Air Liquide
creative oxygen

Carbon Capture utilizing Hybrids: Membrane and Liquefaction

AIChE Carbon Management Technology Conference

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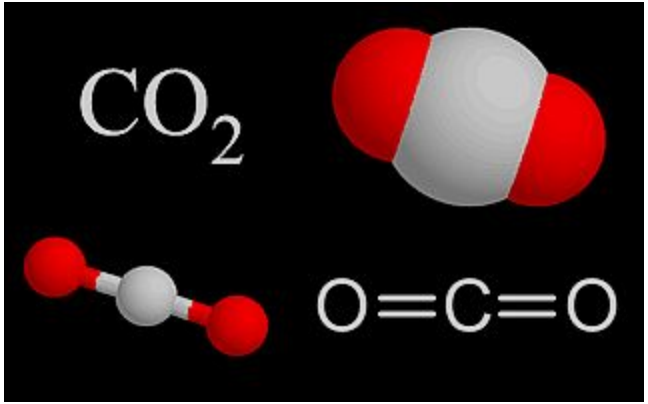
Commercial Membrane Hybrid Solutions for CO_2 Separations

1. Cold Membranes for Air Fired flue gas
2. Cryocap Oxy for Oxy Fired flue gas
3. Cryocap CO_2 for Steam Methane Reforming



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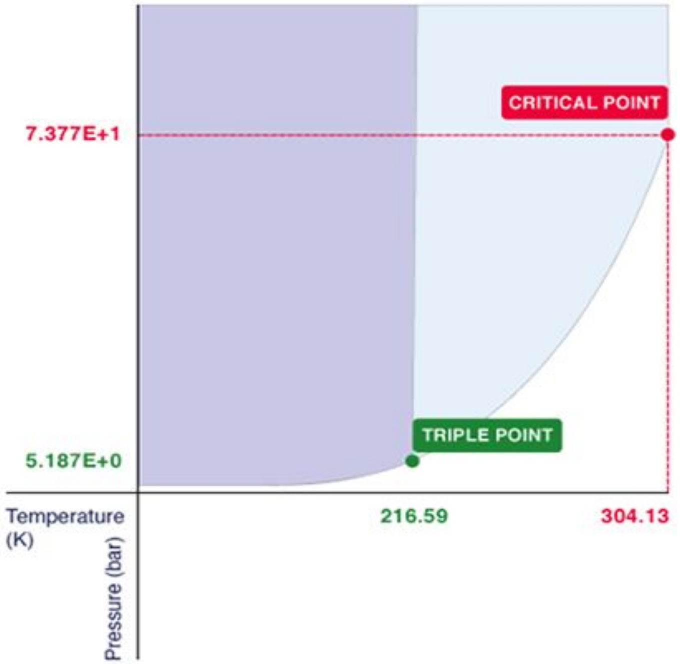
Why Do We Need Hybrids?

Cryogenic Separation of CO_2

CO_2 Distillation at low pressure at -100 °C

- Estimated cost of capture ~ $20/tonne
- Why don't we use this?

The Problem with CO_2



Triple Point prevents liquefaction at low pressures

- Temperature
  - 56.56 °C
- Pressure
  5.1867 bar

- Recovery is low without high pressure

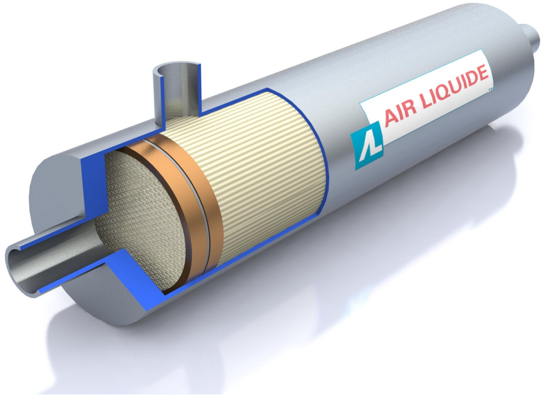
The Problem with Membranes

Purity Specifications of minor components are difficult to reach

Parameter	Limit	Requirement for EOR Pipeline
Temperature	<35°C (95°F)	Transportation pipeline specification
Pressure	152 barg (2200 psig)	Transportation pipeline specification
CO_2	>95% vol	Minimum miscible pressure for enhanced oil recovery (EOR)
N_2	<4% vol	Minimum miscible pressure for EOR
H_2O	dew point <-40°C (-40°F)	Transportation pipeline corrosion / hydrate formation
O_2	**<40 ppmv**	**Transportation pipeline corrosion**
CO	<0.1% vol	Safety and corrosion

Advantages of a Hybrid System

- Cryogenic solutions have two advantages
  - High purity of the CO_2
  - Liquid CO_2 Product



- Membranes have two advantages
  - High recovery of CO_2
  - Simplicity of operation

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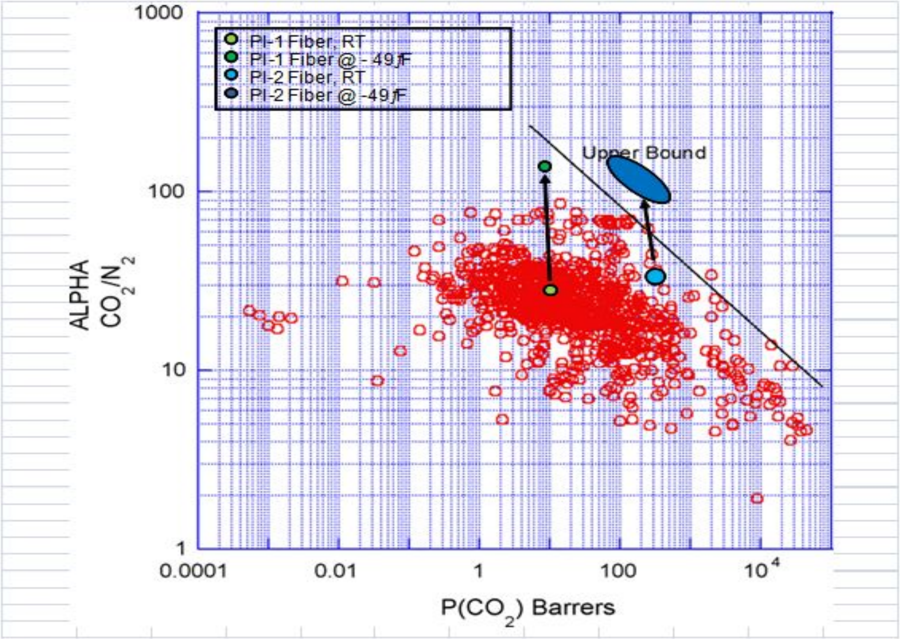
Cold Membrane System

Various polyimides respond favorably to cold temperature operation



Robeson, JMS, 2008

$$\Delta E_P = \Delta E_D + \Delta H_S$$

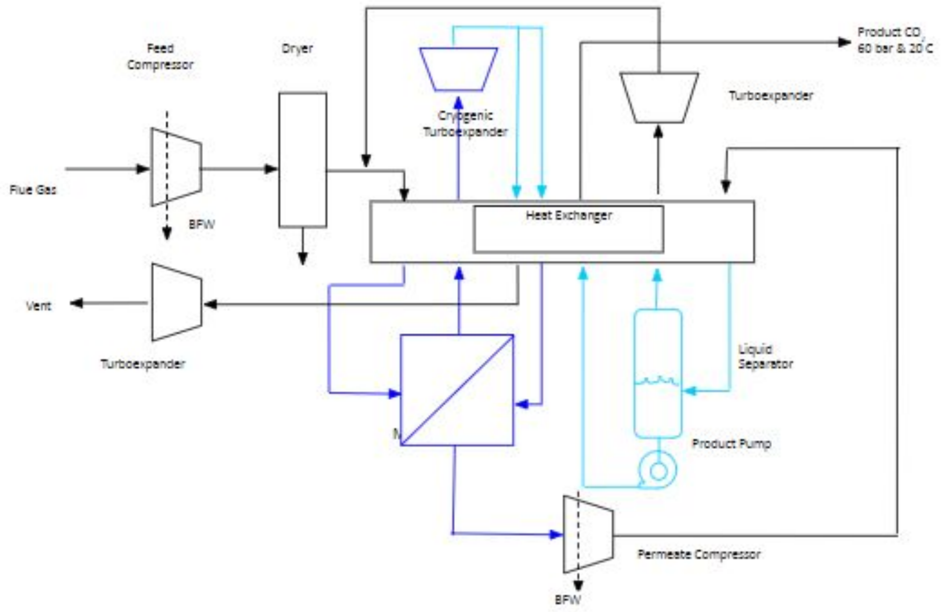
Three polyimides extensively studied: Varying polymer free-volume, plasticization tendency, chain stiffness and CO_2 affinity

Cold Membrane is a Hybrid System

- Highly selective membrane followed by condensation
- Incondensible stream recycled back at pressure to the membrane
- Liquid product pumped to final pressure

Energy Procedia
Volume 37, 2013, Pages 993-1003

Highly Selective Membrane followed by condensation



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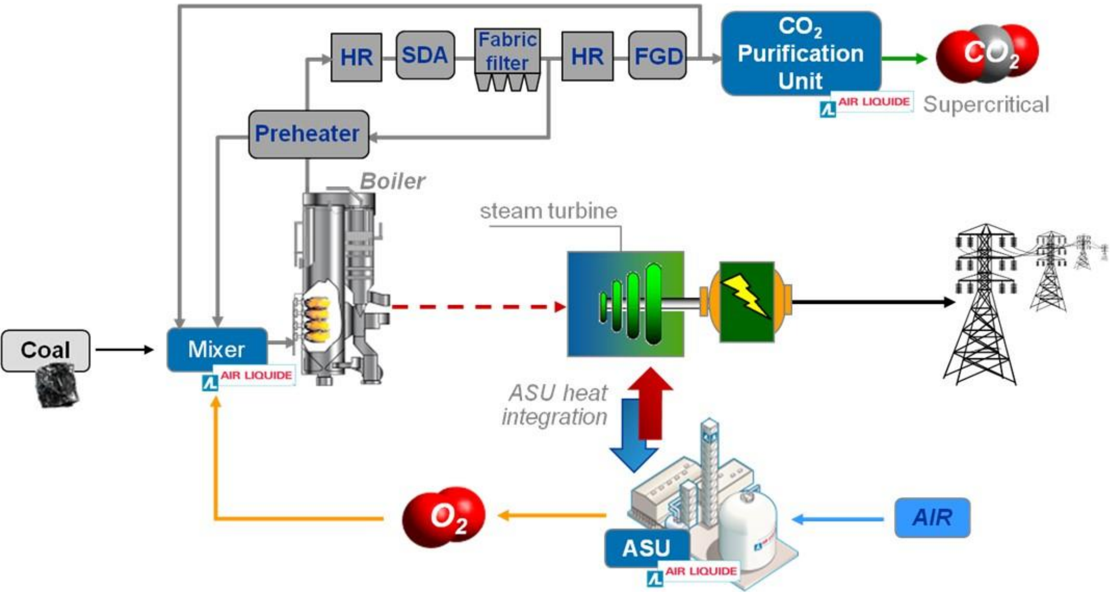
Carbon Dioxide Cryogenic Processing unit (CPU)

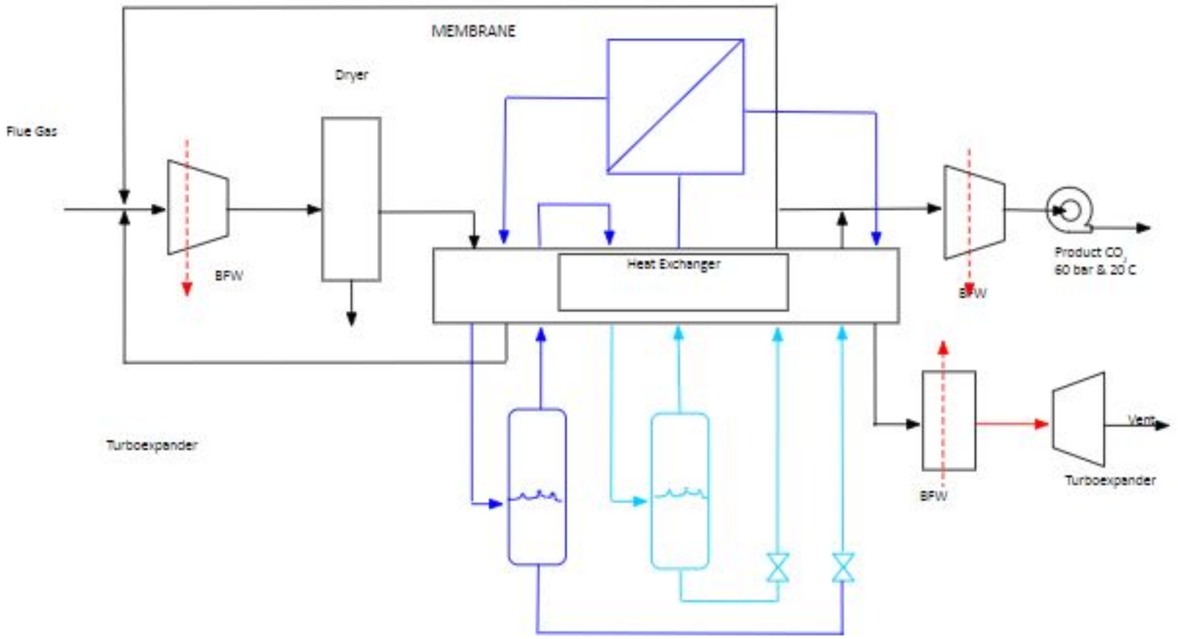
Design for Oxy Combustion of Coal



Liquefaction with membrane recycle of non condensables

Energy Procedia
Volume 63, 2014, Pages 342-351

CPU Process: Condensation before Membrane Separation



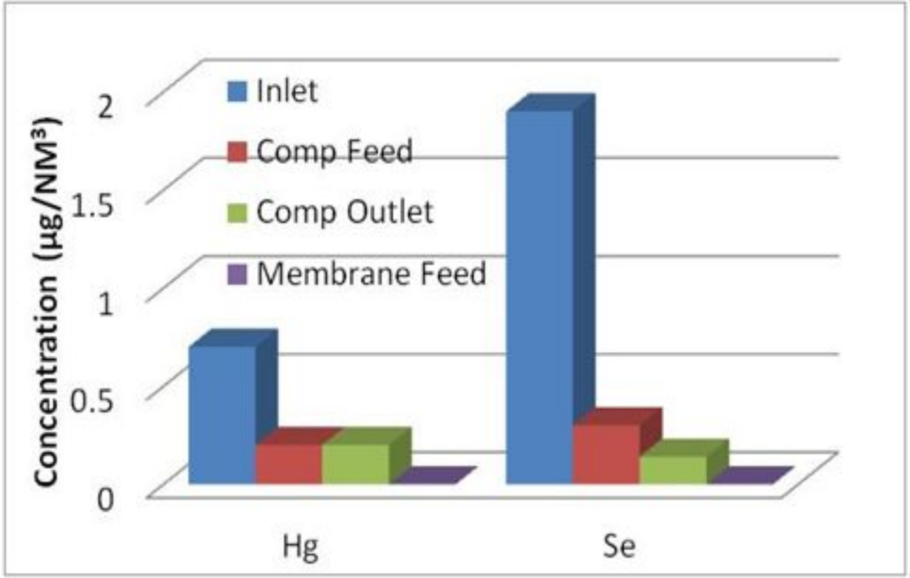
Optimization

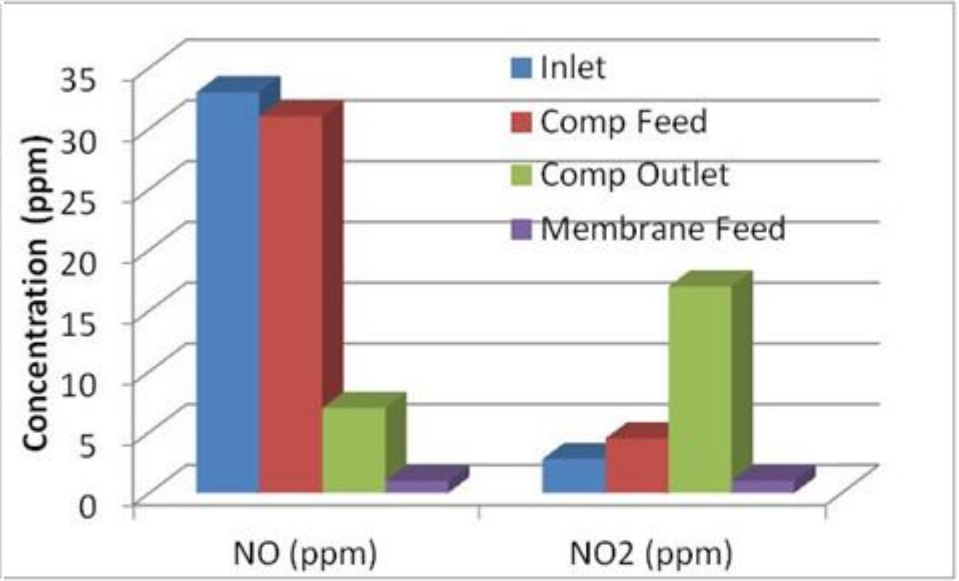
- At low concentrations of CO_2, a cold membrane solution is preferred
- At high concentrations of CO_2, a Cryogenic Processing Unit is preferred

For coal fired power production, the costs are roughly equal if the cost of oxygen production is included (and changes of the DOE calculation factored in)

Technology	Cost of CO_2 ($/tonne)	Year
Cold Membrane	39	2017
Oxy Coal	38	2013

Reduction of Other Impurities





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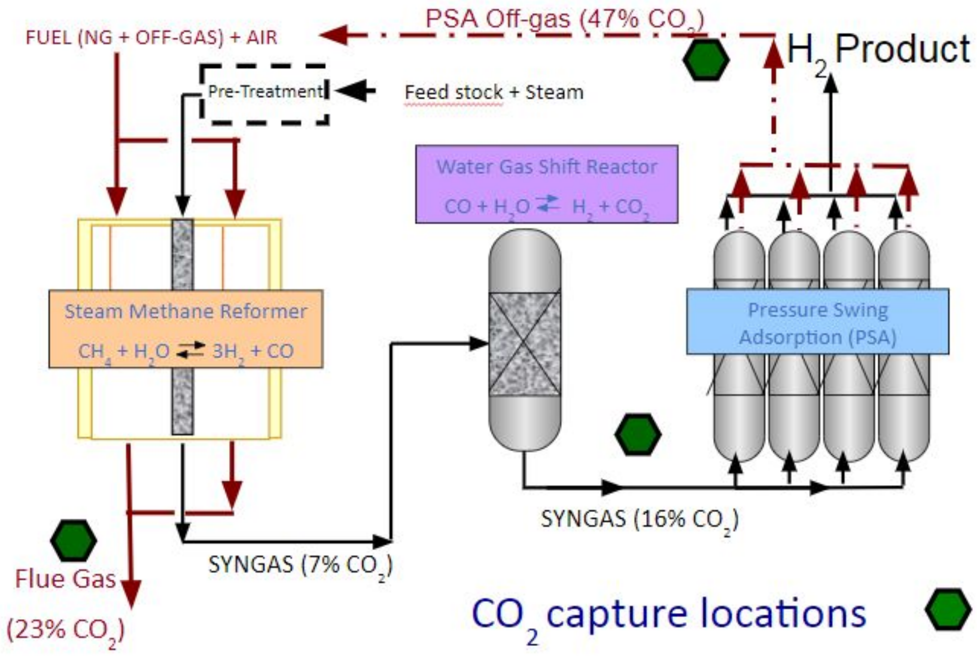
Steam Methane Reforming

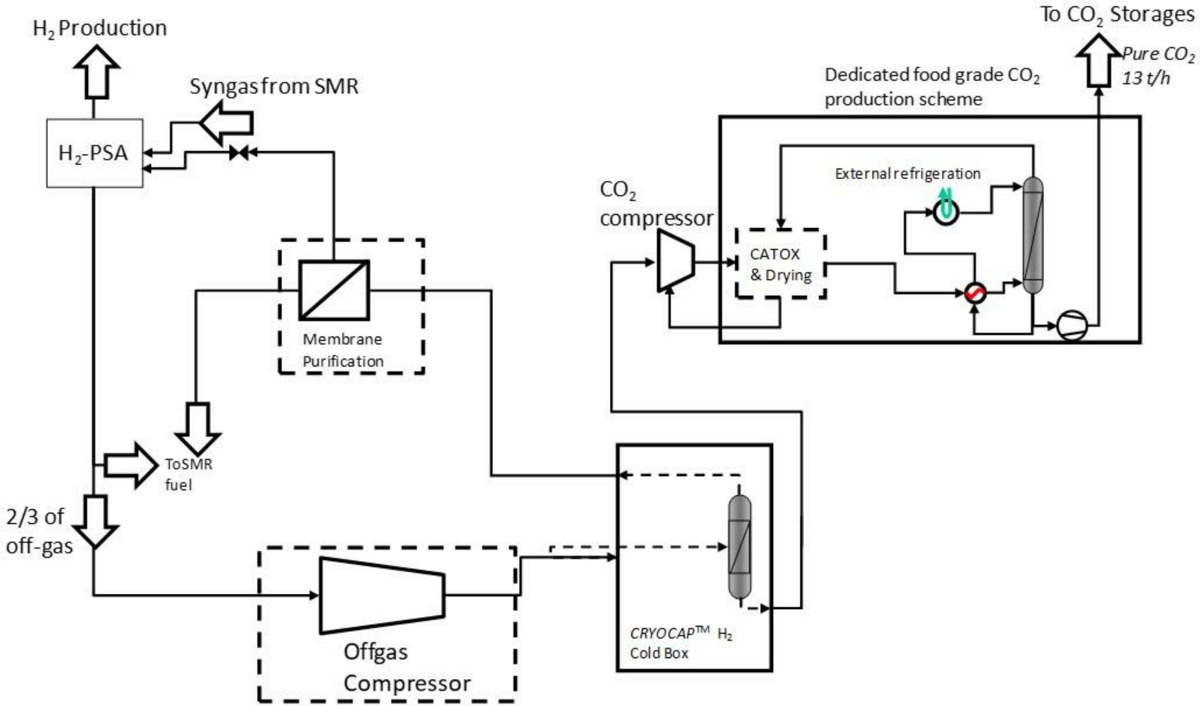
Steam Methane Reforming is Special Case



CO_2 can be captured at three locations

The flue gas is CO_2 with nitrogen, but the other two locations are CO_2 with hydrogen

Hybrid Solution for Capture after Pressure Swing Adsorption



1st Carbon dioxide is removed by condensation

2nd Hydrogen is recycled with a membrane

Commercial Scale Demonstration at Port-Jérôme SMR

The Cryocap™ unit has an annual capture capacity of **100 000 tonnes of CO_2 at this site**.

Energy Procedia
Volume 114, July 2017, Pages 2682-26

Advantages of the Hybrid System

Case	SMR only	SMR + CRYOCAP™ H_2 *Partial CO_2 capture (Port-Jérôme unit)*	SMR + CRYOCAP™ H_2 *Full CO_2 capture*
H_2 production	47 000 Nm^3/hr	50 155 Nm^3/hr	52 480 Nm^3/hr
Additional H_2 production	-	+7%	+12%
H_2 recovery from PSA offgas	0%	87%	87%
Overall H_2 recovery from syngas	88.0%	93.9%	98.3%

Increased H_2 production coupled with industrial scale CO_2 production

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Thank you

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