

Award: DE-FE0026422



**Project Review: Bench Scale Testing of
Next Generation Hollow Fiber
Membrane Modules**



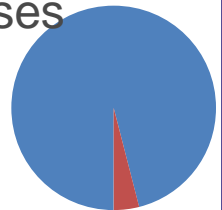
August 11, 2016

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D. Kratzer, M. Bennett | R&D
J.-M. Gauthier | MEDAL**

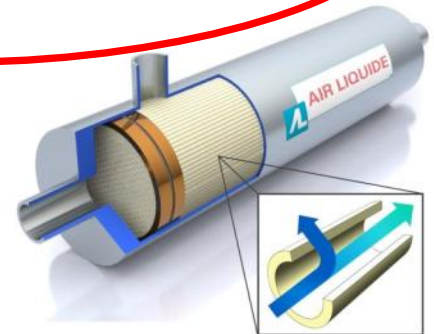
Air Liquide & MEDAL



Air Liquide: world leader in industrial and medical gases
 68,000 employees
 \$18.1 billion sales (2015)



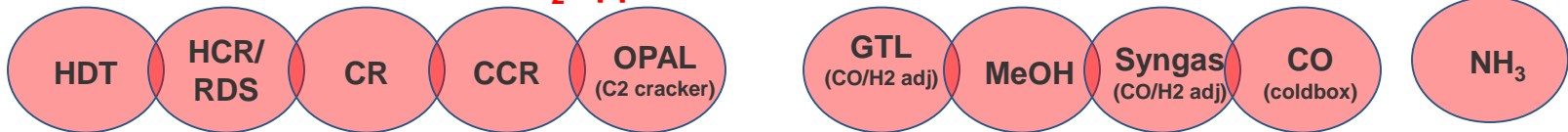
Air Liquide Advanced Separations, MEDAL



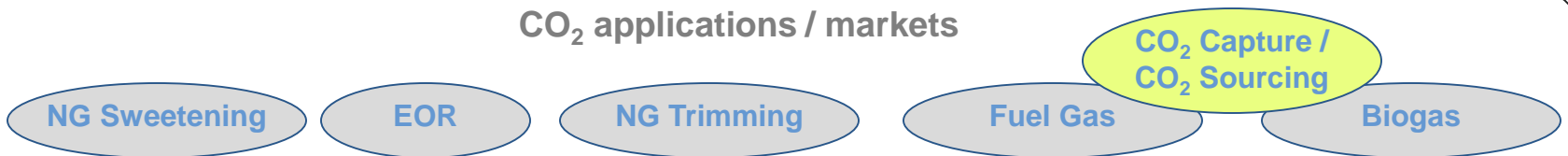
N₂ applications / markets



H₂ applications / markets

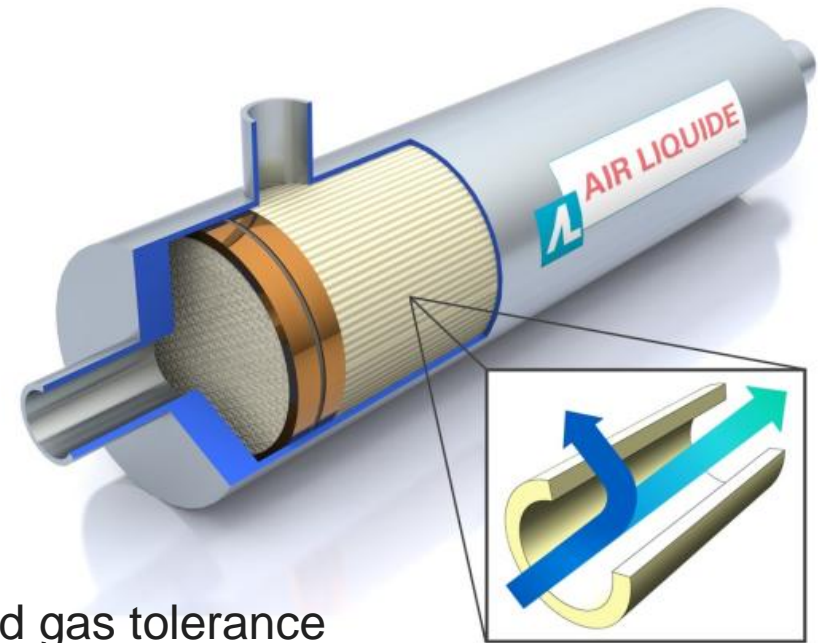


CO₂ applications / markets



Outline

- Project Overview
 - Technology Background
 - Process design
 - PI-2 novel material
 - Project Details / Progress
 - Equipment set-up
 - Formulation development
 - Manufacturing development
 - Conclusions & Future Work
- Acid gas tolerance
 - Hybrid process analysis



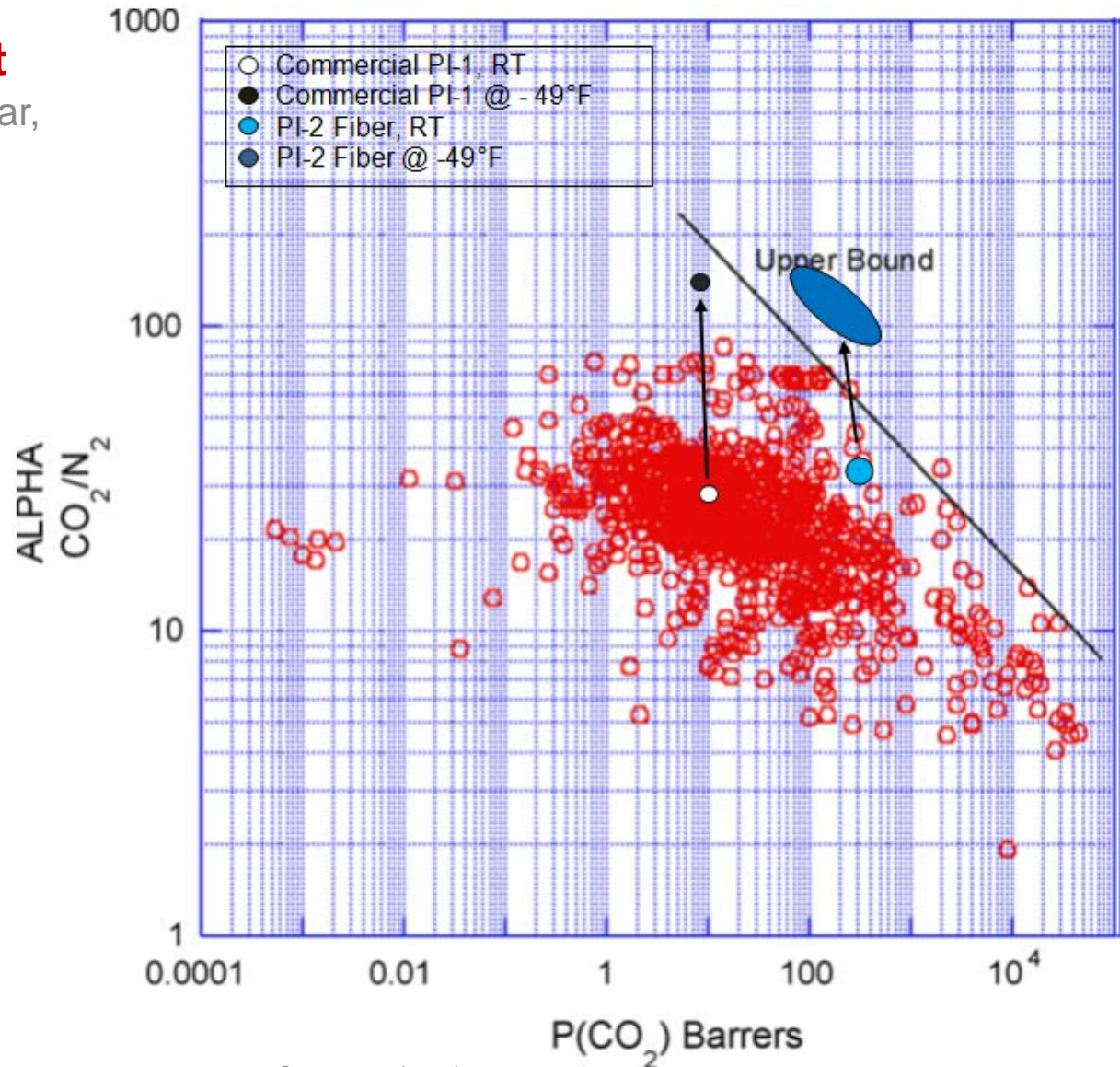
Motivation: Increase Membrane Productivity

PI-1 commercial product

- 1,000's of modules per year, dozens of applications
- Performance improves at low temp

PI-2 novel material

- Thin film properties near Robeson* upper bound
- Spinnable
- Performance at lab-scale over 500+ hours



*Robeson, *J. Membr. Sci.* 2008(320), 390-

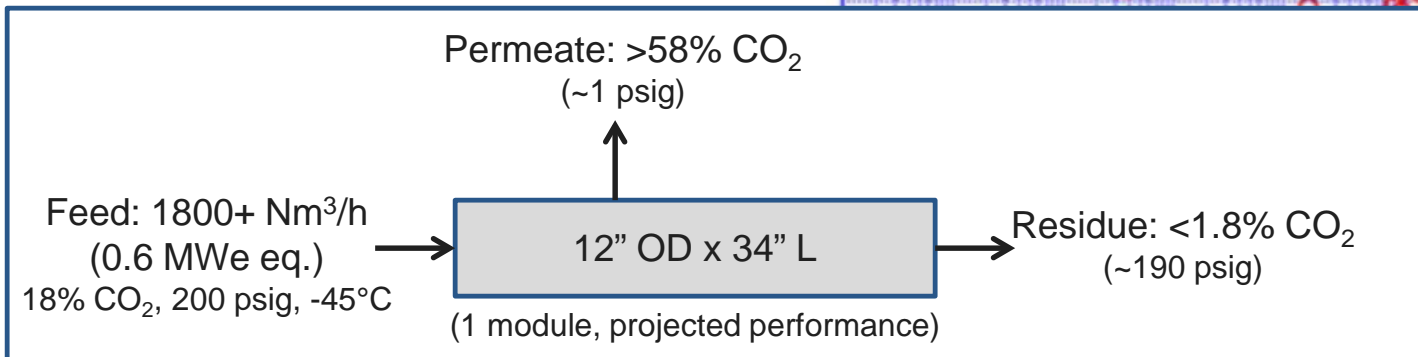
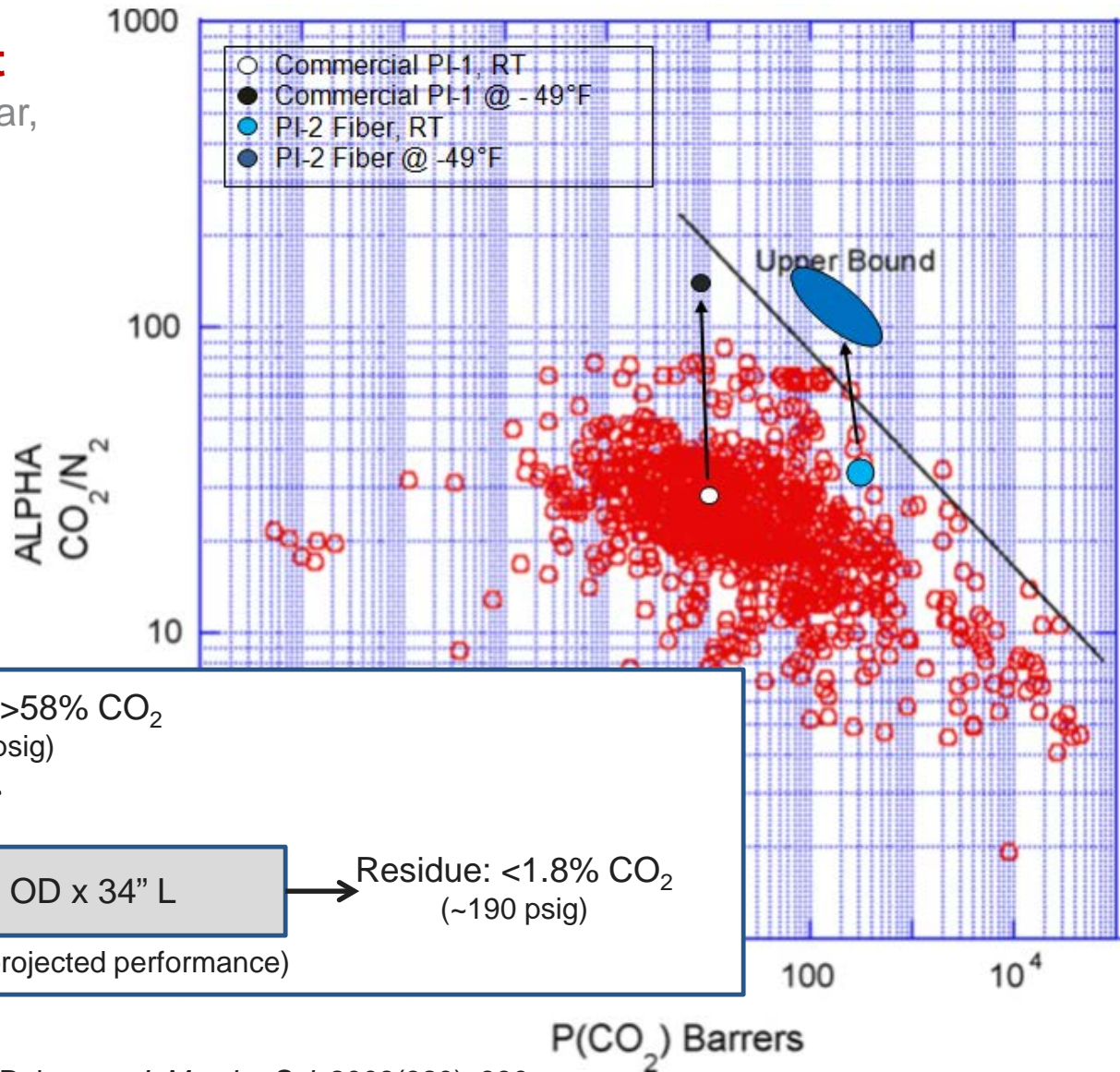
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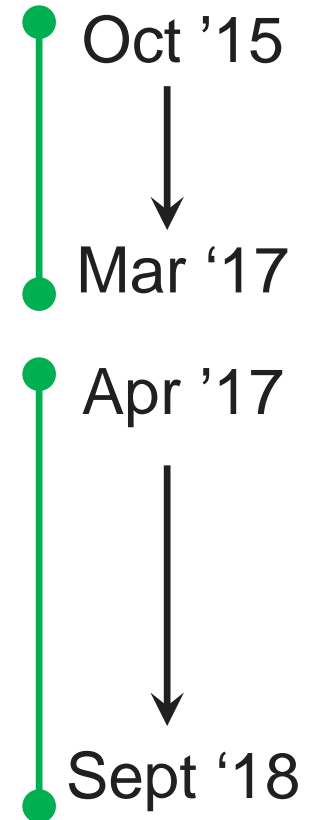
*Robeson, *J. Membr. Sci.* 2008(320), 390-

Project Objectives

■ Objectives (Success Criteria):

- Design/manufacture 4" bundle(s)
 - >90 Nm³/h feed @ 90% CO₂ recovery, >58% CO₂ purity
- Identify other hybrid processes with possibility of economic feasibility

- Design/manufacture 6" bundle(s)
 - >400 Nm³/h feed @ 90% CO₂ recovery, >58% CO₂ purity
 - Manufacture at least one 12" bundle
- Field-test 6" bundles at 0.3 MWe scale with real flue gas at NCCC
- Techno-economic analysis achieving >90% CO₂ capture at a cost of electricity 30% less than DOE baseline



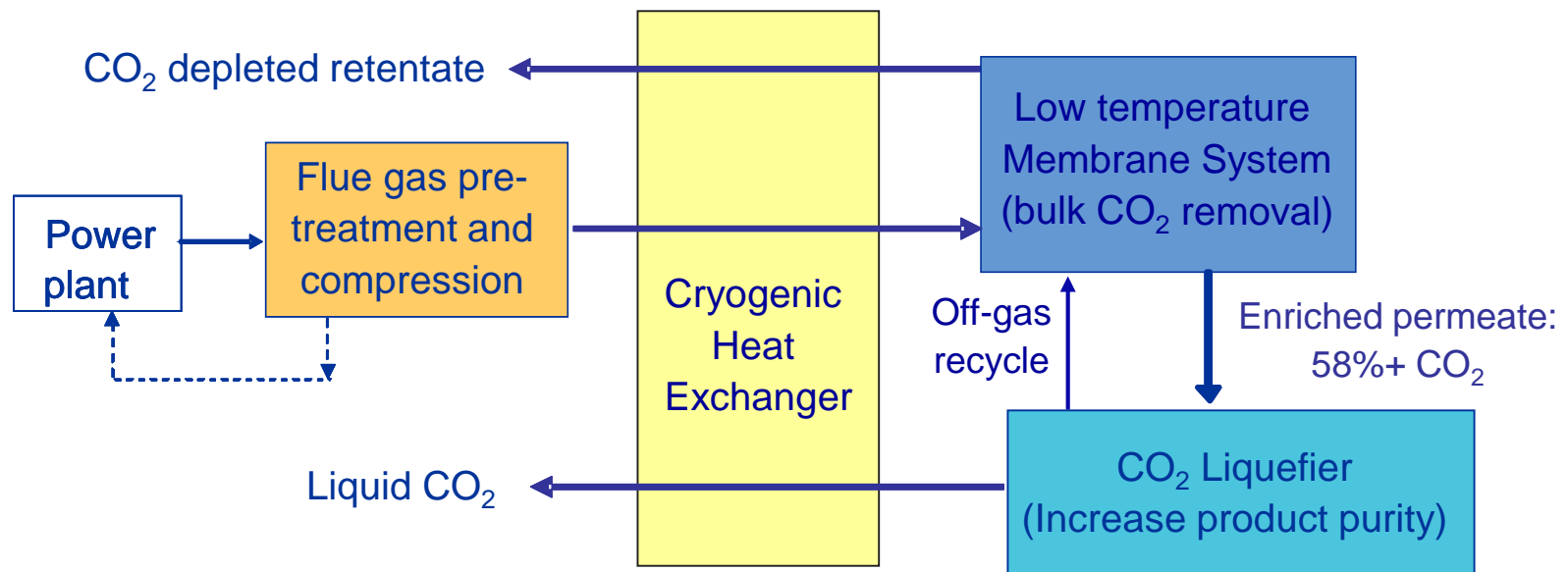
Total Budget - \$3.98 MM (25% cost share), 9.4 man-years total
Partners – DRTC, MEDAL, and Parsons

Technology Background: Process Concept

■ 2010 – 2012 DOE: DE-FE0004278

- Cold membrane hybrid process
- PI-1: synthetic flue gas (TRL 4)
- Techno-economic analysis

- Energy recovery by turbo-expansion and cold production
- Energy integration
- BFW generation
- Pumping liquid CO₂



Technology Background: Capture Cost

■ 2013 – 2016 DOE: DE-FE0013163

■ 2x12” PI-1 bundles, real flue gas

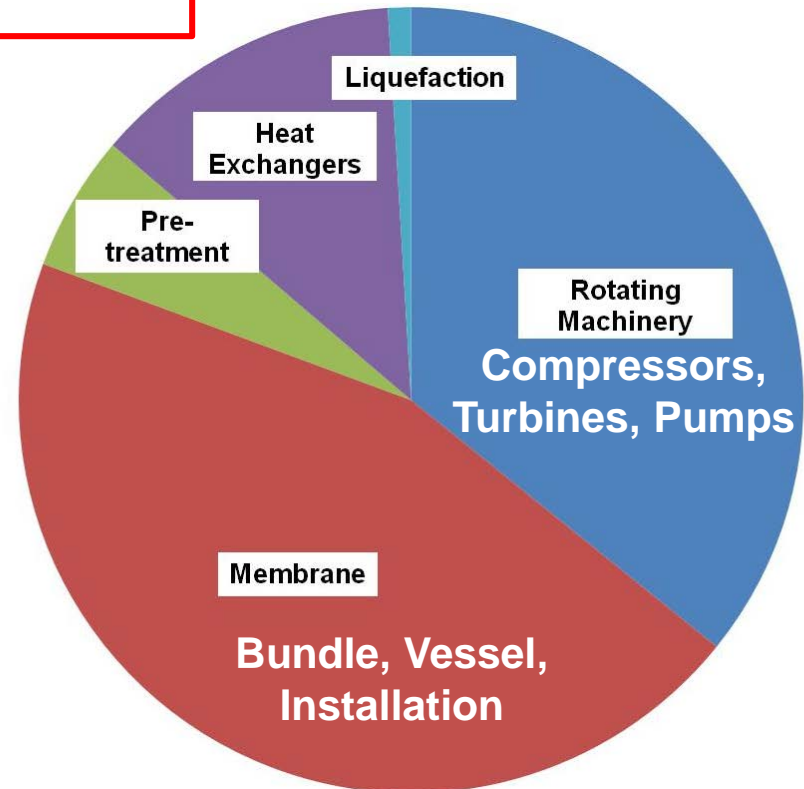
■ TRL 5 (PI-1)

■ Techno-economic analysis

Projected CO₂ capture cost 42 - 48\$/tonne
(DOE Target – 40\$/tonne of CO₂)

Areas of improvement:

- Reduce membrane cost – **improve membrane performance**
- Reduce pre-treatment / compression costs, **lower operating pressure**



Technology Background: PI-2 Fiber Development

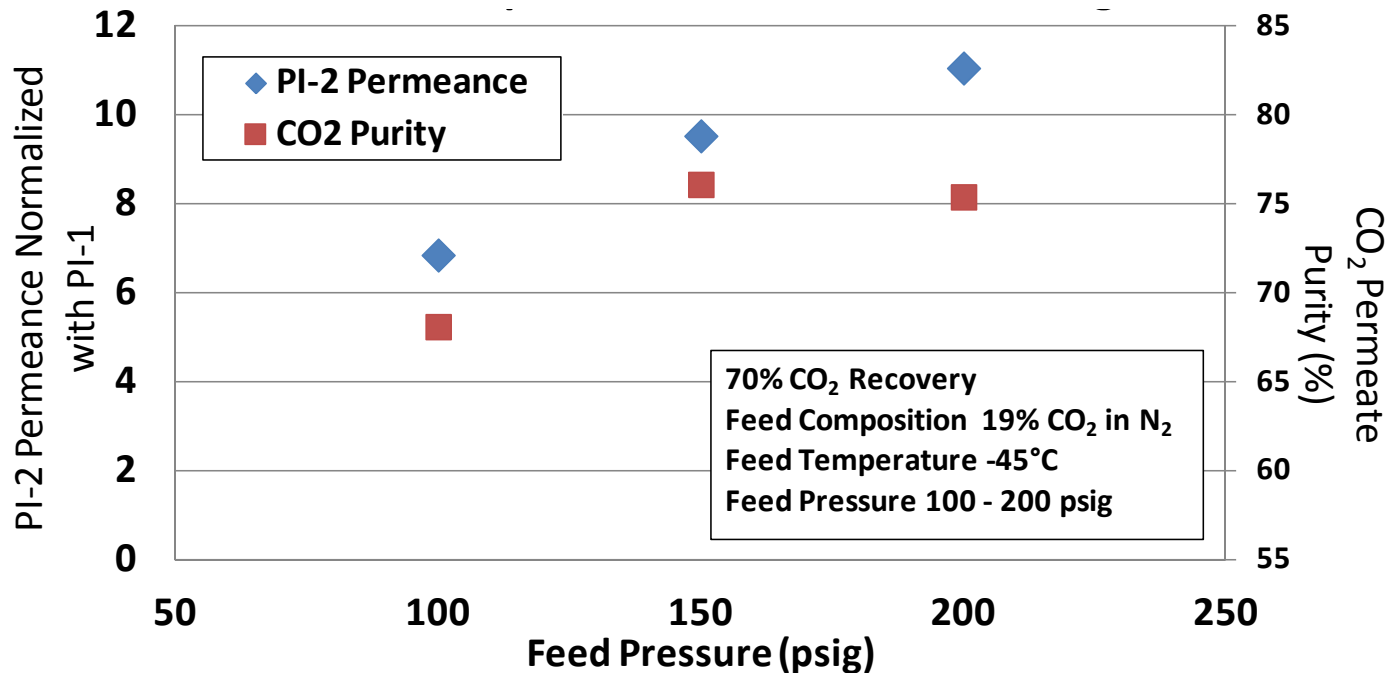
■ 2013 – 2016 DOE: DE-FE0013163

■ 1" PI-2 modules (500+ fibers)

■ TRL 4 (PI-2)

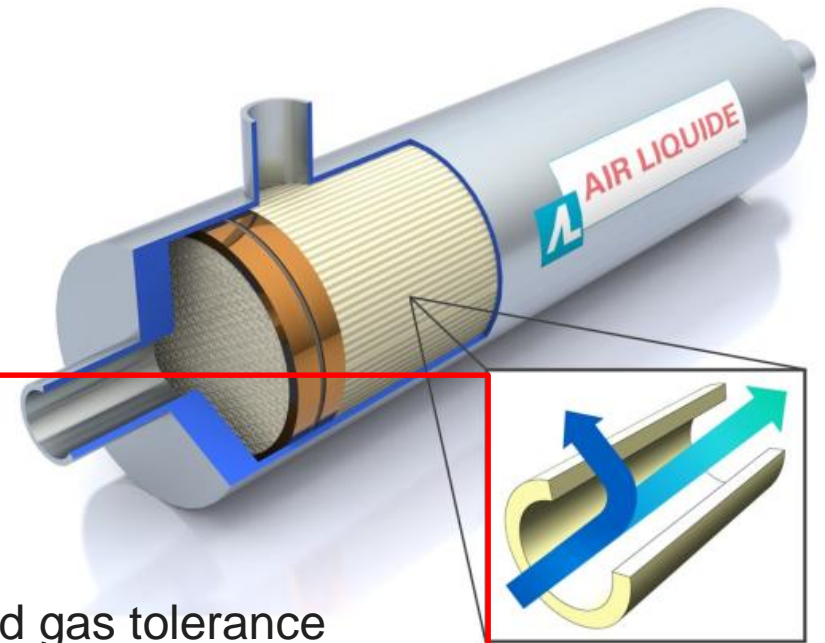
- PI-2 lab-scale spinning methodology

- 1" OD modules (500 fibers) achieved good performance in real flue gas




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Project Milestones & Dates

BP #	Expected	Milestone
BP1	03-31-2016 	Complete prototype manufacturing setup and initiate 4" bundle fabrication
	12-31-2016	Complete prototype bundle testing: >90 Nm ³ /hr productivity @ 18%CO ₂ , 16 bar, 90% CO ₂ recovery, and >58% CO ₂ permeate composition
	03-31-2017	Complete verification of PI-2 flue gas contaminant testing
	03-31-2017	Complete hybrid process analysis comparing different applicable process schemes
GO/NO-GO Decision		
BP2	03-31-2018	Complete PI-2 commercial bundle fabrication and testing: >400 Nm ³ /h productivity @18%CO ₂ , 16 bar, 90% CO ₂ recovery, and >58% CO ₂ permeate composition
	01-31-2018*	Complete installation and commissioning of the 0.3 MWe field-test unit at NCCC
	09-30-2018*	Complete 0.3 MWe field-testing including parametric testing and at least 500 hours for one membrane
	09-30-2018*	Techno-economic analysis of CO ₂ capture at 550 MWe net AFPC plant using cold membrane technology
	09-30-2018*	Environmental, Health, and Safety analysis of cold membrane technology at full scale

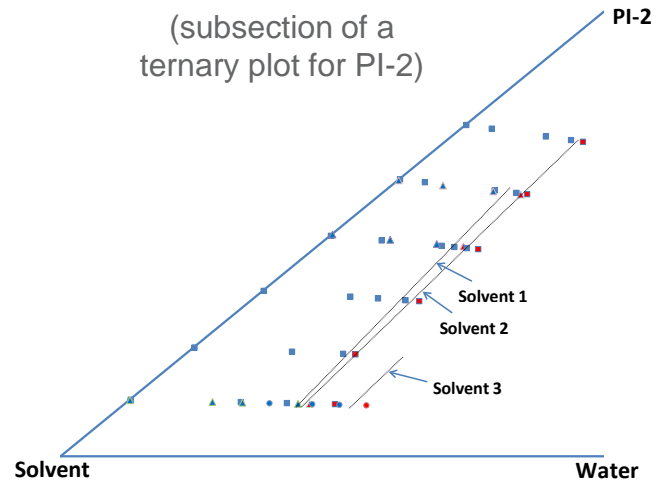


Polymer Formulation Development

Baseline

Normalized Permeance 5
 $\alpha\text{-CO}_2/\text{N}_2$ >70

(subsection of a ternary plot for PI-2)



Alternate Formulations

Normalized Permeance **5 - 15**
 $\alpha\text{-CO}_2/\text{N}_2$ **40 - 85**

Performance Improvement



Cost Reduction

Alternate Formulations

Normalized Permeance **0.5 - 1.5**

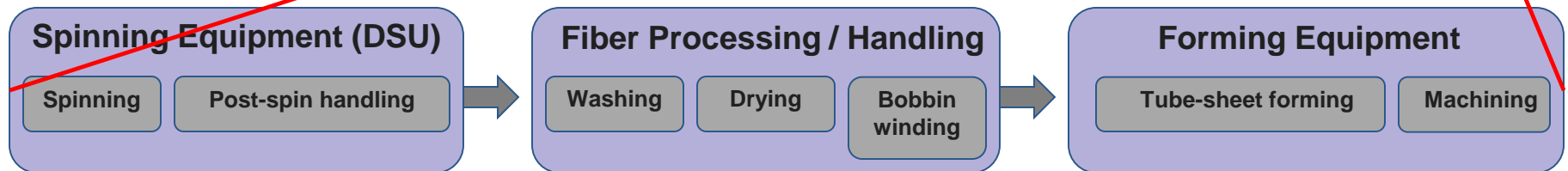
	Blend A	Blend B	Blend C	Blend D	Blend E	Blend F	Blend G
Dope 1	Neg	Neg					
Dope 2			Neg	Pos			
Dope 3				Pos			
Dope 4					Neg		
Dope 5						Neg	
Dope 6							Neg
Dope 7				Pos			

(polymer blending attempts)



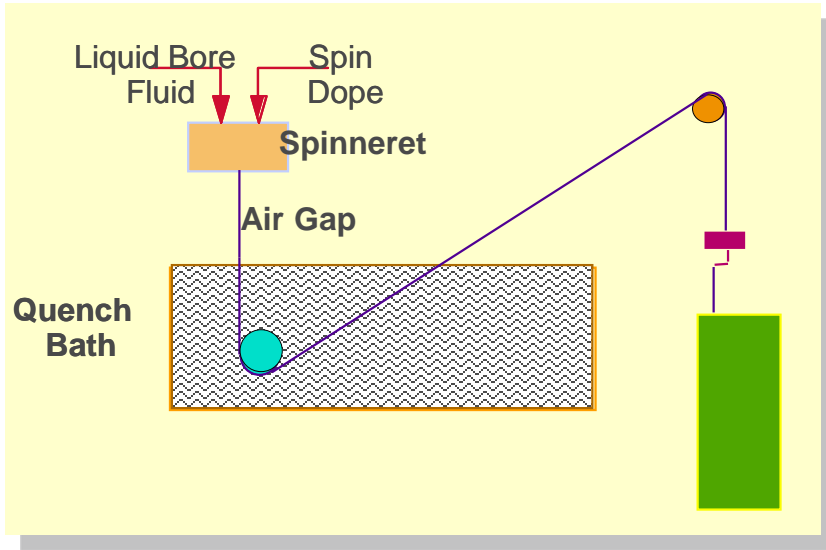
Manufacturing Development

	OD (in)	Length (ft)	Fiber Count	Spinning Device	Fabrication Technique
Mini permeator	0.25 - 0.5"	1.6'	<1000	1-hole lab unit	Hand
Permeator	1"		1 - 5x		12-hole "DSU"
Skein module	2.5"	2.8'	15 - 20x	24/36-hole production unit	
R&D prototype bundle	2.5 - 4"		15 - 20x		
6" bundle (commercial)	6"		50 - 90x		
12" bundle (commercial)	12"		>200x		



Demonstration Scale Fiber Synthesis Equipment

Dry jet wet quench fiber spinning



12-filament Development Spin Unit

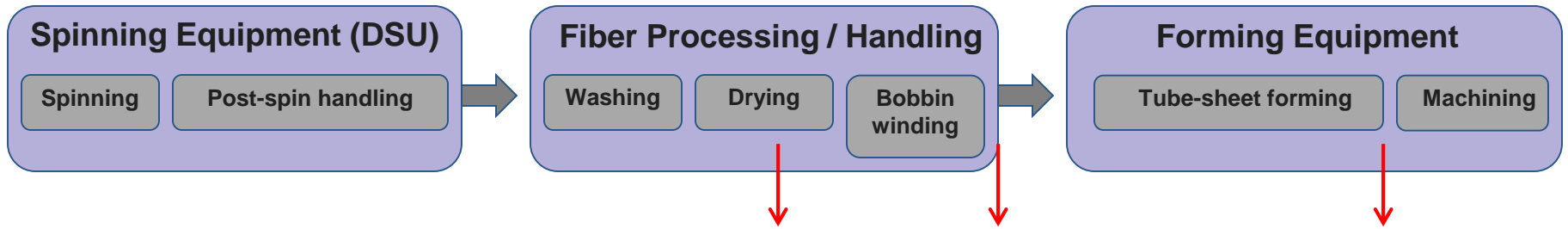


Batches of fiber

MEDAL manufacturing equipment for processing

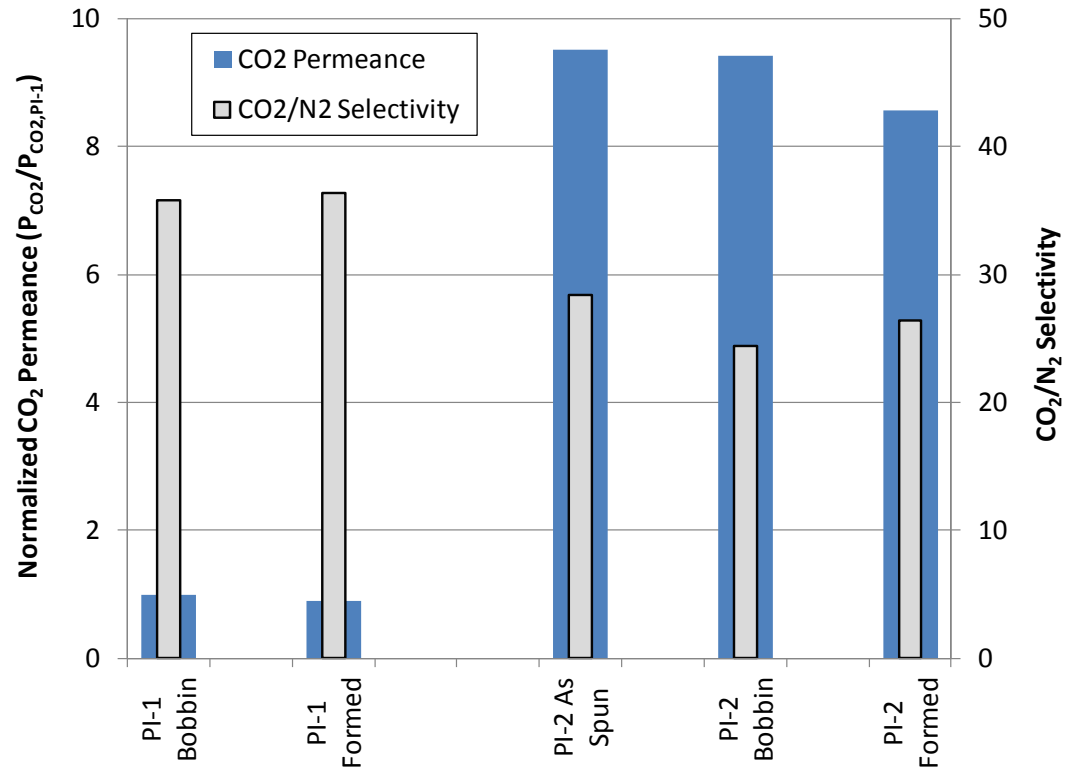


Fiber Synthesis & Handling Damage



Samples taken and quality tested at ambient temperature

- Minor selectivity loss due to bobbin winding: minor handling damage
- No selectivity loss due to forming: little or no further handling damage



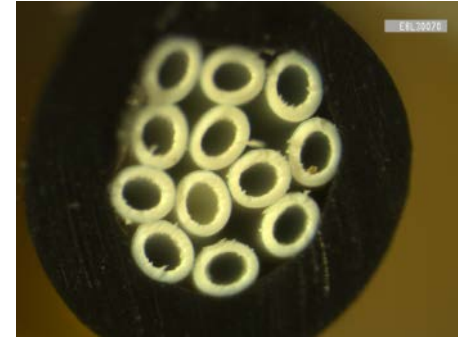
Fiber Synthesis & Bundle Forming

1.9 lbs of PI-2 fiber synthesized on the DSU over 3 hours

Periodic samples for quality control:

Sample #	Normalized CO ₂ Perm	CO ₂ /N ₂ Selectivity	Fiber ID
1	13.1	27.8	*Proprietary
2	11.7	31	
3	14.3	28	
4	11.0	26	
5	13.2	35	
6	9.4	27	
Average	12.1	29.1	
Std Dev	11.6%	14.7%	3.6%

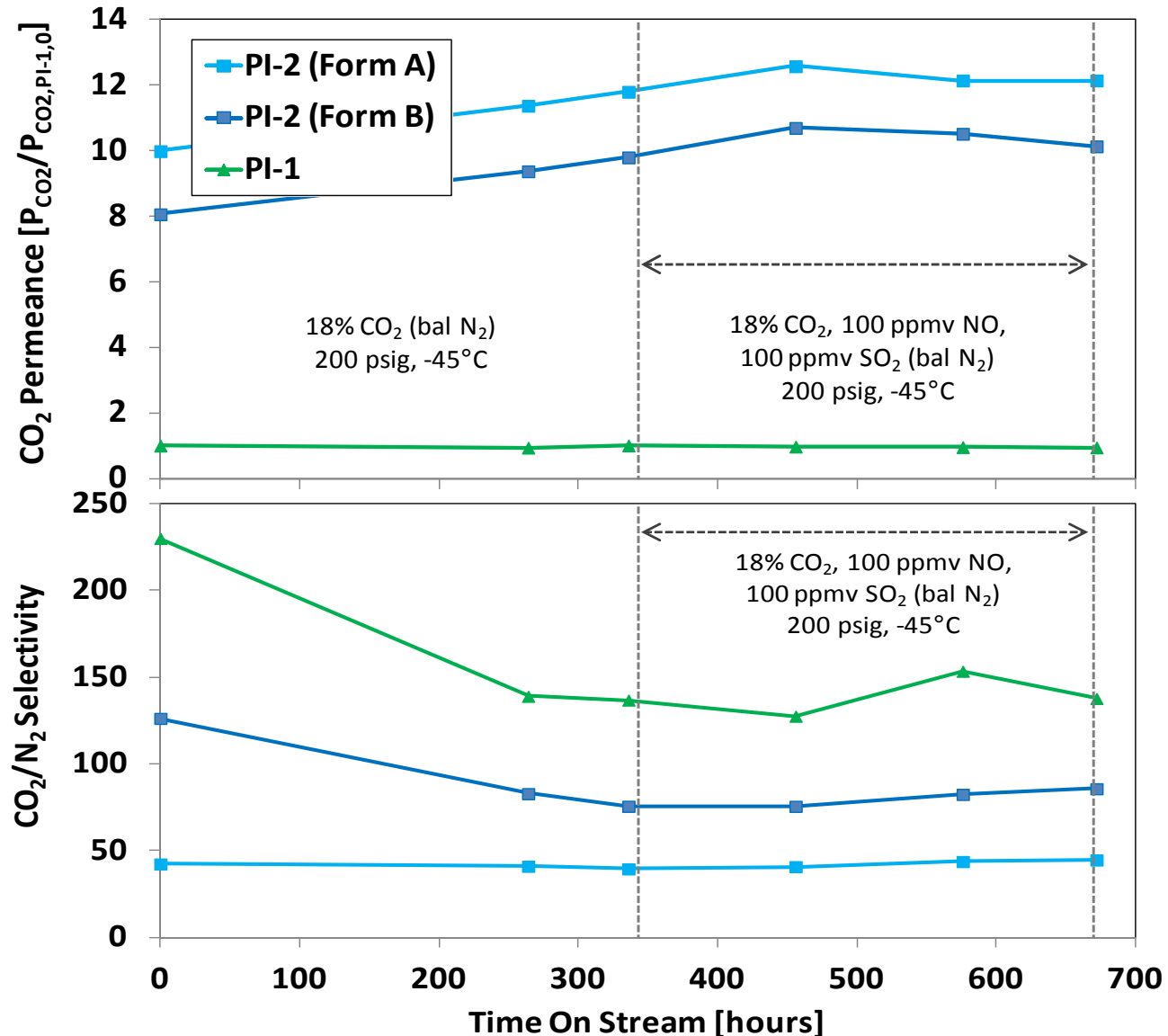
- Fiber performance was consistent and agreed with previous lab-scale results
- Fiber “formed” into two prototype bundles (to be tested at 0.1 MWe skid at DRTC)



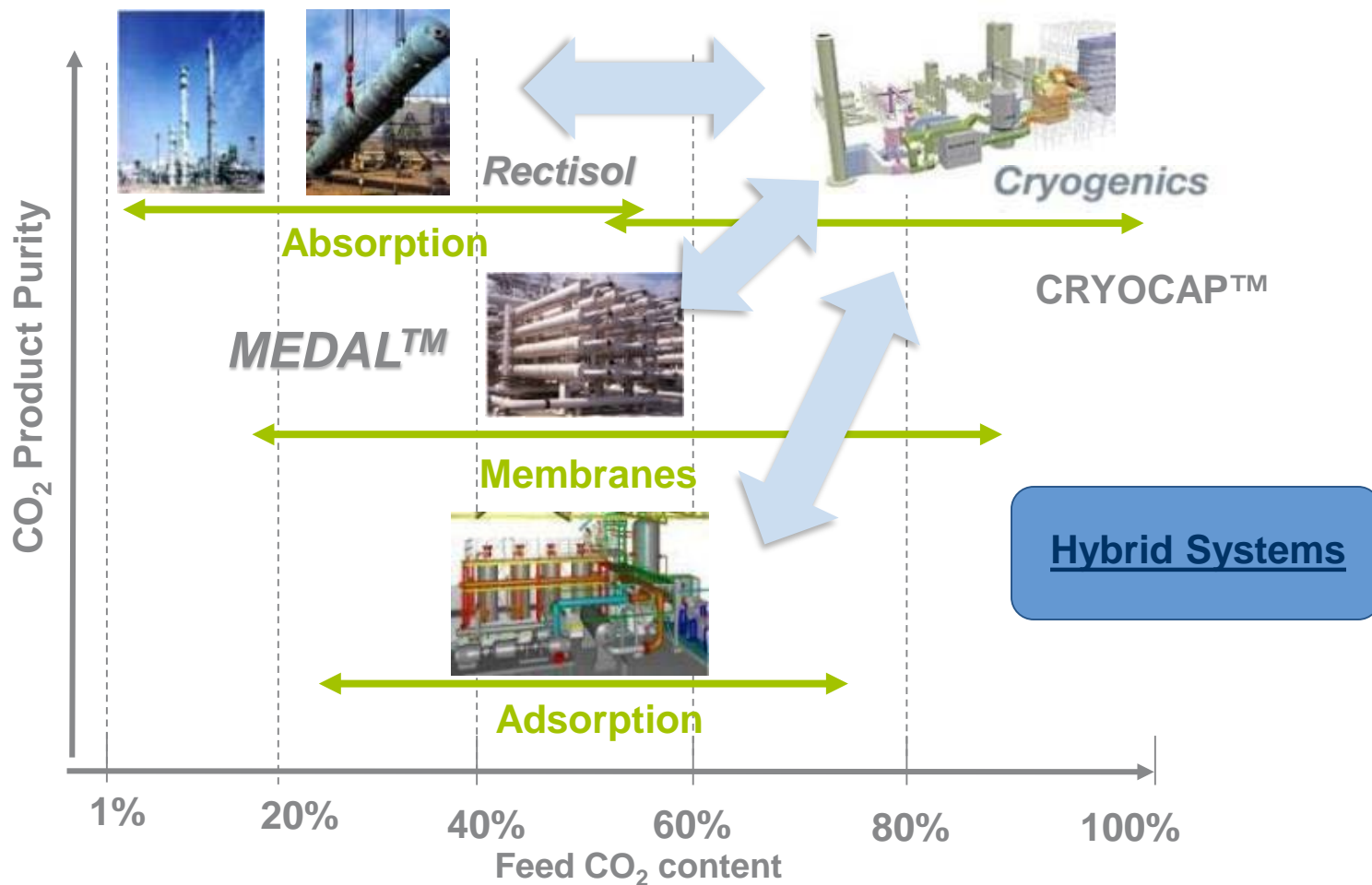
Acid Gas Contaminant Testing

Fiber samples in three mini-permeators simultaneously exposed to 100 ppmv NO and SO₂ over two weeks

- Stable / slightly increasing permeance for all samples
- Stable selectivity for all samples
- No apparent effect of NO or SO₂ on the PI-2 fiber
- Still to do: 100 ppmv NO₂ (not stable in combination with NO & SO₂)

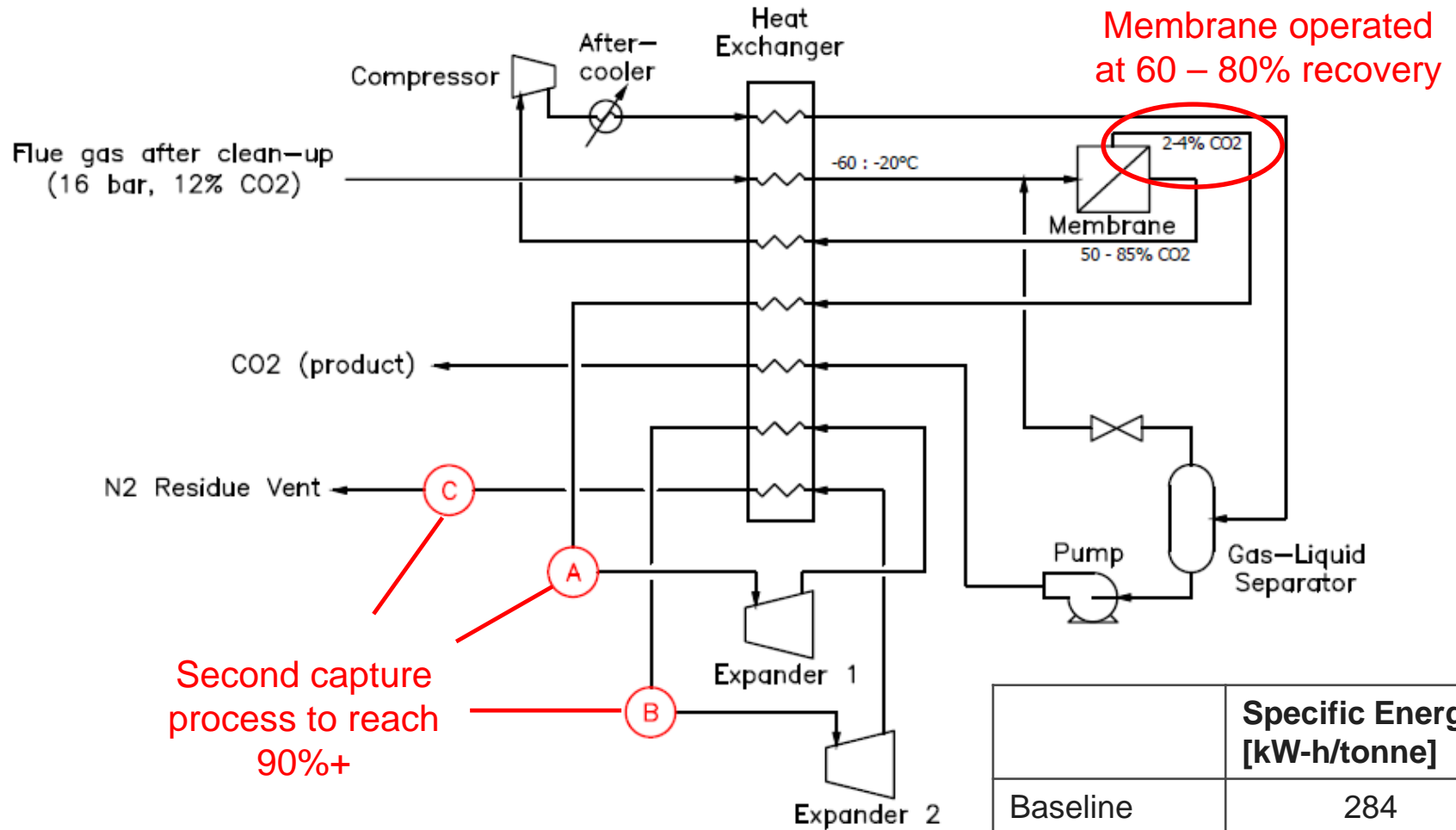


Air Liquide's Unique Position on CO₂



Technology for the whole range of CO₂ feed and product purities from any CO₂ source

Hybrid Process Schemes

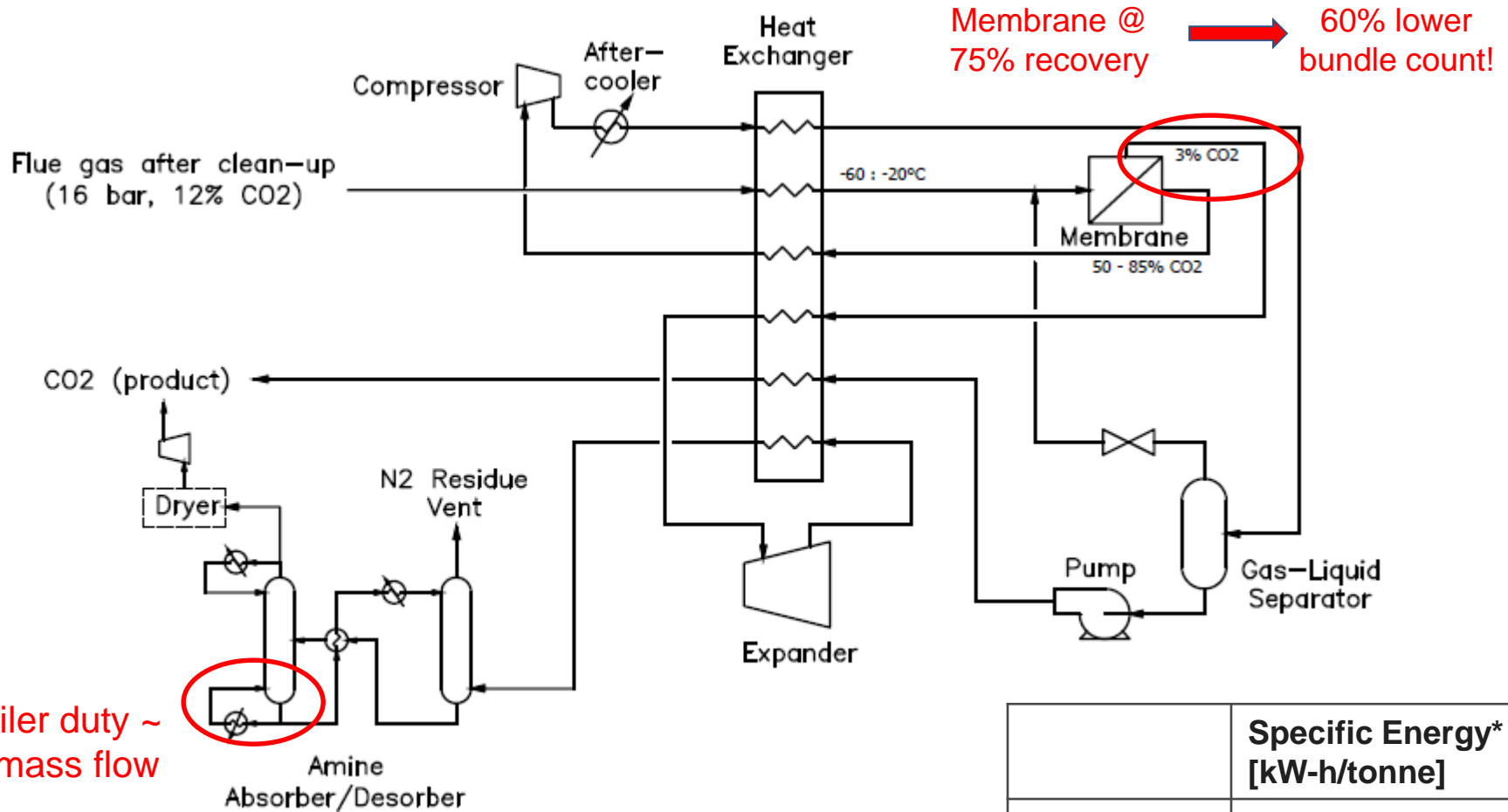


	Specific Energy* [kW-h/tonne]
Baseline	284

*CO₂ capture only



Hybrid Process Schemes (Cold Membrane + Amines)



Membrane @ 75% recovery → 60% lower bundle count!

Reboiler duty ~ CO₂ mass flow

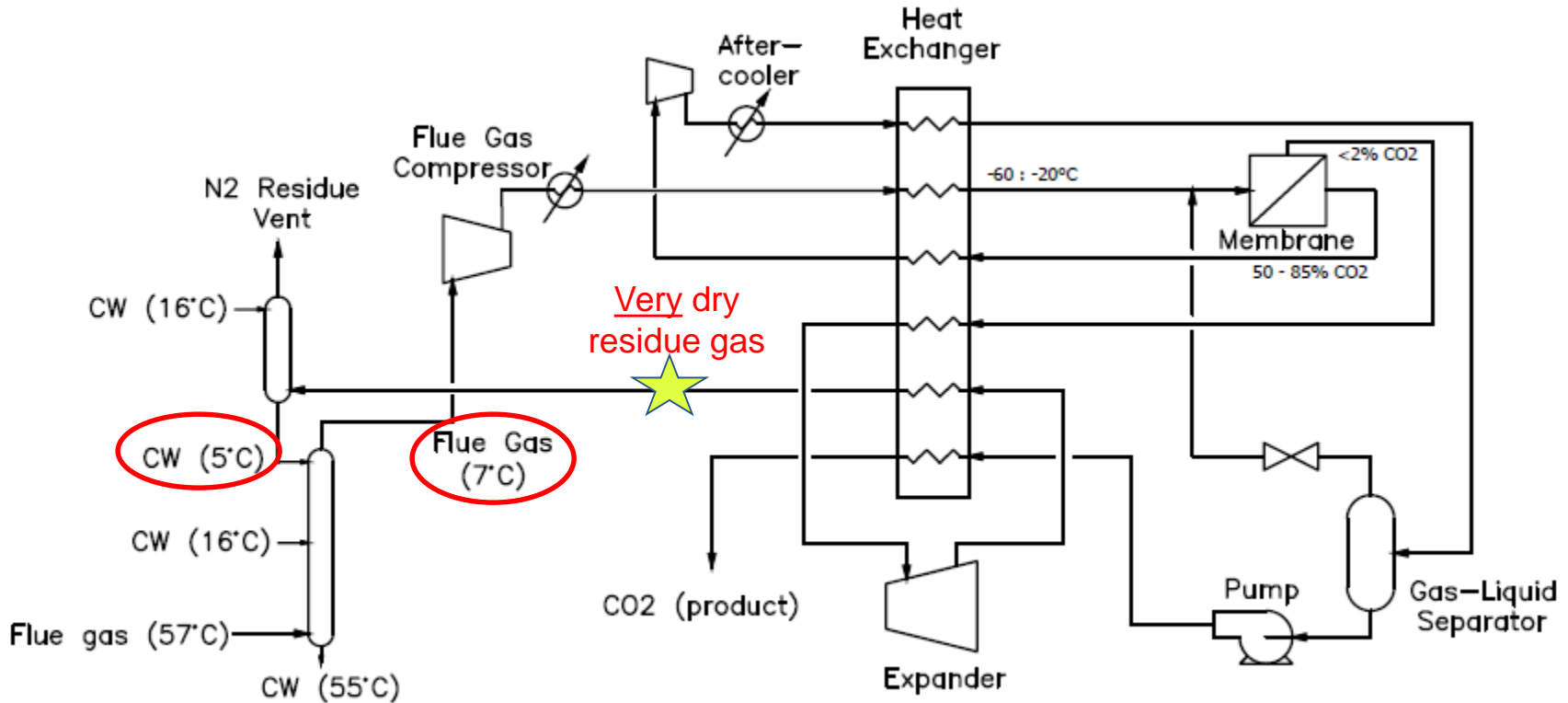
Amine system for 90%+ recovery

	Specific Energy* [kW-h/tonne]
Baseline	284
With Amines	402

*CO₂ capture only



Hybrid Process Schemes (Cold Water)



Direct contact towers for flue gas cooling

	Specific Energy* [kW-h/tonne]
Baseline	284
Cold Water	267

*CO₂ capture only



Conclusions & Future Work

Conclusions

- Prototype bundles fabricated (awaiting testing)
- Fiber tolerance towards NO and SO₂ demonstrated
- Hybrid processes modeled

Future Work (present to Mar '17)

- Prototype bundle fab / test
- Hybrid process development

Budget Period 2 (Apr '17 to Sept '18)

- Manufacturing scale-up (6" and 12" bundles)
- Field-test at NCCC (0.3 MWe unit)
- Techno-economic analysis



0.3 MWe Field-Test Unit at NCCC, Pilot Bay 3
(DE-FE0013163)



Acknowledgments / Disclaimer

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 - NCCC: Frank Morton, Tony Wu
 - Parsons: Brad Knutson
 - Air Liquide: Rob Gagliano, Shilu Fu, Sudhir Kulkarni, Dave Hasse, Dean Kratzer, Dave Edwards, Jean-Marie Gautier
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Opening new ways

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