### **SRI International**





### Project Review (FE0031633)

# DEVELOPMENT AND TESTING OF A HIGH-TEMPERATURE PBI HOLLOW-FIBER MEMBRANE TECHNOLOGY FOR PRE-COMBUSTION CO<sub>2</sub> CAPTURE

Presented by Elisabeth Perea

Advanced Technology and Systems Division

**SRI** International





**Project Team** 

Enerfex, Inc.



**Energy Commercialization, LLC** 



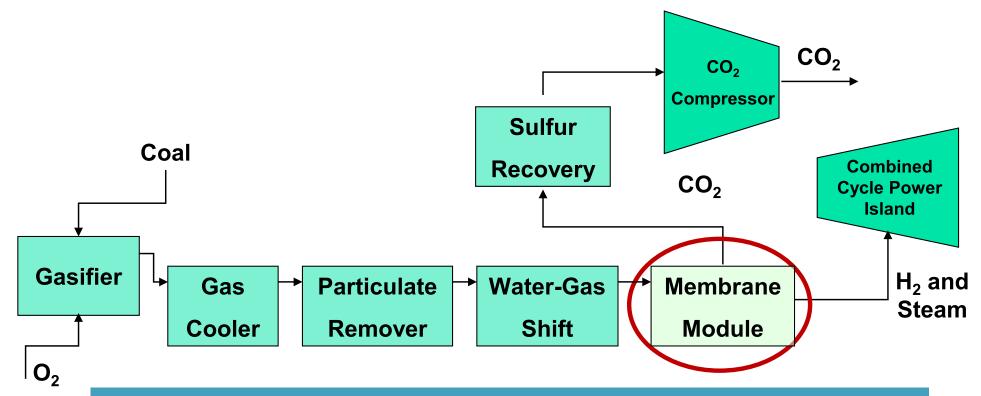
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# Membranes for Pre-Combustion CO<sub>2</sub> Capture

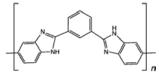
Advantages of High-Temperature Membranes for Separation of CO<sub>2</sub>



Note: PBI hollow fiber membrane (HFM) is a  $H_2O$  and  $H_2$  transporting membrane

### **Advantages of Membrane-Based Separation**

- Reduced costs for syngas cooling
- Reduced CO<sub>2</sub> compression costs
- Emission free, i.e., no solvents
- Decreased capital costs
- Low maintenance
- Modular



m-Polybenzimidazole (m-PBI)

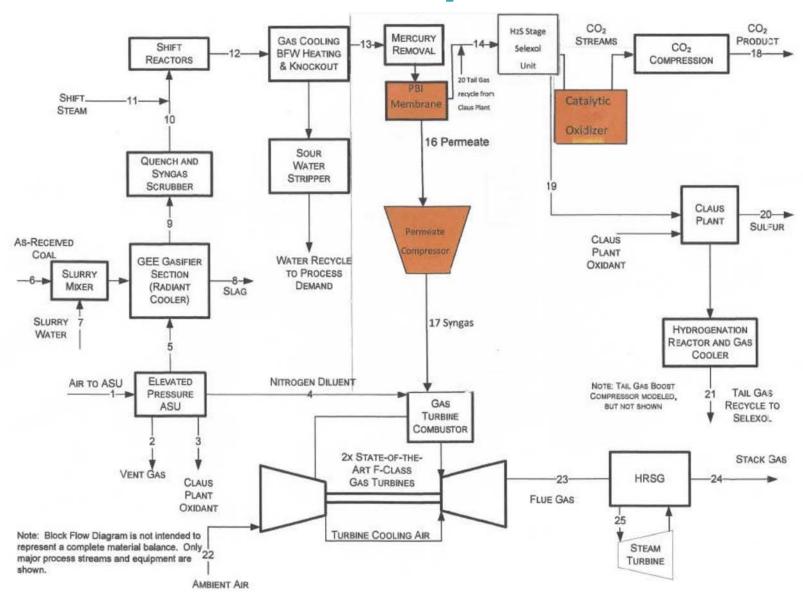
### **Characteristics of PBI Membranes**

- Attractive combination of throughput (permeance) and separation (selectivity)
- Thermally stable up to ~ 300°C and sulfur tolerant
- Tested up to 225°C with simulated gases and with real syngas

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# **PBI** Membrane Integration

### Modification of Case B5B, GEE IGCC with CO<sub>2</sub> Capture



# **Techno Economic Analysis**

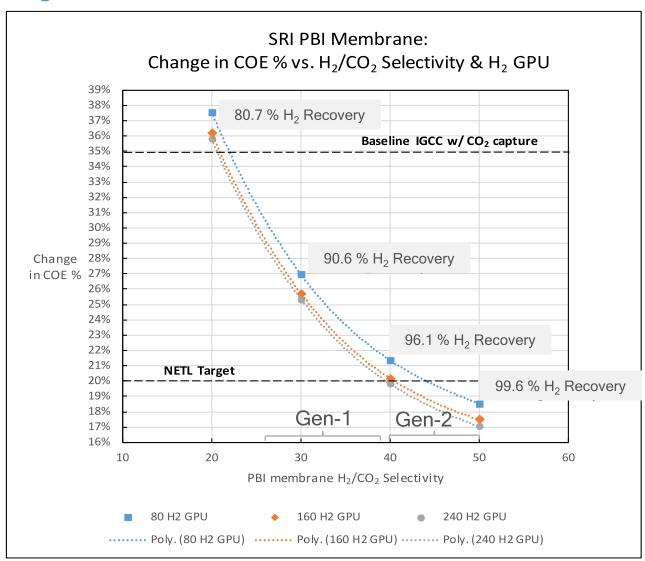
### **Developed by Enerfex**

Case Name	IGCC-B1A Baseline No Capture	IGCC-B5B <sup>1</sup> Baseline CO <sub>2</sub> Capture	Gen-1 Membrane CO <sub>2</sub> Capture	Gen-2 Membrane CO <sub>2</sub> Capture				
CO <sub>2</sub> removal	No	Selexol	PBI me	mbrane				
CO <sub>2</sub> purification	N	<b>1</b> 0	Ye	es				
Sulfur removal	Sulfinol		Selexol					
	Performance	and Economic S	ummary					
H <sub>2</sub> /CO <sub>2</sub> Selectivity	n/a	n/a	40	50				
H <sub>2</sub> GPU	n/a	n/a	80	80				
CO <sub>2</sub> capture	n/a	92.25%	90.0%	90.0%				
CO <sub>2</sub> purity	n/a	99.48%	95.6%	95.6%				
H <sub>2</sub> recovery	n/a	99.98%	96.1%	99.6%				
HHV plant efficiency	42.1%	32.6%	32.6%	34.4%				
LHV plant efficiency	43.7%	33.8%	33.8% 35.6%					
COE w/o T&S (\$/MWh)	\$107	\$135	\$121	\$118				
COE w/ T&S (\$/MWh)	\$107	\$144	\$130 \$127					
% Increase in COE	0.0%	34.9%	21.3% 18.5%					

Cost and Performance Baseline for Fossil Energy Plants Volume 1b: Revision 2b, July 31, 2015

# COE vs H<sub>2</sub>/CO<sub>2</sub> Selectivity and H<sub>2</sub> GPU

90% CO, Capture



# Reduced CO<sub>2</sub> Capture Options:

- 40 selectivity and 100
   GPU recovers 99% H<sub>2</sub>
   with 88% CO<sub>2</sub> capture
- 25 selectivity and 150
   GPU recovers 99% H<sub>2</sub>
   with 82 % CO<sub>2</sub> capture

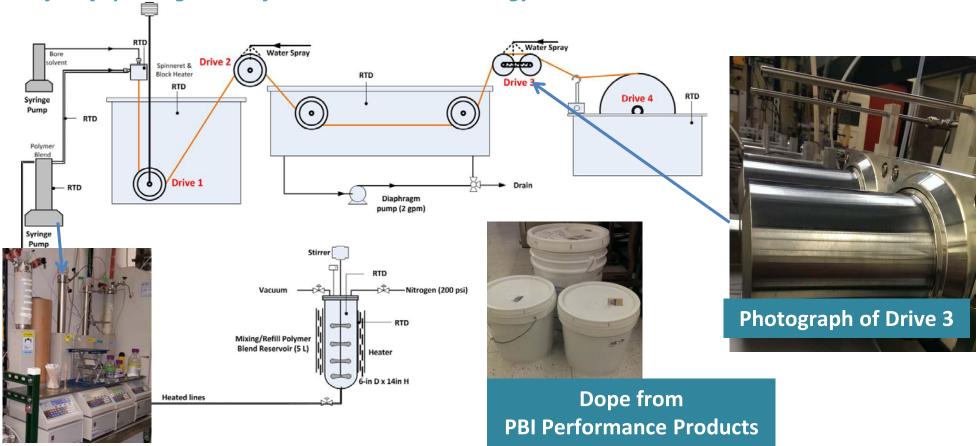
T= 225°C, Pressure ratio= ~12

Illustration of the reduction in COE in moving from Gen-1 to Gen-2 performance.

# Advancements in Spinning Kilometer Lengths of Asymmetric PBI Hollow Fibers with Minimal Defects

# First Spinning Line Installed at SRI in 2015

Transfer of spinning hollow fibers critical to Technology Maturation



The new spinning line was crucial for developing an improved and robust spinning process that can be transferred to industry. The line enabled:

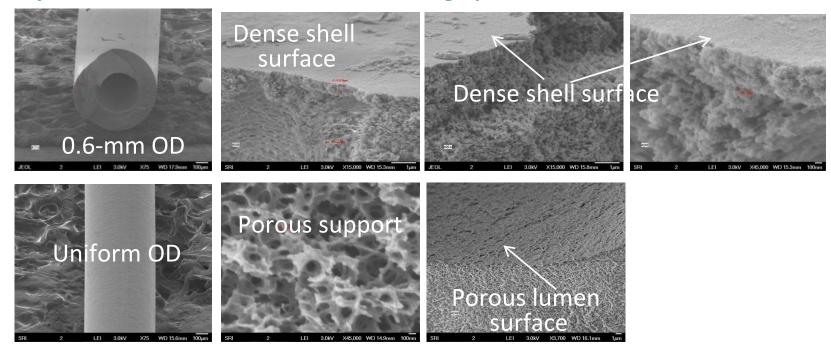
- Use of multiple coagulation solvents
- Increased productivity (1 gal reservoir)
- Process monitoring and data collection
- Precise flow controls and draw ratios

- Optimization of fiber diameter
- Optimization of the fiber dense-layer thickness

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# **Fabrication of Fibers with Good Reproducibility**

Quality control is the KEY to success when scaling-up



- Developed protocols for spinning < 0.3- $\mu$ m dense layer hollow-fiber membranes with membrane OD 450 to 650  $\mu$ m. ABOVE: ~ 0.1- $\mu$ m fibers with ~ 600- $\mu$ m OD.
- Tested more than 100 fiber bundles (1-in) for fiber-spinning optimization of OD and dense layer
- Fabricated Gen-1 hollow-fiber membrane with a very thin, dense layer (< 0.3  $\mu$ m) in kilometer lengths with very good reproducibility
- Spun > 100 km of Gen-1 fibers for both Generon and SRI modules (4-in)

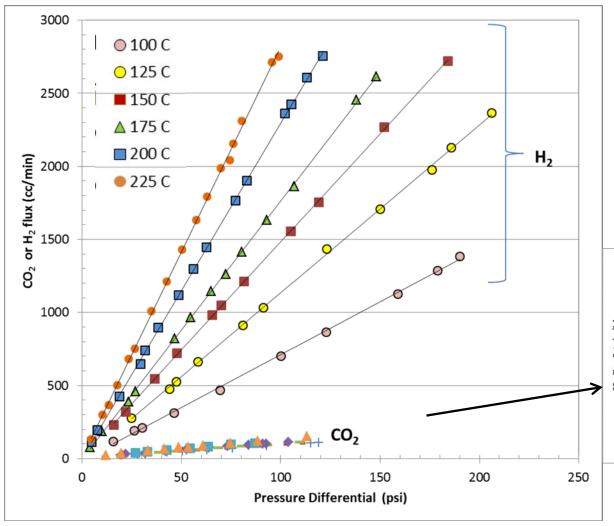
### **Achievements:**

- Dense-layer thickness reduced from 1  $\mu$ m to < 0.3  $\mu$ m
- Fiber diameter reduced from 1 mm to less than 600 μm

### Gen-2:

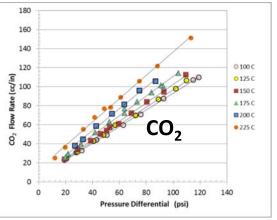
0.5 μm dense layer Reduced defect potential

# **PBI Fiber Withstands High Pressures & High Temperatures**



### **Mixed Gases**

	Selectivity					
H <sub>2</sub> /CO <sub>2</sub>	40					
$H_2/N_2$	98					
H <sub>2</sub> /CO	103					
H <sub>2</sub> /H <sub>2</sub> S	>200					
225 °C and 200 psi ΔP						



Observation:  $H_2/CO_2$  selectivity increases with temperature up to 225 ° C.

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# Fabrication of Large Modules at SRI: 4-inch



Photograph of 5000 fibers (5 m<sup>2</sup>) arranged for potting at SRI



4-in sleeve for fiber potting



Potted 4-in fiber module cross-section (early design)

SRI fiber modules are designed for:

- -Easy fabrication
- -Easy handling
- -Easy drop-in replacement

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# **Critical Asset: Membrane Testing Skid**

Installed and Tested at the NCCC



Photograph of the skid installed at the NCCC (April 2017)



Photograph of the skid installed at SRI (December 2018)

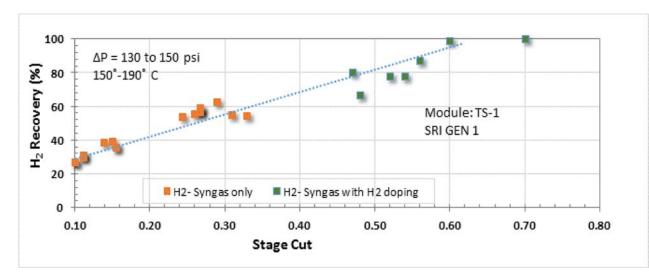
- PBI membrane skid transferred to the NCCC in March 2017
- Test campaign at NCCC conducted in April 2017 at 50 kWth scale
- Skid was removed from the host-site and returned to SRI in March 2018 for inspection and preservation
- Skid will be used in current work

### **Test Results at NCCC**

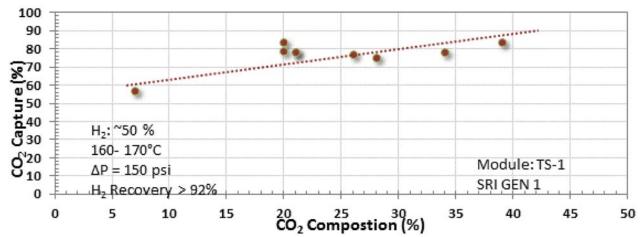
### Air-blown Gasifier

### Sample parametric matrix

Test Parameter	Range	Unit
Temperature	80 to 215	°C
Pressure	50 to 170	psig
Gas composition	Variable	slpm
Stage cut	0.2-0.7	
H <sub>2</sub> in syngas	12 to 50	%
CO <sub>2</sub> in syngas	5 to 40	%

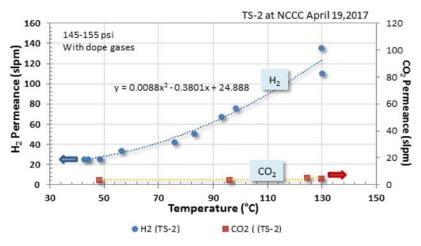


Observed hydrogen recovery with varying stage cuts in the temperature range  $150^{\circ} - 190^{\circ}$ C and pressure differentials of 130 to 150 psi for the syngas-only condition and for syngas with doped with H<sub>2</sub>

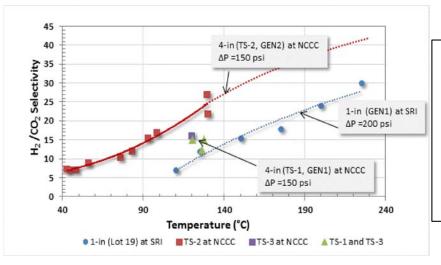


Observed  $CO_2$  capture with varying feed  $CO_2$  composition under fixed hydrogen composition at the temperature range 150 – 190°C and a pressure differential ~ 150 psi for the TS-1 membrane

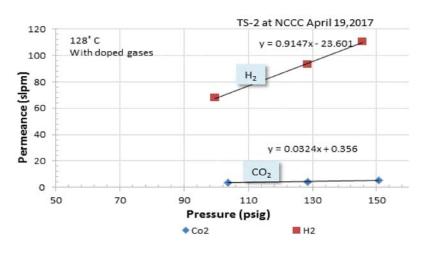
# **Gen-2 at NCCC: Temperature and Pressure Effect on Permeance**



Measured H<sub>2</sub> and CO<sub>2</sub> permeances at the NCCC for the TS-2 (GEN-2) module at varying temperatures under a pressure differential of 145 to 155 psi.



Comparison of measured H<sub>2</sub>/CO<sub>2</sub> selectivity for GEN-1 and GEN-2 modules



Measured H<sub>2</sub> and CO<sub>2</sub> permeances at the NCCC for the TS-2 (GEN-2) module with varying pressures at 128°C

### **Modules tested at NCCC:**

- Membrane element TS-1 consisting of SRI GEN-1 fibers (GPU $^{\sim}$ 150, H<sub>2</sub>/CO<sub>2</sub> selectivity  $^{\sim}$  25 at 150 $^{\circ}$ C) for  $^{\sim}$  500 hr
- Membrane element TS-2 consisting of SRI GEN-2 fibers (GPU  $^{\sim}$  100 , H $_2$ /CO $_2$  selectivity  $^{\sim}$  40 at 200°C, 200 psi) for  $^{\sim}$  48 hr

Performance of GEN-2 at SRI: GPU  $\sim$  80,  $H_2/CO_2$  selectivity  $\sim$  50 at 200°C, 200 psi)

# **Current Project Details**

# **Project Budget and Team for DE-FE0031633**

# Cooperative agreement grant with U.S. DOE Period of Performance:

BP1: 10-1-2018 to 03-31-20

- BP2: 04-01-20 to 09-30-21

### Funding:

- U.S. Department of Energy: \$2.007 million
- Cost share: \$0.505 million (20.1%)
- Total: \$2.512 million

### NETL Project Manager:

Andrew Jones

### **NETL**

Funding and technology oversight

### SRI

- Gen-2 PBI membrane Spinning
- Module fabrication
- Skid installation & testing

### **PBI Performance Products, Inc.**

PBI Dope and industry perspective

### Enerfex, Inc.

 Membrane system modeling and Technoeconomic analysis

### **Energy Commercialization**

Commercialization analysis

### **UKy CAER**

Gasifier facility test site

Current Spending: \$222,527 ( as of 27 July 2019)

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# **Project Objectives**

- Demonstrate that Gen-2 PBI based hollow fiber membranes provide a pathway to achieving DOE's pre-combustion capture targets
  - Bench-scale testing (50 kWth) of Gen-2 with actual syngas feed stream from an OXYGEN BLOWN gasifier
  - Evaluate Techno-economics based on bench-scale test results
- Leverage assets and knowledge generated from previous projects
  - PBI Hollow fiber membrane spinning line
  - Potting of fibers
  - Construction of modules based on PBI fibers
  - Test skid utilized for testing Gen-1 (50 kWe) at the NCCC on an AIR BLOWN gasifier
  - Production of Gen-2 fibers with improved selectivity over Gen-1

# **Project Tasks**

# **Budget Period 1**

Task #	ВР	Task	Status
1	1	Project Management and Planning	On going
1	1	Preliminary Technology Maturation Plan Program Management Plan Preliminary TEA	Submitted
1	1	Installation of Partner Agreements and Sub-awards	Completed
2	1	Modification of the 50 kWth Test Unit - Refurbish and upgrading of the existing skid system - Fabrication of Gen-2 Fibers - Module design and installation of the Modules (4 to 6-in diameter) - Membrane performance testing at SRI - HAZOP and PI&D Review at CAER	Started
3	1	Modeling - Modeling of the Module arrangement - Modeling of the skid performance - Preliminary TEA	Started

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# **Project Tasks**

# **Budget Period 2**

Task #	ВР	Task	Status
4	2	Operation of the Test Unit at a Field -Skid Transport and Installation at the Site - Development of a test plan - Operation of the skid and data collection - Analysis of the data form the skid	Not Started
5	2	EH&S, TEA and other Related Reports  - Techno-Economic Analysis  - Update the State Point Data Table  - Technology Gap Analysis  - Preparation of Technology Maturation Plan  - Environmental Health and Safety Assessment (EH&S)	Not Started
6	2	Skid Decommissioning - Skid decommissioning and Transport - Skid Postmortem and Storage	Not Started

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# **Project Milestone Plan**

### **Budget Period 1**

Task/ Subtask	Milestone Description	Planned Completion	Status	Verification Method
1	Updated PMP	10/31/2018	Completed	PMP file
1	Kick-off Meeting	1/31/2019	Completed	Presentation file
1	Technology Maturation Plan	12/31/2018	Completed	TMP file
3.3	Completion and submission of preliminary TEA	12/31/2018	Completed	Topical report
2.1 to 2.3	Complete the production of at least 100 km of Gen-2 fibers that provide a $\rm H_2/CO_2$ selectivity of about 40 and $\rm H_2$ permeance of 80-120 GPU at > 150°C at a 150 psi pressure differential	11/30/2019	Started	Results reported in QR
2.1	Completion of the updated Basic Engineering Design package for modification of 50 kWth skid	12/30/2019	Started	Results reported in QR
2.1 to 2.4	Completion of bench skid acceptance testing for 50 hrs at SRI and achieve $H_2/CO_2$ selectivity > 35	3/31/2020	Not started	Results reported in QR

We are on schedule to complete the project milestones

# **Project Tasks and Schedule**

BP1: 18 months BP2:18 months			BP1 BP2																							
			10/1/18 1/1			1/1/19		4/1/1	9	7/1/19	10/1/19	1/1/20	4/	4/1/20		7/1/20		20	0 1/1/21		4/1/21		7/1/21		12/31/21	
Task	Start Date	End Date		Q1 Q2		Q3 Q4		Q4 Q5		Q6		Q7	Q8		Q9		Q10		Q11		Q12					
Development and Testing of a High Temperature PBI Hollow Fiber Membrane Technology for Pre-Combustion CO2 Capture	10/1/2018	9/30/2021																								
Task 1.0 (BP1 & BP2) - Project Management and Planning	10/1/2018	9/30/2021																								
Subtask 1.1 - Project coordination and reporting	10/1/2018	9/30/2021																								
Subtask 1.2 - Preparation and Submission of Continuation Report	3/1/2021	3/31/2020				П										П								$\Pi$		
Milestones			а	b c	Т	П						f, h	h			П		П						$\Box$		
Task 2.0 (BP1): Modification of the 50 Kwth Test Unit for the Field Test	10/1/2018	3/31/2020														П		П						$\Pi$	П	
Subtask 2.1 - Refurbish and upgrading of the existing skid system	10/1/2018	8/31/2019				$\Box$																		$\Pi$		
Subtask 2.2 - Fabrication of SRI Generation 2 (GEN 2) Fibers	1/1/2019	3/31/2020	П																					$\Pi$		
Subtask 2.3 - Module design and installation of the Modules (4 to 6-in diameter)	4/1/2019	3/31/2020	П		Т	П									$\sqcap$	П		П		T			$\top$	$\sqcap$		
Subtask 2.4 - Membrane performance testing at SRI	1/1/2019	3/31/2020	П													П							$\top$	$\Box$	$\Box$	
Subtask 2.5 - HAZOP and PI&D Review at CAER	4/1/2020	3/31/2020				П									Ħ								$\top$	$\Box$	ΠŤ	
Milestones						Ħ						d,	ė.		Ħ								$\top$	$\Box$	ΠŤ	
Task 3.0 (BP1) -Modeling	10/1/2018	3/31/2020																					$\top$	$\Box$	П	
Subtask 3.1 - Modeling of the Module arrangement	1/1/2019	3/31/2020	П			П									Ħ								T	$\Box$	ΠŤ	
Subtask 3.2 - Modeling of the skid performance	4/1/2019	3/31/2020	П		Т	П									Ħ	T		П					$\top$	$\Box$		
Subtask 3.3 - Preliminary TEA	10/1/2018	12/31/2018				П																	$\top$	$\Box$	П	
Milestones			П			П						g												$\Box$		
Task 4.0 (BP2) - Operation of the Test Unit at a Field Site	4/1/2020	9/30/2021																								
Subtask 4.1 -Skid Transport and Installation at the Site	4/1/2020	3/31/2021	П			П									П			П					Т	П	П	
Subtask 4.2 - Development of a test plan	10/1/2020	12/31/2020				$\Box$																		$\Pi$	П	
Subtask 4.3 - Operation of the skid and data collection	1/1/2021	3/31/2021																						$\Pi$		
Subtask 4.4 - Analysis of the data form the skid	1/1/2021	6/30/2021	П			П												П						$\Box$	П	
Milstones			П			П										П		i	li		k		$\top$	$\Box$	П	
Task5.0 (BP2) - EH&S, TEA and other Related Reports	1/1/2021	9/30/2021				Ħ												Ĺ						П		
Subtask 5.1 - Techno-Economic Analysis	1/1/2021	6/30/2021				Ħ									Ħ			П					T	Ħ	ΠŤ	
Subtask 5.2 - Update the State Point Data Table	7/1/2021	9/30/2021	П		T	$\top$	7								Ħ	T		П						П		
Subtask 5.3 - Technology Gap Analysis	7/1/2021	9/30/2021	П			П										П								П	$\Box$	
Subtask 5.4 - Preparation of Technology Maturation Plan	10/1/2018	12/31/2018				П										П		П						$\Box$	П	
Subtask 5.5 - Environmental Health and Safety Assessment (EH&S)	7/1/2021	9/30/2021																П								
Submit the State Point Data Table	9/1/2021	9/30/2021																								
Submit the Technology Gap Analysis	9/1/2021	9/30/2021																								
Submit the Technology Maturation Plan	9/1/2021	9/30/2021																								
Milestones			Ш			Ш										Ш		Ш					m	,n,o,p	ρ	
Task 6.0 (BP2) - Skid Decommissioning	9/1/2021	9/30/2021	Ш		L	Ш					$oxed{oxed}$		Ш		$oxed{oxed}$	Ш	oxdot	Ц							$oldsymbol{\sqcup}$	
Subtask 6.1 - Skid decommissioning and Transport			Ш			Ш			Ш	$\bot \bot$			Ш		$\sqcup \!\!\!\! \perp$	Ш	oxdot	Ц	$\bot$				$\bot$	Ш	Щ	
Subtask 6.2 - Skid Postmortem and Storage			Ш			Ш			Ш	$\perp \! \! \perp$			Ш	_	$\sqcup$	Ш	$\sqcup \!\!\!\! \perp$	Ш	$\bot \bot$			$\perp \downarrow \downarrow$	$\bot$	Щ	$\vdash$	
Milestones			$\sqcup$		$\perp$	$\sqcup$	4	_	Ш	$\bot \bot$	+++	$\sqcup \bot \bot$	$\perp$		$\sqcup$	Ш	$\sqcup \!\!\!\! \perp$	Н	$\bot \bot$	$\bot$	$\perp$	$\perp \downarrow$	$\bot$	$\bot$	q,	
Project Reviews	40/4/005		Н			$\sqcup$	_		Ш	$\bot \bot$			$\bot$	_	$\perp \perp$	Ш	$oxed{oxed}$	Н	$\perp$	$\bot$		$\perp$	$\perp$		$\perp$	
Final Report Submission	10/1/2021	12/31/2021	Ш			Ш			Ш						$oldsymbol{ol}}}}}}}}}}}}}}}}}}$	Ш	oxdot	Ш				Ш	丄		ىل	

# **UKy-CAER Pilot Facility**

### **Gasification Unit**

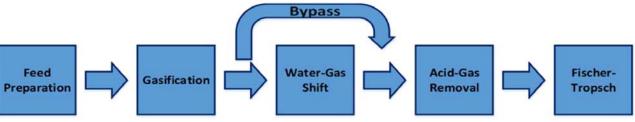
- Multi-burner, entrained flow, oxygen blown, slagging type
- 1 ton/day coal consumption
- Syngas production rate: ~80 m³/hr
- $H_2/CO: \sim .80$

### Water-Gas Shift

- Packed bed
- Sulfur tolerant sour shift catalyst
- $H_2/CO$ : up to 11/1

### **Syngas Compressor**

- Metal Diaphragm
   Compressor
- 450 psi max outlet pressure



Gasifier



Gasifier Operating Parameters							
Temperature (°C)	1350						
Pressure (MPag)	0.1						
CWS Solid (%)	53.0						
Syngas (vol%)							
H <sub>2</sub>	24.51						
$N_2$	2.93						
СО	28.94						
CO <sub>2</sub>	40.89						
H <sub>2</sub> O	2.54						
H <sub>2</sub> S	0.18						
COS	0.02						





**Compressor** 



# **Current project work update**

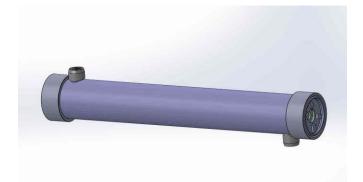
# **Improved Module Design**

Reliable fiber module performance enables maximum collection of high-quality data at UKy-CAER

Previous tube sheet module design



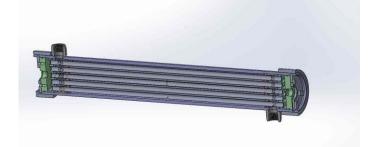




New tube sheet module design



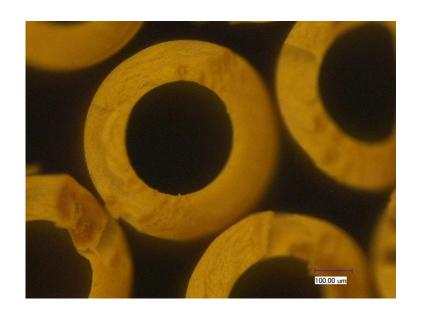




Fast module swapping and reduced gas bypass

# In Progress: Production of Gen-2 Fibers

Reproducible spinning process to provide abundant hollow fibers for installation in skid

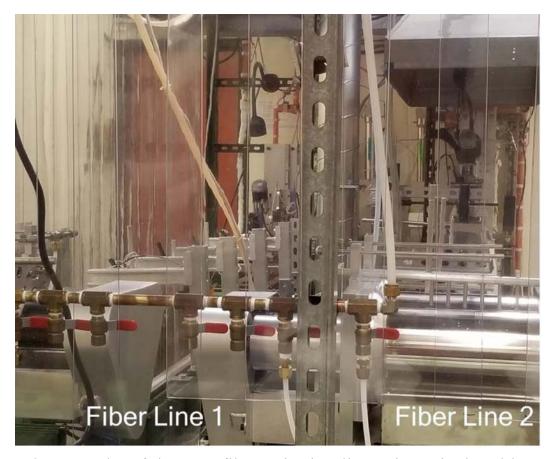




# >10 km Gen-2 fibers produced to date

# A Second Spinning Line Installed at SRI in 2019

Transfer of spinning hollow fibers critical to Technology Maturation



Photographs of the new fiber spinning line. Line 1 is the old line, and Line 2 is the newly installed line.

# **Fiber Spinning Capacity Doubled**

# **Technology Maturation**

# **DOE Funding: Critical to Technology Maturation**

DOE enabled "first-of a kind" hollow fiber membranes of PBI in kilometer lengths

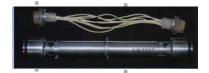
### **Accomplishment**

DE-FC26-07NE43090

Producing Gen-1 PBI based membrane modules

Testing POTTED Gen-1 fiber bundles

Surface area ~ 100 cm<sup>2</sup>



Produce first ever porous hollow fiber membranes of PBI that were kilometers in length AND minimal defects

Dope preparation

High temperature potting

Accomplishment

DE-FE0012965

Producing and testing Gen-1 based membrane modules at NCCC

Developing Gen-2 PBI based fibers

Surface area ~ 5 m<sup>2</sup>



Consistent multi-fiber
bundles that are
kilometers in length of
Gen-1 and Gen-2 with
minimal defects

In Progress

DE-FE0031633

Producing and testing Gen-2 based membrane modules at UKy-CAER

Higher selectivity and new module design

Surface area ~ 20 m<sup>2</sup>



Doubled spin capacity

Production of 100 km of Gen-2 with minimal defects

Figure 22. To about pint between 18 growth and 18 conditions the pint between 18 growth and 18 conditions and 18 conditions and 18 conditions are pint between 18 growth and 18 conditions are pint between 18 conditions are pint

Testing single

tubes

Surface area ~ 10 cm<sup>2</sup>

**Membranes** 

prepared by coating
PBI on porous
metal substrates

LANL demonstrates
PBI is attractive for
pre-combustion
applications

# Acknowledgements

- Andrew Jones, Jose Figueroa, Elaine Everitt, Lynn Brickett, and others at NETL
- Indira Jayaweera (Principal Investigator), and the rest of the SRI team:
   Srini Bhamidi, Regina Elmore, Xiao Wang, William Olson, Gopala Krishnan, Milad
   Yavari, Palitha Jayaweera and Chris Lantman
- Richard Callahan (Enerfex, Inc.)
- Kevin O'Brien (Energy Commercialization, LLC)
- Greg Copeland and Mike Gruende (PBI Performance Products)
- Kunlei Liu and his team (UKy- CAER)
- John Jensvold and his team (Generon IGS)
- The staff at the NCCC

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### **SRI International**

**Contact:** 

Dr. Indira Jayaweera

indira.jayaweera@sri.com

1-650-859-4042

Headquarters
333 Ravenswood Avenue
Menlo Park, CA 94025
+1.650.859.2000

Additional U.S. and international locations

www.sri.com

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