Membrane and Solvent Development for Pre-Combustion Carbon Capture

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U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

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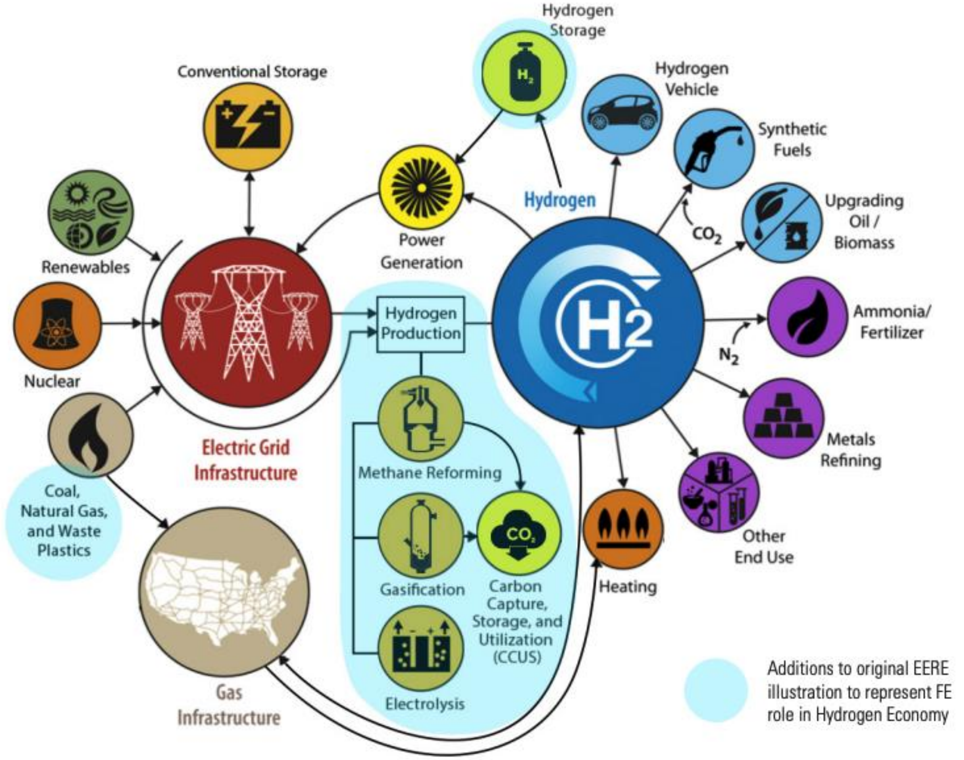
H_2 production & Pre-combustion CO_2 capture

- Demand for H_2 is growing for applications including power, fuels, and chemicals
- Gas reforming and coal gasification are the main technologies for H_2 production today
- CCUS is required to reduce these emissions

- Blue Hydrogen includes H_2 produced from steam methane reforming of natural gas with carbon capture and storage (SMR-CCS)
- Carbon capture options for SMR-CCS can include pre-combustion **membranes** and **solvents**



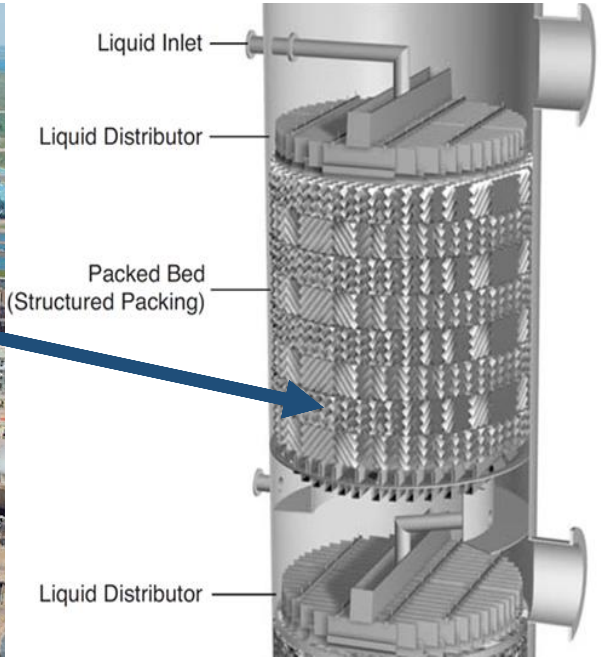
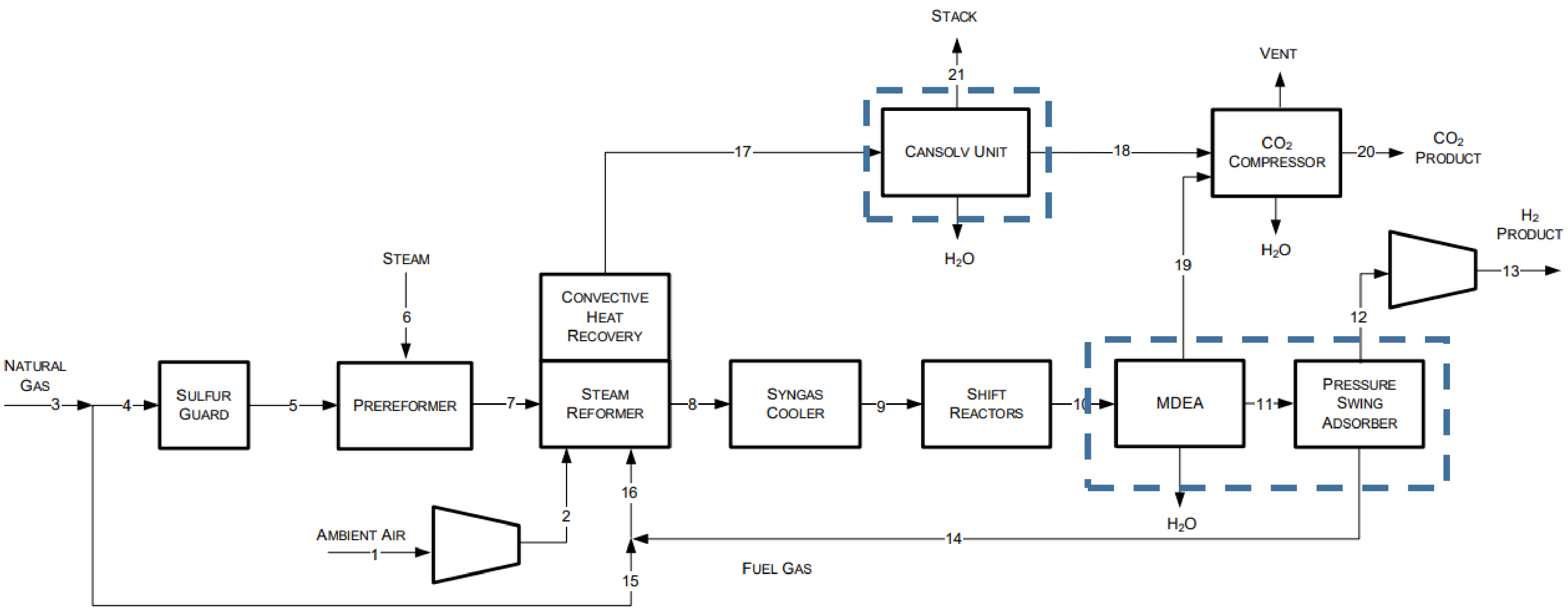


Fig.1 from: https://netl.doe.gov/sites/default/files/2020-12/USDOE_FE_Hydrogen_Strategy_July2020.pdf
Plant image from: https://dakotagas.com/sites/CMS/files/images/home-hero/DGC-aerial-homepage.jpg

NETL SMR-CCS Baseline vs. Proposed R&D

Exhibit 3-17. Case 2 block flow diagram, steam methane reforming plant with CO_2 capture



NETL Baseline study has both pre- and post-combustion CO_2 capture using amine solvents

We propose a pre-combustion-only capture option using a hybrid process with H_2 selective membranes and CO_2 selective solvents.

Hybrid Pre-combustion Capture for Flexible SMR-CCS Operations

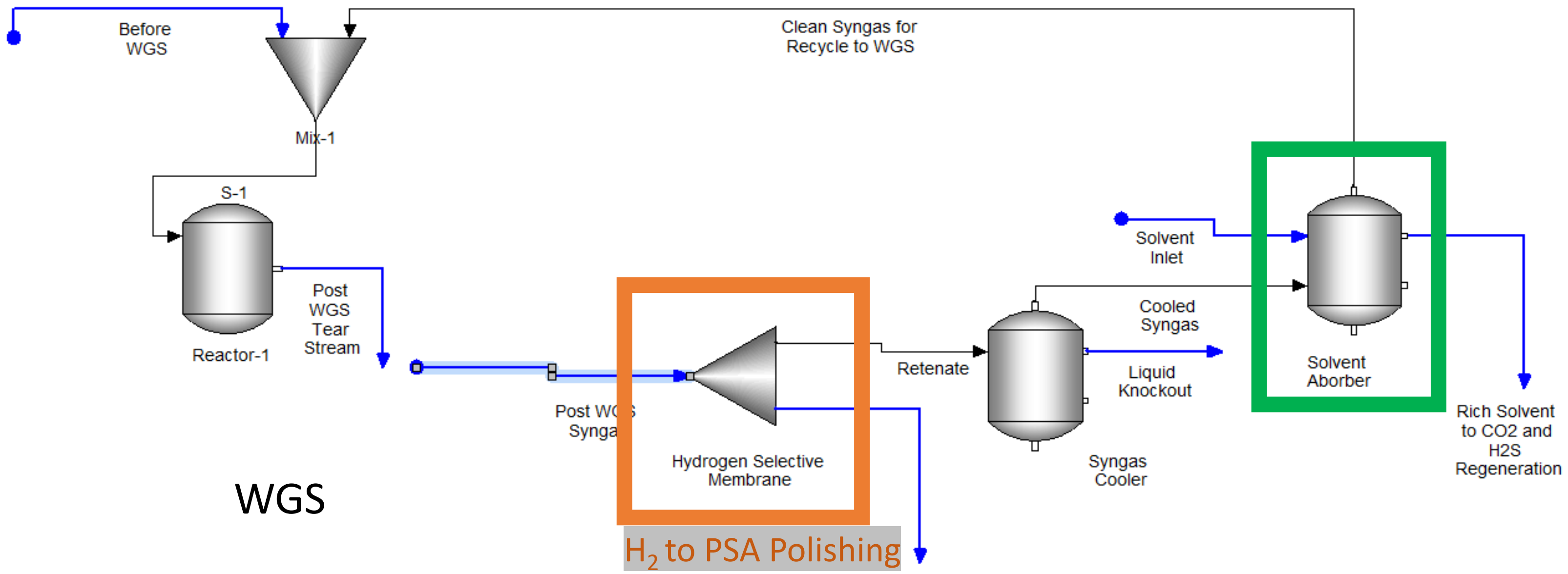
Upstream H_2 selective membrane & Novel Phys-Chem CO_2 selective solvent

Overall objective: Demonstrate small-scale modular pre-combustion CO_2 capture processes by combining H_2-selective membranes with CO_2 selective solvents for H_2 generation from SMR.

What is unique about SMR-CCS compared with previous pre-combustion capture?

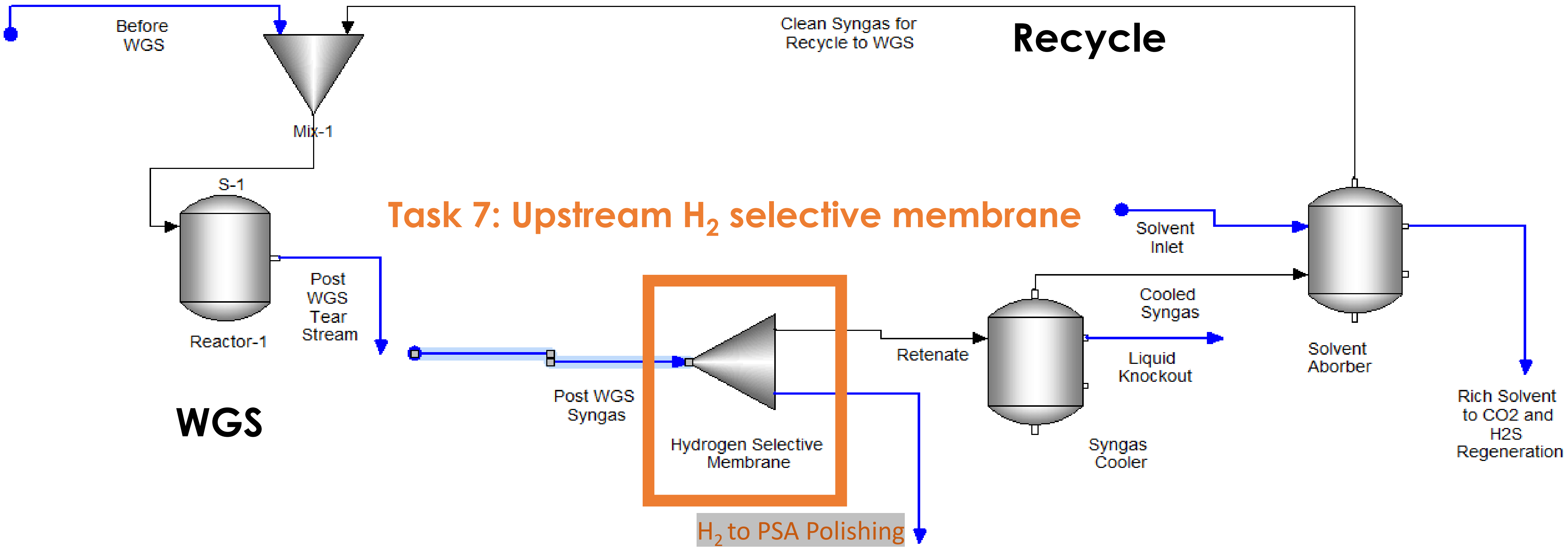
- CO_2 gas partial pressure is lower than for IGCC-CCS (~5 bar vs. ~25 bar)
- Purity requirements are typically high at >99.9% H_2 (i.e. very low contaminant specifications)

➢ Combine **H_2-selective membranes** & novel **phys-chem solvents** (developed by NETL/RIC)

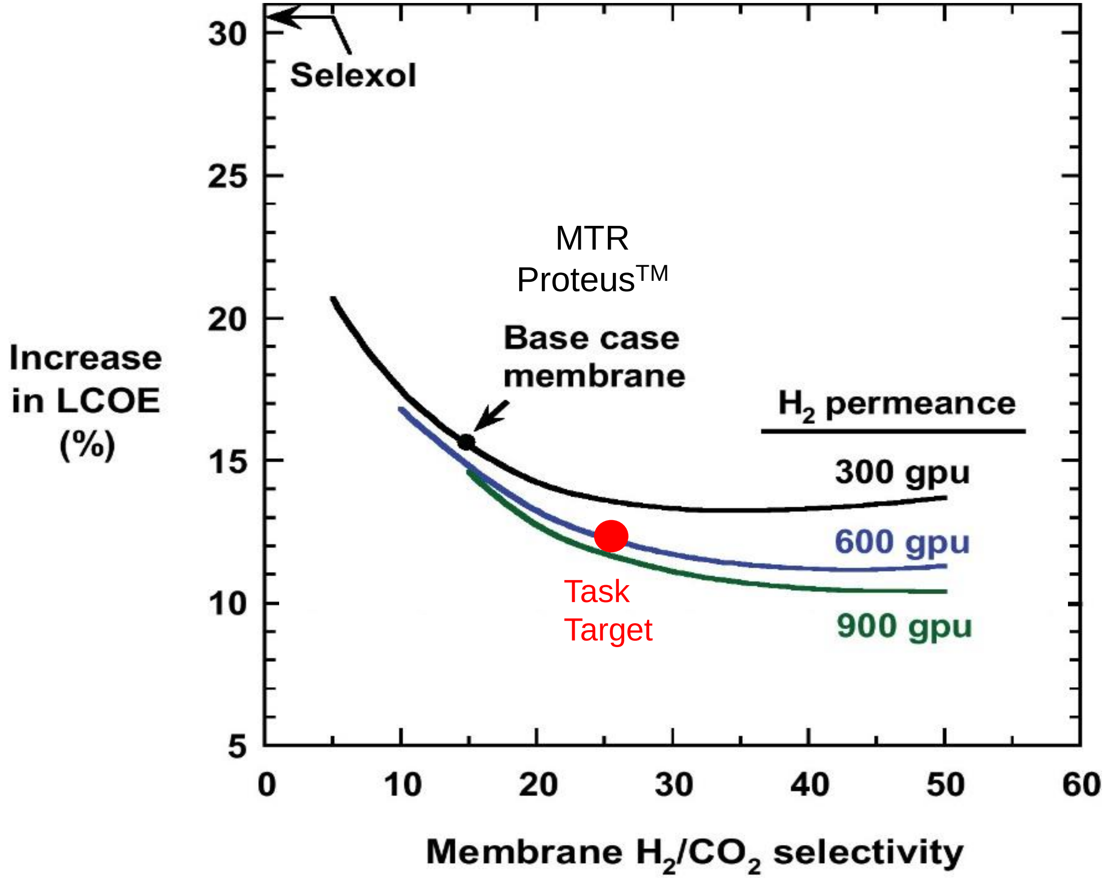


H_2-Selective Membrane Development

Objective: To scale up H_2 selective membranes with H_2 permeance of ≥ 600 GPU and H_2/CO_2 selectivity of ≥ 25, outperforming commercially-available H_2-selective membranes (~300 GPU and ~15 selectivity).

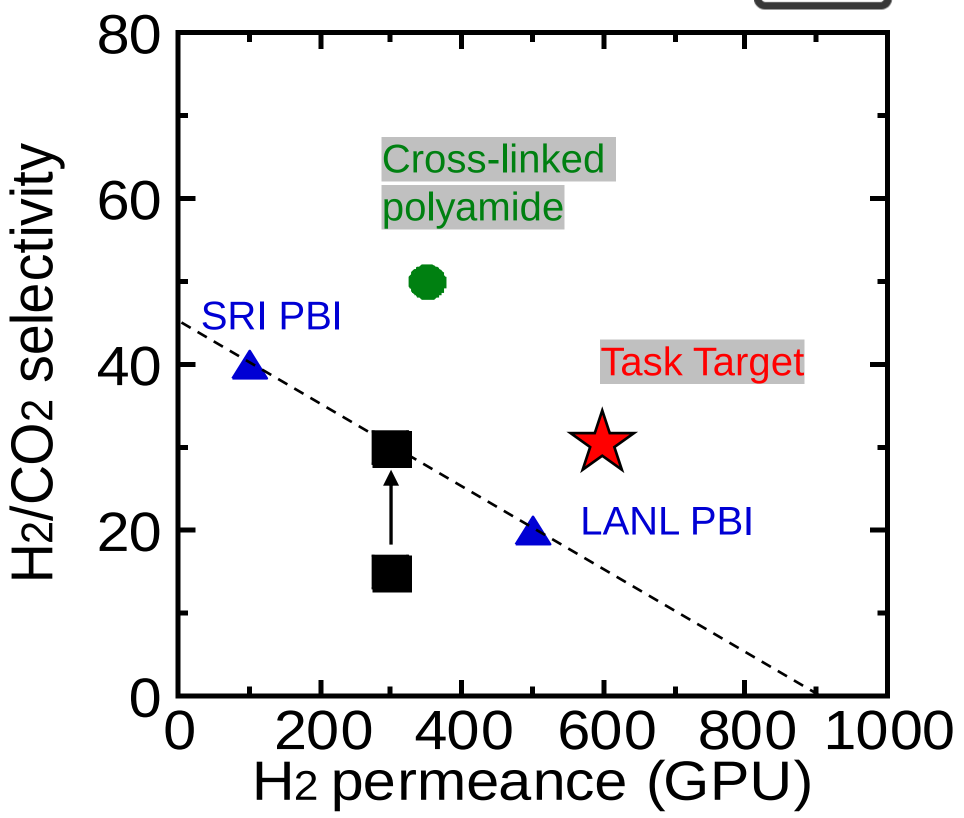


Existing H_2 selective membrane research from literature



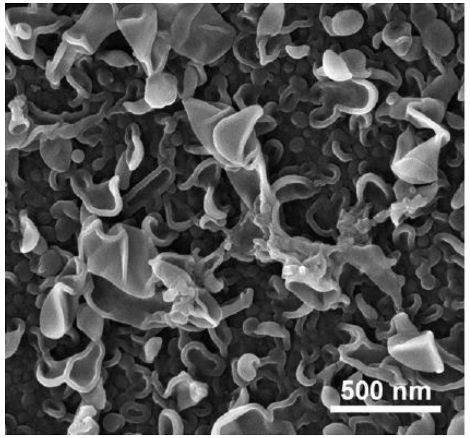
J. Membr. Sci., 2012, 389, 441

MTR
Proteus
@ 150 °C



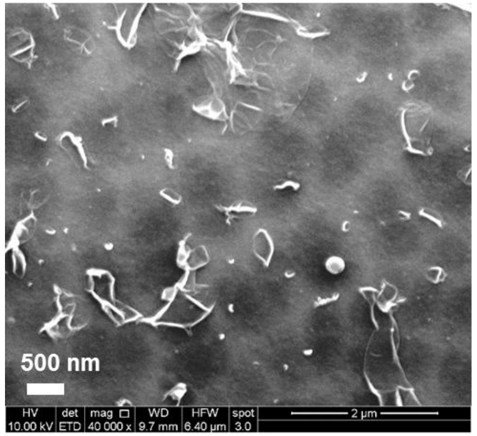
1. *J. Mater. Chem. A*, 2018, 6, 30
2. SRI PBI: https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jayaweera_0.pdf
3. LANL PBI: US patent 2016/0375410 A1
4. Proteus: https://www.netl.doe.gov/sites/default/files/2018-12/DOE-FE0031632-Project-Kickoff.pdf and 1878227 (osti.gov)

H_2-Selective Membrane Development



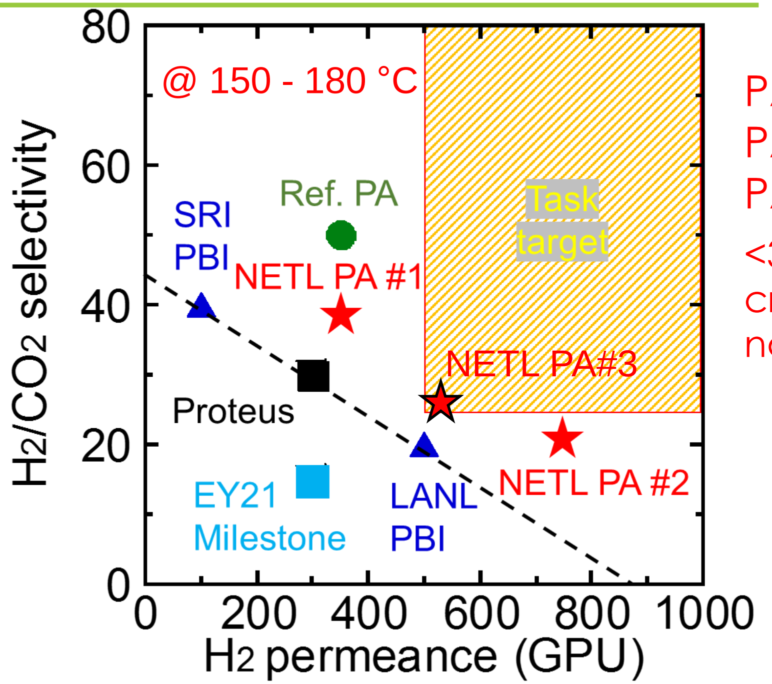
Reference: *J. Mater. Chem. A*, 2018, 6, 30

Rough surface with a polyamide thickness of **100 – 300 nm**

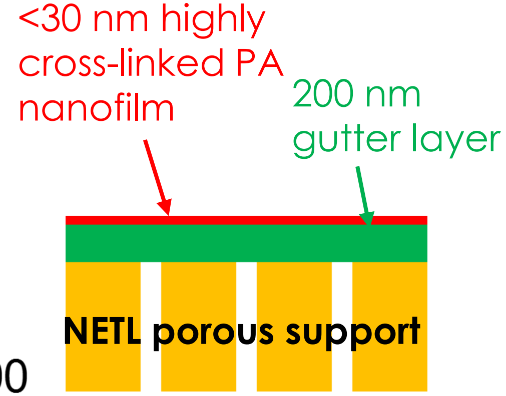


This study

NETL polyamide membranes (**NETL PA**): Smoother surface with a polyamide thickness of **<30 nm**



PA#1 avg. = 26 nm
PA#2 avg. = 15 nm
PA#3 avg. = ~20 nm



Accomplishments

- Demonstrate a polyamide composite membrane with mixed-gas H_2 permeance of ≥ 500 GPU and H_2/CO_2 selectivity of ≥ 25 at 100–250°C, showing no obvious aging for 50 hours.
  [Completed: NETL PA#3 530 GPU + 25.2 selectivity]
- Demonstrate a polymeric composite membrane with mixed-gas H_2 permeance of ≥ 600 GPU and H_2/CO_2 selectivity of ≥ 25 at 100–250°C.
  [In progress]

Novel Phys-Chem CO_2-Selective Solvent

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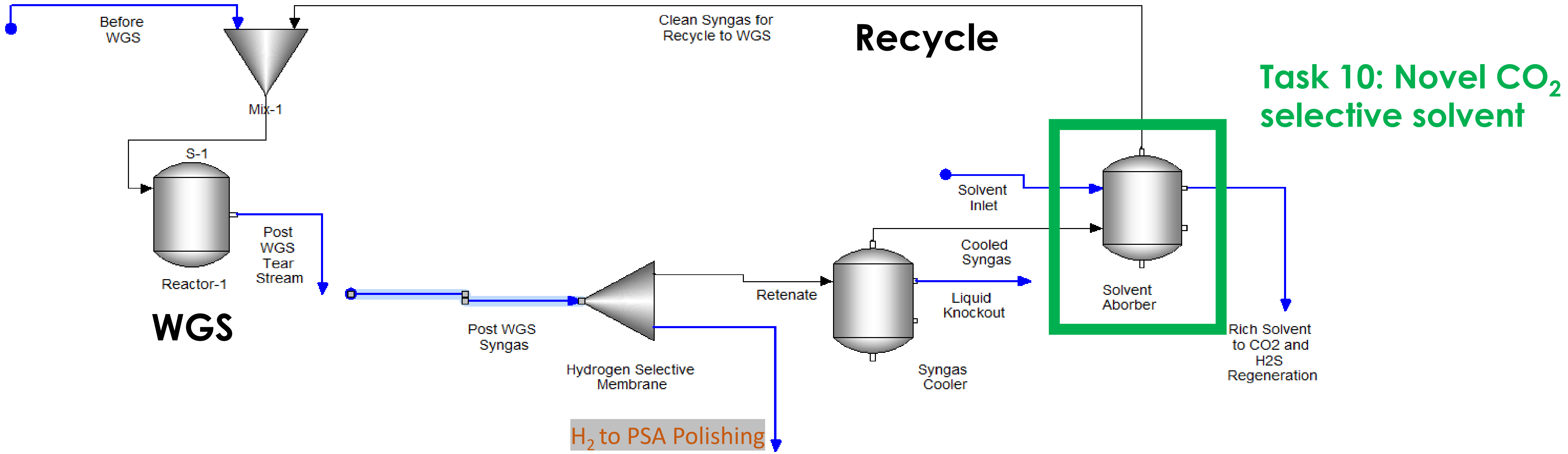
Objective: Determine optimal solvents for SMR-CCS using economic screening, ultimately leading down-selection of solvents and operating conditions for scale-up and higher TRL demonstrations.

Method: Regress experimental solvent properties into Aspen Plus, run model simulations for SMR-CCS with cost estimates, and then use an Artificial Neural Network (ANN) to find optimal solvents and operating conditions for SMR-CCS.

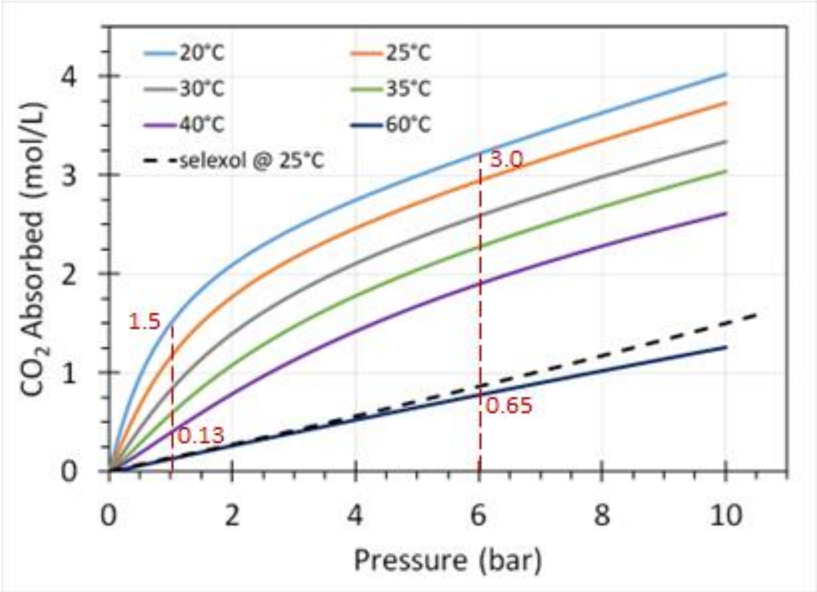


Identification of Optimal Solvents for SMR-CCS

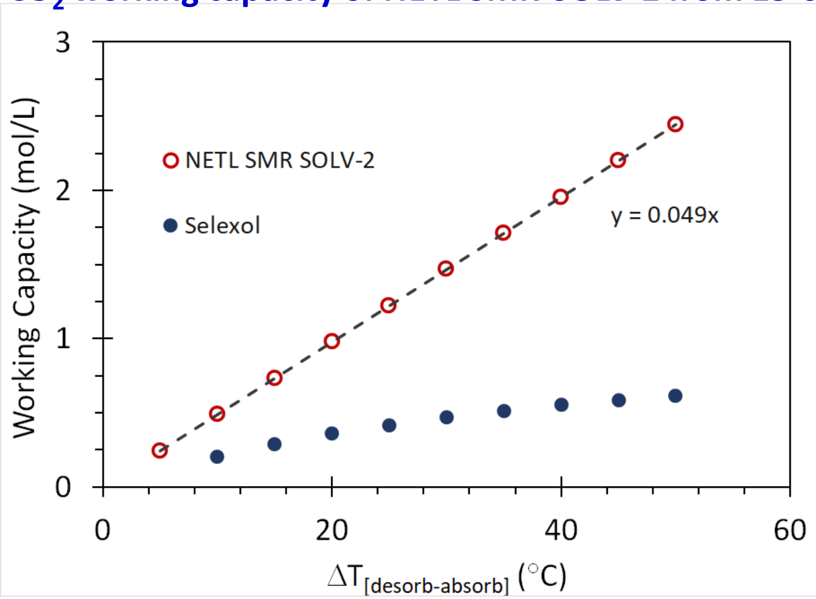
NETL sterically-hindered-amine non-aqueous solvents

- High boiling, low vapor pressure solvents with viscosities at 25°C < 10cPs
- CO_2 absorption behavior tuned by manipulation of the solvent molecular structure

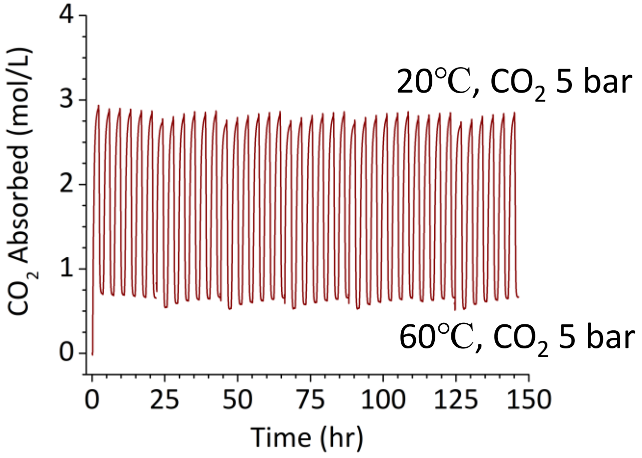
CO_2 absorption isotherms: SMR-SOLV-1 vs. Selexol

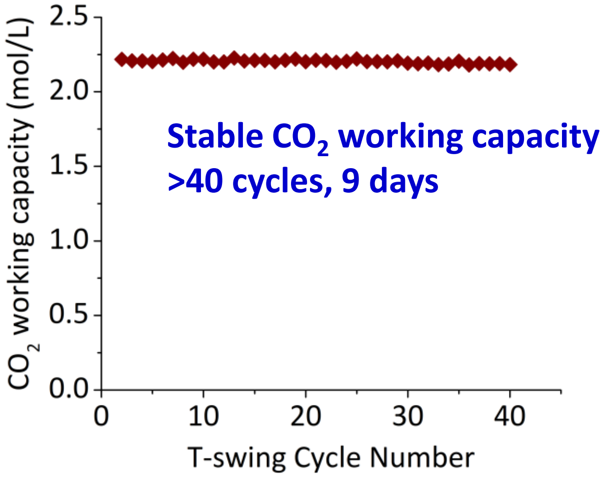


CO_2 working capacity of NETL SMR-SOLV-2 from 15-65 °C



Hold at 5 bar CO_2, cycle 20-60°C



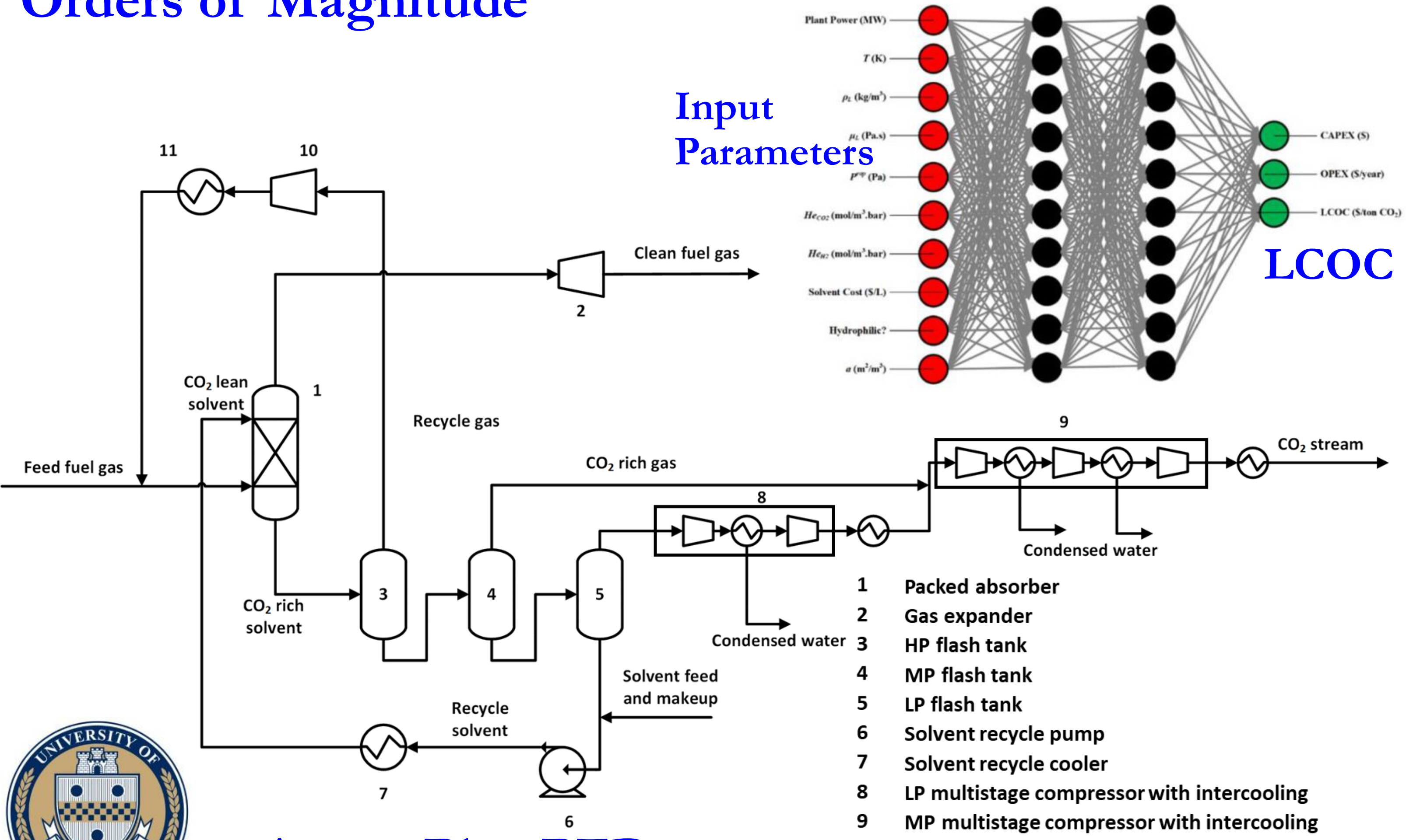


Accomplishments/findings:

- Moderated CO_2 binding energy gives high CO_2 uptake using only low-grade waste heat for regeneration
- > 2 mol/L working capacity @ 5 bar CO_2 with 20-60°C T-swing
- Regenerating at 5 bar minimizes CO_2 compression costs

Economic Screening of Optimal Pre-combustion CO_2 Capture Solvents

Artificial Neural Network: Reduces Computational Time by 3 Orders of Magnitude



Aspen Plus PFD

Input Parameters

LCOC

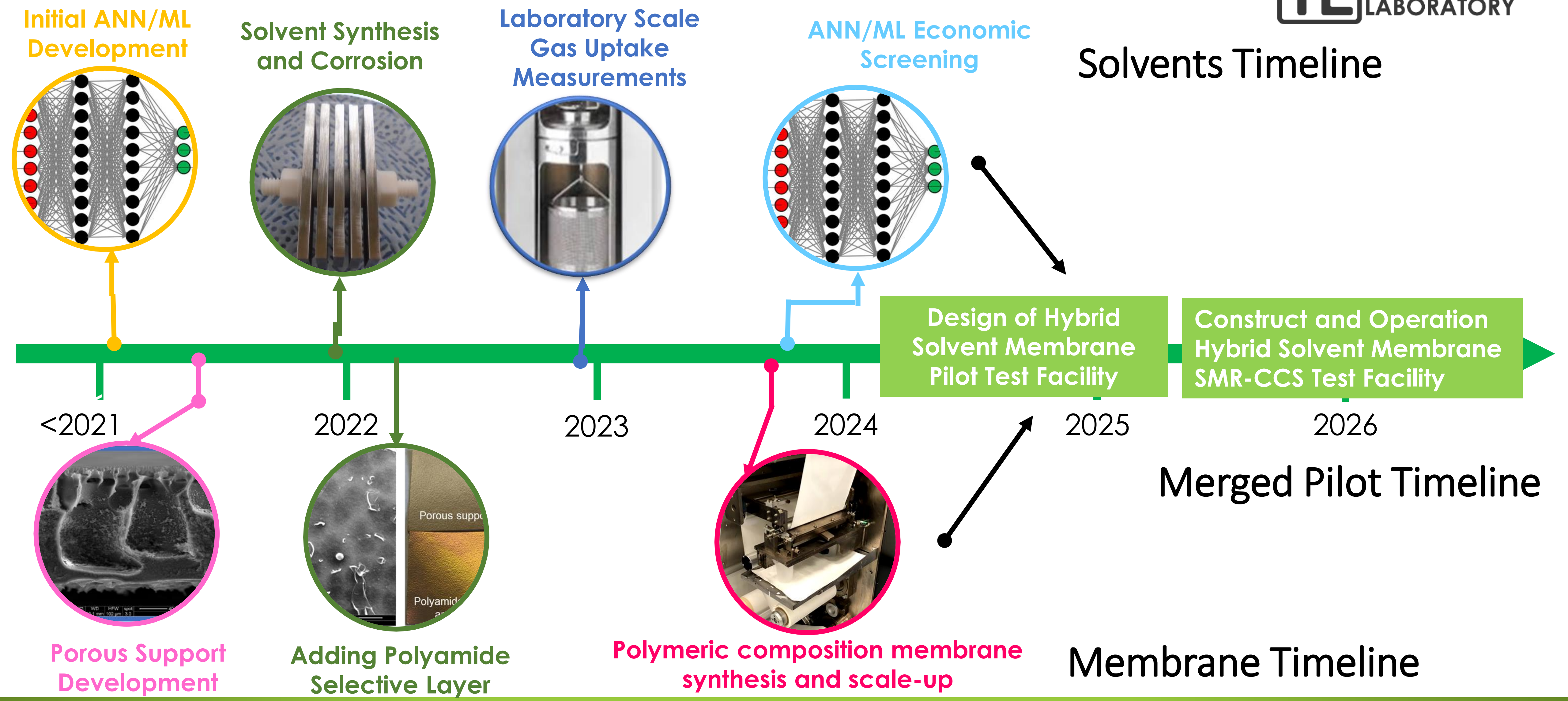
>35 solvents used to train ANN

Category	Solvents	Molecular weight (kg/kmol)	Solvent cost ($/Liter)
Ionic Liquids (ILs)	1. $[aPy][Tf_2N]$	401.33	40.00
	2. $[bmim][BF_4]$	226.02	18.11
	3. $[bmim][MeSO_4]$	250.32	18.14
	4. $[bmim][PF_6]$	284.18	14.65
	5. $[bmim][Tf_2N]$	419.38	14.37
	6. $[bmPyr][Tf_2N]$	422.42	32.17
	7. $[emim][BF_4]$	197.98	17.34
	8. $[emim][Tf_2N]$	391.32	30.38
	9. $[hmim][(C_2F_5)_3PF_3]$	612.30	34.16
	10. $[hmim][Tf_2N]$	448.43	41.50
	11. $[omim][Tf_2N]$	475.48	26.44
Oxygenated-Hydrocarbons (OHCs)	1. 1-Hexanol	102.18	0.82
	2. 1-nonanal	142.24	0.62
	3. 1-Octanol	130.23	0.82
	4. DES	258.36	0.96
	5. NBAc	116.16	0.88
	6. NPAc	102.13	0.88
	7. TBP	266.32	1.96
Cyclic-Hydrocarbons (CycHCs)	1. cis-Decalin	138.25	0.45
	2. Cyclohexanone	98.15	0.94
	3. MNPh	142.20	1.02
	4. NMP	99.13	2.00
	5. PC	102.09	0.60
Hydrocarbons (HCs)	1. 1-Heptene	98.19	1.39
	2. 1-Octene	112.22	2.13
	3. n-Octane	114.23	0.73
	4. n-Decane	142.29	0.70
	5. n-Tetradecane	198.39	0.76
Polymers	1. PEGDME	280.00	4.00
	2. PEGPDMS-1	426.77	4.00
	3. PEGPDMS-3	617.01	4.00
Subcooled	1. Methanol	32.04	0.18
	2. THF	72.11	0.62
nitrogenized-Hydrocarbons (NHCs)	1. DMF	73.10	0.76
	2. PN	55.08	0.78

= NETL Patented Solvents

Ashkanani, H. E. Techno-Economic Analysis of the Carbon Dioxide Capture Process in Pre-Combustion Applications. The University of Pittsburgh, Pittsburgh, USA, 2021.

Precombustion R&D Timeline: Project Progress and Potential EY24+ Scale-up



Acknowledgements

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- Ron Munson, Technology Manager (U.S. Department of Energy, National Energy Technology Laboratory)
- HQ PM (Mani Gavvalapalli) and HQ DD Dan Hancu (U.S. Department of Energy, Office of Fossil Energy)