Washington University in St. Louis
James McKelvey School of Engineering

2024 FECM/NETL Spring R&D Meeting

Project FE0032178:

Intensification of Hydrogen Production Enabled By Electrochemical Pumping Module for Purification and Compression

presented by:

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Team Introduction

Wash U (lead)

Electrochemical Technologies

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Gasification Plant Cost & Performance

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Skyre, Inc.

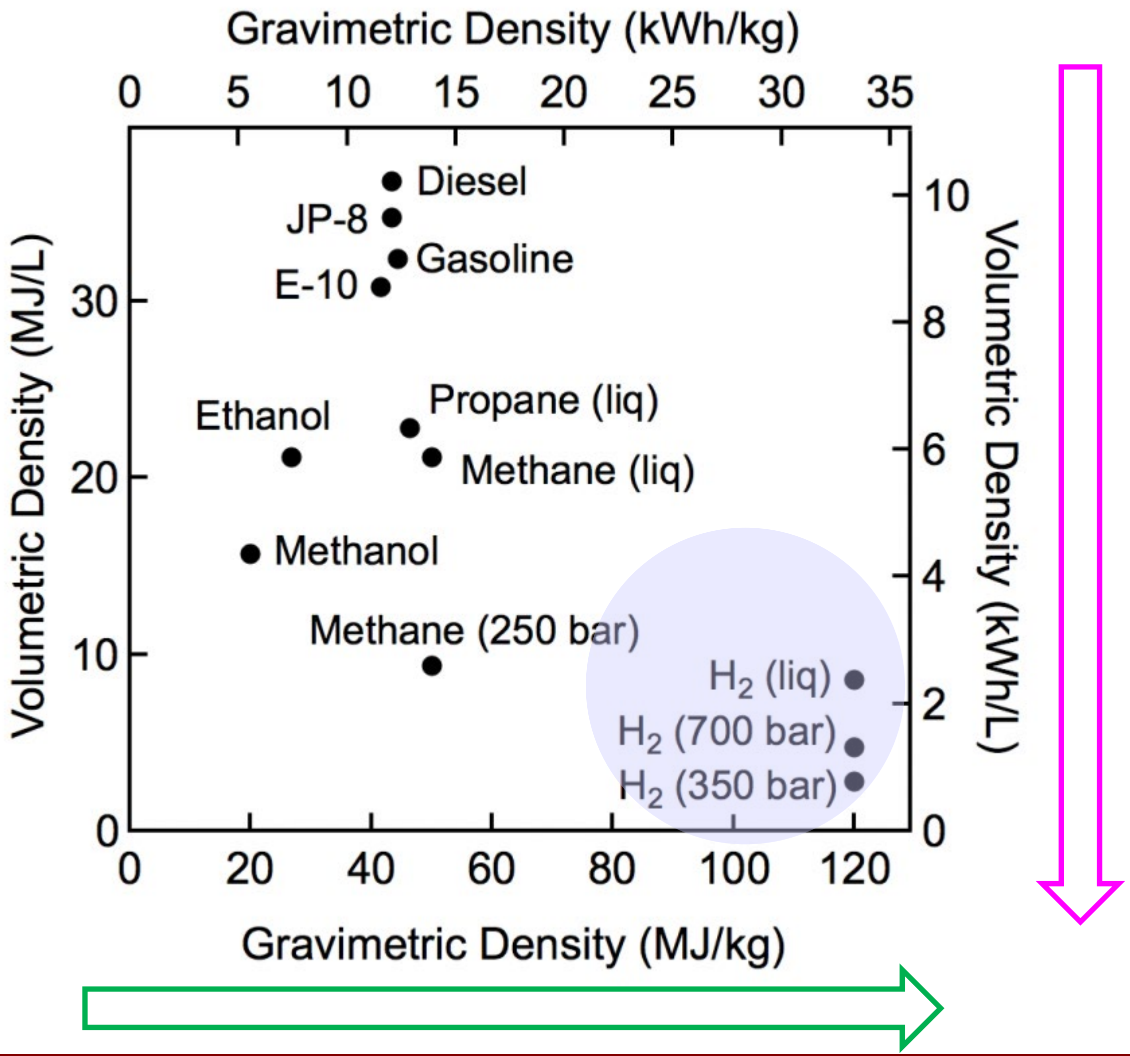
Developer & Supplier of Commercial Electrochemical Systems

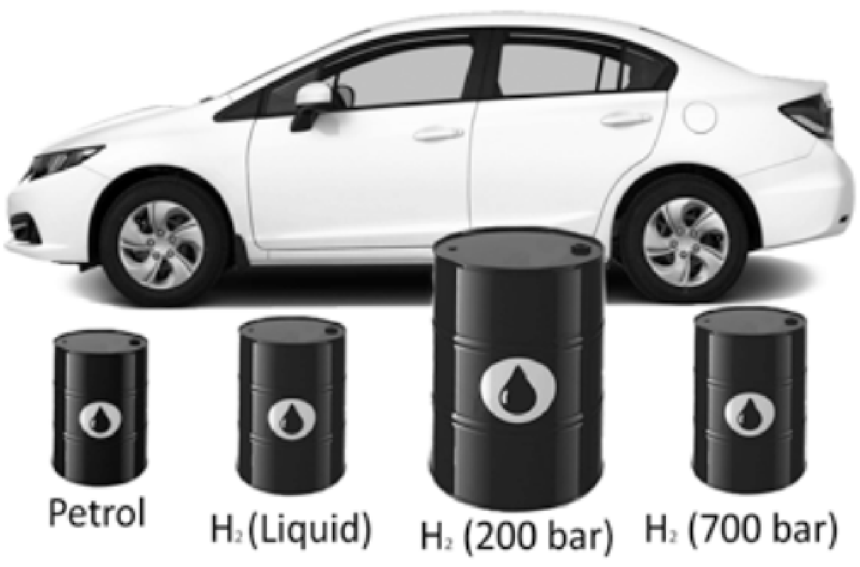
- Trent Molter
  CEO
- Nancy Selman
  VP Business Development
- Tom Maloney
  VP Technology
- Praveen Kolla
  Principal Scientist
- Cesar Oliveira
  Sr. Operations Manager

Motivation

- Clean Hydrogen Energy Earthshot
  - Cost of $1/kg or less (80% reduction)
  - Carbon intensity of 2 kg CO_2e / kg H_2
  - Achieved in 10 years
- Low-carbon, biomass-derived feedstocks are favorable for meeting the clean standard
  - Fossil sources would require CO_2 capture and utilization/sequestration
  - Biomass + CCUS gives potential for carbon negative process
- Geographic distribution of biomass-derived feedstocks suggests ideal scale for gasification plants (5-50 MW)
  - Cost and efficiency must be improved through process intensification and implementation of modular components

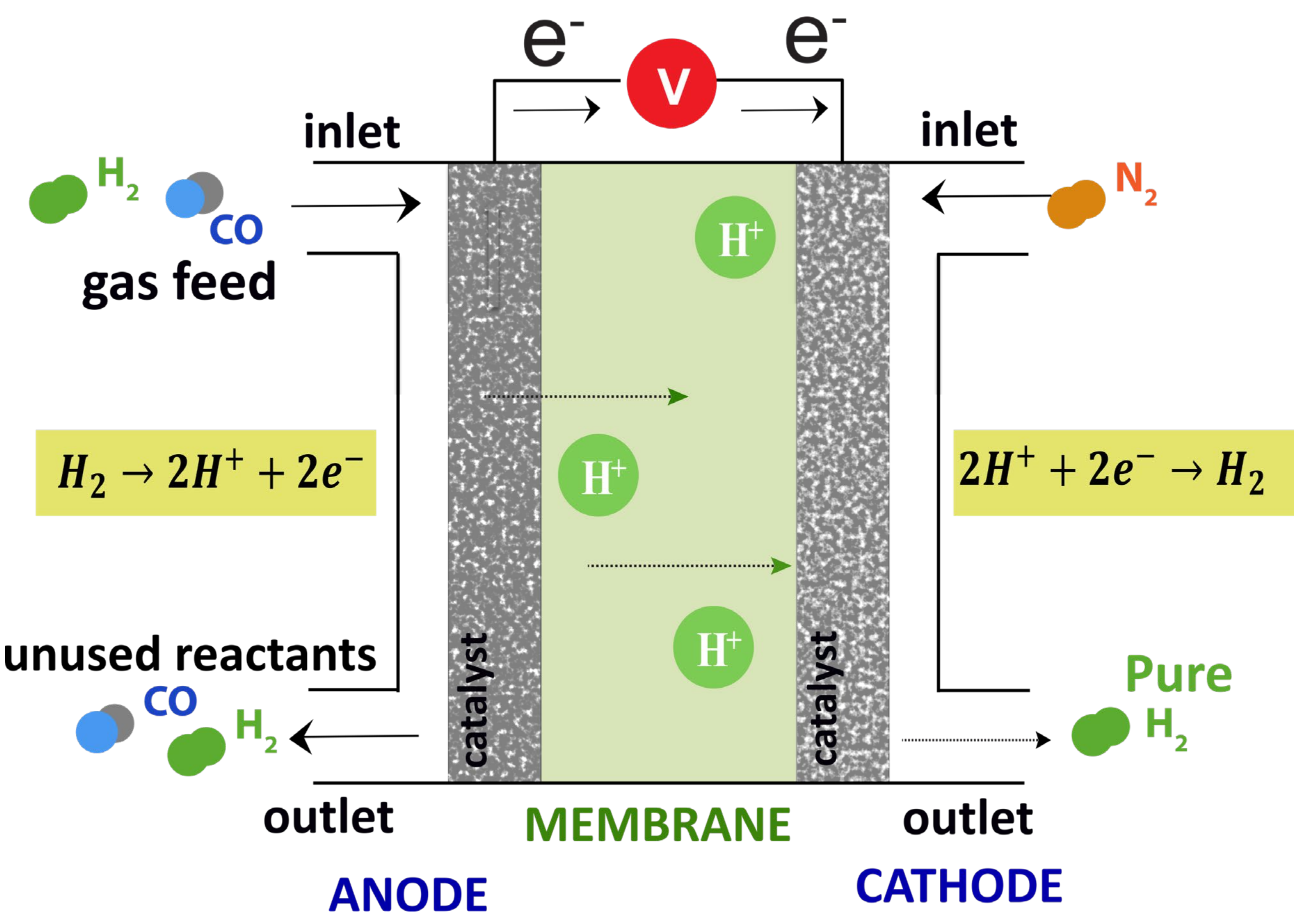
Hydrogen Compression





- Hydrogen has the highest gravimetric energy density
- Hydrogen must be compressed at very high pressure, between 200-950 bar, to be used in technologies such as fuel cell vehicle

Electrochemical Hydrogen Compression



- Anode: Hydrogen oxidation and produces protons (HOR)
- Protons migrate through proton exchange membrane (PEM)
- Cathode: Proton converts to hydrogen (HER)

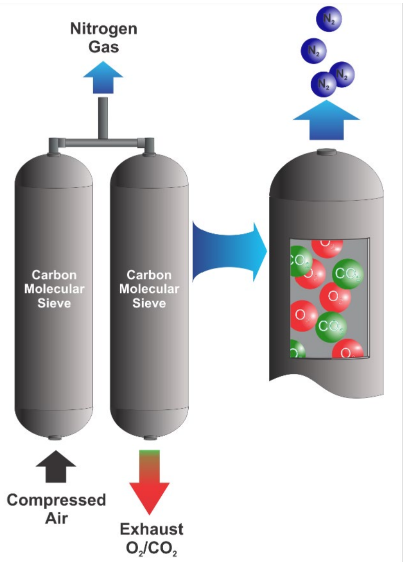
Overall: H_2 (P_a) → H_2 (P_c); Pa <<Pc

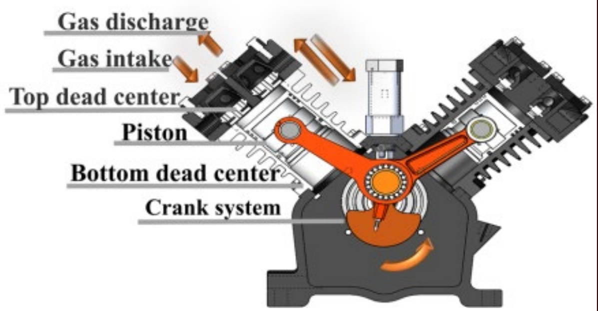
$$E_{Nernst} = E^0 - \frac{RT}{nF} ln\frac{Pcathode}{Panode}$$

Hydrogen oxidation reaction **Hydrogen evolution reaction**

Simultaneous Purification and Compression

Conventional Process





Pressure swing adsorption

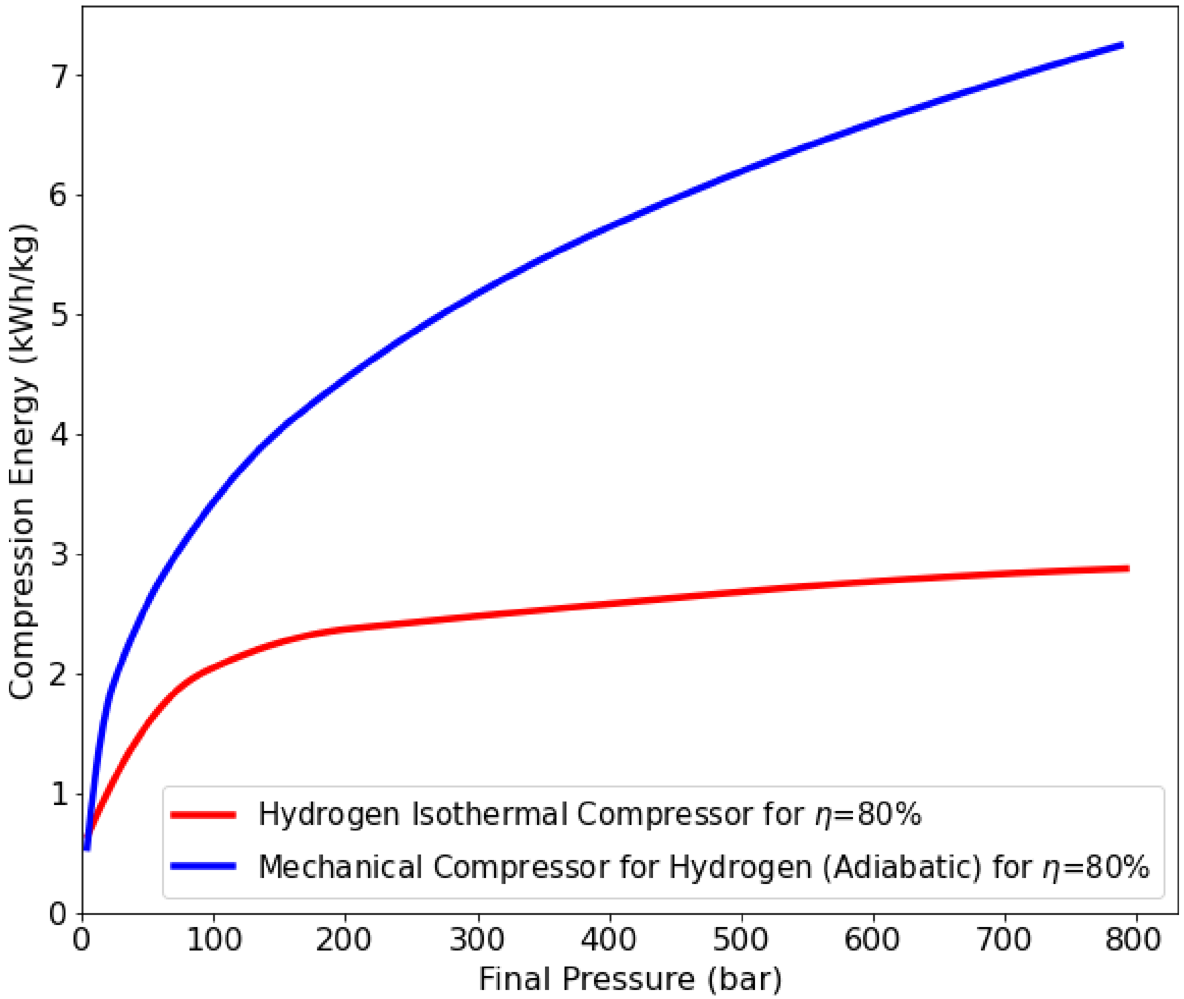
Piston compressor

- ❑ Multi step purification + compression

EHP

- ❑ Simultaneous purification + compression: Single unit
- ❑ No moving parts
- ❑ Modular design
- ❑ Low energy consumption
- ❑ No vibrations

Comparison with Mechanical Compression



Opportunities and Challenges

Potential Process Intensification Benefits:

- Reduced cost of CO_2 and N_2 separation (compared to cryogenic or PSA)
- Reduced oxygen requirements
- Low-temperature purification
- Reduced # components
- Reduced compression energy by over half

Potential Impediments:

- Poisoning of Pt catalyst by CO and H_2S
- Reverse water gas shift reaction CO_2 → CO → catalyst poisoning
- Catalyst deactivation by particulate matter
- PEM degradation
- Limited EHP experience with complex gas mixtures

Project Objectives

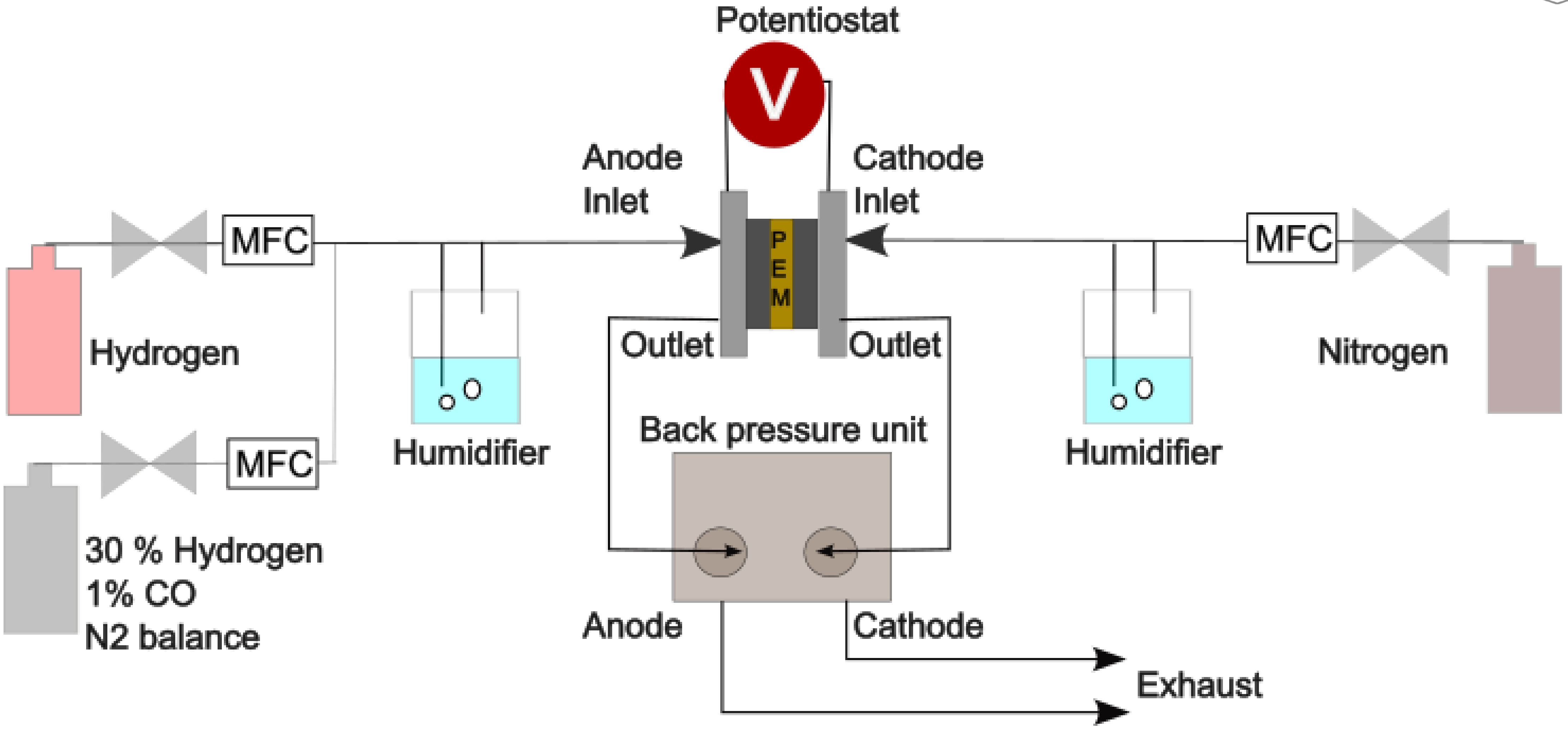
Overall Goal:

To develop and demonstrate an innovative electrochemical hydrogen pump (EHP) technology that will significantly reduce the costs of clean hydrogen production, specifically from small-scale (5- 50MW) biomass gasification units.

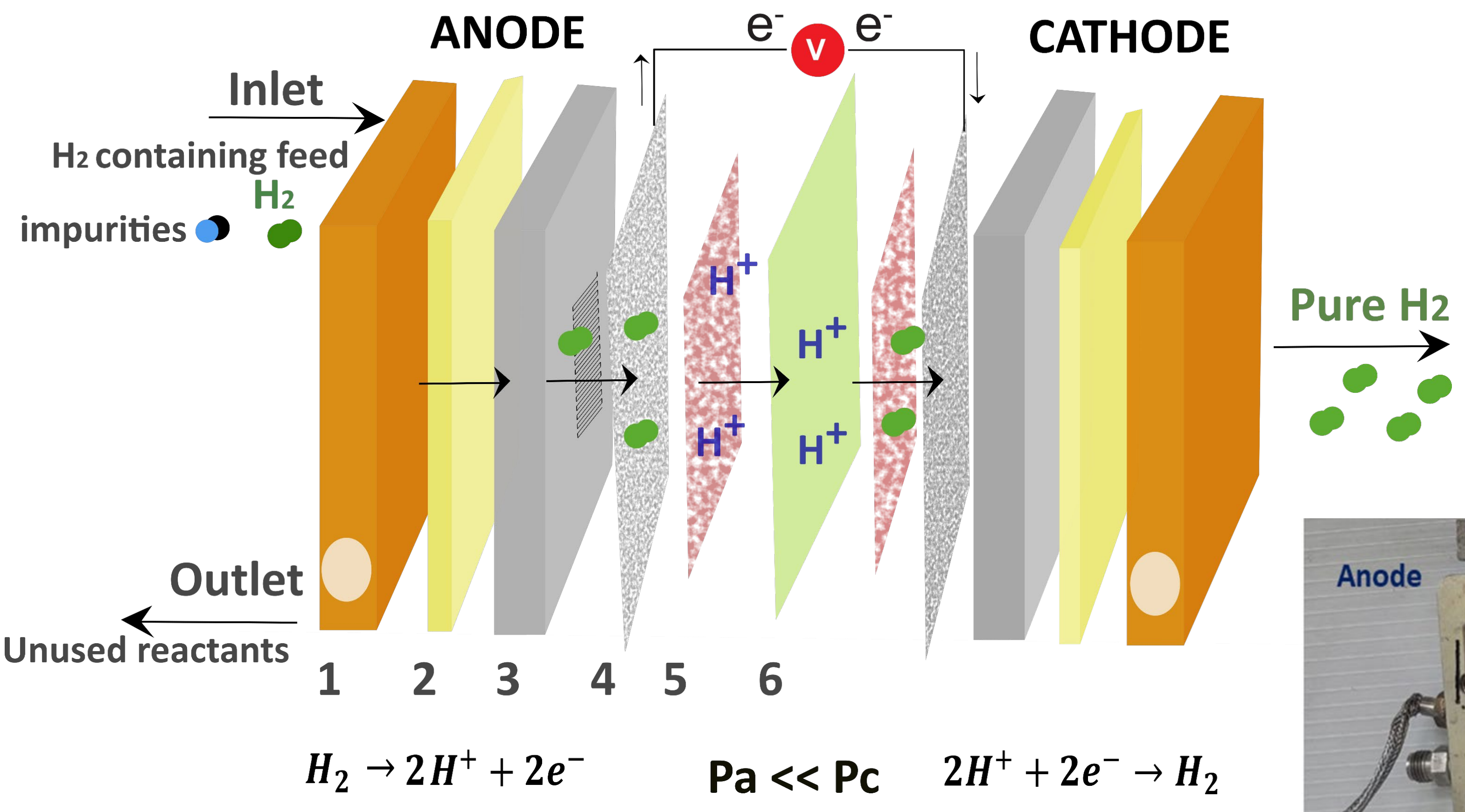
Objectives:

- Demonstration of a custom anode catalyst that is tolerant to CO at concentrations of 0.1- 0.5%.
- Demonstration of hydrogen pressurization in a 10x82cm^2 cell stack up to at least 70 bar, enabled by membrane advancements to reduce contaminant crossover and maintain high purity
- Advance the Technology Readiness Level from TRL 3 to TRL 4
- Generate and disseminate a comprehensive operating dataset and cost analysis for TEA analysis

Experiment Schematic



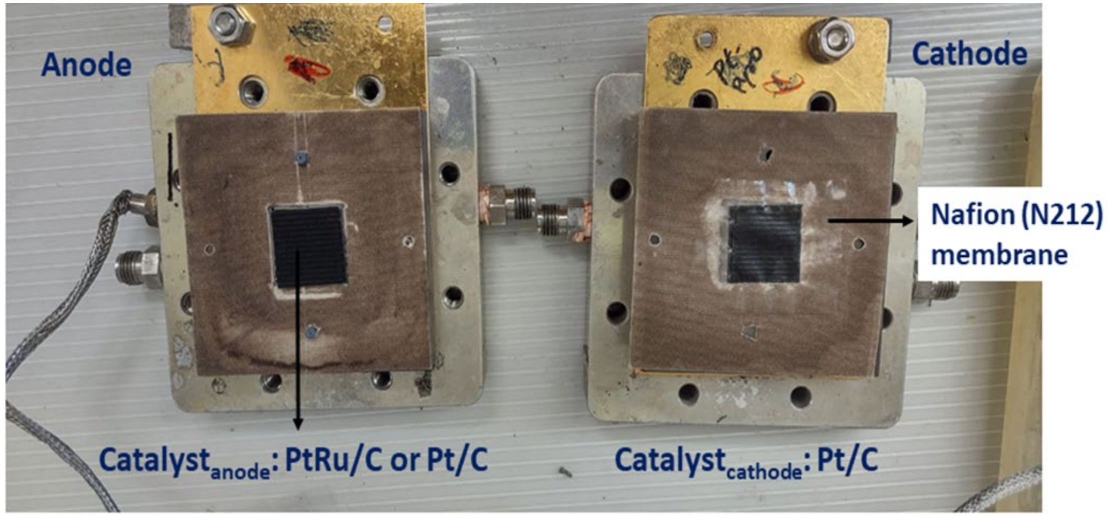
Experiment Test Cell



1- End plate
2- Current collector
3- Single-channel serpentine graphite flow field

4- Gas diffusion layer
5- Catalyst layer
6- Proton exchange membrane (PEM)

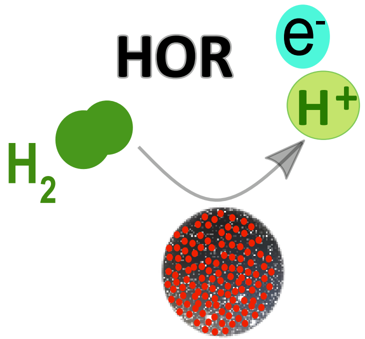
Membrane electrode assembly (MEA)

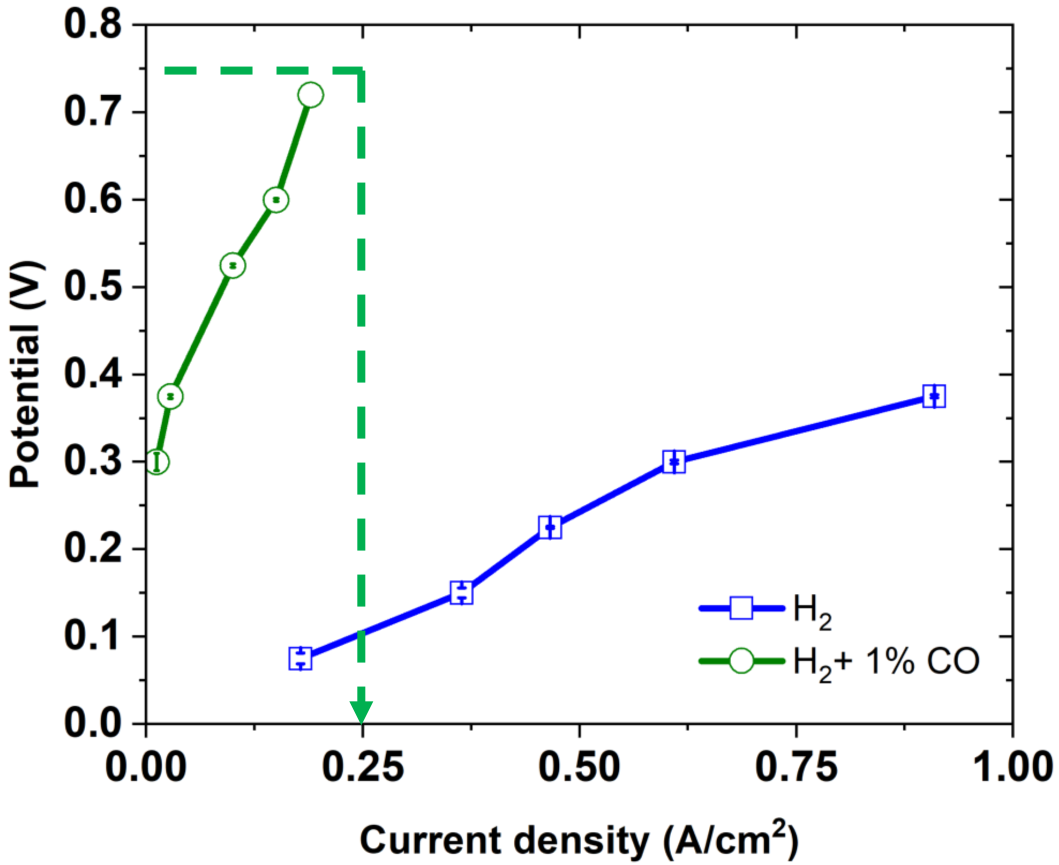


Research Gap: Catalyst Poisoning

No impurities:

$Pt + H_2 \rightarrow Pt\text{-}H + H^+ + e^-$



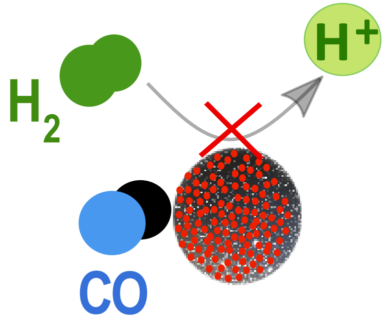


Presence of carbon monoxide (CO):

$Pt + H_2 \rightarrow Pt\text{-}H + H^+ + e^-$

$Pt + CO \rightarrow Pt\text{-}CO$

$2\,(Pt\text{-}H) + 2CO \rightleftharpoons 2\,(Pt\text{-}CO) + H_2$



Goal: **Achieving higher current in lower potential**

- ❑ **H_2:** Requires lower applied potential (0.12 V) for current density (e.g., 0.25 A/cm²).
- ❑ **H_2CO:** Requires high applied potential (> 0.7 V) under similar conditions.
- ❑ PtC is significantly poisoned in the presence of CO

Strategies for Mitigation

Low-Temperature (LT) EHP

- ❑ Temperature range: <100 ^{0}C
- ❑ Membrane: e.g.: Nafion (requires humidification for proton conduction)
  - o Humidifier and back pressure unit

Strategies

1. CO-tolerant catalyst (Platinum/ruthenium on carbon support (PtRu/C))
2. Pulse oxidation
3. Air bleed
4. Increasing temperature (challenge: Nafion humidification)

High-Temperature (HT) EHP

- ❑ Temperature range: 100-220 ^{0}C
- ❑ Membrane: e.g.: PBI-based (No humidification/ no water management)

Strategies

1. Tailoring thermally stable catalyst
   - o PtRu/C (100-150 ^{0}C)
   - o PtRu/RTO (>150 ^{0}C) (thermally stable support)
2. Fabricating thermally stable membrane
3. Pulse oxidation
4. Air bleed

Strategy 1: CO Tolerant Electrocatalyst PtRu/C

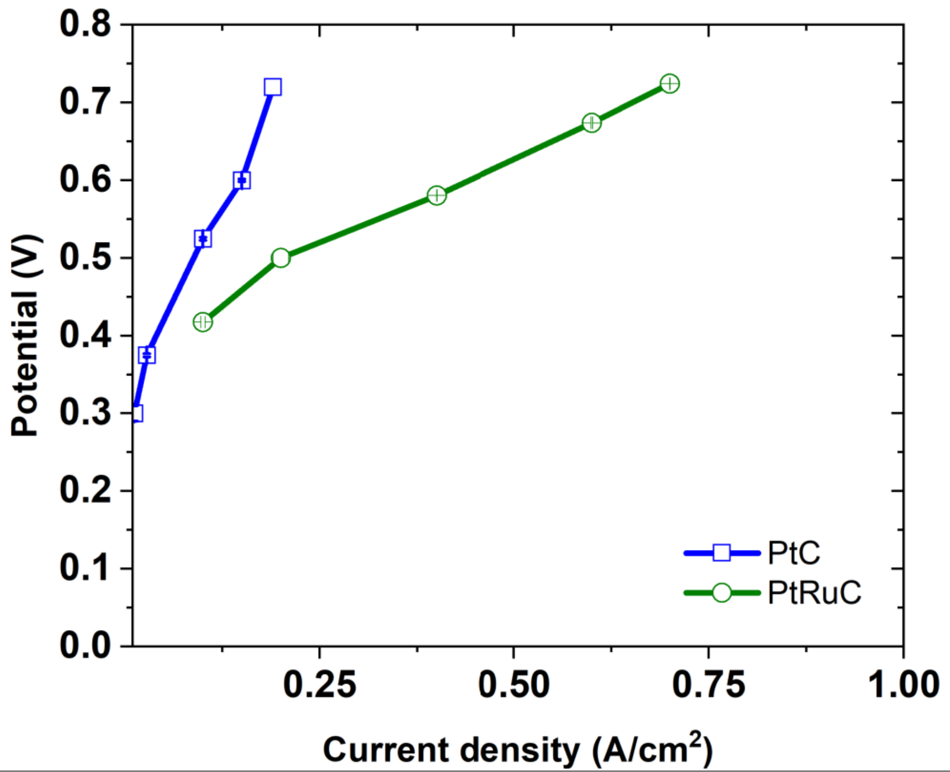
CO-tolerant electrocatalyst (PtRu/C)

$$Pt + CO \rightleftharpoons Pt\text{–}CO$$

$$Ru + H_2O \rightarrow (Ru\text{–}OH) + H^+ + e^-$$

$$(Pt\text{–}CO) + (Ru\text{–}OH) \rightarrow Pt + Ru + CO_2 + H^+ + e^-$$

- ❑ Anode: PtRu/C $_{3\ mg/cm^2}$
- ❑ Membrane: N212 (58 μm)
- ❑ Cathode: Pt/C $_{3\ mg/cm^2}$
- ❑ Temperature: 80 ^{0}C



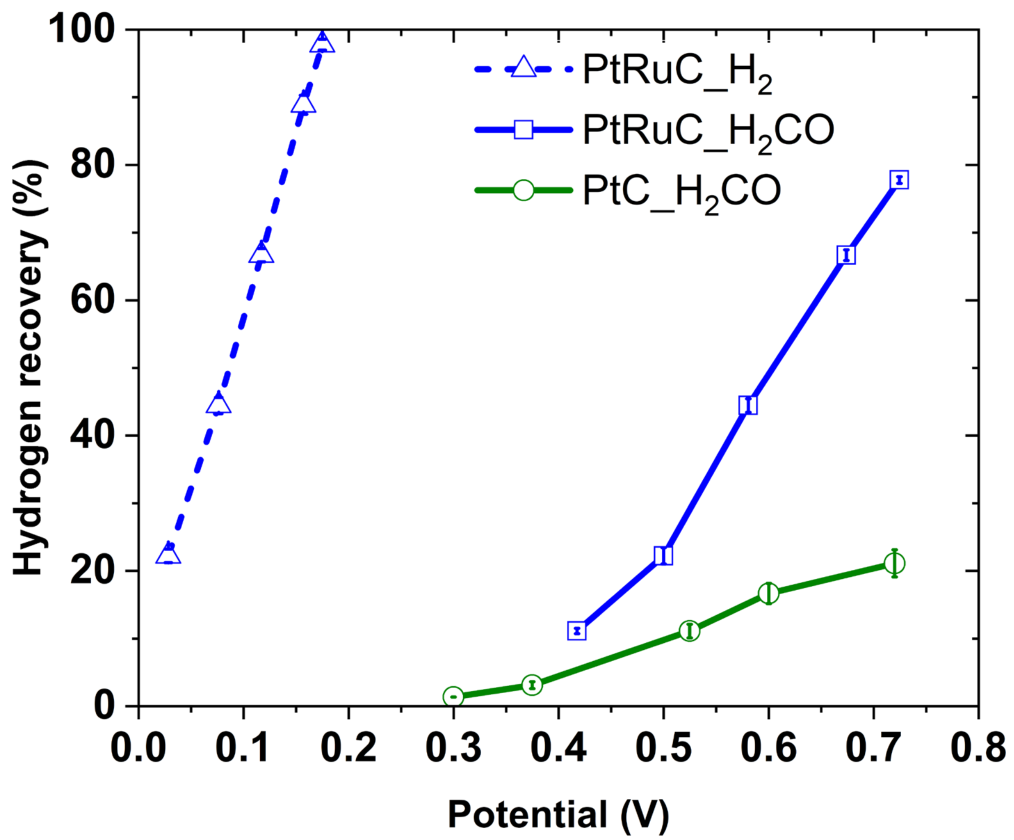
H_2CO_PtC vs PtRuC

- ❑ **PtC:** Requires high applied potential (> 0.7 V) for current density (e.g., 0.25 A/cm²).
- ❑ **PtRuC:** Requires lower applied potential (0.48 V) under similar conditions.
- ❑ PtRuC significantly mitigates CO poisoning compared to PtC.

Experiment Results: Hydrogen Recovery

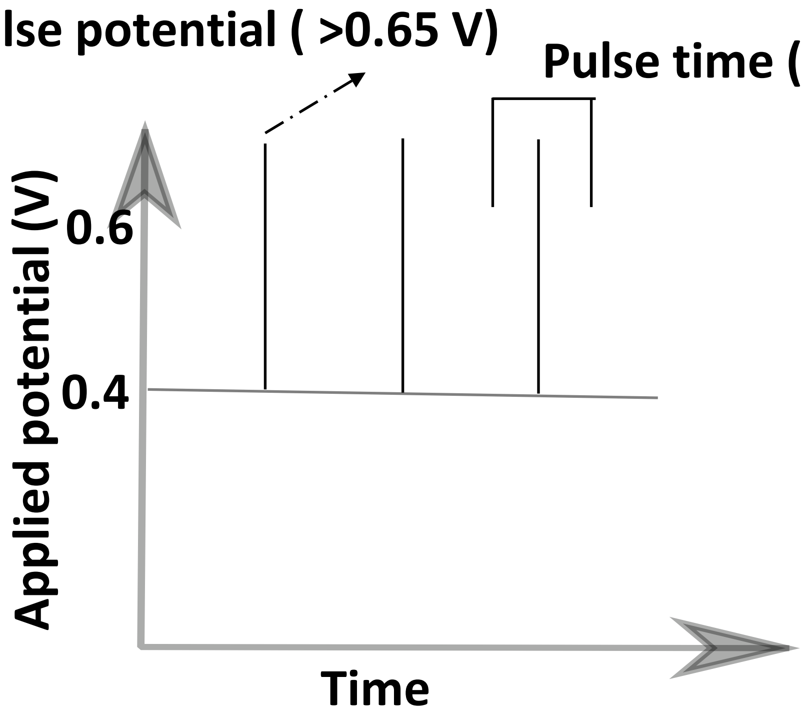
Test Gas: 30% H_2 + 1% CO

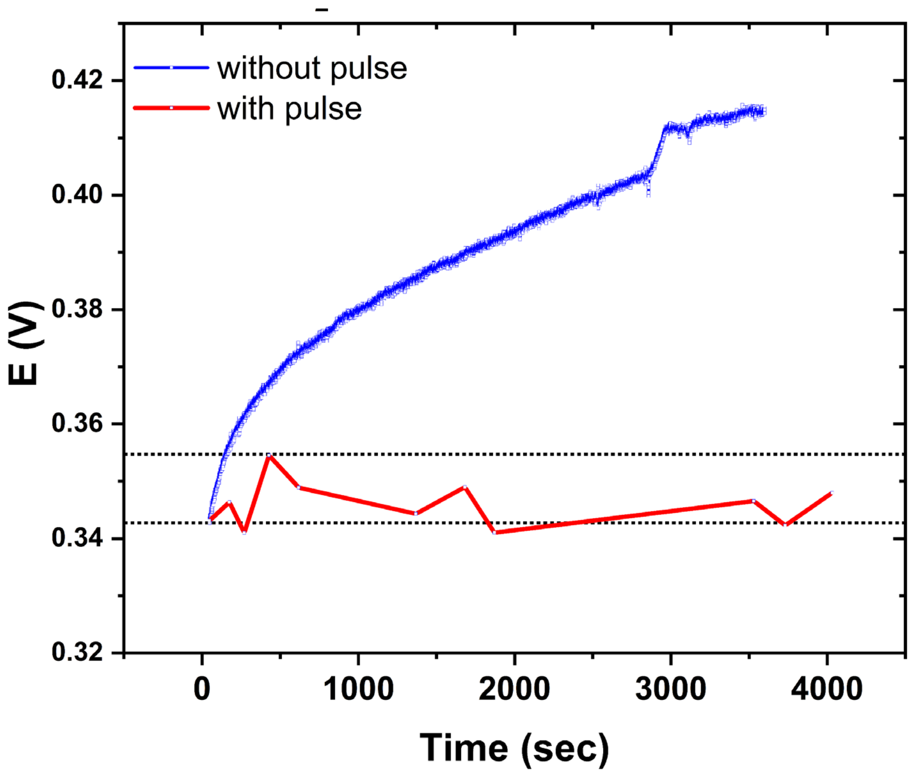
$$\textbf{HR}\ (i_{measured}) = \frac{H_{2\,out}}{H_{2\,in}} == \frac{i_{measured}}{i_{theoretical}}$$



- **H_2CO_PtC vs PtRuC:** PtRuC shows improved hydrogen recovery compared to PtC in the presence of H_2CO
- **PtRuC_H_2 vs H_2CO:** Further advancements are required for PtRuC to enhance recovery compared to H_2

Strategy 2: Pulsed Oxidation





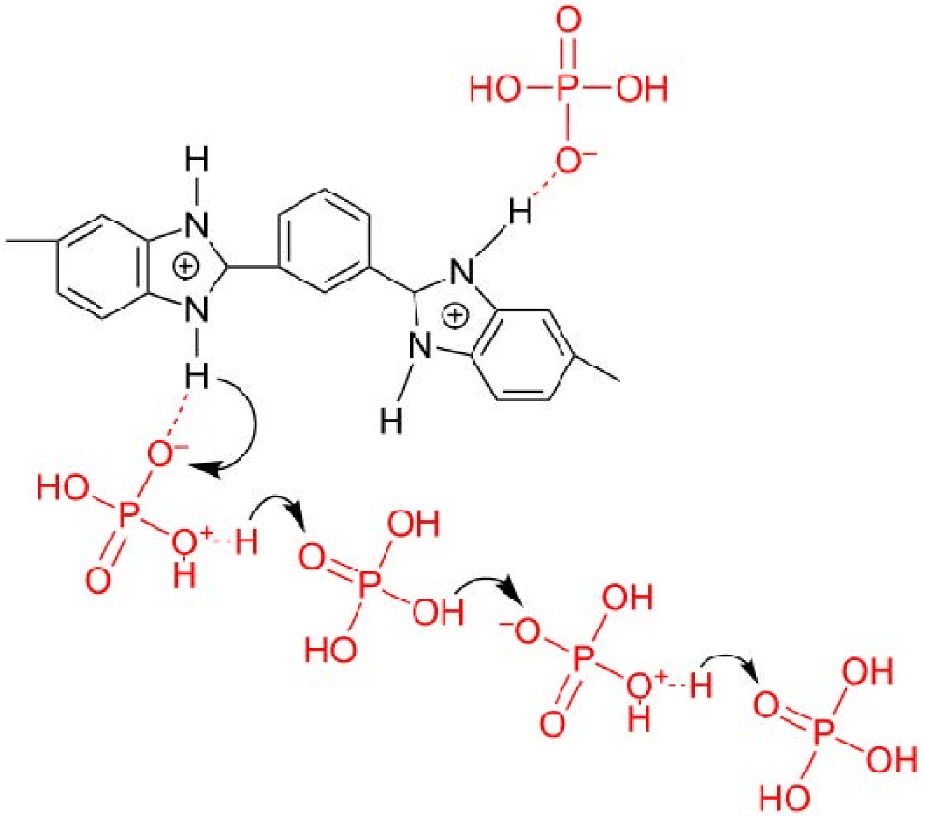
Blue line: Transient poisoning of the catalyst by 1% CO contamination at a constant current density of 0.2 A cm^{-2} for one hour

Red line: Pulsed oxidation technique on PtRu/C catalyst operated at 0.2 A/cm^2 for 1 hr with a 5 A pulsing current; 0.3 s pulse width (pulse applied are not shown for clarity)

- ❑ Frequent periodic pulsing: Oxidizes CO to CO_2, significantly mitigating CO poisoning.

Strategy 3: High Temperature Membrane

WashU-In house fabrication of thermally stable membrane

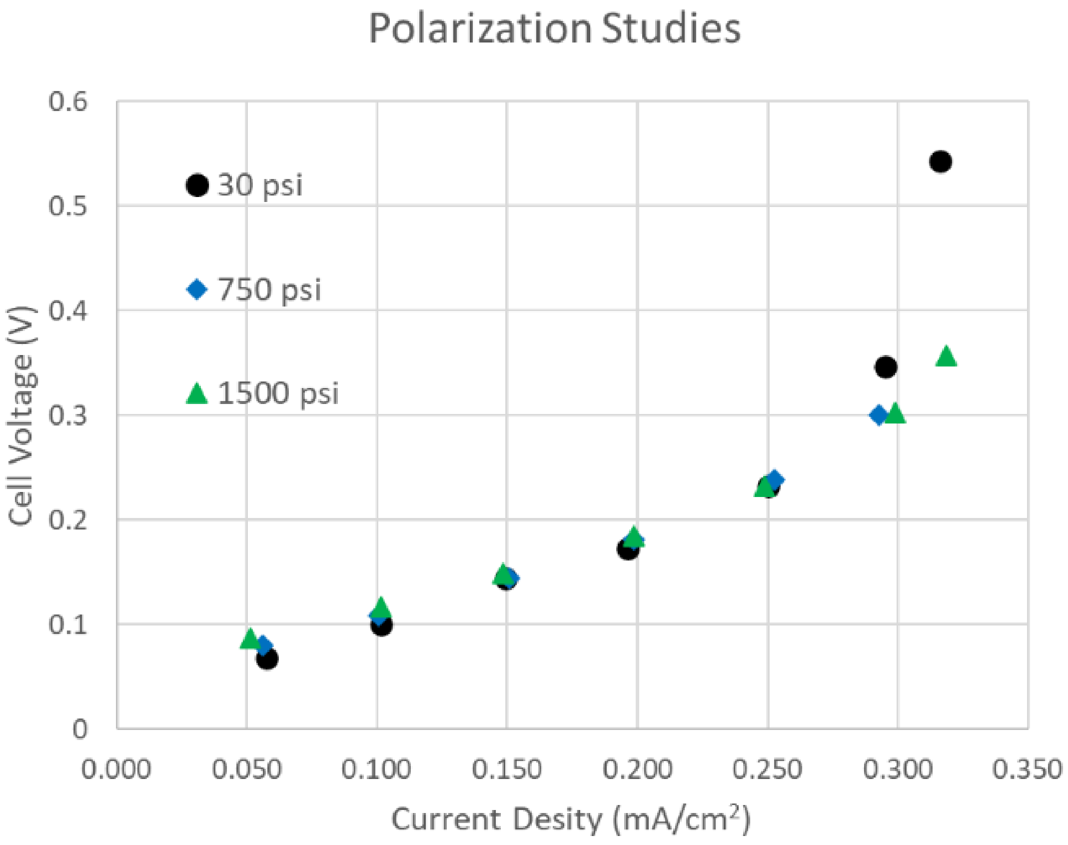


- ❑ Poly benzimidazole (PBI) membrane (dimension: 3” x3”)
- ❑ 20 µm thickness
- ❑ Doping agent: Phosphoric acid (for proton conduction)

High Pressure Test Stand

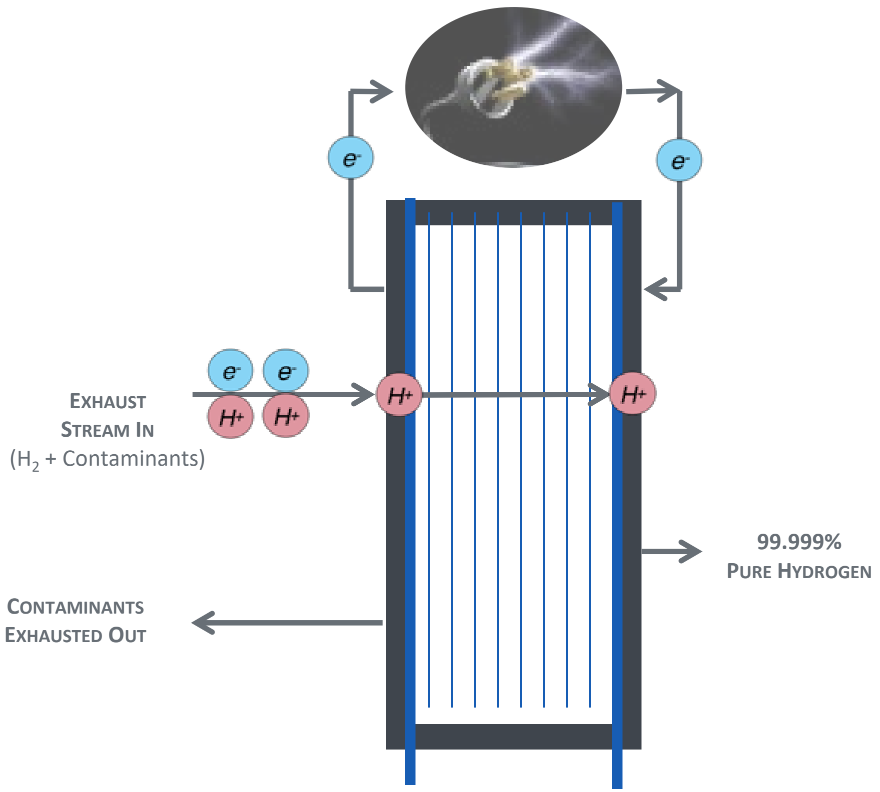
Test conditions:

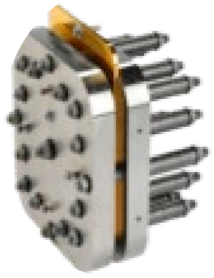
- Anode @10-15 psi (~ 1bar); 500 SCCM of H_2 (UHP)
- Humidification @ 40°C and cell @50°C
- H_2 is pumped to desired cathodic pressure by applying 0.1-0.2 A/cm^2 prior to polarization study



Proven, Patented, Electrochemical Technology Purifies and Compresses H_2

H2RENEW™ Hydrogen Electrolyzer





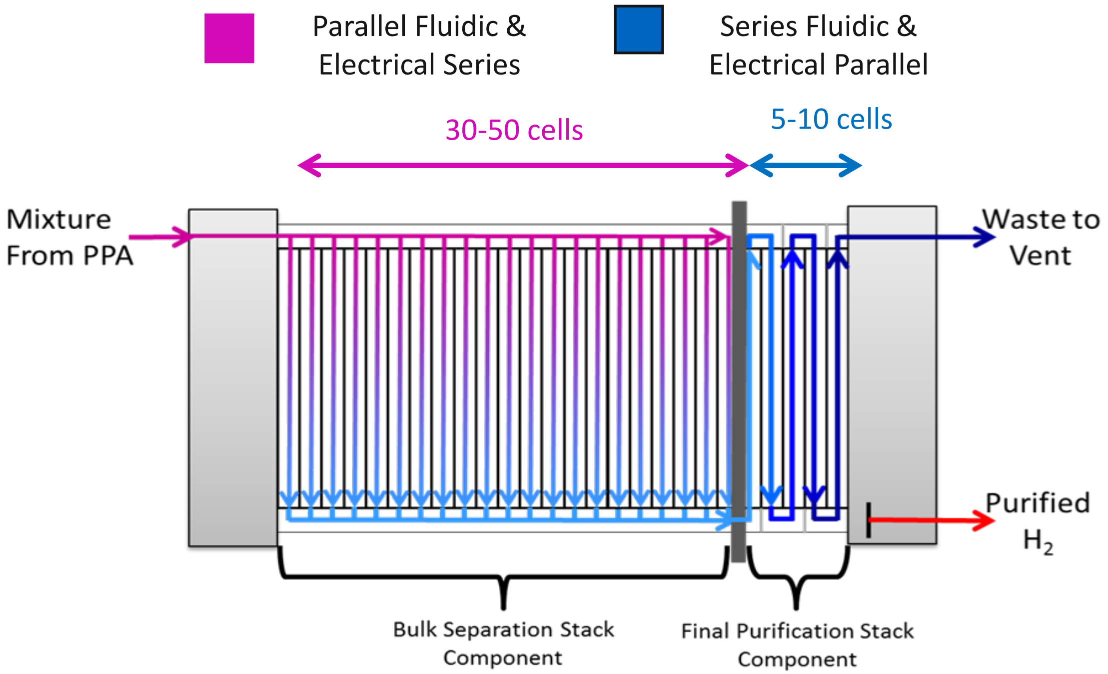
High Pressure Separation & Compression

Separation & Compression 100 kg/Day Output

Helium Reclamation (H_2-He Separation)

50% cost advantage and a 50% reduction in emission of greenhouse gases

H2RENEW™ - Advanced Stack Design Approach

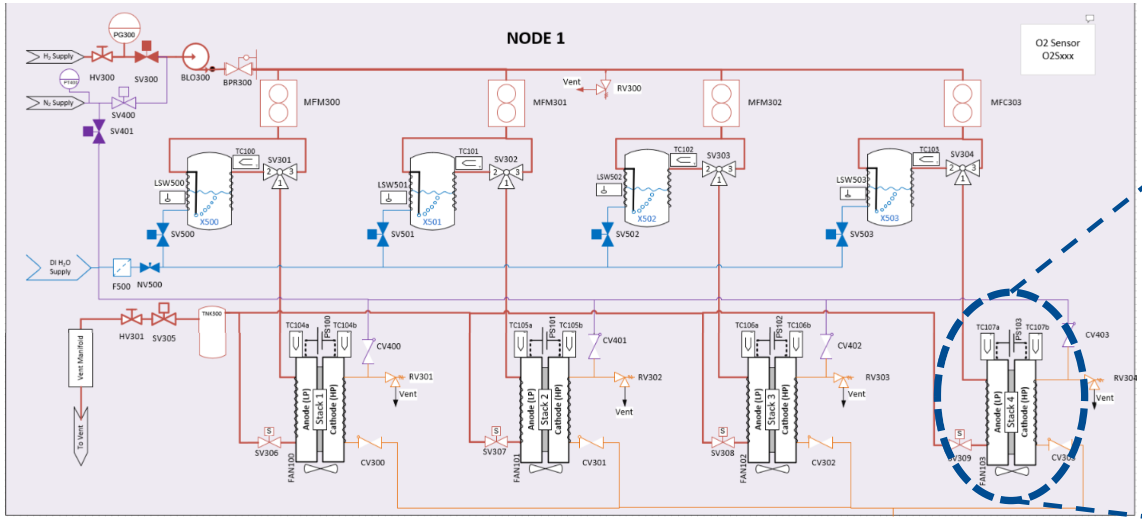


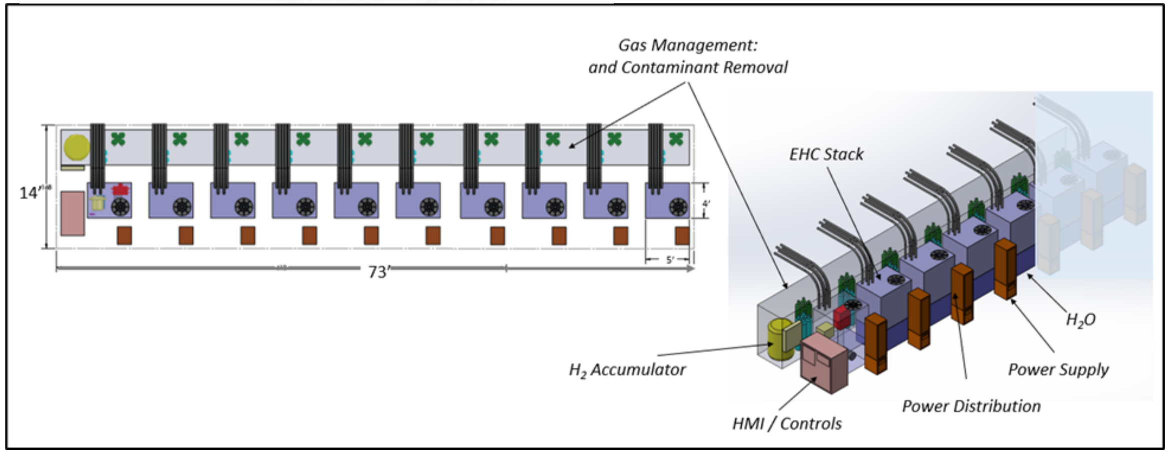
Concept 1				Concept 2		
Primary Stack				Primary Stack		
Active Area:	81.6	cm2		Active Area:	81.6	cm2
Cell Count:	50	cells		Cell Count:	25	cells
Current Density:	0.224	A/cm2		Current Density:	0.448	A/cm2
H2 Consumption	6.946	L/min		H2 Consumption	6.946	L/min
Utilization	90.205	%		Utilization	90.205	%
Remaining H2	0.754	L/min		Remaining H2	0.754	L/min
Total Flow	1.706	L/min		Total Flow	1.706	L/min
% H2 Out	44.21191			% H2 Out	44.21191	
Clean-Up Stack				Clean-Up Stack		
Active Area:	81.6	cm2		Active Area:	81.6	cm2
Cell Count:	5	cells		Cell Count:	5	cells
Current Density:	0.244	A/cm2		Current Density:	0.244	A/cm2
H2 Consumption:	0.755045	L/min		H2 Consumption:	0.755045	L/min
Purification:	100	%		Purification:	100	%

- Bulk H_2 removal stage promotes efficiency
  - Electrically serial cells
  - Parallel flow-cells
  - Constant current (Voltage float)
- Maximize utilization with final purification stage
  - Electrically parallel cells
  - Serial flow-cell
  - Constant voltage (Current float)

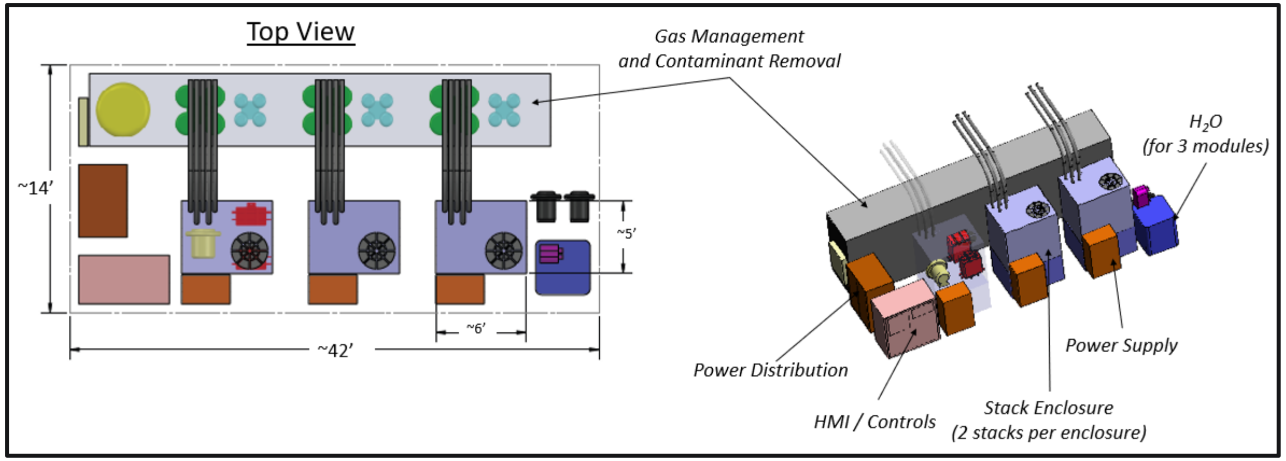
The integrated advanced stack design resulted in maximum H_2 recovery (>99%)

H2RENEW™ - Modular System Approach





Conceptual Design for 1 MT H_2/day System (non-optimized)



Conceptual Design for 1 MT H_2/day System (improved packaging)

SKYRE

Technology Roadmap Drives Pressure, Capacity, Contaminants, Cost

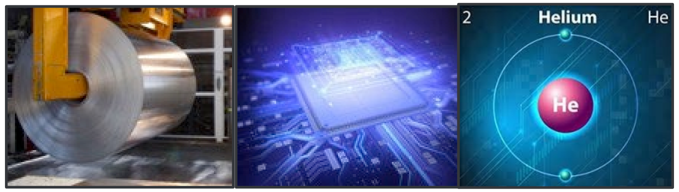
Pressure (bar)

10

100 kg-H_2/day Platform

1K kg-H_2/day Platform

10K kg-H_2/day Platform



350

100 kg-H_2/day Platform

1K kg-H_2/day Platform

10K kg-H_2/day Platform

750

100 kg-H_2/day Platform

1K kg-H_2/day Platform

10K kg-H_2/day Platform

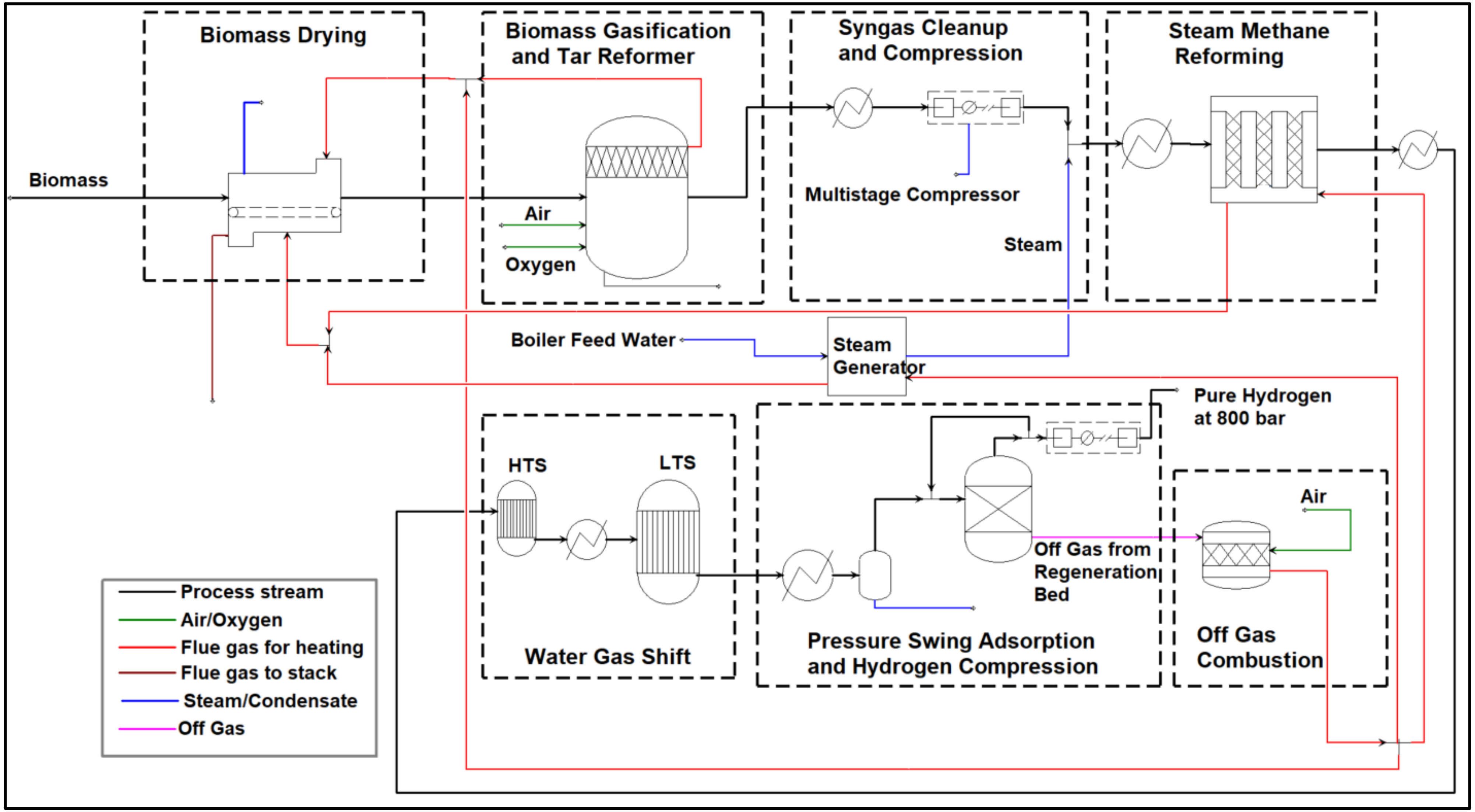
Development

Commercialization

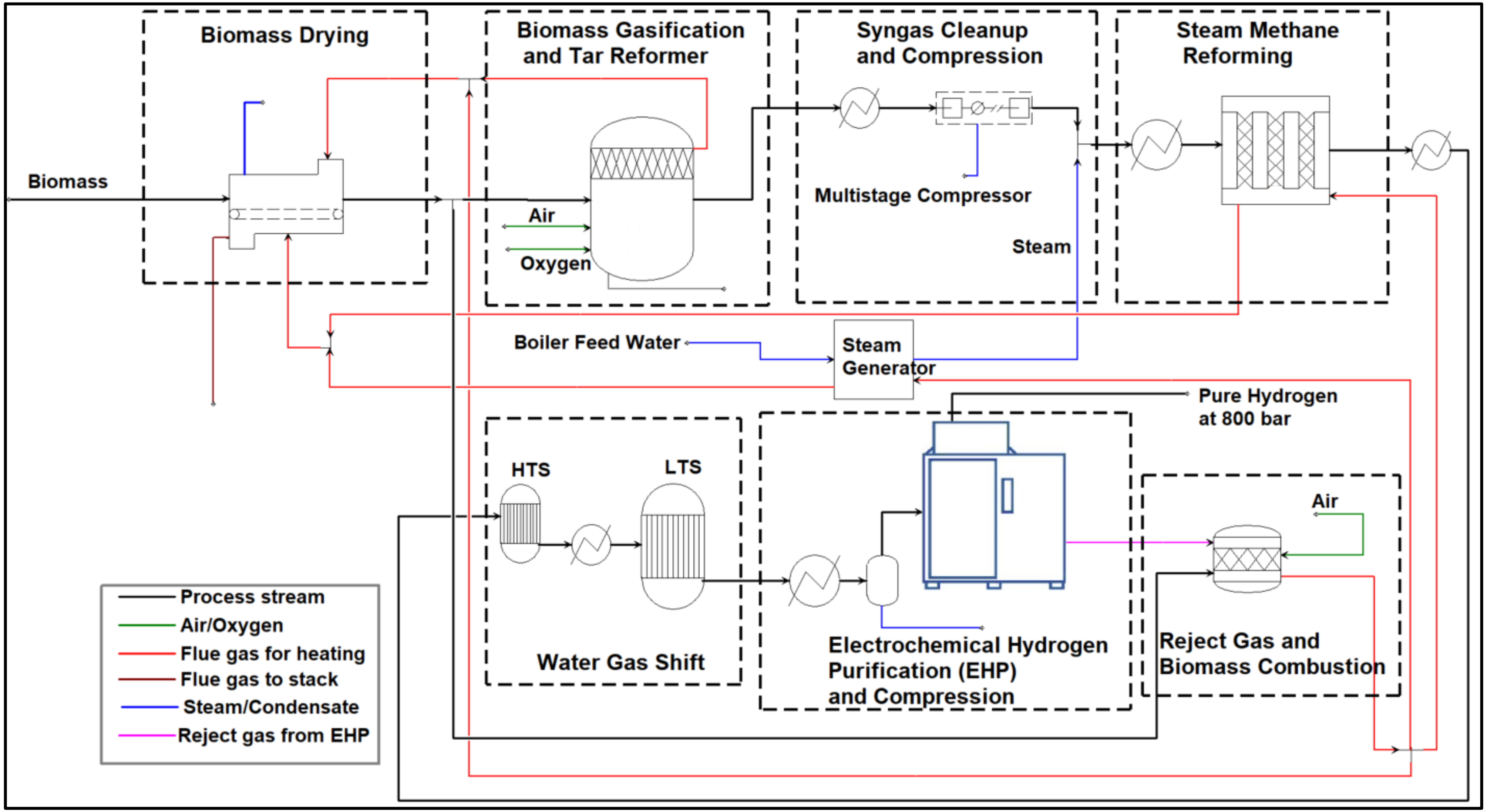
2022 **2023** **2024** **2025** **2026**

Over Time Our H2RENEW Product Technology Will Grow In Pressure and Capacity

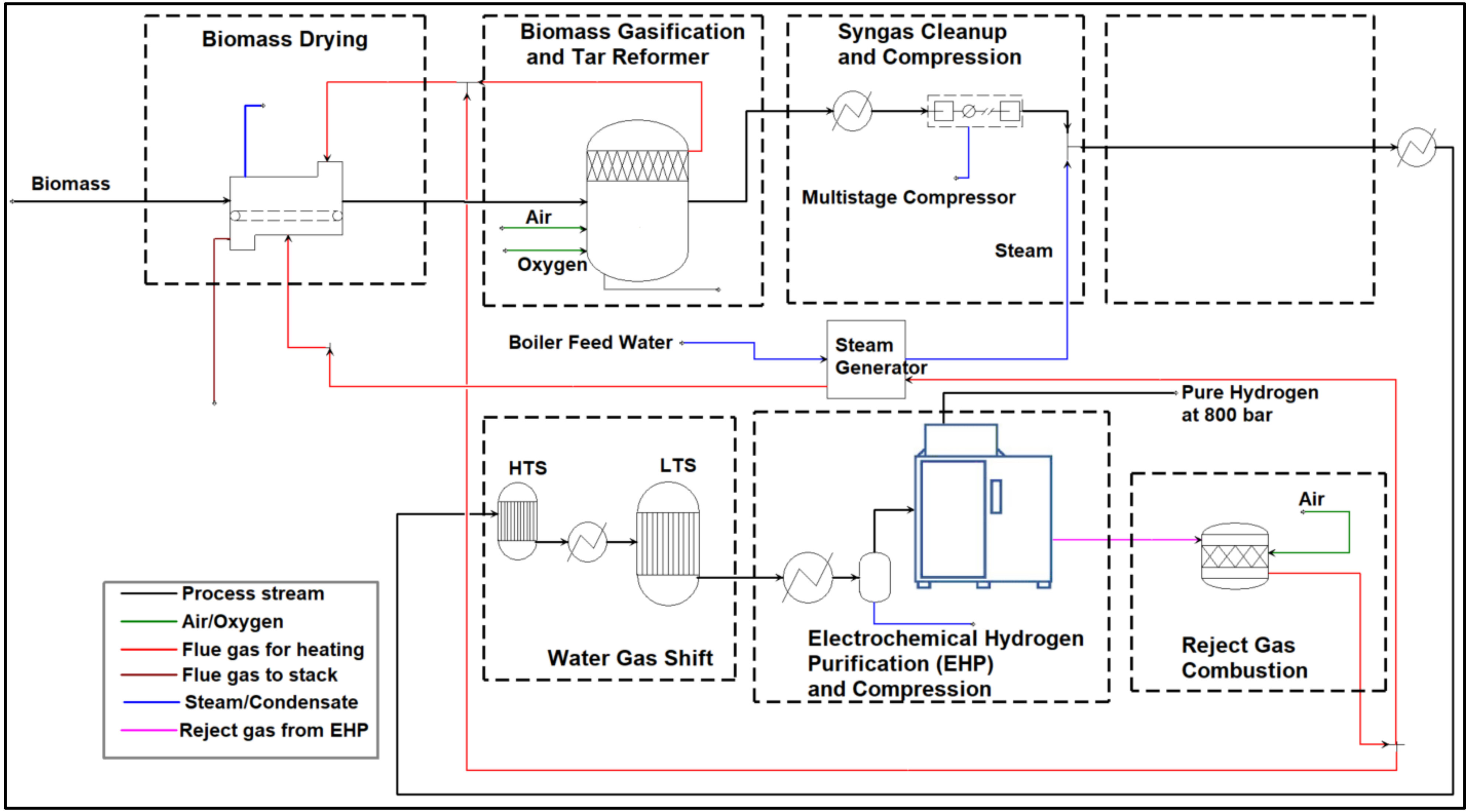
Biomass to Hydrogen Process: Case 1 Baseline



Case 2: Intensified Process



Case 3: Intensified Process w/o SMR



Design Basis

- Feedstock is wood with 50% moisture on As-Received (AR) basis.

Component	C	H	N	S	O	Ash
Wt% (dry basis)	46.64	6.02	0.35	0.14	46.52	0.31

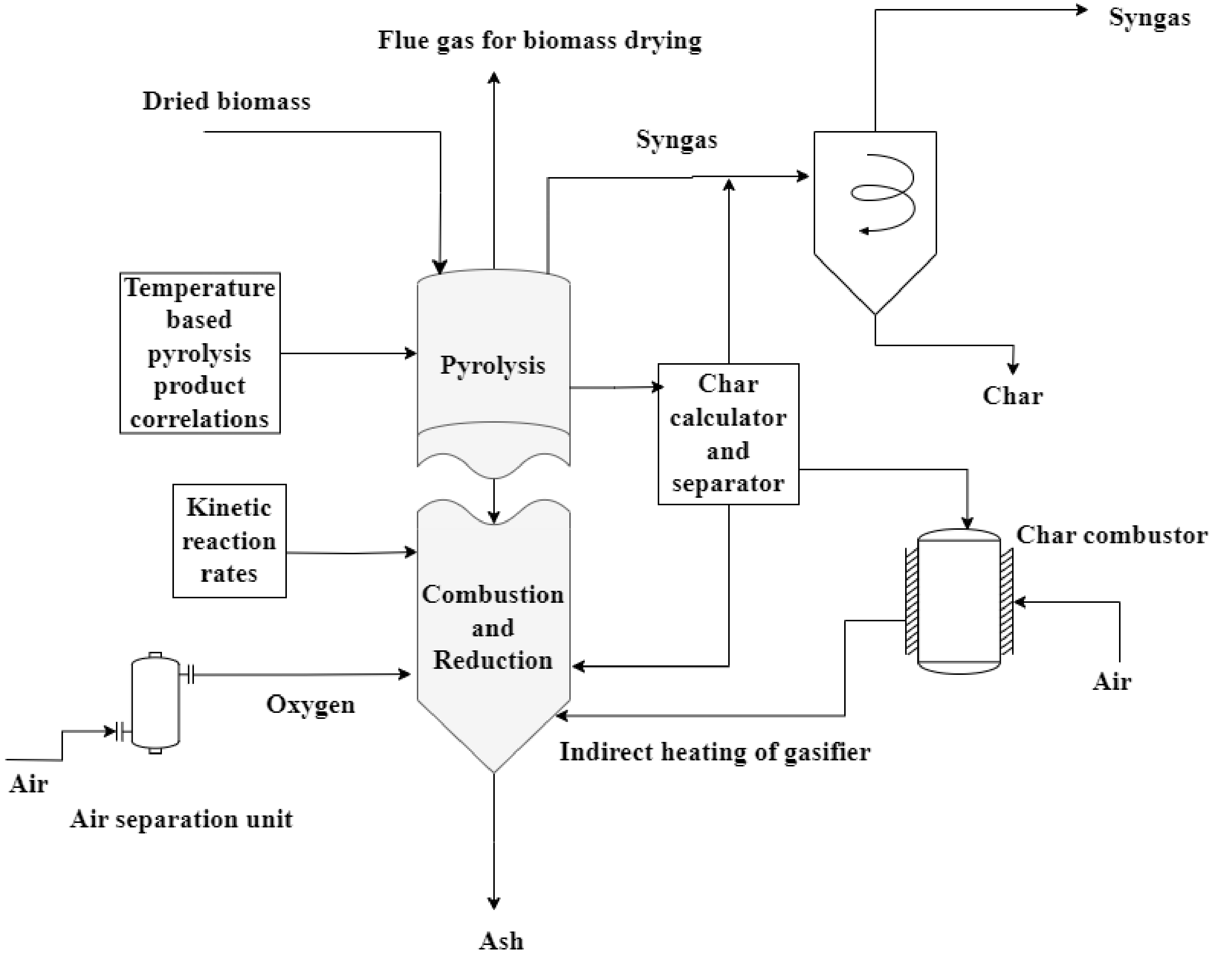
- LHV = 33.3 kWh/kg
- 336 TPD or 14000 kg/hr of bone-dry biomass.
- Equivalent size: 25 MWe (assuming 60% efficiency of conversion of H_2)
- Compression to 800 bar
- ASU specific power consumption: 213 kWh/t O_2
- PSA and balance of plant guided by NREL Model:

  Spath, P. et al. (2005) . NREL/TP-510-37408

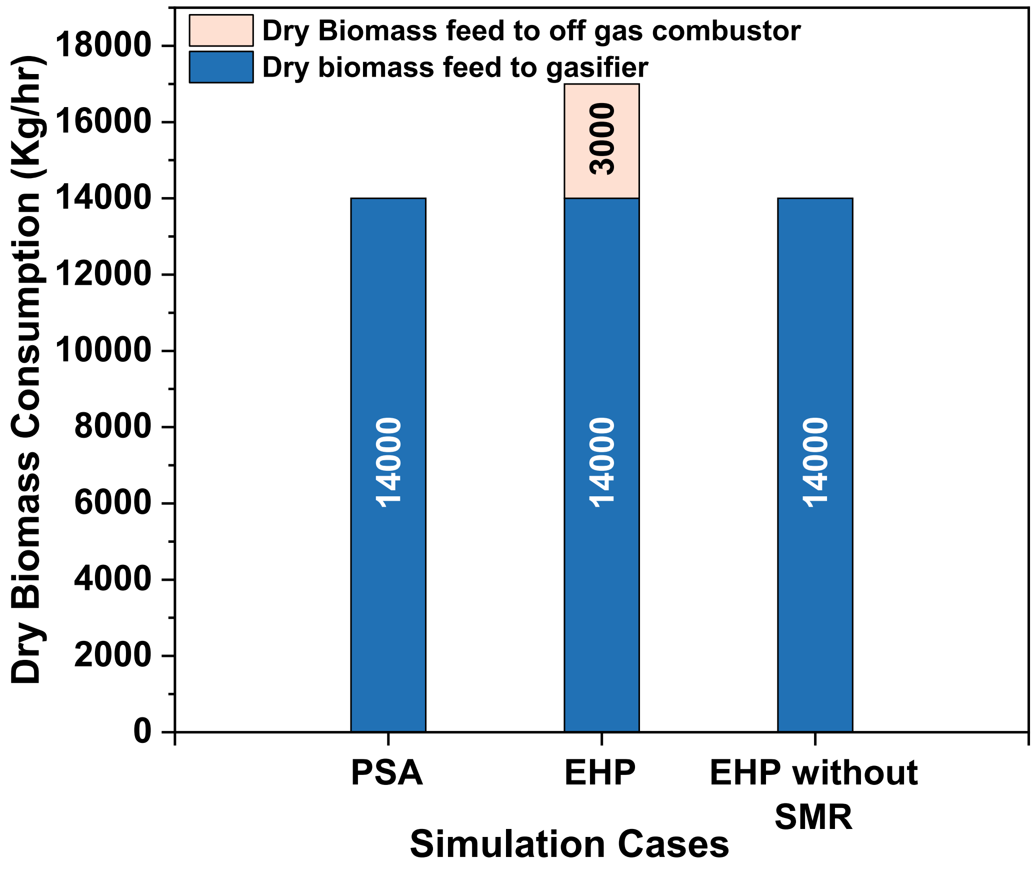
Gasifier Model

- Pyrolysis model: Abdelouahed, L. et al. (2012)
  Products include tar: – benzene, phenol, toluene, naphthalene.
- Combustion and gasification kinetic model (PFR): Abdelouahed, L. et al. (2012), Puig-Gamero, M. et al. (2021)

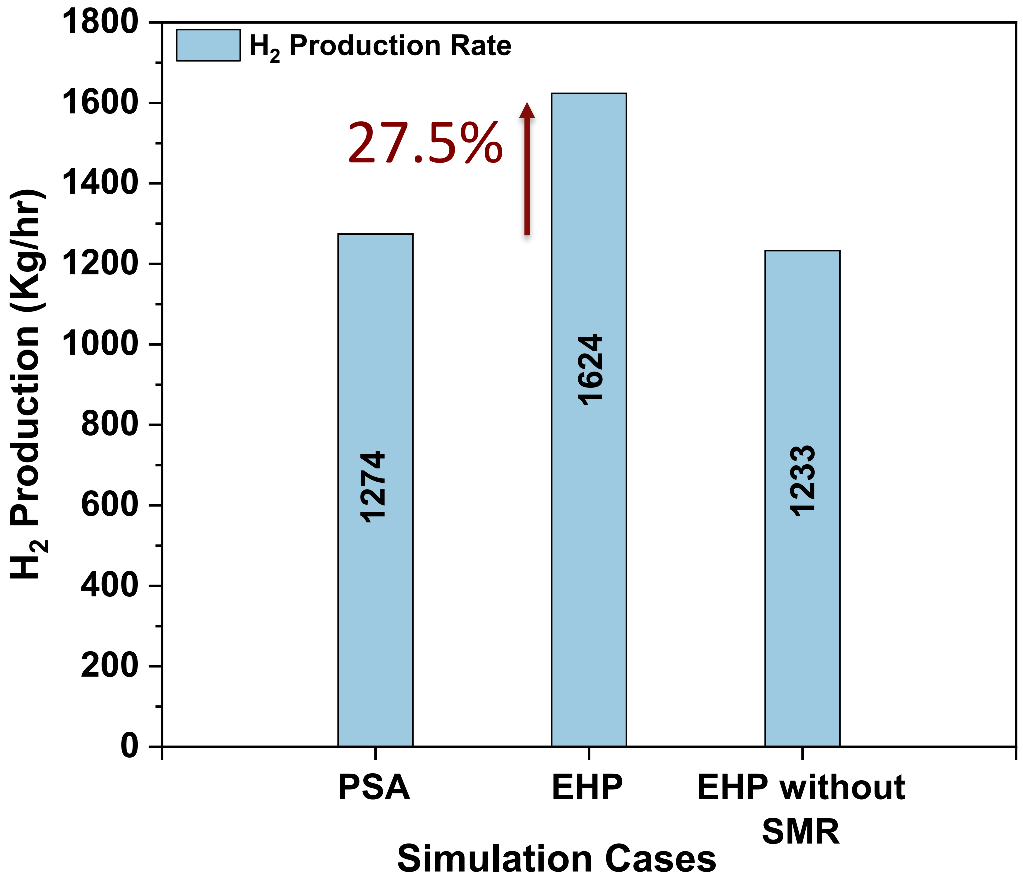
Gasifier Specifications	
Parameter	**Value**
Operating Temperature °C	800
Energy Source	Indirectly heated from char combustion
Gasifier type	Oxygen blown
Cold Gas Efficiency (LHV Basis)	83 %



Results

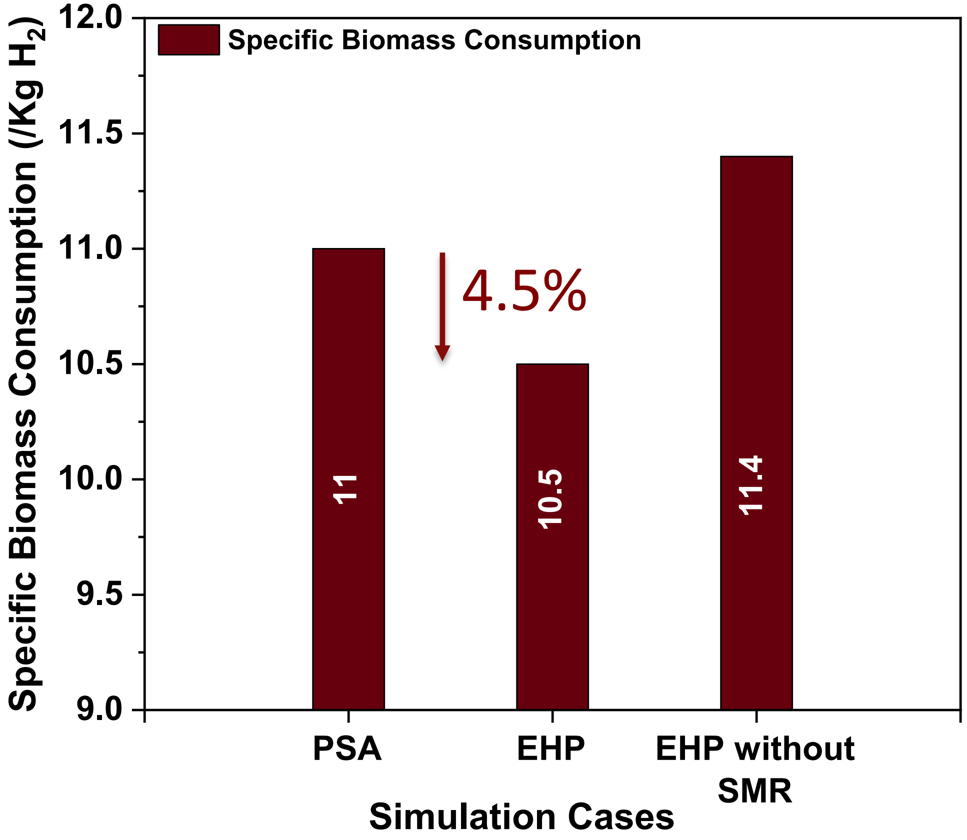


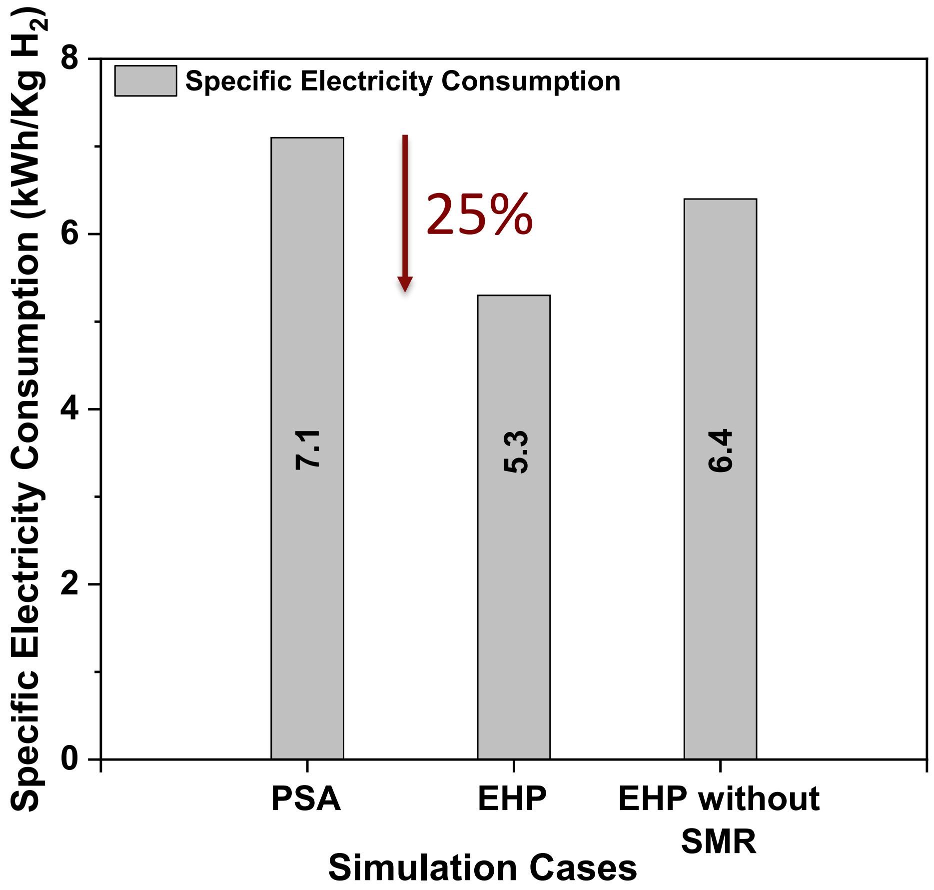
Dry Biomass feed to off gas combustor
Dry biomass feed to gasifier
Dry Biomass Consumption (Kg/hr)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
14000
14000
3000
14000
PSA
EHP
EHP without SMR
Simulation Cases



H_2 Production Rate
H_2 Production (Kg/hr)
1800
1600
1400
1200
1000
800
600
400
200
0
27.5%
1274
1624
1233
PSA
EHP
EHP without SMR
Simulation Cases

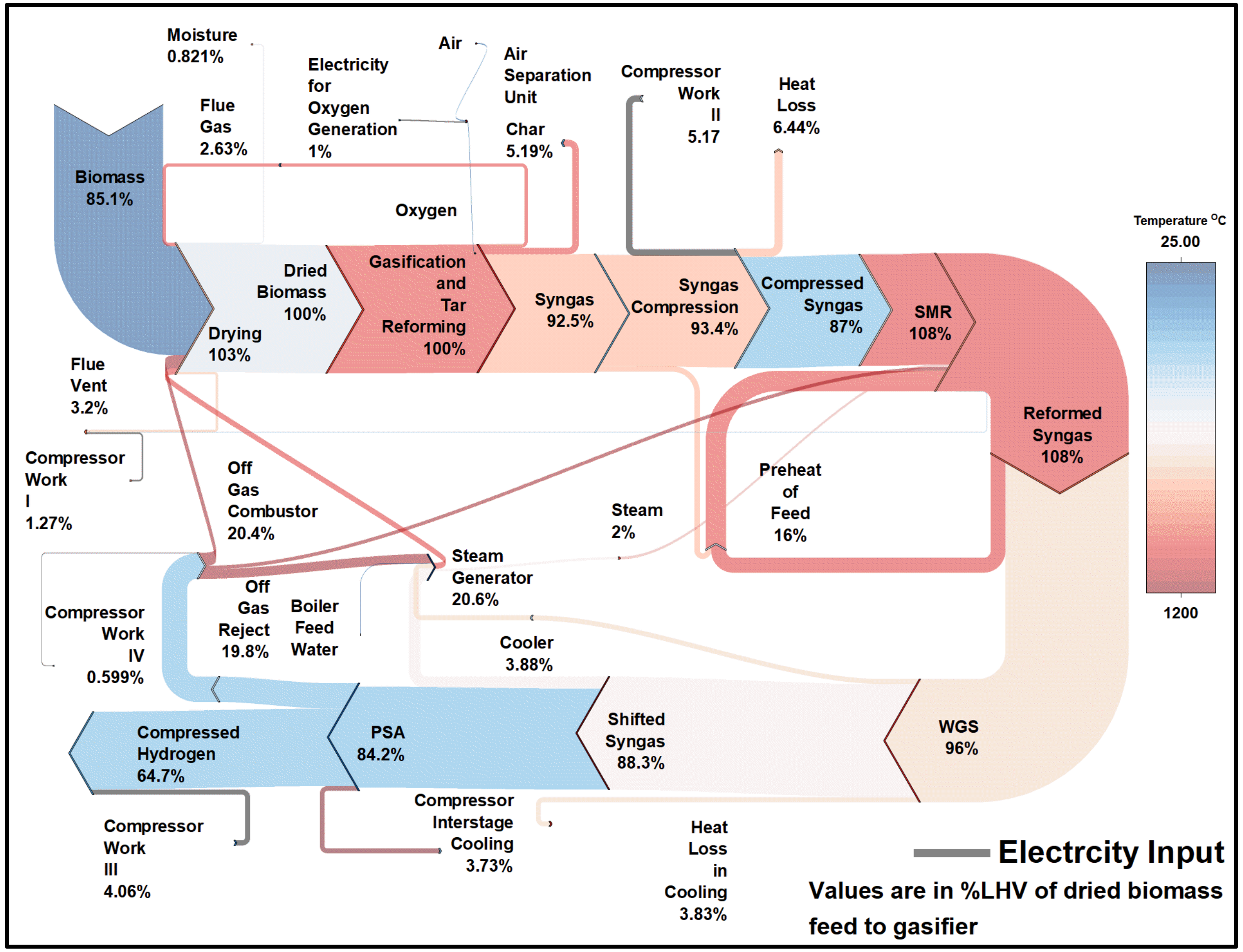
Results


Specific Biomass Consumption
Specific Biomass Consumption (/Kg H2)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
11
10.5
11.4
4.5%
PSA
EHP
EHP without SMR
Simulation Cases

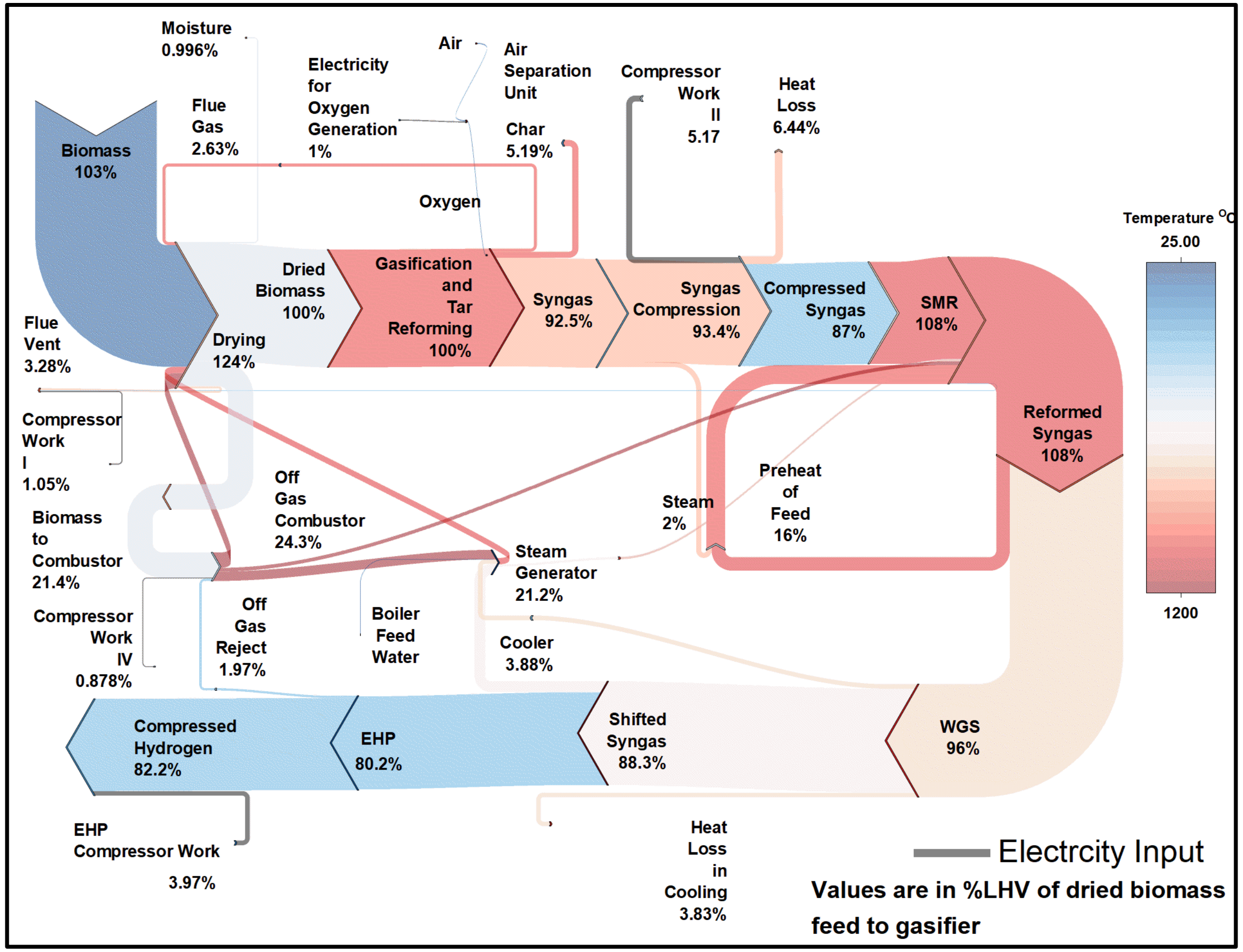

Specific Electricity Consumption
Specific Electricity Consumption (kWh/Kg H2)
8
6
4
2
0
7.1
5.3
6.4
25%
PSA
EHP
EHP without SMR
Simulation Cases

Results

Case 1: PSA



Case 2: EHP



Thank you

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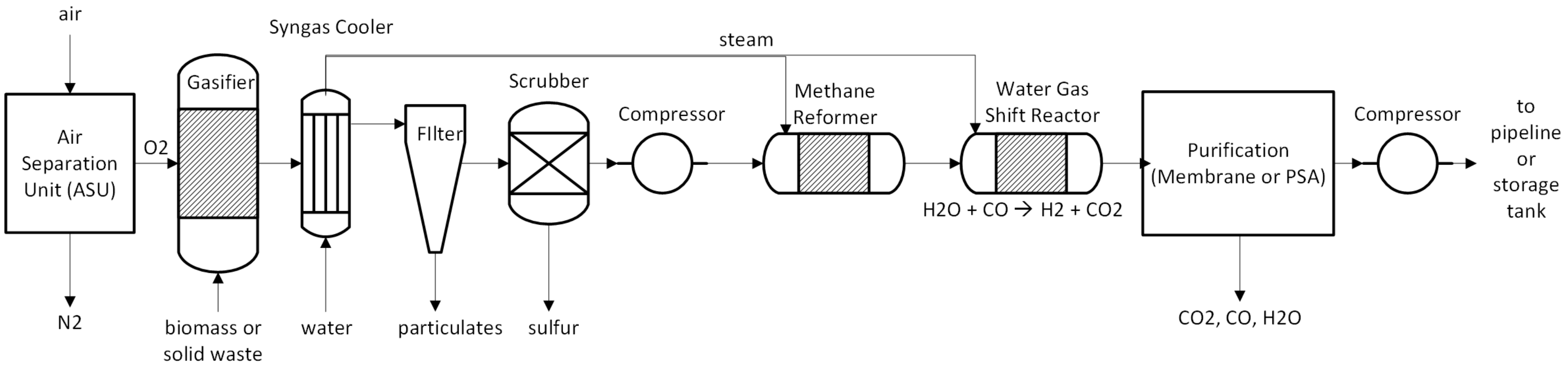
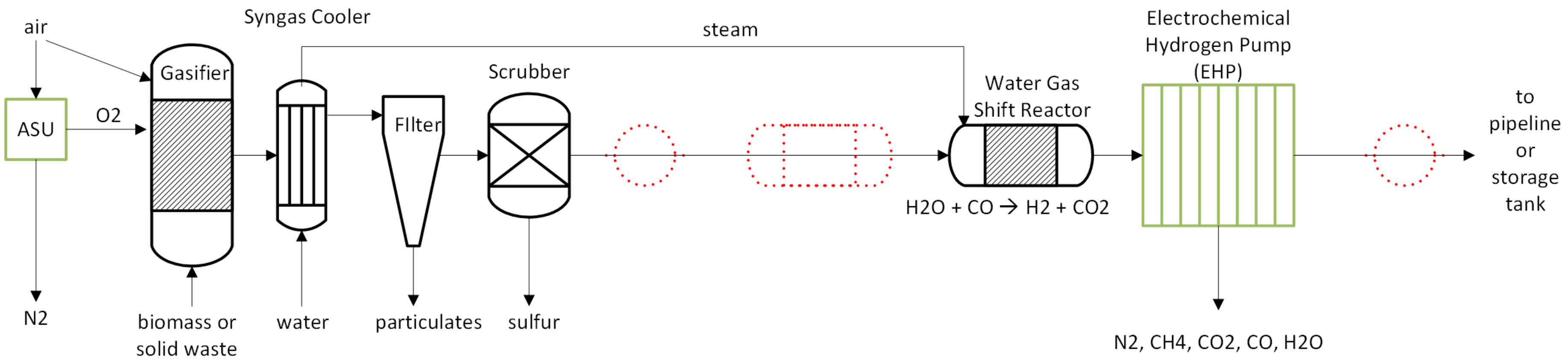
- **EXTRAS**

Application to Biomass Gasification Plant

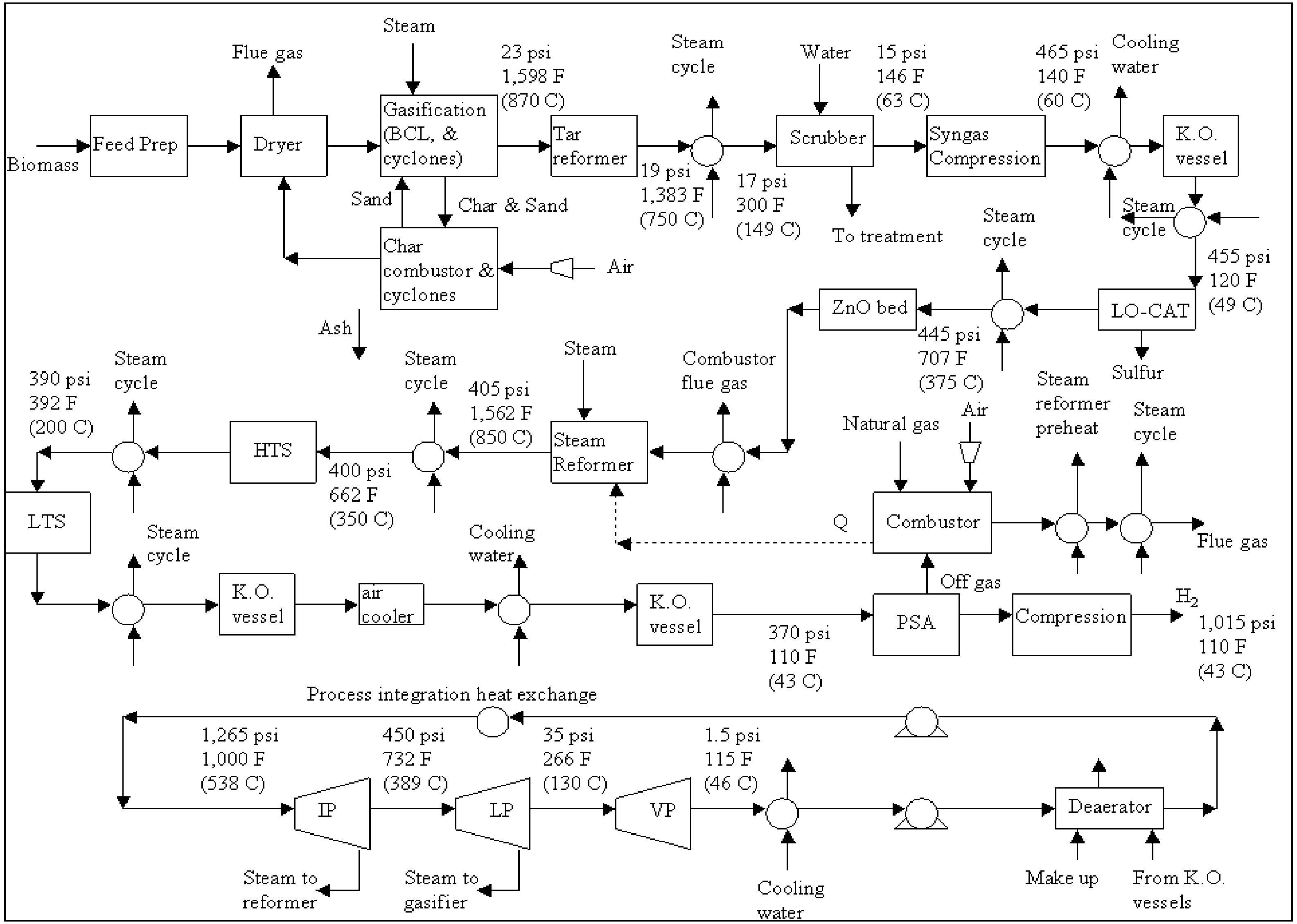
REFERENCE PROCESS FOR HYDROGEN PRODUCTION VIA BIOMASS GASIFICATION



INTENSIFIED PROCESS ENABLED BY ELECTROCHEMICAL HYDROGEN PUMP



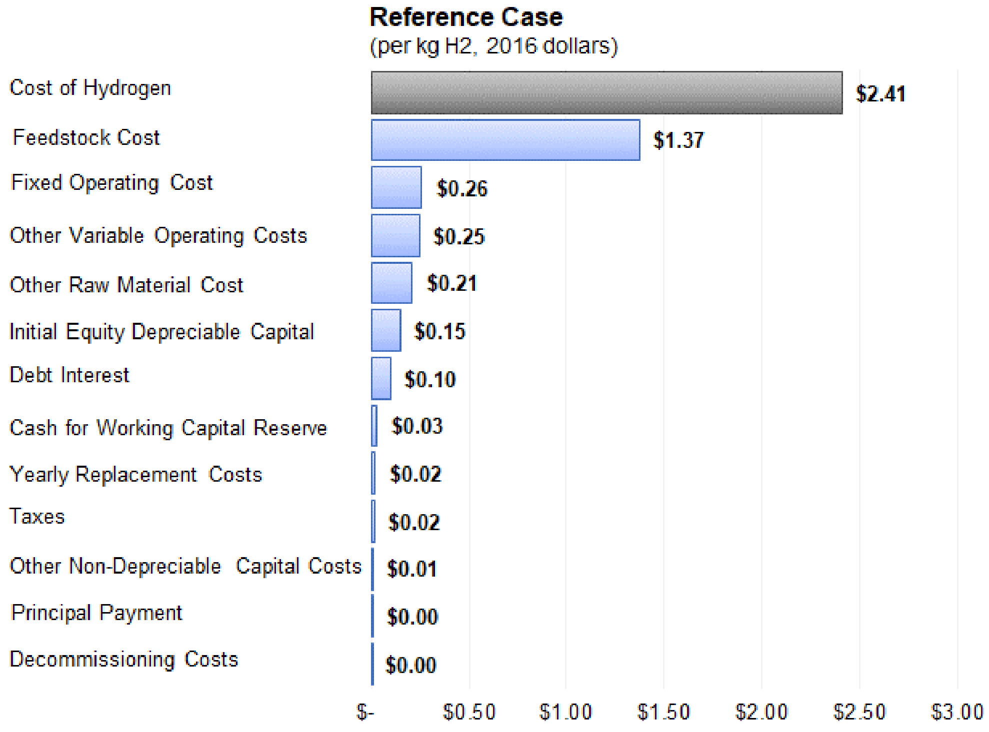
NREL Reference Plant Model

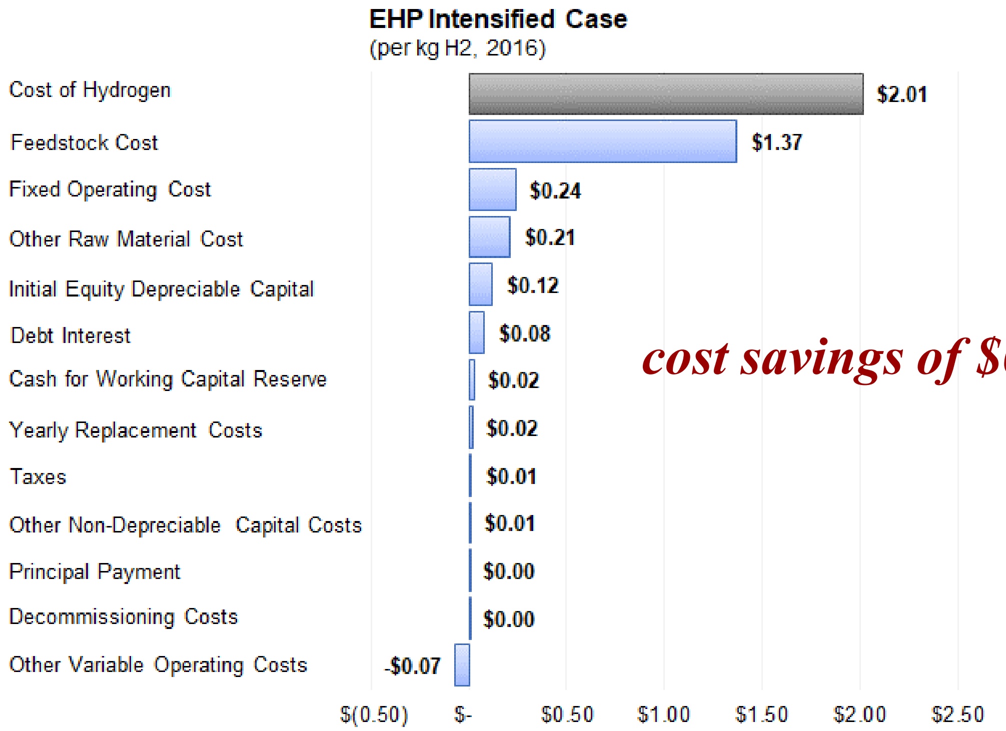


Mann, M. and D. M. Steward (2018) Current Central Hydrogen from Biomass via Gasification and Catalytic Steam Reforming: H2A Hydrogen Performance Analysis Model, NREL.

Preliminary Cost Savings Estimates

- Estimated 20% reduction in total capital (installed) costs
- Reduced specific power consumption by more than 60%:
  4.54 kWh/kg (for PSA and compression) to → 1.75 kWh/kg





cost savings of $0.47/kgH$_2$