Modular biomass Gasification for Co-Production of Hydrogen and Power

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U.S. Department of Energy

National Energy Technology Laboratory

Fossil Energy and Carbon Management

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UNIVERSITY OF NORTH DAKOTA
COLLEGE OF ENGINEERING & MINES

Project Overview

Objective

Demonstrate the technical and economic feasibility of a novel, process-intensified and modular Combined Hydrogen Heat and Power (CH^2P) technology, targeting scales less than 50 MW_e (~60 MTPD hydrogen)

Funding

- Federal: $1,600,000
- North Dakota Industrial Commission $500,000
- Singularity Energy Technologies: $20,000

Team Funding

- UND: $1,470,056
- Envergex LLC: $579,944
- Singularity Energy Technologies: $70,000

Period of Performance

- Start: 10/01/2022
- Stop: 09/30/2024

Small Scale Biomass to Hydrogen

- Small scale (5 - 50 MW_e) H_2 production from biomass requires sufficient biomass (~200 – 2,000 mptd)
- Abundant biomass residues available in ND and MN
- Combustion for facility steam/heat/power does not consume all biomass residues produced

Sunflower Processing facilities;

- ADM Northern Sun Division, SunOpta, Smude's Sunflower Oil, CHS Sunflower

Sugar Beet Processing facilities;

- American Crystal Sugar Company, Southern Minnesota Beet Sugar Cooperative, Minn-Dak Farmers Cooperative

RDF/MSW Facilities;

- Minnesota Resource Recovery Facility


Sunflower hulls


Beet pulp Shreds


Refuse derived fuel

Property	Beet pulp[1]	Sunflower hulls[2,3]	RDF[4]
% MC	6.9	9.61	5.5
% AC	6.2	1.2	16
% VM	75.4	82.7	57.5
% FC	18.5	16.1	15
S	0.2	-	0.35
C	51.1	46.21	37.5
H	6.7	6.06	6.5
N	3.4	0.88	3
O	38.7	46.58	27.5
HHV , MJ/Kg	20.29	18.11	-
LHV, MJ/Kg	18.92	-	-

[1]Cao, X., et al. (2013). Journal of agricultural and food chemistry, 61(39), 9401-9411.
[2]Brachi, P., et al. (2017).. Combustion Institute-Sezione Italiana.
[3]Turzyński, T., et al. (2021). Materials, 14(10), 2484.
[4]Ganesh, T., Vignesh, P., & Kumar, G. A. (2013). Carbon, 35, 40-0.

Steam-Iron 2.0!

- Steam-Iron Process: Patented by Howard Lane in the early 1900s
- First large-scale production of H_2 from H_2O was by Lane Hydrogen Producer
- Iron-oxide was the active component used in the process

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \quad \Delta H_{800°C} \; -50.5 kJ/mol$$

$$Fe + H_2O \rightarrow FeO + H_2 \quad \Delta H_{800°C} \; -15.0 kJ/mol$$

The steam-iron process was abandoned over time:

- H_2 produced low purity
- Poor stability of oxide material
- H_2 via hydrocarbons cheaper/Better economies of scale
- Thermodynamically limited

UNITED STATES PATENT OFFICE.

HOWARD LANE, OF BIRMINGHAM, ENGLAND, ASSIGNOR TO INTERNATIONALE WASSERSTOFF AKTIENGESELLSCHAFT, OF FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY.

PROCESS FOR THE PRODUCTION OF HYDROGEN.

1,078,686. Specification of Letters Patent. Patented Nov. 18, 1913.

No Drawing. Original application filed June 16, 1910, Serial No. 572,411. Divided and this application filed December 9, 1911. Serial No. 664,809.

To all whom it may concern:

Be it known that I, Howard Lane, a subject of the King of Great Britain, and resident of 125 Edmund street, Birmingham, in the county of Warwick, England, have invented certain new and useful Improvements in a Process for the Production of Hydrogen, of which the following is a specification.

This application is a division of my application for patent for the same invention filed the 16th June 1910 Serial No. 572,411.

This invention relates to the well-known method of producing hydrogen in which a

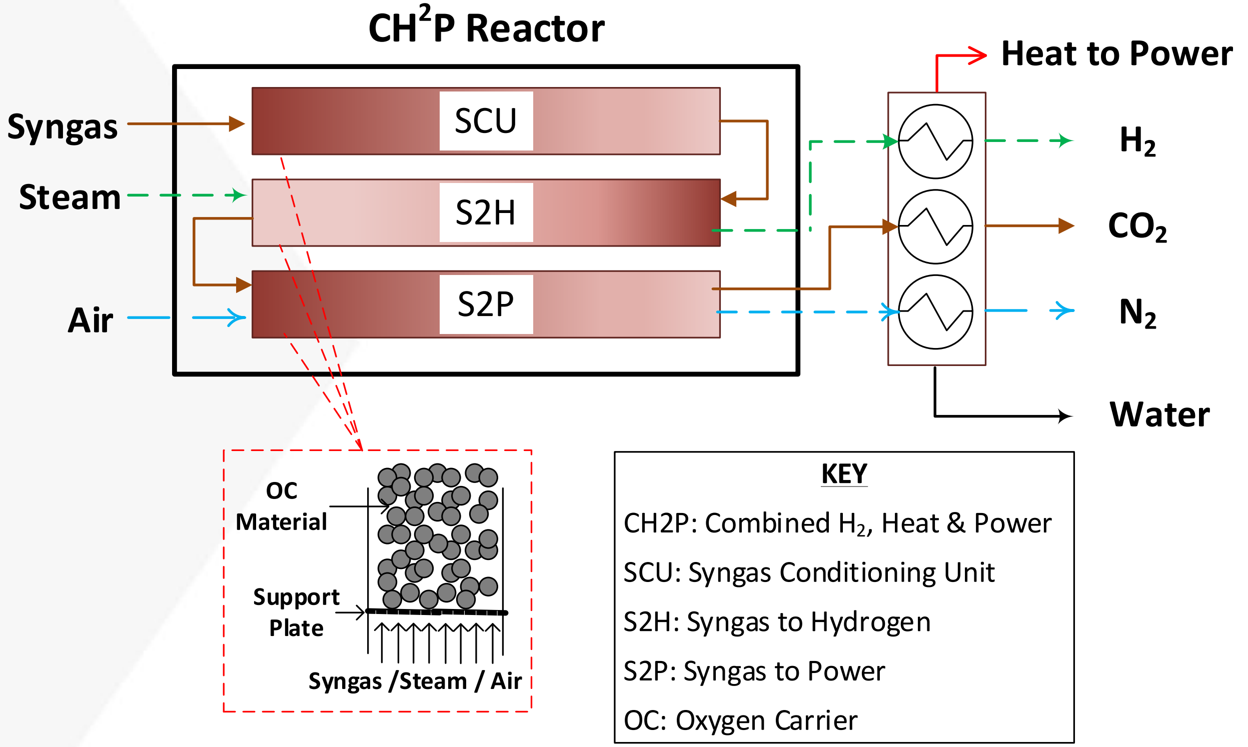
will be assumed that the metal has just been oxidized during the hydrogen producing phase. The sulfur, carbon and other impurities left by the preceding reduction phase are thereupon got rid of by admitting air under pressure to the retort and the products of combustion being discharged into the atmosphere. The admission of air to the retort and the discharge of the products of combustion are then cut off and reducing gas admitted and passed through and out of the retort to a gas-washing and regenerating apparatus. When the reduction stage

Lane, H. (1913). *U.S. Patent No. 1,078,686*. Washington, DC: U.S. Patent and Trademark Office.
Voitic, G., et al. (2016). High purity pressurised hydrogen production from syngas by the steam-iron process. *RSC advances*, *6*(58), 53533-53541.
Thursfield, A., & Metcalfe, I. S. (2013). High temperature gas separation through dual ion-conducting membranes. *Current Opinion in Chemical Engineering*, *2*(2), 217-222.

Combined Hydrogen, Heat & Power

CH²P (Combined Hydrogen, Heat and Power)

- Three step process: 1) Oxy-gasification of low carbon fuel, 2) Syngas oxidation with oxygen carrier, and 3) Oxidation of oxygen carrier with steam/air
- Leverages advances in chemical looping combustion and high temperature systems to improve stability and purity
- Interest in distributed, small-scale H_2 production
- Intensification for co-production of heat and power



Project team

- UND's College of Engineering and Mines Research Institute (CEMRI)
  - Mr. Junior Nasah (PI), Dr. Johannes (Hannes) Van der Watt
  - Two research engineers and three graduate students
- Envergex LLC (small business partner)
  - Dr. Srivats Srinivasachar
- Singularity Energy Technologies (Small business, Sandwich™ Gasifier consultant)
  - Dr. Nikhil Patel

Team Organization

Dr. Daniel Laudal – Director
Mr. Junior Nasah (PI) – Assoc. Director
College of Engineering & Mines Research Institute

US Dept. of Energy
National Energy Technology Laboratory

Sub-contractor
Dr. Srivats Srinivasachar, Envergex

Task 1 – Project Management and Planning
- Nasah (Lead)
- Laudal
- Srinivasachar

Task 2 – Development and Evaluation of Novel OCM
- Srinivasachar (Lead)
- Nasah
- Van der Watt
- Graduate Student

Task 3 – Laboratory Scale Evaluation of Oxygen-Blown Gasifier
- Van der Watt (Lead)
- Nasah
- Patel (SET)
- Engineer / Scientist
- Graduate Student

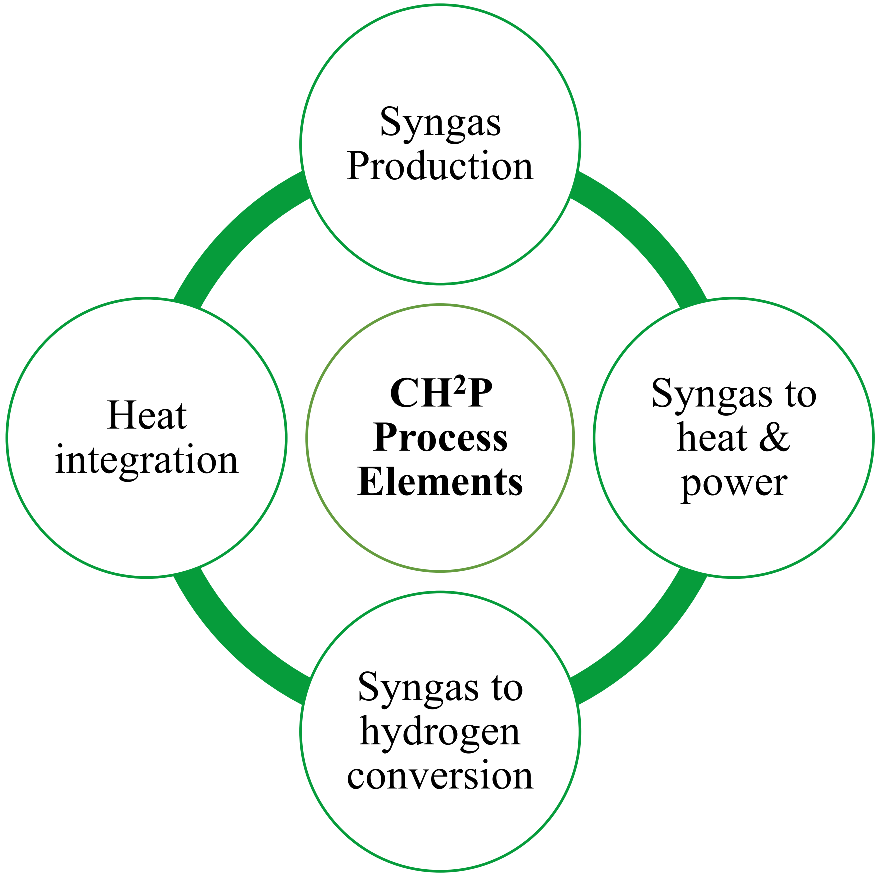
Task 4 – Integrated Hydrogen Production
- Van der Watt (Lead)
- Nasah
- Srinivasachar
- Engineer / Scientist
- Graduate Student

Task 5 – Preliminary TEA
- Nasah (Lead)
- Laudal
- Srinivasachar
- Patel (SET Consultant)
- Van der Watt
- Graduate Students

Technical Approach

Five Key Focus Areas

1. Develop oxygen carrier materials (OCM) and evaluate cyclic performance with syngas and steam (Task 2)
2. Characterize syngas quality from oxy-blown Sandwich™ gasification (Task 3)
3. Produce high purity H_2 and compression-ready CO_2 (Task 2, 4)
4. Test integrated laboratory unit of Sandwich™ gasifier and CH2P reactor (Task 4)
5. Perform TEA of process including pathway to $1/kg of H_2 (Task 5)



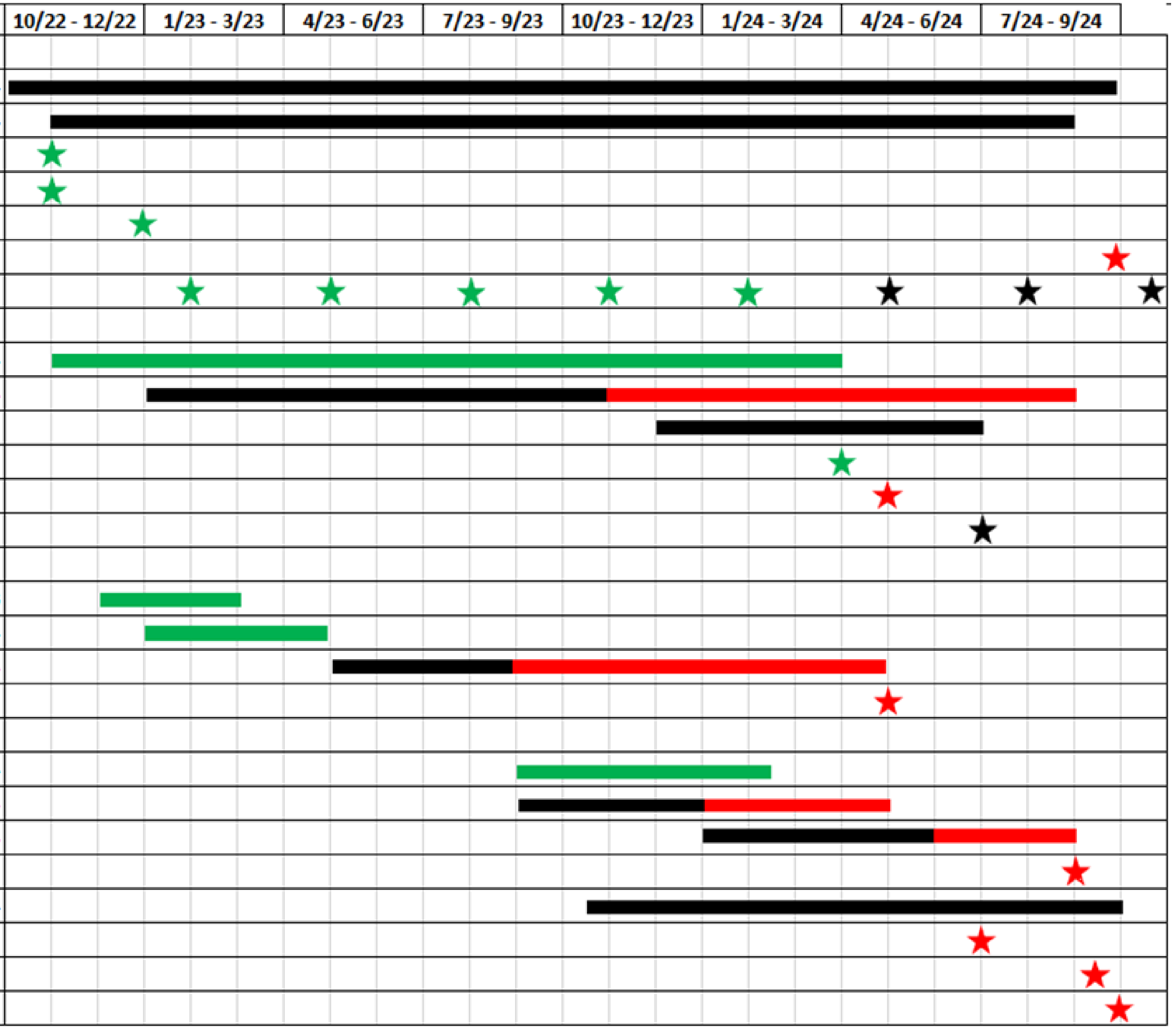
Project Status

- Activities ongoing in all focus areas
- Oxygen Carrier Material (OCM) development
- Gasification testing
- OCM testing in a tube reactor
- Construction of bench CH^2P
- Techno-economic analysis

Milestone Title and Description	Due Date
Project Management Plan	**10/30/2022**
Technology Maturation Plan	**12/28/2022**
Synthesis Gas Characterization	4/30/24
Down-selection of OCMs	**3/28/24**
Extended cycling of OCM completed	7/1/24
Gasifier Heat Mass Balance Completed	6/30/24
Integrated Testing Completed	9/1/24
Integrated Heat Mass Balance Completed	9/16/24
Final TMP	9/30/24
OCM Development Report	4/25/24
Techno-Economic Analysis	9/30/2024

Project Schedule

		Start Date	End Date
Task 1	**Project Management and Planning**		
1.1	Project Management Plan	10/1/22	9/30/24
1.2	Technology Maturation Plan	11/2/22	8/1/24
	Mileston 1 - Kickoff	11/2/22	
	Milestone 2 - PMP Updated	10/28/22	
	Milestone 3 - Preliminary TMP	12/29/22	
	Milestone 10 - Final TMP	9/30/24	
	Quarterly and Final Reports		
Task 2	**Development & Evaluation of Novel Oxygen Carrier Materials**		
2.1	Laboratory Scale OCM Manufacturing	11/2/22	3/28/24
2.2	Characterization and Performance Testing	1/9/22	3/29/24
2.3	OCM Lifetime Evaluation	12/1/23	6/31/24
	Milestone 5 - Downselection of OCM	3/28/24	
	Deliverable A - OCM Development Report	4/25/24	
	Milestone 6 - 1000 hr cycle completed on downselect	7/1/24	
Task 3	**Lab Scale Evaluation of Oxy-Blown Gasifier**		
3.1	Feedstock Procurement & Characterization	11/2/22	1/31/23
3.2	Heat Distribution Modelling and Equipment Upgrade	1/3/23	1/15/24
3.3	Synthesis Gas Production	5/15/23	4/30/24
	Milestone 4 - Synthesis Gas Characterization	4/30/24	
Task 4	**Integrated Hydrogen Production**		
4.1	Catalyst Manufacturing	9/1/23	2/15/24
4.2	Hydrogen Reactor Fabrication	9/1/23	4/30/24
4.3	Integrated Testing	1/2/24	9/1/24
	Milestone 8 - Integrated Testing Completed	9/1/24	
Task 5	**Preliminary Techno-Economic Analysis**	10/15/23	9/30/24
	Milestone 7 - Gasifier Heat Mass Balance	6/30/24	
	Milestone 9 - Integrated Heat Mass Balance	9/16/24	
	Deliverable B - Techno-Economic Analysis	9/30/24	



Green is completed
Red is changes
Black is original

Technical Approach

Focus Area 1

1. Develop oxygen carrier materials (OCM) and evaluate cyclic performance with syngas and steam (Task 2)
2. Characterize syngas quality from oxy-blown Sandwich™ gasification (Task 3)
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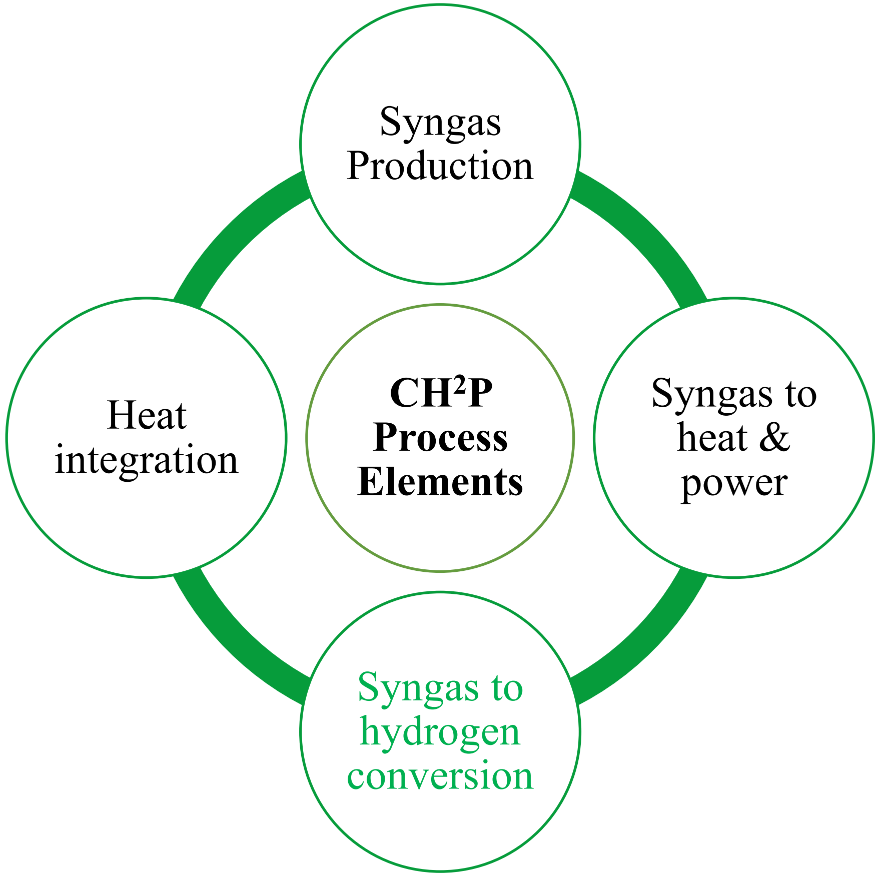


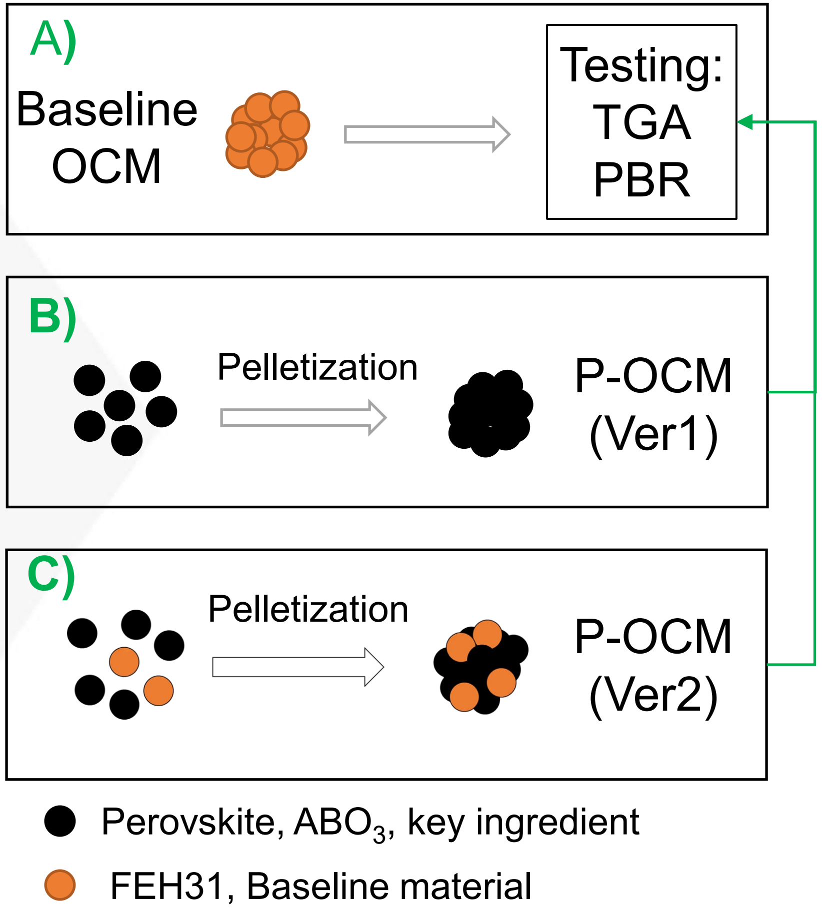
Focus Area 1

Evaluate OCM Performance

A. Baseline OCM – H_2 Production
- ❑ Determine cyclic syngas conversion performance
- ❑ Evaluate reaction rates in packed bed
- ❑ Determine effect of impurities

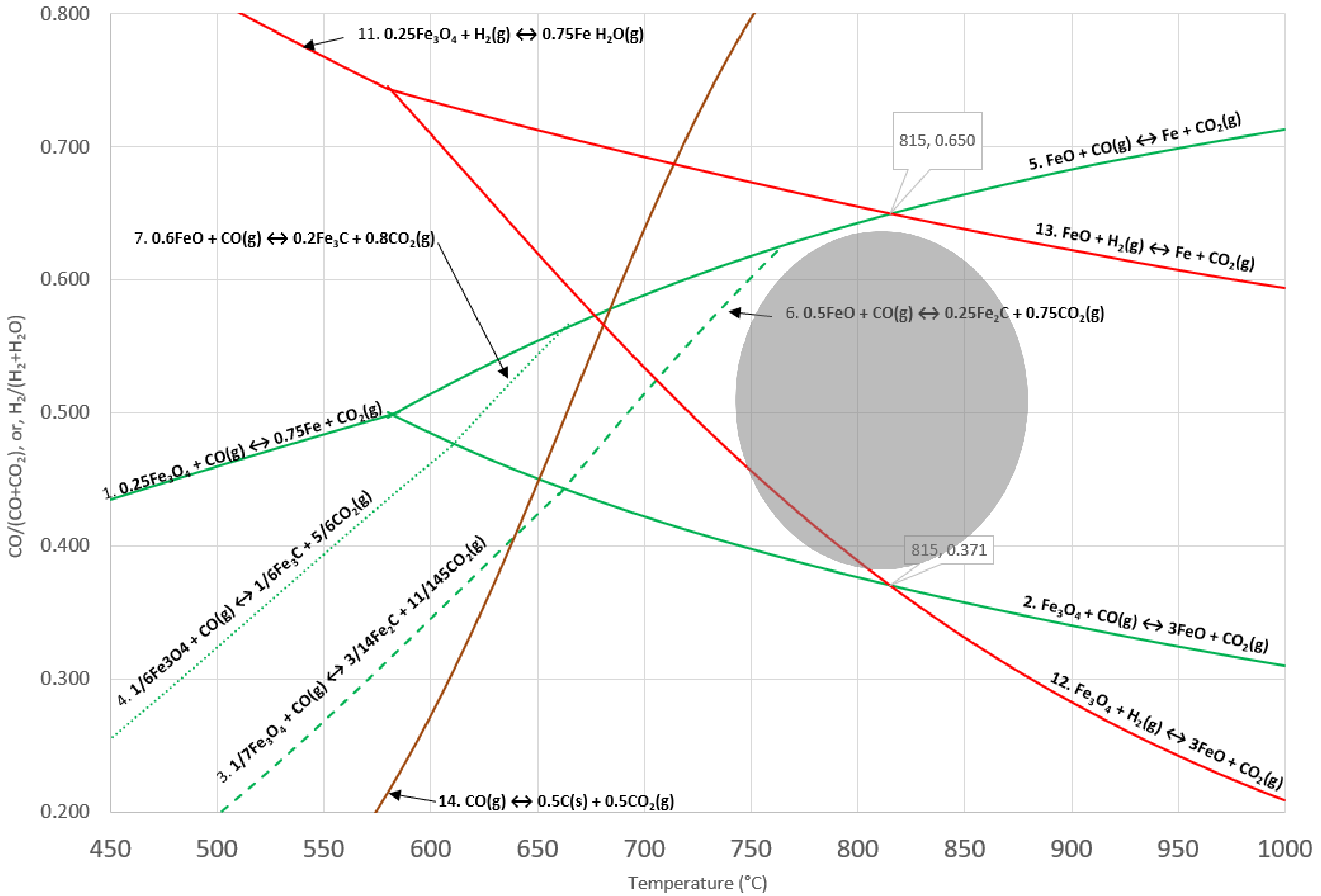
B. Perovskite – Syngas Conversion
- ✓ Prepare perovskites by
  - ✓ Pechini method
  - ✓ Mechanical mixing
- ❑ Evaluate syngas conversion in packed bed

C. P-OCM – H_2 & Syngas
- ❑ Prepare perovskite-baseline blend and evaluate



Thermodynamics

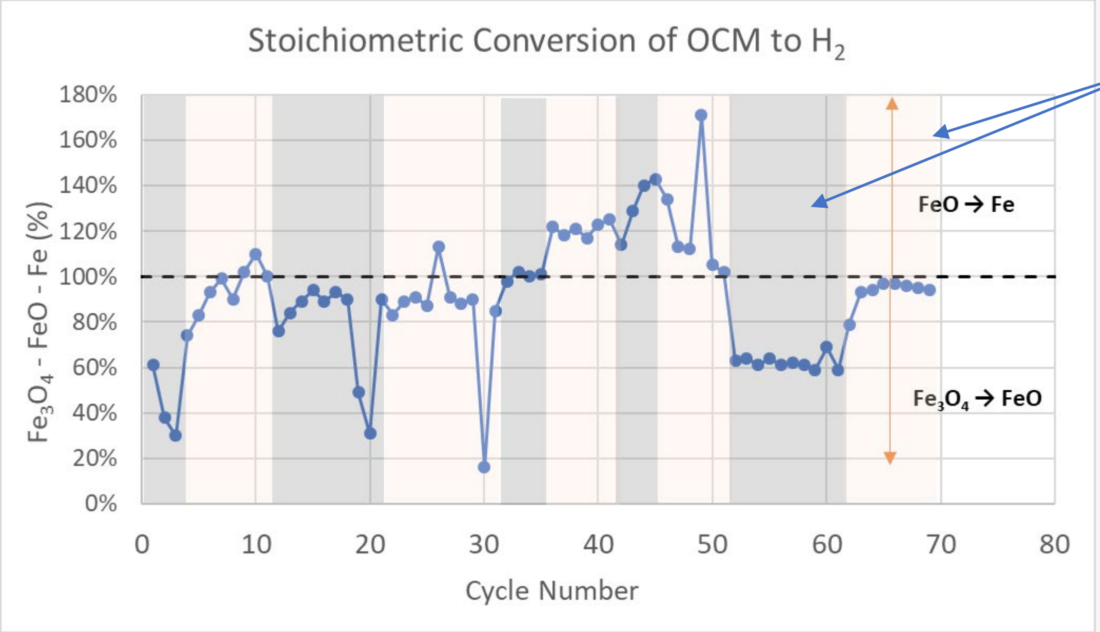
- Thermodynamics determined by Baur-Glaessner diagram
- Diagram identifies equilibrium CO and H_2 conversion as function of temperature
- Also identifies conditions for carbide formation



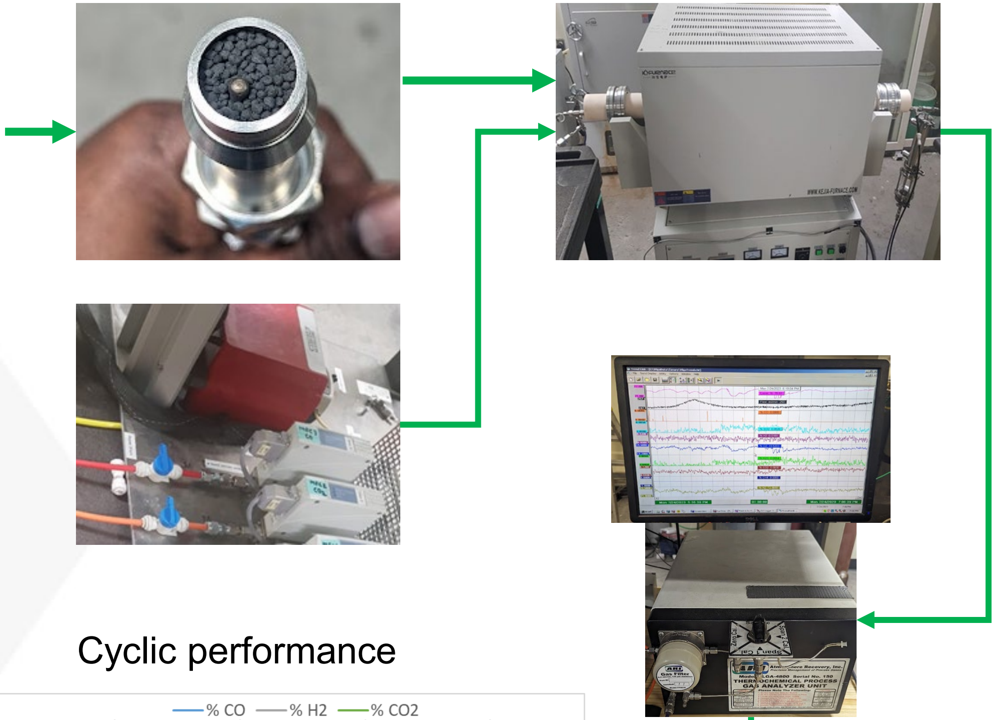
Focus Area 1A

Baseline OCM (FEH31, developed in FE0031534)

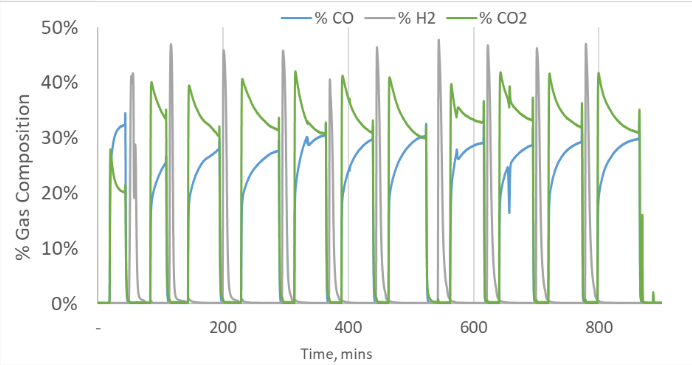
- Developed in previous project (FE00031534)
- Multi-cycling tests ongoing (~70 cycles of 1000) with 100% CO/CO2 (reduction) and 100% steam (oxidation)



Varying test conditions



Cyclic performance



Focus Area 1A

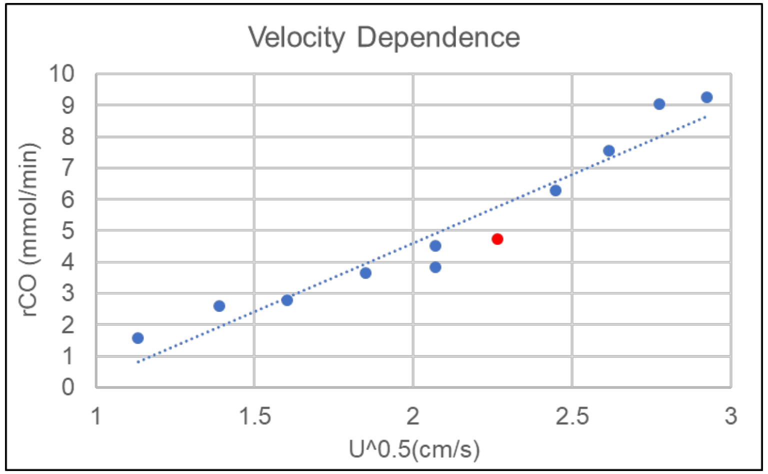
Baseline OCM (FEH31)

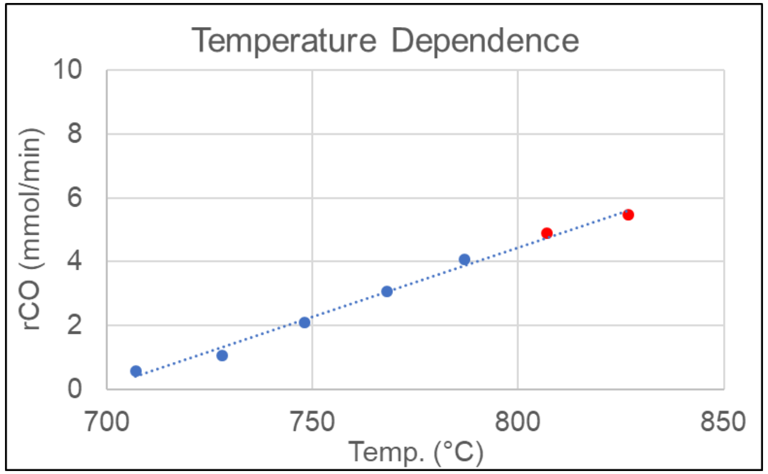
- ❑ Developing model for reactor performance
  - ❑ Temperature dependence
  - ❑ Pressure dependence
- ❑ Determine effect of impurities

$$\frac{dT}{dW} = \frac{r'_A \Delta H_{Rx} - \dfrac{Ua(T - T_a)}{\rho_b}}{\sum F_i C_{P_i}}$$

Type of Limitation	Variation of Reaction Rate with:		
	Velocity	Particle Size	Temperature
External diffusion	$U^{1/2}$	$(d_p)^{-3/2}$	≈ Linear
Internal diffusion	Independent	$(d_p)^{-1}$	Exponential
Surface reaction	Independent	Independent	Exponential

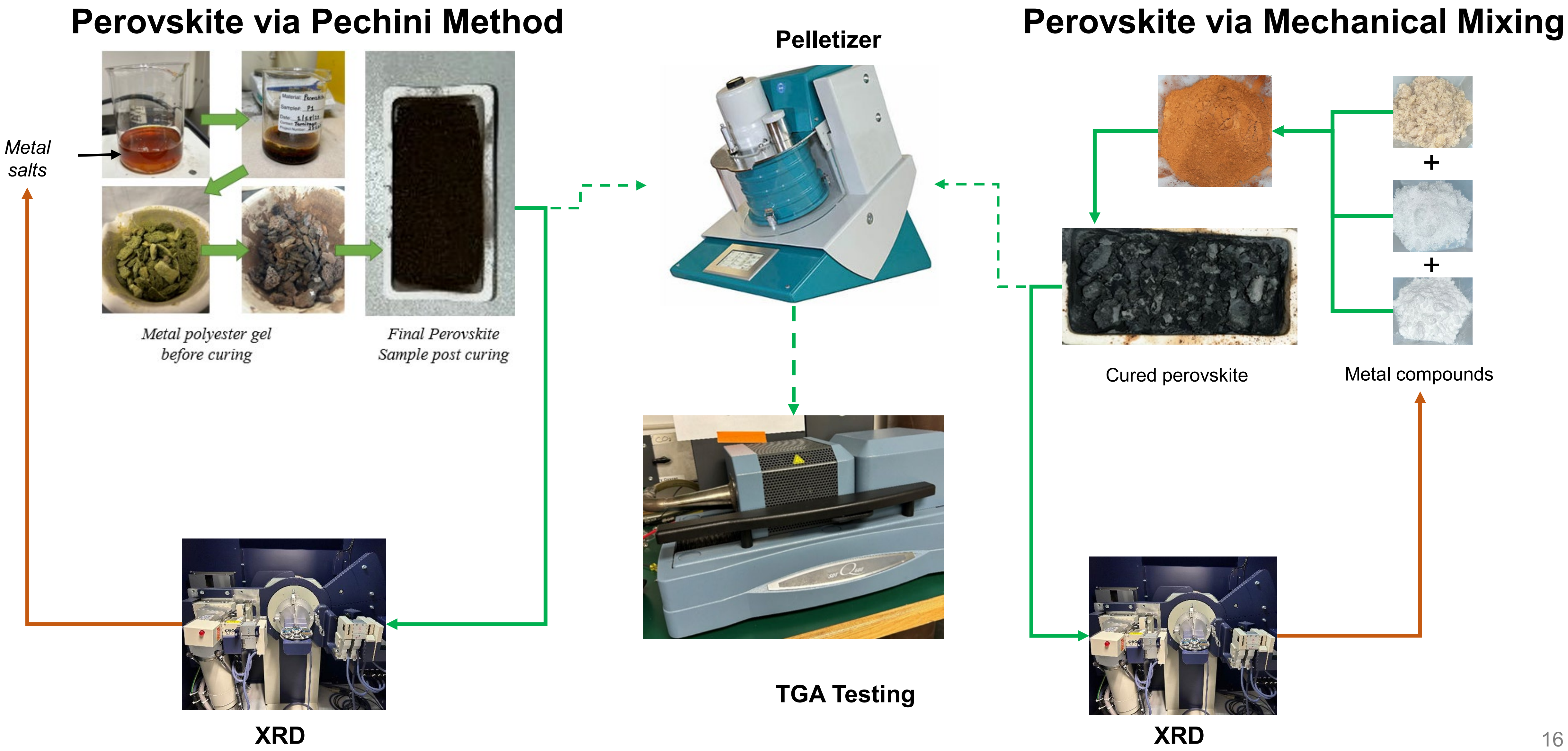
$$\frac{dP}{dz} = -\frac{G}{\rho g_c D_P}\left(\frac{1-\phi}{\phi^3}\right)\left[\overbrace{\frac{150(1-\phi)\mu}{D_P}}^{\text{Term 1}} + \overbrace{1.75G}^{\text{Term 2}}\right]$$





Fogler, H. S. (2010). *Essentials of chemical reaction engineering: essenti chemica reactio engi*. Pearson Education.

Focus Area 1B



Focus Area 1B

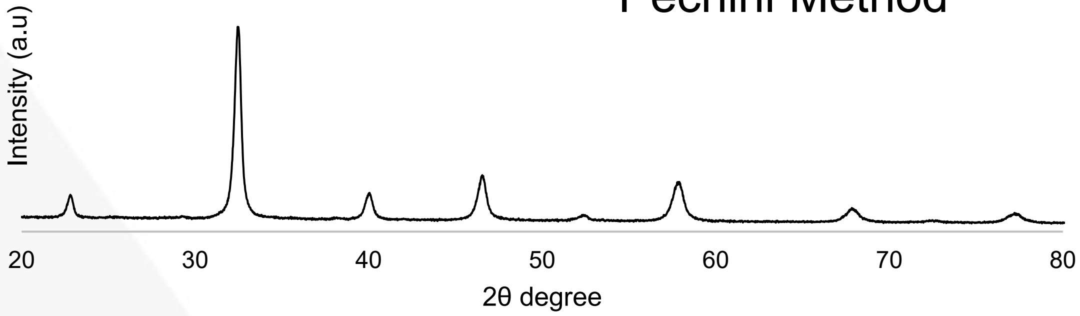
- Preparation methods for perovskite completed
- Both production pathways showed similar purity
- Testing of perovskite for syngas conversion ongoing

Pelletized Perovskite Material

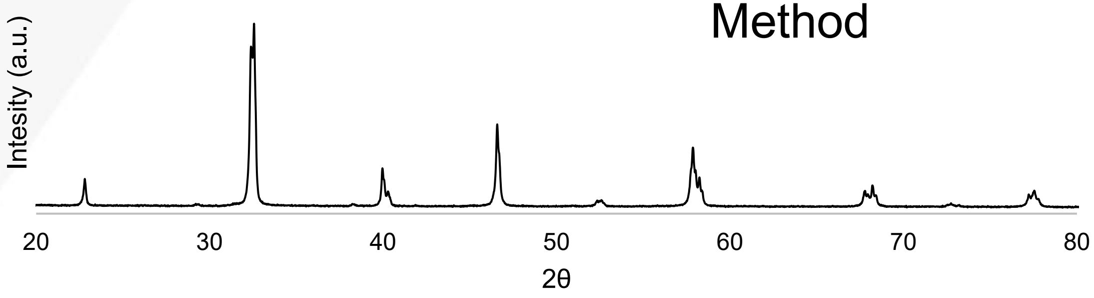
Before curing

After curing

Pechini Method



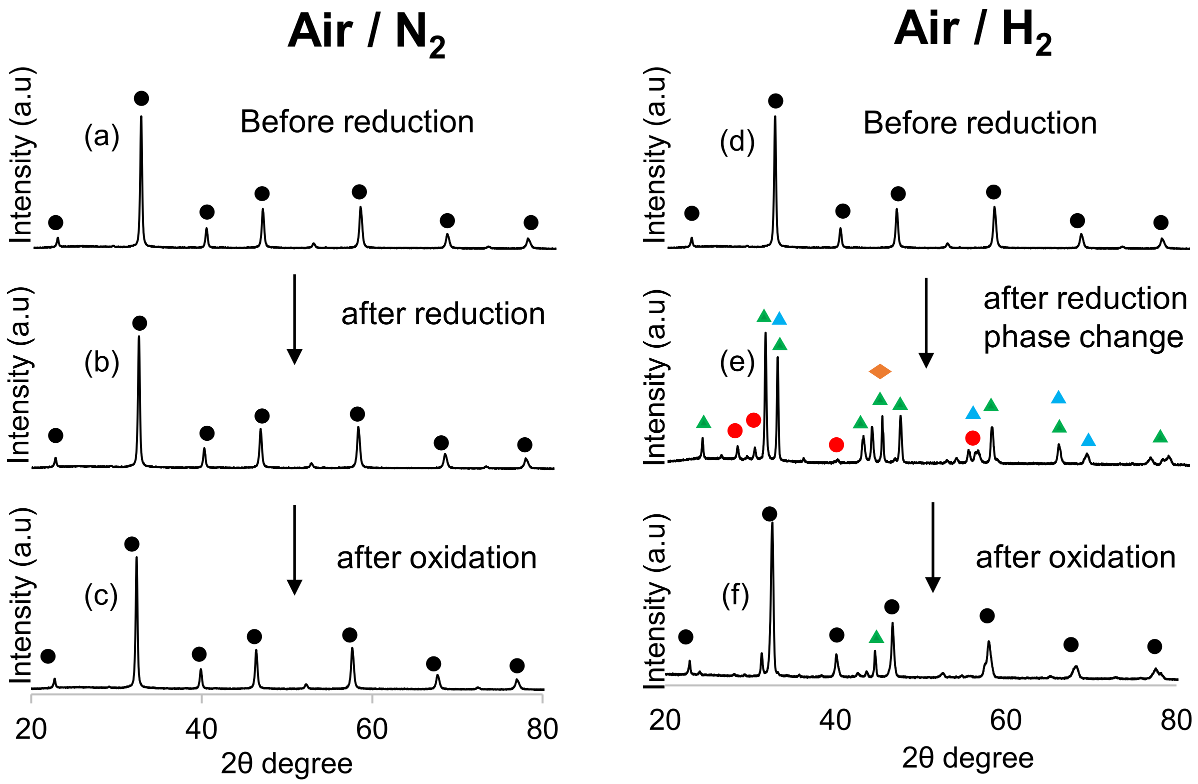
Mechanical Mixing Method



Focus Area 1B

Reversibility Tests

- Evaluated phase changes due to redox reactions on perovskite powders

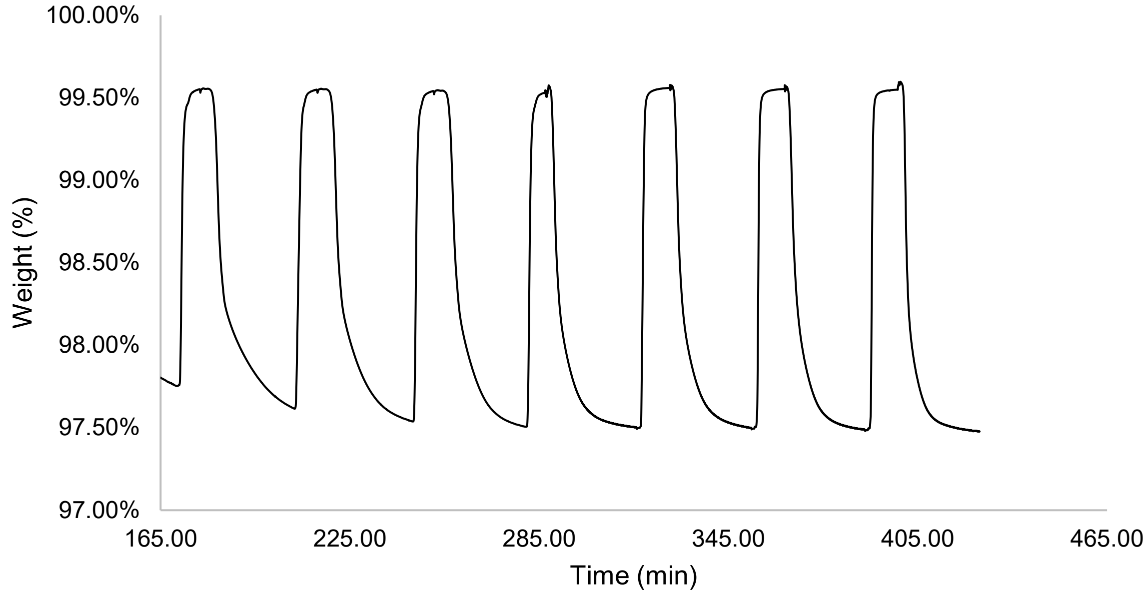


N_2 reduction and air oxidation runs: diffractogram of sample (a) before reduction; (b) after reduction; (c) after oxidation. H_2 reduction and air oxidation runs: (d) before reduction; (e) after reduction; (f) after oxidation

Cyclical Stability Tests

Objectives:

- Evaluated cyclical stability of perovskite in
  - Reducing atmosphere: CO/CO_2 (N_2 background)
  - Oxidizing atmosphere: Air



Technical Approach

Focus Area 2

1. Develop oxygen carrier materials (OCM) and evaluate cyclic performance with syngas and steam (Task 2)
2. Characterize syngas quality from oxy-blown Sandwich™ gasification (Task 3)
3. Produce high purity H_2 and compression-ready CO_2 (Task 2, 4)
4. Test integrated laboratory unit of Sandwich™ gasifier and CH2P reactor (Task 4)
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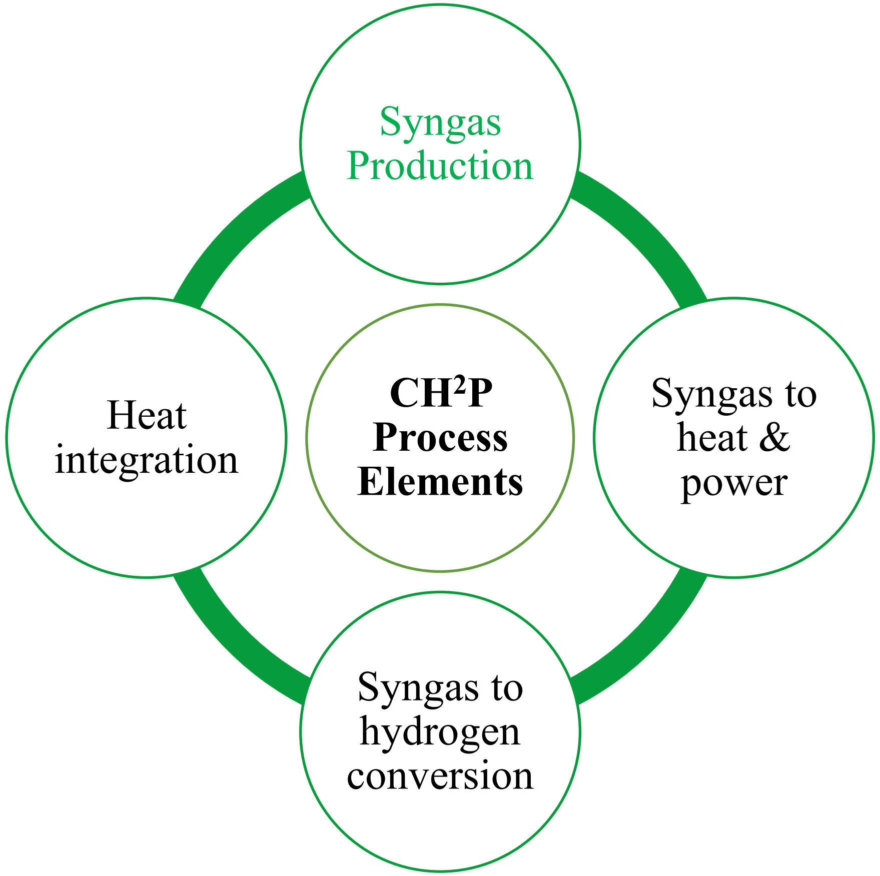
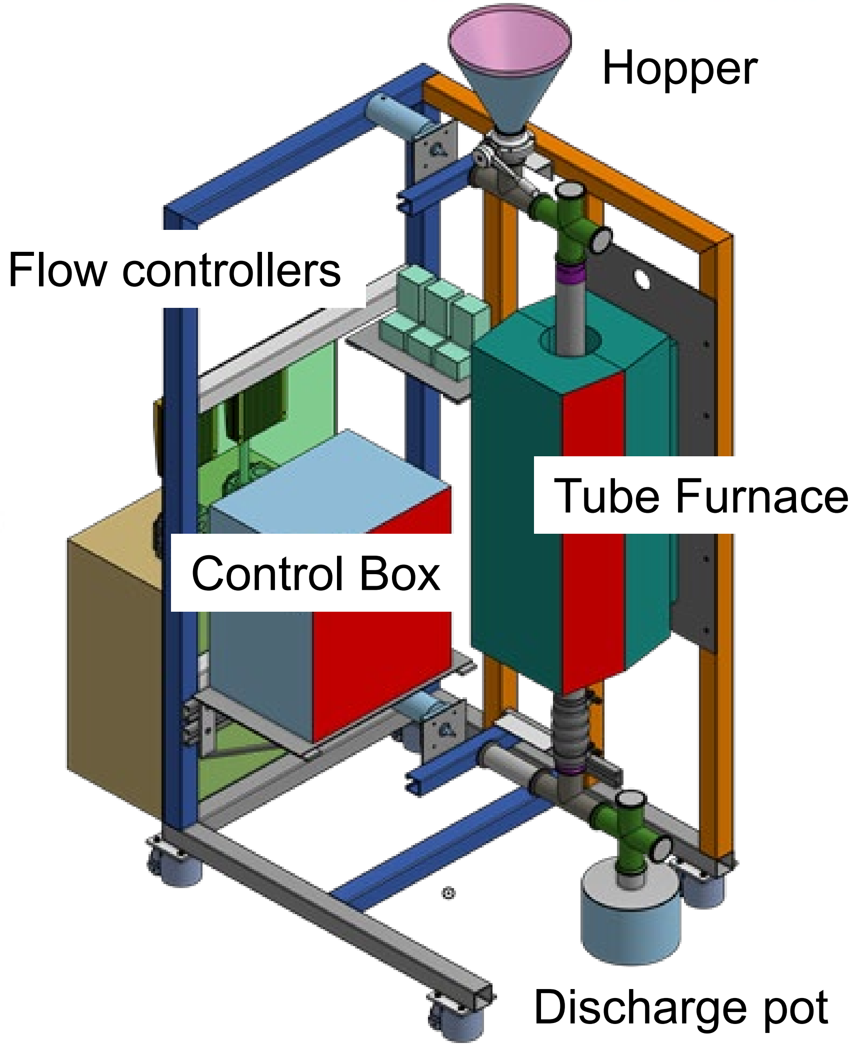


Focus Area 2

Objective: Characterize syngas quality

A. Process simulation of Sandwich™ gasification (ASPEN Plus)
   - ✓ Evaluate multiple equivalence ratios
   - ✓ Validate with experimental data

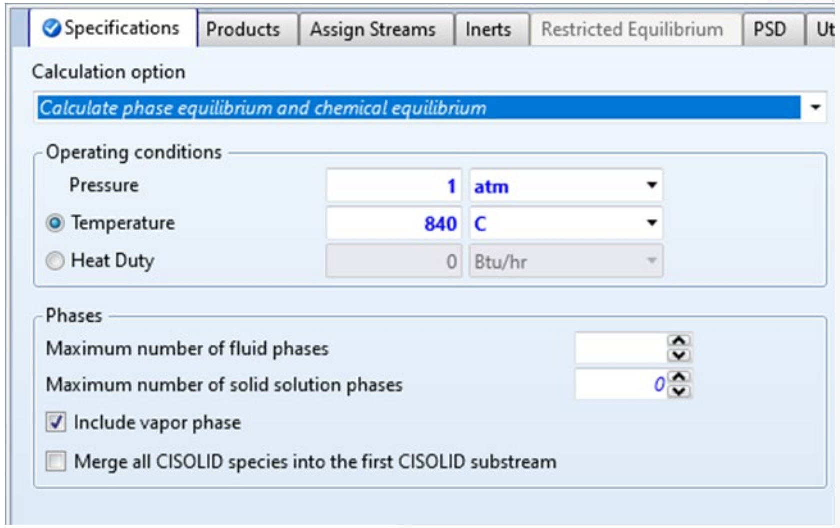
B. Produce Syngas Using Sandwich™ Gasification technology
   - ❑ Oxy-gasification with CO_2 & H_2O
   - ❑ Evaluate two biomasses (wood pellets & ag-waste)
   - ❑ Tar sampling and analysis

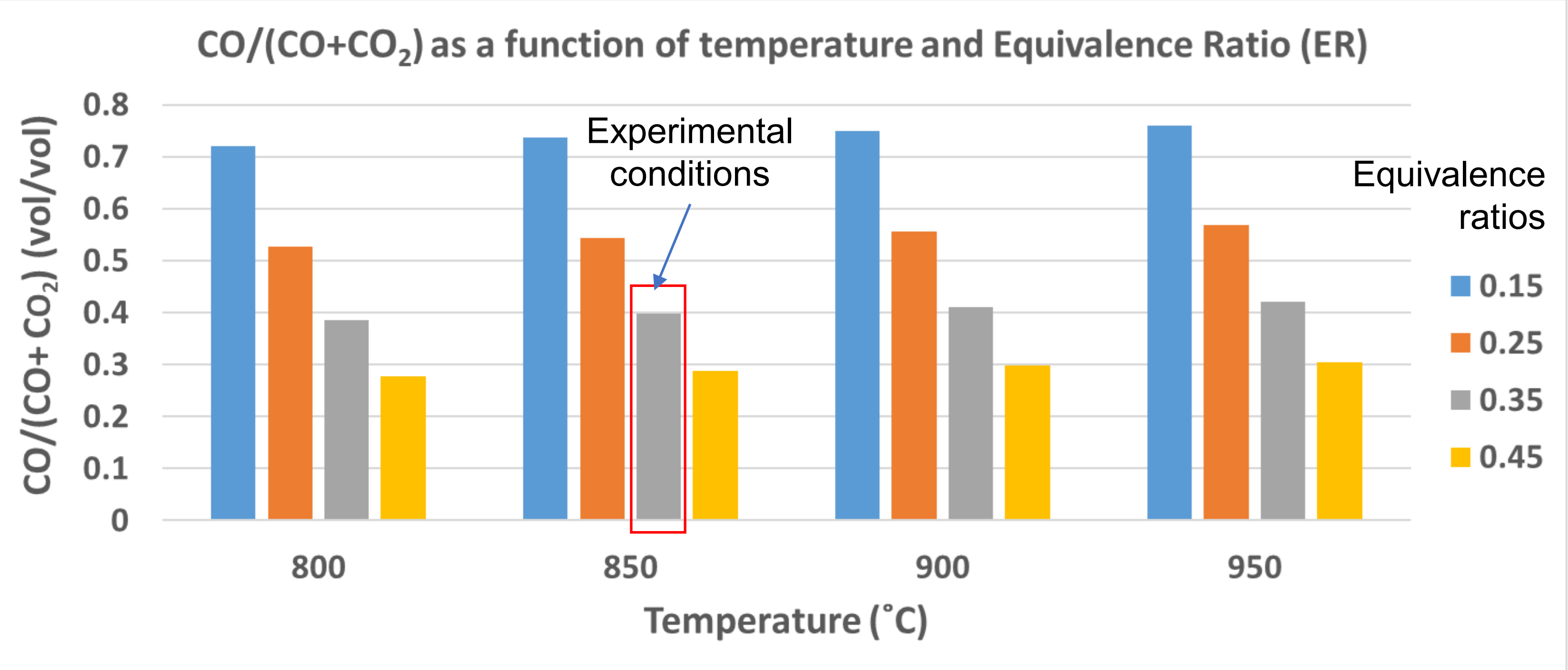


Focus Area 2A – Process Model

- Evaluated multiple equivalence ratios (ER)
- ER of 0.35 selected
- Oxidant ratios: O_2 / CO_2 of 0.35 / 0.65

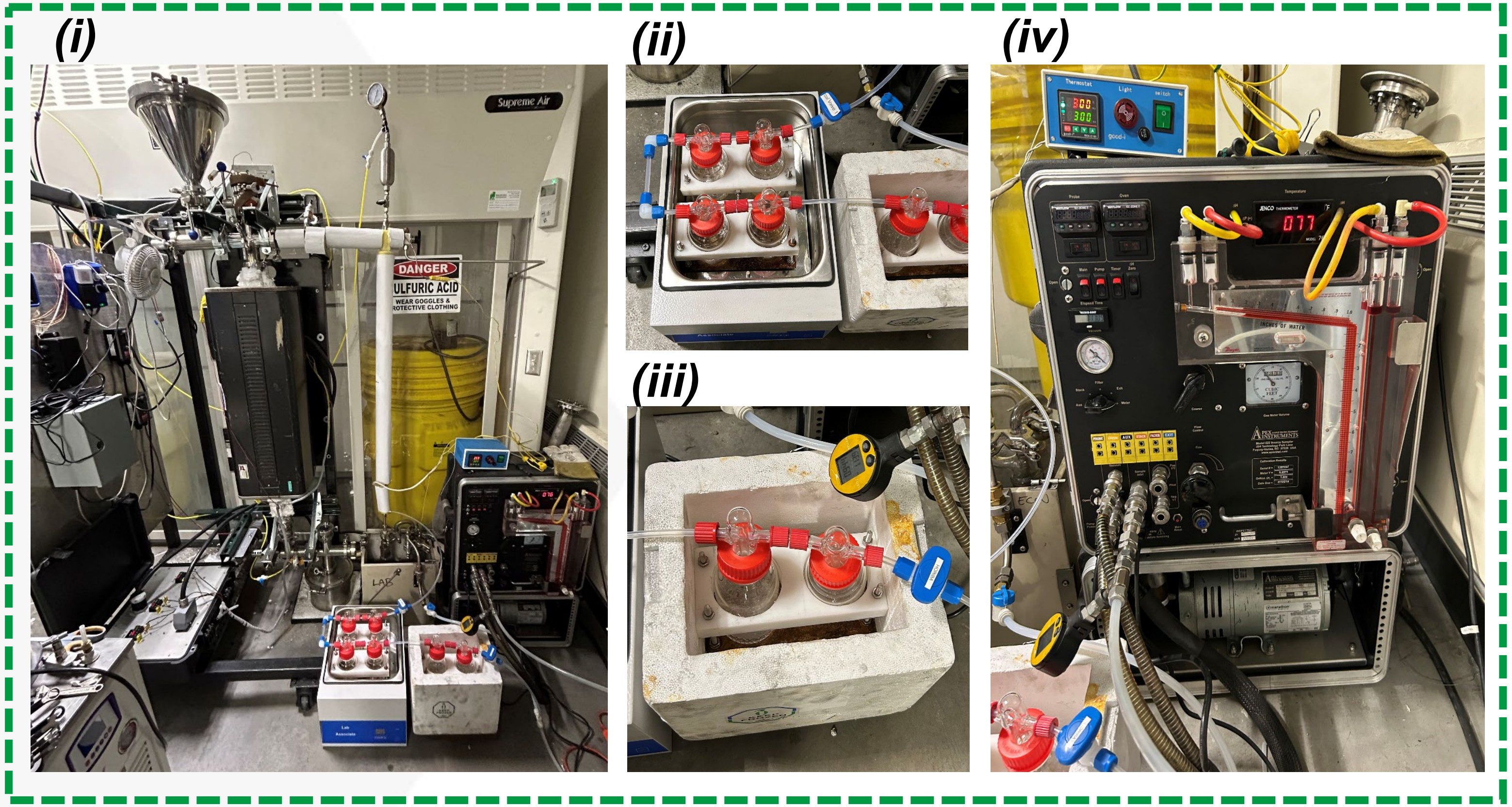
$$\frac{CO}{CO + CO_2} = \text{Extent of Fe conversion}$$





Focus Area 2B – Gasification

- Biomass gasification
  - Woodchips at 850 ˚C
  - ~0.5 lb./hr feed rate
- Sandwich™ Gasifier Design
  - Multi-zone gasification
  - $CO_2 + O_2$; $H_2O + O_2$
- Tar sampling
  - Tar Protocol (CEN/TS 15439:2006)[1]
  - DCM under consideration



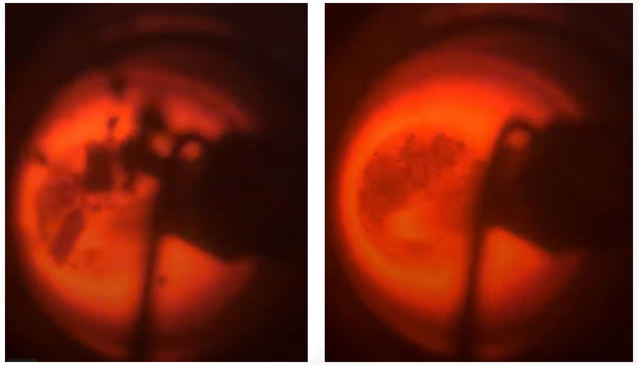
(i) Gasification unit; Tar sampling equipment – (ii) hot bath, (iii) cold bath, (iv) pump and gas metering console

1. Anca-Couce, A. et al. (2022). *Biomass and Bioenergy*, *163*, 106527.

Focus Area 2B - Gasification

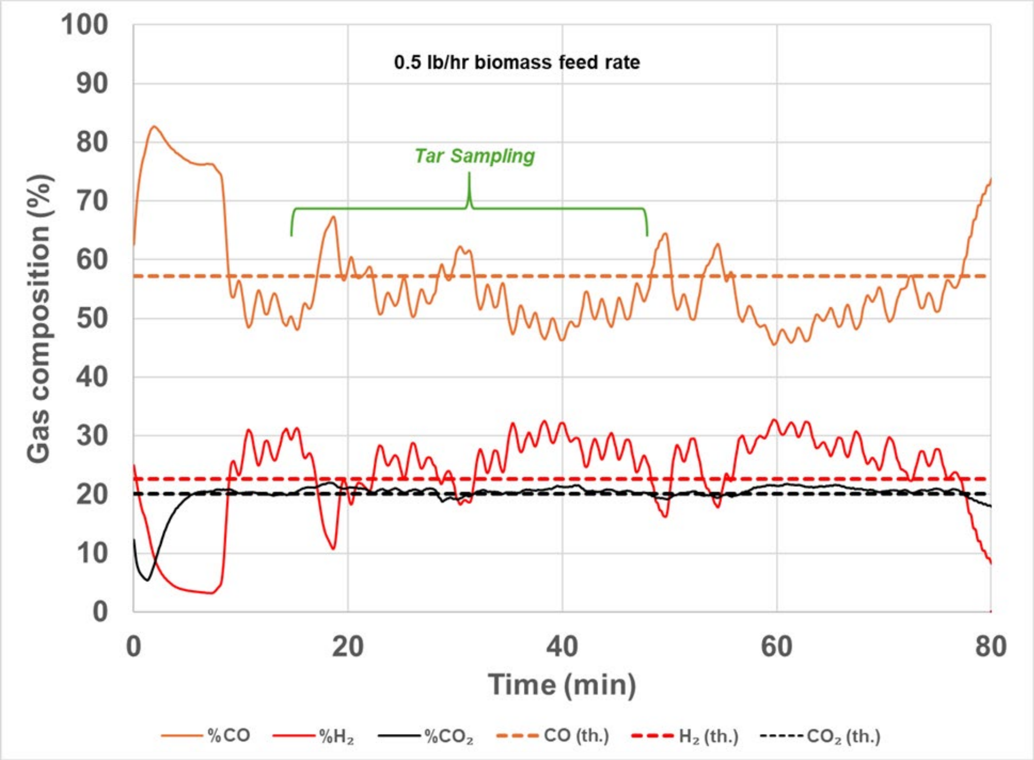
0% O_2 | 6% O_2 | 35% O_2

Addition of O_2



Addition of wood pellets

Sampling train (no filter)



Saw good agreement between experimental and ASPEN simulation

Technical Approach

Focus Area 3 – 5 (future activities)

1. Develop oxygen carrier materials (OCM) and evaluate cyclic performance with syngas and steam (Task 2)
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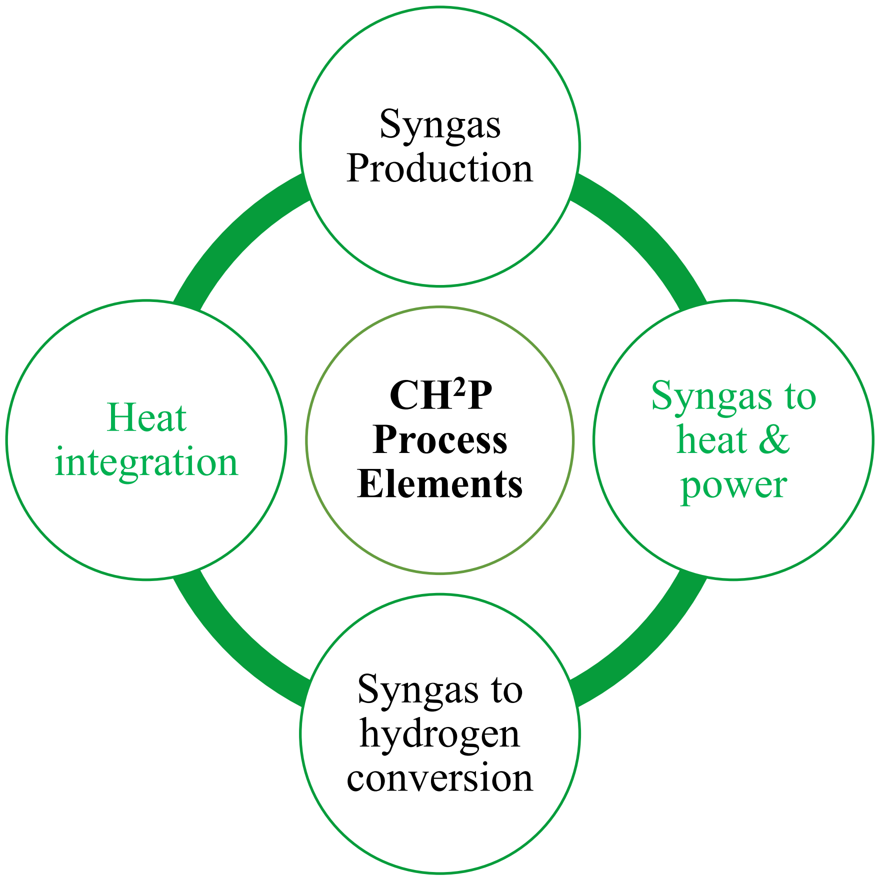
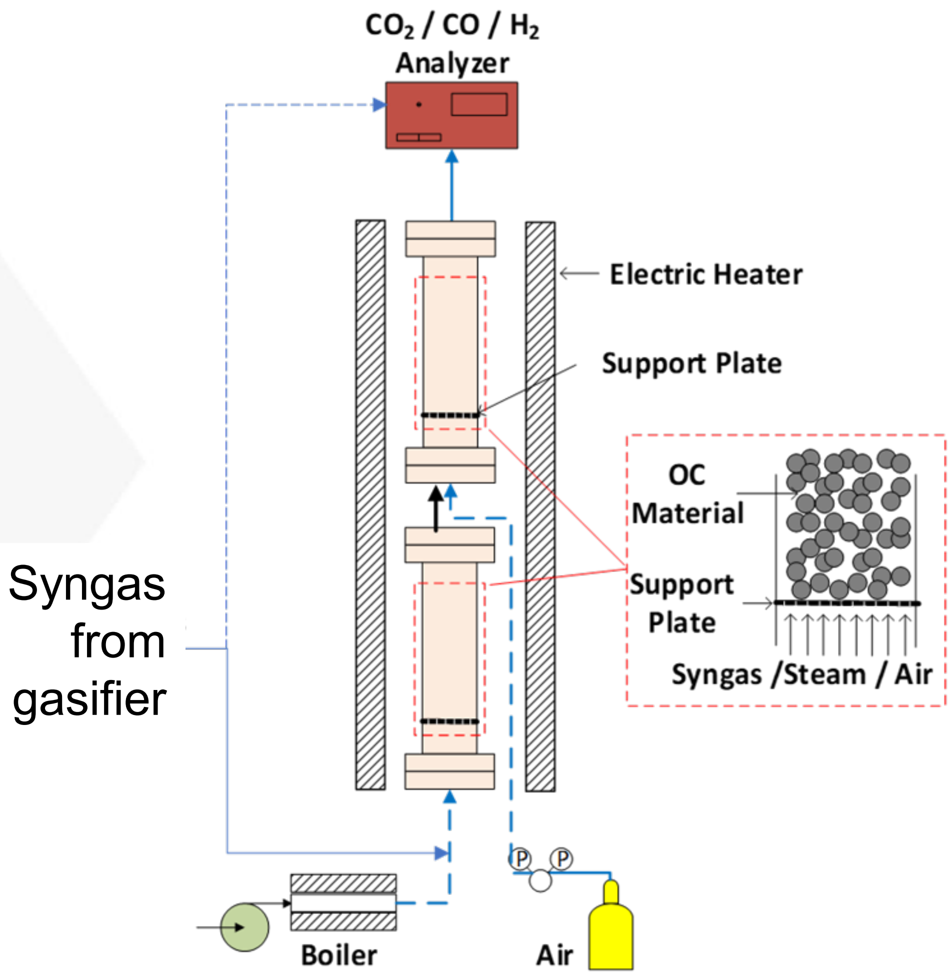


Future Activities

- Focus Area 3 & 4
  - Construct a CH^{2}P bench unit and integrate with lab gasifier unit
  - Evaluate H_2 and CO_2 purity
- Focus Area 5
  - Preliminary design of commercial reactor
  - Techno-economic analysis



Questions?

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