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DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Renewable Natural Gas from Carbonaceous Wastes via Phase Transition CO_2/O_2 Sorbent Enhanced Chemical Looping Gasification

Date: April 6th, 2023
Organic Waste Conversion

Principal Investigator: Fanxing Li
Organization: North Carolina State University

U.S. DEPARTMENT OF ENERGY

CHEMICAL & BIOMOLECULAR ENGINEERING
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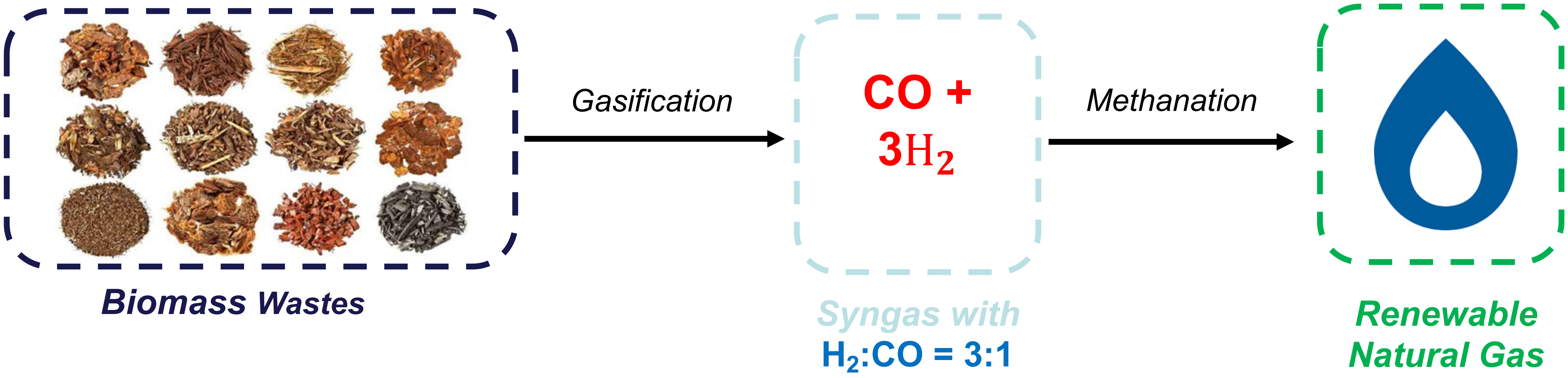
Project Overview

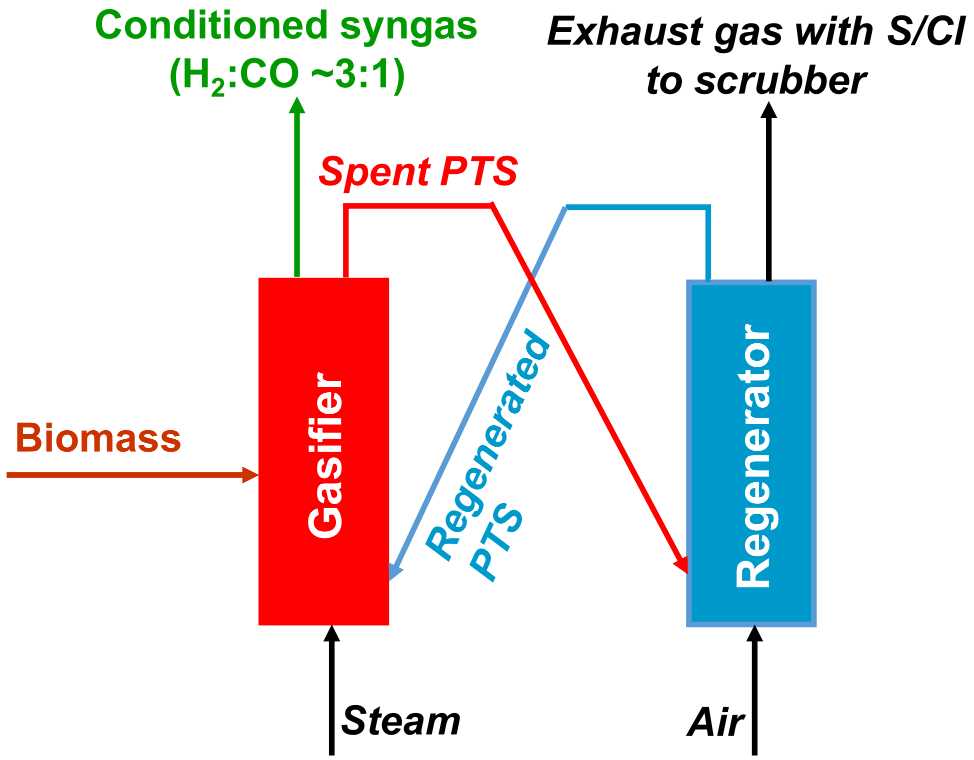
Biomass derived **syngas** ($CO + H_2$) can be used for the sustainable production of **renewable natural gas**, **hydrogen, and beyond**.

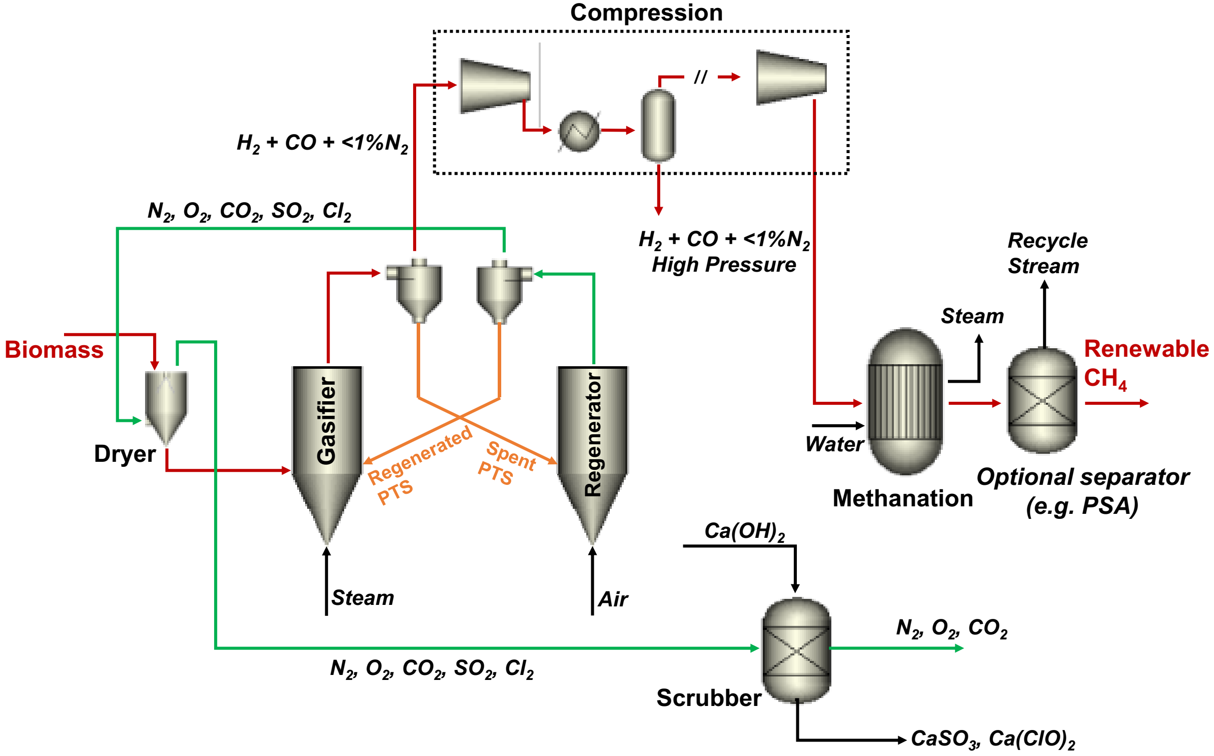


Project Goals: (i) developing multi-functional, mixed oxide based phase transition sorbents (PTS) for biomass gasification with integrated air separation and CO_2 sorption; (ii) demonstrating the ash and contaminant resistances, stability, activity, and cost/performance of the PTS; (iii) 5 kW_{th} circulating fluidized bed (CFB) gasifier demonstration; (iv) validate >35% decrease in LCOE and >10 energy return on investment (EROI).

1 – Approach: Concept Overview

Sorption Enhanced Chemical Looping Gasification (SE-CLG)





Gasifier: $C_nH_mO_x + SrFeO_3 \rightarrow SrCO_3 + FeO/Fe + CO + 3H_2$ ($\Delta H = -14$ kJ/mol H_2)

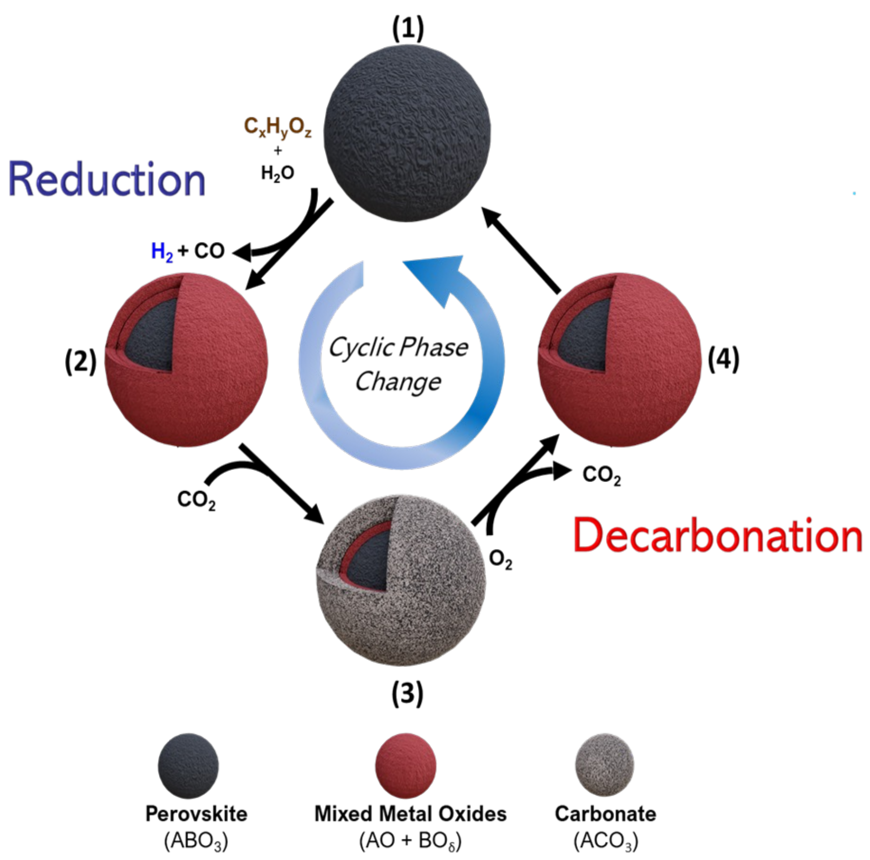
Regenerator: $SrCO_3 + Fe/FeO + Air \rightarrow SrFeO_3 + CO_2 + N_2$ ($\Delta H = -150$ kJ/mol $SrFeO_3$)

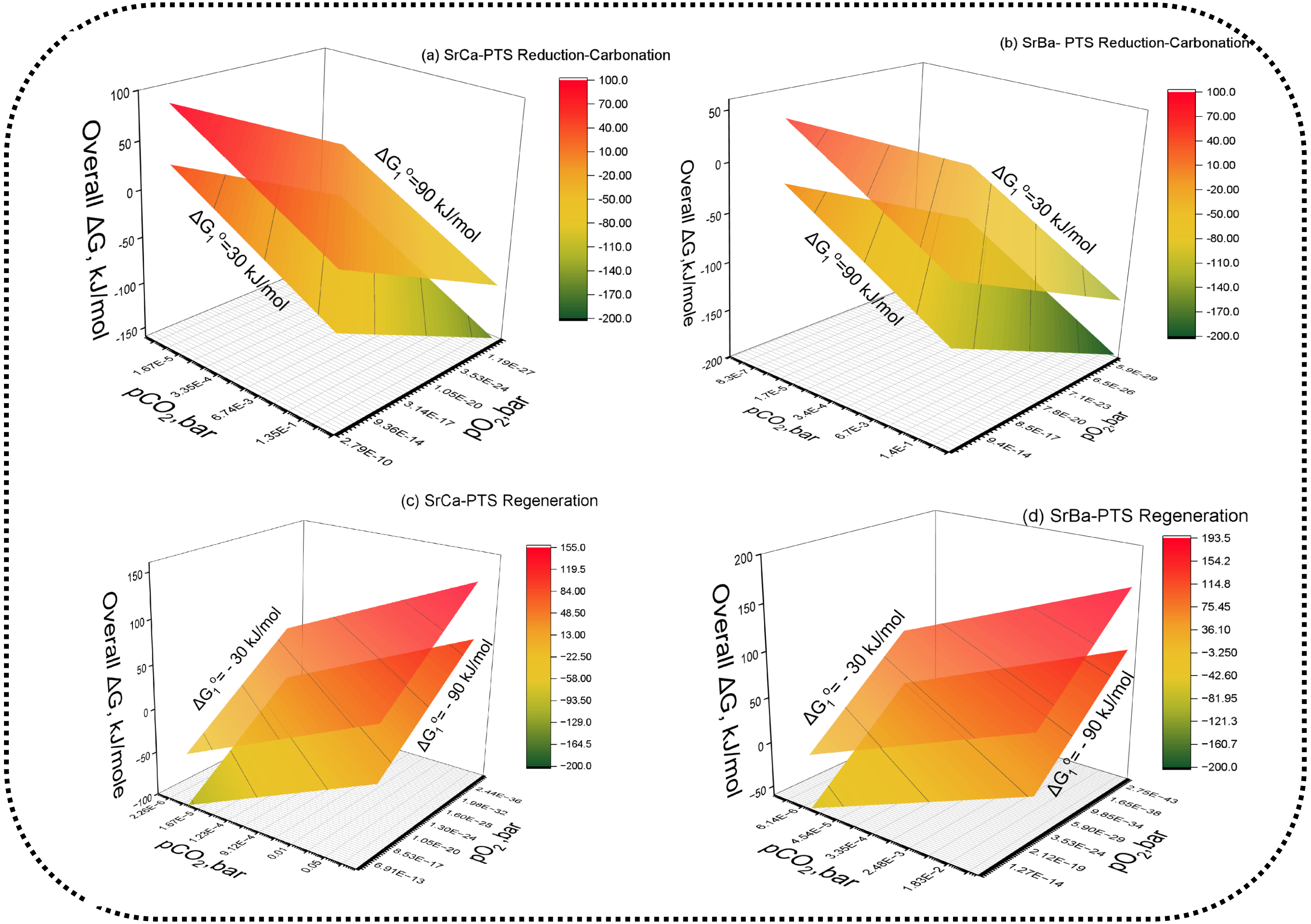
Process intensification enabled by a new class of multi-functional mixed oxide sorbents with for redox-triggered CO_2-sorption and desorption.

Advantages vs SoTA:

- *In-situ* CO_2 capture and integrated oxygen separation for significantly higher efficiency;
- Elimination of water-gas-shift and CO_2 removal;
- Hydrogen rich syngas ready for methanation;
- Catalytic activity for tar removal;
- Tunable sorbent thermodynamics.

1 – Approach





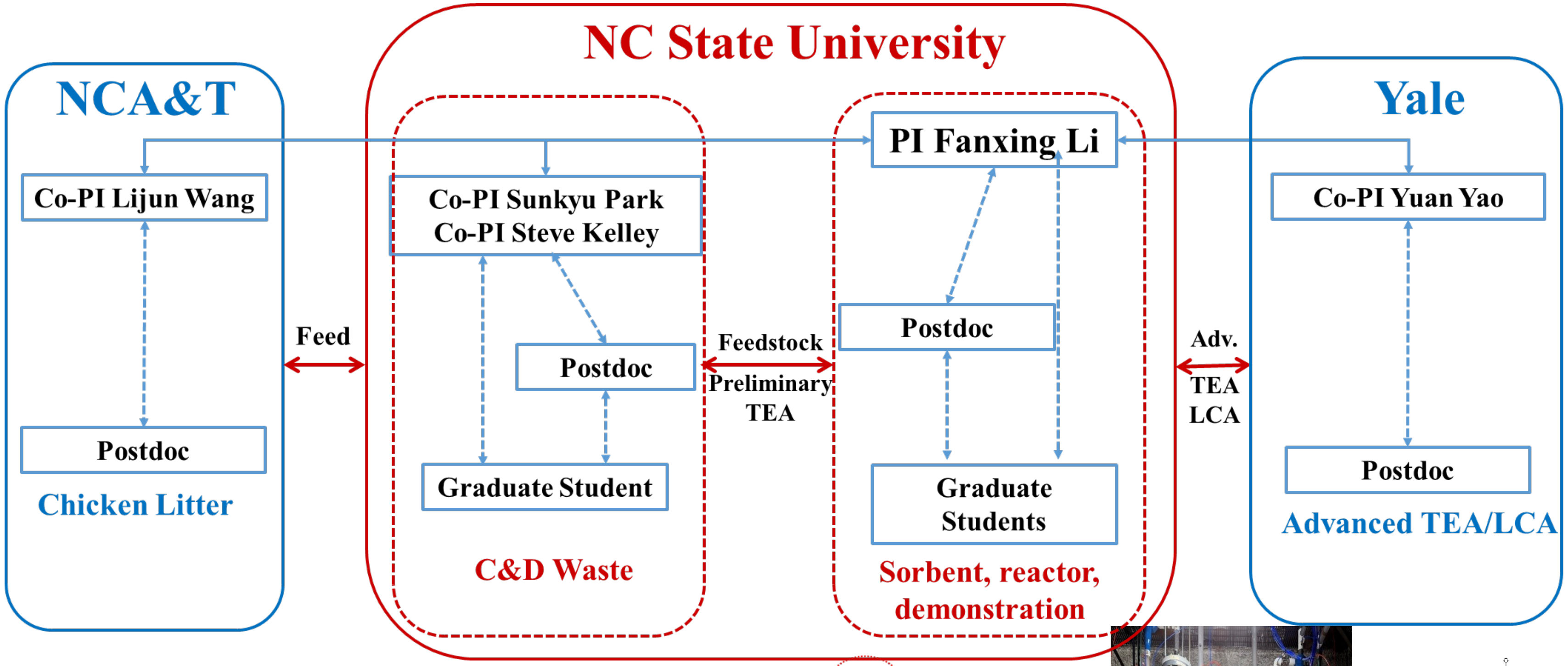
Overall Gibbs free change of **absorption step** (a) SC, (b) SB PTS as a function of pO_2, p_{CO_2} and $\Delta G1^0$ at **T=750 and P=1 atm**

Overall Gibbs free change of **regeneration step** (c) SC, (d) SB PTS as a function of pO_2, p_{CO_2} and $\Delta G1^0$ at **T=750 and P=1 atm**

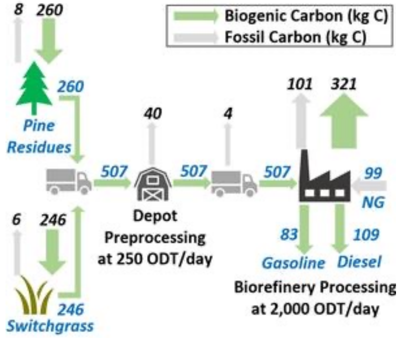
1 – Approach

- ***Key success factors:*** *i. Phase transition sorbents (PTSs) performance, i.e. sorption capacity and kinetics, redox activity and oxygen carrying capacity, activity for biomass (tar) conversion, and long-term stability; ii. Reactor design: satisfactory solids circulation rates and sorbent residence times;*
- ***Overall approach:*** *(a) biomass waste sample collection, characterization and pretreatment; (b) Design, characterization and optimization of PTSs; (c) preliminary process and cost analysis; (d) cold model design/ operation and hot unit design; (e) hot unit construction; (f) scale up synthesis of PTS particles; (g) system demonstration; (h) comprehensive TEA/LCA;*
- ***Potential risks and mitigation:*** *i. PTS performance (Phase I work resulted in high performance sorbents); ii. Reactor performance (Phase I cold model operation met the design requirements); iii. Reactor cost inflation (the team is working closely with the vendor for cost reduction). The team has ample technical expertise and promising data. The tasks were specifically designed to de-risk these challenges;*
- ***Go/No-Go:*** *Finalized gasifier hot model design with detailed P&ID, HAZOP analysis, and cost estimate.*
- ***Team:*** *PI Fanxing Li, expert in mixed oxides, chemical looping and reaction engineering; Co-PI and key personnels: Stephen Kelley (NCSU), Sunkyu Park (NCSU), and Lijun Wang (NC A&T), experts in biomass characterization, conversion and pretreatment; Yuan Yao (Yale), expert in TEA and LCA; Wyatt Casey LaMarche and Raymond Cocco(PSRI), particle technology and reactor design. A diverse team involving public and private educational institutions, HBCU, and an industrial collaborator).*

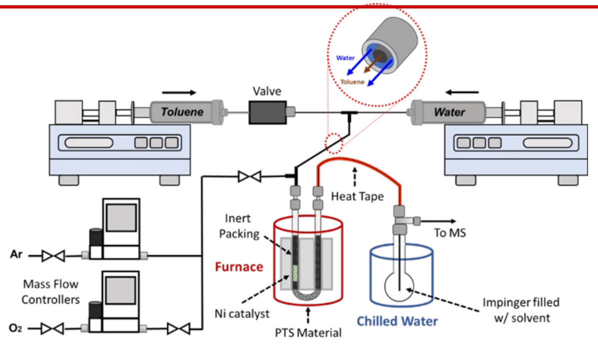
1 – Approach



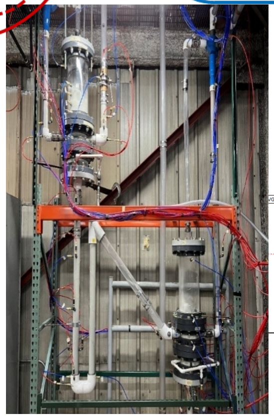
NC State University
NCA&T
Co-PI Lijun Wang
Postdoc
Chicken Litter
Feed
Co-PI Sunkyu Park
Co-PI Steve Kelley
Postdoc
Graduate Student
C&D Waste
Feedstock
Preliminary
TEA
PI Fanxing Li
Postdoc
Graduate Students
Sorbent, reactor, demonstration
Adv.
TEA
LCA
Yale
Co-PI Yuan Yao
Postdoc
Advanced TEA/LCA

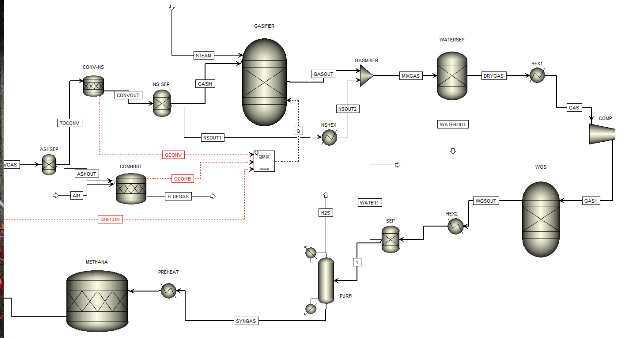


Biogenic Carbon (kg C)
Fossil Carbon (kg C)
8 260
260
Pine Residues
6 246
246
Switchgrass
507
40
Depot Preprocessing at 250 ODT/day
507
4
507
101 321
99
NG
83 109
Gasoline Diesel
Biorefinery Processing at 2,000 ODT/day



Toluene
Valve
Water
Heat Tape
Inert Packing
To MS
Furnace
Ar
Mass Flow Controllers
O₂
Ni catalyst
PTS Material
Chilled Water
Impinger filled w/ solvent





2 – Progress and Outcomes

Budget Period 1 (Q1-Q7; currently ongoing): (i) biomass waste feedstocks collection, characterization, and pretreatment; (ii) phase transition sorbents (PTSs) design, characterization, and optimization; (iii) preliminary process and cost analysis; (iv) PTS performance evaluation and improvements; (v) design of a 5 kW_{th} SE-CLG gasifier.

(Go/No-Go) Hot model design: Finalized gasifier hot model design with detailed P&ID, HAZOP analysis, and cost estimate, ready to proceed.

Budget Period 2 (Q8-Q13): (i) construction of gasifier hot unit; (ii) scale up synthesis of PTS particles; (iii) gasifier hot unit demonstration and methanation; (iv) comprehensive process and life cycle analyses.

(End of project targets) >25% decrease in LCOE compared to indirect steam gasification technology and >5 EROI (our internal targets for the project are 35% decrease in LCOE and >10 EROI).

2 – Progress and Outcomes

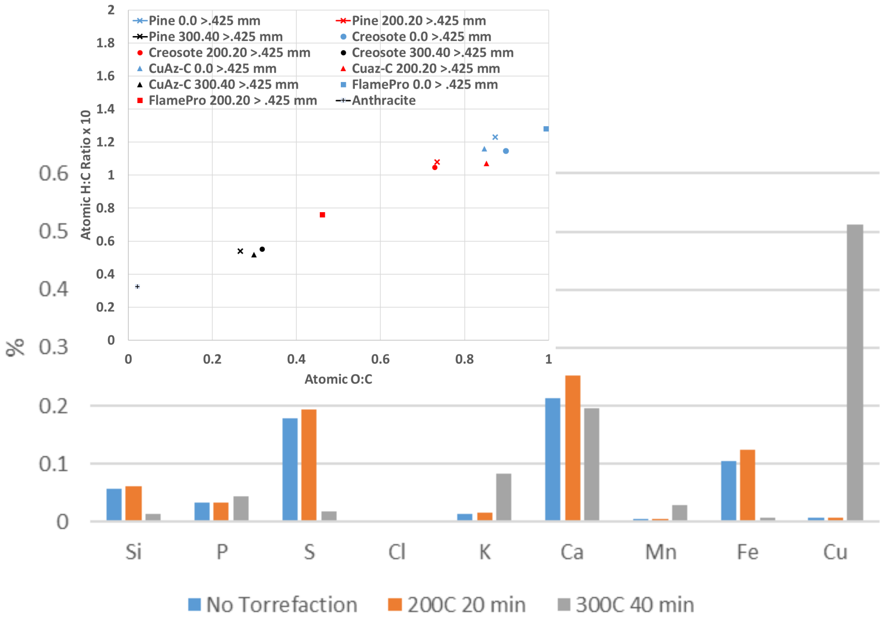
Milestone	Type	Description
1.1: Sample collection and characterization (Task 1.1.1 and 1.1.2)	Technical	(Q1) Collect consistent and representative biomass waste feedstocks and characterize their key properties for thermochemical conversion.
1.2: Feedstock pretreatment (Task 1.1.3)	Technical	(Q3) Determine the effect of torrefaction on the feedstock
1.3: CO_2 sorption of sorbent (Task 1.2.1 and 1.2.2)	Technical	(Q3) Develop six PTSs with >5 w.t.% oxygen capacity and CO_2 uptake/release kinetics two times greater than a baseline CaO sorbent while maintaining high stability (<3% degradation of CO_2 uptake/release kinetics) over 25 CO_2 capture and release cycles.
1.4: Sorbent development (Task 1.2.3)	Technical	(Q3/4) Develop six PTSs showing >95% methane and biomass volatile conversion while producing syngas with H_2/CO ratio >2.5
1.5: Sorbent robustness (Task 1.2.4)	Technical	(Q4) Develop four PTSs showing < 5% degradation over 50 cycles in the presence of ash and contaminants
1.6: Cost benefit for SE-CLG (Task 1.3.1 and 1.3.2)	Technical	(Q4) Validate 35% reduction in Levelized Cost of Energy (LCOE) for methane production compared to state-of-the-art
1.7: Fluid bed performance (Task 1.4.1 and 1.4.2)	Technical	(Q7) Develop four PTSs showing >95% biomass waste conversion on a carbon basis
1.8: Sorbent fluidized bed stability (Task 1.4.3)	Technical	(Q7) Develop one PTS with < 5% degradation in activity and <1 wt.% attrition over a 24 hour testing period
1.9: Cold model design (Task 1.5.1)	Technical	(Q6) Complete the design of a CFB gasifier cold model
1.10: CFB cold model operations (Task 1.5.1)	Technical	(Q6) 24 hour stable and continuous operation of the CFB cold model
1.11: Hot model design (Task 1.5.2)	Go/No Go	(Q7) Finalized gasifier hot model design with detailed P&ID, HAZOP analysis, and cost estimate, ready to proceed.

Achieved Milestones

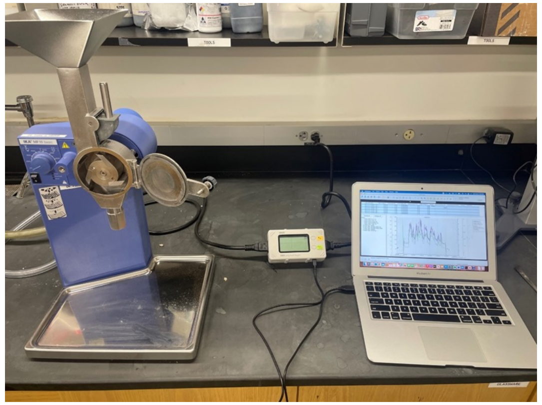
On-schedule, nearly completed

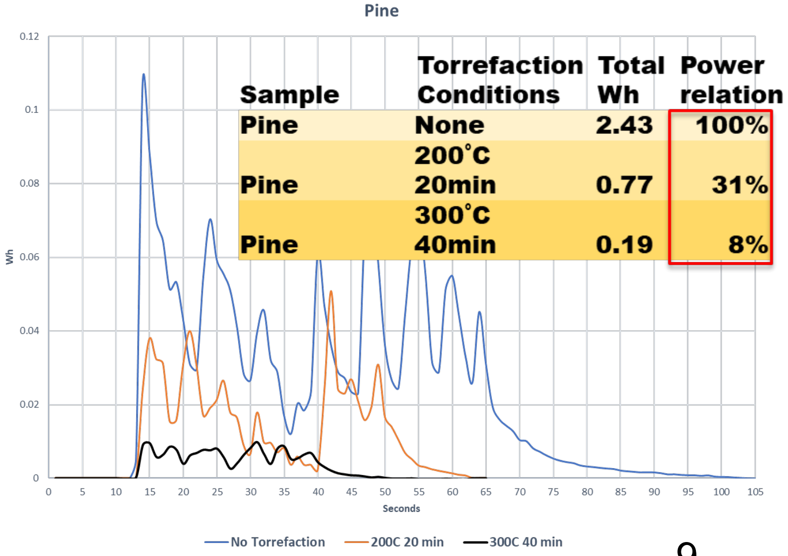
2 – Progress and Outcomes: Biomass Waste Collection and Pretreatment

Sample	Torrefaction Conditions	Purpose
Southern Yellow Pine	No Torrefaction 200˚C 300˚C	Chosen as a control, for its wide spread use and common as the starting material for most treated lumber
CuAz-C	No Torrefaction 200˚C 300˚C	Inorganic treatment common in residential use for preventing biological degradation
Creosote	No Torrefaction 200˚C 300˚C	Organic treatment abundant in industrial use, ex. railroad ties
FlamePro	No Torrefaction 200˚C 300˚C	Inorganic flame resistant treatment chosen for it's unlike thermal qualities.



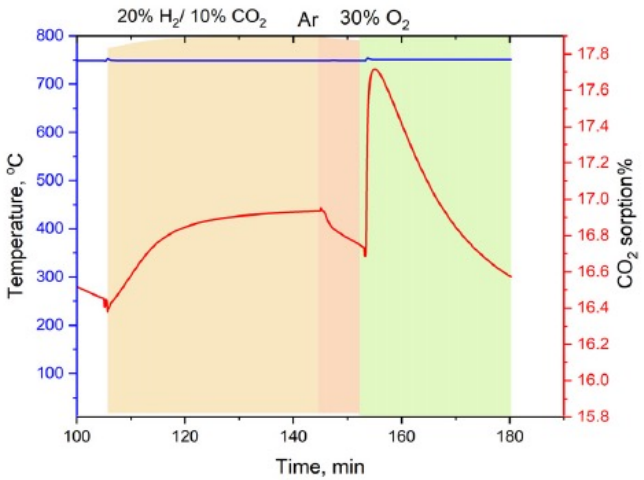
	C%	H%	N%	O%	Ash%
Pine 0.0 >.425 mm	50.04	6.16	0.14	43.66	0.96
Pine 200.20 >.425 mm	54.26	5.86	0.00	39.88	0.77
Pine 300.40 >.425 mm	75.60	4.08	0.17	20.15	2.37
Creosote 0.0 >.425 mm	49.62	5.69	0.13	44.56	1.86
Creosote 200.20 >.425 mm	54.50	5.71	0.07	39.72	0.96
Creosote 300.40 >.425 mm	72.61	4.01	0.31	23.07	1.24
CuAz-C 0.0 >.425 mm	50.91	5.91	0.06	43.12	1.091
Cuaz-C 200.20 >.425 mm	51.04	5.47	0.02	43.47	1.56
CuAz-C 300.40 >.425 mm	73.94	3.83	0.10	22.13	3.49
FlamePro 0.0 > .425 mm	46.86	6.00	0.58	46.56	4.56
FlamePro 200.20 > .425 mm	64.42	4.90	0.95	29.73	3.79
FlamePro 300.40 > .425 mm	48.10	3.16	0.45	48.29	4.89

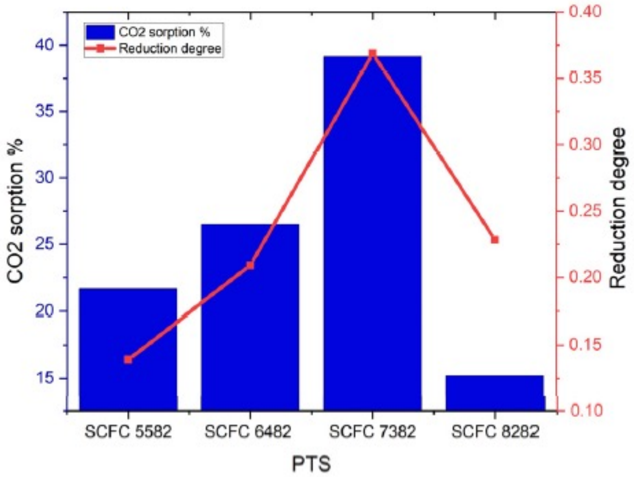


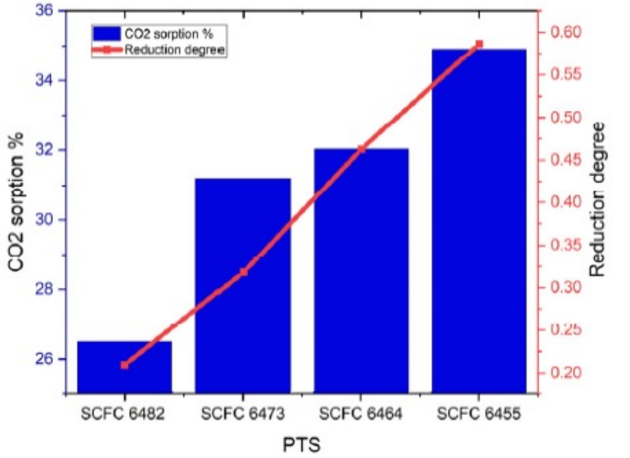


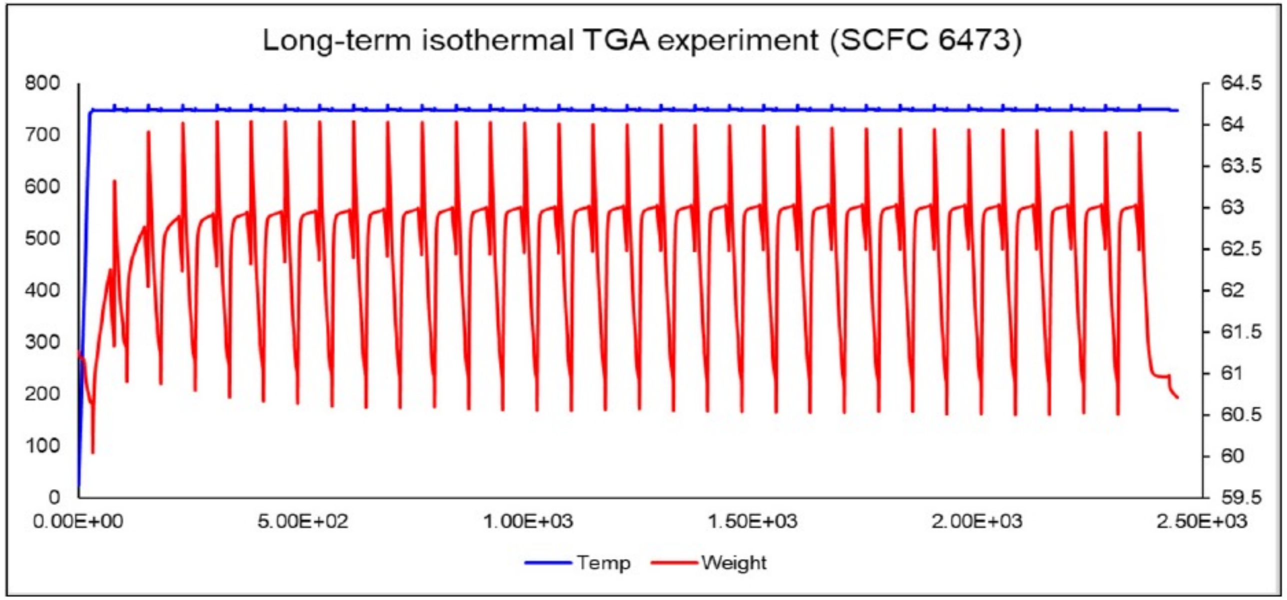
Sample	Torrefaction Conditions	Total Wh	Power relation
Pine	None	2.43	100%
Pine	200˚C 20min	0.77	31%
Pine	300˚C 40min	0.19	8%

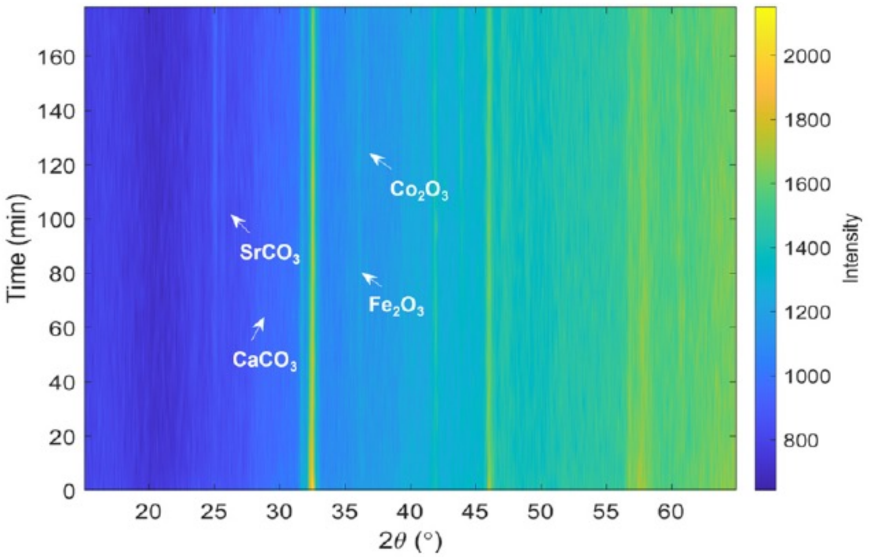
2 – Progress and Outcomes: PTS Bi-Functionality and Tunability







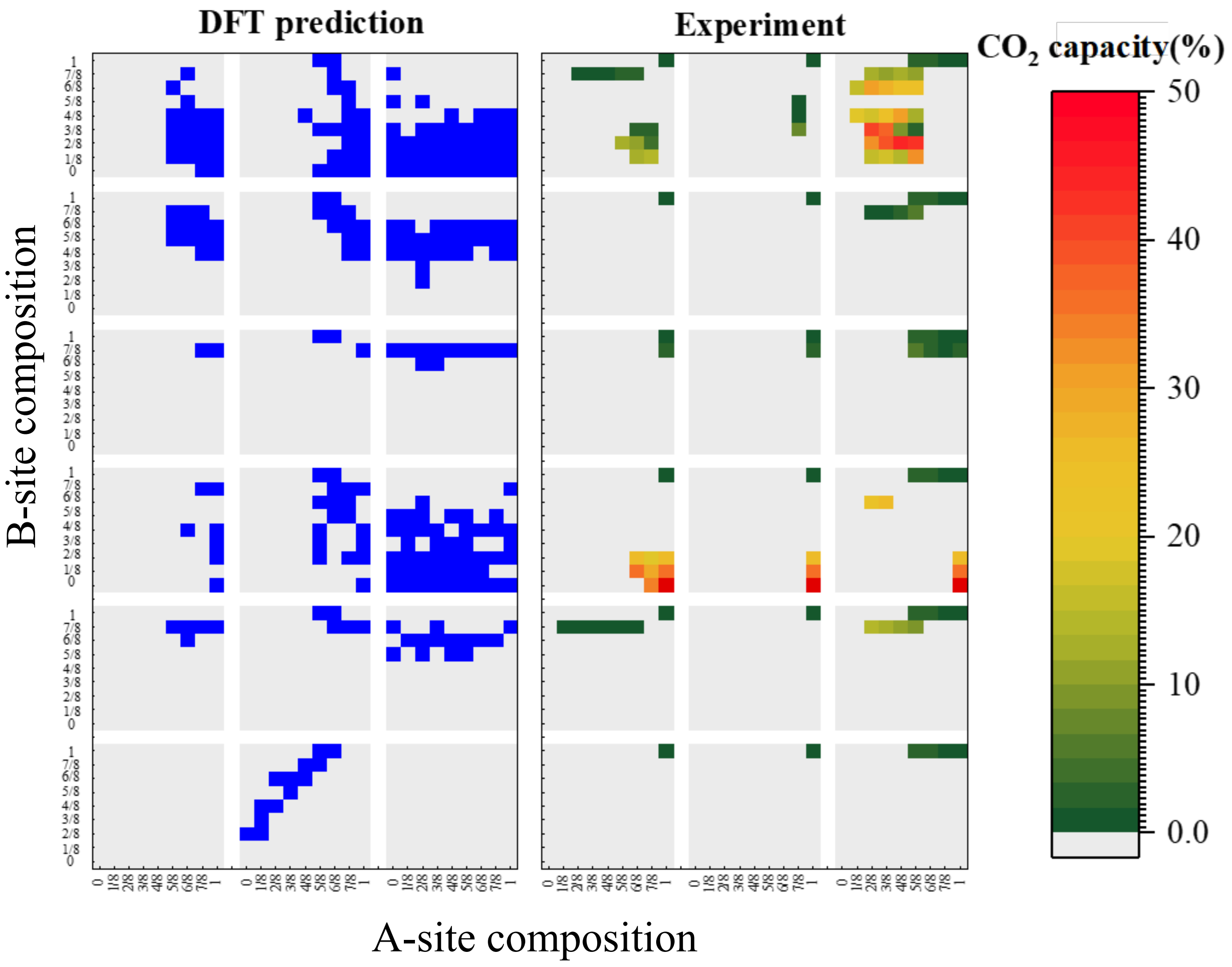




Isothermal TGA experiments confirmed the feasibility of the proposed concept, and correlation between reduction degree and CO_2 sorption.

2 – Progress and Outcomes: Computationally Guided PTS Design

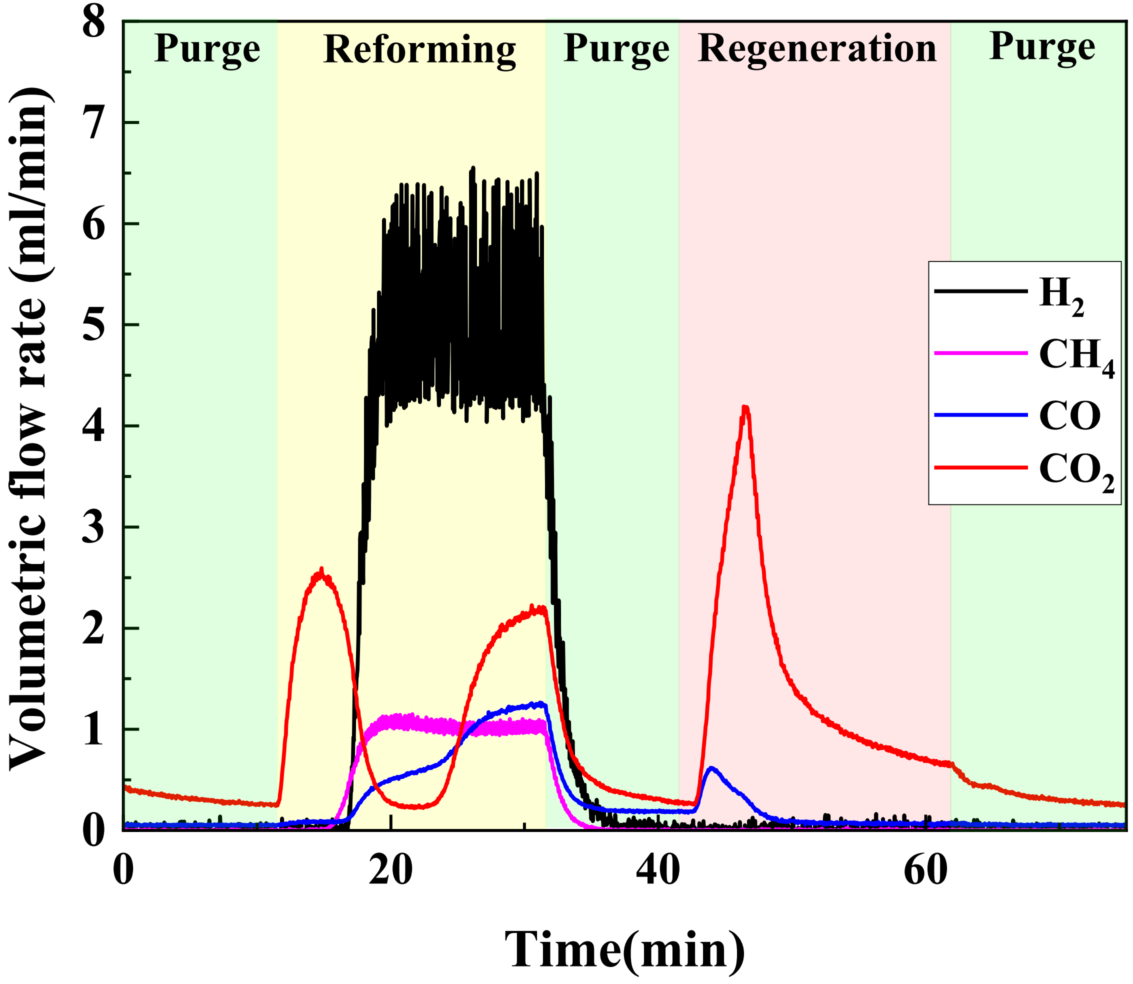
➢ Sorption capacity

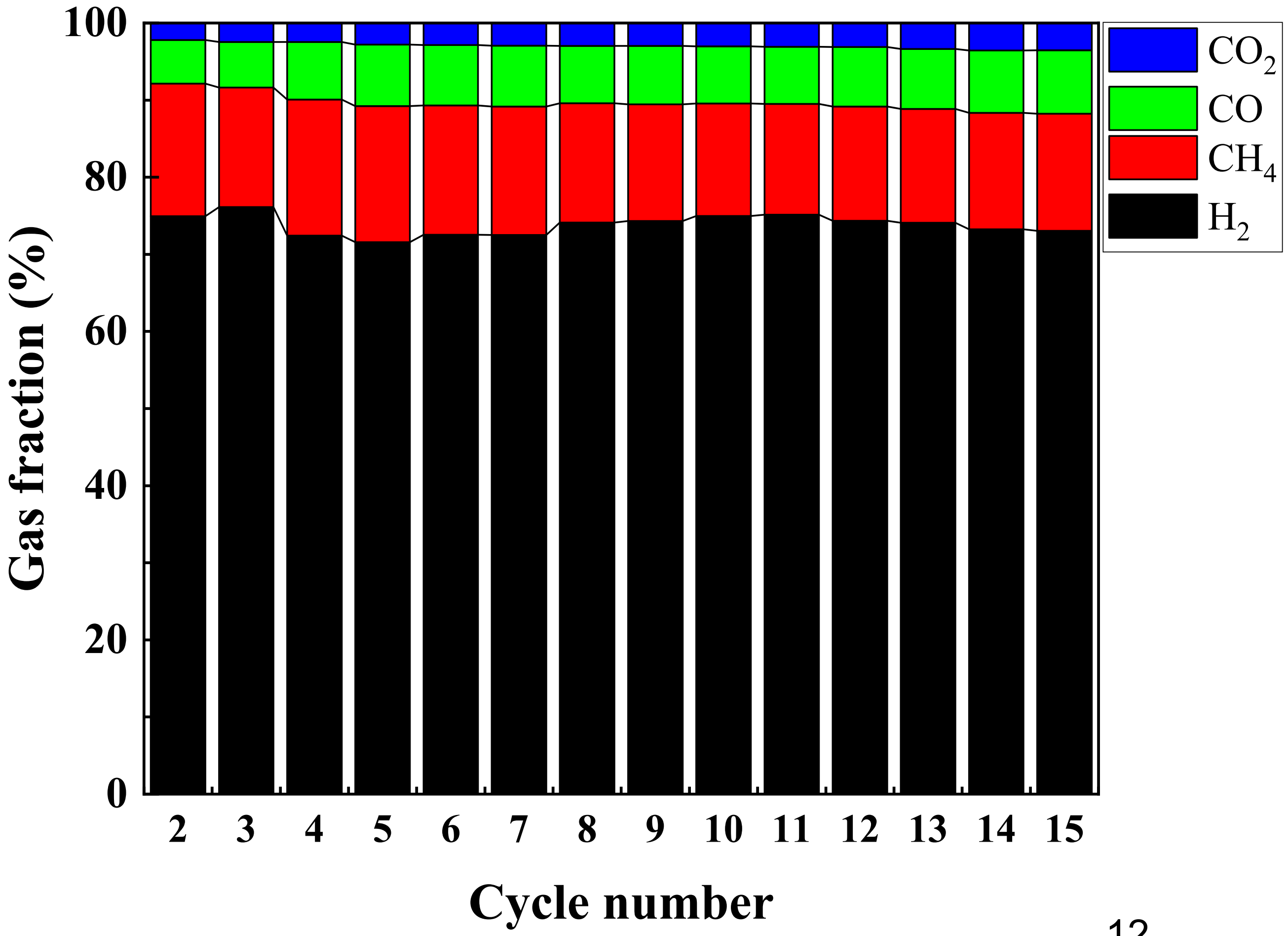


- Based on DFT computation, 91 samples were tested
- Isothermal operation at 850 °C
- DFT predicted samples show a better performance
- Doping in the B-site of $SrFeO_3$ is necessary to achieve isothermal operation

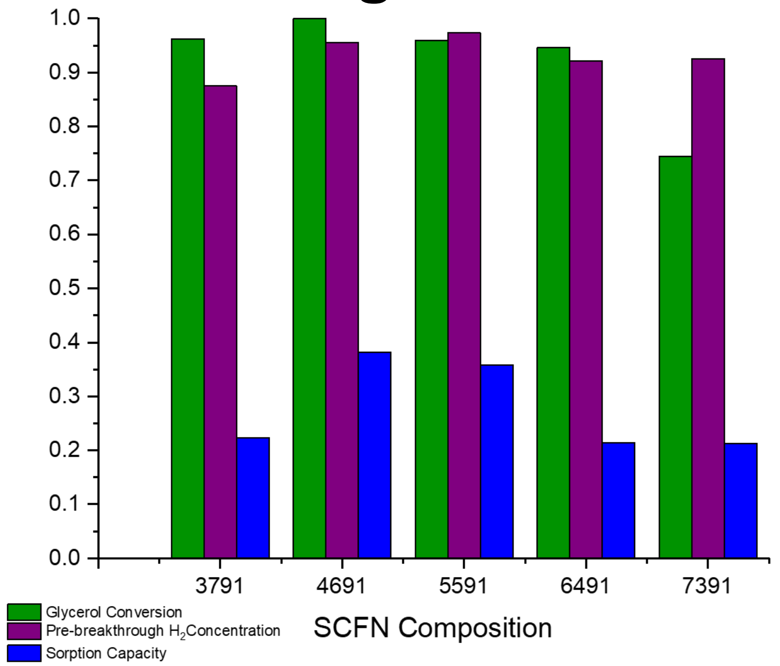
2 – Progress and Outcomes: Computationally Guided PTS Design

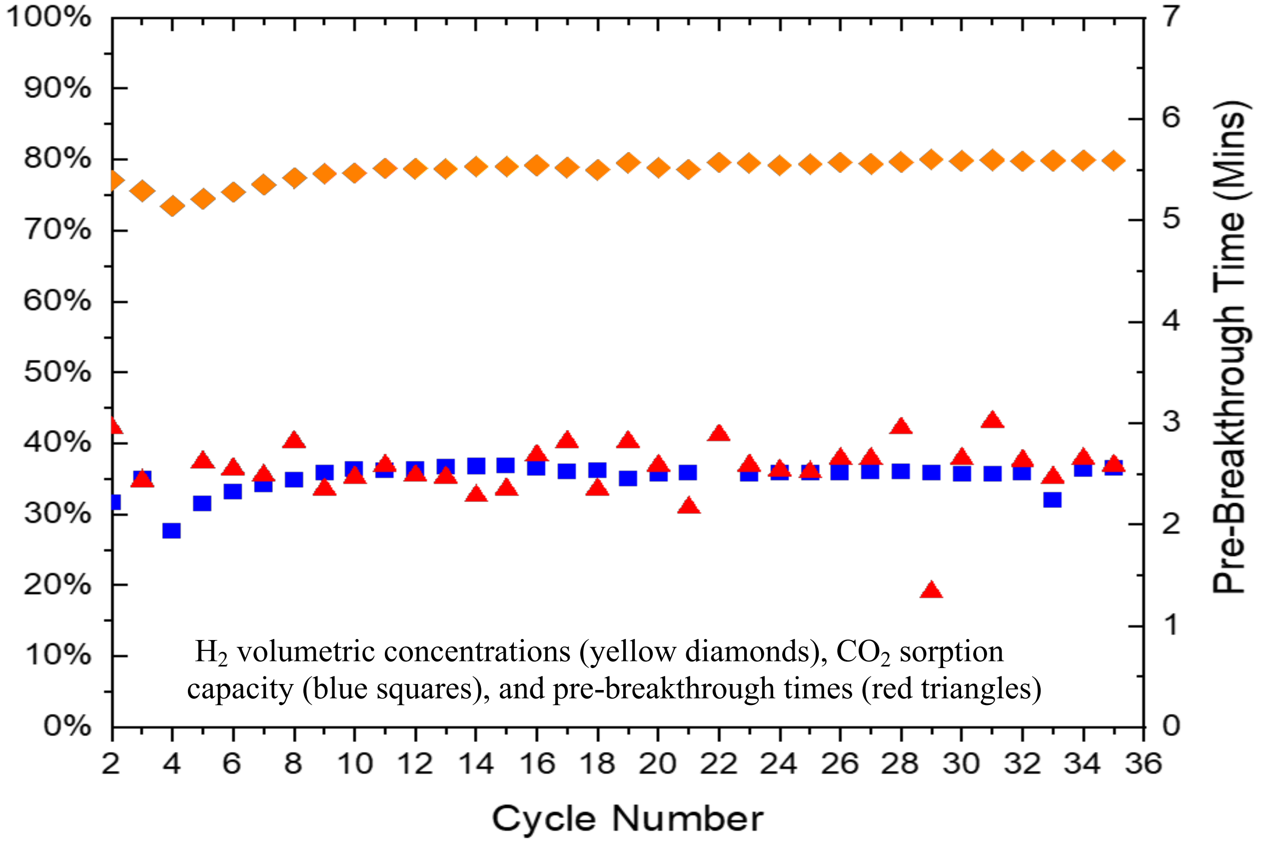
- Demonstration of a SCFM sorbent in a packed bed
  - Successful isothermal operation:



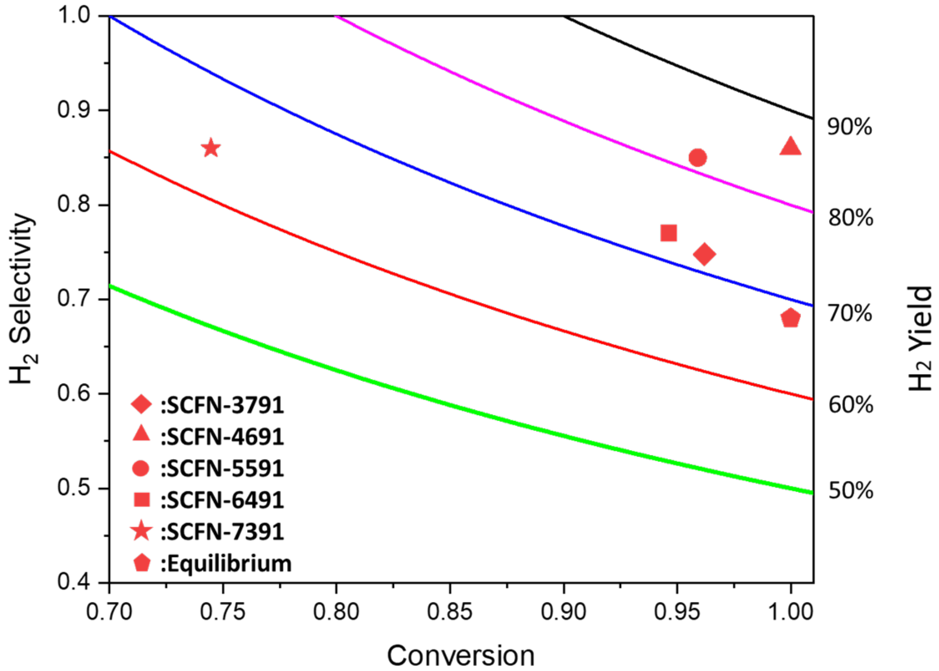


2 – Progress and Outcomes: PTS Conversion of Tar/Model Compounds



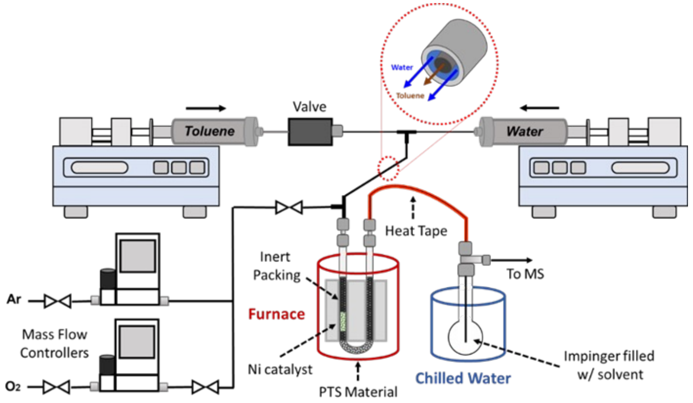


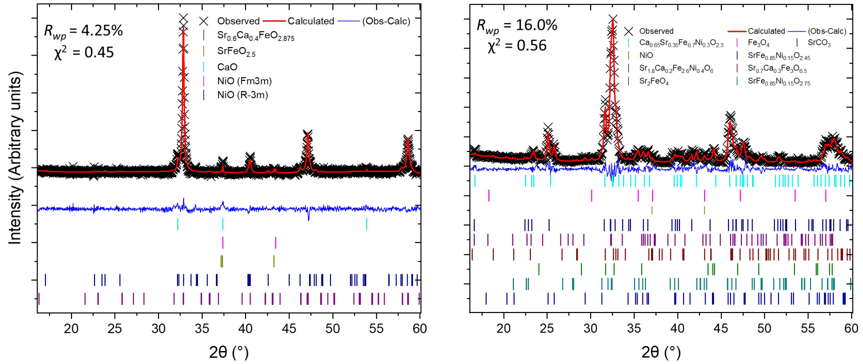
H_2 volumetric concentrations (yellow diamonds), CO_2 sorption capacity (blue squares), and pre-breakthrough times (red triangles)

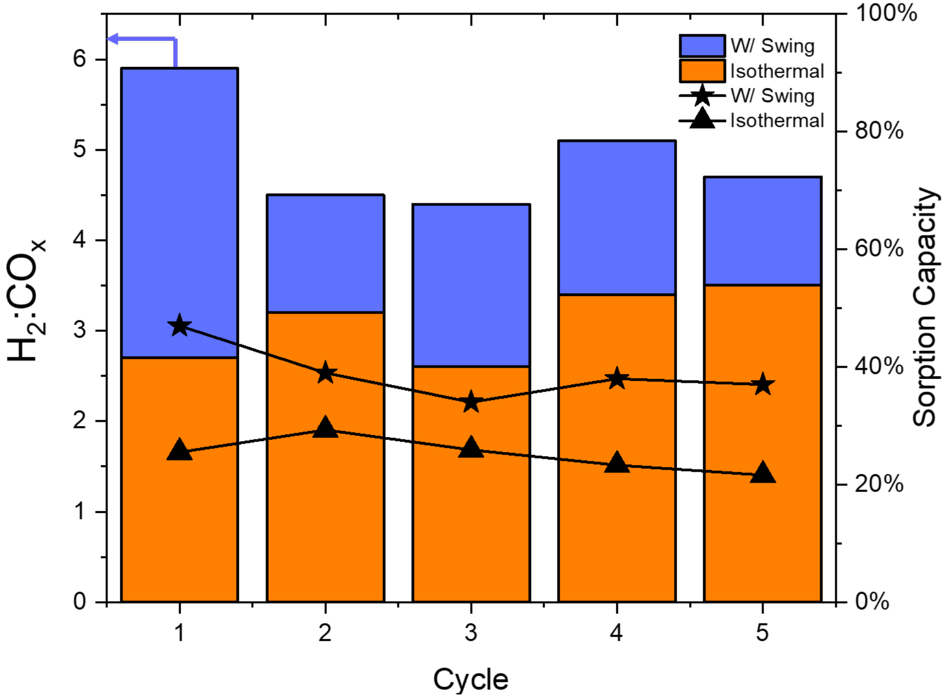


Material	H_2:CO_x	Molar [CO_2]
SCFN-3791	2.63	13.0%
SCFN-4691	**4.07**	**9.1%**
SCFN-5591	**3.53**	**9.3%**
SCFN-6491	2.27	15.0%
SCFN-7391	2.38	14.9%

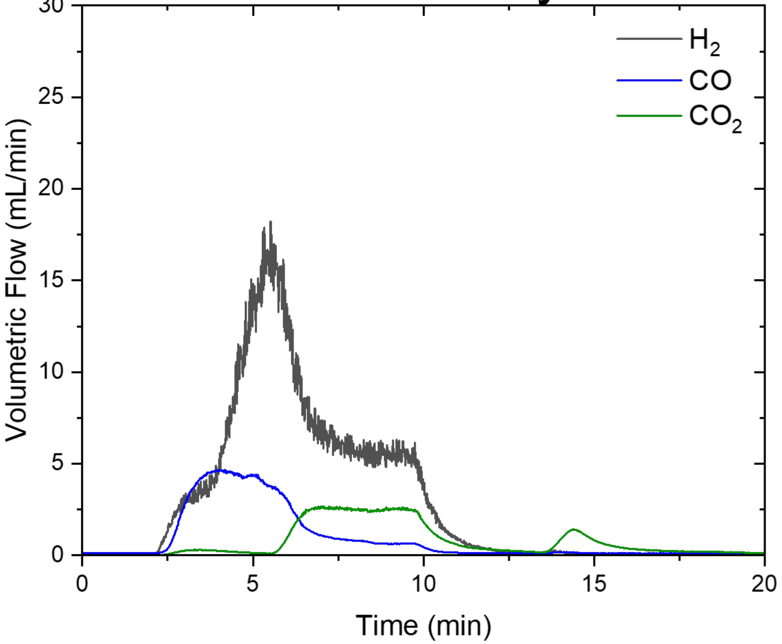
2 – Progress and Outcomes: PTS Conversion of Tar/Model Compounds



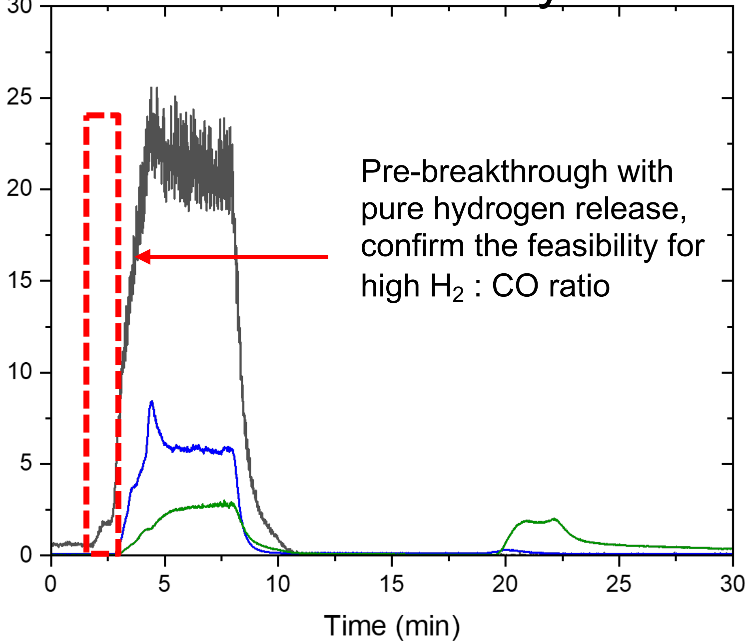


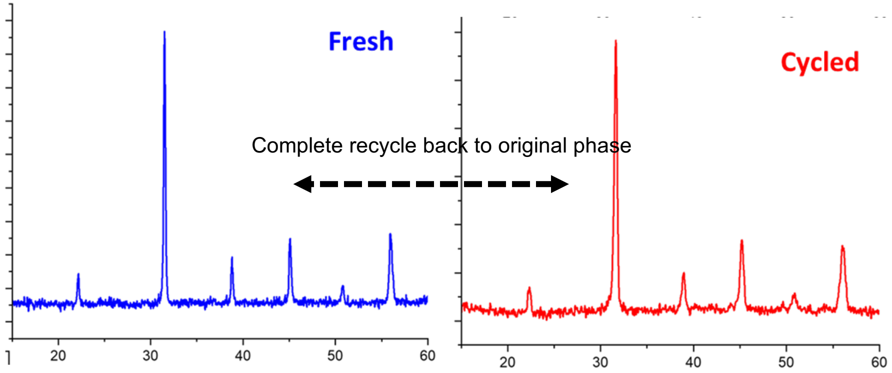


Without Ni catalyst



With Ni catalyst

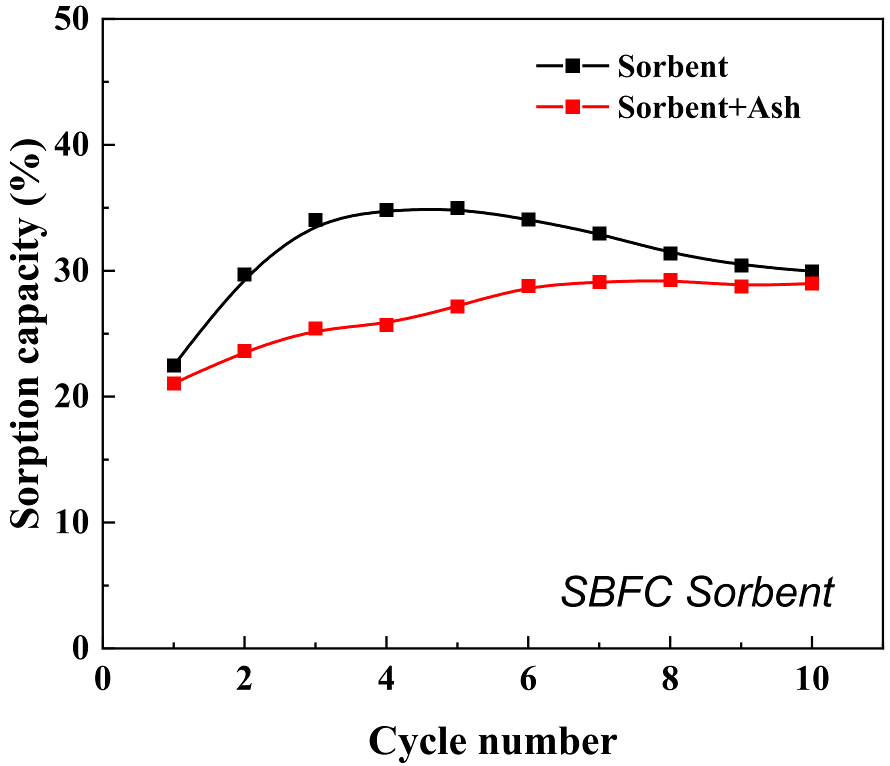


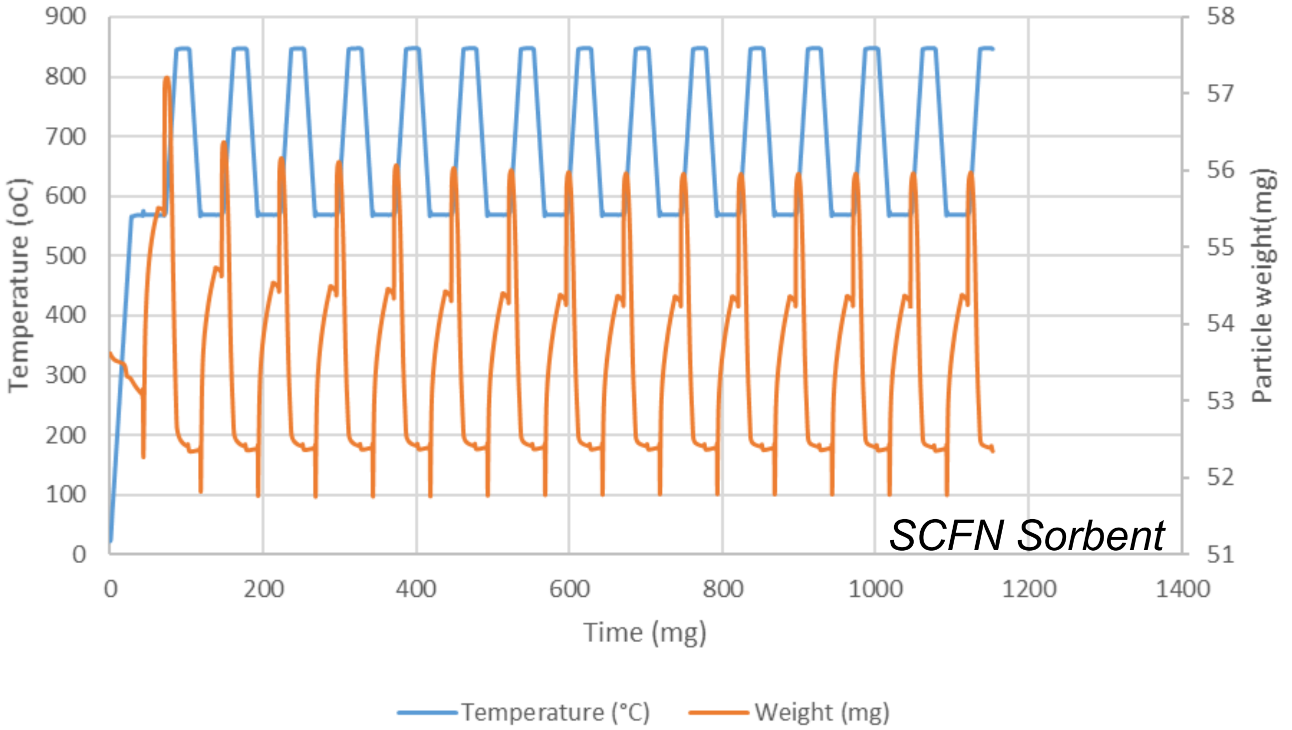


With the Ni catalyst, sorption capacity greatly increased (38%), with a toluene conversion ~98% with $H_2:CO_x$ at 3 or higher for all cycles, ideal for methanation.

2 – Progress and Outcomes: PTS Stability in the Presence of Ash

- 850 ^{o}C isothermal operation



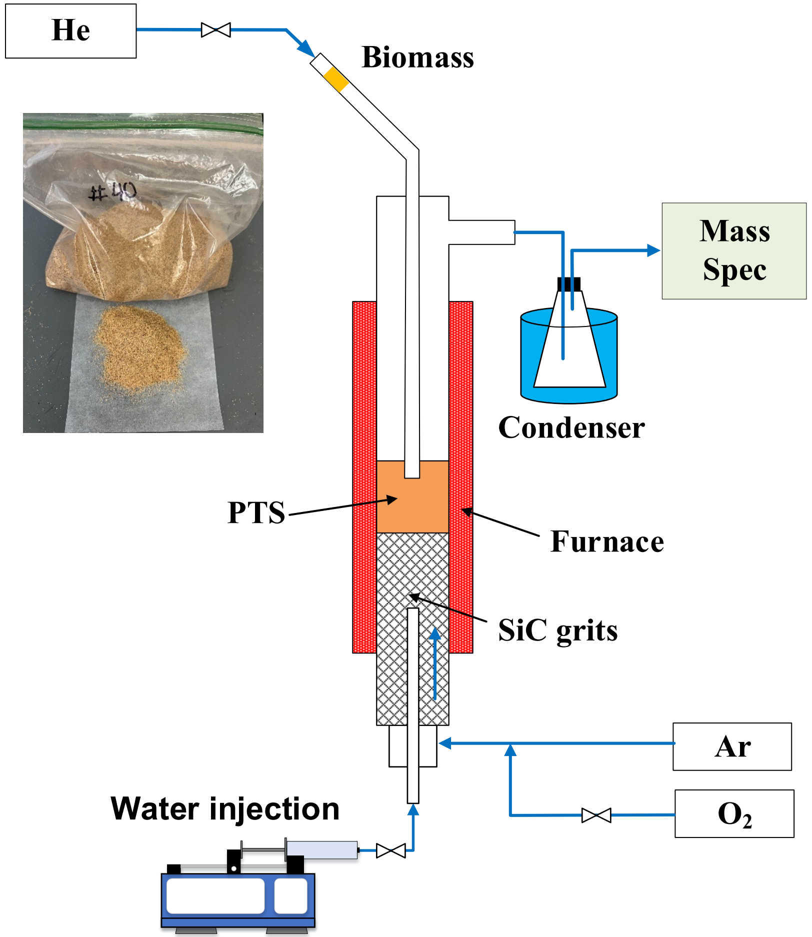


1 wt.% Ash in sorbent: 29% CO_2 capacity vs. pure sorbent: 29.9%

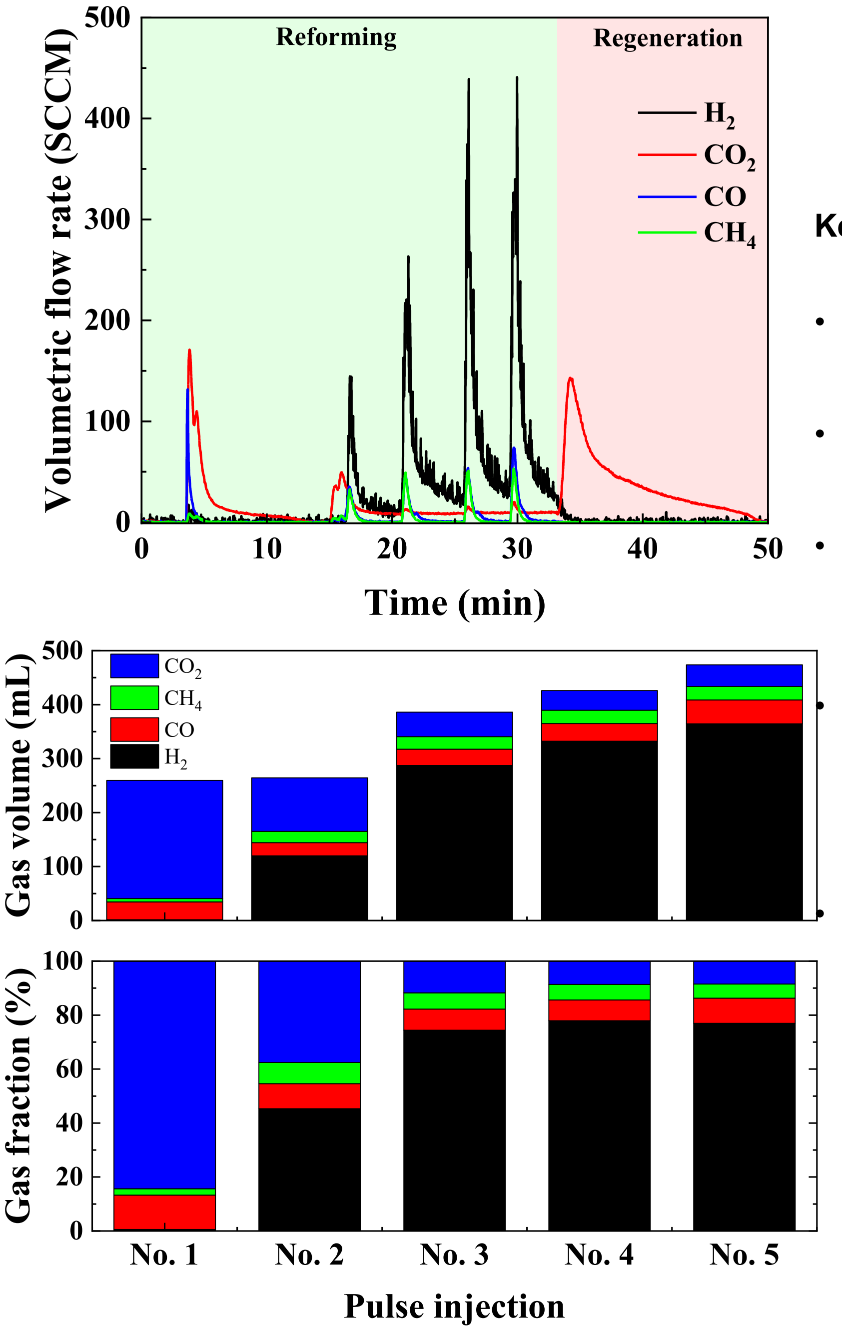
25 wt.% Ash in sorbent: slight deactivation followed by stabilization

Ash would have a negligible impact on the sorbents in the gasifier since ash is estimated to be ~0.03 wt.% (the current test was 30 – 600 X of the anticipated amount).

2 – Progress and Outcomes: PTS Conversion in a Lab-Scale Fluidized Bed



- Fluidized bed reactor with 15g sorbent particles (180~425 µm)
- Woody biomass (200~500 µm)
- Biomass injection: pressurized pneumatic transport in a batch mode
- Total fluidizing gas volume: 1.2 SLM; fluidizing velocity: 0.18 m/s

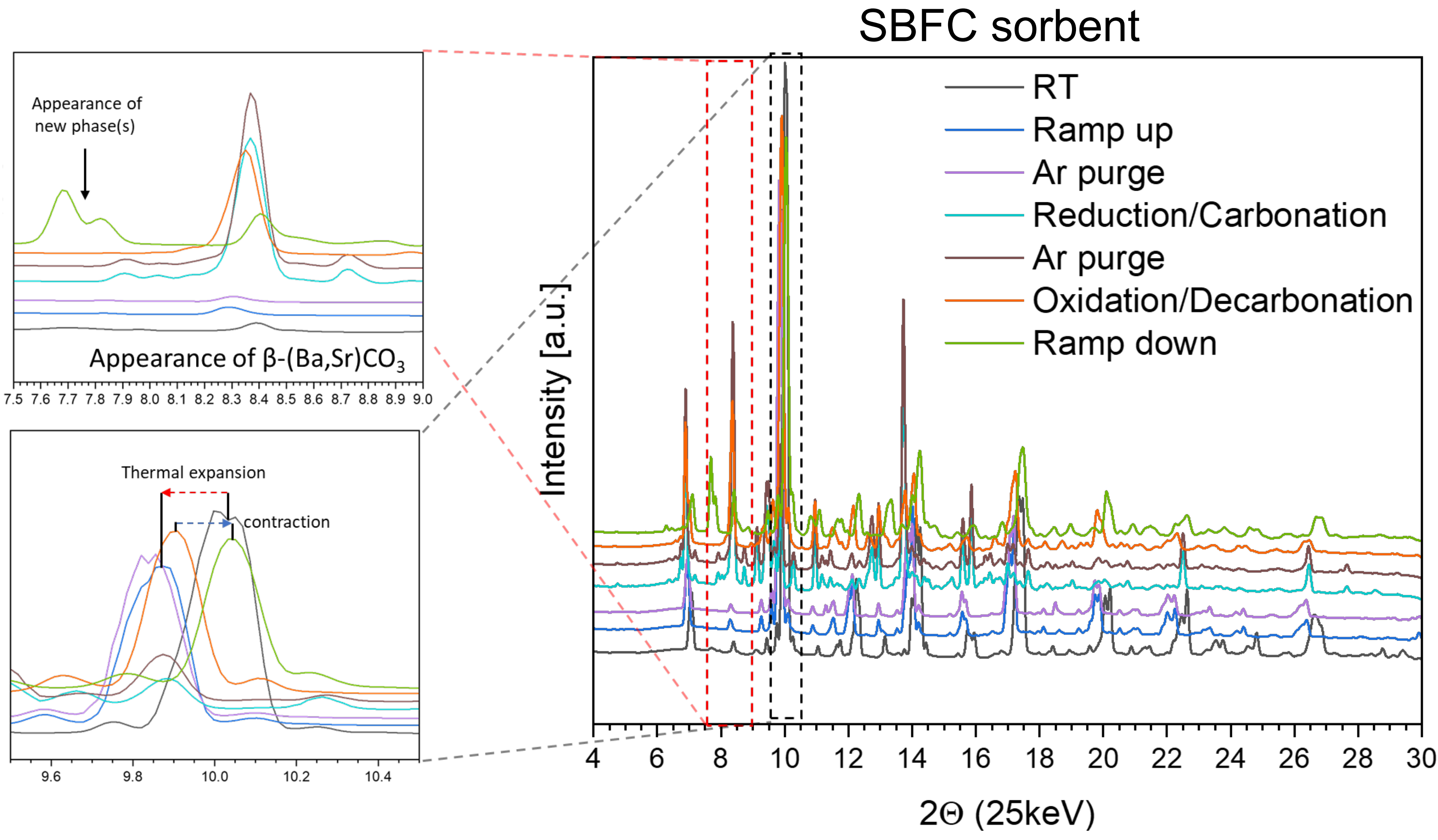


Key findings:

- ~100% carbon balance and carbon conversion;
- H_2 concentration reached 80%, minimal tar production;
- Variable H_2: CO_x ratios, higher CO_x for more oxidized sorbent under the batch mode of operation;
- Continuous CFB operation would allow controlled yet tunable oxidation and carbonate states to allow ideal H_2 : CO_x ratios for methanation;
- Excellent sorbent renderability and stability over 40 hours of fluidized bed operation.

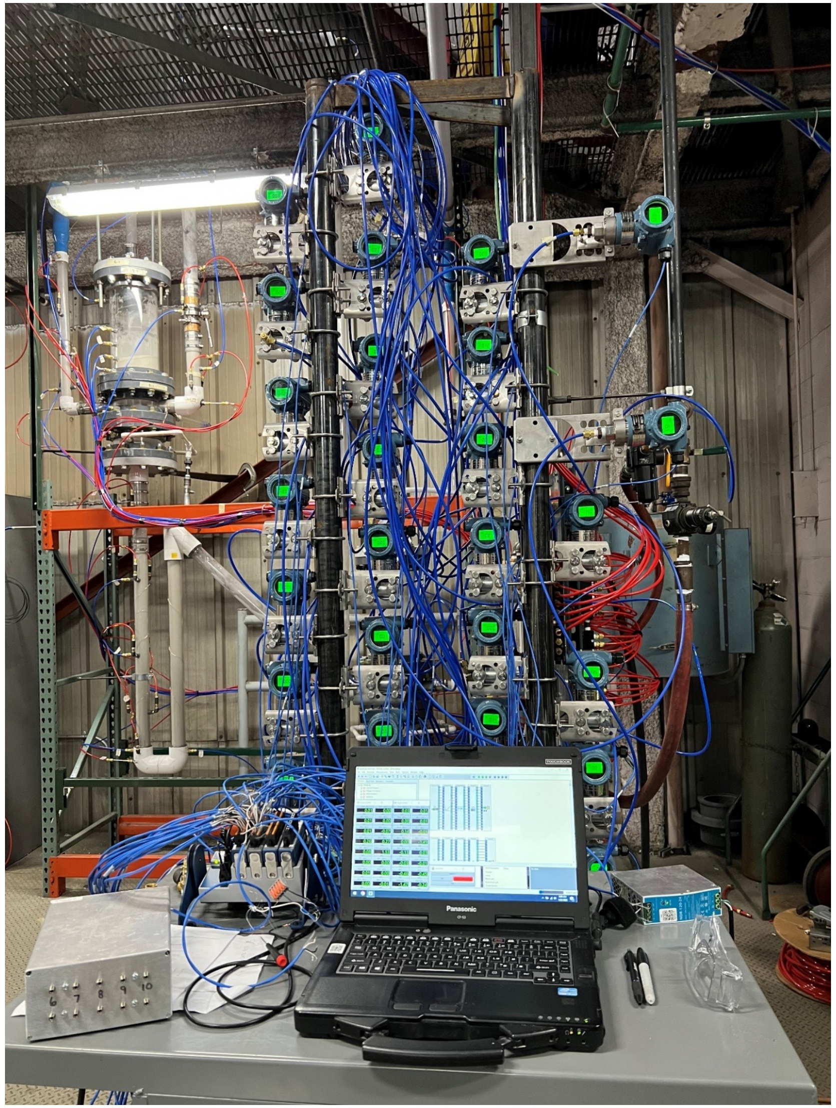
2 – Progress and Outcomes: PTS Characterizations

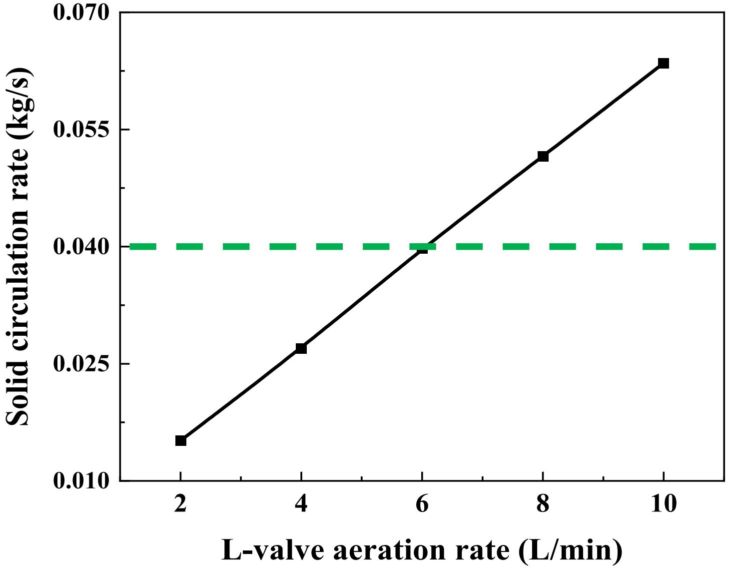
- In-Situ XRD results from the advanced light source (ALS) at LBNL reveal fast-forming intermediates linked to the performance of the PTS materials.
- Rietveld refinement is being used to identify which phases impede further CO_2 capture.
- Results of this detailed characterization will be coupled with *in-situ* TEM and DFT to assist future optimizations.

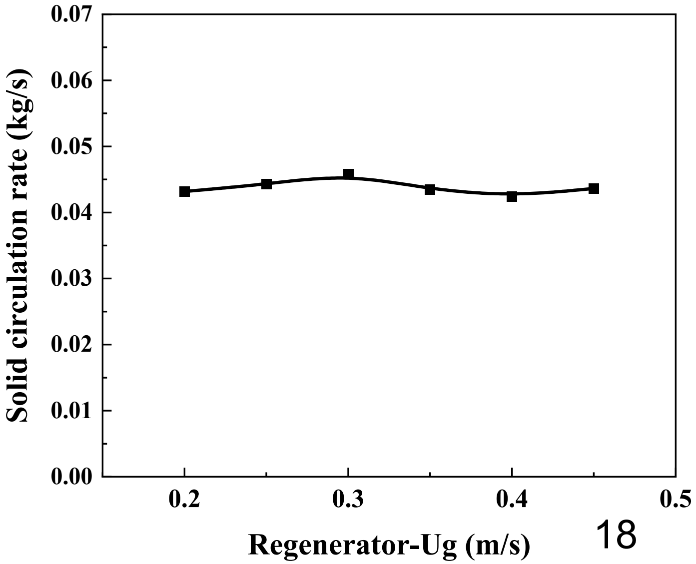


2 – Progress and Outcomes: (Cold) Reactor Design and Operation

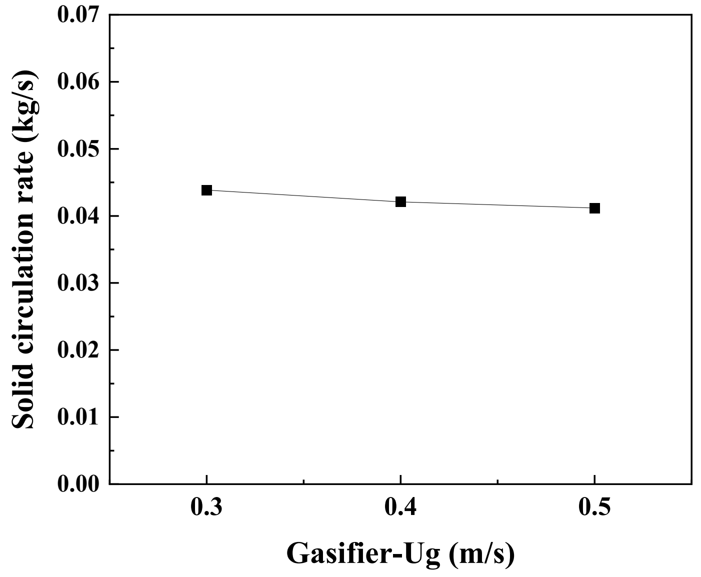
- Dual-fluidized bed gasifier

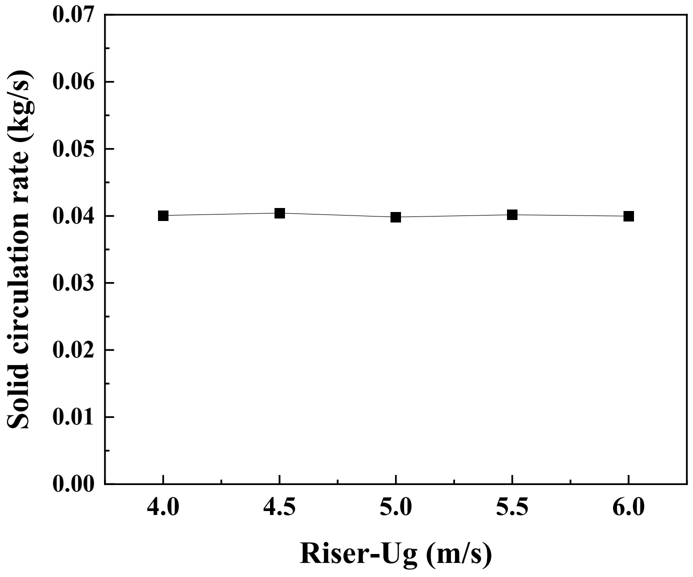


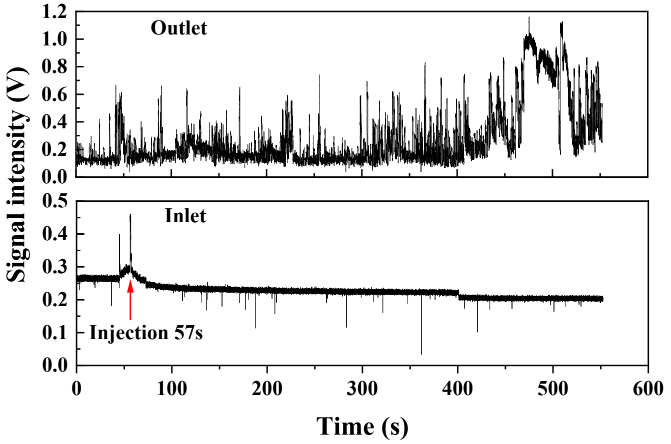


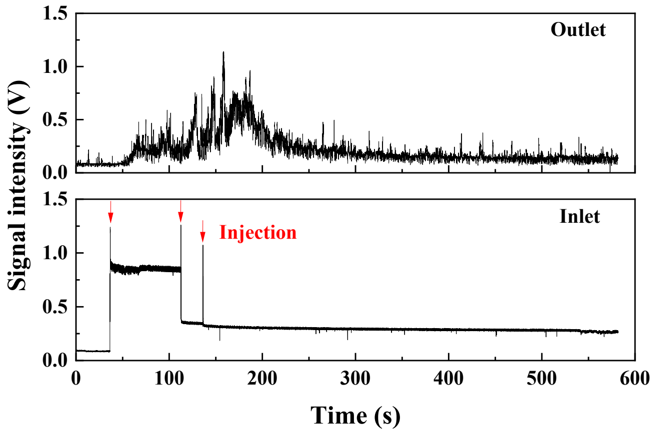


2 – Progress and Outcomes: (Cold) Reactor Design and Operation





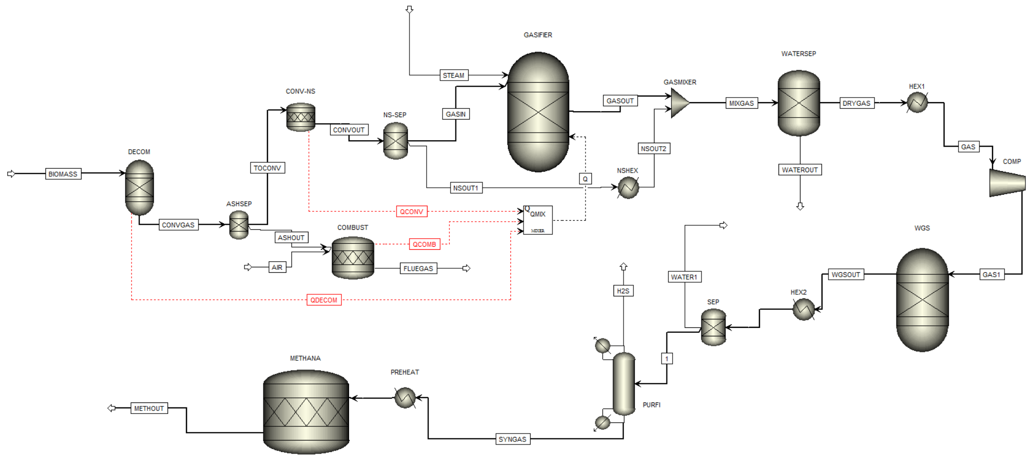


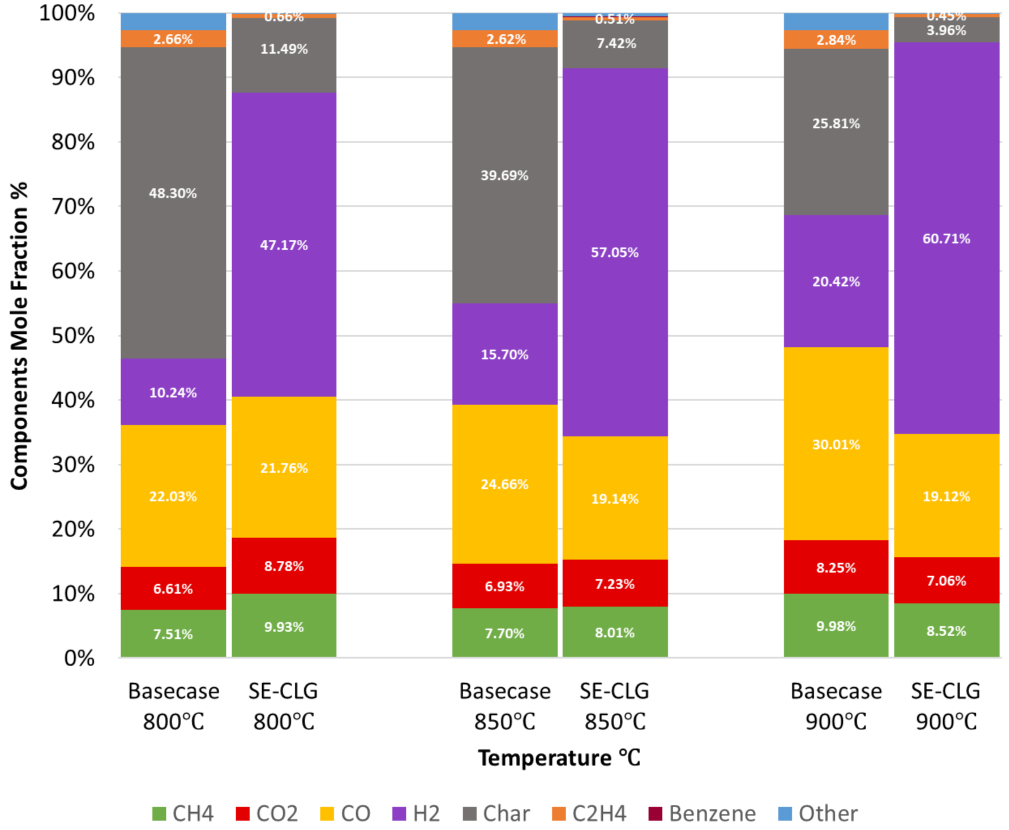


- Solid circulation rate linearly increased with the aeration rate in the L-valve
- Ability to achieve desired solids circulation rates
- Strong anti-interference ability: remained almost unchanged with the variation in the gas velocities in the regenerator, gasifier and riser
- 400 – 450 s sorbent residence time and 60 – 80 s biomass residence time in the gasifier, suitable based on sorbent kinetics

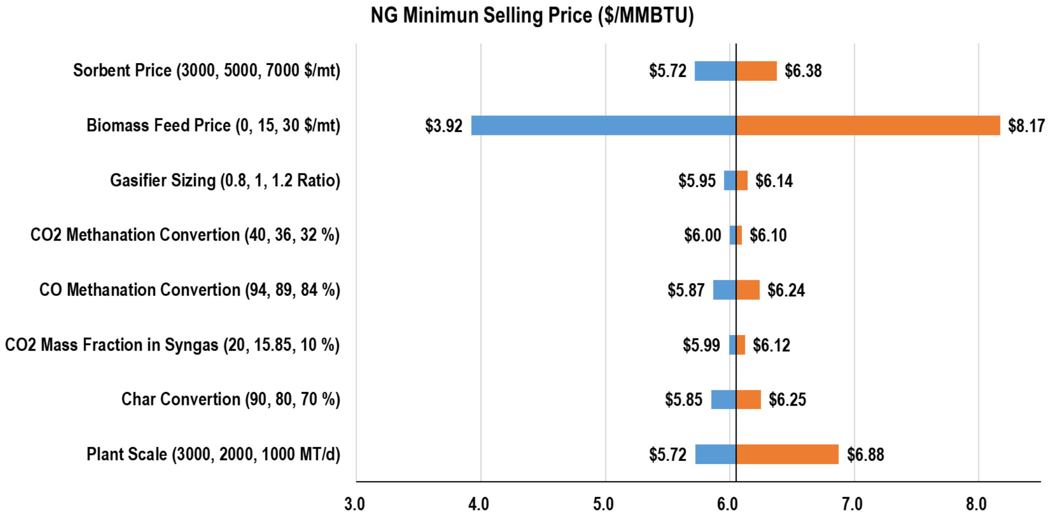
Five hot unit vendors have been contacted, initial bid from one vendor has been received, on track to meet Phase I go/no-go

2 – Progress and Outcomes: Preliminary Process Analysis





Plant Scale: 2000 MT/d Biomass Feed	Basecase	SE-CLE
Minimum Fuel Selling Price ($/MM BTU)	**8.58**	**6.05**
Fuel Production (MM BTU/hr)	**459.27**	**622.07**
Capital Cost $		
Feedstock Handling	$8,801,293	$8,801,293
Gasification and gas conditioning	$31,850,393	$18,770,129
Compression	$7,937,094	$9,748,066
Methanation	$12,407,887	$15,389,026
Steam System and Power Generation	$7,718,126	$7,718,126
Others	$910,571	$910,571
Total Installed Equipment Cost	$69,625,364	$61,337,211
Added Direct + Indirect Cost	$64,574,636	$56,462,789
Total Capital Investment (TCI)	**$134,200,000**	**$117,800,000**
Manufacturing Cost $/yr		
Biomass	$10,512,500	$10,512,500
Catalyst	$4,285,125	$4,070,869
Other Materials	$2,516,928	$2,516,928
Electricity	$1,335,162	$1,272,013
Waste Disposal	$1,830,676	$1,830,676
Fixed Costs	$5,200,000	$ 4,700,000
Total Operating Cost	**$25,700,000**	**$24,900,000**



3 – Impact

- *The proposed SE-CLG approach can greatly intensify the biomass gasification process since it combines syngas conditioning, oxygen separation, and catalytic tar removal in a single step, leading to an efficient, autothermal gasification process.*
- *Studies to date confirmed the feasibility and superior performance of the proposed sorbent. Excellent sorbent stability, CO_2 and oxygen capacities, and biomass ash resistance were demonstrated.*
- *>3:1 H_2:CO_x ratio was achieved, ideal for methanation;*
- *A novel dual fluidized bed gasifier cold model was designed and demonstrated.*
- *One peer-reviewed article has been published in ACS Sustainable Chemistry and Engineering. One more under review, and two other are being finalized for submission.*
- *Outreach to potential industrial partners have generated substantial interests.*
- *The team has previously filed invention disclosures covering relevant mixed oxide compositions. A patent application is being prepared.*

Summary

- Feasibility of the SE-CLG concept was validated;
- Advanced phase transition sorbents (PTSs) were developed with multi-functionalities and capable of isothermal CO_2 sorption and regeneration;
- The PTSs showed excellent cyclic stability and capable of converting various biomass/biomass derived feedstocks into high quality syngas with >3 H_2:CO ratios, ready for methanation;
- Reactor design and cold model operation were successful, meeting the SE-CLG requirements;
- The team is ready to move to BPII after selecting the vendor for the hot unit.

Quad Chart Overview

Timeline
- *08/01/2021*
- *11/30/2024*

	FY22 Costed	Total Award
DOE Funding	*$383,861*	*$2,499,411*
Project Cost Share *	$278,937	$636,099

TRL at Project Start: TRL-3
TRL at Project End: TRL-5

Project Goal
Develop a significantly intensified, sorbent enhanced – chemical looping gasification (SE-CLG) technology, which combines biomass gasification, air separation, and syngas conditioning and cleaning into a single circulating fluidized bed (CFB) gasifier to produce methanation ready syngas with an ideal H_2/CO ratio (~3:1) from biomass waste such as C&D waste and chicken litter.

End of Project Milestone
Design and demonstrate a 5 kW_{th} CFB based SE-CLG gasifier for 100 h continuous operation, as well as methanation of the syngas product for pipeline quality renewable natural gas (RNG) production.

>35% decrease in levelized cost of energy (LCOE) compared to the baseline indirect steam gasification technology.

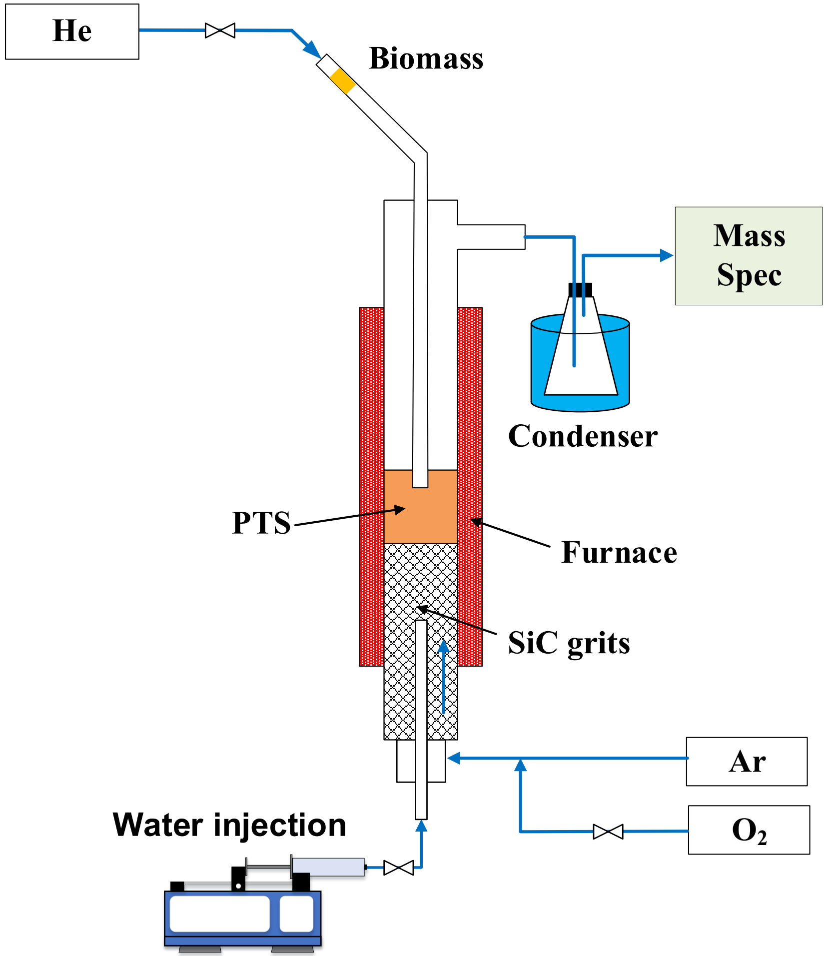
>10 energy return on investment (EROI).

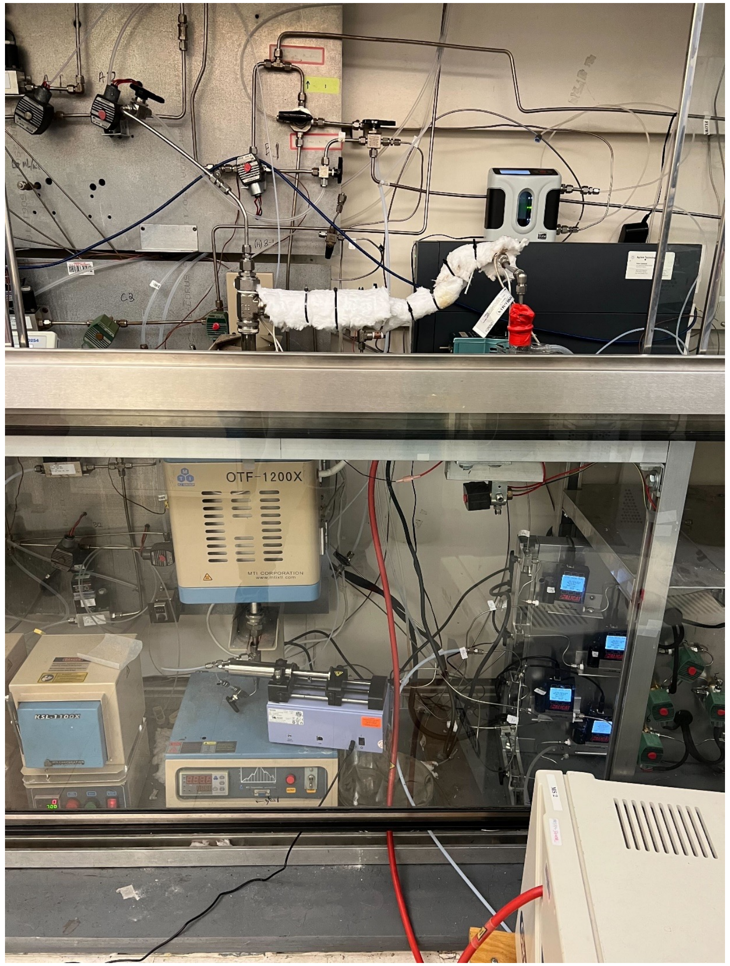
Funding Mechanism
DE-FOA-0002044, AOI 1b, 2019.

Project Partners
- NC A&T State University
- Yale University

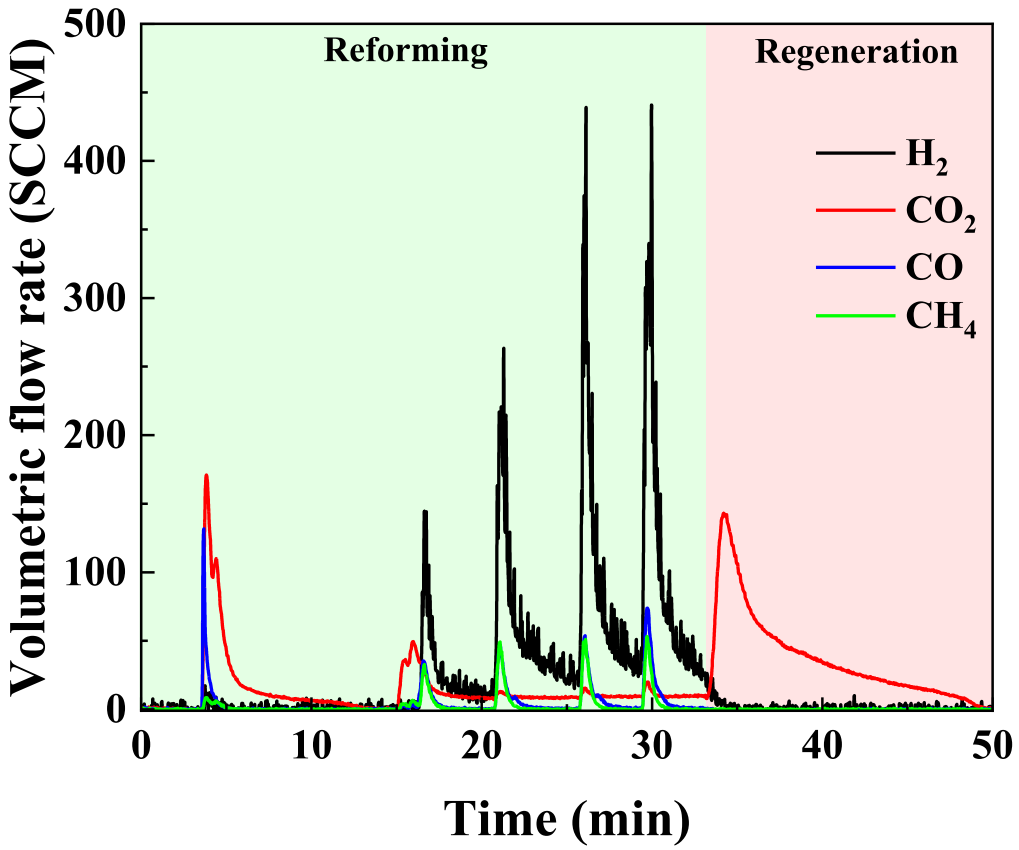
Additional Slides

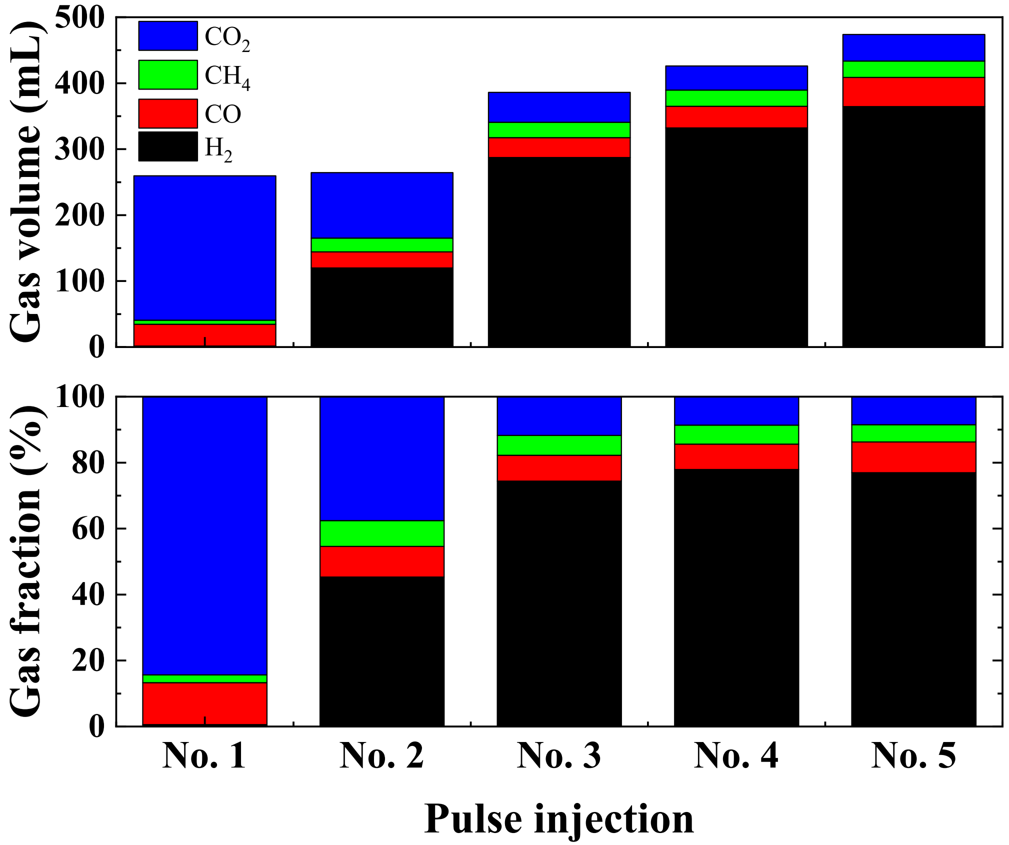
- Fluidized bed reactor with 15g sorbent (180~425 μm)
- Woody chips (200~500 μm)
- Biomass injection: pressurized pneumatic transport
- Total fluidizing gas volume: 1.2 SLM; fluidizing velocity: 0.18 m/s



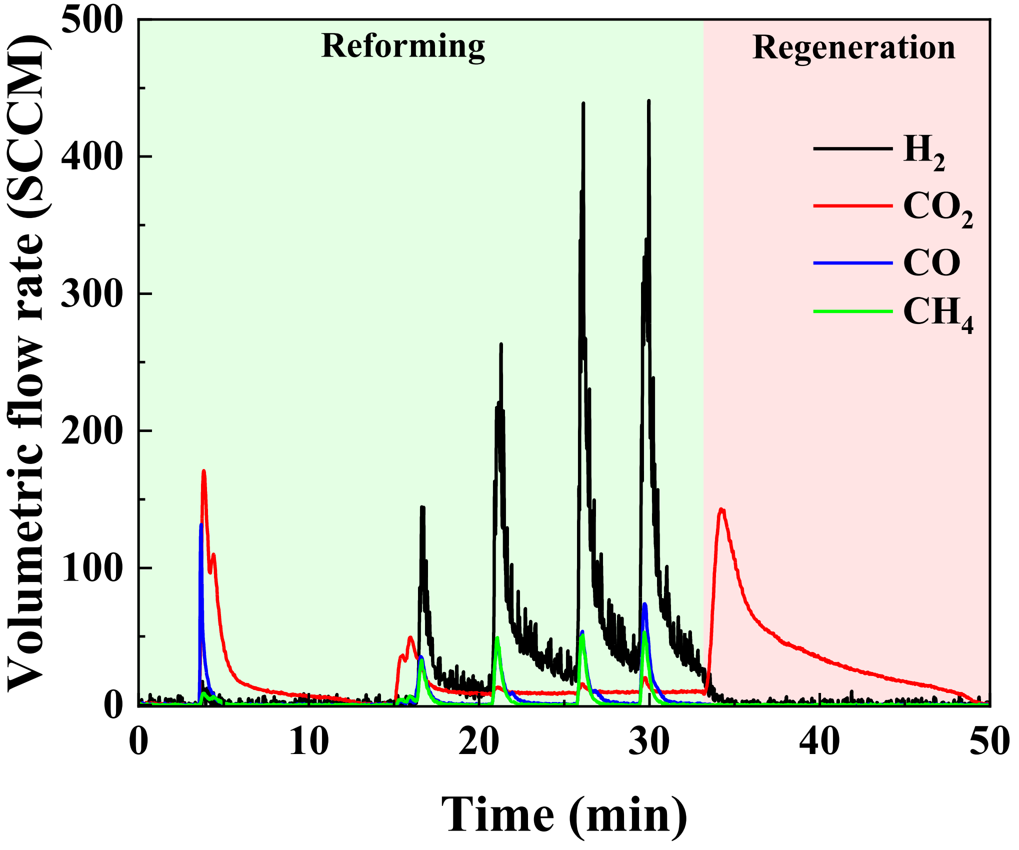


- Reforming: Steam flow rate: 0.21 ml/min, Ar: 923 SCCM;
- Regeneration: Steam flow rate: 0.21 ml/min; Ar: 683 SCCM; O_2: 240 SCCM
- Woody biomass injection: 0.3 g each time, multiple injections each half cycle
- H_2 and syngas concentration increased with injection numbers
- Carbon balance: ~100% based on the C-species released under oxygen combustion condition
- H_2 concentration reached ~80%

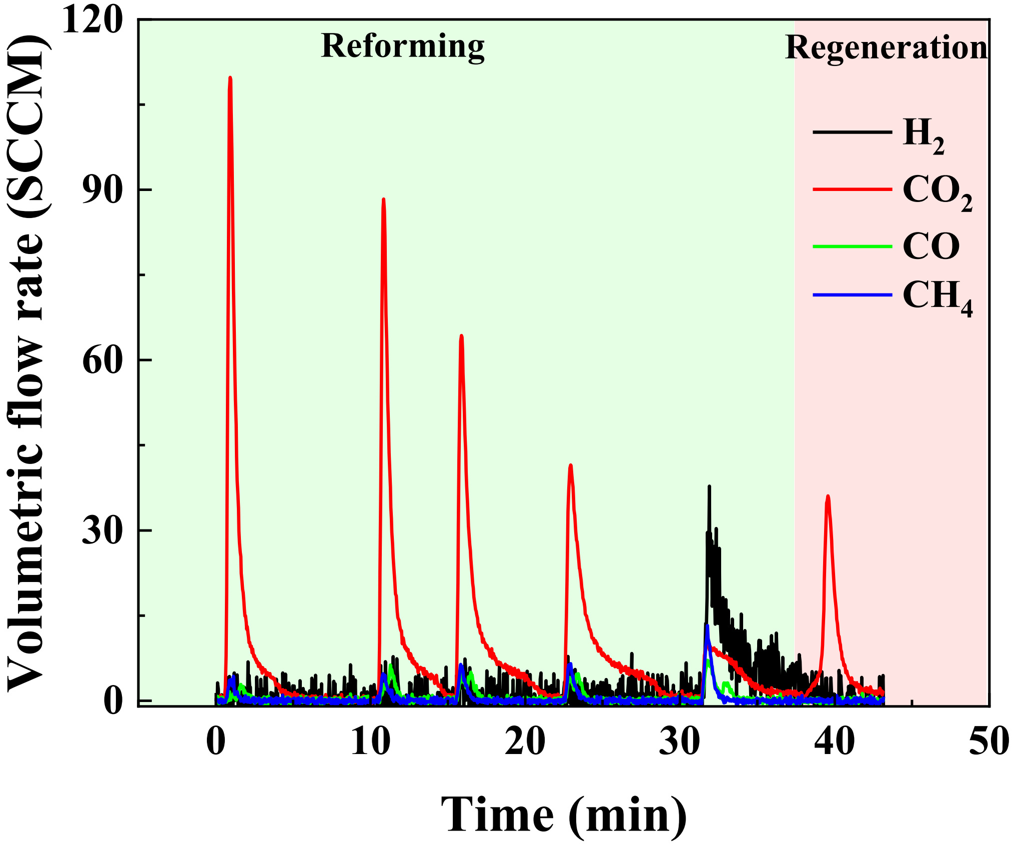




- Comparison between 0.3 g and 0.1 g injection
- Carbon balance: both ~100% based on the C-species release under oxygen combustion condition
- Only a slightly amount of H_2 was produced at the 5th injection
- No syngas (or hydrogen) was observed without steam injection
- Key parameters: Steam-carbon ratio and reduction extent



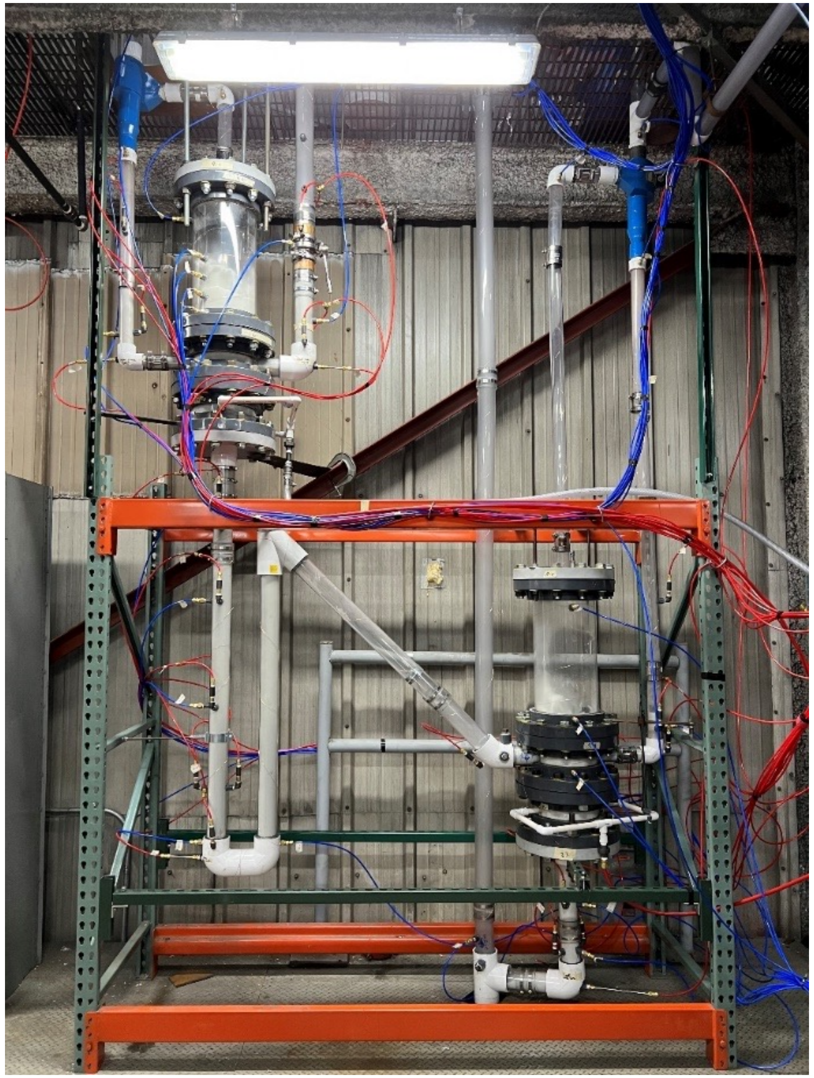
0.3 g injection

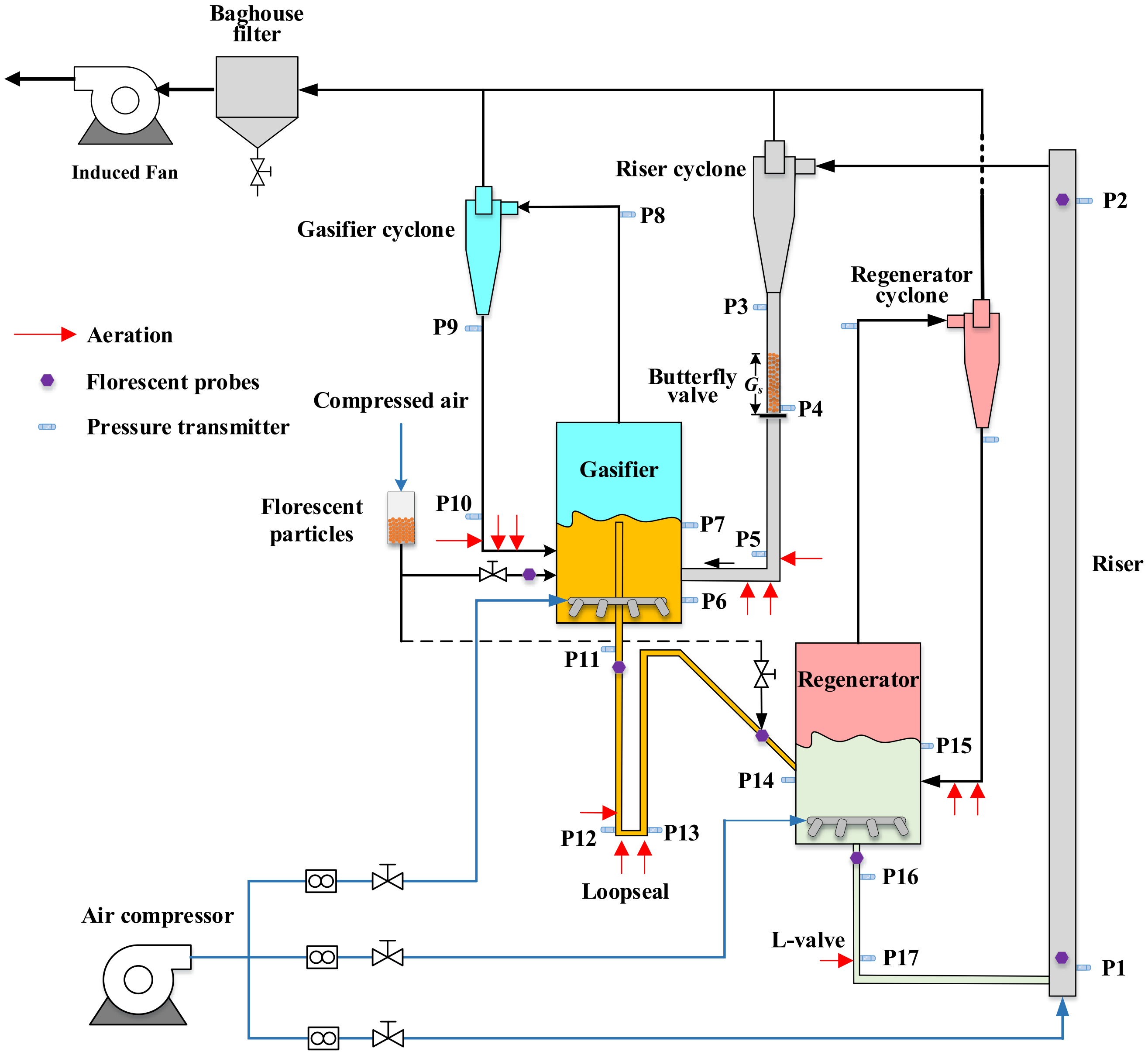


0.1 g injection

Cold flow model

- Dual-fluidized bed gasifier





Publications, Patents, Presentations, Awards, and Commercialization

Accepted Publication:

Leo Brody[#], Runxia Cai[#], Alajia Thornton, Junchen Liu, Hao Yu, Fanxing Li. (2022) "Perovskite-based Phase Transition Sorbents for Sorption Enhanced Oxidative Steam Reforming of Glycerol." ACS Sustainable Chemistry and Engineering. 10(19): 6434-6445. DOI: doi.org/10.1021/acssuschemeng.2c01323

Publication under review:

Leo Brody, Mahe Rukh, Runxia Cai, Azin Saberi Bosari, Reinhard Schomacker, and Fanxing Li. (2023) "Sorption-enhanced steam reforming of toluene using multifunctional perovskite phase transition sorbents in a chemical looping scheme"

A patent application is being compiled, along with two more journal articles.

Commercialization outreach:

In discussion with a large chemical company about potential application for flexible syngas generation;

In discussion with a leading catalyst manufacturer for sorbent synthesis.