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

Jian Dou, Sunkyu Park, Stephen Kelley, and Fanxing Li (PI)

North Carolina State University

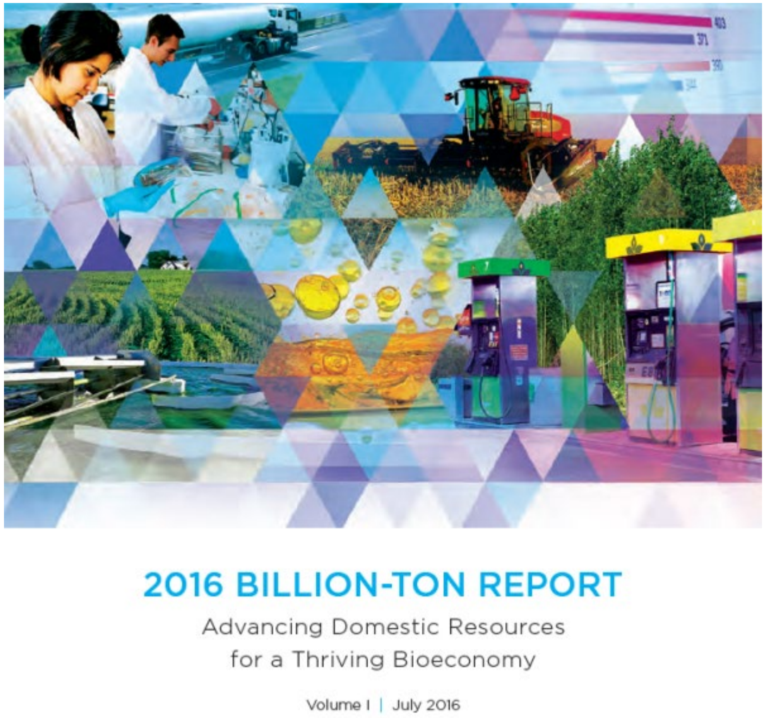
Project Partners: NCA&T and PSRI

Particulate Solid Research, Inc.

Outline

- **Background**
- Preliminary Data
- Project Objectives and Tasks
- Market Transformation Plan
- Collaborations

Biomass Waste to Renewable Energy



2016 BILLION-TON REPORT

Advancing Domestic Resources
for a Thriving Bioeconomy

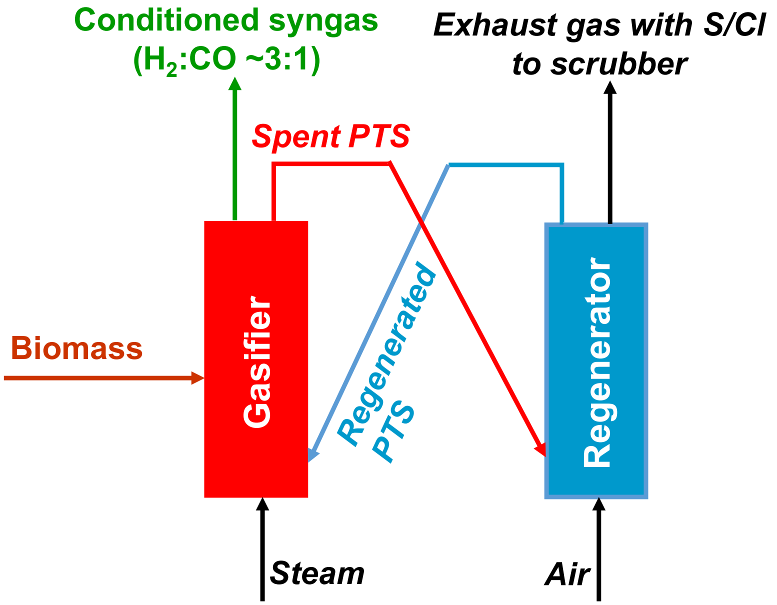
Volume I | July 2016

- Renewable energy mitigates global climate change
- More than 40 million dry ton biomass available every year[1]
- Conventional anaerobic digestion encounters problems of incomplete conversion of feedstock
- State-of-the-art partial oxidation gasifier suffers from high capital and energy cost for air separation

---

[1] Langholtz, M. H.; Stokes, B. J.; (Leads), L. M. E. In *ORNL/TM-2016/160. Oak Ridge National Laboratory, Oak Ridge, TN. 448p. doi: 10.2172/1271651.*

Sorbent-Enhanced Chemical Looping Gasification (SE-CLG)



Conditioned syngas (H_2:CO ~3:1)

Exhaust gas with S/Cl to scrubber

Spent PTS

Biomass

Gasifier

Regenerated PTS

Regenerator

Steam

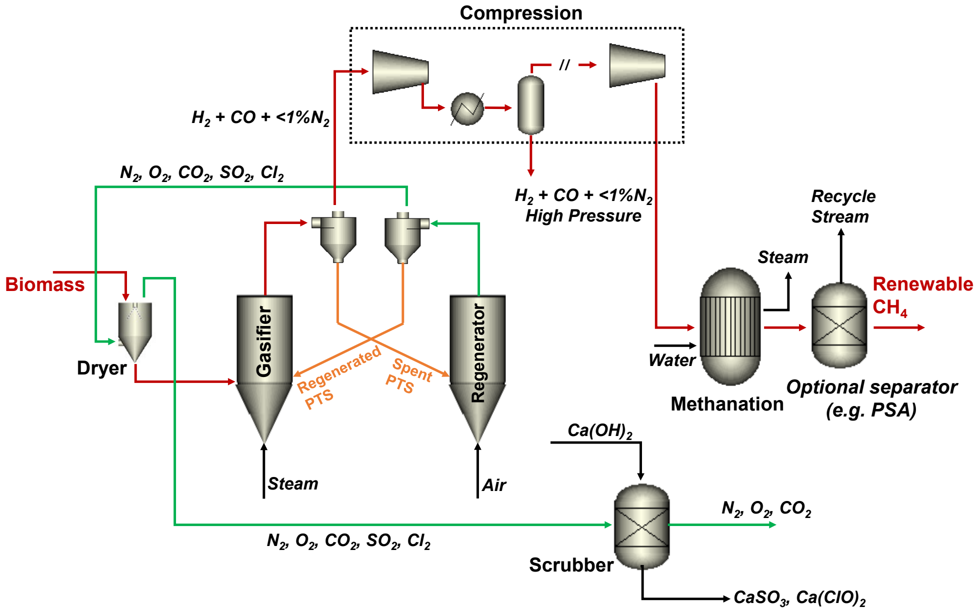
Air

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 $SrFeO_3$)

- Intensified sorbent enhanced chemical looping Gasification (SE-CLG) using circulating fluidized bed
- SE-CLG integrates together biomass gasification, air separation, and syngas conditioning and cleaning
- Production of syngas with H_2/CO ratio of 3:1, ready for methanation
- >35% reduciton in LCOE comparing to indirect steam gasification

Sorbent-Enhanced Chemical Looping Gasification (SE-CLG)



- Mixed oxide phase transition sorbent (PTS) for biomass gasification
- Particles fluidized by steam
- PTS donates lattice oxygen to oxidized biomass to H_2, CO, along with steam, CO_2
- PTS reduced to alkaline oxide and metal/metal oxide
- Alkaline oxide (i.e., CaO) absorbs CO_2 to form carbonate, and absorbs contaminants to form CaS, and $CaCl_2$

Reactions in SE-CLG Process

Unit	Key Reactions ($SrFeO_3$ is used as a simplified PTS example)
Gasifier	$4SrFeO_3 \rightarrow 2Sr_2Fe_2O_5 + O_2$ Biomass + $Sr_2Fe_2O_5 + O_2 \rightarrow CO + H_2 + CO_2 + H_2O + SrO + FeO + Fe + SrS/SrCl_2/FeS/FeCl_2$ $CO + H_2O \leftrightarrow CO_2 + H_2$ $CO_2 + SrO \rightarrow SrCO_3$ $NH_3 + FeO \rightarrow Fe + N_2 + H_2O$
Regenerator	$SrCO_3 + FeO + Fe + SrS/FeS/SrCl_2/FeCl_2 + O_2 \rightarrow SrFeO_3 + CO_2 + SO_2 + Cl_2$
Methanation unit	$CO + 3H_2 \rightarrow CH_4 + H_2O$
Scrubber	$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$ $2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O$

PTS is the key to biomass gasification and syngas cleaning and conditioning

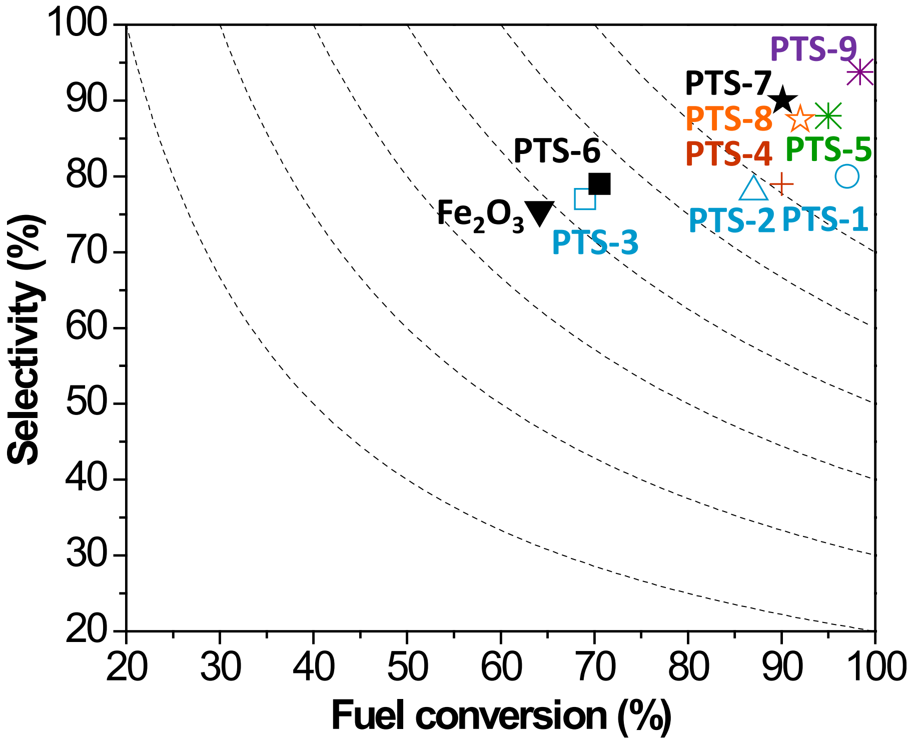
SE-CLG vs Indirect Steam Gasification vs Anaerobic Digestion

	AD	SG	SE-CLG
Status	Mature	Developing	Developing
Capacity	Small	Large	Large
Biomass conversion	Low	High	High
Contaminants and CO_2 content	High	High	Low
Air separation Unit	N.A.	Required	Not required
Syngas cleaning and conditioning	Required	Required	Not required
H_2/CO ratio	N.A.	<2:1	3:1
Methanation	Not required	Required	Required

Outline

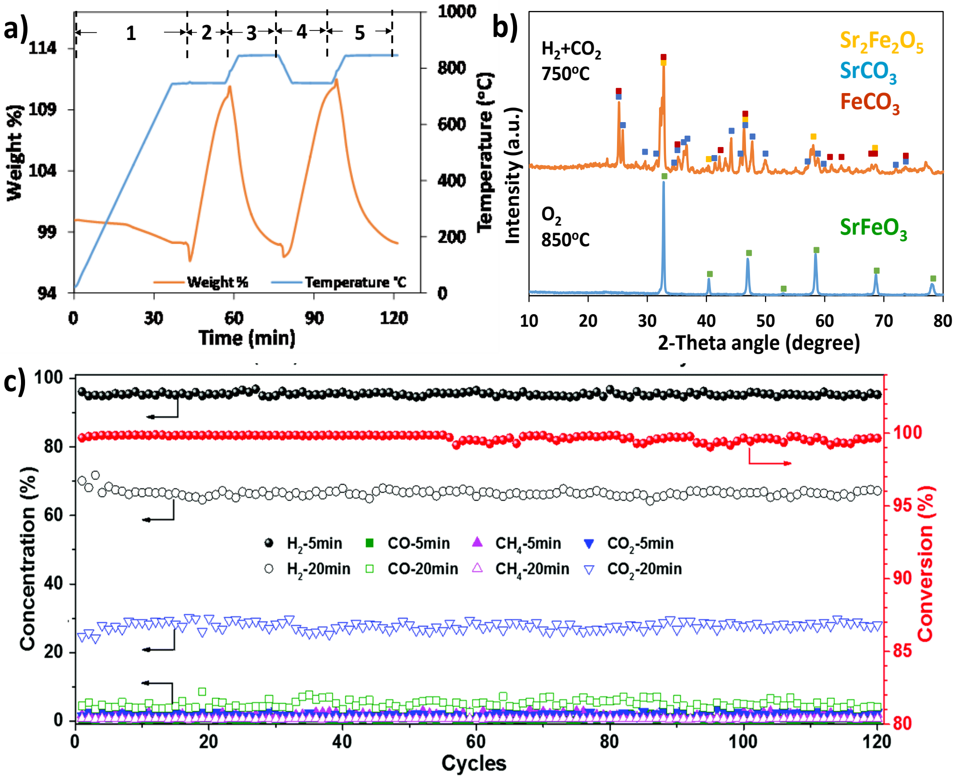
- Background
- **Preliminary Data**
- Project Objectives and Tasks
- Market Transformation Plan
- Collaborations

PTS Design-Methane Conversion and Syngas Selectivity



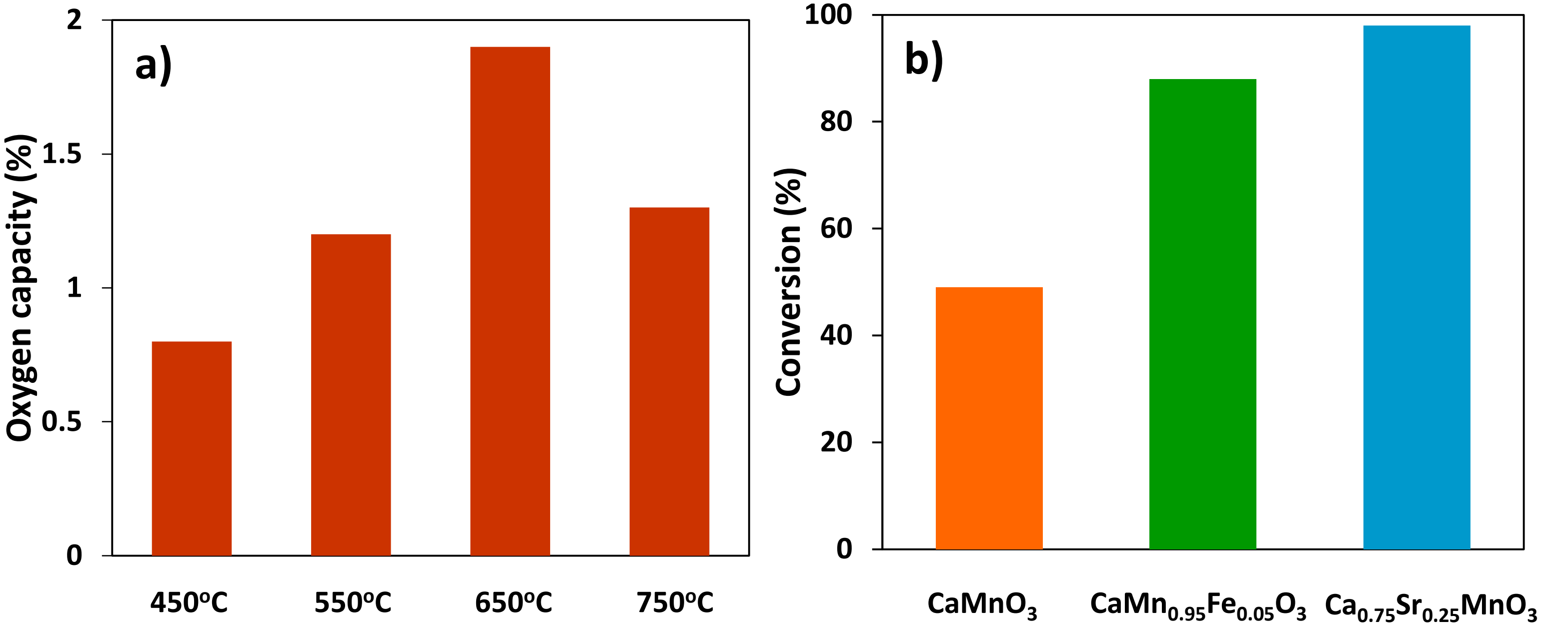
- PTS sorbents effectively donates lattice oxygen to convert methane into syngas
- Integration of air separation with gasification
- CaO modified $SrFeO_3$ sorbents and $BaMn_xFe_{1-x}O_3$ sorbents with up to 90% syngas yield

PTS Design-CO_2 Sorption and Release



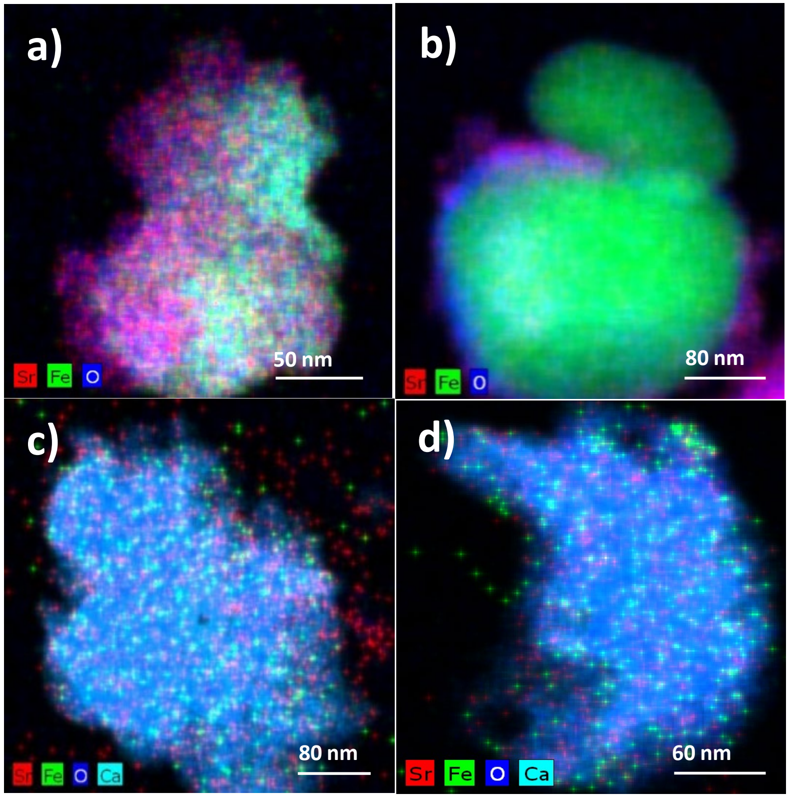
- *in-situ* syngas conditioning via CO_2 sorption
- $SrFeO_3$ donates its lattice oxygen in the presence of a H_2 and CO_2 mixture
- Reversible CO_2 uptake and release via formation of $SrCO_3$ and $FeCO_3$ in H_2/CO_2, and regeneration of $SrFeO_3$ in air
- $Ca_{0.5}Co_{0.5}O$ PTS effectively conditioned syngas produced from glycerol to increase H_2:CO ratio from 1.8:1 to 20:1

PTS Design-Spontaneous Oxygen Release



- Kinetics for biomass gasification is critical to determine reactor sizing and capital cost
- Phase transition of $SrFeO_{2.5}$ to $SrO/SrCO_3$ and Fe is ideal for syngas generation
- PTS like $SrFeO_3$ has significant amount of O_2 release capacity (0.8-1.9 w.t.%) at 450-750°C
- PTS increases char gasification kinetics by an order of magnitude comparing to steam gasification alone

PTS Design-Stability



- Develop PTS with excellent chemical and physical stabilities for fluidized bed operation
- Improve PTSs's physical stability by adding support and/or binding materials
- CaO enhances well dispersion of Fe in the PTS oxide, allowing facile and reversible phase transitions with good stability

Outline

- Background
- Preliminary Data
- **Project Objectives and Tasks**
- Market Transformation Plan
- Collaborations

Project Objectives

- Develop phase transition sorbents (PTSs) for biomass gasification with integrated air separation and CO_2 sorption
- Demonstrate ash and contaminants resistance of PTS for C&D waste and poultry litter feedstock
- Design, construction and demonstration of 5 kW CFB gasifier to produce clean and conditioned syngas from biomass
- Validate >35% reduction in LCOE comparing to steam gasification process

Technical Approach

- **Year I:** Collect, characterize, and pretreat biomass waste feedstocks. Design, characterize and optimize PTS for SE-CLG. Perform preliminary process and cost analysis.
- **Year II:** Demonstrate robustness of PTS for various biomass wastes including poultry and C&D wastes. Design and construct a 5 kWth CFB based SE-CLG gasifier.
- **Year III:** Synthesize 20 kg batches of PTS sorbents. Demonstrate a 5 kW_{th} CFB to produce methanation ready syngas for 100+ hours. Perform detailed techno-economic and life cycle analyses.

Biomass Waste Characterization and Pretreatment

- Feedstock characterization and handling is critical for biorefinery.
- characterize the woody and poultry litter feedstock to determine solid, volatile, moisture, and ash contents as well as elemental composition.
- Pretreat feedstock by torrefaction to reduce moisture content, increase carbon content, decrease grinding energy, and enhance flow properties in CFB gasifier.

Milestone: *Collect consistent and representative biomass waste feedstocks and characterize their key properties for thermochemical conversion; Determine the effect of pretreatment on the feedstock.*

Phase Transition Sorbent Design, Characterization, and Testing

- Preliminary studies have already resulted in a number of promising PTSs
- Investigate redox kinetics of PTSs under reducing and oxidizing conditions, followed by optimization through doping and/or secondary phase addition
- Improve PTSs' CO_2 uptake/release rates and sorption capacities by incorporation of alkaline earth or alkali metal cations and/or tuning the strength of interactions between alkaline earth metals and transition metal oxides
- Tailor PTSs' composition and structure for spontaneous oxygen release to improve gasification kinetics
- Stability of PTSs in the presence of contaminants and ash will also be established.

Milestone: *Develop PTSs showing >95% methane conversion while producing syngas with* H_2/CO *ratio >2.5 and < 5% degradation over 50 cycles in the presence of ash and contaminants.*

Scale up Synthesis of Phase Transition Sorbents

- Prepare PTS particles at 1 kg/batch scale using scalable methods such as solid-state reaction method at NCSU or spray-dry method through collaborations with VITO
- Evaluate PTS particles in the lab scale fluidized bed reactor and optimize PTS composition
- Synthesize larger batches of PTS particles at 20 kg/batch based on optimized PTS composition
- Validate the reactive and hydrodynamic properties as well as attrition resistances of PTS particles prior to operation of the gasifier.

Milestone: *Synthesize PTS particles with a scalable method and showing <5% activity degradation and <1 wt.% attrition over 24 hrs; Prepare two 20 kg batches of PTS particles.*

SE-CLG of Biomass Wastes

- Evaluate PTSs with biomass feedstocks to validate their performance and stability under an operational environment
- Characterize PTSs before and after gasification using the lab-scale fluidized bed
- Optimization of the sorbents to improve biomass conversion kinetics, enhance the H_2/CO ratio in the syngas products, and reduce tar and other contaminants in the syngas product stream
- Investigate the effect of contaminants (i.e., S and Cl) to validate the PTS particles' robustness
- Demonstrate stability of PTSs in the lab scale fluidized bed for 24 hours under a cyclic redox mode with the injection of biomass waste particles.

Milestone: *Develop PTSs showing >95% biomass waste conversion and <5% degradation in activity and <1 wt.% attrition over a 24 hour testing period in a lab-scale fluidized bed.*

Circulating Fluidized bed (CFB) Gasifier Design and Construction

- Design and construct a 1:1 scale cold model of the 5 kW$_{th}$ unit through collaboration with PSRI.
- Operate cold model with model glass beads and inert gases to validate the design
- Design CFB gasifier based on the finalized cold model
- Fabricate CFB hot model components at PSRI
- Assembly CFB hot model at NCSU

***Milestone**: Complete the construction of the CFB gasifier hot unit.*

Shakedown and Operation of the 5 kW_{th} Gasifier

- Test CFB gasifier with inert simulants at room temperature to validate the reactor hydrodynamics and operability
- Operate gasifier at high temperature using inert fluidization gas
- Demonstrate SE-CLG process using PTS particles and biomass powders
- Validate methanation step based on syngas composition from CFB gasifier

Milestone: *100 hrs CFB demo with >95% biomass conversion to syngas (H_2:CO ratio >2.5); methanation of the syngas to >95% CH_4.*

Comprehensive Techno-economic and Life Cycle Analyses

	Baseline	***SE-CLG***
Biomass processing rate (MW_{th})	462.7 (MW_{th}, HHV)	
CH_4 production rate (MW_{th}, HHV)	215.5	275.7
Capital Costs (in Millions, 2007 $)		
Gasifier	43.3	43.3
Tar reforming/quench	26.9	n.a.
Scrubbing	28.5	10.4
Compression	32.5	30.1
methanation	33.1	33.1
power generation	22.9	24.7
cooling water/utilities	9.6	5.7
Total installed cost	*196.8*	*147.3*
Land, site, contingency	133.2	100.2
Working Capital	16.4	12.3
Total Capital Cost (TCI)	***346.5***	***259.8***
Operating Costs (million $/year)		
Biomass cost	10.5	10.5
Catalyst cost	3.8	1.9
PTS particle cost	0.0	1.9
Other raw materials	0.4	0.4
Waste disposal	0.5	0.5
Fixed cost	18.6	14.8
Total Operating Cost	***33.8***	***30.0***
Levelized Cost of Energy Calculation (in Millions, 2007 $)		
Annualized financing cost	30.5	22.9
Total annual cost	64.3	52.9
Discounted cost over 30 years	520.2	427.6
Discounted energy production (GJ)	52756897.1	67474315.0
LCOE ($/GJ)	***$9.86***	***$6.34***

- Develop Aspen model and Excel-based economic model based on the experimental results to optimize the proposed process.
- Quantify the impacts of uncertainty and identify scenarios with minimum financial risks using Monte Carlo simulation
- Perform LCA using system boundaries including waste collection and transportation, RNG production, and use in commercial trucks
- Integrate results of TEA and LCA into a Cost Benefit Analysis framework to understand the trade-offs between economic attractiveness and environmental benefits

Milestone: *Confirm 35% LCOE reduction and >10 EROI using the 5 kW_{th} CFB data.*

Outline

- Background
- Preliminary Data
- Project Objectives and Tasks
- **Market Transformation Plan**
- Collaborations

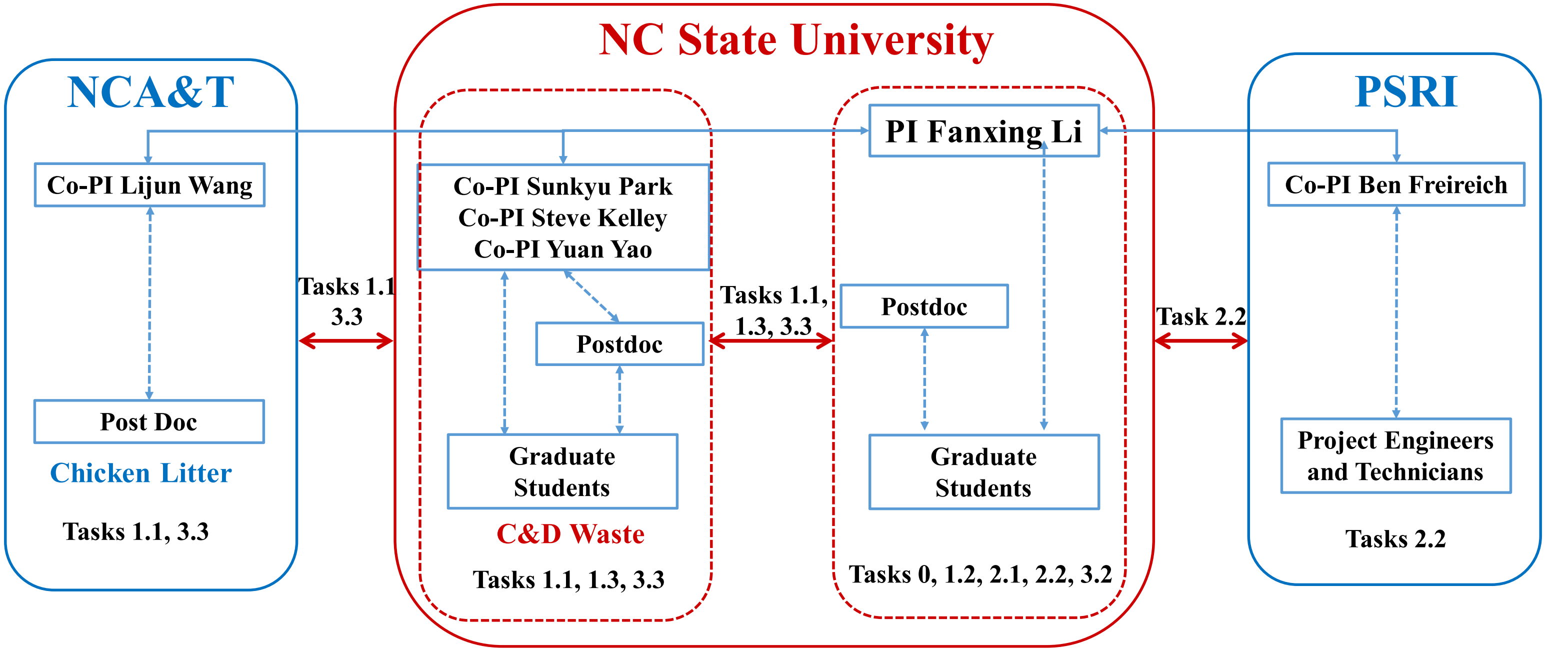
Market Transformation Plan

- RNG cost from SE-CLG technology including byproduct (i.e., fertilizer via chicken litter pretreatment and electricity co-product) credits is estimated as $2.39/mmBtu, competitive to conventional natural gas prices
- Aim to either enter a joint technology development agreement with commercial partners (candidates include Duke Energy and Aries Clean Energy) or license out the technology
- Demonstrate auto-thermal, long term operation of the SE-CLG gasifier (4 – 7 year timeline) prior to full-scale commercialization

Outline

- Background
- Preliminary Data
- Project Objectives and Tasks
- Market Transformation Plan
- **Collaborations**

Collaborations



NCA&T

Co-PI Lijun Wang

Post Doc

Chicken Litter

Tasks 1.1, 3.3

Tasks 1.1
3.3

NC State University

Co-PI Sunkyu Park
Co-PI Steve Kelley
Co-PI Yuan Yao

Postdoc

Graduate Students

C&D Waste

Tasks 1.1, 1.3, 3.3

Tasks 1.1,
1.3, 3.3

PI Fanxing Li

Postdoc

Graduate Students

Tasks 0, 1.2, 2.1, 2.2, 3.2

Task 2.2

PSRI

Co-PI Ben Freireich

Project Engineers and Technicians

Tasks 2.2

Particulate Solid Research, Inc.

Related References

1. Zhang, J.; Haribal, V.; Li, F. *Sci. Adv.* **2017**, *3*, e1701184.
2. Haribal, V. P.; He, F.; Mishra, A.; Li, F. *ChemSusChem* **2017**, *10*, 3402.
3. Galinsky, N.; Sendi, M.; Bowers, L.; Li, F. *Applied Energy* **2016**, *174*, 80.
4. Dang, C.; Li, Y.; Yusuf, S. M.; Cao, Y.; Wang, H.; Yu, H.; Peng, F.; Li, F. *Energy Environ. Sci.* **2018**, *11*, 660.
5. Ou, L.; Kim, H.; Kelley, S.; Park, S. *Biofuels, Bioproducts and Biorefining* **2018**, *12*, 442.
6. Galinsky, N. L.; Shafiefarhood, A.; Chen, Y.; Neal, L.; Li, F. *Appl. Catal. B* **2015**, *164*, 371.
7. Li, F.; Luo, S.; Sun, Z.; Bao, X.; Fan, L.-S. *Energy Environ. Sci.* **2011**, *4*, 3661.
8. He, F.; Linak, W. P.; Deng, S.; Li, F. *Environ. Sci. Technol.* **2017**, *51*, 2482.
9. Shafiefarhood, A.; Zhang, J.; Neal, L. M.; Li, F. *J. Mater. Chem. A* **2017**, *5*, 11930.
10. Neal, L. M.; Shafiefarhood, A.; Li, F. *ACS Catal.* **2014**, *4*, 3560.
11. Park, J.; Meng, J.; Lim, K. H.; Rojas, O. J.; Park, S. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 199.
12. Meng, J.; Park, J.; Tilotta, D.; Park, S. *Biores. Technol.* **2012**, *111*, 439.
13. Yao, Y.; Graziano, D. J.; Riddle, M.; Cresko, J.; Masanet, E. *Environ. Sci. Technol.* **2015**, *49*, 14704.
14. Yao, Y.; Graziano, D.; et al. *Curr. Opin. Chem. Eng.* **2014**, *6*, 90.

Acknowledgement

NCSU:
Sunkyu Park (co-PI), Stephen Kelley (co-PI), Yuan Yao (co-PI)

NCA&T: Lijun Wang (co-PI)

PSRI: Ben Freireich (co-PI)

Thank you!