Advanced Reaction Systems

Jonathan W Lekse

Research Team: Mehrdad Shahnam, Mary Ann Clarke, Omer Dogan, Yuhua Duan, Mark Smith, Pranjali Muley, Ping Wang, Ranjani Siriwardane, Eric Lewis, Robert Stevens

NATIONAL ENERGY TECHNOLOGY LABORATORY

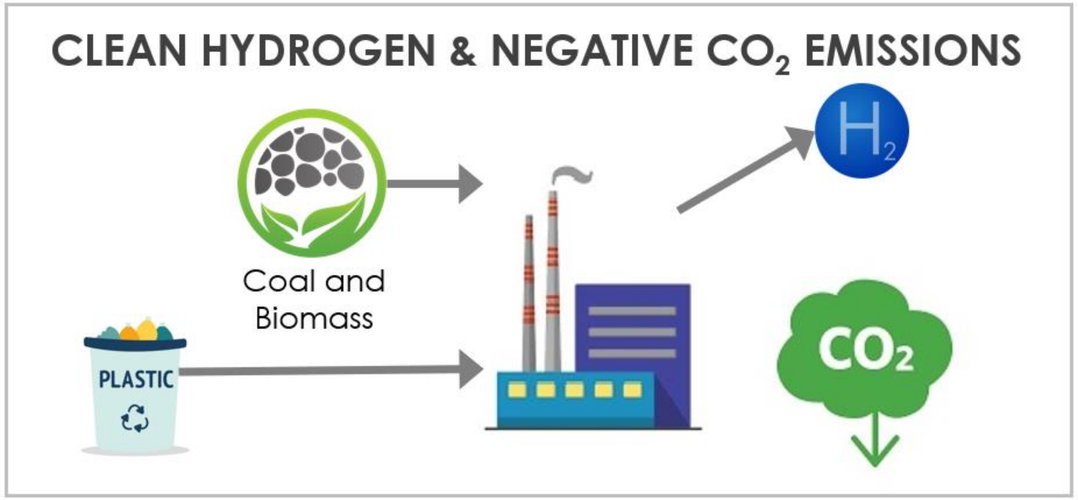
U.S. DEPARTMENT OF ENERGY

Research Objective

Portfolio Objective

Value Proposition: Gasification technologies offer promising opportunities to generate value from waste materials with minimal carbon emissions

The objective of the Advanced Reaction Systems Portfolio is to design, develop, and analyze technologies to support the mission of the Gasification Program to enable the use diverse feedstocks to produce hydrogen and other value-added products with net-zero carbon emissions



Current Research

Overview

- Task 3: Advanced Reactor Design
- Task 4: Refractory Materials for Multi-Fuel Gasification
- Task 5: Oxygen Integration for Net-Zero Carbon
- Task 7: Process Development to Mature Oxygen Sorbent-Based Technology
- Task 6: Microwave Reactions for Gasification
- Task 8: Gasification of Waste Plastic to Enable a Circular Economy
- Task 11: Production of H_2 from Biomass, Plastics, and MSW via Catalytic and Non-Catalytic Processes
- Task 13: Hydrogen Production from Gasification Assessment

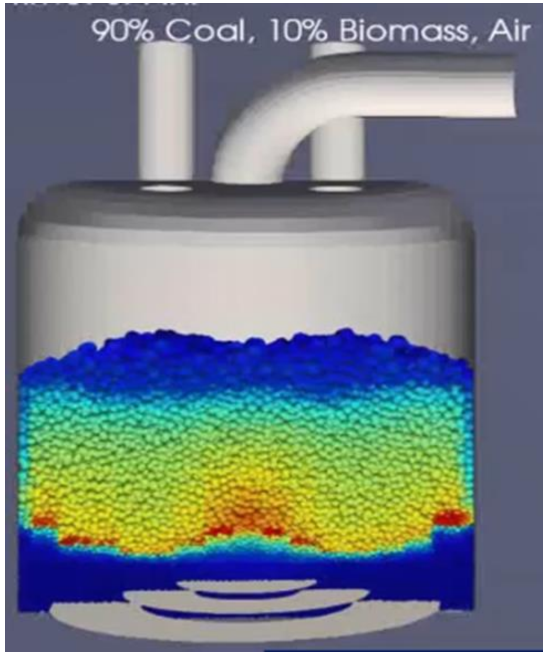
Task 3: Advanced Gasifier Design

Overview

- **Task Objective: Use Simulation-based Engineering Tools to decarbonize gasification-based processes for production of power, syngas, and hydrogen using mixed feedstocks including biomass, plastics, and MSW**

- **Project Activities:**

- Develop detailed kinetic models for pyrolysis and gasification of plastics and MSW in collaboration with Polytechnique University of Milan
- Validate the kinetic models with experimental data provided from Task 8 of ARS FWP
- Develop and validate a CFD model for pyrolysis and gasification of mixed feedstock of biomass and plastics in a pilot scale air blown fluidized bed reactor with thermal output of 400 kW in collaboration with Sotacarbo S.p.A.
- Simulate the operation of a pilot scale updraft moving bed gasifier operating on a mixed blend of coal, biomass, and waste plastic in collaboration with Hamilton-Maurer International, EPRI, and Sotacarbo S.p.A.
- Characterize the mixing and fluidization behavior of biomass, plastics and MSW in a fluidized bed experimentally and use the data to improve the fluidization behavior of mixed feedstocks in gasifiers.

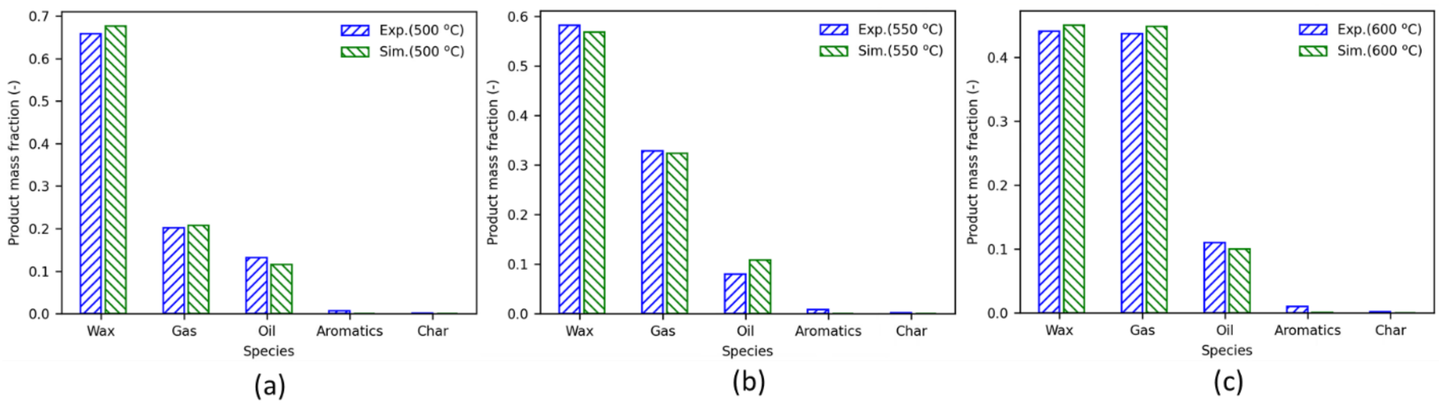


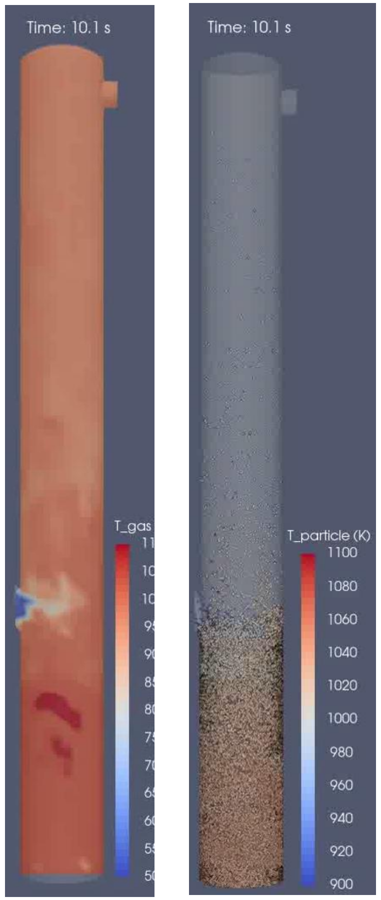
Hamilton-Maurer International

Task 3: Advanced Gasifier Design

Accomplishments

- CFD model for pyrolysis and gasification of Eucalyptus biomass and plastic feedstock is validated against data from 400 kW fluidized bed gasifier at Sotacarbo.
- Kinetic models for pyrolysis of HDPE has been developed and validated against drop tube data from Task 8 of ARS FWP and data for a laboratory- and pilot-scale gasifier from literature.



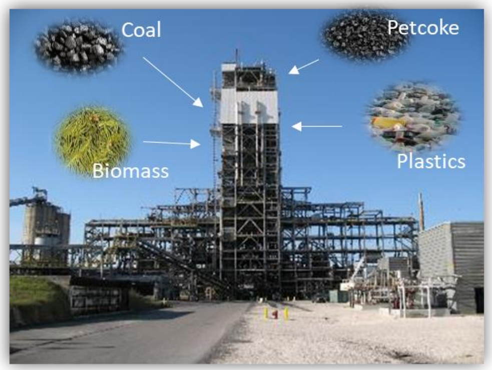


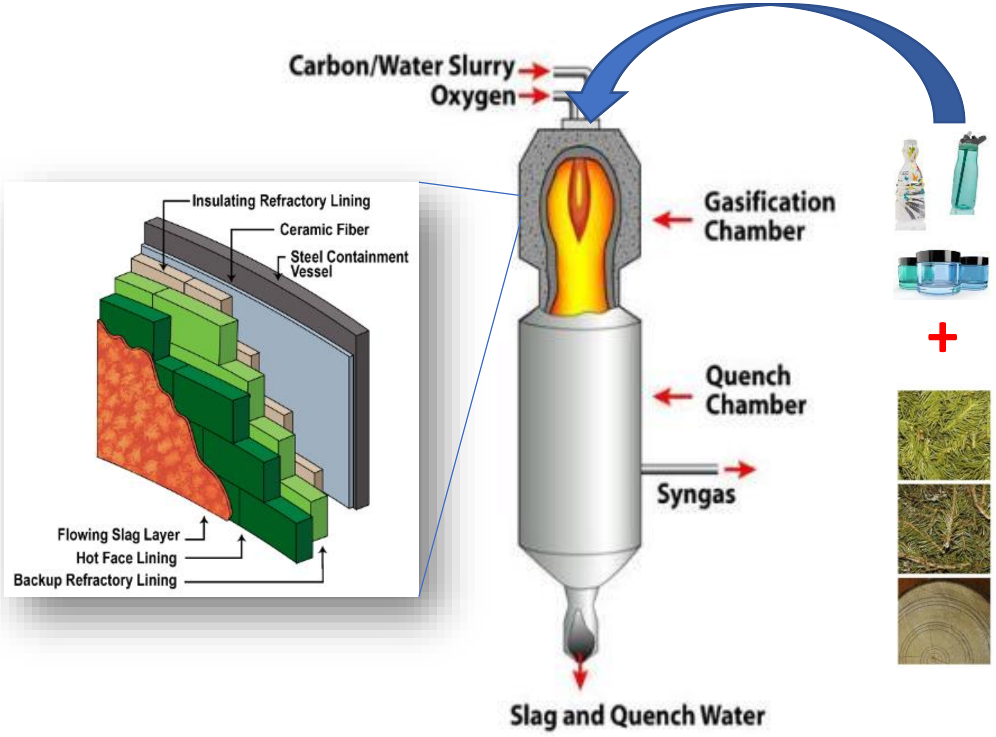
Particle and bed temperature (K) in the 400 kW fluidized bed gasifier

Task 4: Refractory Materials for Multi-Fuel Gasification

Overview

- **Objective: Develop novel refractory materials that enables multi-fuel gasification**
- **Project Goals:**
  - Develop refractories that can withstand gasifier conditions with waste **plastics** feedstock options
  - Facilitate the use of a carbon-diverse fuel in gasification for production of chemicals, power, and $\mathbf{H_2}$
  - Contribute to **a circular economy** and **net-zero carbon** goal by enabling plastic recycling





NATIONAL ENERGY TECHNOLOGY LABORATORY

Accomplishments

Current Accomplishments (EY22)

- Working with HarbisonWalker International, six refractory materials encompassing high to low chrome, alumina, and magnesia were manufactured and machined into testing coupons. These coupons were fired along with synthetic plastic slag under simulated gasifier conditions for 50 hours.
- A wide selection of waste plastics, from household sources and additive manufacturing, and waste materials from a retired computer were fired in air at temperatures of 800-1000 °C per ASTM. Ti, Al, Si, Ca, and Mg were primarily found in most ashed plastics while polypropyrene (PP) exhibited Ti content as high as 93 wt%Alumina- and mullite-based refractories were fired against 20% plastic slag; the former tended to degrade while the latter exhibited some resistance.
- Slag viscosity of the different plastic ashes was estimated and compared to that of coal- and biomass-based slags. LDPE and PP slags indicated higher viscosity than coal slag. Most plastic slags exhibited higher fluidity than coal, but spruce slag showed the lowest viscosity among the compositions examined.

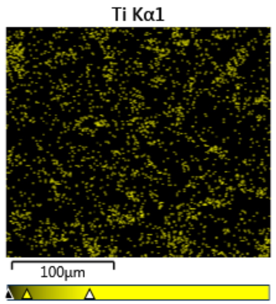
Future Accomplishments (EY23 – future)

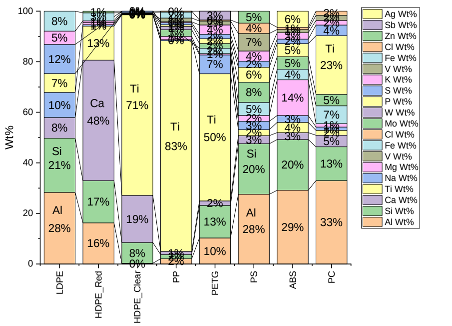
- Establish novel refractory composition that enables sustainable plastics gasification

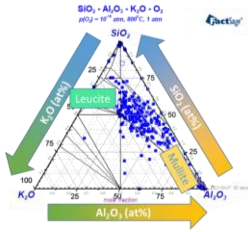
ALLIED MINERAL PRODUCTS

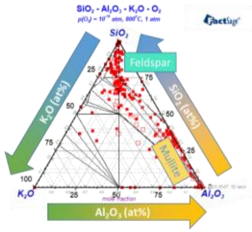
EASTMAN

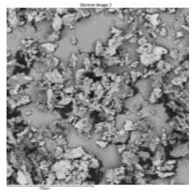
HWI HarbisonWalker International

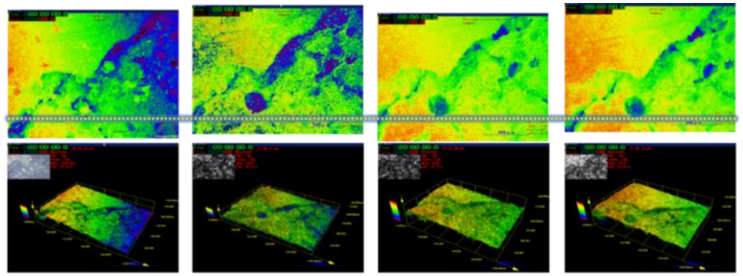










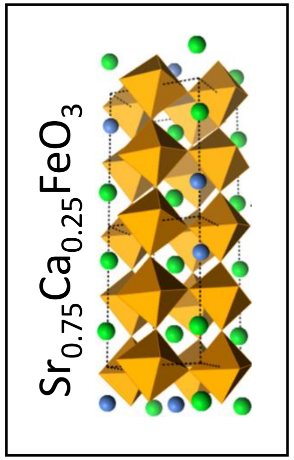


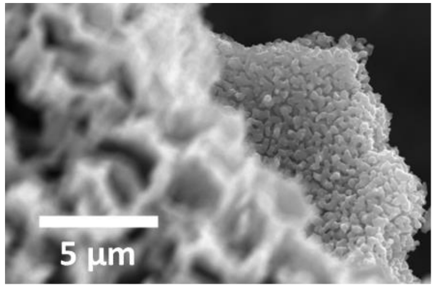
Before After Ramp Up After 1 Hour After Cool Down

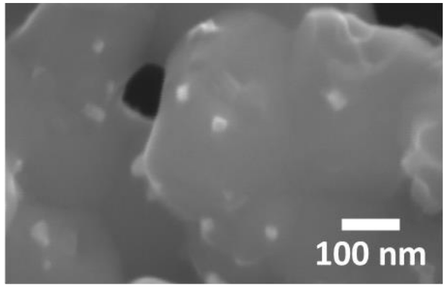
Task 5: Oxygen Integration for Net-Zero Carbon

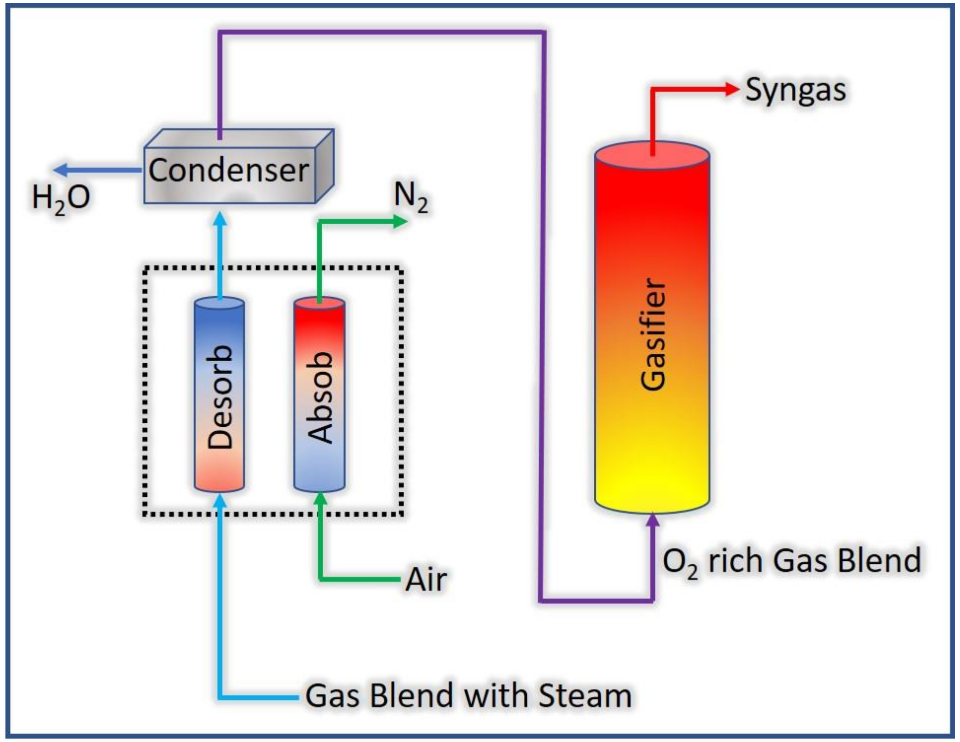
Overview

- **Objective: Design a metal oxide carrier material capable of separating oxygen from air and develop a reactor based on NETL developed carrier materials**
- **Project Goals:**
  - Develop a carrier material that can rapidly and reversibly store and release oxygen
  - Create a knowledge base and machine learning modelling tool for the optimization of carrier materials
  - Contribute to scaling efforts of an oxygen production reactor based on NETL carrier materials









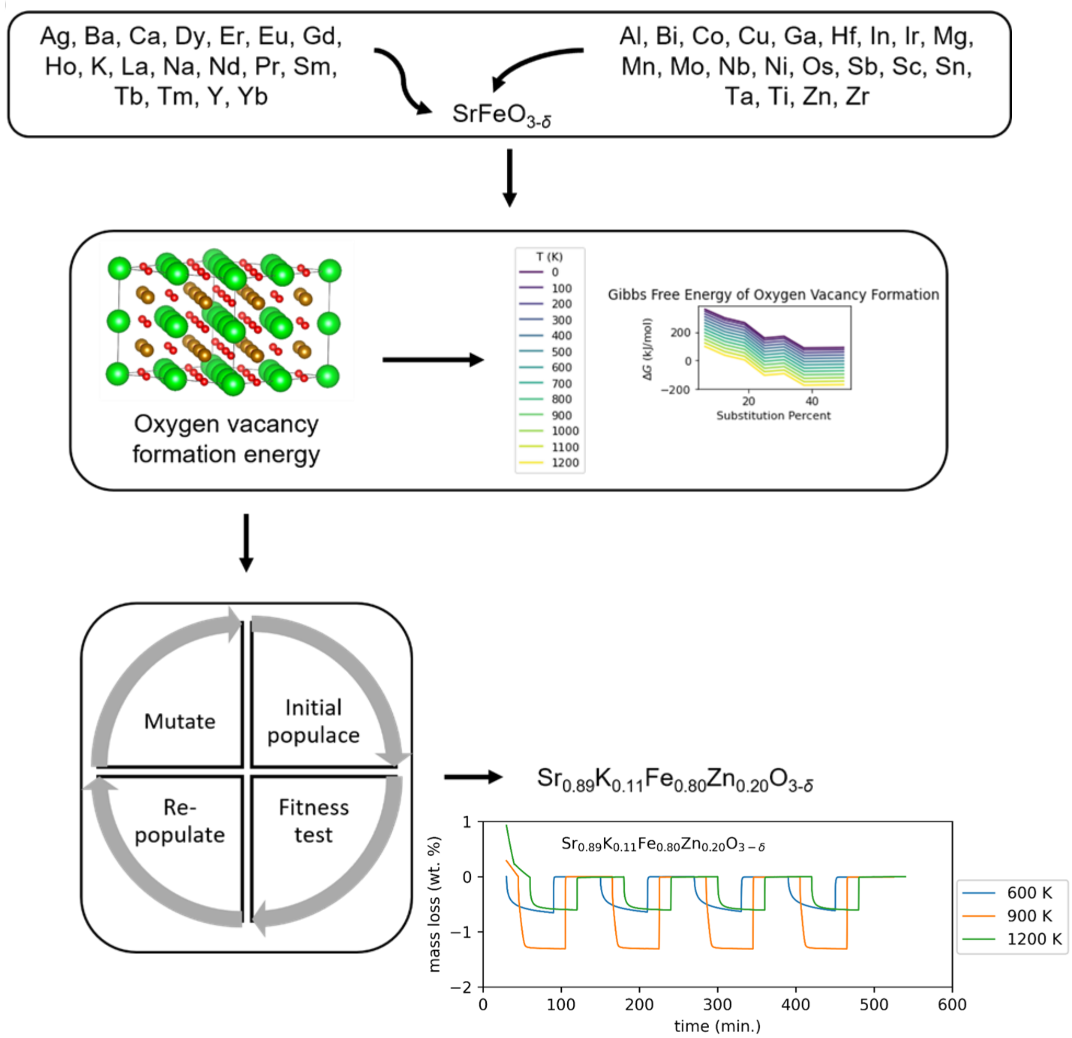
$$Sr_{0.75}Ca_{0.25}FeO_3 \xleftrightarrow{\delta(T,P_{O_2})} Sr_{0.75}Ca_{0.25}FeO_{3-\delta} + \frac{\delta}{2}O_2$$

Task 5: Oxygen Integration for Net-Zero Carbon

Accomplishments

Current Accomplishments

- Demonstrated ability to control capacity, desorption temperature, and rate through compositional changes
- Designed and tested a carrier with greater than 2 wt% oxygen capacity with rates in excess of 2.0 wt%/min and demonstrated stability over more than 10,000 cycles
- Identified a candidate material for scale-up testing
- Ellingham diagrams for perovskite carriers have been calculated and experimentally validated
- Two machine learning models have been generated using DFT calculated Ellingham diagrams
- Used ML models to predict, test, and validate an improved carrier composition



Task 7: Process Development to Mature Oxygen Sorbent Technology

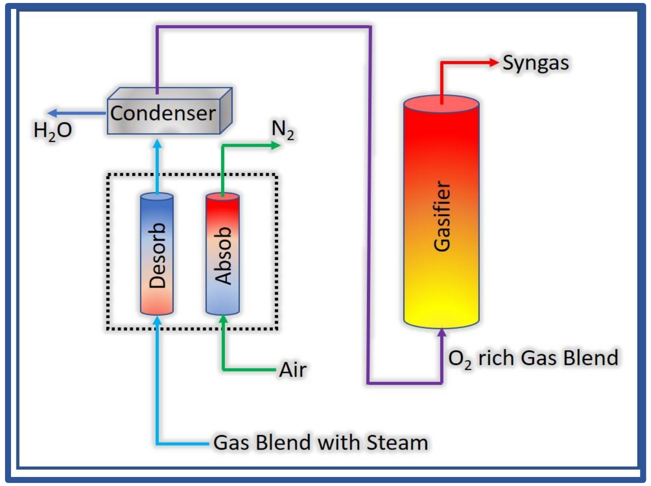
Overview

- **Objective: To develop a computational model that captures the oxygen storage/release potential of NETL designed materials and to leverage simulation to design a pilot-scale fixed bed, perovskite sorbent oxygen separation reactor.**

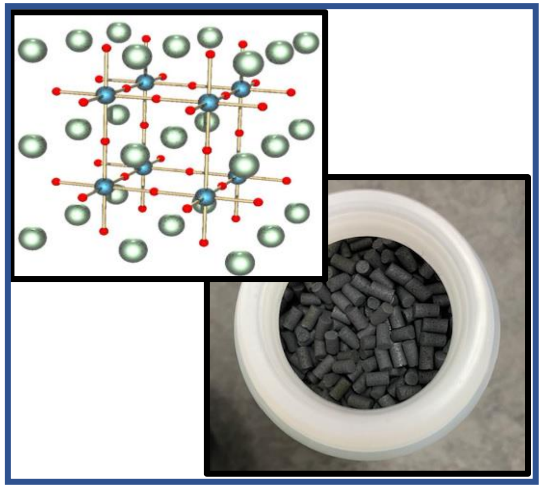
- **Project Goals:**

- Create kinetic rates for O_2 adsorption from physical TGA and bench-scale experiments.
- Validate rates through computational comparison to experiments.
- Computationally bridge scale from 3g -> 100g -> 100kg reactor models.
- Optimize O_2 production rates at pilot scale through investigation of adsorption swing time and geometric reconfiguration to reduce pressure drop.

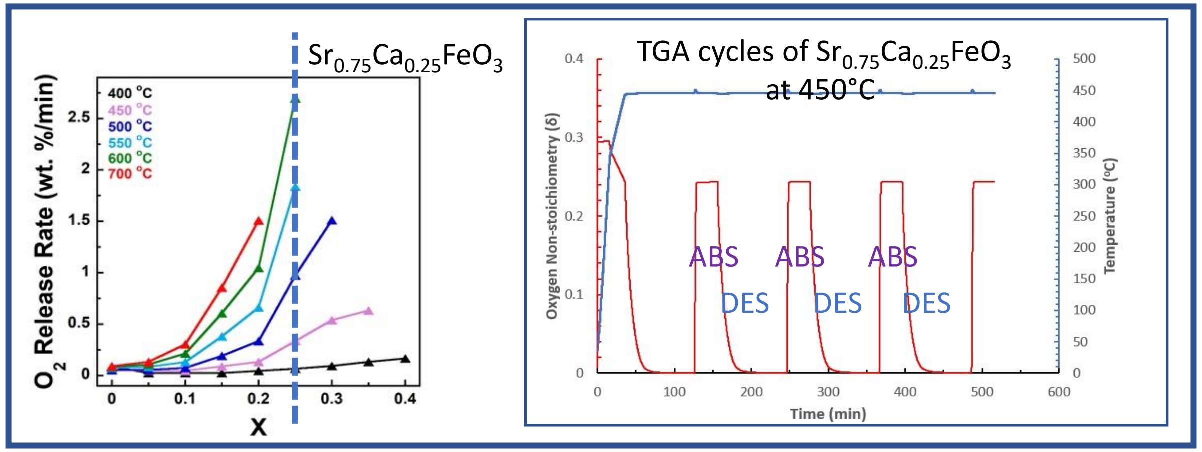
Process Concept



Material Structure



Chemistry Foundation



Task 7: Process Development to Mature Oxygen Sorbent Technology

Accomplishments

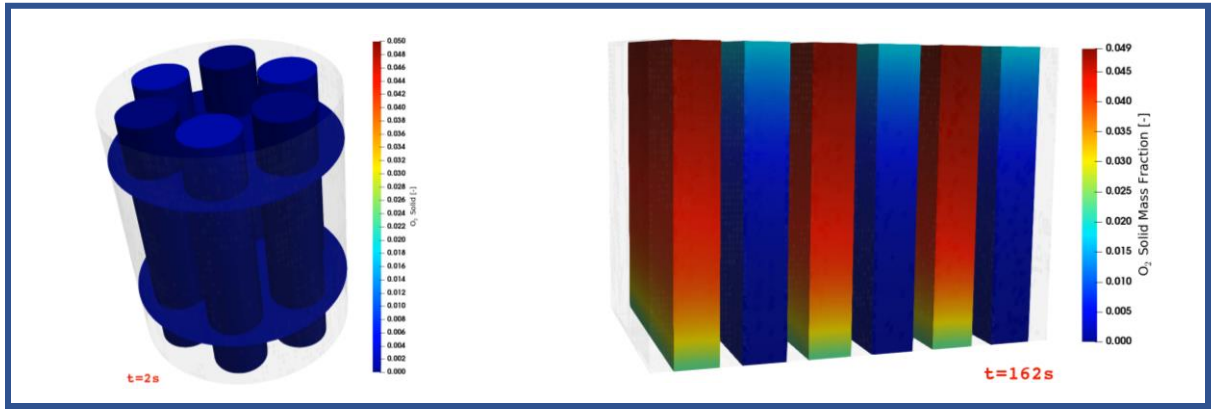
Accomplishments:

- Kinetic rates to describe O_2 adsorption/desorption for $Sr_{0.75}Ca_{0.25}FeO_{3-\delta}$ were derived and applied at 50g and 50kg simulation scales.
- Physical experiments verified that desorption driven by N_2 match kinetic rates.
- Multiple modular geometries with 50kg $Sr_{0.75}Ca_{0.25}FeO_{3-\delta}$ investigated and compared for performance measures.
- CFD Simulations of fixed bed configurations of $Sr_{0.75}Ca_{0.25}FeO_{3-\delta}$ demonstrate comparable O_2 production rates with similar fill weights; slight variation based on thermal management and pressure drop.

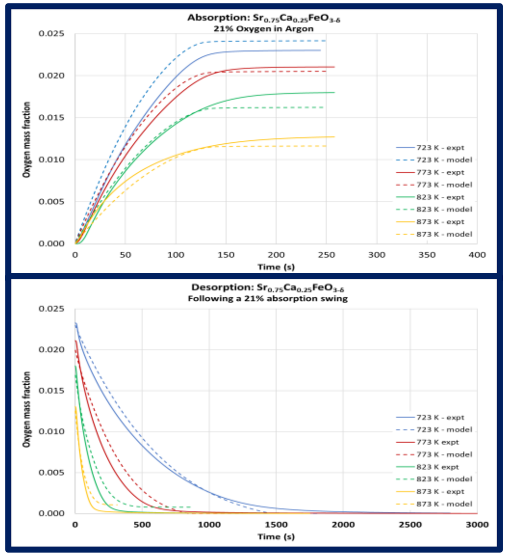
Impact:

- Simulations demonstrate O_2 production from perovskite materials may effectively supplant cryogenic process.
- Risk-averse processing scenarios are examined through simulation.

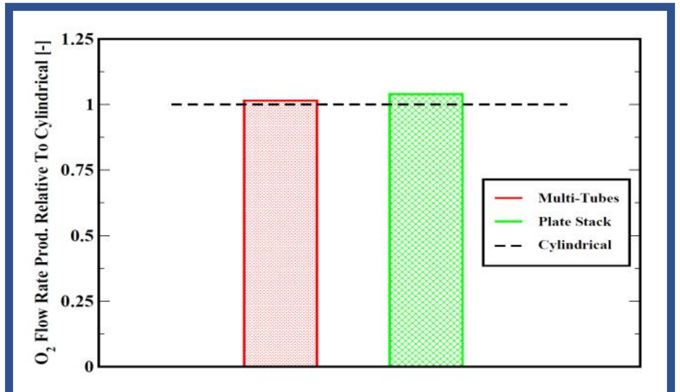
Modular Reactor Computational Fluid Dynamics Simulations



Derived Rates



Data Analysis



Average O_2 production with "Cylindrical" design is 0.201 $g_{O_2}/h/g_{perov}$

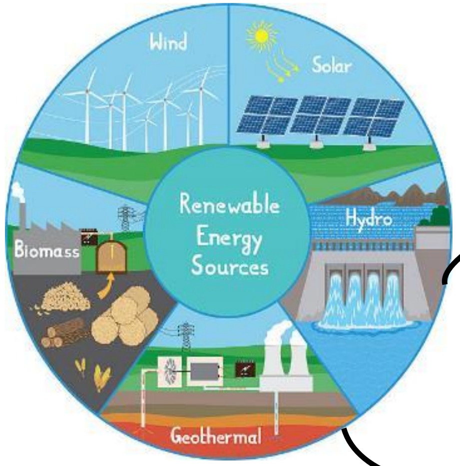
Task 6: Microwave Reactions for Co-Gasification of Plastic and Biomass

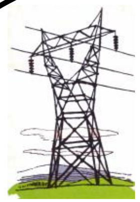
NATIONAL ENERGY TECHNOLOGY LABORATORY

Overview

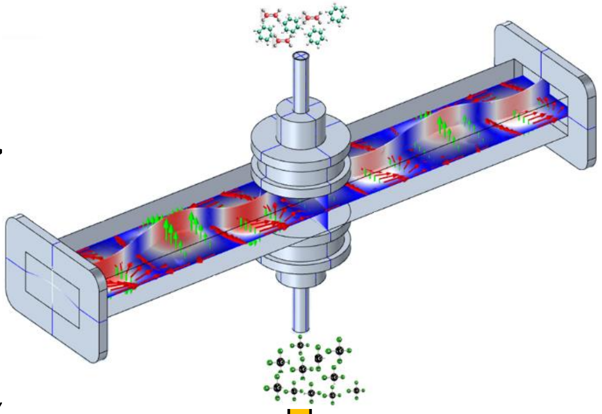
Feedstocks: biomass, plastics, MSW, Coal

Coupling with intermittent energy resources





Microwave Reactor



Process Intensification

- Modularity
- Reduction in capex (mild reaction conditions)
- Efficient rapid heating and promote favorable reaction
- Reduced CO_2 emissions – cleaner H_2

H_2, Syngas

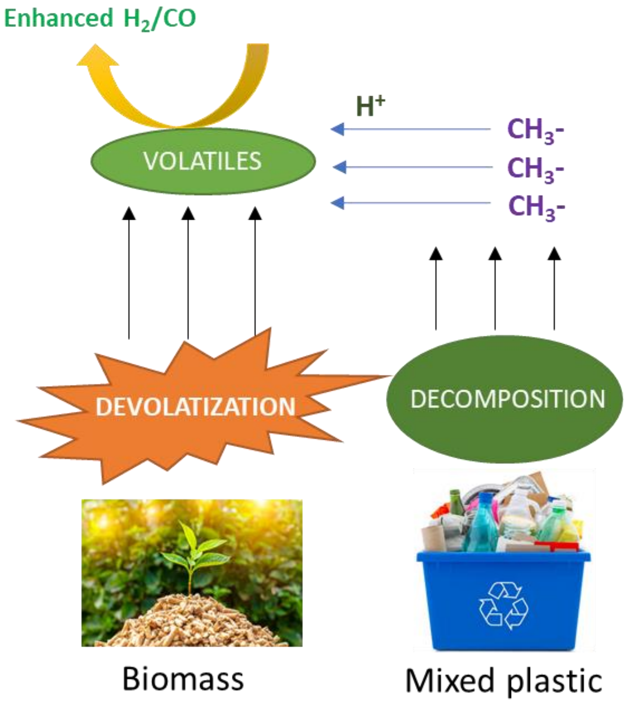
Fuels & Chemicals

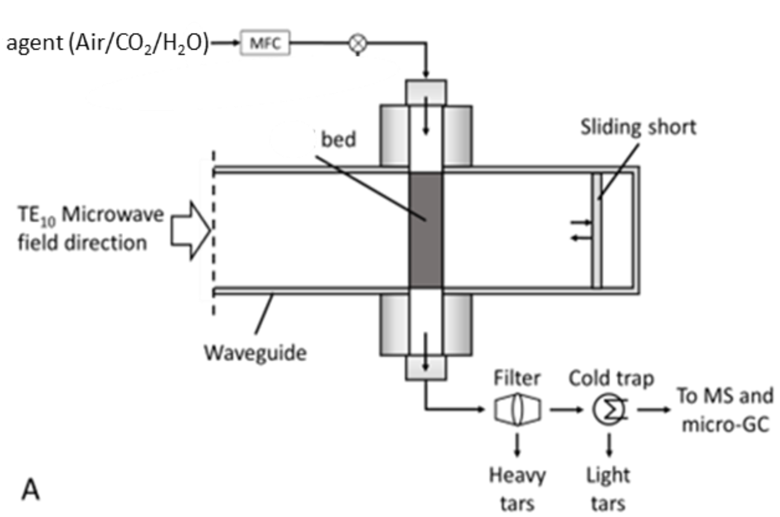
Task 6: Microwave Reactions for Co-Gasification of Plastic and Biomass

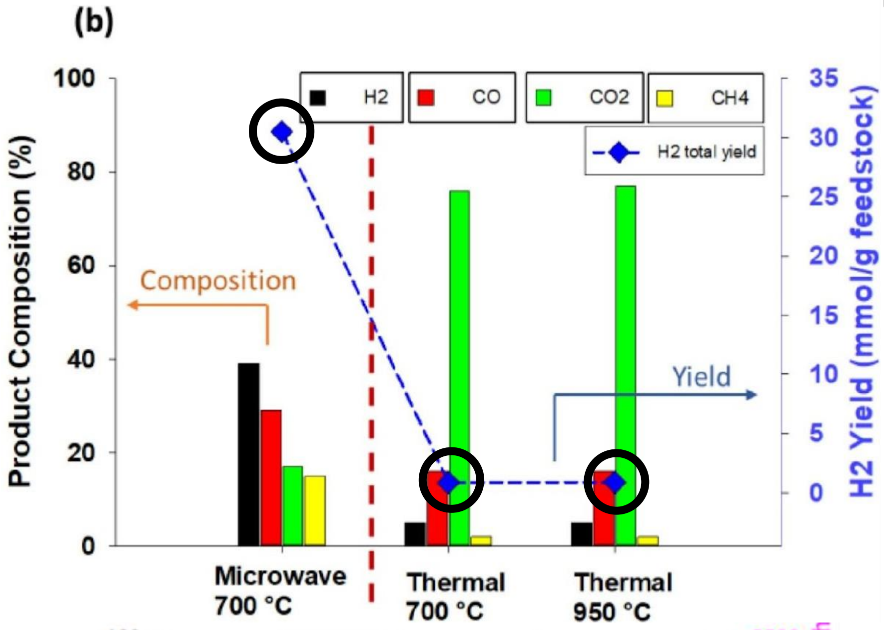
NATIONAL ENERGY TECHNOLOGY LABORATORY

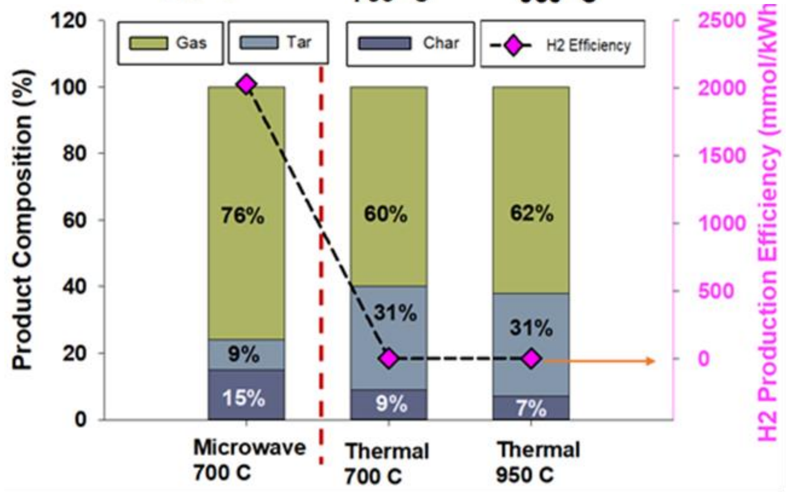
Accomplishments

- **4 times higher hydrogen yields** and **~20% higher syngas yields** with microwave heating
- Findings published in high impact journal article
- Demonstrated moving bed microwave gasifier at lab-scale









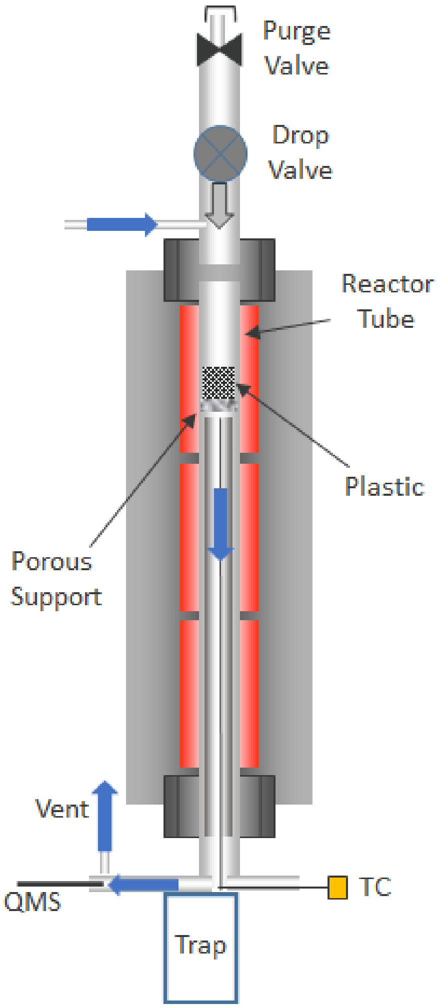
Ashraf Abedin, Xinwei Bai, Mark Smith, Pranjali Muley, Microwave-assisted co-gasification of mixed plastics and corn stover: A synergistic approach to produce clean hydrogen, Energy Conversion and Management, Volume 280, 2023, 116774, ISSN 0196-8904

Task 8: Gasification of Waste Plastic to Enable a Circular Economy

Overview

- **Objective: To explore the gasification of alternative feedstocks, such as waste plastics, waste coals, and biomass, to generate H_2/syngas with minimal CO_2 emissions.**

- **Project Goals:**
  - **Co-gasification of waste plastic and waste coal/biomass in steam gas environment to generate H_2/syngas**
    - Study the feasibility of co-feeding of waste plastic and waste coal/biomass in DTR by pelletizing plastic and feedstocks
    - Evaluate process conditions such as catalyst, feed blend ratio, and temperature to further optimize syngas conversion
  - **Co-pyrolysis of waste plastic and/or biomass for model development and validation through collaboration with ARS Task 3 Team**
    - Investigate pyrolysis of waste plastic and/or biomass at different operation conditions (such as temperature and residence time)
    - Analyze condensable (tar) product composition (hydrocarbons up to C40) using gas chromatography-mass spectrometry (GC-MS) to understand mechanism of pyrolysis and tar cracking for generating more syngas from gasification
    - Conduct kinetics of plastic pyrolysis in a simultaneous thermal analyzer (thermogravimetric analyzer-differential scanning calorimeter, TGA-DSC) to determine kinetic parameters (such as heat of fusion/pyrolysis, and activation energy)



Accomplishments

- **Investigated steam co-gasification studies with pellets containing low-density polyethylene (LDPE) and coal refuse (CR) in a DTR-MS**
  - Pelletized feed blend LDPE/CR ratios by weight covered a wide range: 0/100, 10/90, 20/80, 40/60, 60/40, 80/20, and 100/0, to overcome issues associated with feeding and handling plastics with a low melting temperature
  - Evaluated operating conditions, such as feed blend ratios, pellet characteristics, and reaction temperature (800, 900, and 1000 °C), on the gasification performance such as carbon conversion, product yield/selectivity, and syngas quality (H_2/CO molar ratio)
  - Performed co-gasification of LDPE and CR with an iron oxide (Fe_2O_3) catalyst to mitigate tar formation and to further develop the low cost catalyst for improving H_2/syngas production while minimizing tar formation
- **Studied pyrolysis of high-density polyethylene (HDPE) plastic pellets in a DTR-MS**
  - Conducted various operating conditions, such as long residence time (LRT) and reaction temperatures (400, 500, 600, 700, 800, and 900 °C) to understand their effects on the pyrolysis performance
  - Characterized tars using Fourier-transform infrared spectroscopy (FTIR) and GC-MS, and chars (scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)) formed at different pyrolysis temperatures
- **Developed a protocol for GC-MS analysis tar composition that allowed the identification and quantification of hydrocarbons up to C40 collected from a cold trap located at the exit of a DTR**

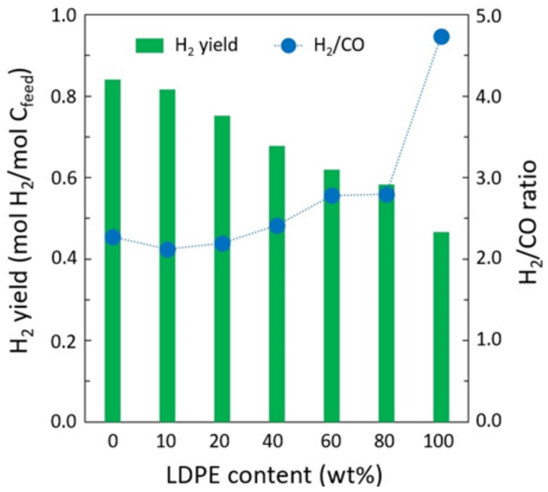


Figure 1: H_2 yields and H2/CO molar ratio obtained from H2O-gasification at 900 °C as a function of LDPE content in CR-PE pellets

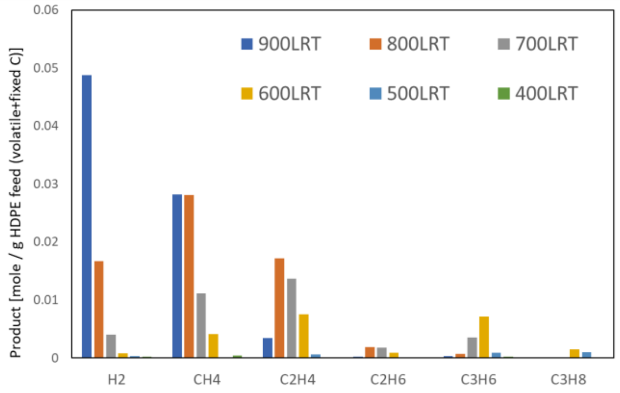


Figure 2. Product distribution at different pyrolysis temperatures under an LRT reactor configuration

Task 11: Production of H_2 from Biomass, Plastics, and MSW via Catalytic and Non-Catalytic Processes

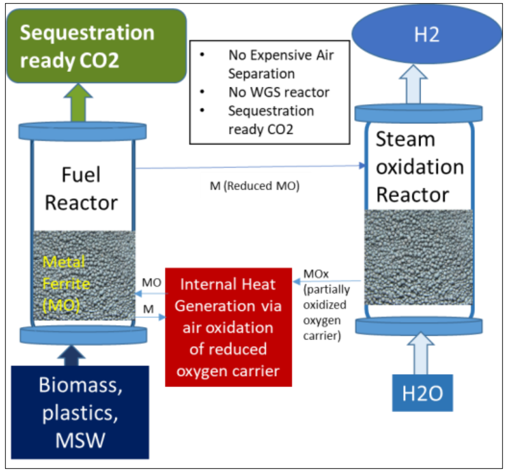
NATIONAL ENERGY TECHNOLOGY LABORATORY

Overview

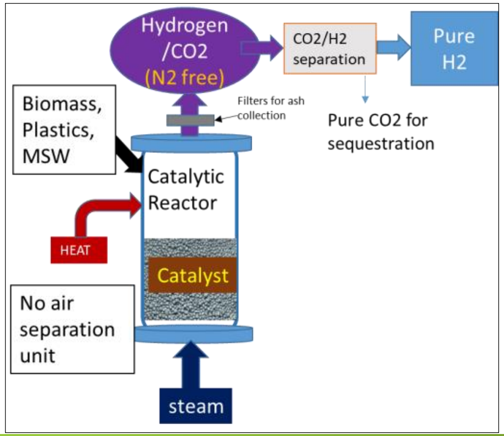
- **Objective: Develop optimized systems with inherent carbon capture that can be used in H2 production from solid fuels such as biomass, plastics, coal, and municipal solid waste (MSW) via two novel patented and patent pending processes.**

- **Project Goals:**
  - Produce parameters to develop integrated H_2 production systems
  - Scaled-up reactor design based on sub-pilot scale and pilot scale test data
  - Obtain parameters necessary for TEA and commercialization.

Non catalytic H2 production



Catalytic H2 production

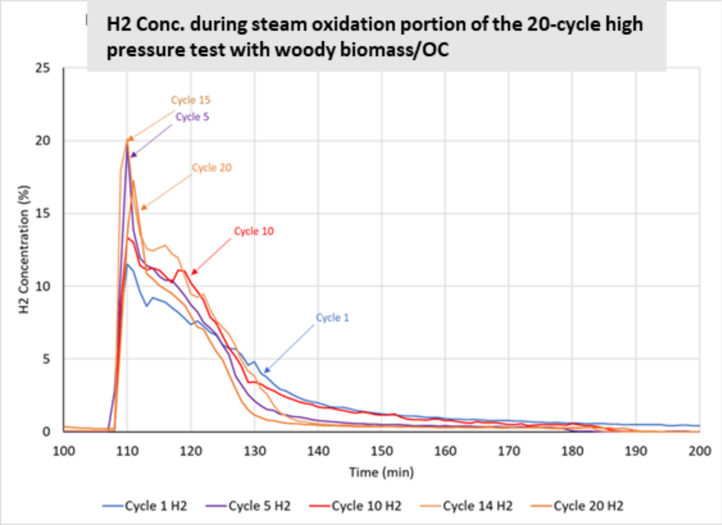


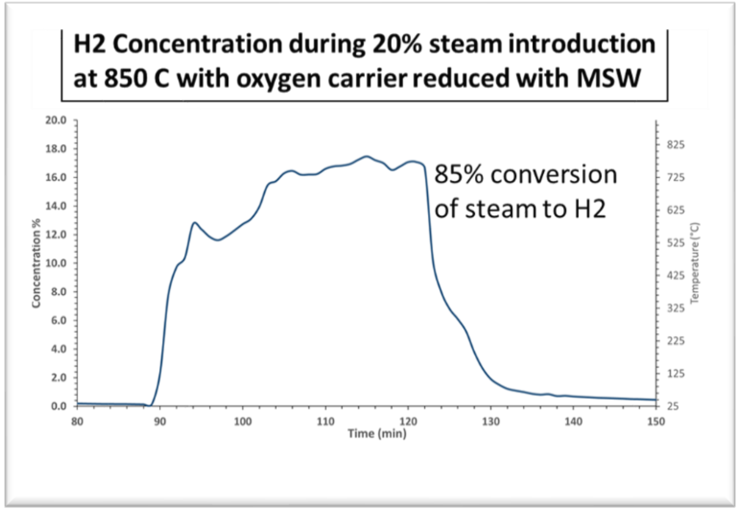
Task 11: Production of H_2 from Biomass, Plastics, and MSW via Catalytic and Non-Catalytic Processes

Accomplishments

Current Accomplishments

- Promising H_2 production tests with metal ferrite were demonstrated using plastics (PE/PP mixture), MSW (municipal solid waste) and biomass
  - Steam to H_2 conversion rate of about 75-85%.
- Stable high pressure H_2 production using biomass demonstrated during a 20 cycle test with metal ferrite
  - Production of H_2 at high pressure will lower the compression costs of H_2 for transportation.
- Metal ferrites and catalysts are capable of tar decomposition that would eliminate the tar processing units required with fuels in regular gasification.
- Preliminary systems studies with both non catalytic and catalytic processes indicated many advantages over the H_2 production with base line steam gasification systems.
- Two non-provisional patent applications based on the work was submitted to the U.S. patent office:
- An industrial partner signed an NDA and submitted documents to NETL tech transfer team for a funds-in-CRADA to advance the H_2 production technology for commercialization.

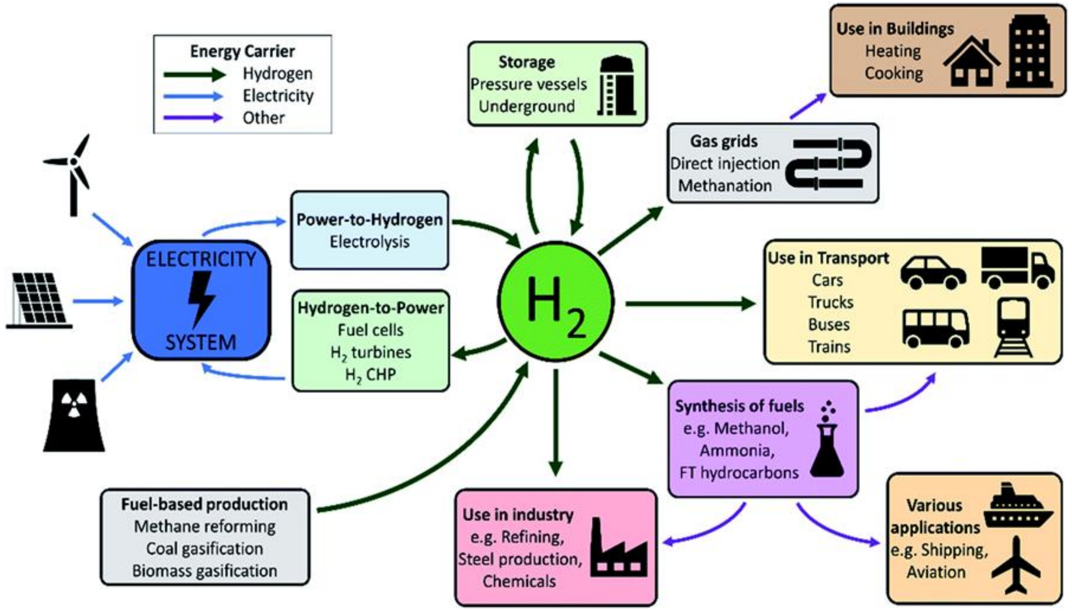




Task 13: Hydrogen Production from Gasification Assessment

Overview

- **Objective: Support the Gasification Program by developing a reference study for commercial, gasification-based hydrogen production technologies analyzing market conditions of carbonaceous feedstocks, and formulating strategies to reduce the levelized cost of hydrogen**
- **Project Goals:**
  - Develop reference study for commercial, gasification-based H_2 production technologies
    - Using alternative feedstocks
    - Estimate levelized cost of hydrogen
  - Identify key R&D areas to improve performance and cost of H_2 production technologies
  - Support ongoing and future research by furthering current understanding of the cost and performance of gasification-based H_2 production plants



C.J. Quarton, et. al. Sustainable Energy & Fuels DOI: 10.1039/C9SE00833K

NATIONAL ENERGY TECHNOLOGY LABORATORY

Accomplishments

- CONFERENCE PRESENTATIONS
  - Presentation at the Gasification Technology Status and Pathways for Net-Zero Carbon Economy Workshop - "Techno-economic and Lifecycle Greenhouse Gas Assessments of H2 Production from Coal, Coal/Biomass, and Biomass," November 30, 2022
- INTERNAL PRESENTATIONS
  - "Market Investigation of MSW and Plastics for Hydrogen Production – Final Presentation"
- INTERNAL REPORTS
  - "Market Investigation of MSW and Plastics for Hydrogen Production"

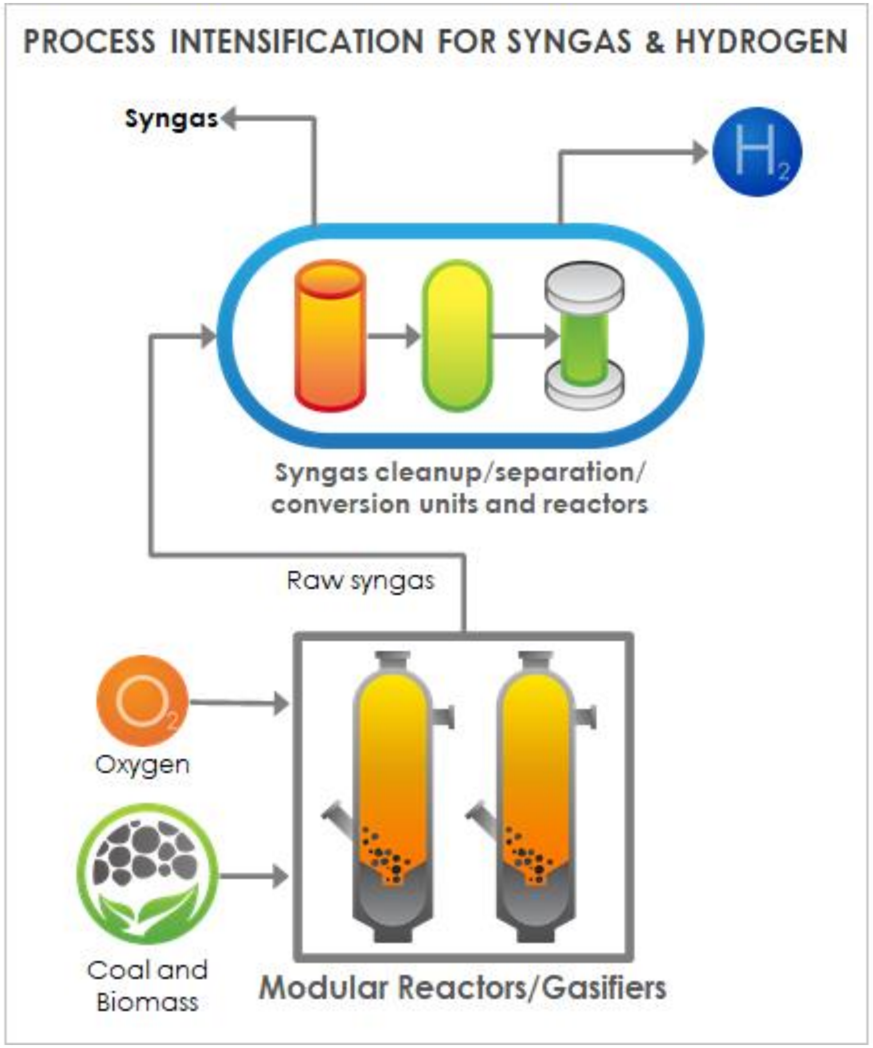
Acknowledgments

NATIONAL ENERGY TECHNOLOGY LABORATORY

- Acknowledgment
  - This material is based upon work supported by the Department of Energy research under the Gasification Research Program. The research was executed through the NETL Research and Innovation Center's Advanced Reaction Systems field work proposal. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.

Conclusion

The Advanced Reaction Systems portfolio supports the Gasification Program by designing and developing technologies and tools to enable modular gasification systems that can convert waste materials into valuable products with net-zero carbon emissions



?Questions?