Advanced Reaction Systems

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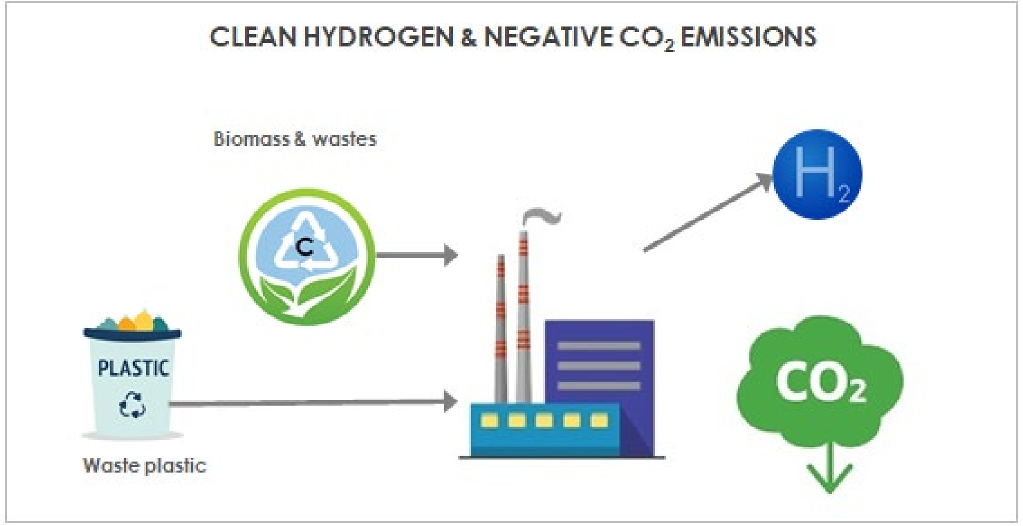
U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

Research Objective

Portfolio Objective

Value Proposition: Gasification technologies offer promising opportunities to generate value from biomass and 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 of diverse feedstocks to produce hydrogen and other value-added products with net-zero greenhouse gas emissions

Current Research

Overview

- Task 3: Advanced Gasifier Design
- Task 4: Refractory Materials for Multi-Fuel Gasification
- Task 5: Oxygen Integration for Net-Zero Carbon
- Task 6: Microwave Reactions for Gasification
- Task 7: Process Development to Mature Oxygen Sorbent-Based Technology
- Task 8: Gasification of Waste Plastic to Enable a Circular Economy
- Task 11: Maturing Oxygen Carrier and Catalyst Technologies for Hydrogen Production
- Task 13: Pathways to Minimize Clean Hydrogen Cost
- Task 14: Feedstock Control for Gasification

Task 3: Advanced Gasifier Design

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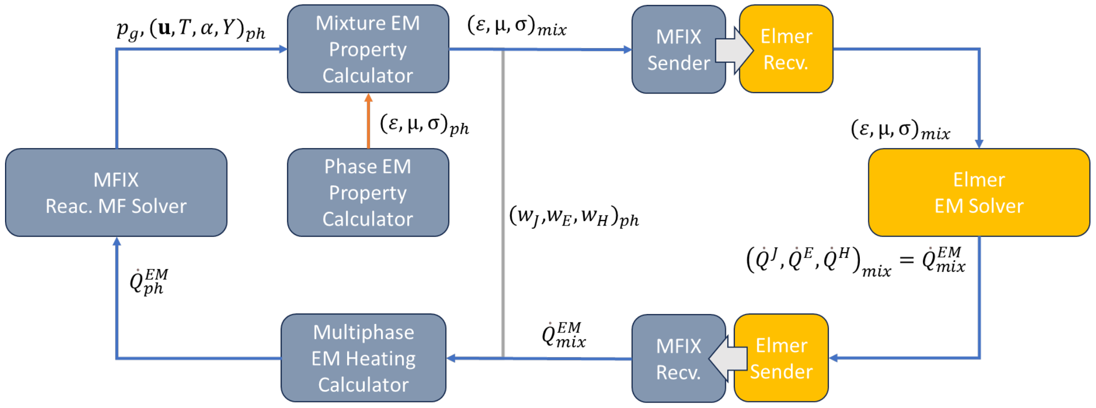
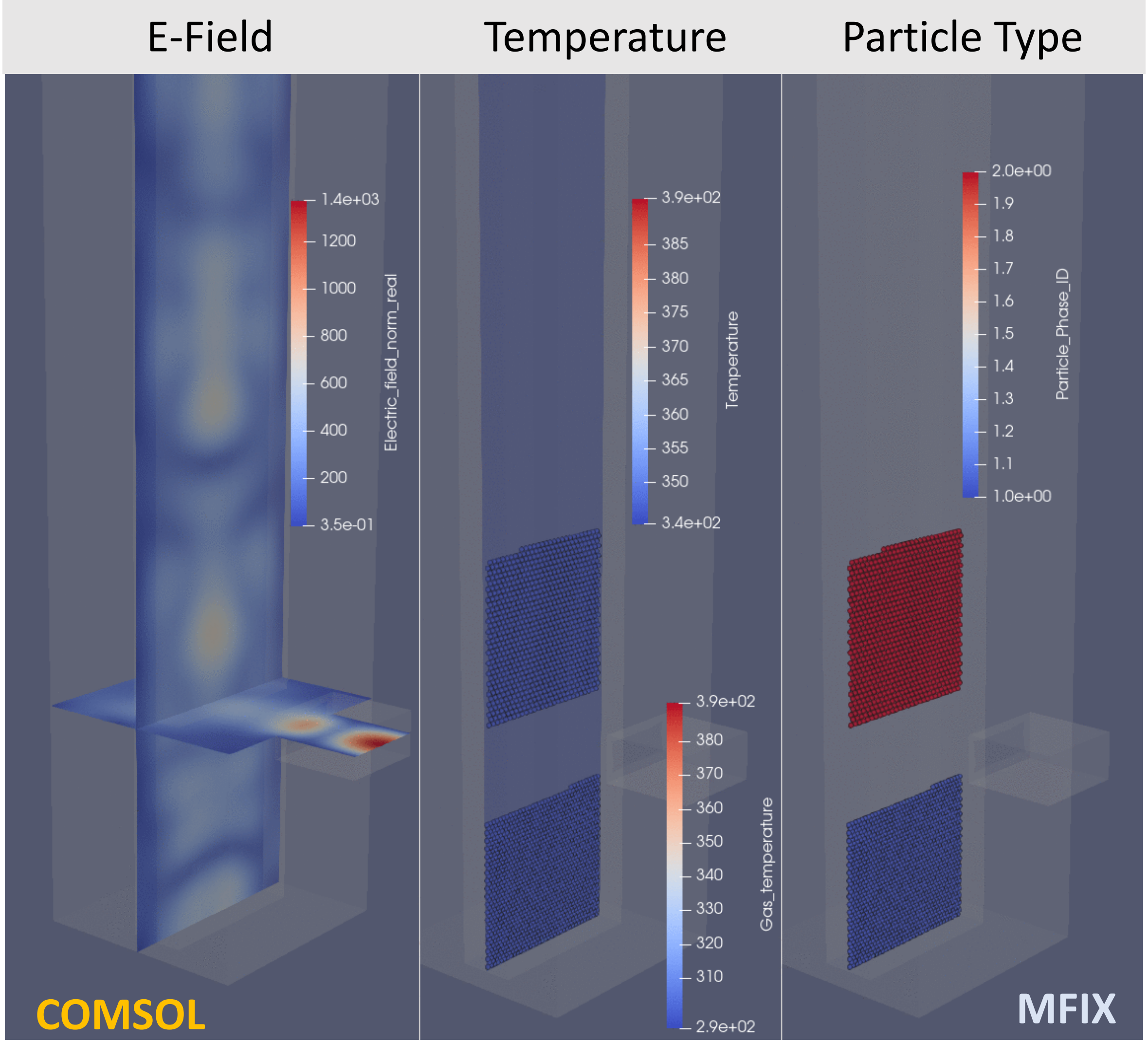
Microwave Heating for Fluidized Bed Reactors

- Combined computational electromagnetics (CEM) and computational fluid dynamics (MFIX/CFD) to predict the performance of MW interactions in fluidized be reactors.
- (Right) – Loosely coupled spouted fluidized bed simulation using MFIX and COMSOL
  - Note temperature difference between the MW absorber (Blue) and MW transparent (Red) particles.
- (Below) - A fully coupled approach using MFIX and Elmer is in progress.





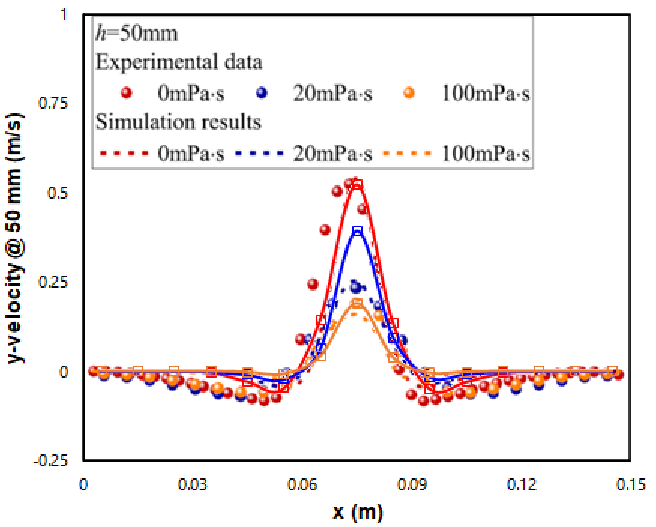
Task 3: Advanced Gasifier Design

Development of Liquid Bridge Model for Agglomeration of Melted Plastic

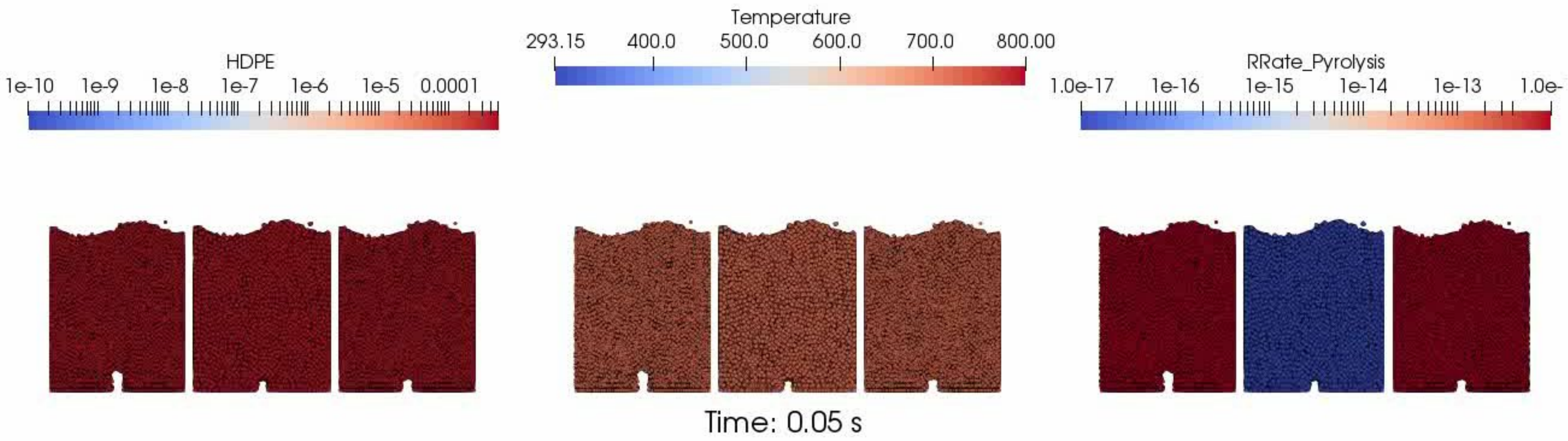
- Several studies have reported issues associated with agglomeration of the bed material when coated with fused (melted) plastic during pyrolysis of plastic or municipal solid waste and consequent defluidization of the fluidized bed
- The liquid bridge model implementation was validated for cold flow against Tang et al. (2019) for different viscosities

Defluidization increases with increasing liquid viscosity

Left animation: pyrolysis model is on, and agglomeration model is off
Center animation: pyrolysis model is off, and agglomeration model is on
Right animation: both pyrolysis and agglomeration models are on



Cold flow validation



Mass fraction of plastic Temperature Reaction rates pyrolysis

Task 4: Refractory Materials for Multi-Fuel Gasification

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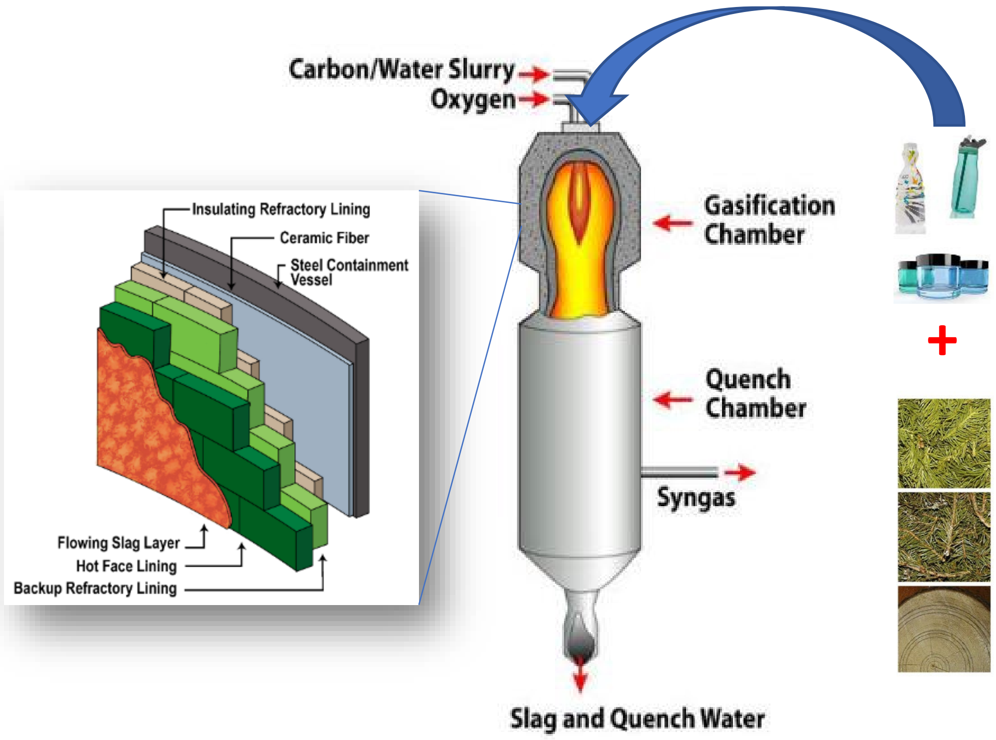
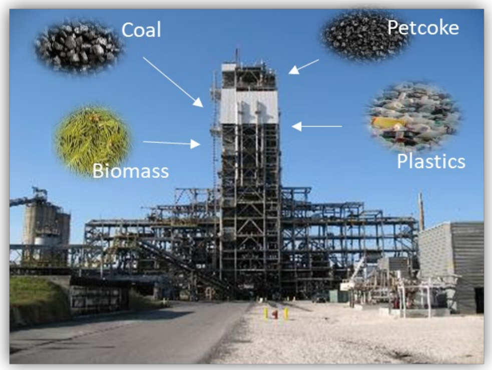
Overview

- **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





Task 4: Refractory Materials for Multi-Fuel Gasification

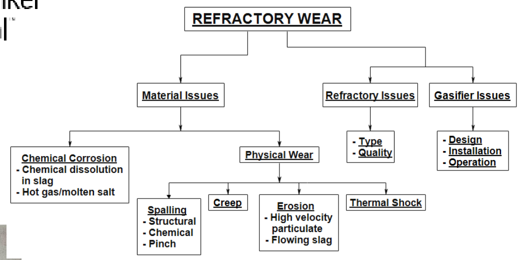
Accomplishments

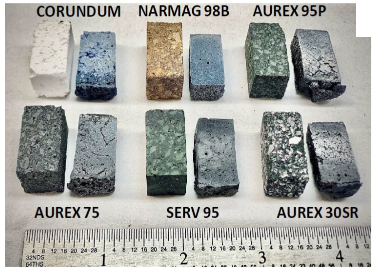
Current Accomplishments (EY23)

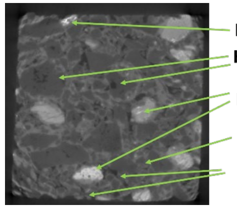
- Continued working with HarbisonWalker International to evaluate six ceramic bonded refractories for use as gasifier liner materials when HDPE plastic is a carbon feedstock. These refractories include low - high chromia, alumina, and magnesia sintered materials. Test coupons were exposed to molten synthetic plastic ash at 1500°C under simulated gasifier conditions for 50 hours. Samples were studied using the SEM, EDX, and XRD. Initial results indicate chromia and alumina provide no significant advantages over other materials, probably due to the lack of Fe and V found in coal and petcoke feedstocks.
- The use of computed tomography (CT) is being evaluated as a means of determining how slag penetrates into refractory liner material. Plastics may require different, possible new, liner materials for gasifiers if used in high concentrations as a carbon feedstock.
- Arrangements have been made to use transmission electron microscopy (TEM) at Oregon State University to study molten plastic ash/refractory interactions beyond what can be learned using a SEM.

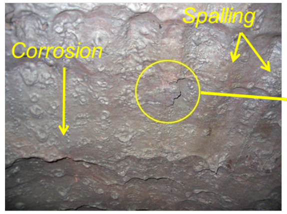
Future Research Plans (EY24 - - -➝)

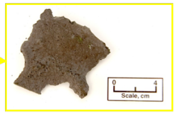
- Finish laboratory studies evaluating potential refractory liner materials for plastic ash (HDPE) gasification. Laboratory studies will include limited TEM, CT, viscosity and additive research.
- Write a final report summarizing conclusions of studies evaluating HDPE molten plastic ash/refractory interactions related to potential liner materials in plastic gasification.
- Begin identification of potential refractory liner materials for use in the ASURE gasifier and design a research approach to study those materials.



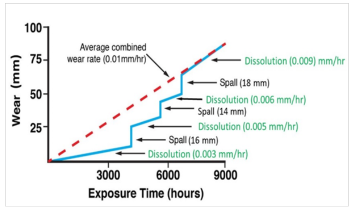






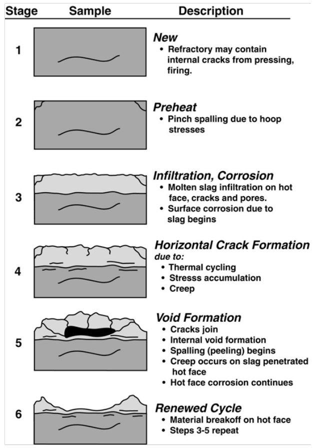


Spalled Material



Spalling Process

W.T. Bakker, "Refractories for Present and Future Electric Power Plants," Key Engineering Materials, Trans Tech Publications, (1993), Vol. 88, pp. 41-70.

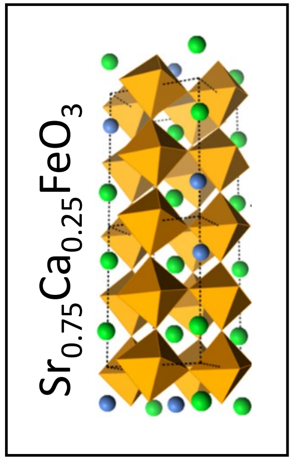


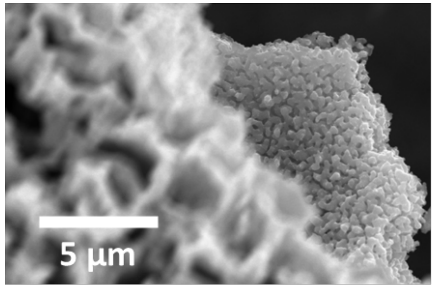
Repetitive Cycle of Spalling

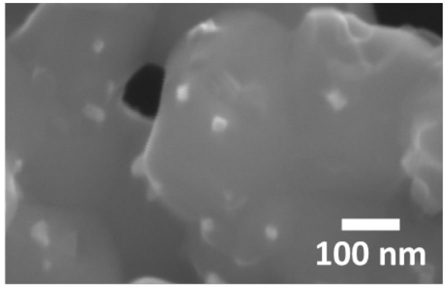
Task 5: Oxygen Integration for Net-Zero Carbon

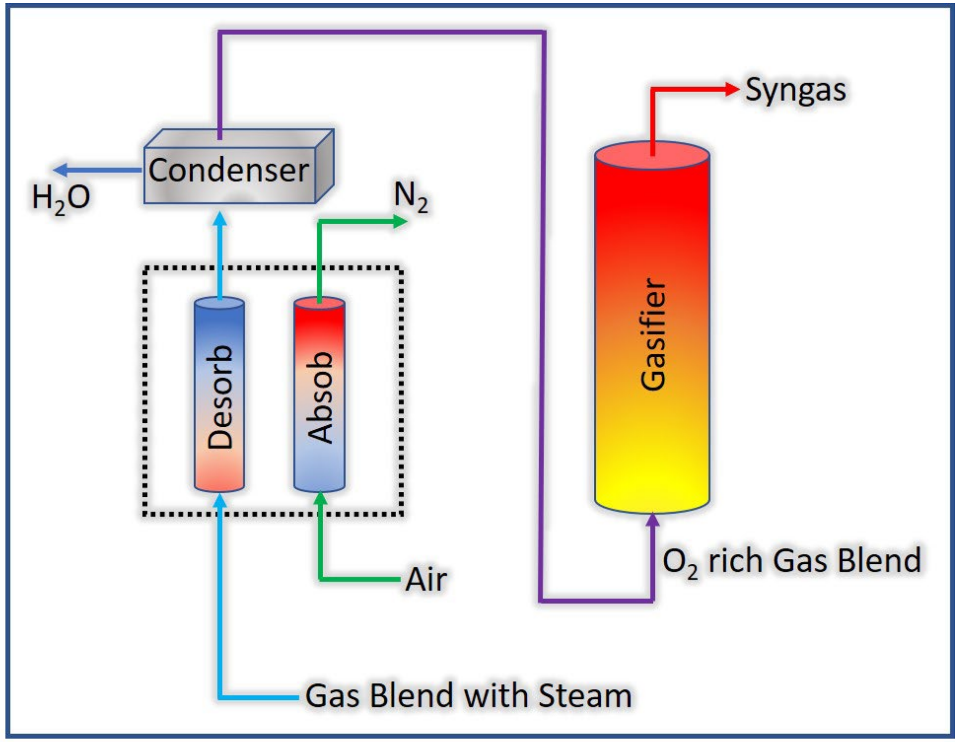
Overview

- **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









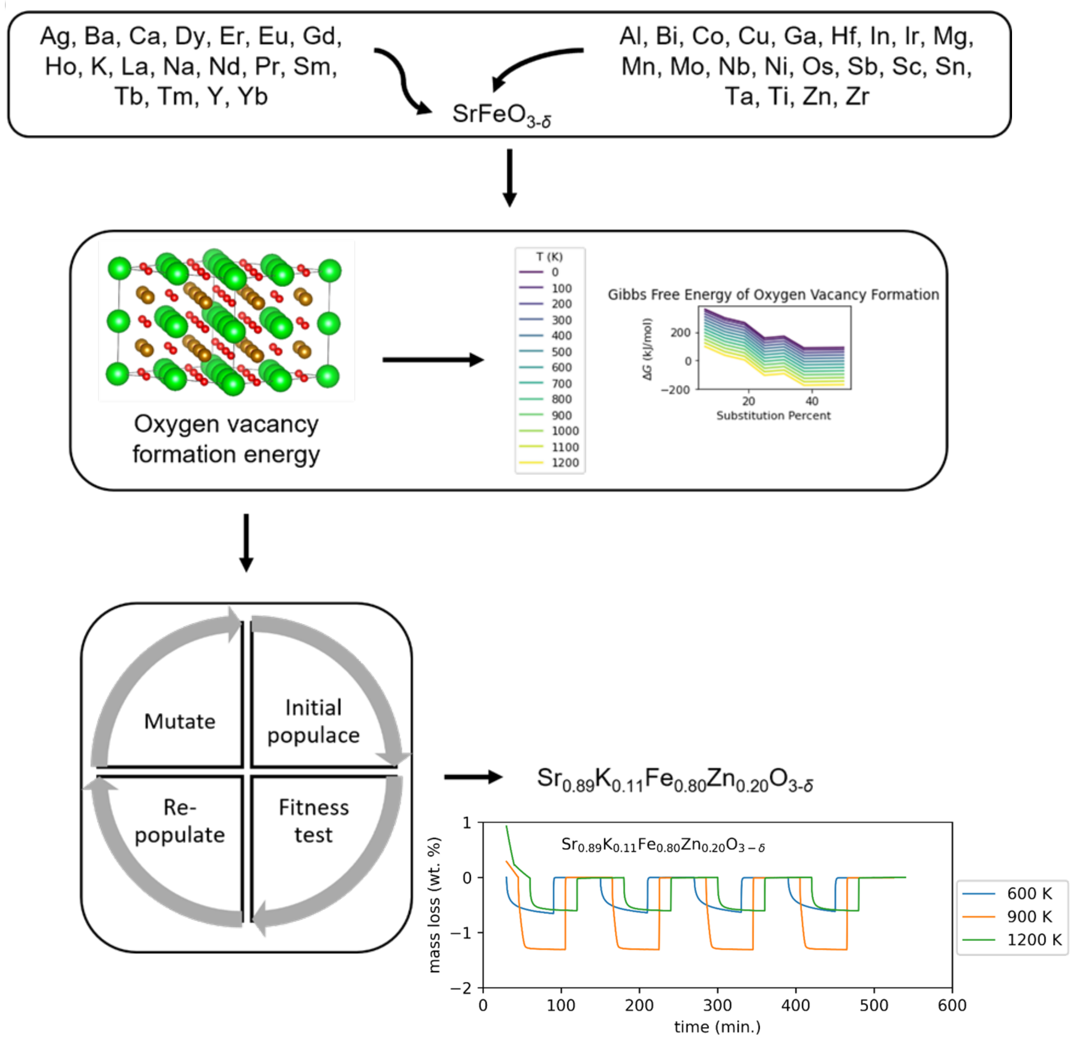
$$Sr_{0.75}Ca_{0.25}FeO_3 \xleftrightarrow{\delta(T,P_{O_2})} Sr_{0.75}Ca_{0.25}FeO_{3-\delta} + \frac{\delta}{2}O_2$$

Task 5: Oxygen Integration for Net-Zero Carbon

Accomplishments

Current Accomplishments

- Demonstrated ability to control capacity, desorption temperature, and rate through both compositional and surface area 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
- Developed computational models to accurately describe diffusion pathways within carrier structures with varying oxygen compositions

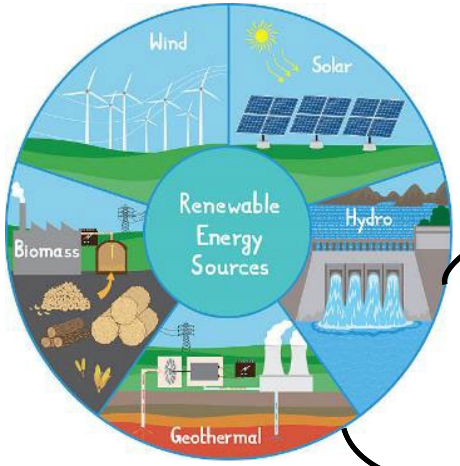


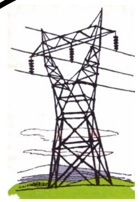
Task 6: Microwave Reactions for Co-Gasification of Plastic and Biomass

Overview

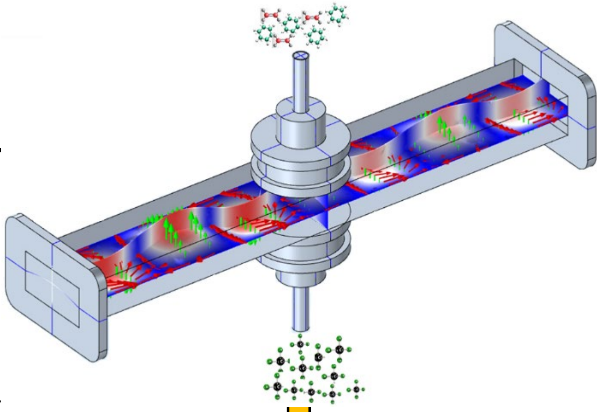
Feedstocks: biomass, plastics, MSW, Coal

Coupling with intermittent energy resources





Microwave Reactor



H_2, Syngas

Fuels & Chemicals

Process Intensification

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

Task 6: Microwave Catalytic Co-Gasification of Plastic & Biomass

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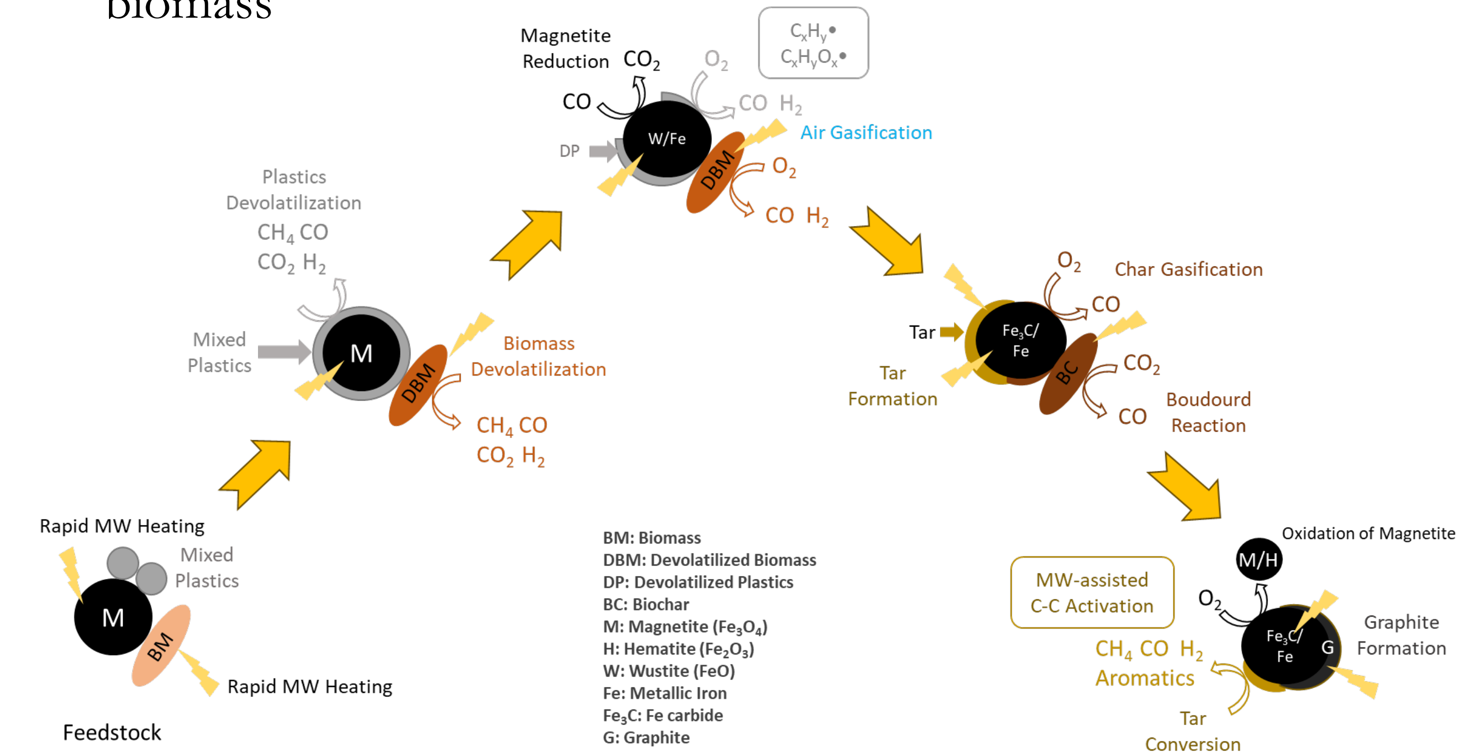
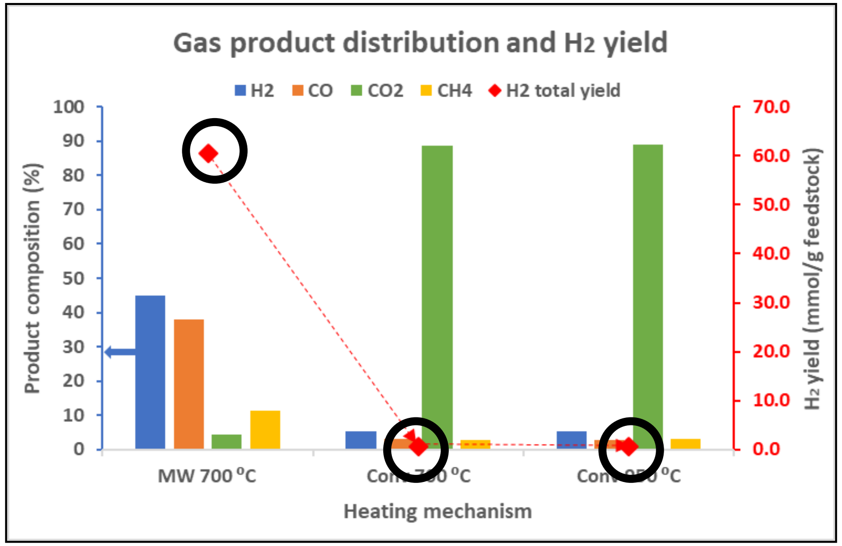
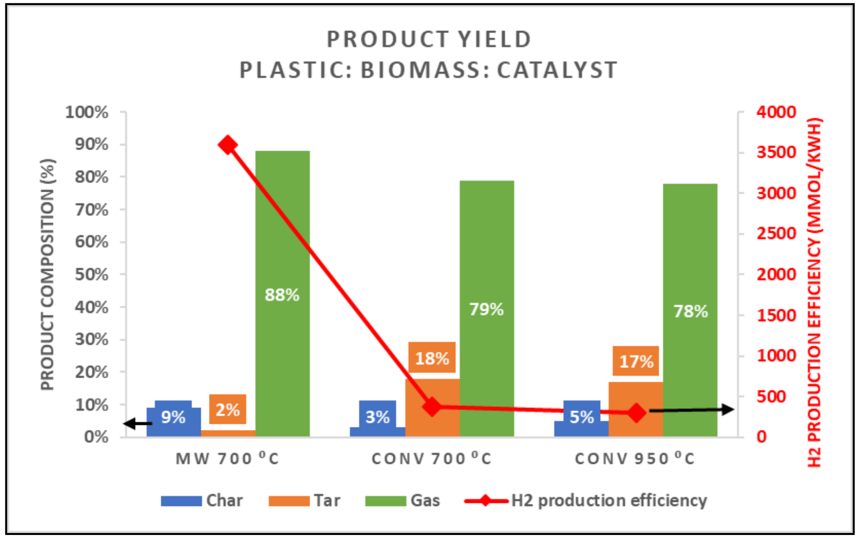
Accomplishments

- **4 times higher hydrogen yields** and **~20% higher syngas yields** with microwave heating
- Tar generation < 2%
- Fe oxide catalyst enhances MW synergy between plastics and biomass







Abedin et al., 2024 submitted

Task 7: Process Development to Mature Oxygen Sorbent Technology

Overview

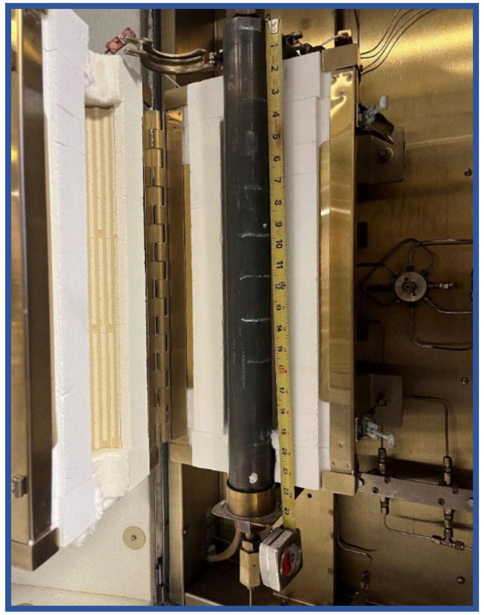
Objective:

- **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.**

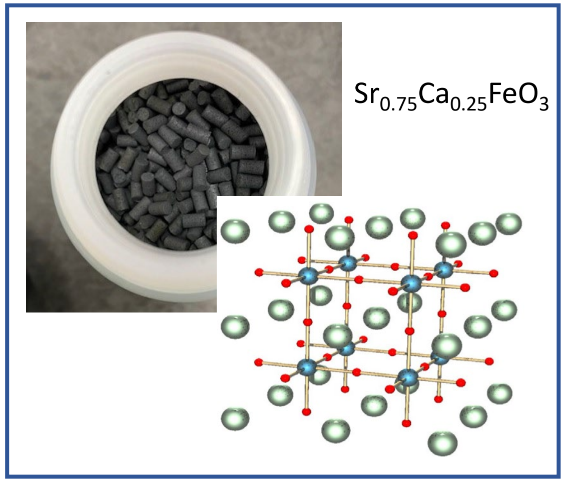
Project Goals:

- Create detailed kinetic rates for O_2 adsorption/desorption from physical TGA and bench-scale experiments.
- Validate rates through computational comparison to experiments.
- Computationally bridge scales to examine modular reactor
- Optimize O_2 production rates at pilot scale through investigation of adsorption swing time and geometric reconfiguration to reduce pressure drop.

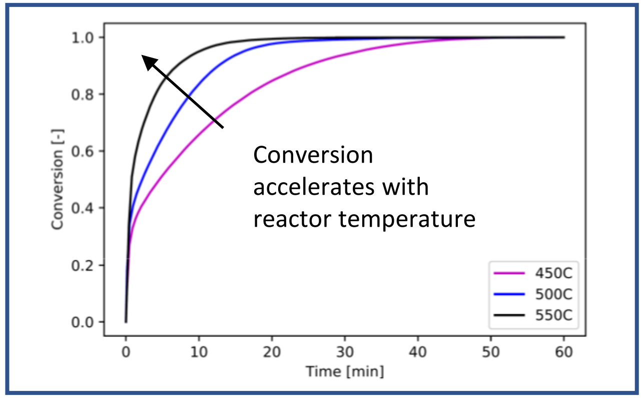
Bench Unit



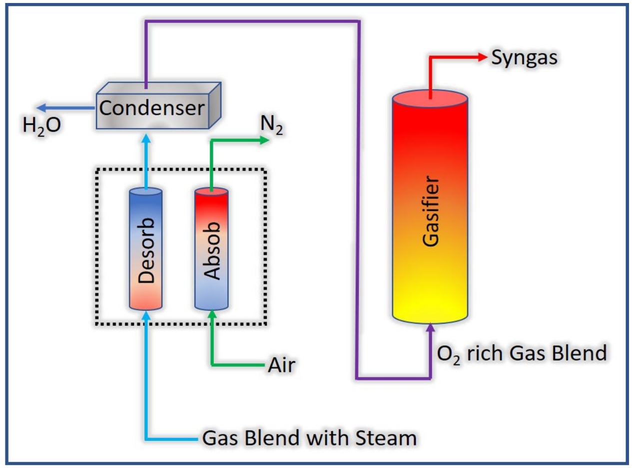
Test Material



Conversion Curves



Process Concept



Task 7: Process Development to Mature Oxygen Sorbent Technology

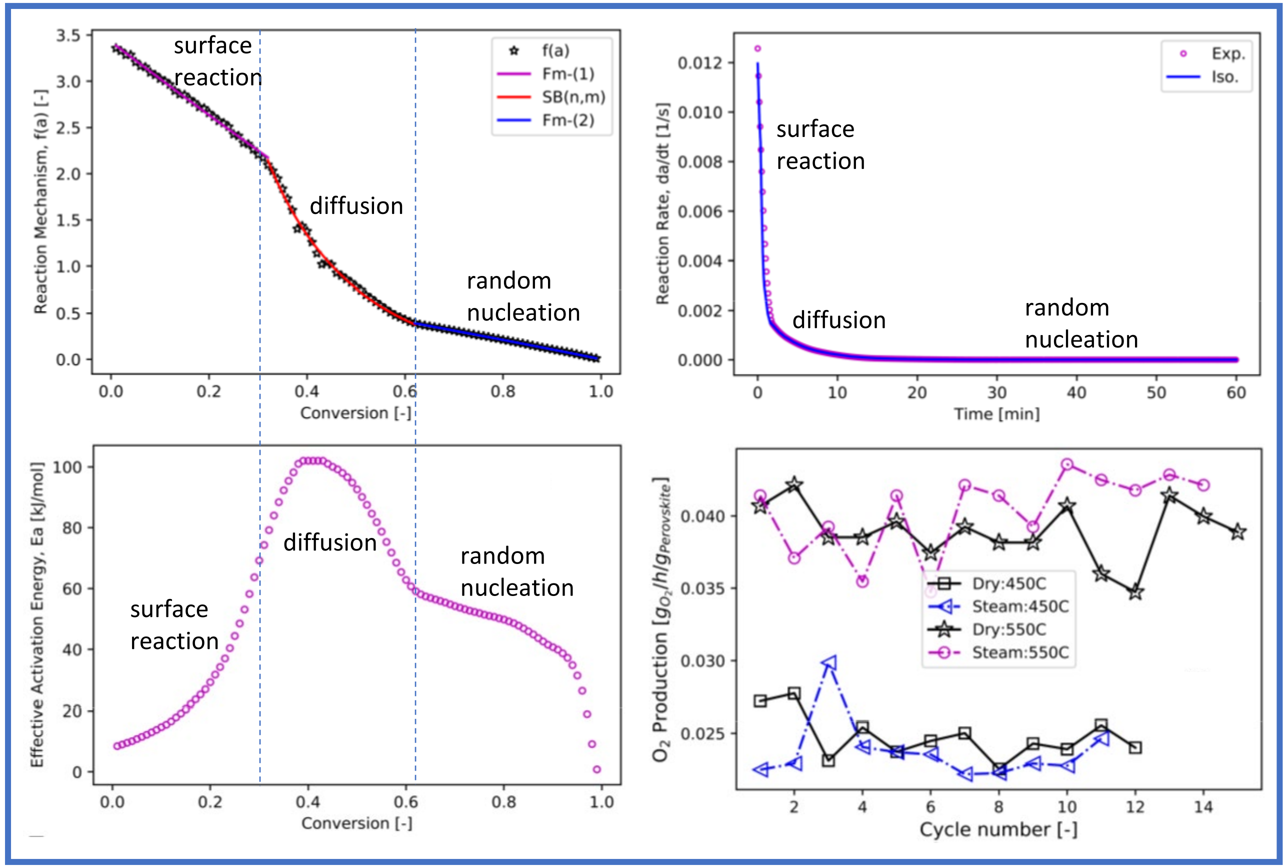
Accomplishments

Accomplishments:

- Iso-conversional desorption kinetic analysis reveals a three-stage desorption mechanism related to conversion extent (surface reaction → diffusion → random nucleation).
- Quantified effective activation energy dependence on conversion extent.
- Experiments indicate that steam is an effective effluent for desorption mechanism and results in near equivalent oxygen production as N_2.

Impact:

- Simulations better capture kinetics and produce improved device performance metrics.
- Simulations demonstrate O_2 production from perovskite materials may effectively supplant some cryogenic processes.
- Risk-averse processing scenarios are examined through simulation.



Publications:

- "Redox-based chemical looping large-scale air separation unit designs using perovskite material," Konan, A; Clarke, M; Aziz, H; Shahnam, M; Energy&Fuels, 2023, 37(21), 16729-16743, DOI: 10.1021/acs.energyfuels.3c02759
- "Dry and steam-based desorption kinetic analysis and derivation for $Sr_{0.75}Ca_{0.25}FeO_{3-\delta}$ perovskite using iso-conversional method with fixed bed redox reactions experimental data," internal review.

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

Overview

- **Objective: Explore the gasification of alternative feedstocks, such as waste plastics, waste coal, and biomass, to generate H_2/syngas with minimal CO_2 emissions**
- **Project goals:**
  - **Co-gasification of waste plastic and waste coal/biomass in a steam environment to generate H_2/syngas**
    - Study the feasibility of co-feeding of pelletized waste plastic and waste coal/biomass in a drop tube reactor (DTR) under nearly isothermal conditions
    - Evaluate process conditions such as feed blend ratio, temperature, and catalyst 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 operating conditions including temperature and gas/volatile residence time
    - Analyze tar composition (hydrocarbons up to C_{45}) using gas chromatography-mass spectrometry (GC-MS) to understand mechanisms of pyrolysis and tar cracking for generating more syngas from gasification
    - Conduct pyrolysis kinetics in a thermal analyzer (simultaneous thermogravimetric analyzer-differential scanning calorimeter, TGA-DSC) to determine kinetic parameters (i.e., heat of fusion and activation energy)

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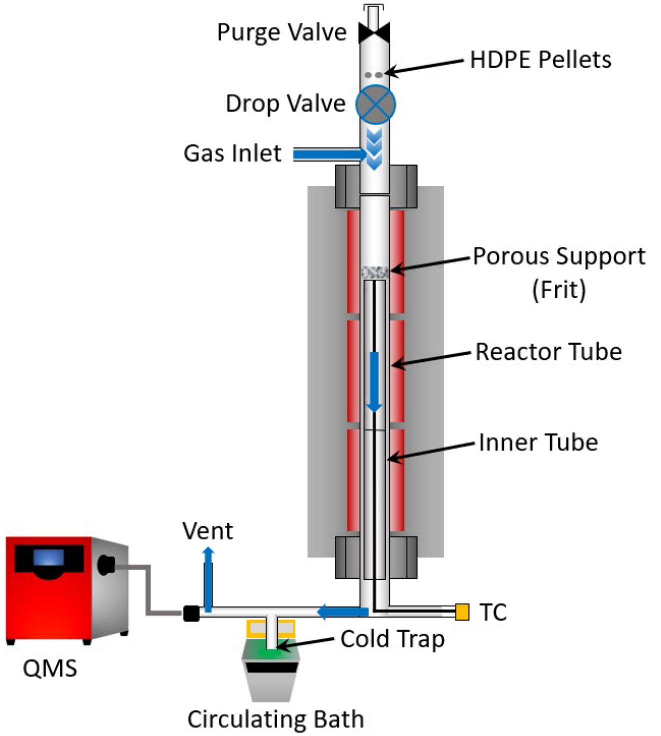

* QMS, Quadrupole Mass Spectrometer
TC, Thermocouple

LDPE Powder

Coal refuse

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

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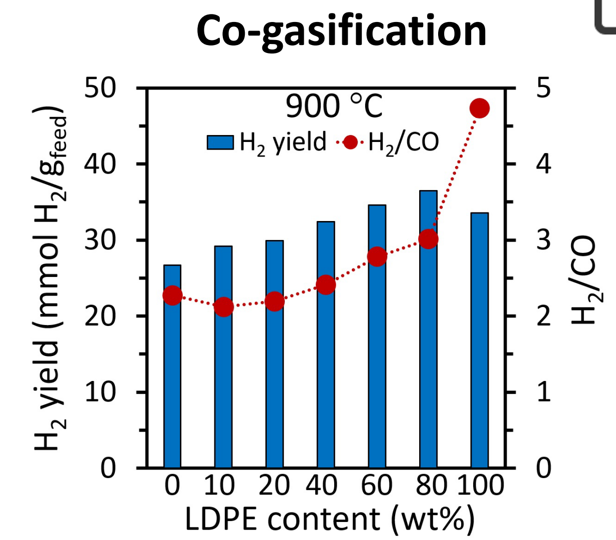
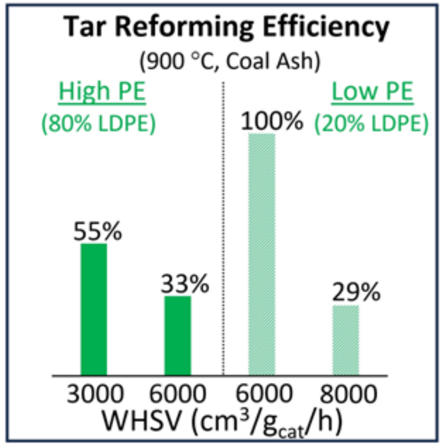
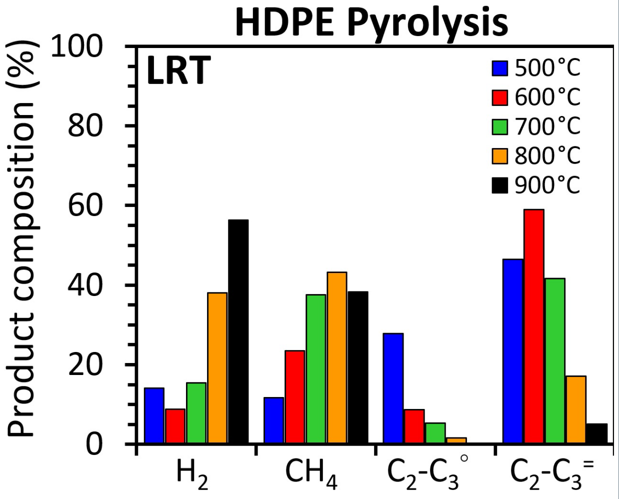
EY23 Accomplishments

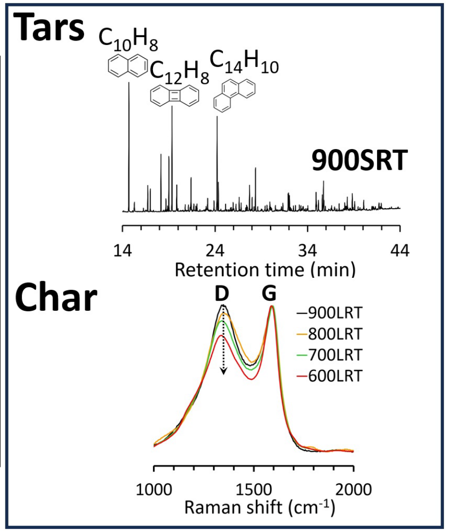
- **Co-gasification of pelletized low-density polyethylene (LDPE) and coal refuse (CR) or biomass with 10% H_2O/Ar in the DTR**
  - Completed optimization of syngas production and quality with various LDPE/CR feed blend ratios (0, 10, 20, 40, 60, 80, and 100 LDPE) and temperature (800-1000 °C)
  - Demonstrated up to 100% tar reforming efficiency during catalytic co-gasification with Fe_2O_3 or coal ash
  - Initiated co-gasification of LDPE and pine dust with select feed blends
- **Pyrolysis of high-density polyethylene (HDPE) pellets and MSW in the DTR**
  - Completed investigation of temperature (500-900 °C) and gas/volatile residence time (4-32 s) effects on carbon conversion and product distribution from HDPE pyrolysis
  - Utilized various analytical techniques, such as GC-MS, Raman spectroscopy, and scanning electron microscopy/energy-dispersive X-Ray spectroscopy (SEM/EDS), to characterize HDPE pyrolysis products: gases (H_2, C_1-C_3), tars (C_{10}-C_{45}), and char and established correlations between their formation and process parameters
- **Determination of pyrolysis kinetic parameters using non-isothermal TGA-DSC**
  - Developed standardized protocols to examine thermal degradation behaviors of pure and mixed feedstocks (plastics, biomass, and MSW)
  - Determined kinetic triplets (activation energy, pre-exponential factor, and reaction mechanism) from collected TGA data using a combination of isoconversional and master-plot
- **Co-gasification and pyrolysis findings presented in ACS and AIChE**







LRT, Long Residence Time
SRT, Short Residence Time



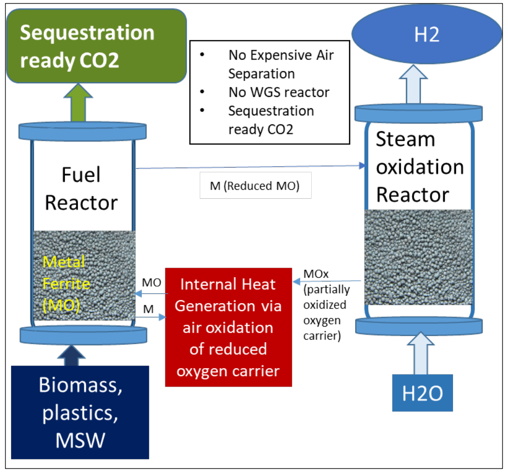
Task 11: Production of H_2 from Biomass, Plastics, and MSW via Catalytic and Non-Catalytic Processes

Overview

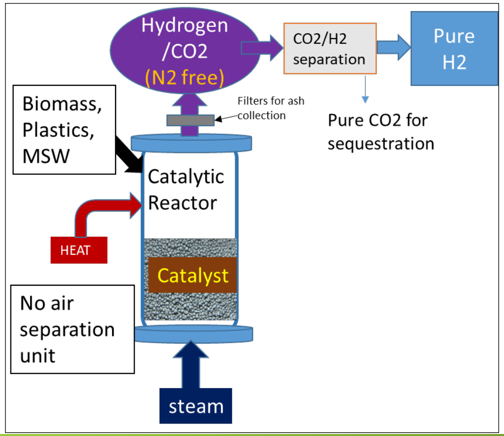
- **Objective: Develop optimized systems with inherent carbon capture that can be used in H2 production from solid fuels such as biomass, plastics, coal, and municipal solid waste (MSW) via two novel patented and patent pending processes.**

- **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.

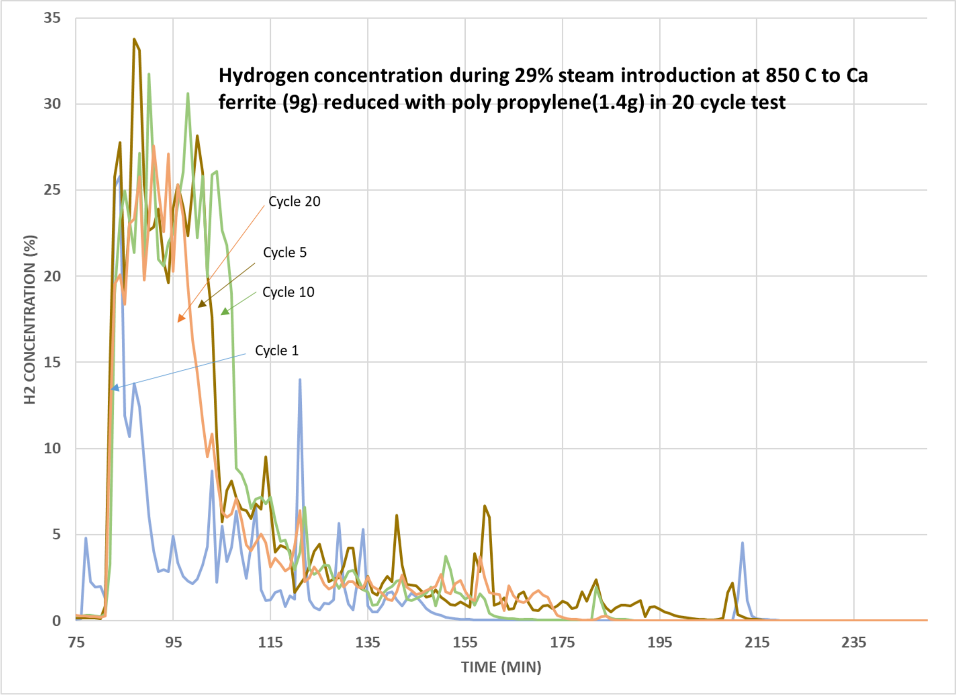
Non catalytic H2 production

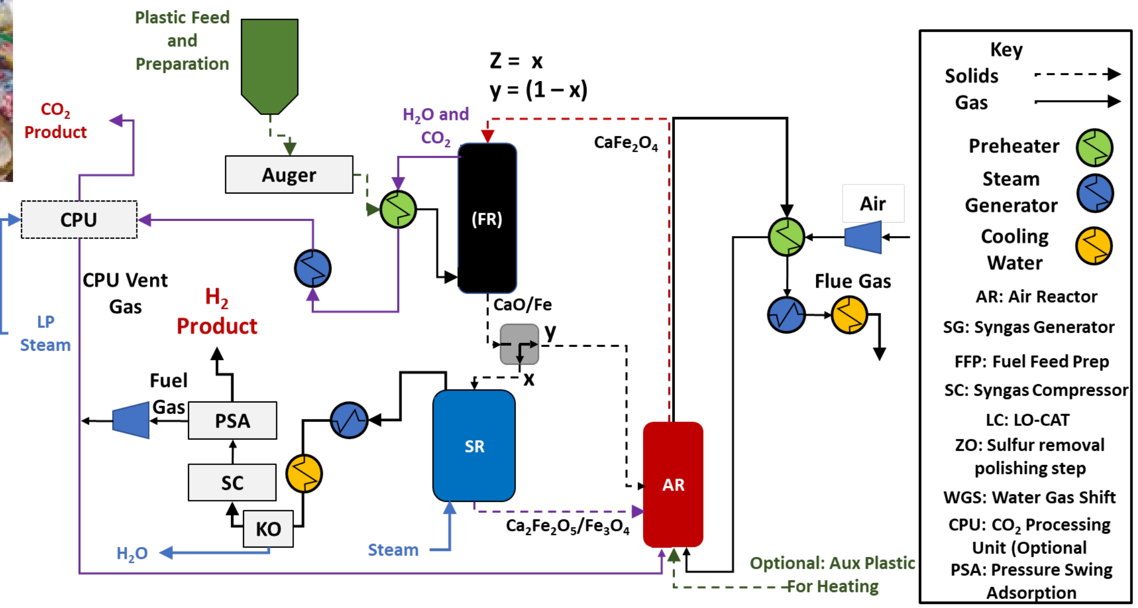


Catalytic H2 production



Task 11: Multi Cycle H2 Production with Ca Ferrite Oxygen Carrier using Poly Propylene (Plastic) as Fuel.





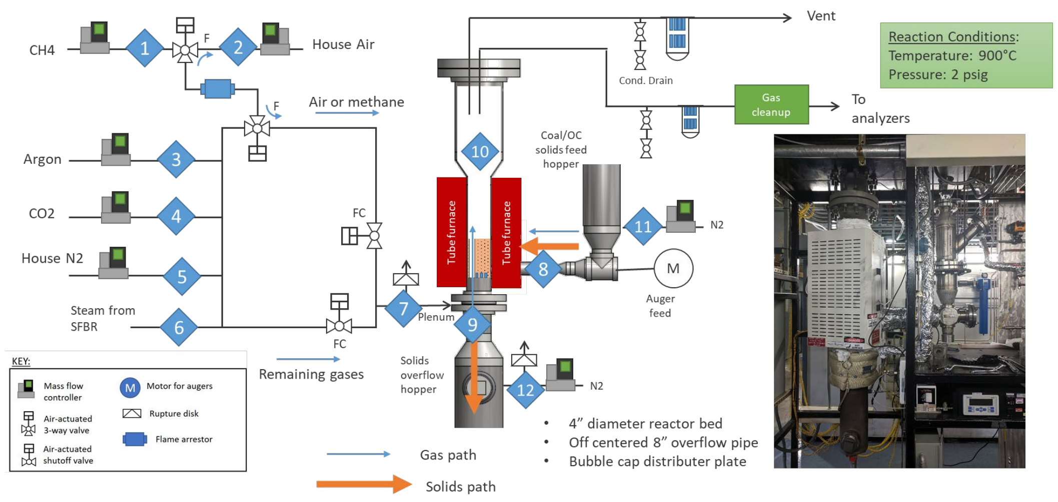
Power/Steam Cycle Included but not displayed

- Stable H2 production during 20 cycle test at a rapid rate with steam to H2 conversion rate of about 85%.
- PP is suitable fuel for the process

Preliminary energy analysis compared to gasification baseline

- Higher Yield (~30% more kg H_2/kg Plastic fuel)
- More efficient thermal management (79% reduction in fuel heating requirements)
  - 10-15w% of H_2 could be used to satisfy thermal requirements
- More efficient usage of process water (29% reduction)
- Less net electricity usage (64% reduction)

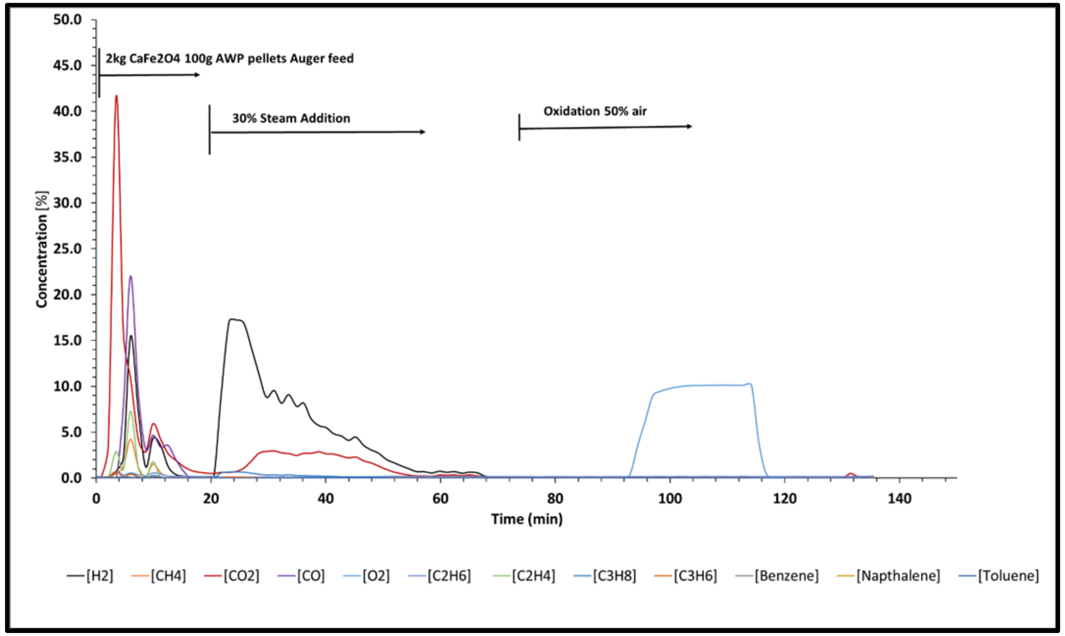
Task 11: Sub-pilot scale tests of Ca ferrite oxygen carrier with woody biomass (AWP)



Initiated sub pilot scale tests-

- Determine the feasibility of process scaling – Initiated H2 production with oxygen carrier tests with woody biomass in sub-pilot scale unit (2-5 Kg material processing)
- Initial data showed promising results
- Future tests - Multi cycle tests and parametric evaluation

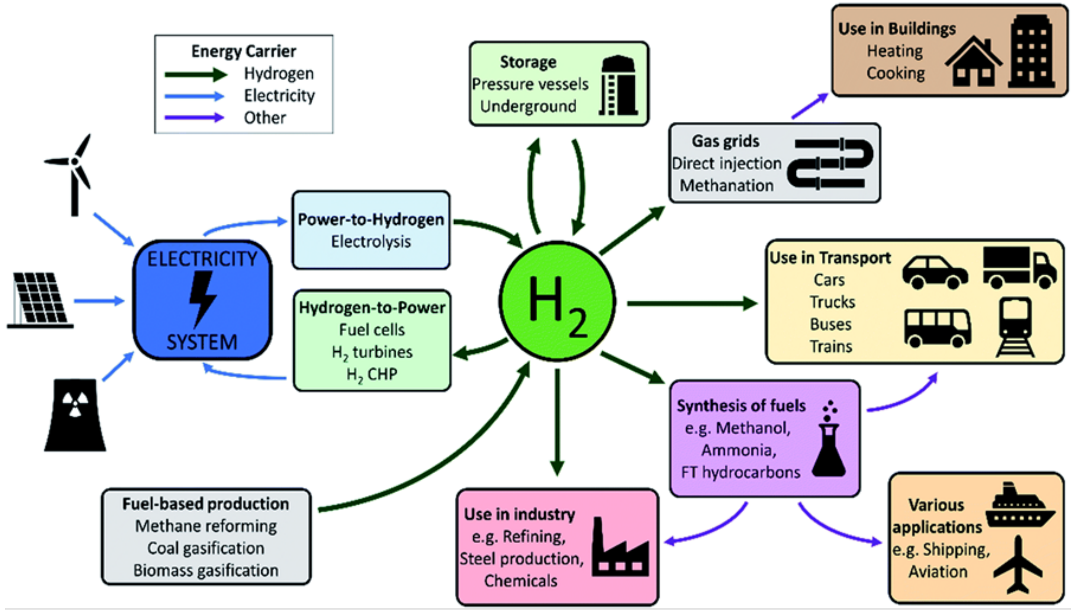
Effluent gas concentrations during the test with 100 g biomass wood pellets and 2.5 Kg of Ca Ferrite at 850 C



- Formation of CO2 (major component), CO, H2 were observed when biomass was injected to Ca ferrite
- Rapid formation of H2 was observed when steam was introduced to the reduced Ca ferrite
- Demonstrated feasibility of H2 production in sub-pilot scale unit

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

Accomplishments

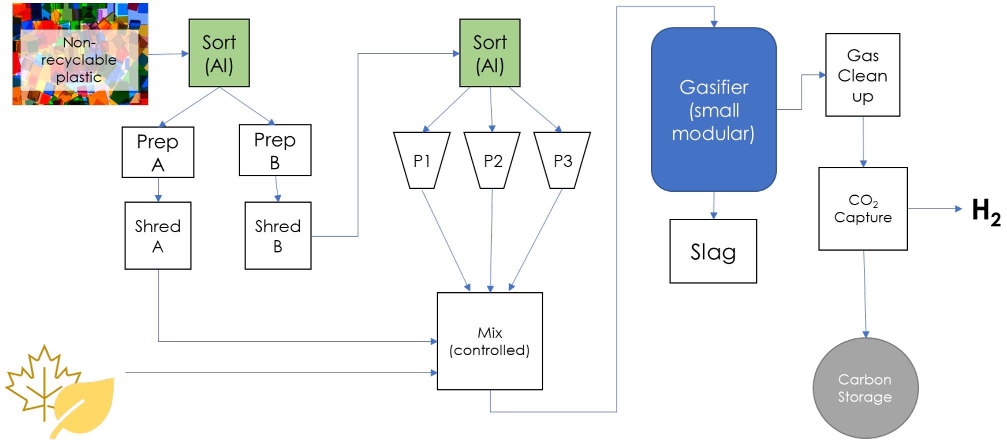
- McNaul, S.; White, C.; "Hydrogen Shot Technology Assessment: Thermal Conversion Approaches," December, 2023
  - Co-sponsored by FE-20 & FE-30
  - Internal review included HFTO/EERE and Office of Policy
  - Deputy Secretary announcement at COP28
- Wallace, B.; Toetz, V.; "Hydrogen Potential from Biomass in the United States" – publication pending review
- McNaul, S.; Keairns, D.; "Biomass Gasification to Hydrogen Net-Zero Scenario Reference" – publication pending review

Task 14: Feedstock Control for Gasification

Overview

- **Objective: Support the development of intelligent systems capable of controlling the blend of mixed plastic waste, biomass, MSW, and waste coal supplied to a modular gasification system for production of H2 with CCS.**

- **Project Goals:**
  - (EY23) With NREL develop a State-of-Technology Report on existing tools for imaging and spectroscopic characterization of biomass, MSW, and fossil energy feedstocks.
  - Collect data to link waste plastics to gasification properties
  - Develop prototype system for actively controlling feed to small pilot gasifier



Accomplishments

- Worked with NREL to develop the State-of-Technology Report

Acknowledgments

- 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.
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