Advanced Reaction Systems

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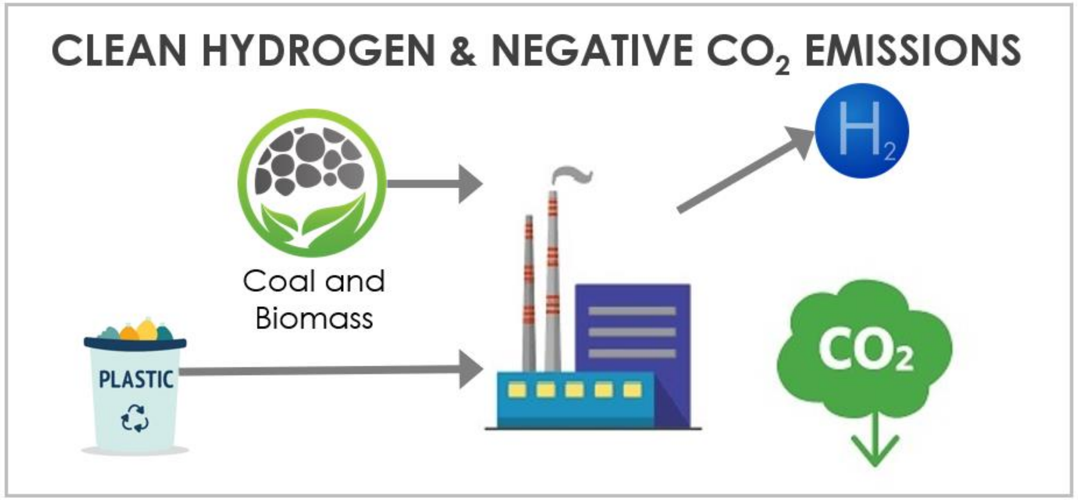
Research Objective

Portfolio Objective

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



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

Current Research

Overview

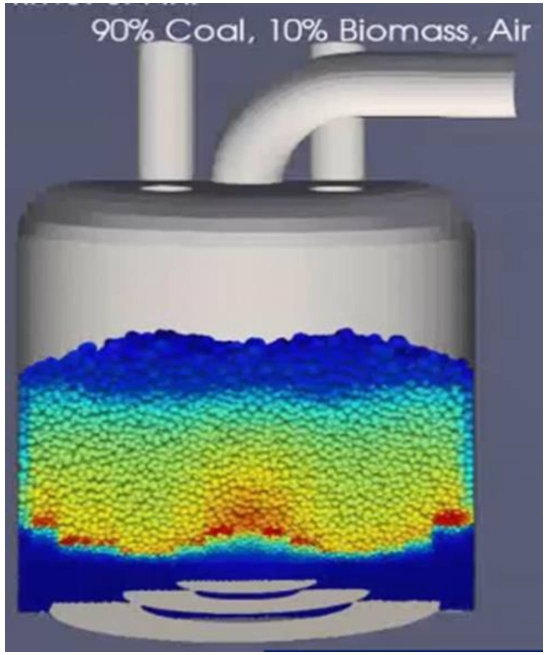
- Task 3: Advanced Reactor Design
- Task 4: Refractory Materials for Multi-Fuel Gasification
- Task 5: Oxygen Integration for Net-Zero Carbon
- Task 7: Process Development to Mature Oxygen Sorbent-Based Technology
- Task 6: Microwave Reactions for Gasification
- Task 8: Gasification of Waste Plastic to Enable a Circular Economy
- Task 13: Hydrogen Production from Gasification Assessment
- Task 14: Syngas Conversion to Industrial Chemicals

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**

- **Project Goals:**
- **Use CFD simulations to guide commercial scale-up and optimization of a moving-bed gasifier design**
  - Application to the proposed University of Alaska, Fairbanks (UAF) modular plant
  - Evaluate gasifier performance for a range of feedstock and operating conditions
  - Optimize operation for production of H_2 with Net-Zero to negative Carbon
  - Evaluate gasifier performance for low-tar application – tar reinjection
- **Evaluate novel fluid bed gasifier performance for mixtures of biomass and waste plastic feedstocks**



Hamilton-Maurer International

Task 3: Refractory Materials for Multi-Fuel Gasification

Accomplishments

Current Accomplishments (EY21)

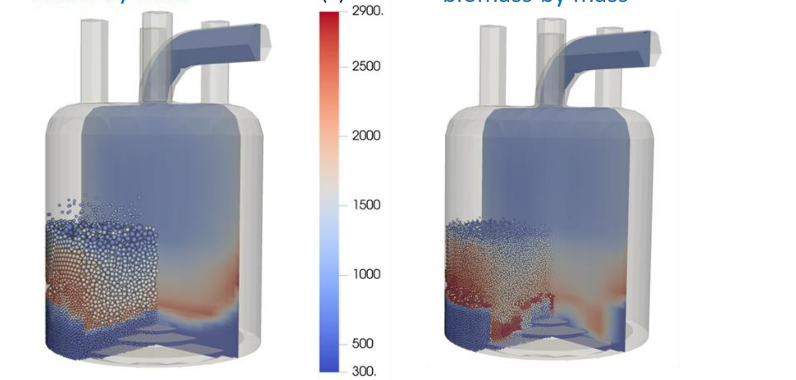
- Simulations were performed on a gasifier with coal/biomass mixtures to determine operating conditions for hydrogen production with net-zero carbon emissions
- Re-Injection of tar into a gasifier was modelled and found to create local regions of high temperature which crack the tar and increase the rates of gasification and char/tar oxidation reactions
- Gasification of Cypress biomass in Sotacarbo's pilot-scale fluidized air blown experimental reactor (FABER) was simulated and gasification reaction kinetics were developed and validated against experimental results
- A HDPE pyrolysis scheme was developed compatible with CFD applications as the first step in modelling the gasification of waste plastic

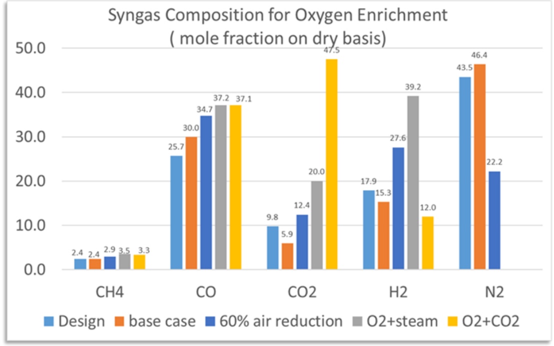
Future Accomplishments (EY22 – future)

- Complete the modelling for a pilot-scale fluidized bed gasifier
- Implement the plastic pyrolysis model into existing gasifier models to determine the performance of these systems on a waste plastic feedstock

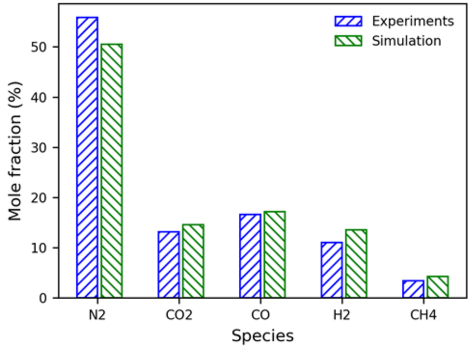
Base Case: 90% coal/10% biomass by mass

Tar Re-Injection: 90% coal/10% biomass by mass





Syngas composition of coal/biomass blends

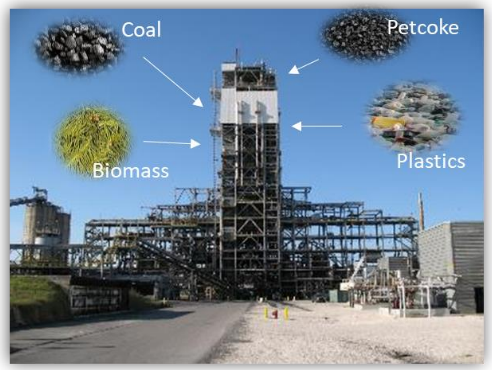


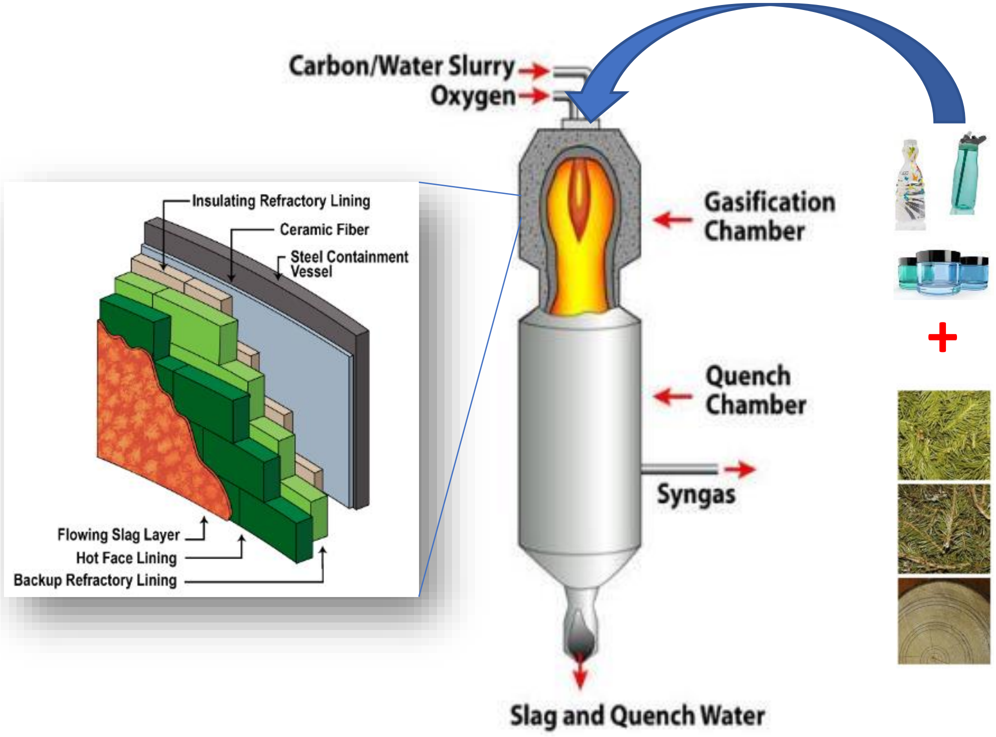
Biomass syngas composition

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



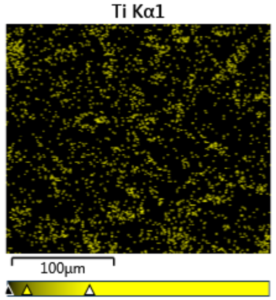


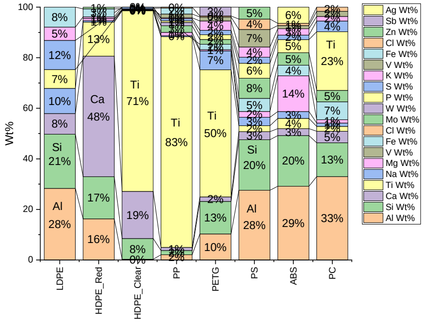
Task 4: Refractory Materials for Multi-Fuel Gasification

Accomplishments

Current Accomplishments (EY21)

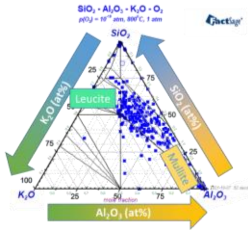
- Industrial partnerships with Eastman (gasifiers), Allied Mineral Products (castable refractories), HarbisonWalker International (sintered bricks)
- Developed own plastic ash composition database for various plastic types (HDPE, LDPE, PP, PS, PET, etc.) by ashing based on ASTM D5630-13.
- Alumina- and mullite-based refractories were fired against 20% plastic slag; the former tended to degrade while the latter exhibited some resistance.
- Two refractory compositions were successfully identified to be used in mixed coal-biomass modular gasifier environments (up to 100% biomass)

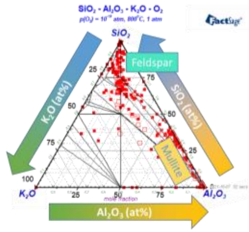


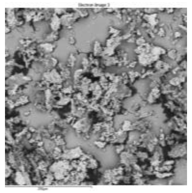


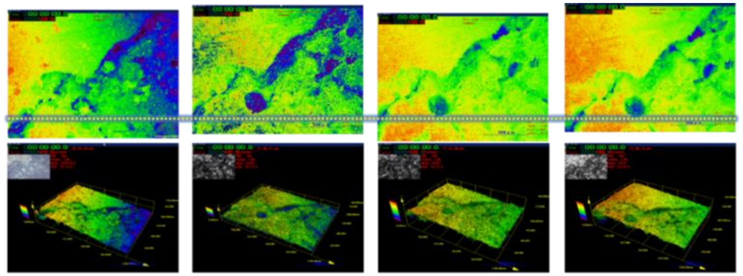
Publications/presentations (EY21)

- **Kristin Tippey, Anna Nakano, Jinichiro Nakano, Hugh Thomas, Ömer N. Doğan, Matthew Lambert, and Dana G. Goski, 'In-operando Interactions of Refractory Materials with Ash/Slag from Mixed Feedstock Gasification,' was presented at TMS2022, 2/27-3/3, 2022, Anaheim, CA.**
- **Kristin Tippey, Jinichiro Nakano, Anna Nakano, Hugh Thomas, Ömer N. Doğan, Matthew Lambert, and Dana G. Goski, 'In-situ observations of alumina- and mullite-based refractory materials interacting with ash in coal-biomass gasification environments,' was presented at UNITECR2022, 3/15-18, 2022, Chicago, IL.**
- **A conference proceedings, Kristin Tippey, Jinichiro Nakano, Anna Nakano, Hugh Thomas, Ömer N. Doğan, Matthew Lambert, and Dana G. Goski, 'In-situ observations of alumina- and mullite-based refractory materials interacting with ash in coal-biomass gasification environments,' was published in UNITECR2022, 3/15-18, 2022, Chicago, IL.**









Before · After Ramp Up · After 1 Hour · After Cool Down

Future Accomplishments (EY22 – future)

- Establish novel refractory composition that enables sustainable plastics gasification

Task 5: Oxygen Integration for Net-Zero Carbon

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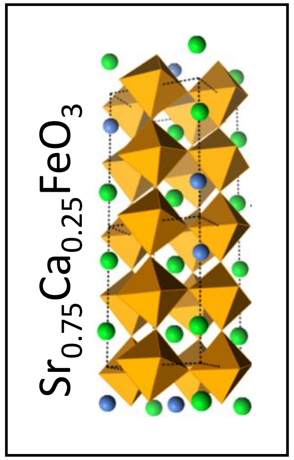
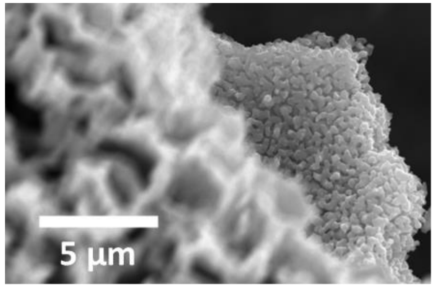
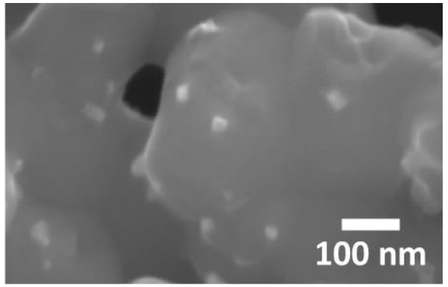
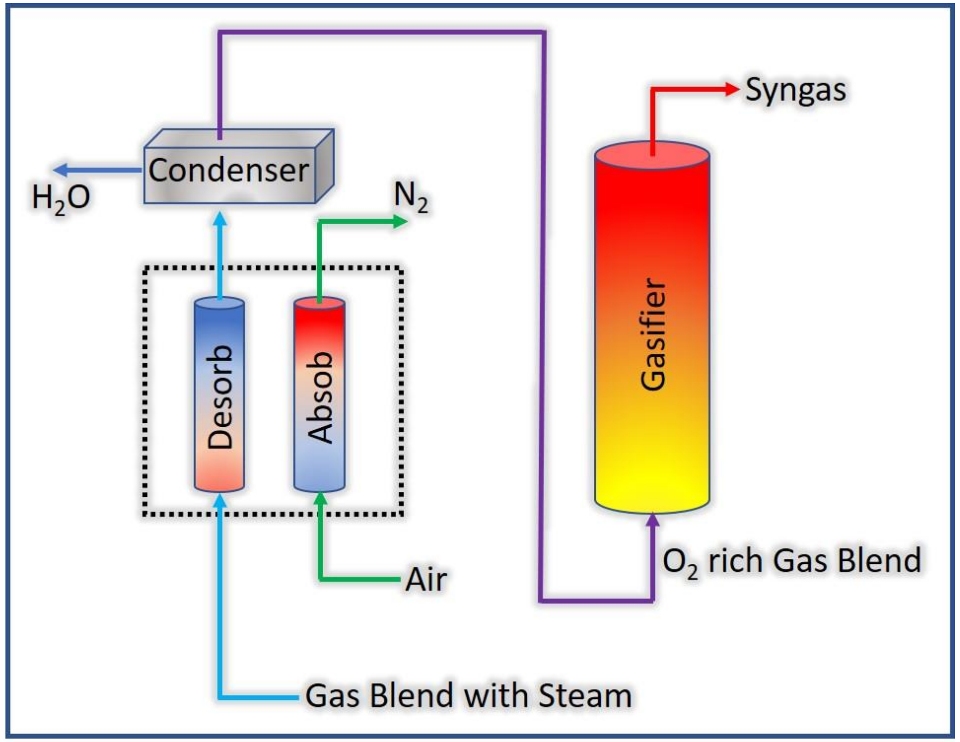
Overview

- **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 modelling tool for the optimization of carrier materials
  - Design 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

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Accomplishments

Current Accomplishments (EY21)

- 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
- Ellingham diagrams for perovskite carriers have been calculated and experimentally validated
- Preliminary reactor design completed using NETL's MFiX software

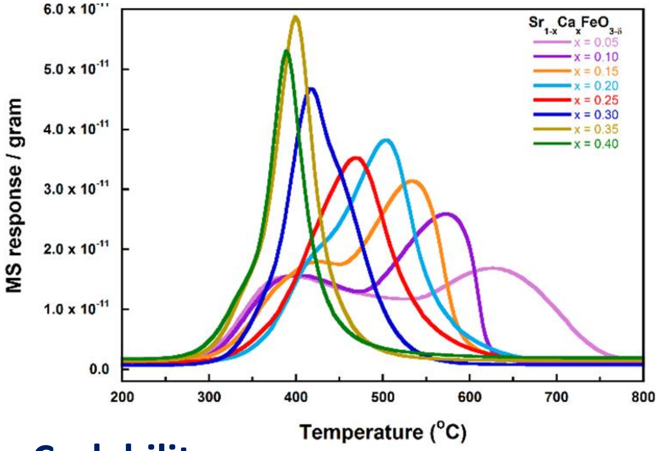
Publications/presentations (EY21)

- Ali Ramazani, Eric Popczun, Sittichai Natesakhawat, Jonathan Lekse, Yuhua Duan "Deep Learning Method to Accelerate Discovery of Effective Doping in Sr1-xRxFe1-yMyO3-d Oxygen Carriers for Chemical Looping Air Separation" Bulletin of the American Physical Society *in progress*.
- Eric J. Popczun, Ting Jia, Wenqian Xu, Chris M. Marin, Yuhua Duan, Jonathan W. Lekse "Nickel B-Site Substitution in Bulk Sr1-xCaxFeO3 Perovskite Oxygen Carriers: Benefits and Limitations" Journal of Alloys and Compounds 896, 162783.
- Eric J. Popczun, Ting Jia, Sittichai Natesakhawat, Chris M. Marin, Thuy-Duong Nguyen-Phan, Yhua Duan, Jonathan W. Lekse "Investigation of Sr0.7Ca0.3FeO3 Oxygen Carriers with Variable Cobale B-Site Substitution" ChemSusChem 14, 1893-1901.

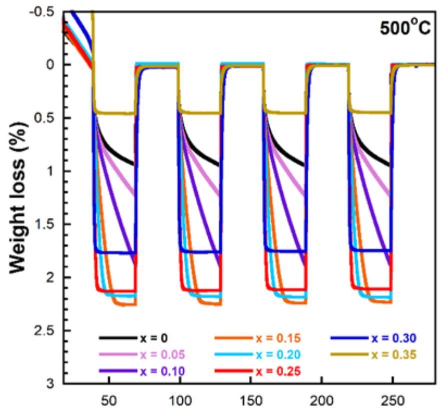
Future Accomplishments (EY22 – future)

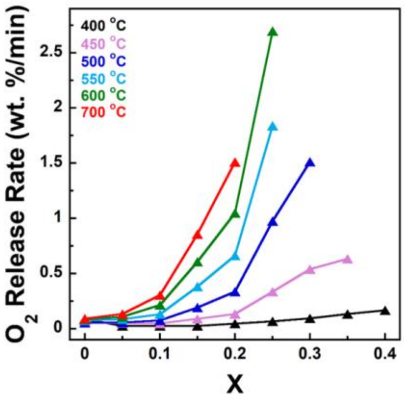
- Develop a machine learning model for carrier materials optimization

Tuneable



Cyclability



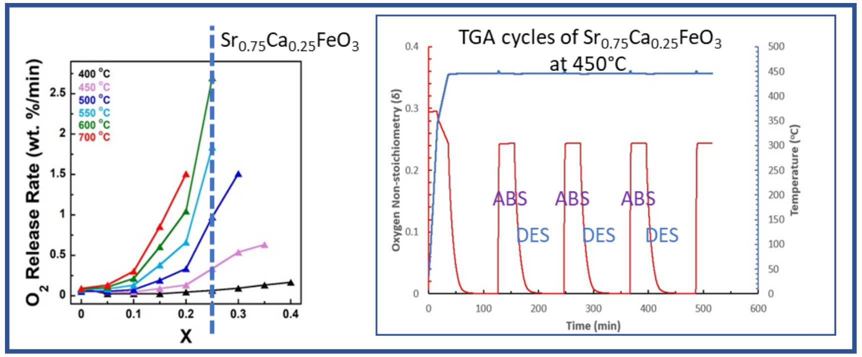


Rapid Kinetics

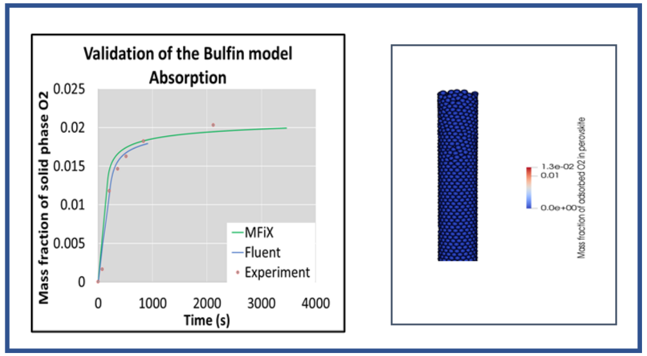
Task 7: Process Development to Mature Oxygen Sorbent Technology

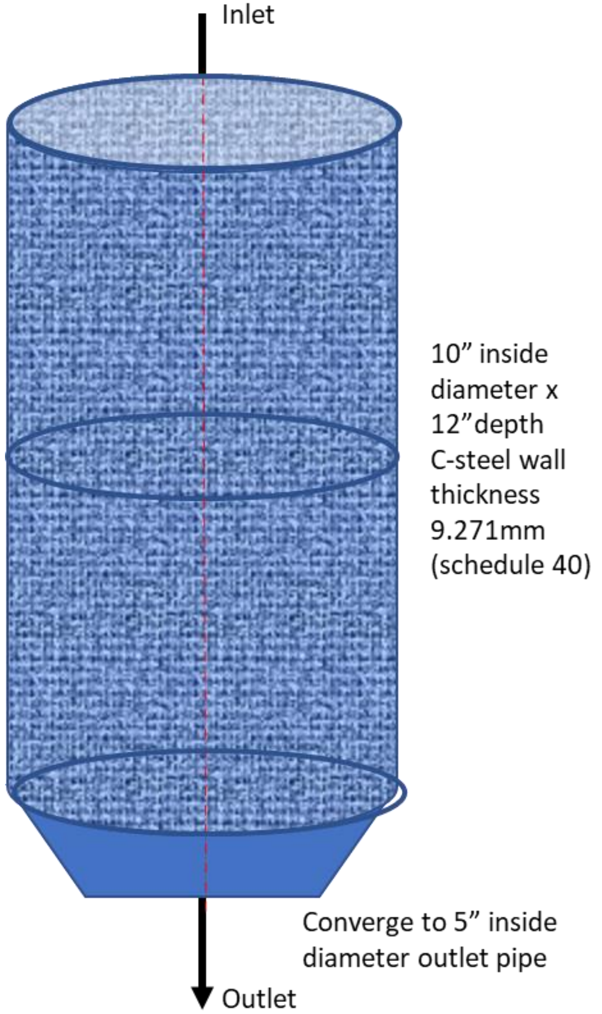
Overview

- **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:**
  - Develop a kinetic model that accurately describes the behavior of NETL designed materials
  - Design and validate a reactor model that maximizes oxygen production
  - Use simulation tools to scale the reactor design from bench scale to a pilot-scale reactor system



Experiments inform CFD models





Task 7: Process Development to Mature Oxygen Sorbent Technology

Accomplishments

Current Accomplishments (EY21)

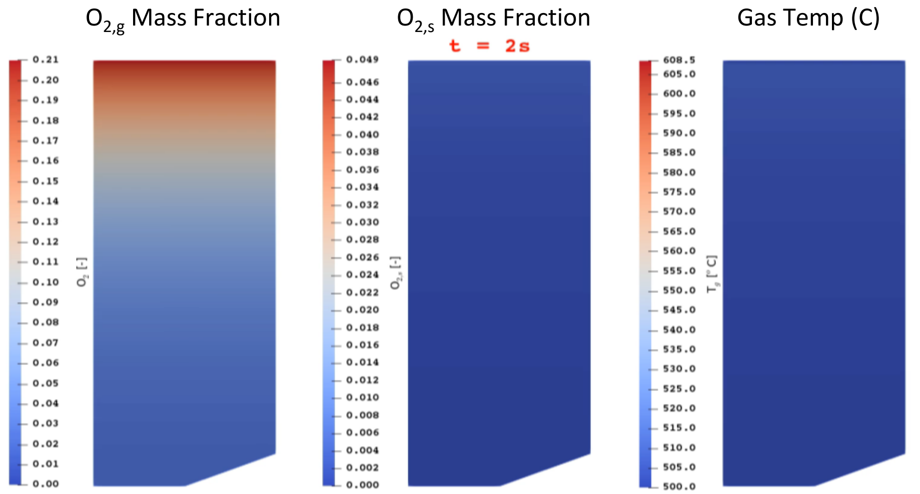
- NETL scientists ran TGA experiments over a range of O_2-gas concentrations and temperatures that were subsequently used to derive the kinetic constants described in the Bulfin model
- Multiple simulations of O_2 absorption and desorption swings at a 50 kg scale were conducted to gain an understanding of how a simple change in reactor mass loading can affect O_2 production in a fixed bed device
- The reactor design was scaled to 100 kg of material and additional simulations were performed and compared to performance at 50 kg

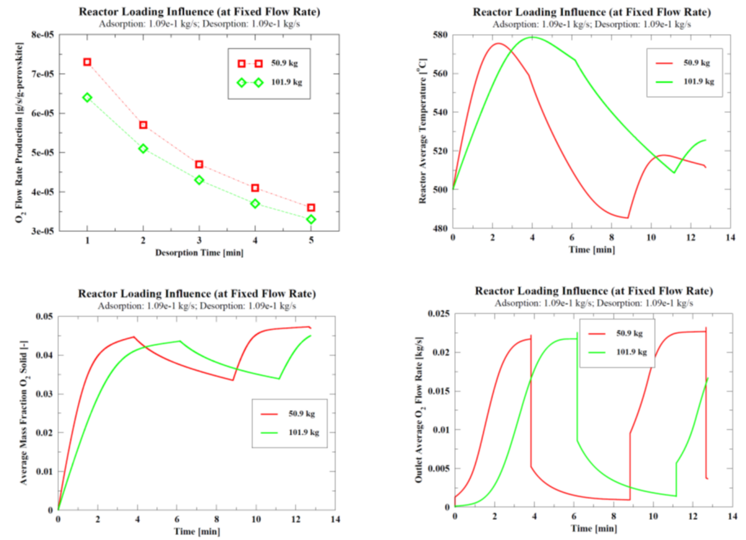
Publications/presentations (EY21)

- **D.Chandramouli, M. Clarke, "Perovskite sorbent oxygen separation modeling with MFiX," NETL Technical Report Series; U.S. Department of Energy, National Technology Laboratory: Morgantown, WV, 2021; p. 25.**
- **M. Clarke, A. Konan, D. Chandramouli, S. Ramesh, E. Popczun, "Derivation and Implementation of Kinetic Rates for $Sr_{0.75}Ca_{0.25}FeO_{3-\delta}$," NETL Technical Report Series; U.S. Department of Energy, National Technology Laboratory: Morgantown, WV, 2022; in review.**

Future Accomplishments (EY22 – future)

- A bench scale system is being built to perform steam desorption at the 300 g scale for model validation
- Optimization of the 50/100 kg reactor including flow rates, thermal management, and swing timings

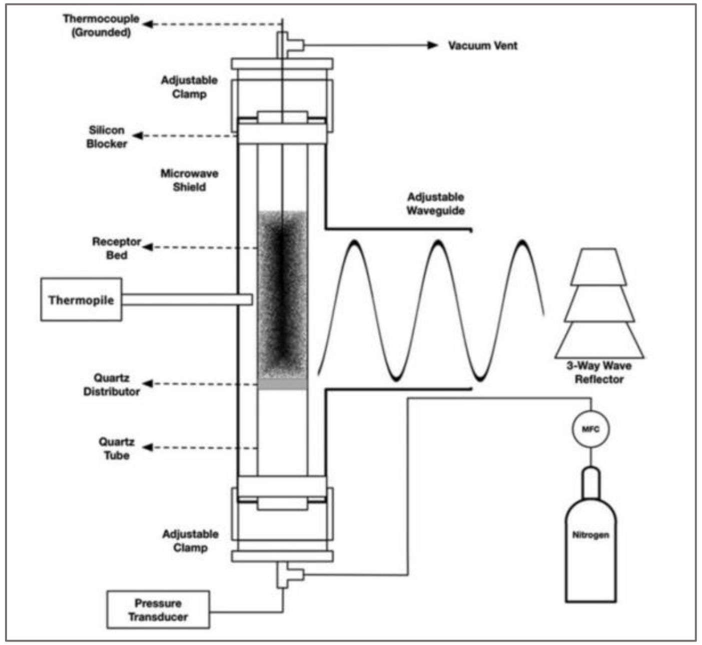


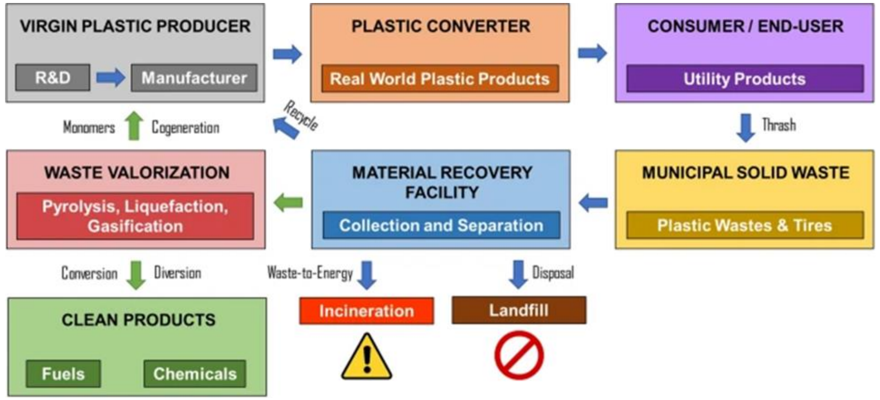


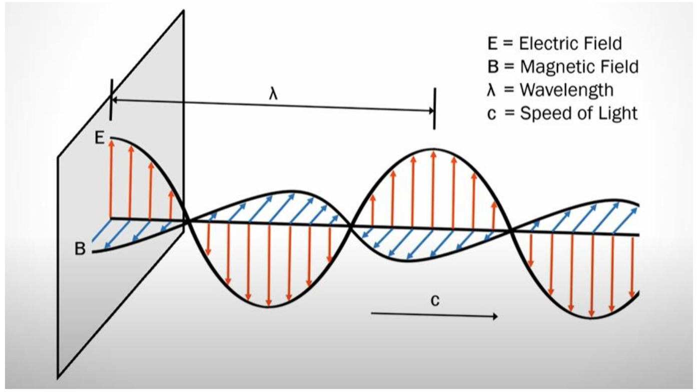
Task 6: Microwave Reactions for Co-Gasification of Plastic and Biomass

Overview

- **Objective: To investigate microwave reactions of plastic and biomass mixtures, determine the benefits afforded by utilization of microwaves, and design a microwave gasification system.**
- **Project Benefits:**
  - Synergy exists for co-gasification of plastic and biomass, depending on
    - ✓ Plastic to biomass ratio
    - ✓ Moisture content of biomass
    - ✓ Plastic type (HDPE > PP > PS)
    - ✓ Temperature
    - ✓ Catalysts (Ni based)
  - With increasing PE, PP or PS, syngas yield increases, tar and char decrease, H_2 increases







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

Accomplishments

Current Accomplishments (EY21)

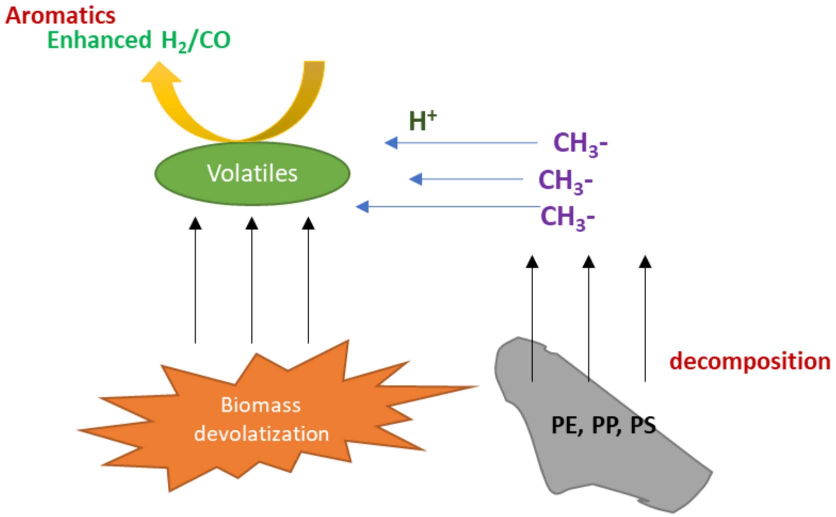
- Complete gasification and high hydrogen production with mixed plastic and biomass
- High H_2 and CO selectivity with biomass + plastic gasification
- Low H_2 production and incomplete gasification with plastic only (no biomass) – confirming synergy
- MW reduced the reaction time for complete gasification ~15 min for 6g sample

Publications/presentations (EY21)

- **P.D. Muley, Y. Wang, J. Hu, D. Shekhawat "Microwave Assisted Heterogeneous catalysis" Catalysis, 2021, 33, 1–37**

Future Accomplishments (EY22 – future)

- Test the effect of a gasifying agent (CO/air/Steam) on microwave gasification of biomass and mixed plastics
- Perform a parametric optimization to obtain data for system design



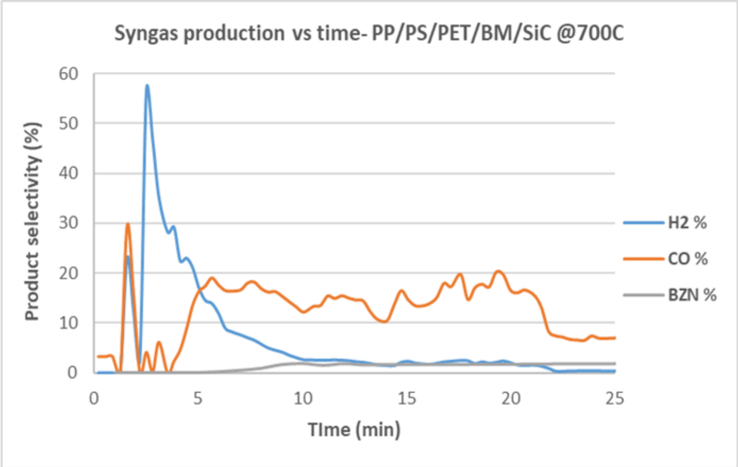
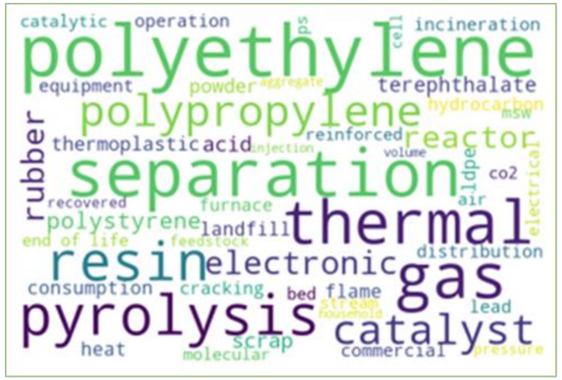


Fig. Product Selectivity of plastic (3g) and biomass (1g) MW gasification with SiC (2g), 200 SCCM air, 700⁰C

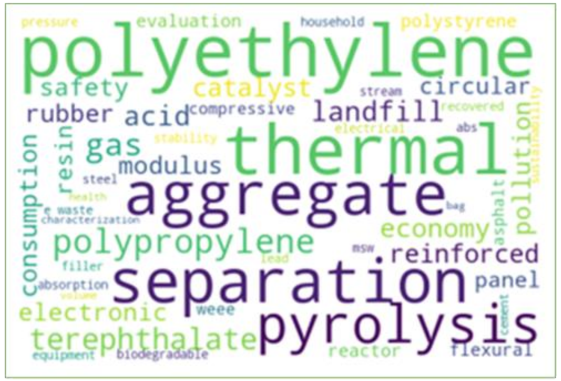
Task 8: Gasification of Waste Plastic to Enable a Circular Economy

Overview

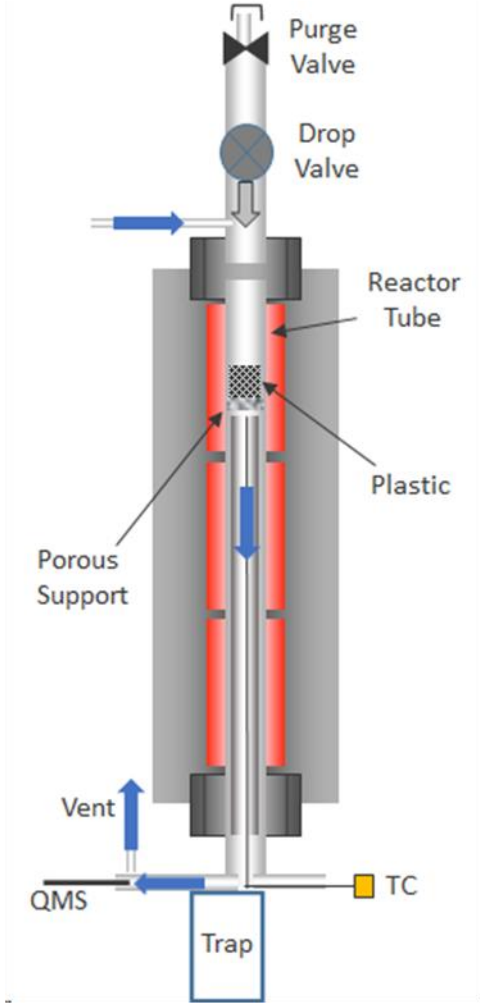
- **Objective: To study the thermal gasification of waste plastic to determine syngas yields and compositions and design a machine learning tool to predict reactor performance based on feedstock and operating conditions.**
- **Project Goals:**
  - Determine syngas composition and yield for various plastic and plastic/waste coal/biomass blends
  - Conduct a literature analysis to gather data on emerging trands in plastic recycling
  - Develop a machine learning tool to predict gasification reactor performance



2000 – 2010



2010 - today



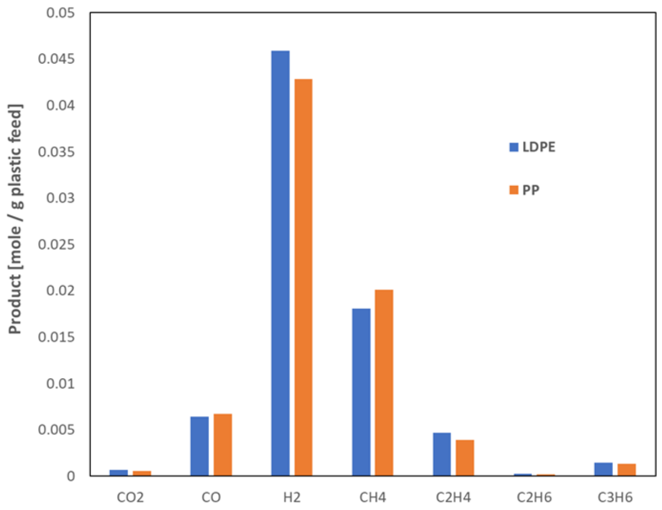
Drop Tube Reactor Schematic

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

Accomplishments

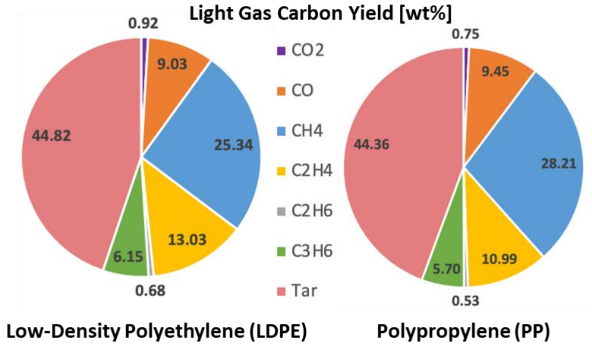
Current Accomplishments (EY21)

- Studied the gasification of alternative feedstock of waste plastic and waste coal to generate enhanced H_2/syngas in a drop tube reactor
- Identified key parameters for product composition
  - Temperature
  - Residence time
  - Plastic/H_2O feed ratio
  - Gas environment (H_2O, inert gas)
- Analyzed approximately 10,000 papers on plastic recycling/upcycling to explore emerging trends using Big-data tool



Future Accomplishments (EY22 – future)

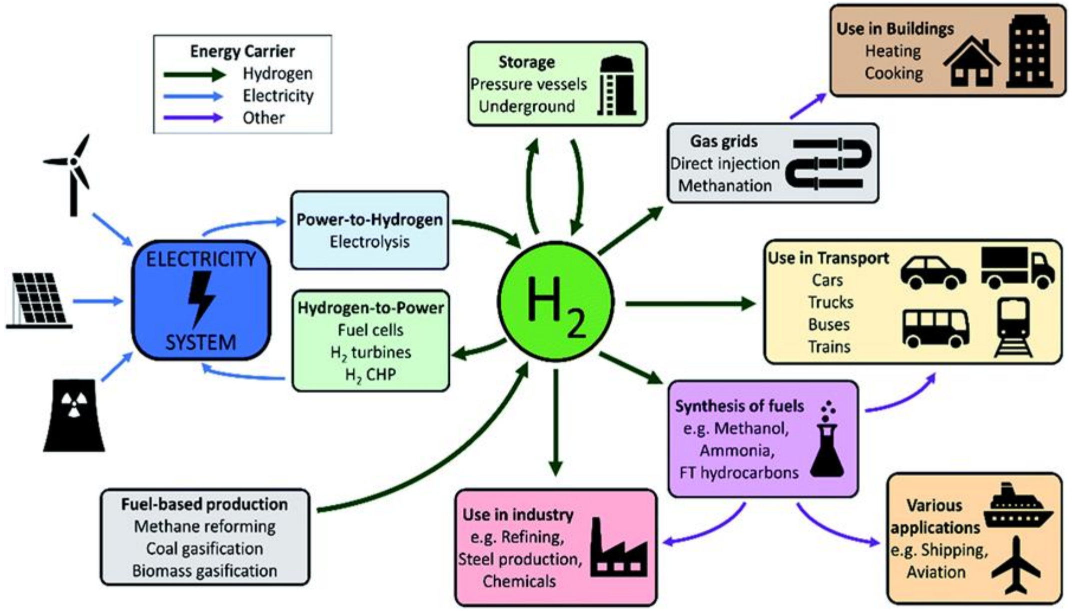
- Investigate biomass and plastic blends for potential of net-zero carbon emissions
- Continue to develop the machine learning model



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**
- **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
- **Accomplishments:**
    - The hydrogen baseline study was completed and is currently being prepared for publication



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Acknowledgments

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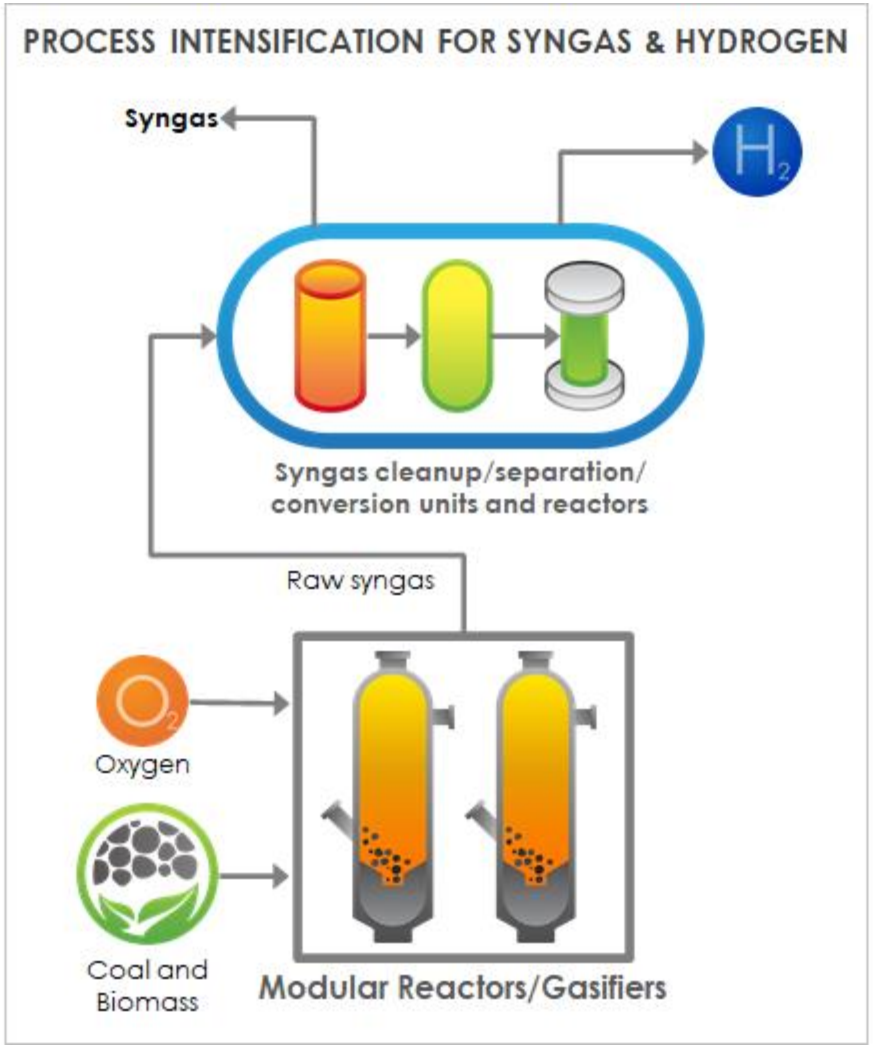
Conclusion

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?