Microwave Reactions for Gasification

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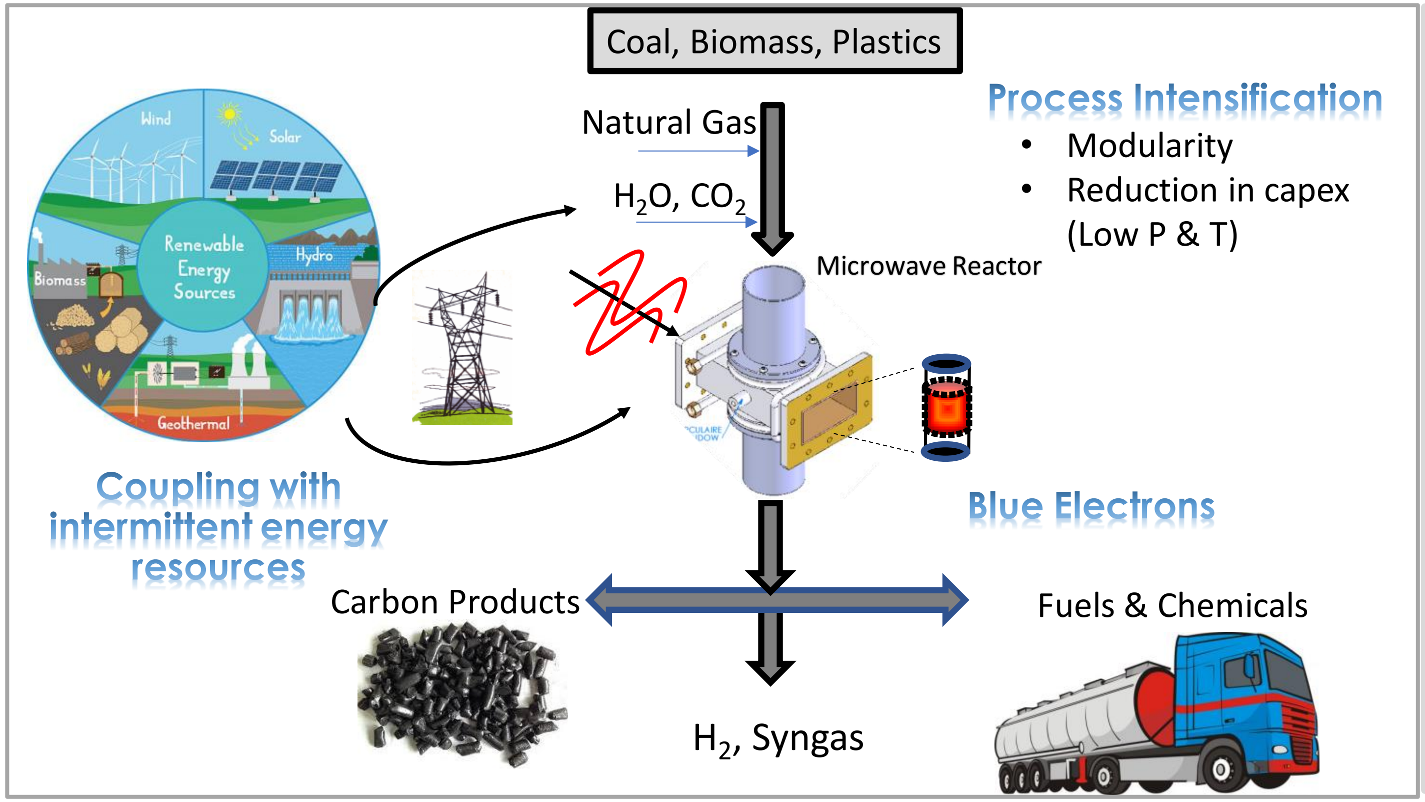
Presentation Outline

- **Background of Microwave Conversion**
- **Microwave Approaches for Gasification**
- **Supporting Tasks**
- **Results and Accomplishments**
- **Future Work**
- **NETL Microwave Capabilities**

Objective

Evaluate the benefits of applying microwave technology to multiple steps in a modular-scale gasification processes



- Rapid, selective heating with microwaves provides process intensification by reducing reactor size and downstream separation units
- Treatment of gasification products/outputs with microwaves can mitigate process upsets from off-spec operation
- Flexibility & tunability of microwave fields allow system to respond to variations in feed rate and composition, as well as to intermittent periods of reduced resource availability (eg. rapid start-up/shut-down)

Microwave Interaction with Materials

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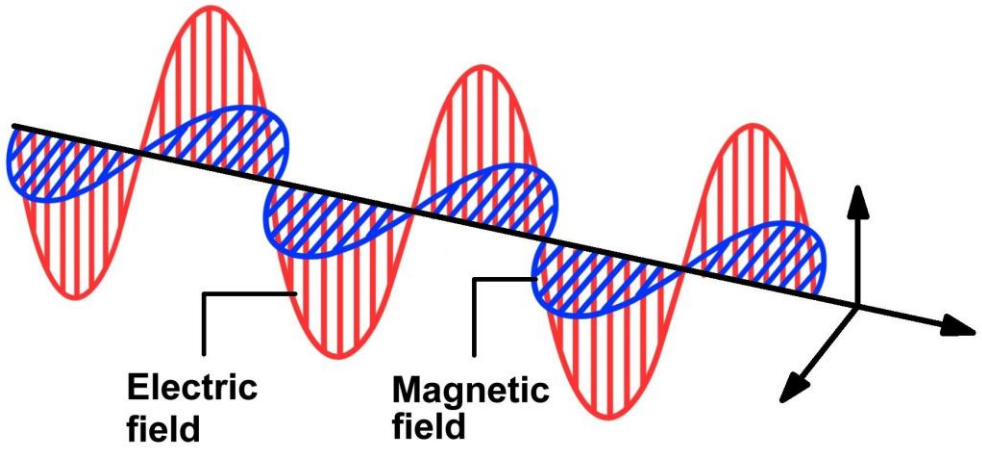


Real part represents the ability of the dielectric to store the energy

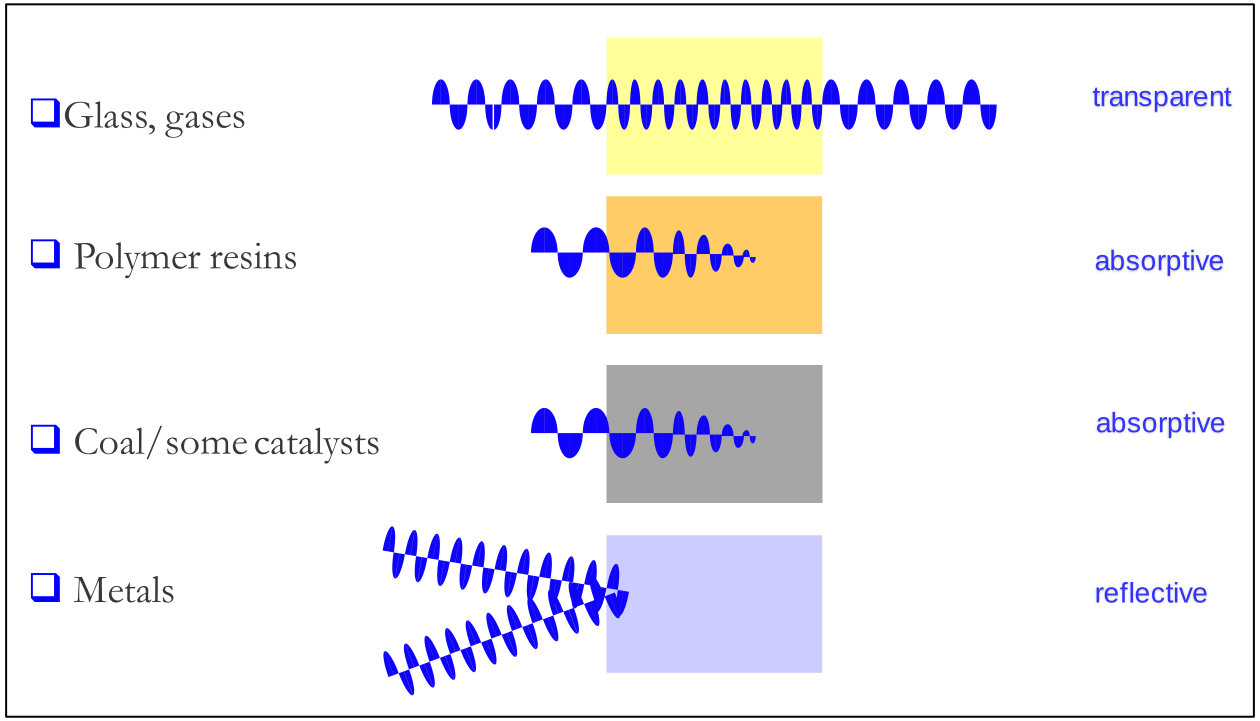
Permittivity → $\hat{\varepsilon}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Loss tangent measures the magnitude of the loss process

Imaginary part represents the ability of material to dissipate the energy

Magnetic field: Permeability
Magnetic loss tangent: $tan\delta_m = \mu''/\mu'$



MW frequency range between 0.3 GHz and 300 GHz (1 m to 1 mm)

$\upsilon =$ 2.45 GHz

$\lambda =$ 12.25 cm

E = 0.098 cm^{-1} (0.978 J/mol)

Opportunities Identified

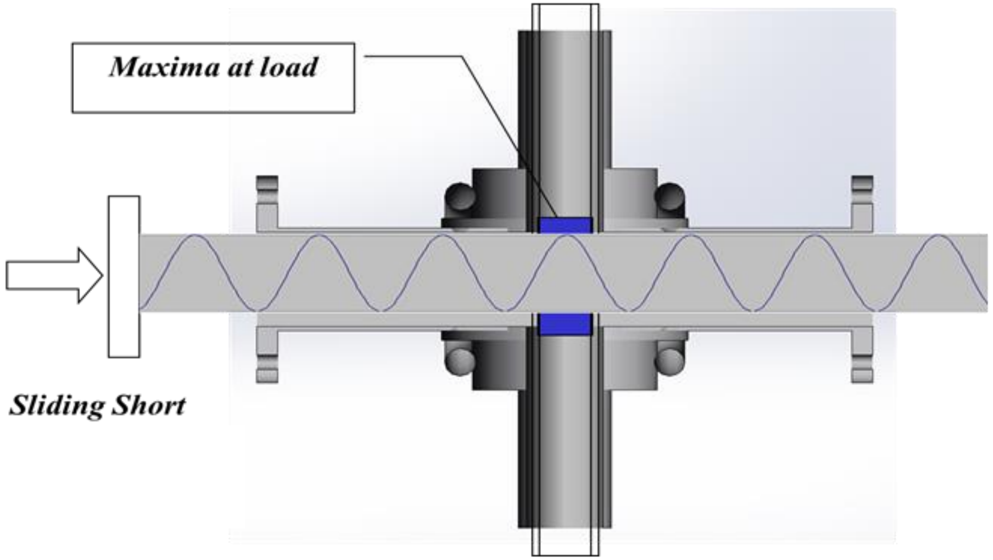
Three Microwave-based Approaches

1. **Modular microwave gasification in moving-bed gasifier**
2. **Microwave-enhance conversion of carbon in dry bottom ash from fluidized-bed gasifier**
3. **Microwave-enhanced, catalytic conversion of tars in syngas from conventional moving-bed gasifier**

Supporting Efforts:

- Microwave Reactor Model Development
- In-situ Characterization Technique for Microwave Processes

Approach #1: Moving-bed Microwave Gasification



Standing Wave applicator

<u>Test conditions:</u>
Temperature = 700°C
Pressure = 1 atm
Feed gas = 67% CO_2/bal N_2

Proximate analysis, dry basis	Lignite	Sub-bit.	Bituminous
Fixed Carbon, wt%	30.5	48.2	77.7
Volatile Matter, wt%	43.8	44.7	17.9
Ash	25.7	7.6	4.6
Ultimate analysis, dry basis	**Lignite**	**Sub-bit.**	**Bituminous**
Carbon, wt%	51.7	76.2	90.6
Hydrogen, wt%	3.57	6.2	4.9
Nitrogen, wt%	1.3	N. D.	N. D.
Sulfur, wt%	0.7	0.4	0.7
Oxygen, wt% (by difference)	17.0	9.6	~0

Goal: Test the effect of coal rank on CO_2 gasification performance in microwave reactor

Gasification Product Yields

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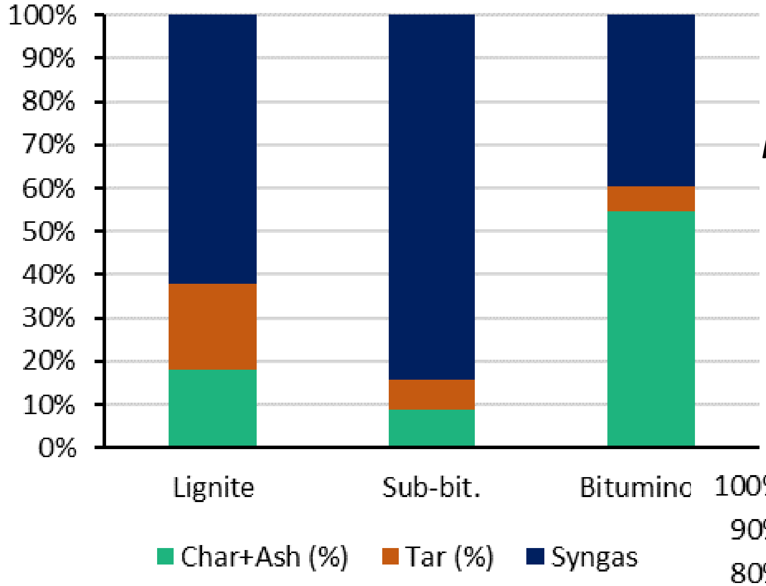
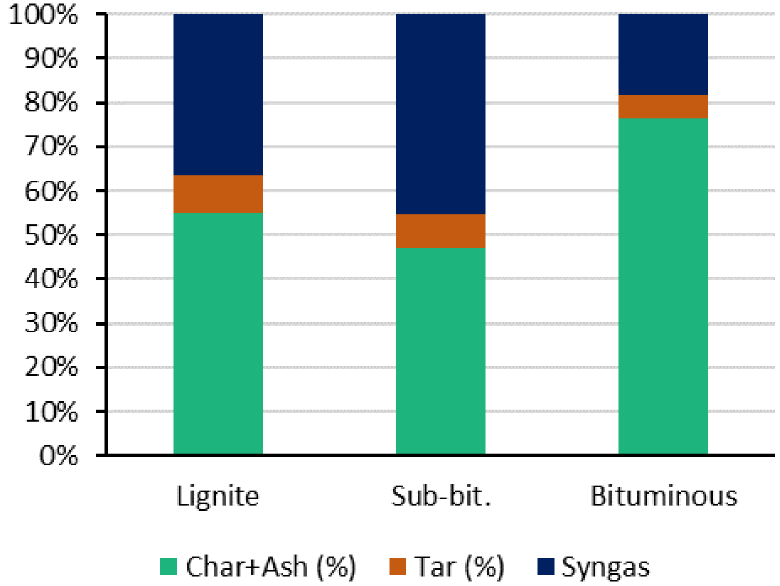
Effect of microwave:

- In all cases, microwave gasification led to greater syngas yields
- Much greater coal conversion (lower char yield) under microwave



Microwave

Conventional



Effect of coal rank:

- Sub-bituminous coal led to the greatest syngas yields
- High tar yield from lignite coal
- Low conversion of bituminous coal into syngas (highest fixed carbon content)

Syngas Production

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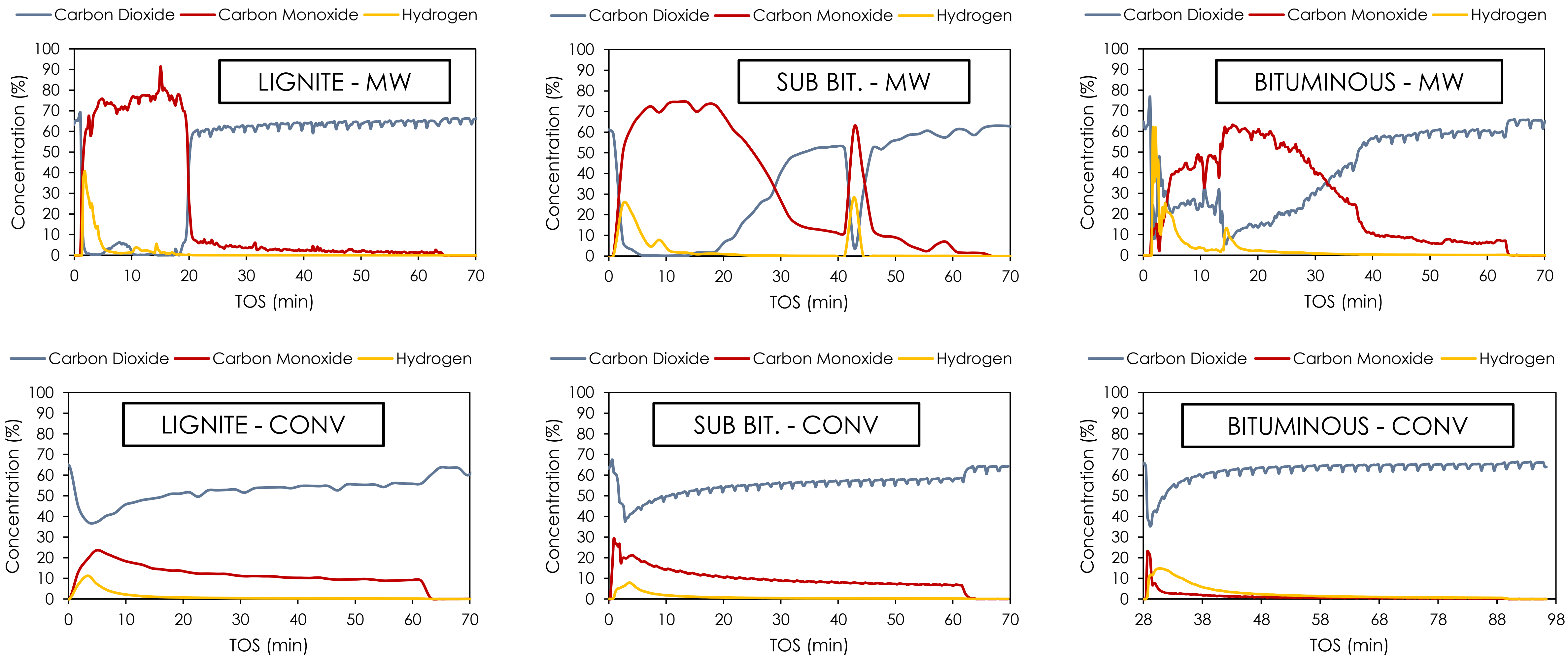
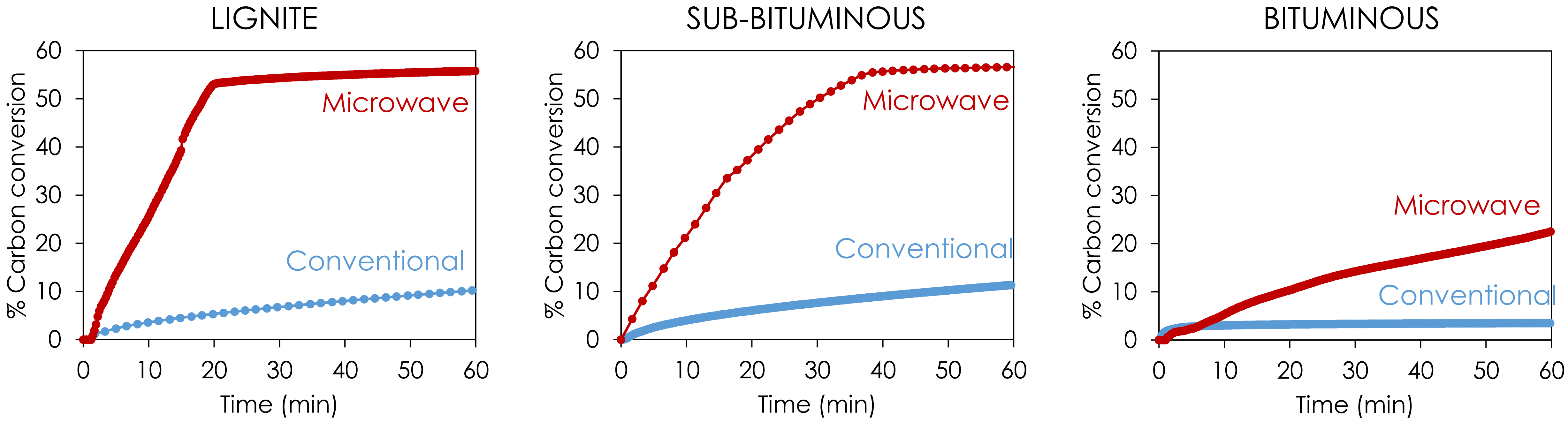


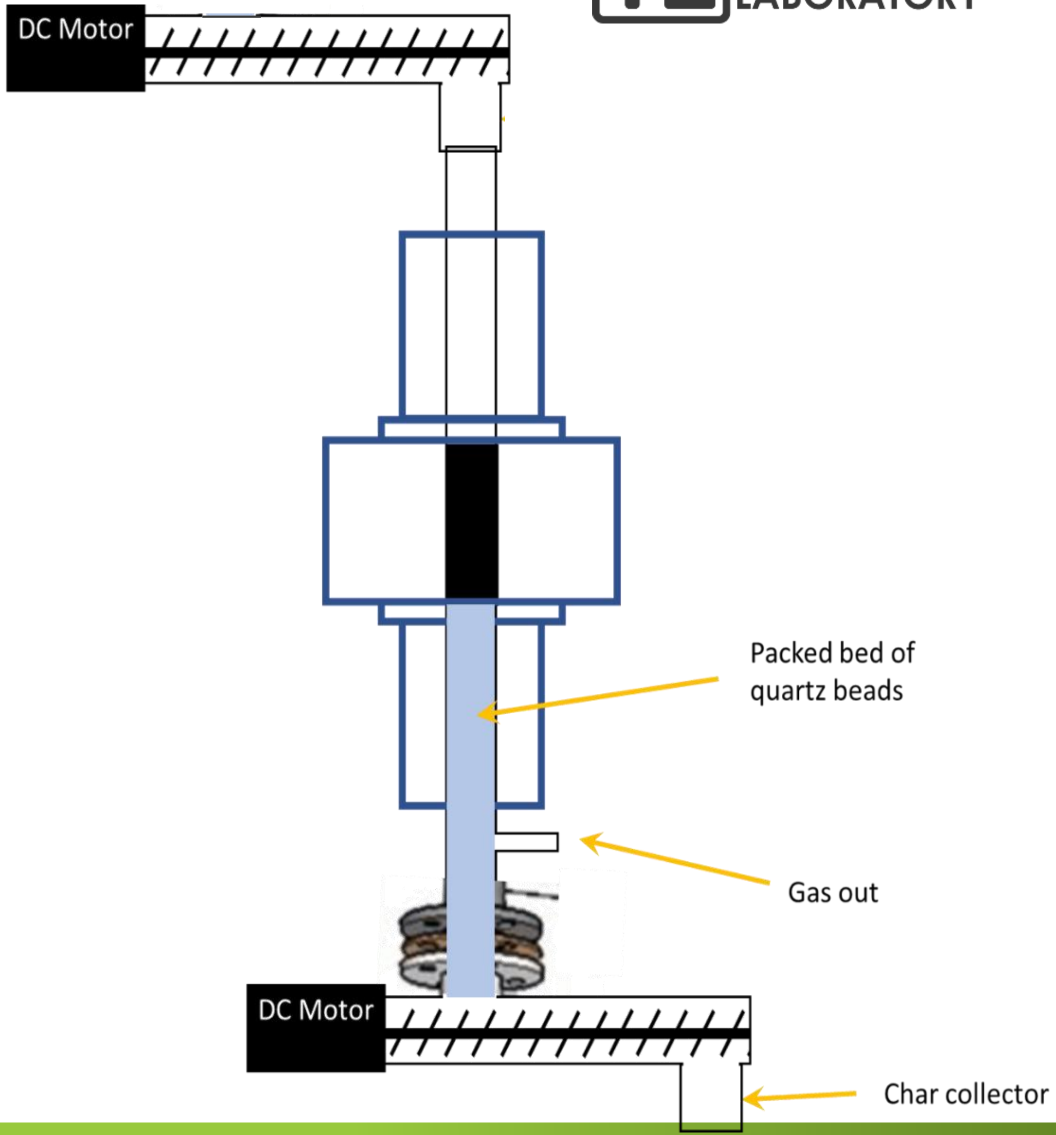
Carbon Conversion Efficiency

- **The percent of carbon in coal converted into gas ($CO+CH_4$)**
  - Lignite: max conversion in 20 mins
  - Sub bit.: max conversion in 40 mins
  - Bituminous: low conversion efficiency after 60 mins

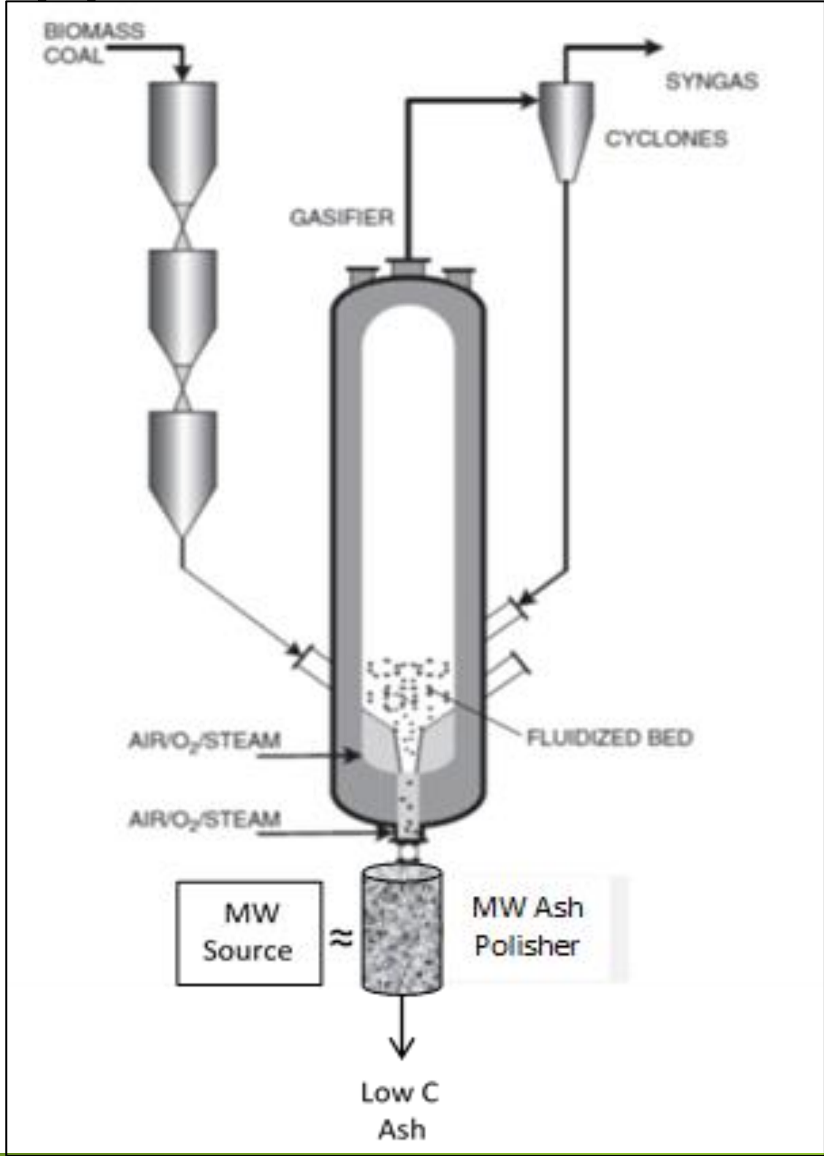


Recent Efforts

- **Modification of current microwave reactor for continuous solid and gas feeds**
  - Develop energy balance model for CGE comparisons
  - Optimize gas feed (CO_2/H_2O/air) to maximize CGE and CGE for a selected coal rank
  - Utilize testing results to develop model for reactor scale-up and design
- **COMSOL model for scaled-up design of microwave reactor(s)**
- **Additional co-gasification concepts: biomass, waste coal materials, waste plastics, MSW**
- **Go/No-Go decision to be made at end of EY2021 based on CGE calculations**



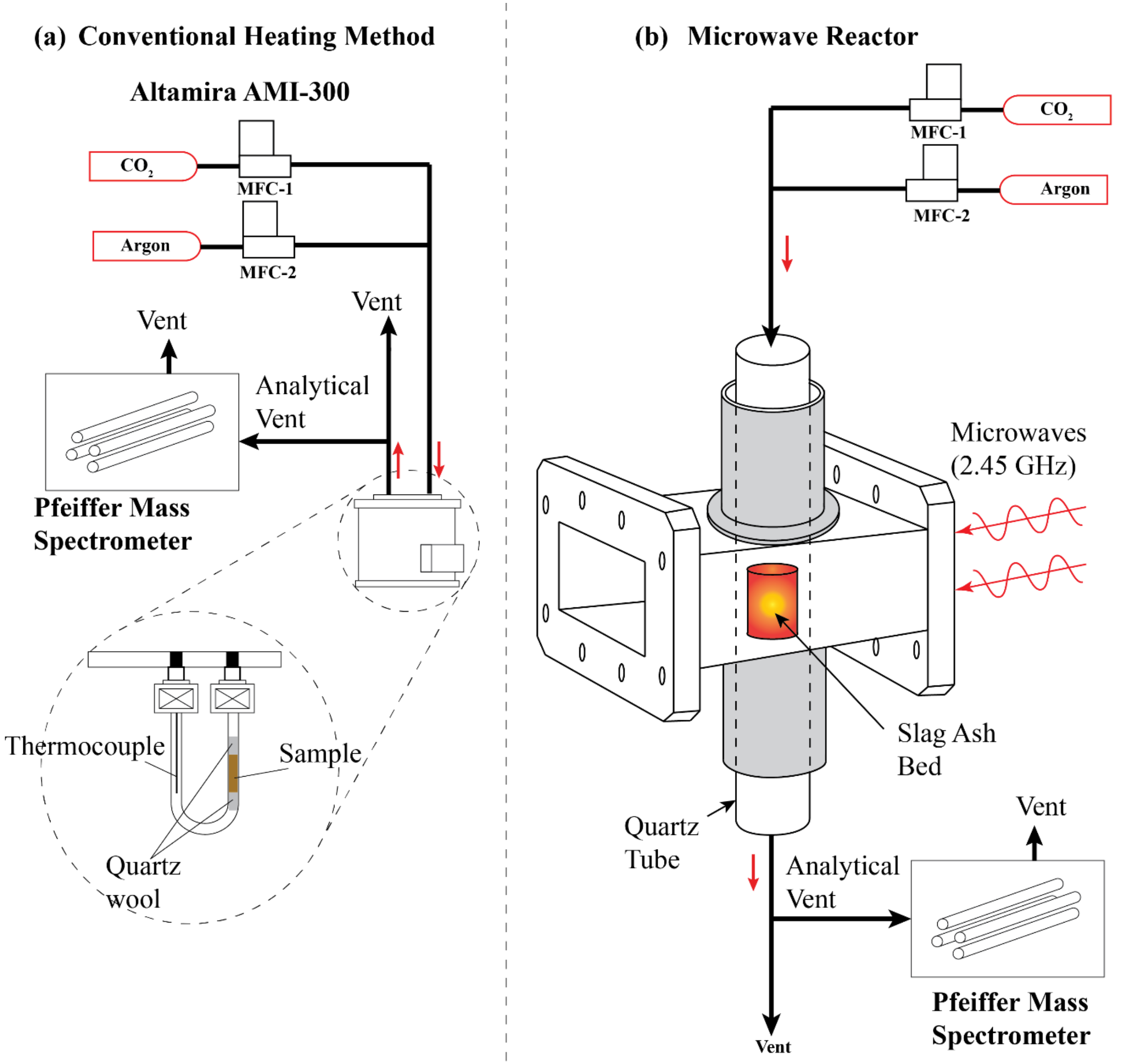
Approach #2: Carbon Conversion in Bottom Ash



- **Potential Benefits:**
  - Reduce size of fluidized-bed or entrained flow gasifier
  - Produce low-carbon ash material suitable for construction

- MW reactor technology can lower the gasification temperature and shorten the reaction time for gasification of carbon in bottoms ash
- Provides an opportunity for CO_2 utilization to help mitigate waste CO_2 in gasifier technology while increasing carbon monoxide yields
- MW increases the accessibility and reactivity of the carbon in the bottom ash samples
- Demonstrated MW enhanced the CO_2 gasification of the carbon in the GTI bottom ash at much lower temperatures (650, 700, 750 C) relative to the conventional heating method (800, 900, 1000 C)

CO_2 & Steam Conversion of Carbon in Ash



Enhanced Microwave (MW) gasification of bottoms ash from GTI coal gasifier

Experimental apparatus:

A. Conventional heating in the SSITKA unit
B. MW heating in plug flow reactor

CO_2 Conversion of Carbon in Ash

Results

Conventional

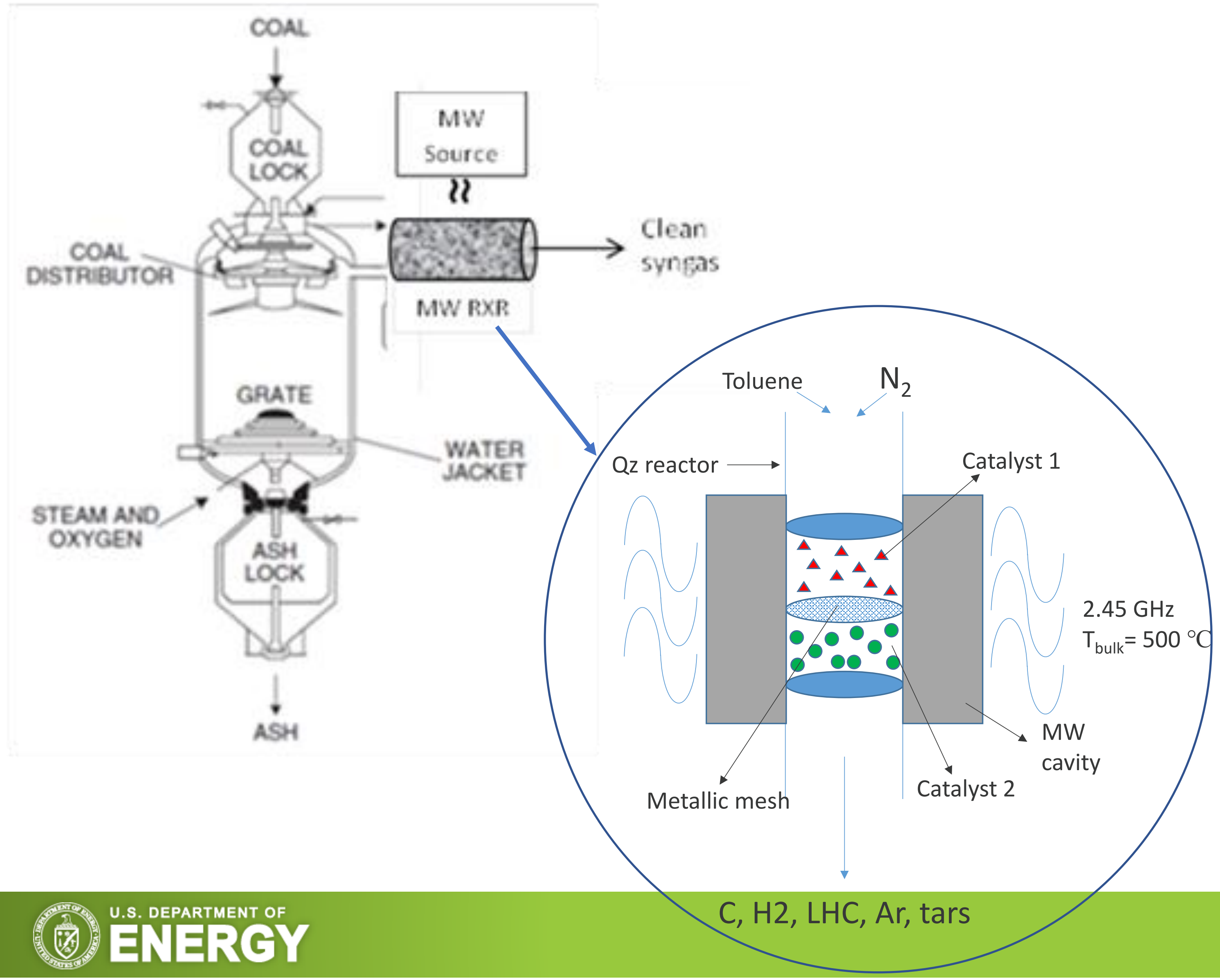
Temp. (°C)	CO_2 Conc. (%)	Reaction Time (min)	Carbon Conversion (wt%)
800	100%	60	2.5
900	100%	60	7.9
1000	100%	60	30.1
800	50%	60	0.7
900	50%	60	3.9
1000	50%	60	23.9
800	25%	60	0.0
900	25%	60	3.3
1000	25%	60	15.3

Microwave

Temp. (°C)	CO_2 Conc. (%)	Reaction Time (min)	Carbon Conversion (wt%)
650	100%	60	5.9
700	100%	60	7.1
750	100%	60	38.8
650	50%	60	30.6
700	50%	60	34.1
750	50%	60	21.8
650	25%	60	18.2
700	25%	60	28.2
750	25%	60	23.5

- Conventional heating method requires higher temperature.
- MW heating method can lower reaction temperature by 250 C
- Higher conversion using MW heating method

Approach #3: Tar Conversion in Syngas

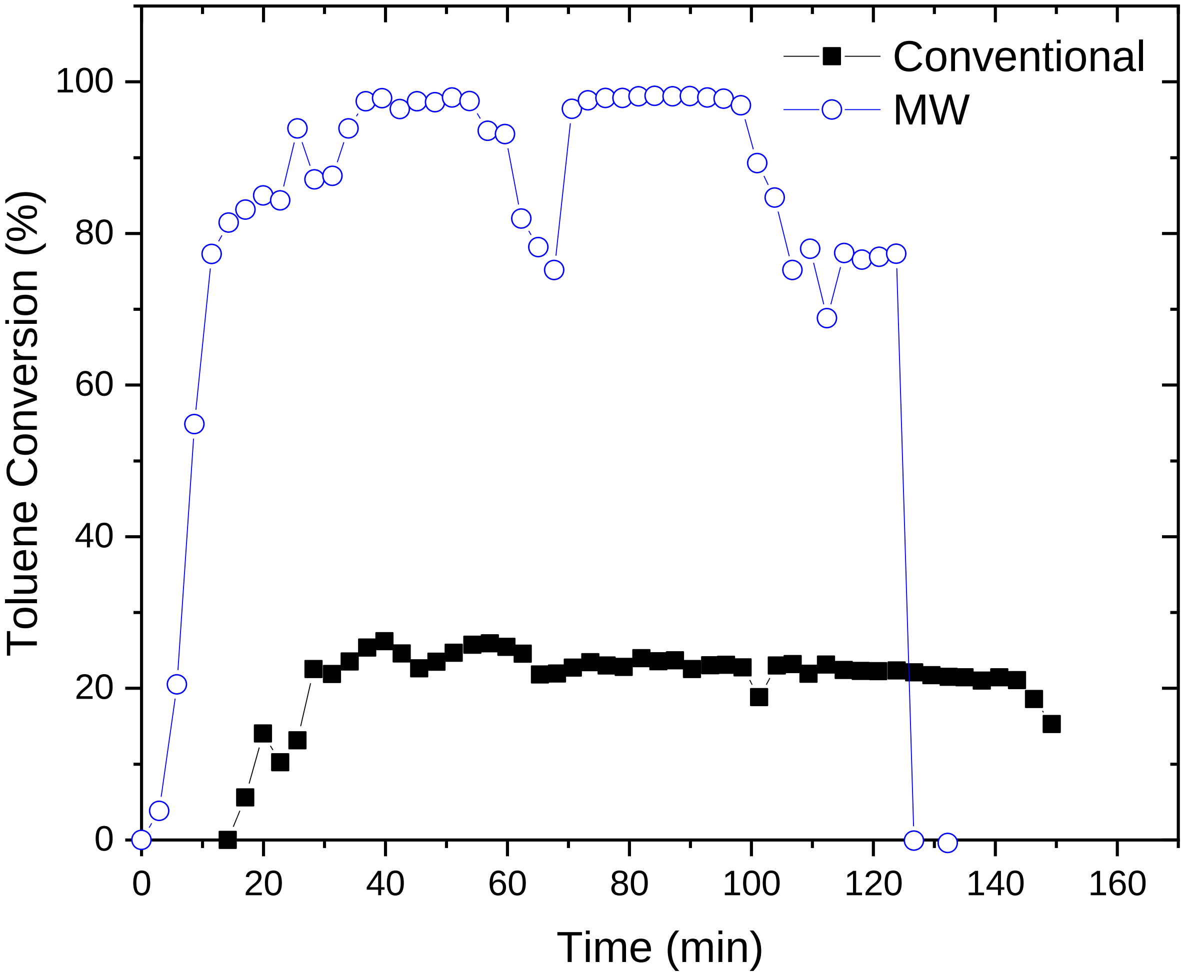


- **Potential Benefits:**
  - Address upstream process upsets and off-spec operation (i.e. spikes in syngas tar concentration
  - Prevent plugging and damage to downstream units that lead to unscheduled shutdowns
  - Reduce quantity of steam needed for tar conversion in gasifier

Tar Conversion

Model tar compounds

- **Experimental Conditions:**
  - Reduced Fe_2O_3/alumina – 100 sccm 20% H_2/N_2, 700°C, 4 hours
  - 1 vol% toluene
  - T = 500°C, 100 sccm N_2, 1000 W max
- **Main Findings:**
  - Microwave decomposition of toluene nearly 100% compared to <30% for conventional
  - Mostly converted to methane and soot without oxidant
  - Addition of steam and/or CO_2 needed to produce syngas and low mol. weight HCs



COMSOL Model of Gasification Reactor

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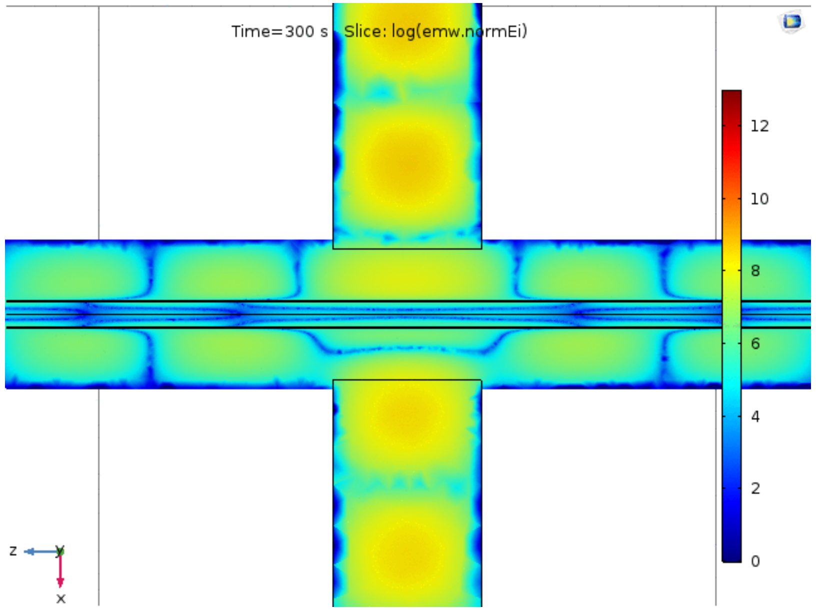
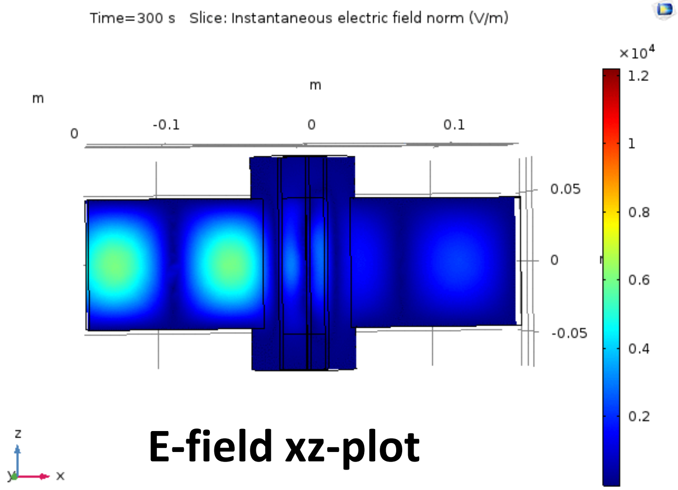
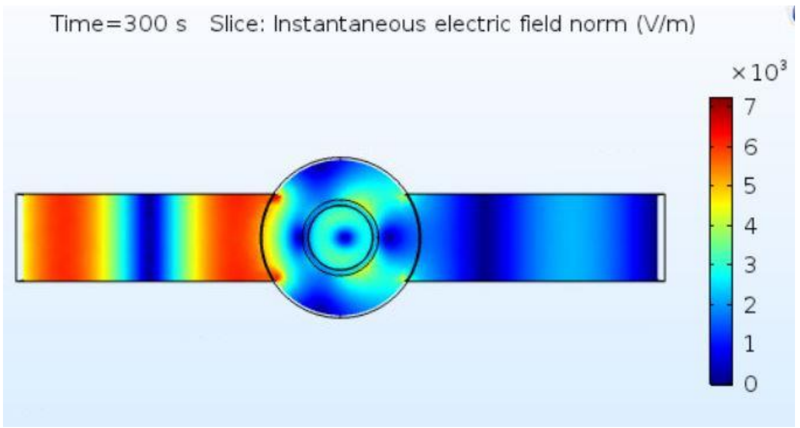


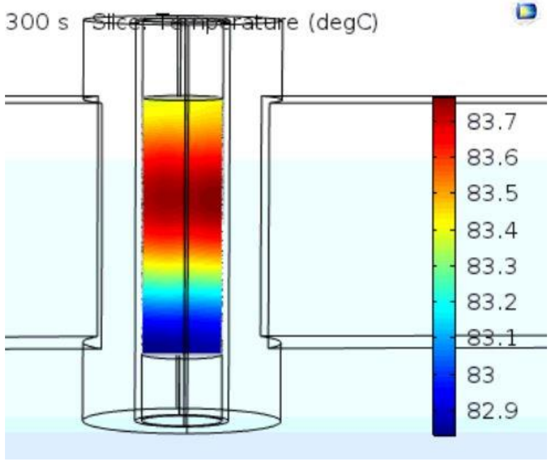
TM01 cavity diameter



E-field xz-plot



E-field xy-plot

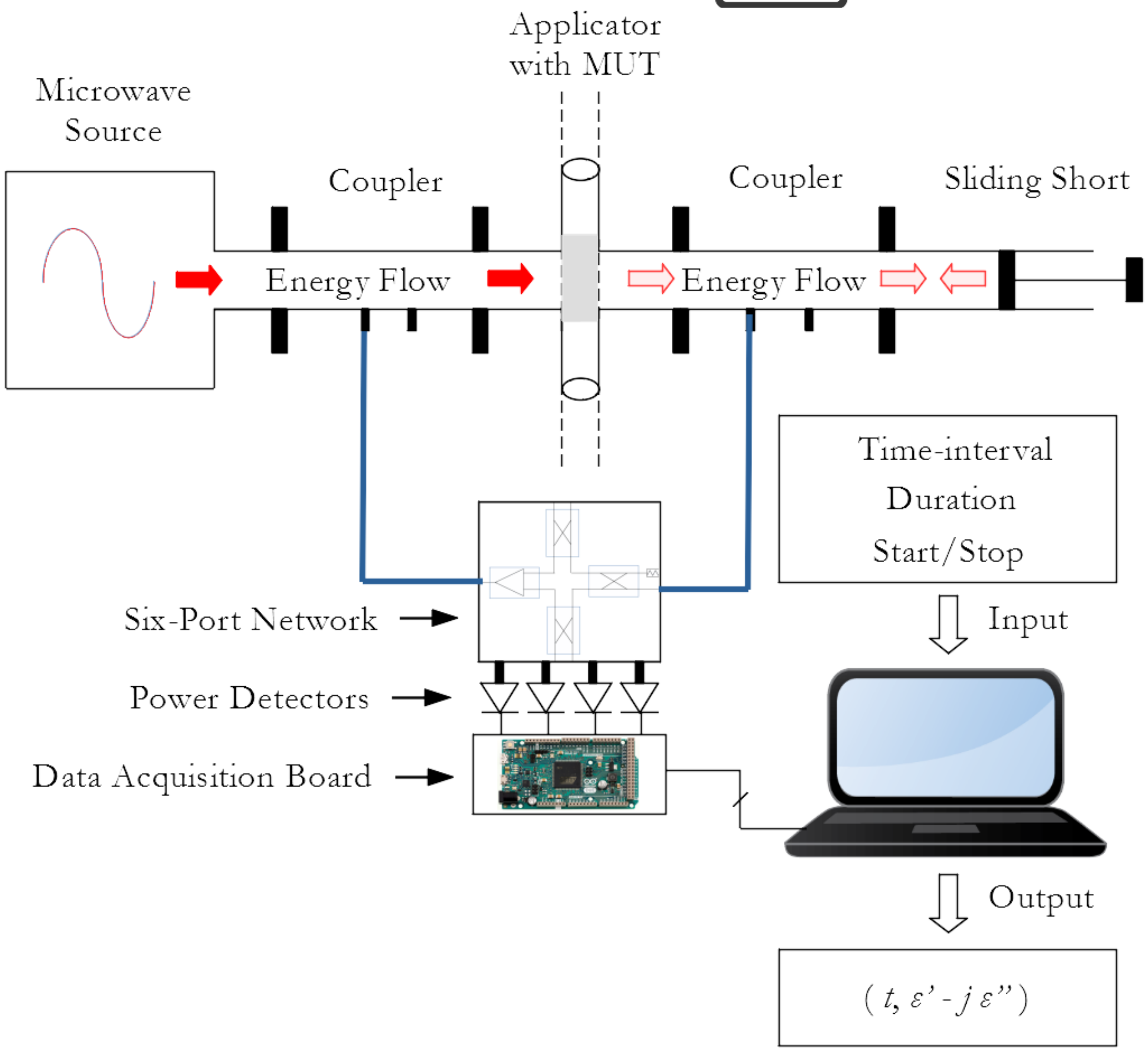


Temperature-plot

- Predict and visualize temperature profiles within the coal bed
- Predict hotspots and maximum temperatures reached
- Electric field distribution inside the reactor
- Optimize microwave reactor geometry and design
- T-profile and heating rate with changing frequency (VFMWR), power (MSU)

Six-Port *In situ* Characterization Method Development

- **Accurate material characteristics enable design of hardware to efficiently transfer energy to the material**
- **Current measurements:**
  - Room temperature with low power: coaxial two port and VNA, or a probe and one port VNA
  - High temperature with low power using a separate heating system
  - Coaxial two port using VNA while heating coaxial fixture to a higher temperature (500°C max.)
  - Resonant cavity with heated sample and accompanying VNA
  - Movement of sample leading to dissimilar heating & characterization environment
  - Time lag/delay between temperature measurement & properties characterization
- **Always in a different configuration than when used under power in the reactor**
- **Cost < $5000 compared to $30k**



Summary & Future Work

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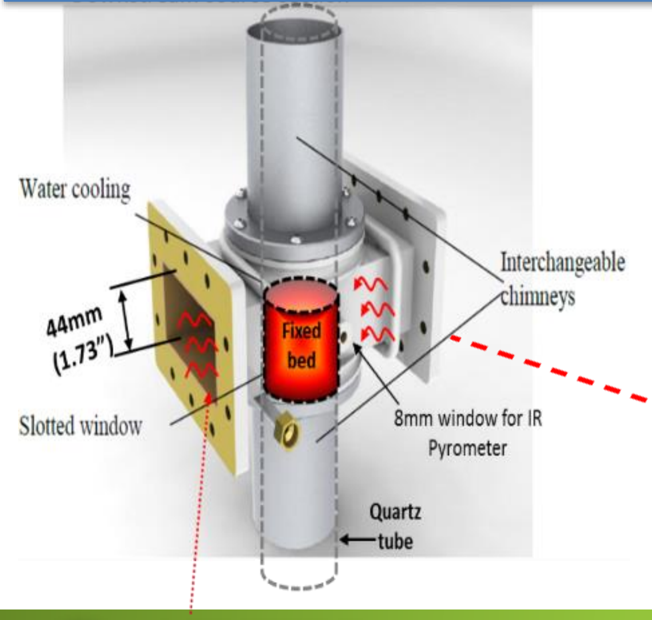
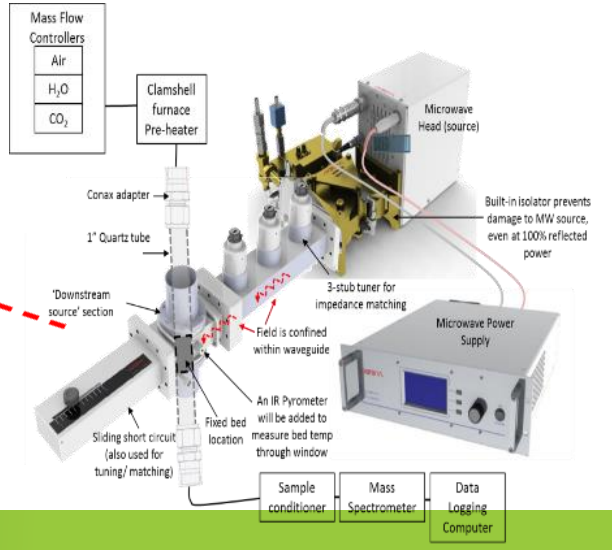
- **Microwave gasification of 3 different coal ranks using CO_2 demonstrated highest syngas yield for sib-bituminous sample**
- **Most rapid conversion under microwave energy was observed for lignite coal**
- **Microwave gasification produced significantly more syngas than conventional, thermal gasification for all three coal ranks**
- **System energy balances will be used during upcoming optimization studies with air and steam addition to compare modular microwave gasification to conventional**

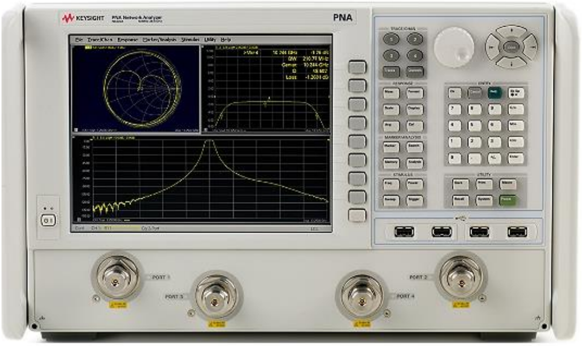
NETL Microwave Capabilities

- **Reactor Systems**
  - CEM Discover Microwave System
    - Frequency: 2.45 GHz
    - Small scale (batch)
  - Fixed frequency MW system
    - Frequency: 2.45 GHz & Power: 0 - 2kW
  - Variable frequency MW system
    - Frequency: 2 to 8 GHz & Power: 0 – 0.5 kW
    - Two different applicator configurations: Horizontal & vertical





VSM magnetometry



Vector Network Analyzers

Cell for EM measurement

- **Microwave Characterization**
  - Vector Network Analyzer (Keysight)
    - Maximum Frequency: 43.5 GHz
    - To measure electromagnetic (EM) properties of materials
  - Developing a cell to measure the electromagnetic properties up to 1200°C
  - VSM magnetometry and field dependent electrical transport properties from cryogenic up to elevated temperatures

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Questions?

Publications

- D. D. Miller, M.W. Smith, D. Shekhawat (2021) Microwave-induced selective decomposition of cellulose: Computational and experimental mechanistic study, *Journal of Physics and Chemistry of Solids* 150, 1098548.
- V. Abdelsayed, M. Smith, C. Ellison, D. Shekhawat (2020) Microwave-assisted Coal Conversion under Different Reactive Gas Environments and Temperatures, *Fuel*, In Final Review with Editor.
- V. Abdelsayed, C. Ellison, A. Trubetskaya, M. Smith, D. Shekhawa (2019) Effect of Microwave and Thermal Co-pyrolysis of Low-Rank Coal and Pine Wood on Product Distributions and Char Structure, *Energy & Fuels* 33 (8) 7069-7082.
- V. Abdelsayed, D. Shekhawat, Mark Smith, S. Hammache (2019) Microwave-Assisted Conversion of Low Rank Coal under Methane Environment, *Energy & Fuels* 33 (2) 905-915.
- V. Abdelsayed, D. Shekhawat, M.W. Smith, D. Link, A.E. Stiegman (2018) Microwave-assisted pyrolysis of Mississippi coal: A comparative study with conventional pyrolysis, *Fuel* 217, 656-667,
- T. Musho, C. Wildfire, N. Houlihan, E. Sabolsky, D. Shekhawat, (2018) Study of Cu2O particle morphology on microwave field enhancement, *Materials Chemistry and Physics* 216, 278-284.

Patents

- D. Shekhawat, D.A. Berry, M.W. Smith, C. Wildfire, V. Abdelsayed, M. Spencer (2019) Electromagnetic Field-Assisted Method for Chemical Conversion, U.S. Patent Application S-148,049.
- D. Shekhawat, M.W. Smith, C. Wildfire, V. Abdelsayed, M. Spencer, T.D. Musho (2020) Method of Chemical Conversion Using Microwave-Active Catalyst, U.S. Patent Application S-149,462.
- D.A. Berry, M. Spencer, M.W. Smith (2021) Method of Electromagnetic-Enhanced Chemical Reactions (S-164,474, S-164,475, S-164,516 - combined), *In preparation – Approved by NETL Invention Review Board April 23, 2021*.