Microwave-Enhanced Coal Gasification

Mark W. Smith
National Energy Technology Laboratory, U.S. Department of Energy, Morgantown, WV 26507

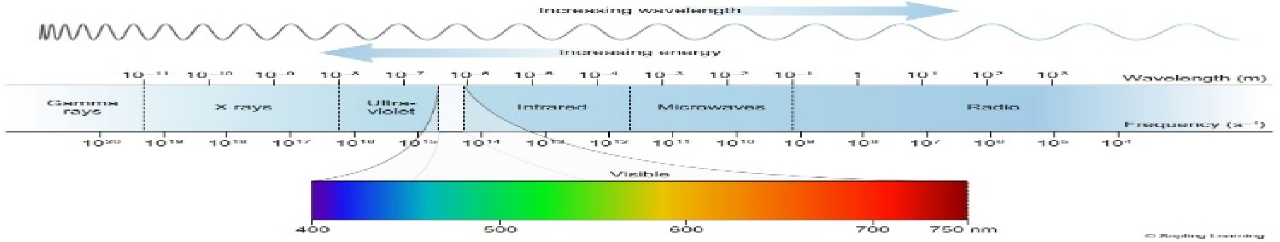
April 10, 2019

Objective

Demonstrate the benefits of microwave-enhanced coal conversion into syngas and char in a modular-scale gasification process

- Characterization of powder samples
- Computational modeling of particles and reactor
- Coal gasification reaction experiments

Changing the Conversion Paradigm



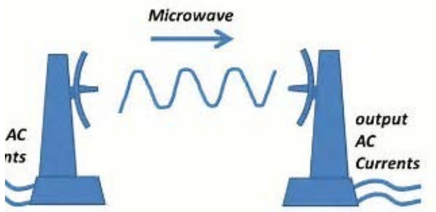
Fossil Fuels

Traditional Thermal Approach

Plasma

Fossil Fuels

Laser



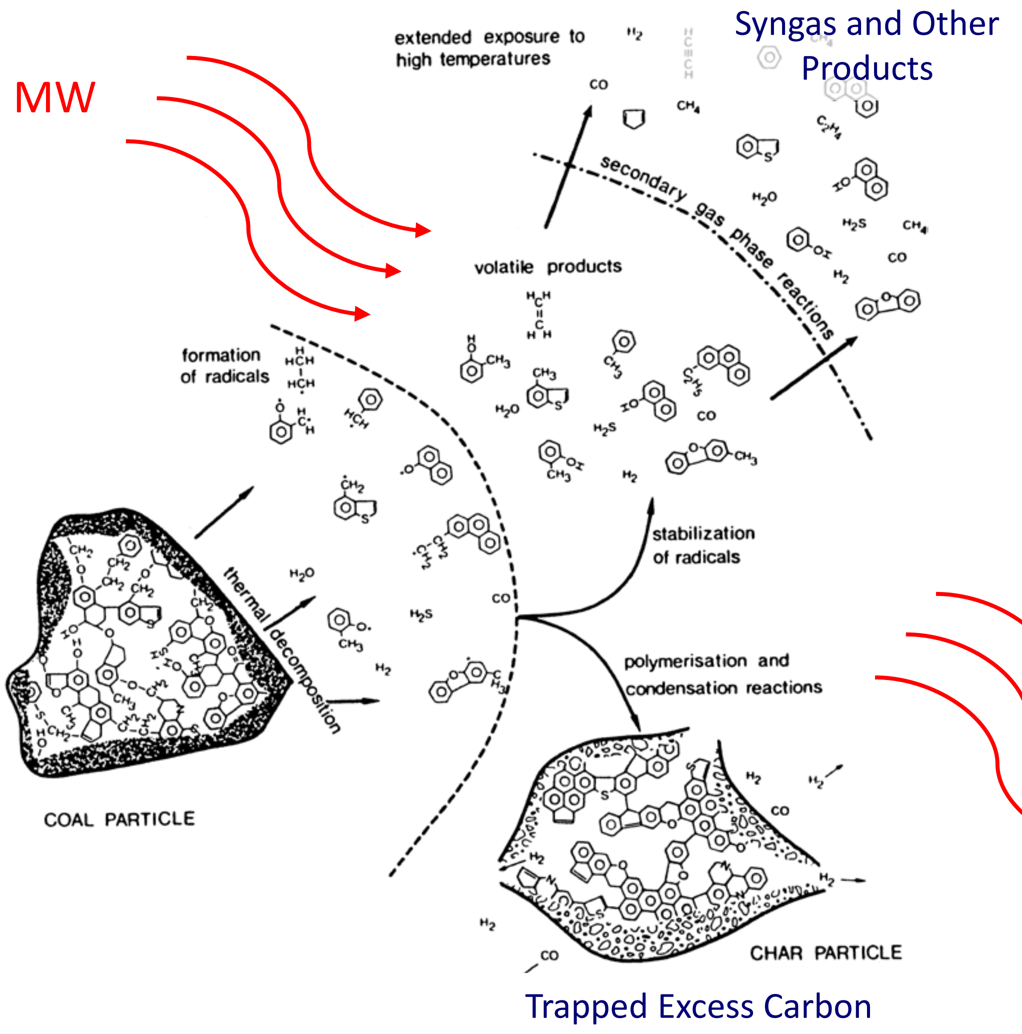
Microwave

Non-Traditional EM Processes

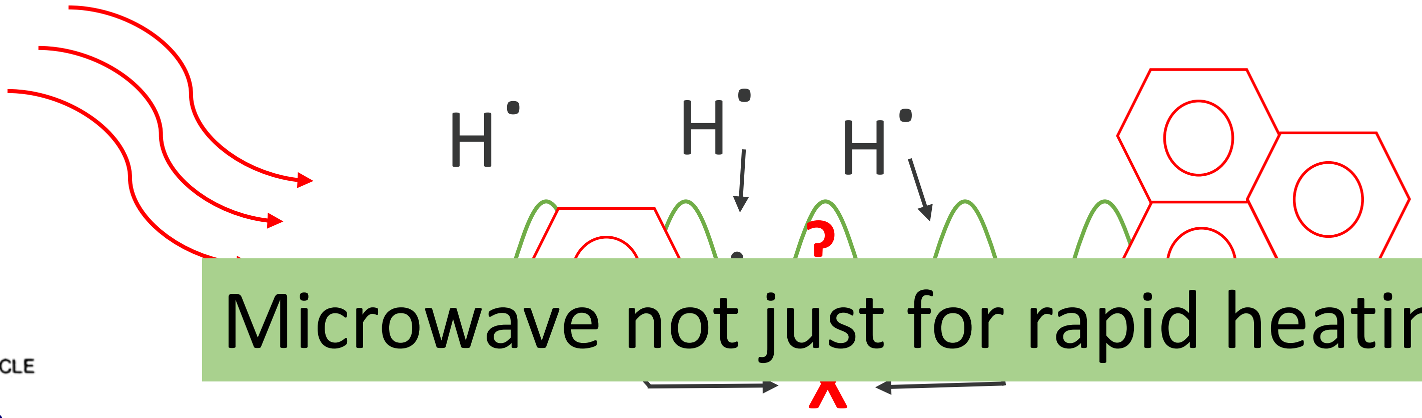
Benefits of Microwave-Assisted Processes

- **Rapidly achieve desired temperature (seconds to minutes)**
  - Minimize start-up and shut-down times
- **Selective activation/heating of coal and other reacting species**
  - Improve product distribution and selectivity
  - Reduce size of reactors
  - Reduce catalyst deactivation that occurs from bulk heating
- **Eliminate or reduce size of other process units (e.g. separations, compressors, heat exchangers)**

Microwave-Assisted Coal Conversion



- Microwaves induces
  - Thermal effect
  - Microwave-specific effects associated with loss processes
- Presence of chemical radicals specially H• in presence of MW could behave differently
- Recombination of radicals under MW could results in:
  - Altering the condensation pathways and hence the product distribution
  - Less trapped carbon under MW pyrolysis

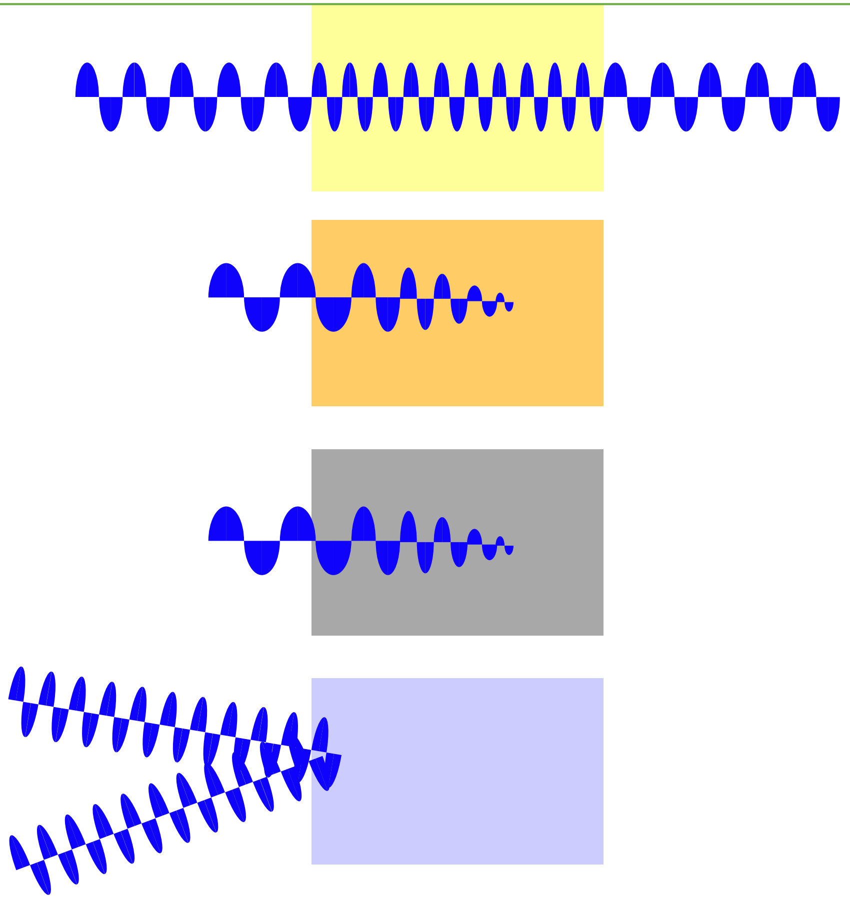


Microwave not just for rapid heating

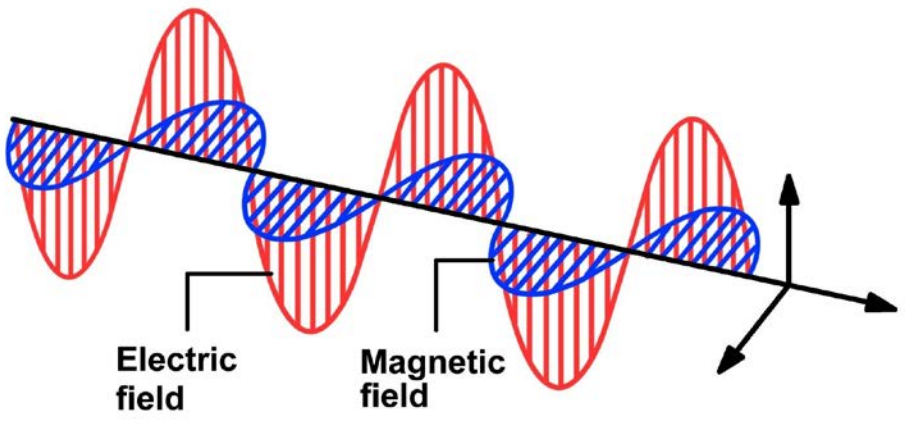
K. Miurar (2000) Fuel Process. Tech. 62, 119–135.

Microwave Interaction with Materials

- Glass, gases — transparent
- Polymer resins — absorptive
- Coal/some catalysts — absorptive
- Metals — reflective



Microwave Energy



MW frequency range between 0.3 & 300 GHz
$\upsilon = $ 2.45 GHz
λ = 12.25 cm
E = 0.098 cm^{-1} (0.978 J/mol)

A material's ability to absorb microwave depends on:

- Dielectric properties
- Frequency of microwave energy
- Temperature of material

Real part represent the ability of the dielectrics to store the energy

Permittivity

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

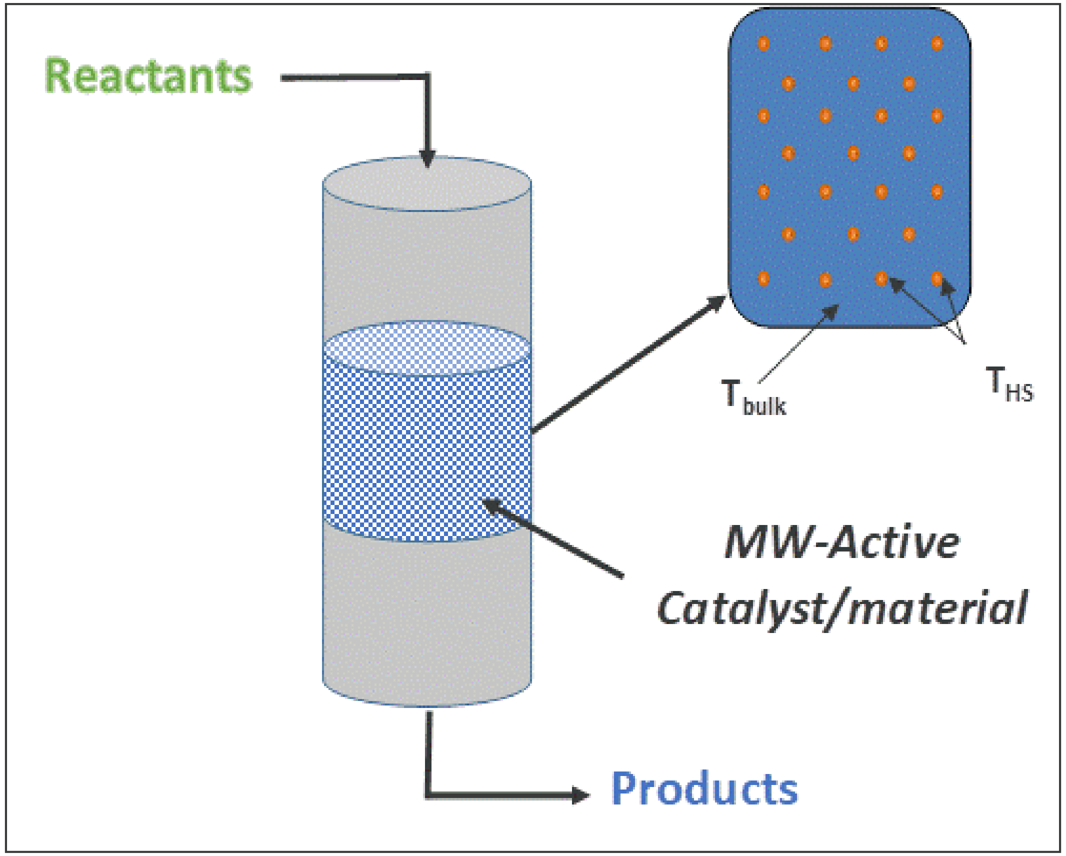
$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Loss tangent to measure the magnitude of the loss process

Imaginary part represents the ability of material to dissipate the energy

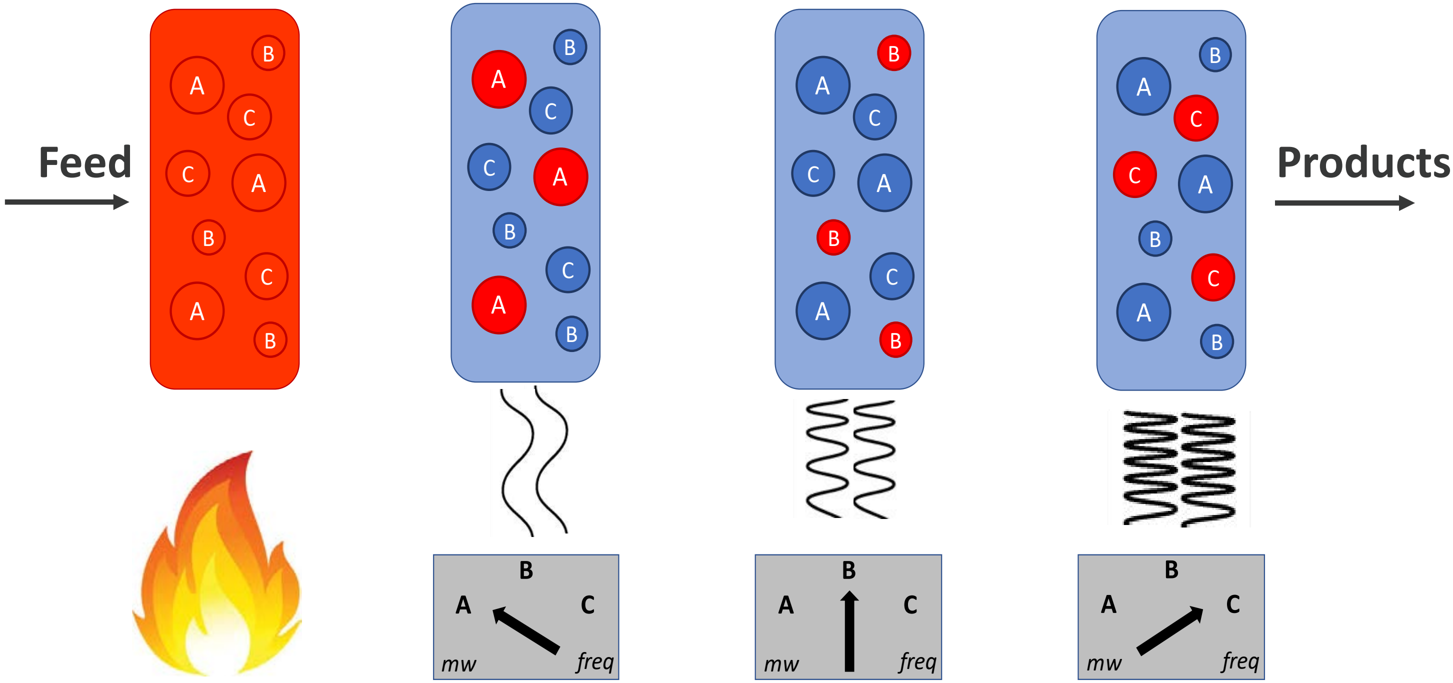
Magnetic field: Permeability
Magnetic loss tangent: $tan\delta_m = \mu''/\mu'$

Microwave-Enhanced Reactions



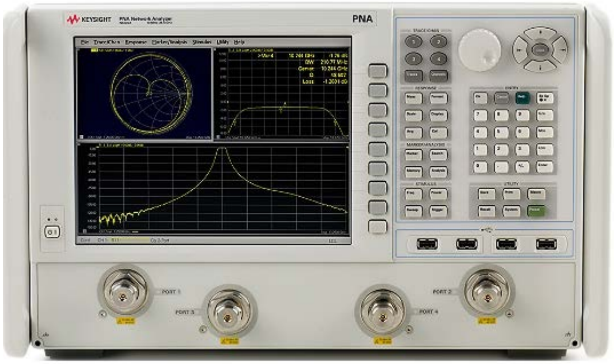
Microwave Input Strategies:

- Power and intensity; optimized pulsing method
- Variable frequency for selective activation of reacting species
- Microwave-active catalysts (dielectric and/or magnetic interaction)



NETL MW Capabilities
Characterization

- **Microwave Characterization**
  - Vector Network Analyzers (Keysight N5231A PNA-L & N5222A PNA)
    - 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
  - Spectrometers



Vector Network Analyzers

VSM magnetometry

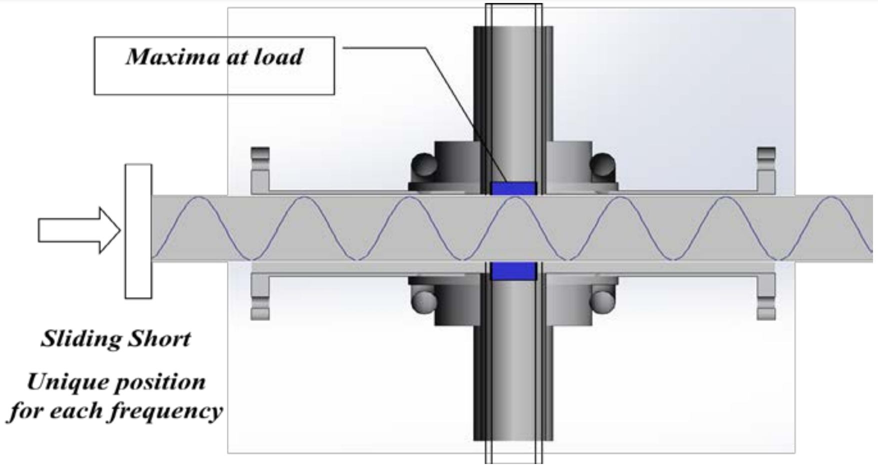
OceanOptics Spectrometer

Cell for EM measurement

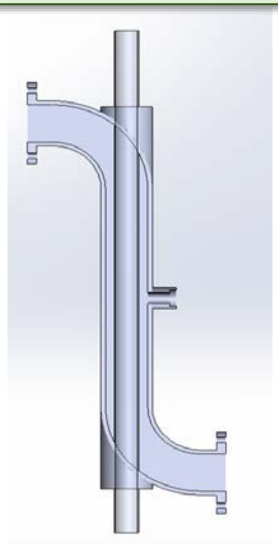
NETL MW Capabilities
Reactors

NATIONAL ENERGY TECHNOLOGY LABORATORY

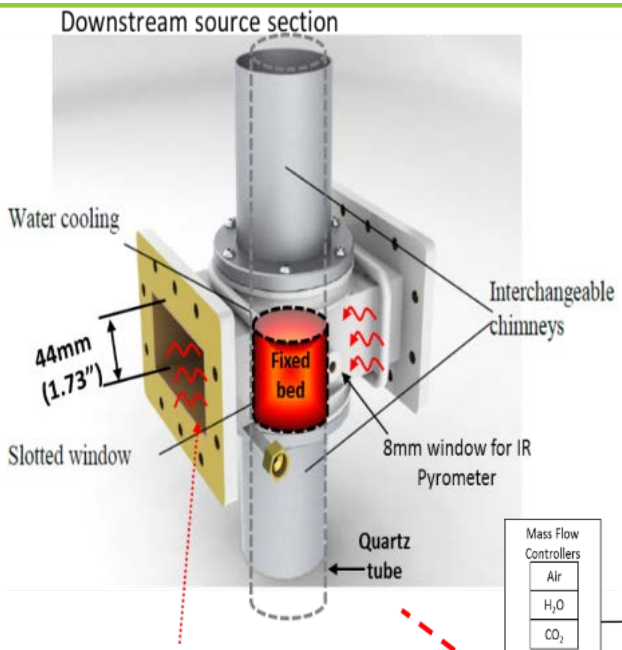
- **Reactor Systems**
  - **CEM Discover Microwave System**
    - Frequency: 2.45 GHz
    - Small scale (batch)
  - **Fixed frequency MW system**
    - Frequency: 2.45 GHz & Power: 0 - 2kW
  - **Variable frequency MW system**
    - Frequency: 2 to 8 GHz & Power: 0 – 0.5 kW
    - Two different applicator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

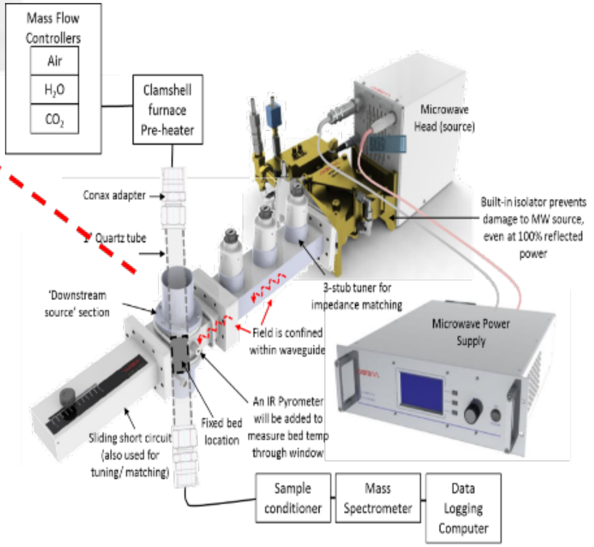


Standing Wave applicator



Dual E-Band Applicator

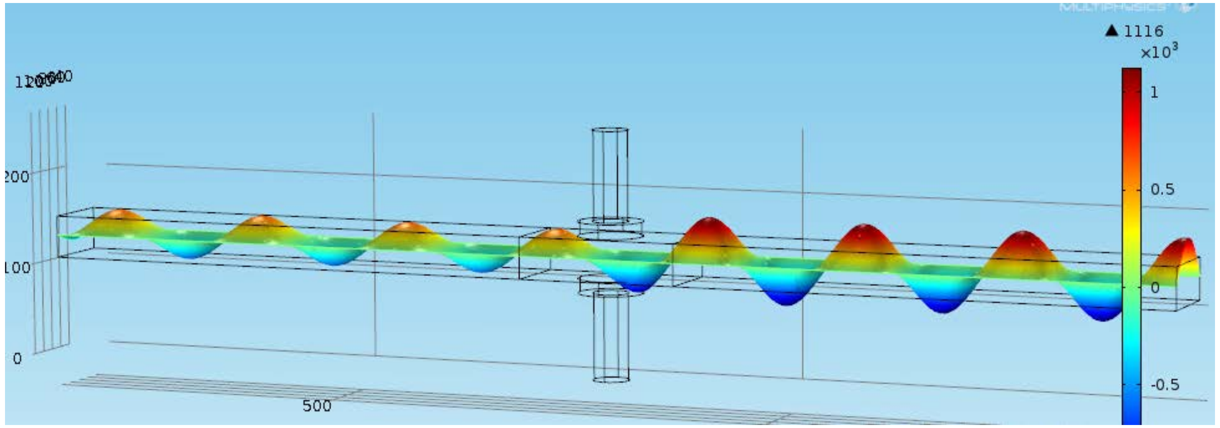


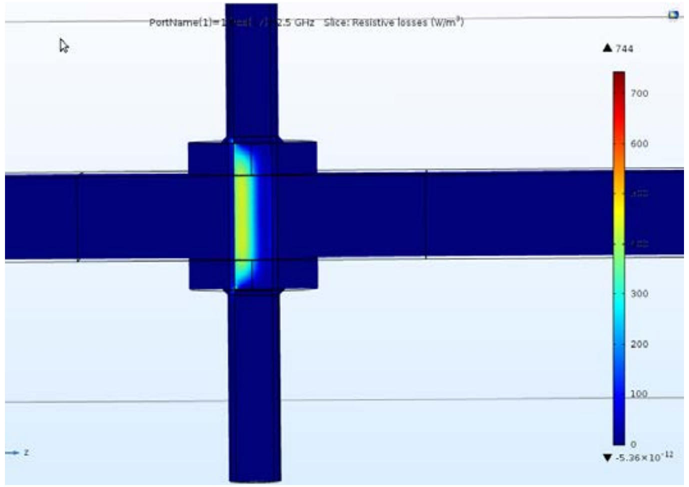


Multi-scale FDTD Simulations of Microwave Interactions

Macroscopic Electromagnetic Waveguide Interaction

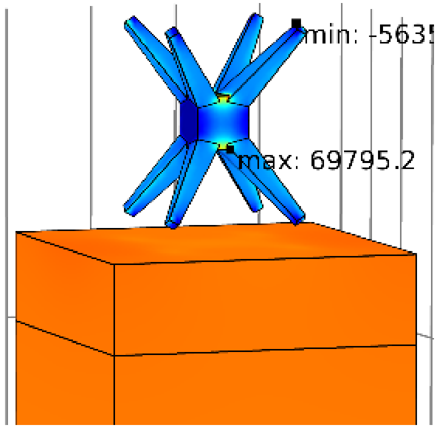
Electric Field Y-dir Contours
Electric Field Deformed Shape
f=2.45Ghz





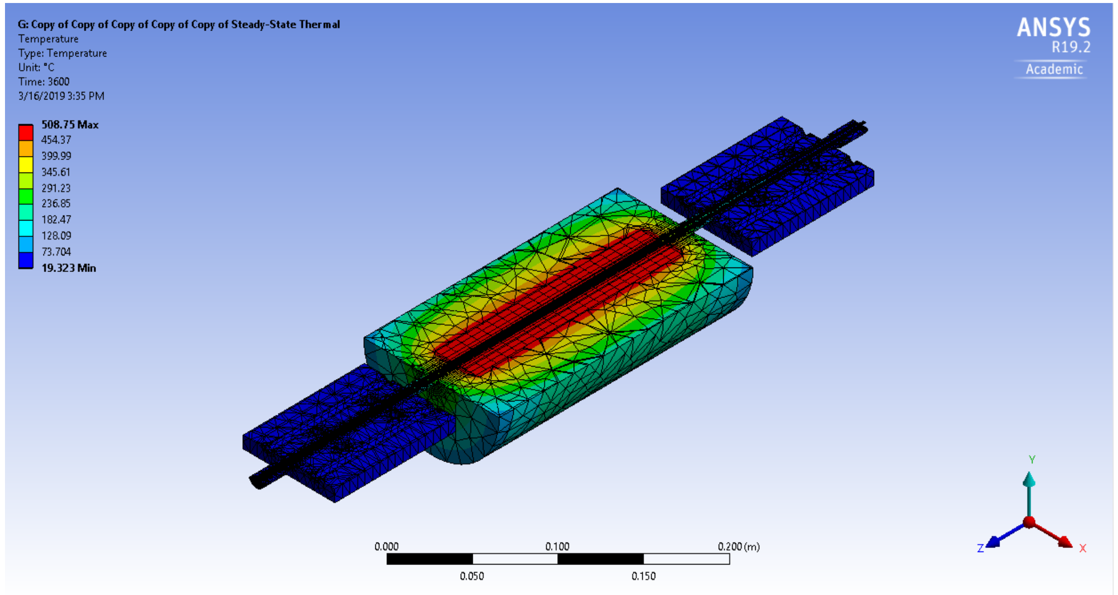
Prediction of Local Heat Flux and Energy Deposition

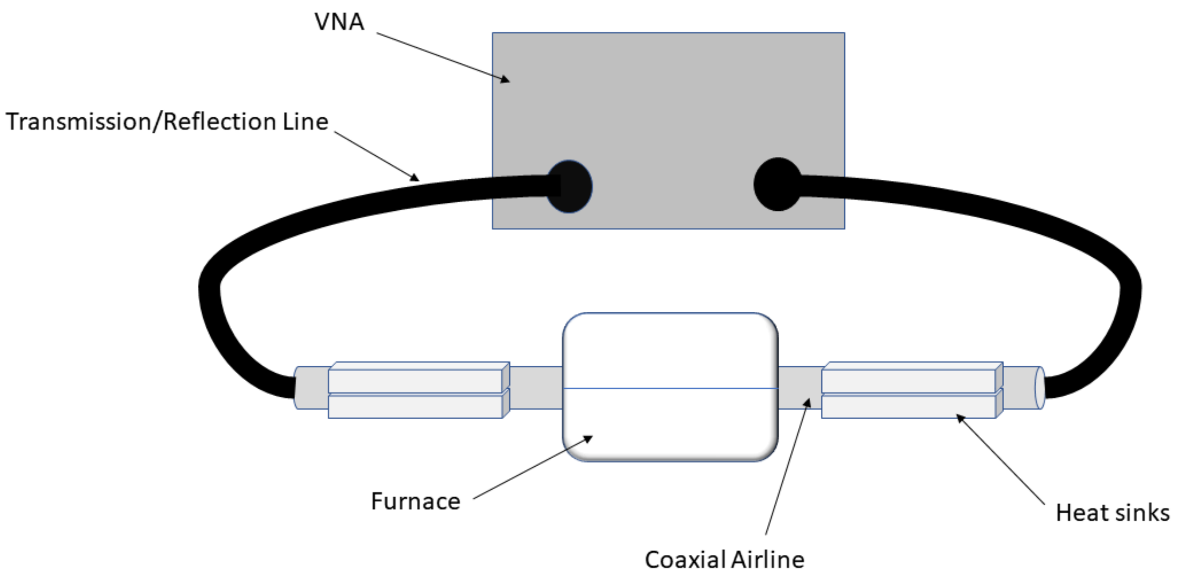
Microscopic Electromagnetic Material Interaction



Complex Material Characterization

- Modeled and validated method for complex material testing
- High temperature testing cell
- Temperature dependent microwave reaction

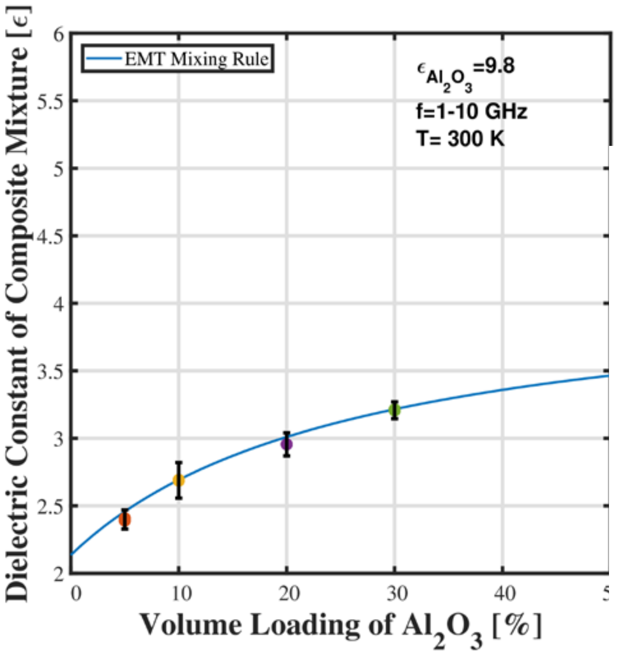


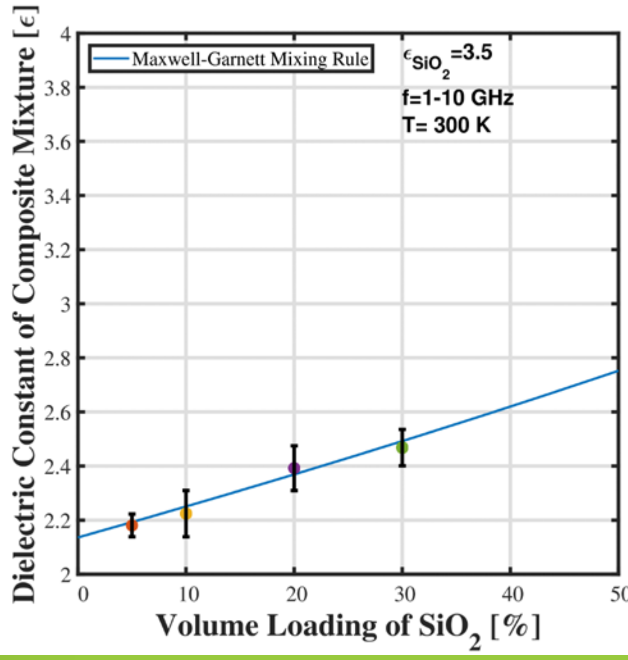


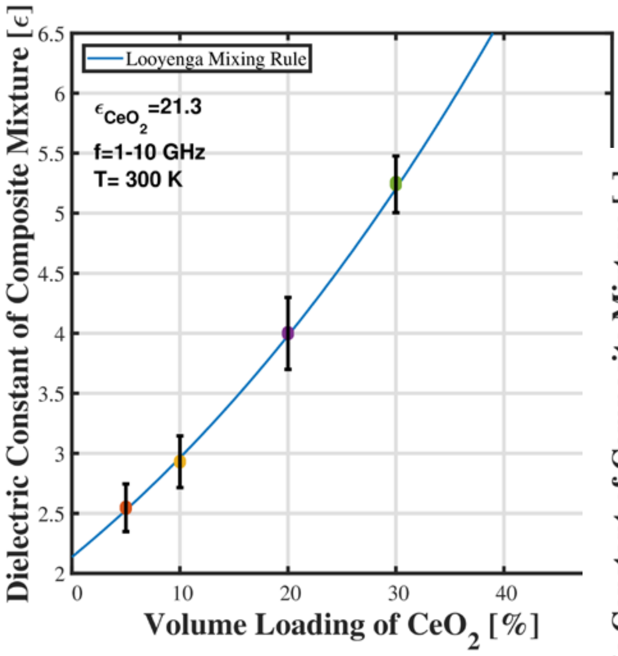
MW Reaction Simulation Modeling

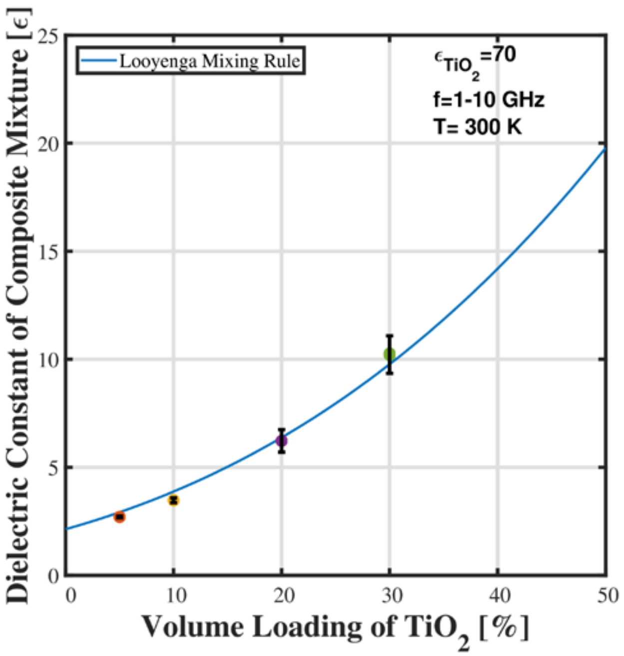
NATIONAL ENERGY TECHNOLOGY LABORATORY

- Predicting properties related to interaction
- Machine learning prediction of coal in MW field
- In-situ monitoring of reactions

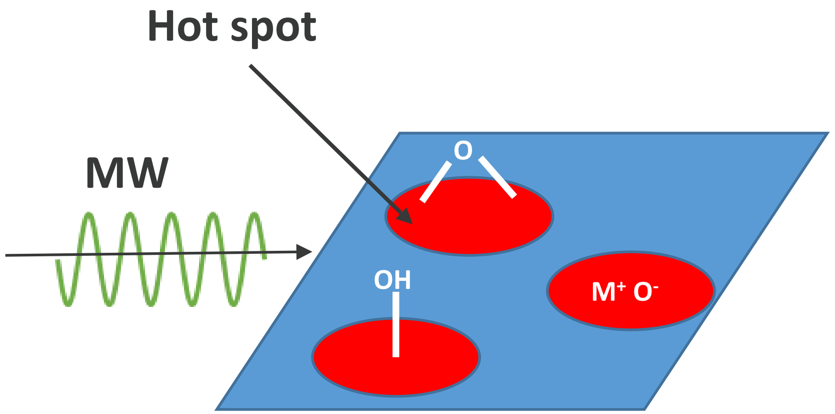






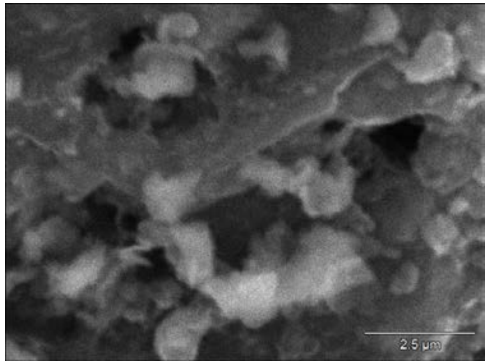


Microwave Generation of Coal Chars

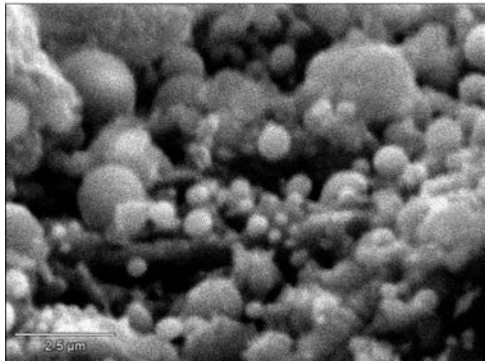


Formation of hot spots during MW pyrolysis due to dipolar polarization

Mississippi raw



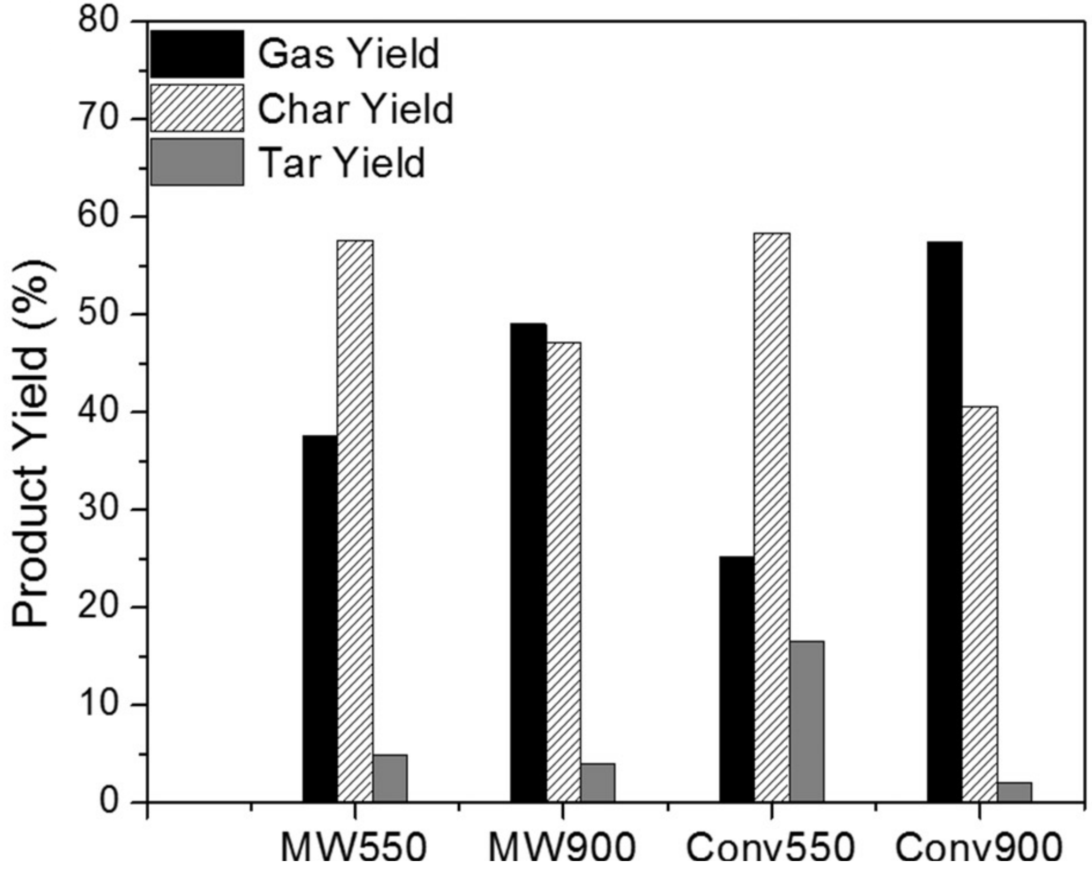
C-conv550

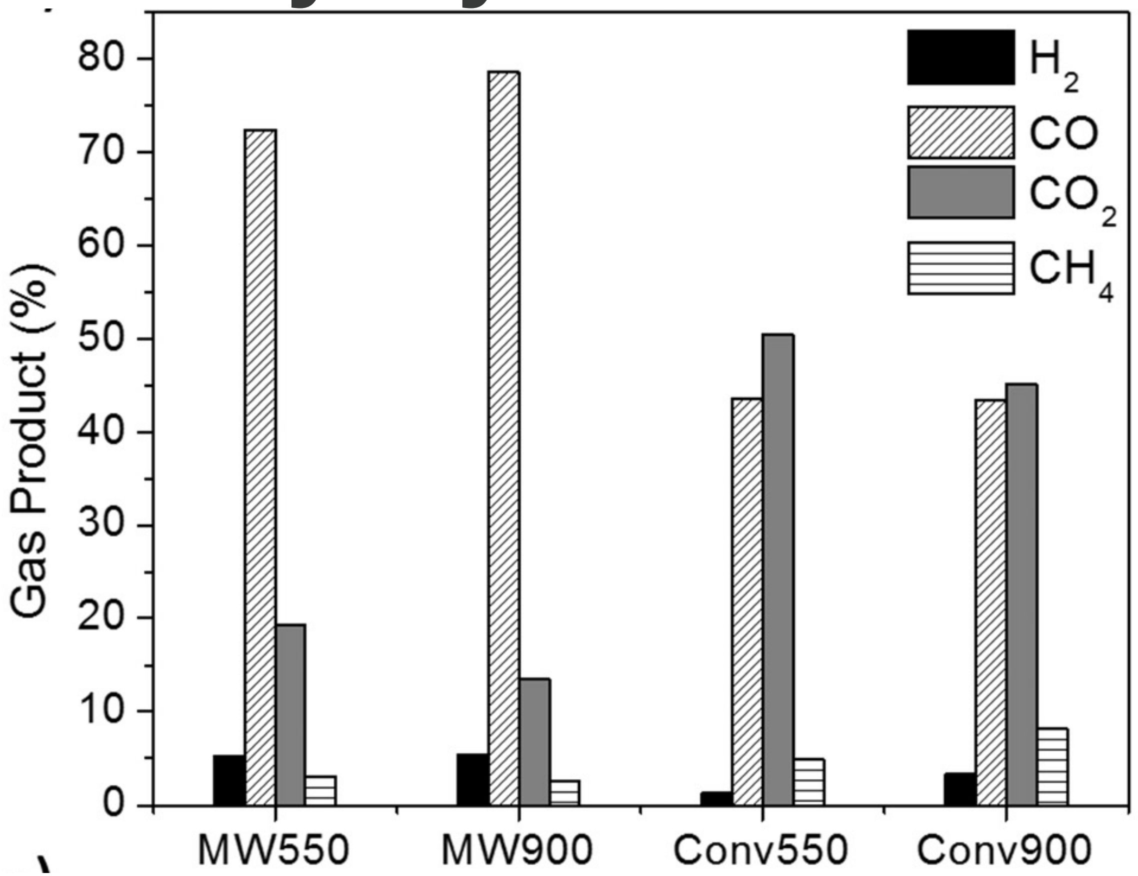


C-MW550

- Porosity increased after MW pyrolysis compared to conventional
- MW can gasify trapped carbon due to selective heating
- Functional groups could act as surface sites that couple with MW energy and results in localized heating

Effect of MW over Conventional Pyrolysis





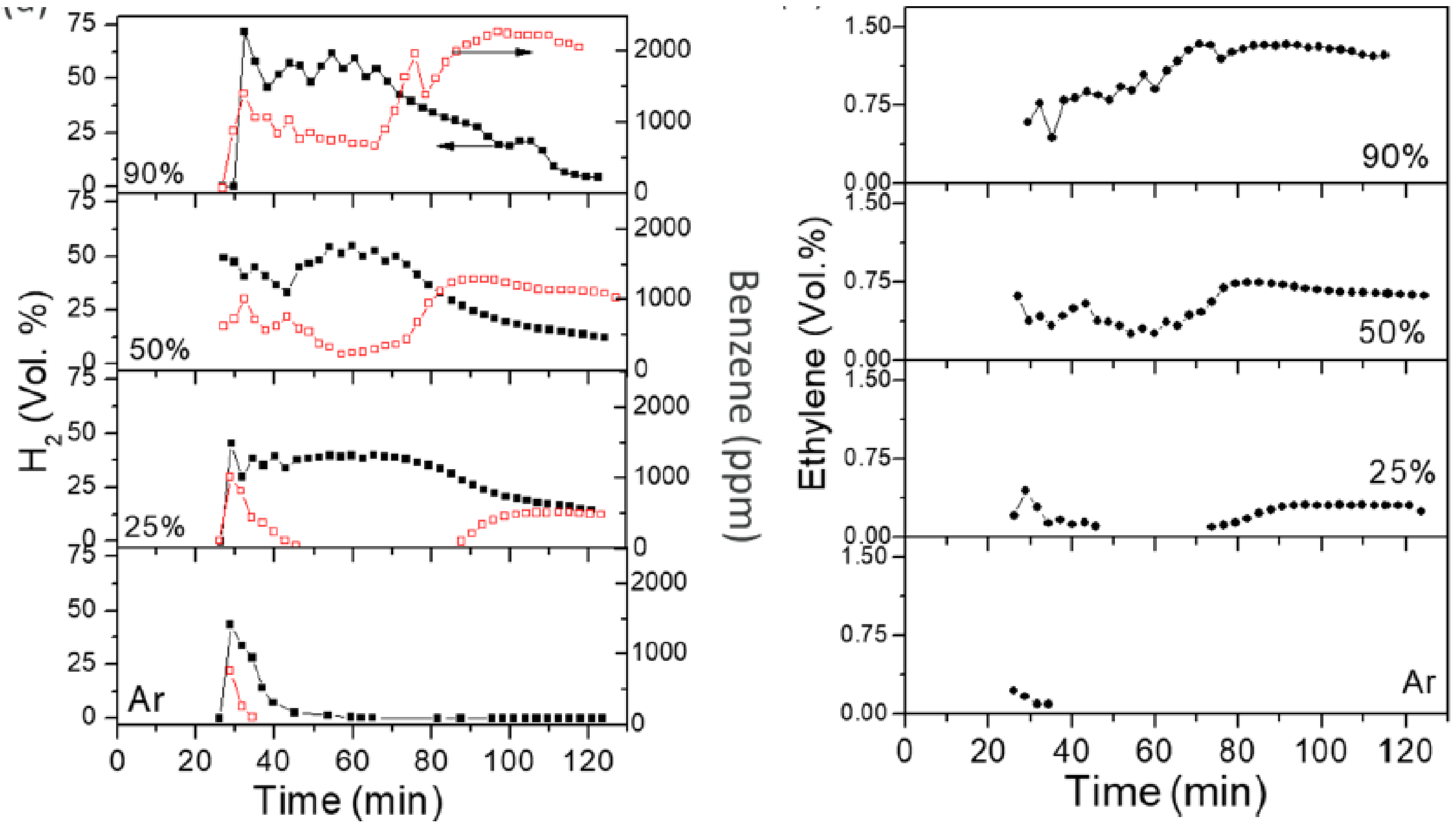
MW favored gas products more than conventional at low temperature & produced high quality char

MW conditions produced higher CO/CO_2 ratio attributed to CO_2 gasification of carbon

V. Abdelsayed et al. (2018) Microwave-assisted pyrolysis of Mississippi coal: A comparative study with conventional pyrolysis, *Fuels* 217, 656-667.

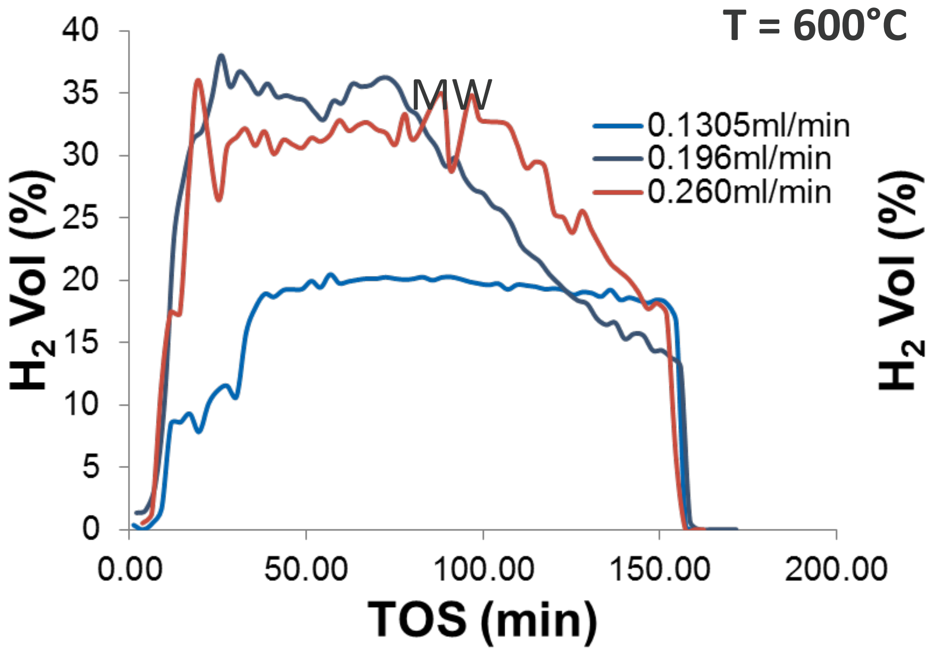
Effect of Methane Addition with Microwave

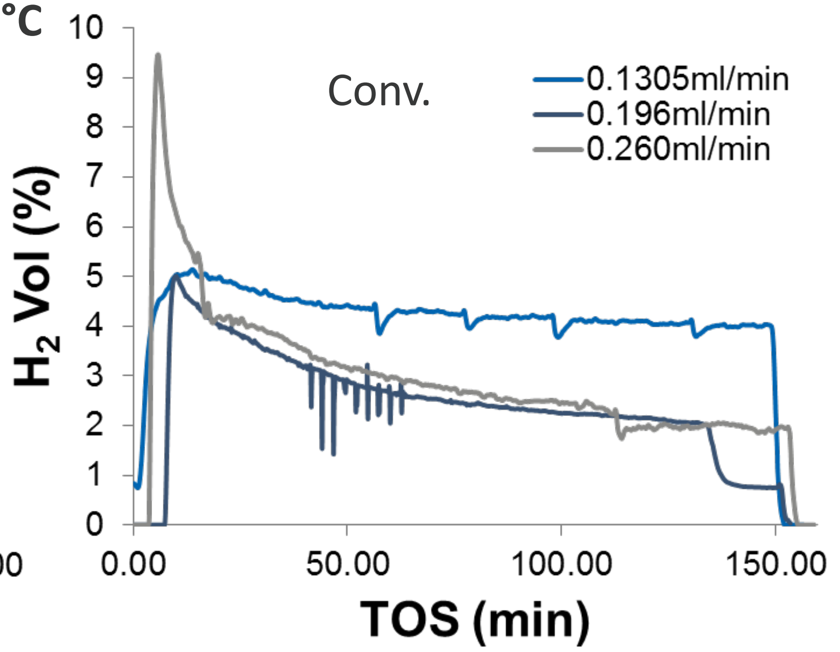
- Increase in CH_4 concentration led to increase in H_2 product that decreased over time
- Carbon/char more amorphous and lower quality
- Increase in CH_4 also led to higher C_6H_6 products that increased with time and leveled off at 2 hrs
- Ethylene production trended the same as benzene

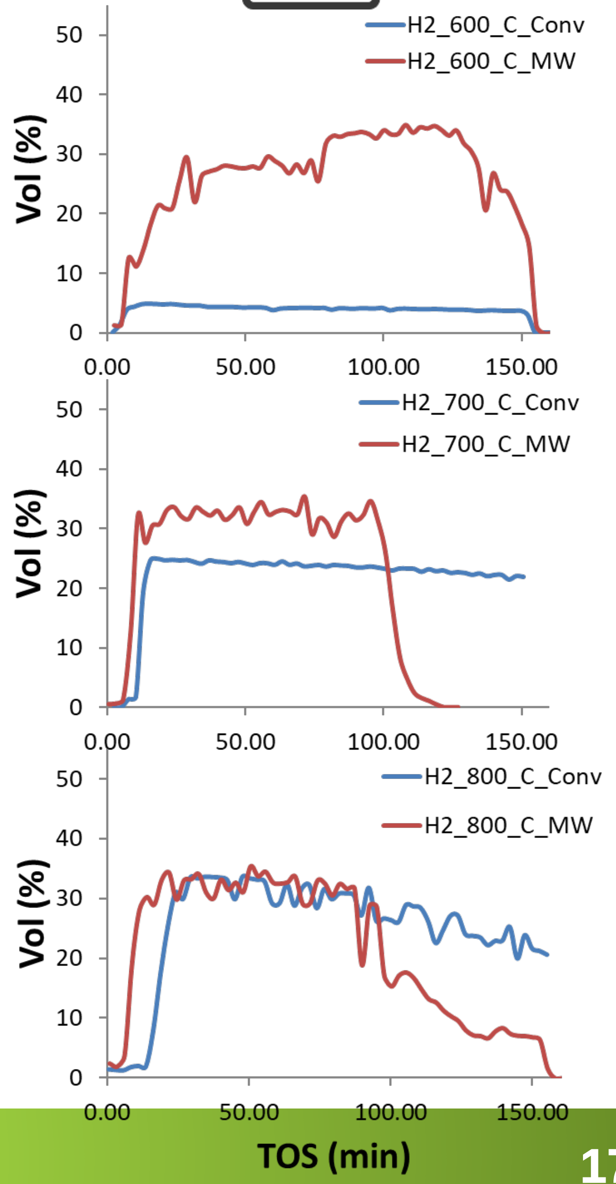


V. Abdelsayed et al. (2019) Microwave-Assisted Conversion of Low Rank Coal under Methane Environment, *Energy Fuels* doi:10.1021/acs.energyfuels.8b03805.

Microwave Steam Gasification

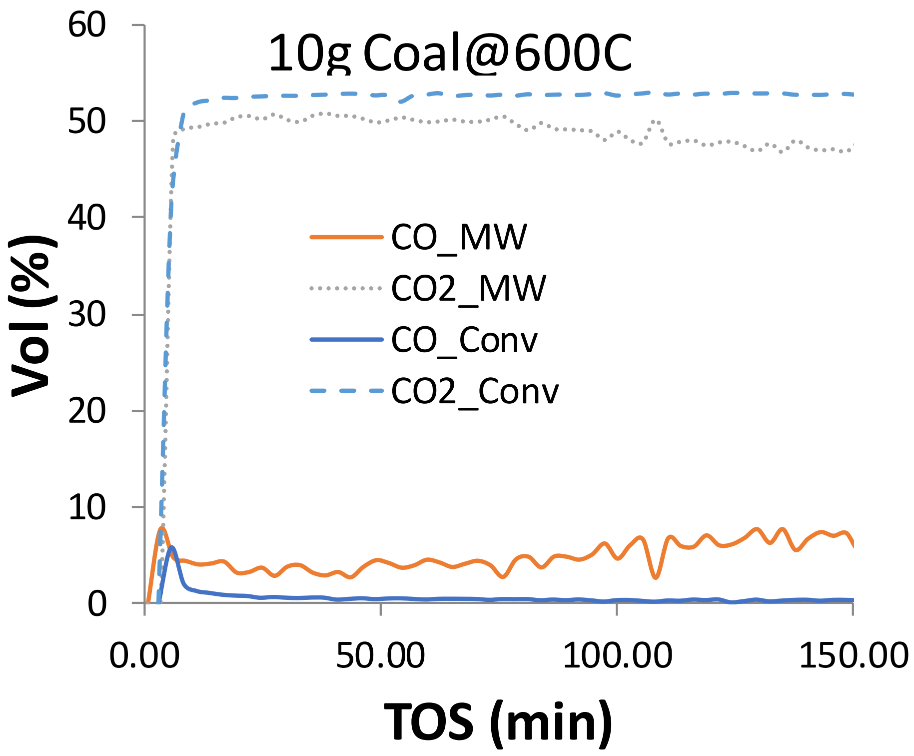


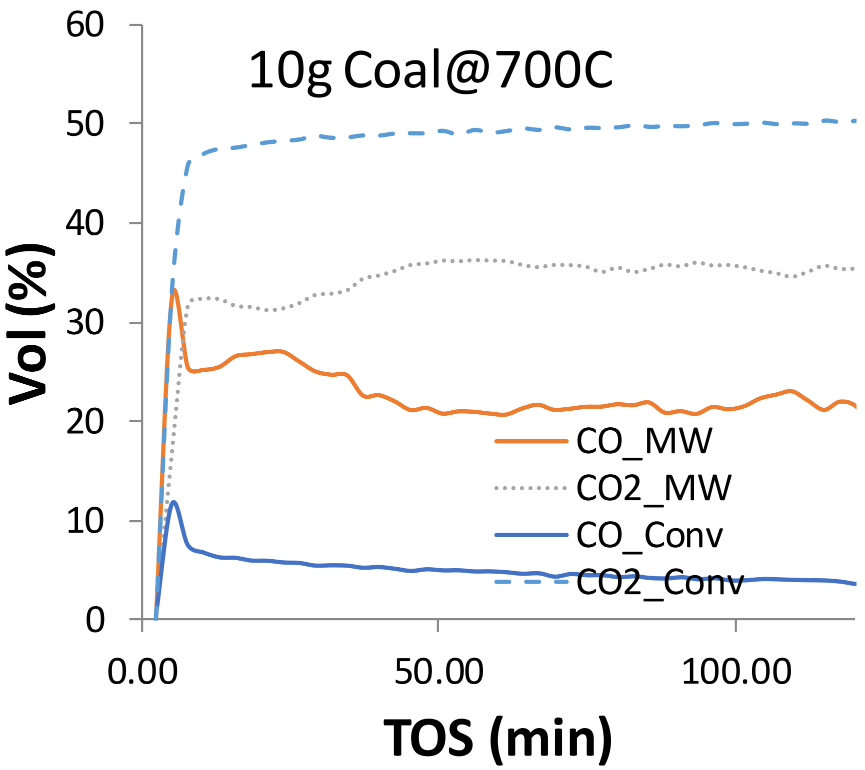




- Microwave produced more gases than conventional thermal energy
- Microwave demonstrated advantages in coal gasification due to its selective heating and enhanced reaction rates
- Addition of higher levels of steam produced rapid coal gasification with microwave; however, conversion decrease with conventional method

Microwave CO_2 Gasification



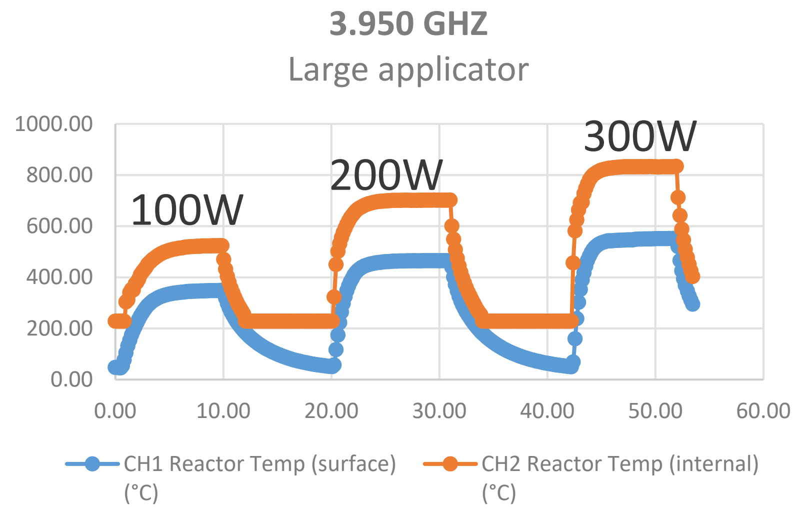


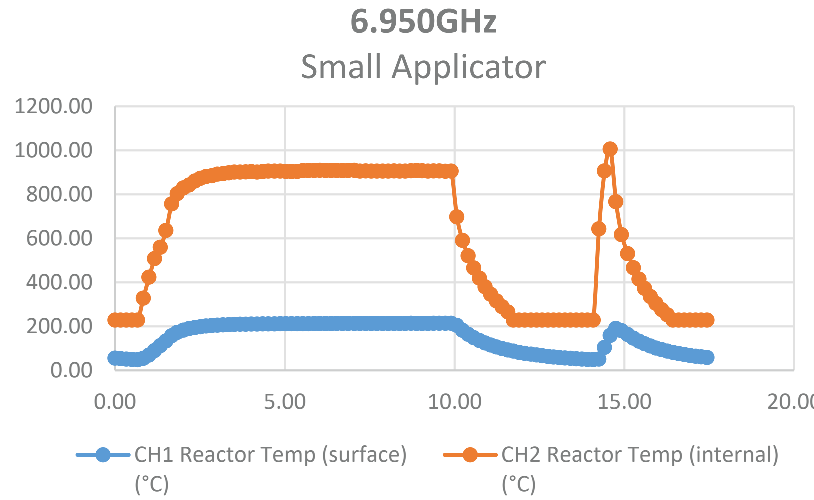
- Preliminary studies to identify operating ranges (PRB)
- Significantly higher CO_2 gasification and CO production with microwave starting at temperature of 700 °C compared to thermal process
- Continued experiments will vary power and CO_2/coal ratio

Microwave Coal Conversion in VFMWR

Examine the frequency effect on carbon black, as a model material for coal, and develop corresponding temperature profiles.

Gas composition	N_2 flow: 100 (sccm)		
Catalyst:	Carbon black	300-600 micron	
Applicator	Frequency (fixed)	Sweep Time	MW Power
Large applicator /low range	2.4-3.95 GHz	155 min (10 min/100MHz)	Repeat the sweep at 100, 200, 300 W and 400 W (if applicable)**
Mid range	3.95-5.85 GHz	190 min (10 min/100MHz)	Same as **
Small applicator/ High range	5.85-8 GHz		Same as **
Temperature limit	Not to exceed 1000 C		For either the reactor or catalyst surface temperatures
MW Power steps	100 W steps up to 400W*		*Middle band can go up to 400W





Summary and Future Work

- **Benefits of microwave energy are being examined for gasification**
  - Reduce time and energy for materials conversion
  - Improve product yields and distribution in chemical reaction
  - Reduce number and size of process units
- **Continue developing fundamental understanding of various microwave interactions with processes (power, pulse, frequency)**
- **Reactor design and scale-up studies**
- **Define and calculate realistic process efficiency (continuous operation)**
- **Develop and demonstrate lab-scale continuous microwave coal gasifier unit for scale-up to pilot system (100 kg/day)**

Acknowledgements

Reaction Engineering Team

Dushyant Shekhawat

Christina Wildfire (ORISE)

Victor Abdelsayed (Leidos)

Michael Spencer (Leidos)

Candice Ellison (Leidos)

Robert Tempke (WVU)

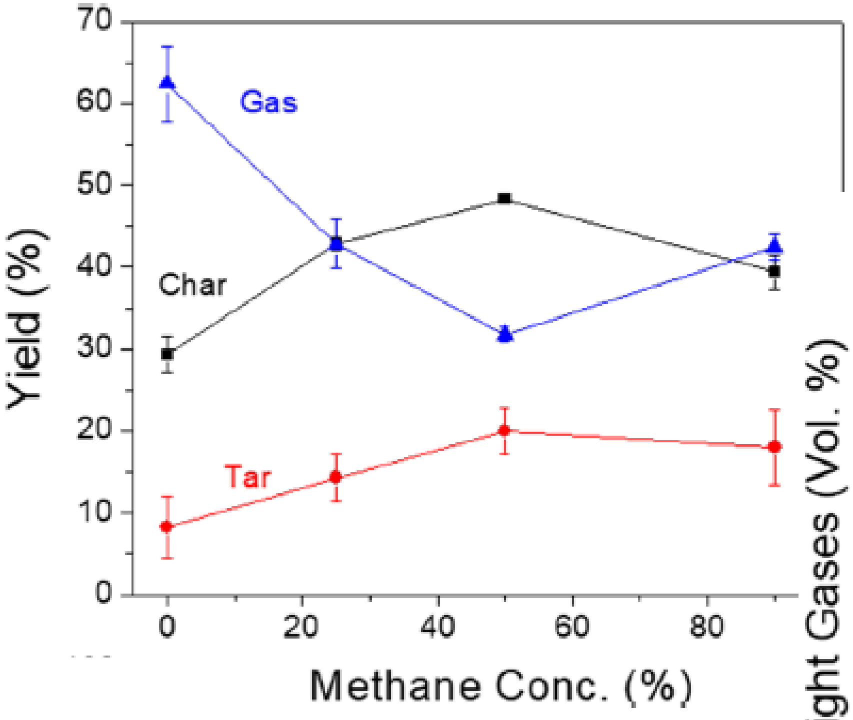
Terry Musho (WVU)

Questions?

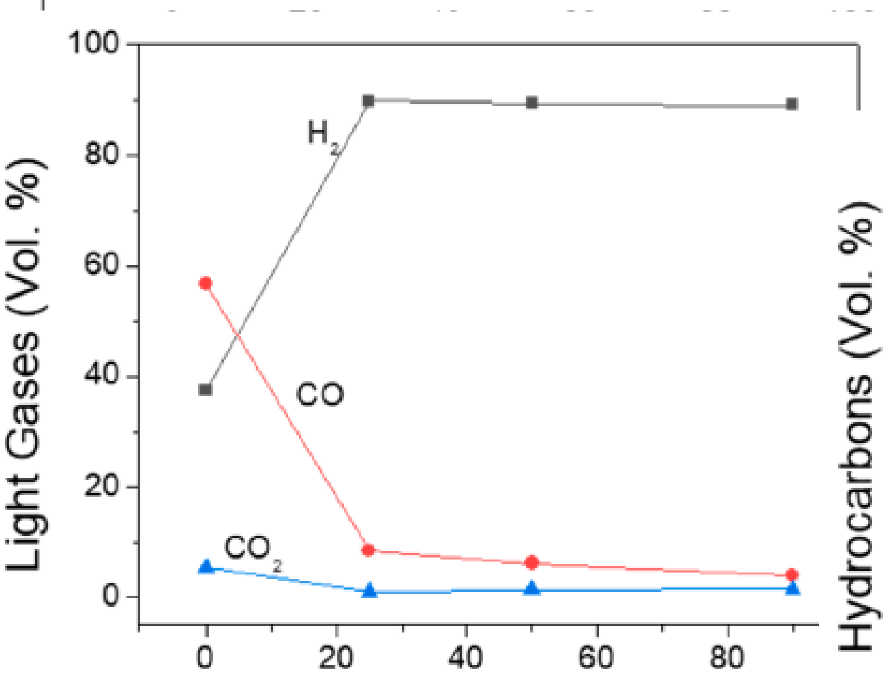
Extra Slides

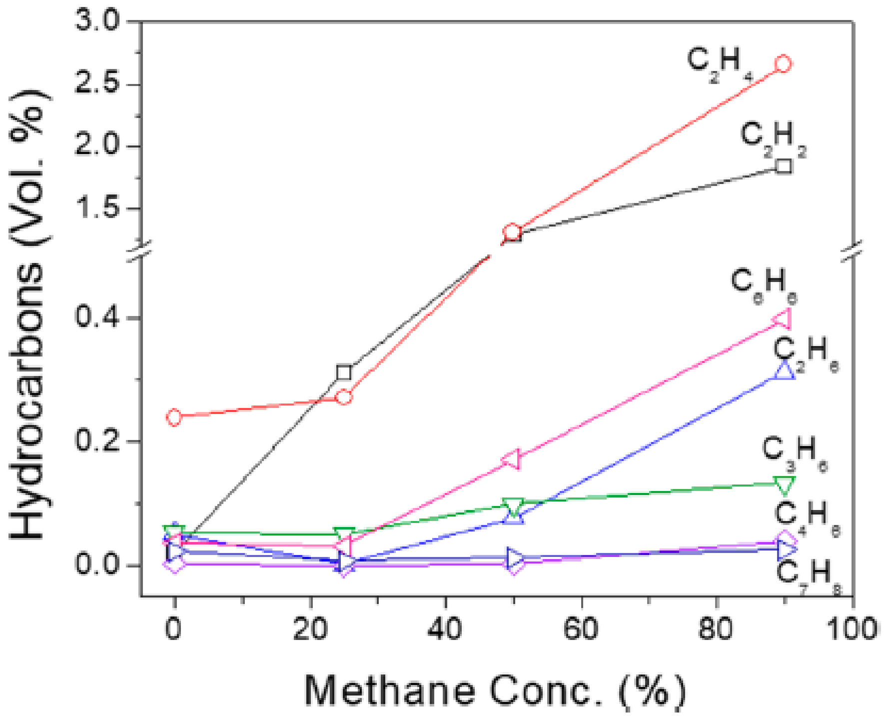
Publications, Presentations, & Patents

Effect of Methane Addition under Microwave



- Overall, increasing methane up to 50% led to higher yield of tar products and char; at 90% gas product yield was higher



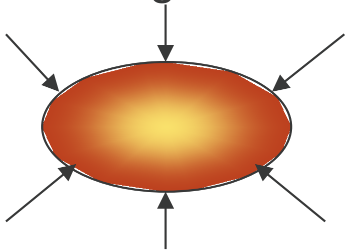


- Hydrocarbon gas yields increased with increasing methane concentration; C2+, benzene, toluene; coal activated by microwave?

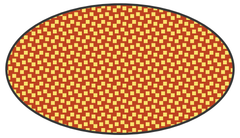
Microwave-Assisted Materials Processing

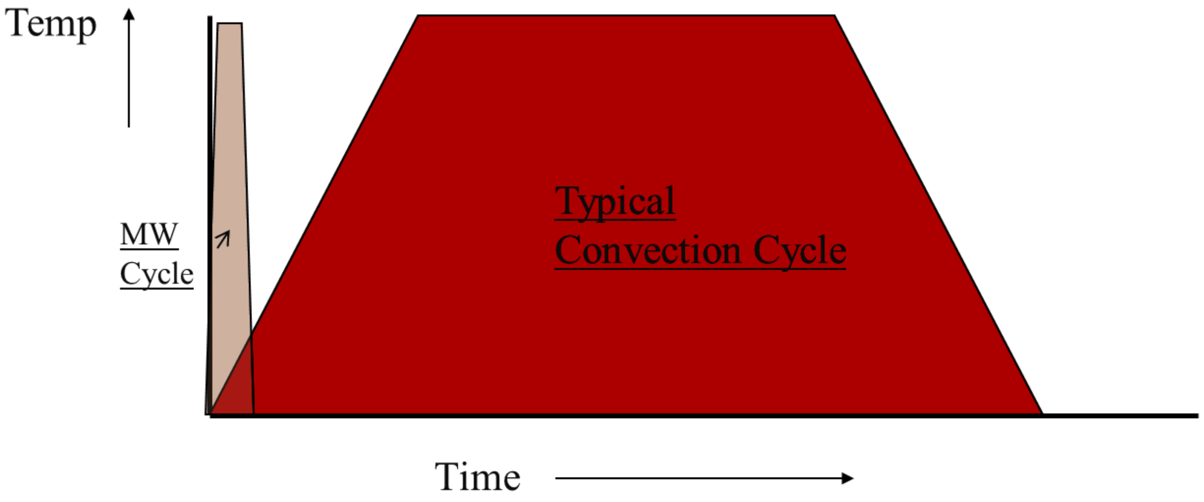
Rapid heating and cooling

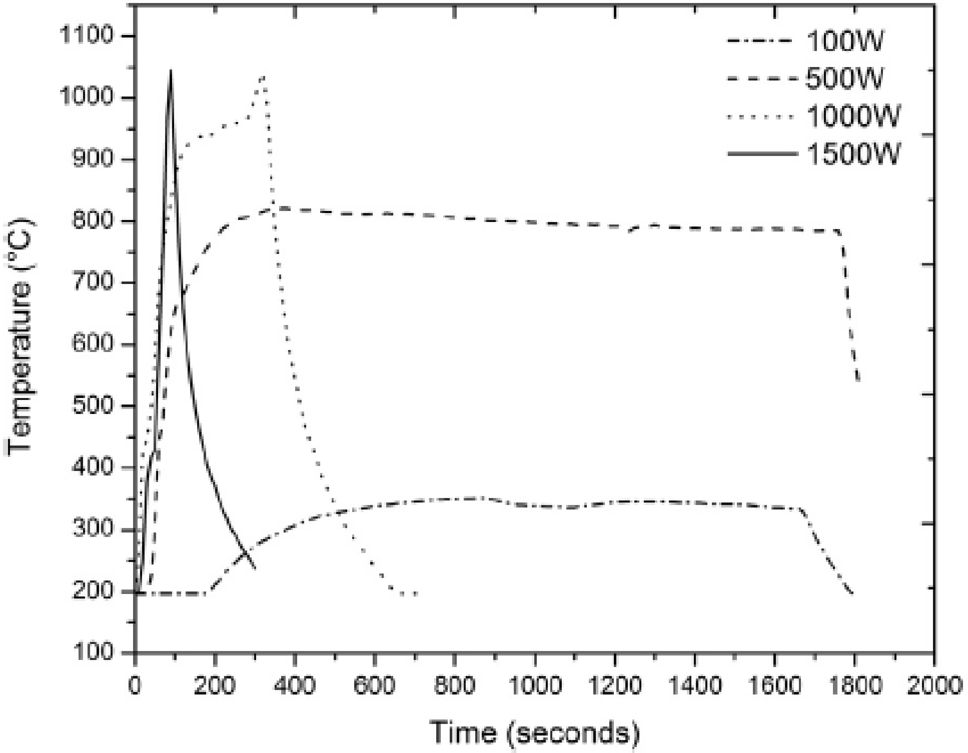
Conventional Heat
-Outside - In



Microwave Heat
-Molecular level





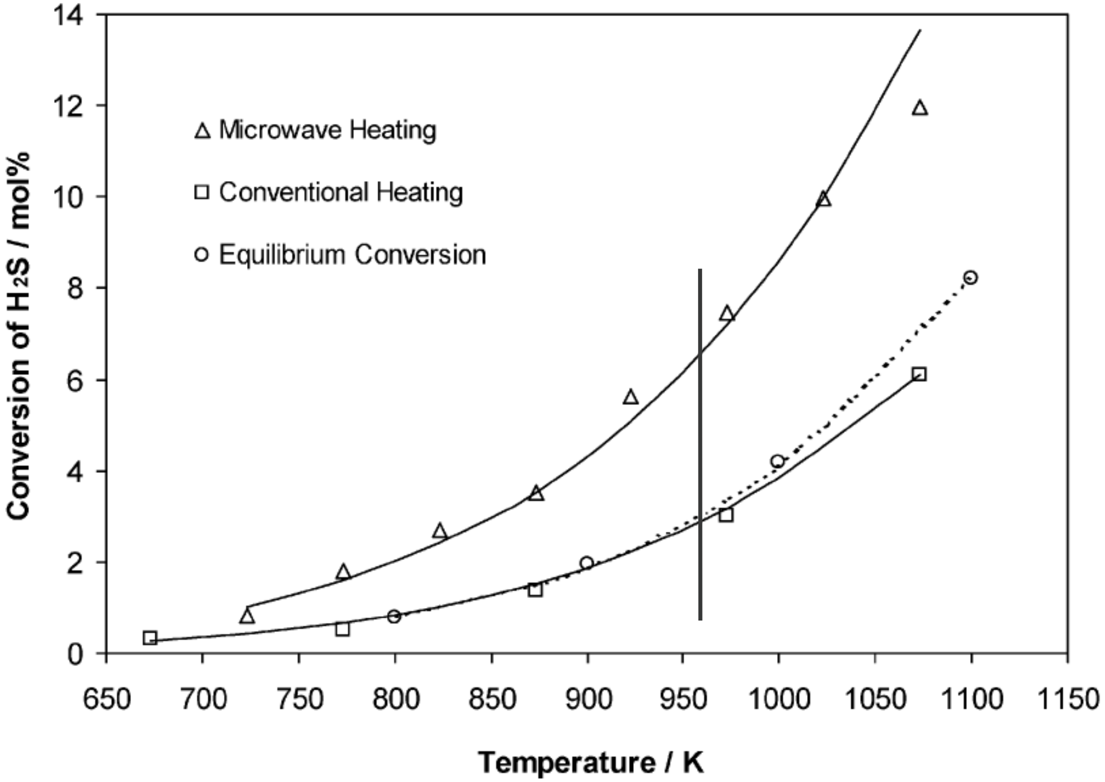


C. Wildfire et al. (2017) Ceram. Intern. 43, 11455-11462.

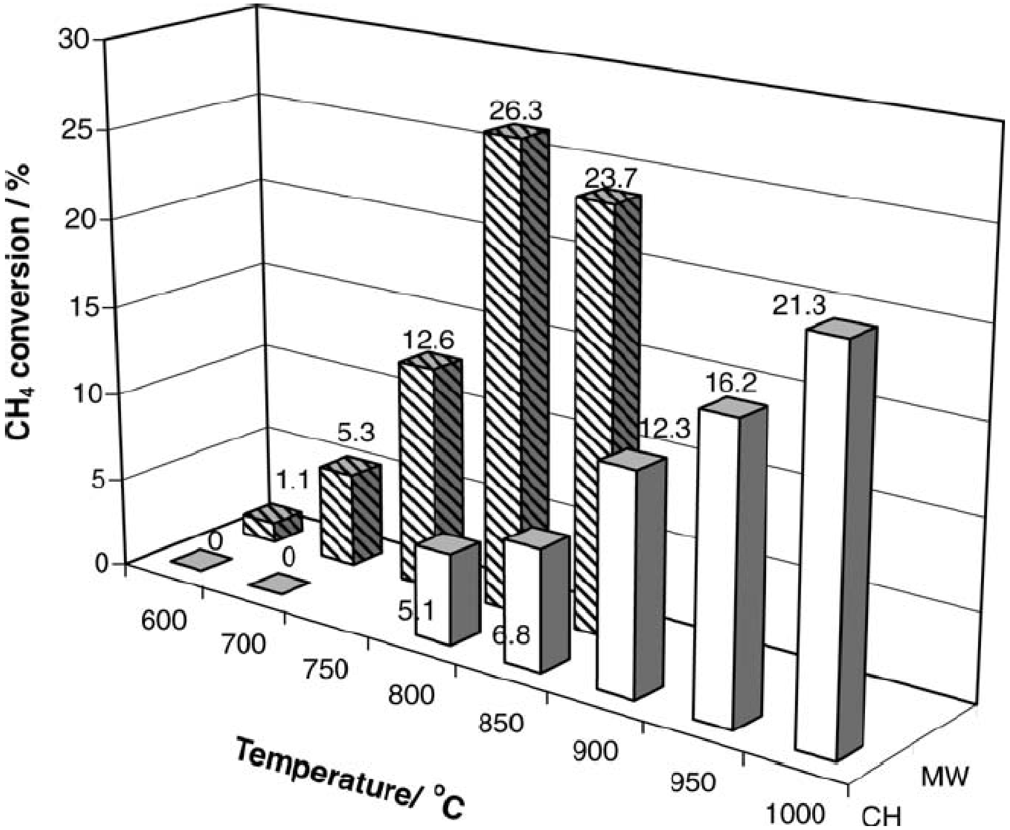
Microwave-Assisted Reactions

Improve conversion and selectivity

$H_2S \rightarrow H_2 + S$



Oxidative Coupling of Methane



- MWs, plasmas, etc. deposit energy in "non-thermal" manner
- Products higher than bulk T thermodynamic predictions & traditional thermal reactors

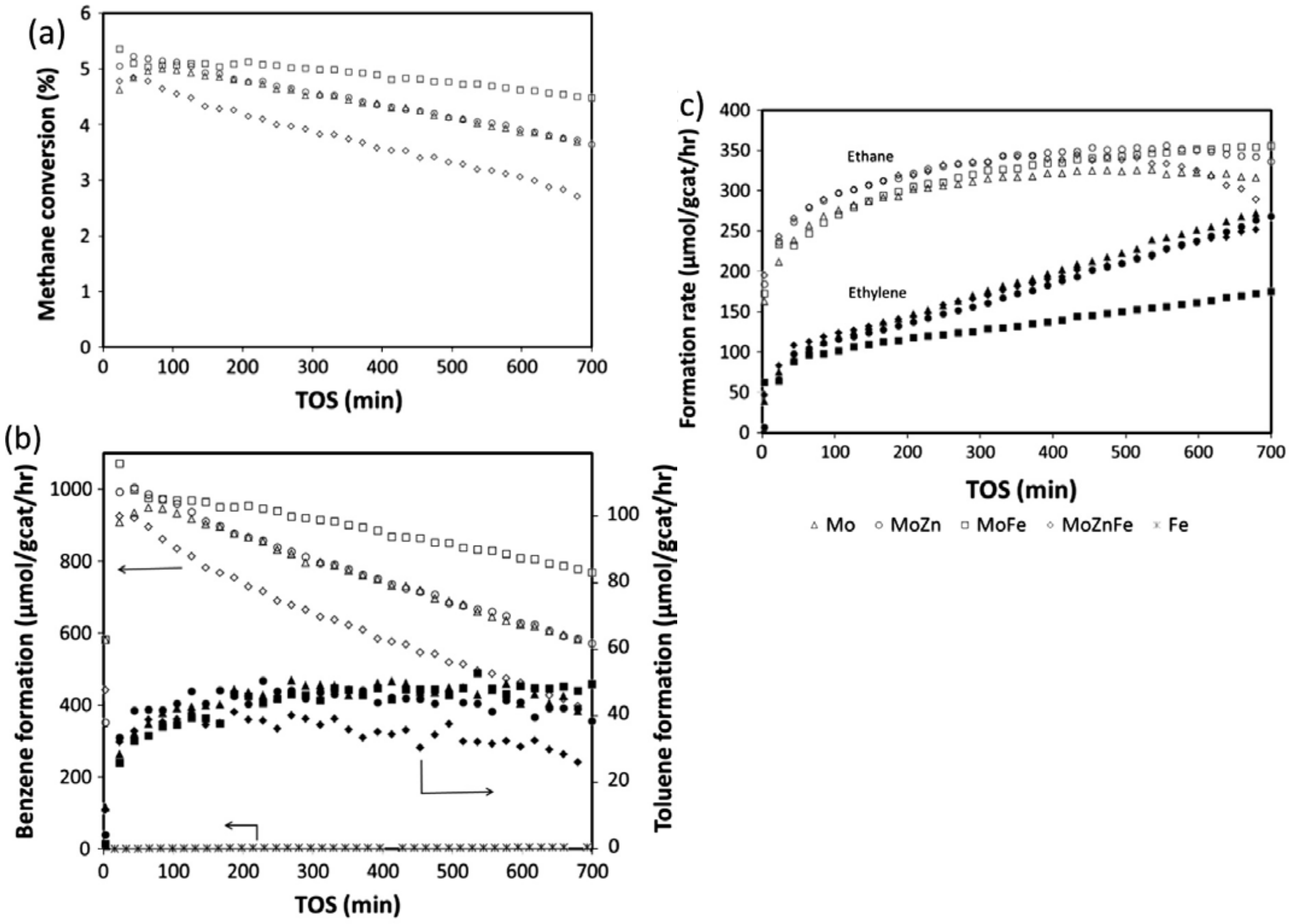
X. Zhang et al. (2003) Catal. Lett. 88 (1-2), 129.

Zhang et al. (2003) Appl. Catal. A, 249, 151

Methane Dehydroaromatization

$$6\ CH_4 \leftrightarrow C_6H_6 + 9\ H_2$$

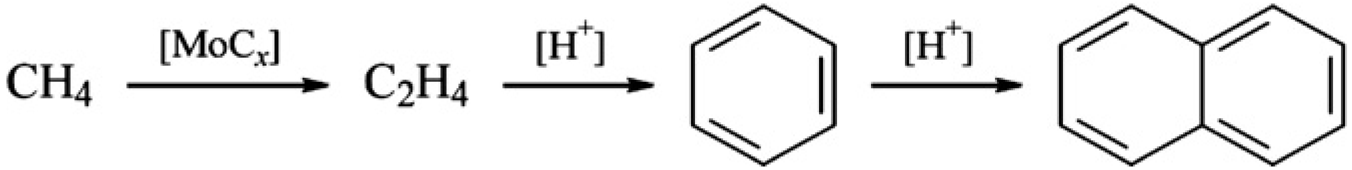
- **Indirect conversion of methane to higher hydrocarbons**
  - Reforming to syngas → Fischer-Tropsch synthesis
- **Issues with direct conversion**
  - Equilibrium yield limited ~10% at 750°C
  - Increasing temperature to improve conversion leads to rapid catalyst deactivation

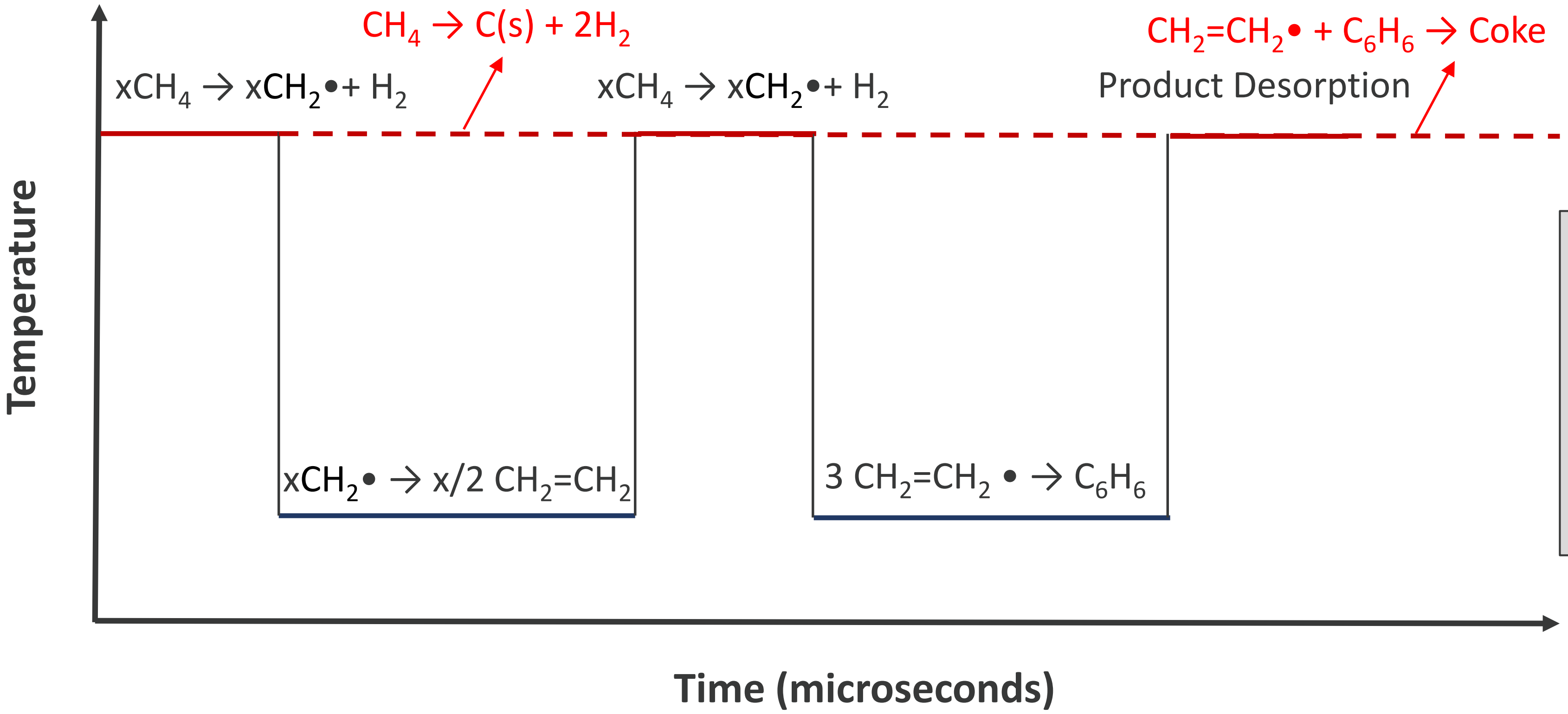


V. Abdelsayed et al. (2015) Fuel 139, 119–135.

Selective Conversion

Example: Methane to Benzene



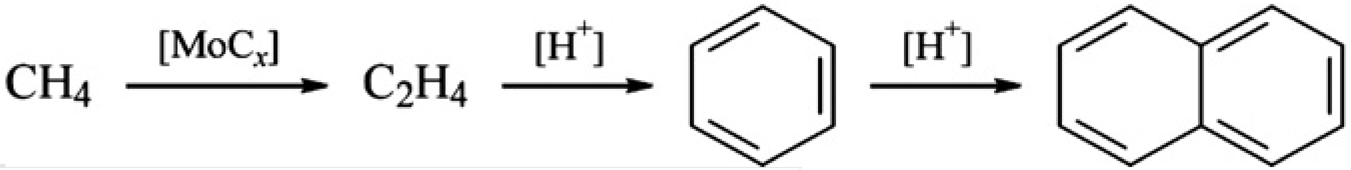


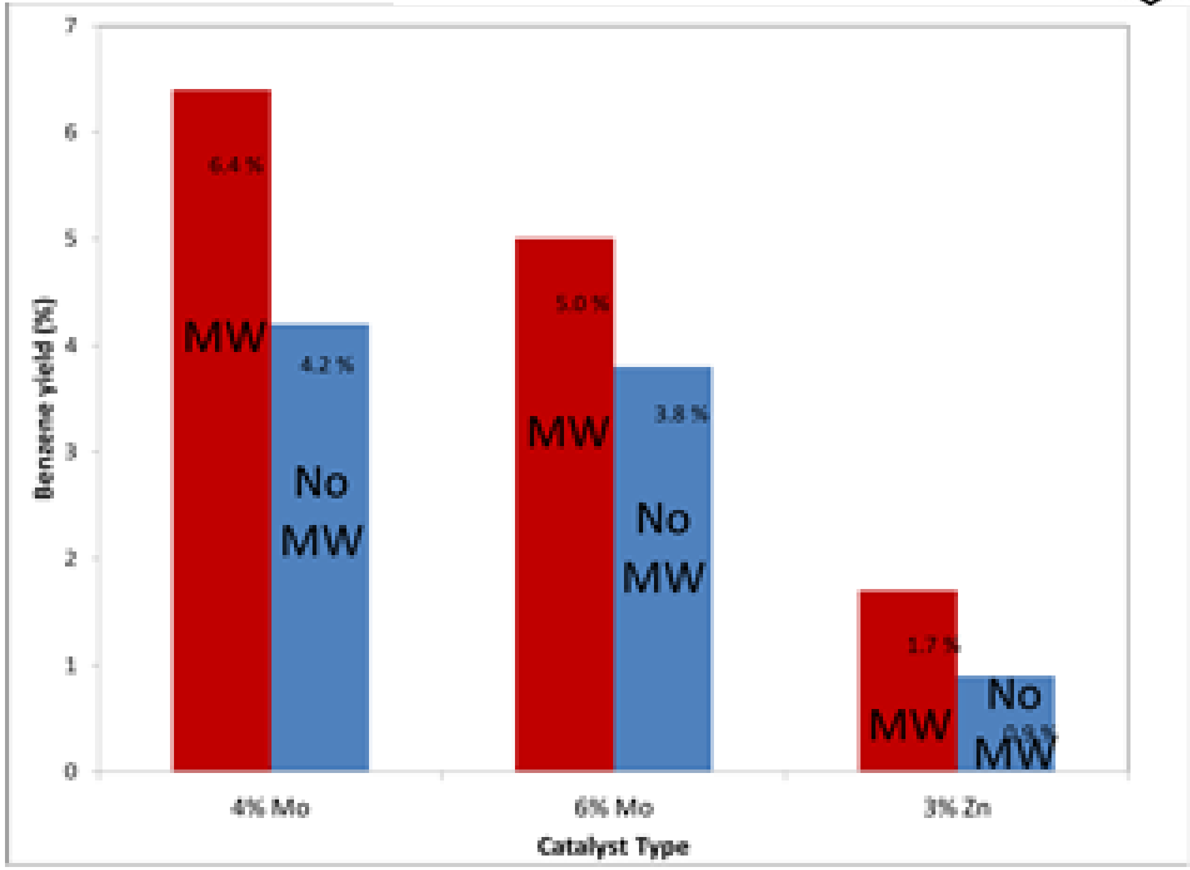
Microwave Effect:

- Intended to promote or prevent the endothermic steps of the overall reaction mechanism, depending on the desired products.

Methane Dehydroaromatization

NATIONAL ENERGY TECHNOLOGY LABORATORY





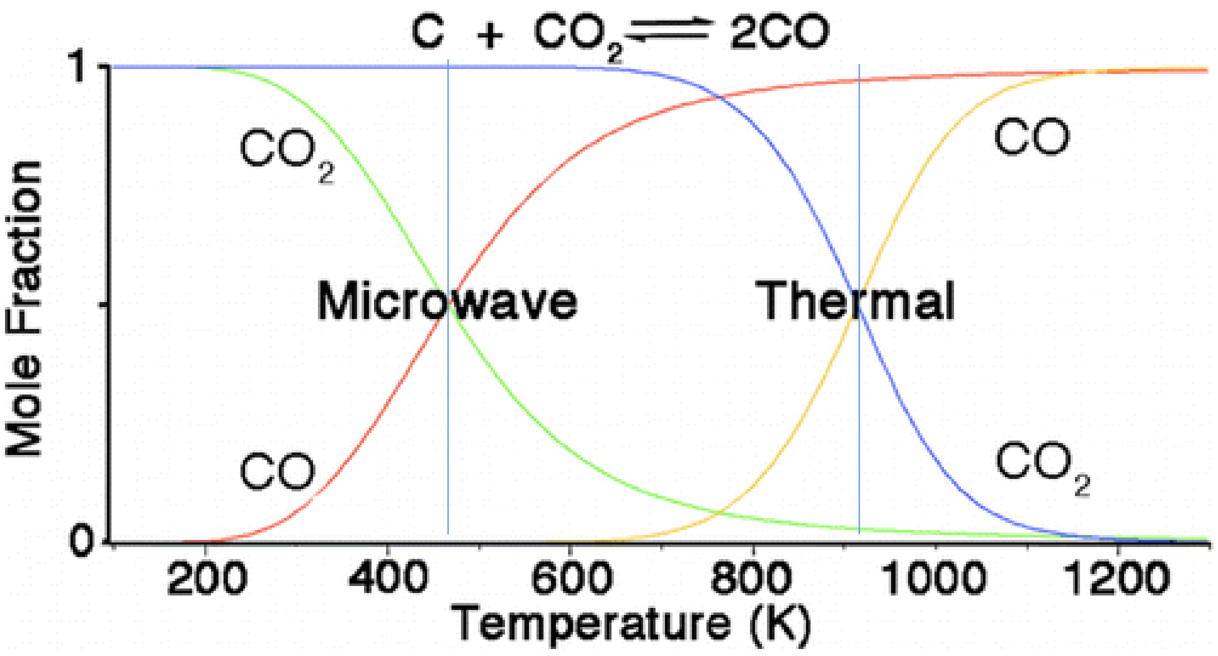
- Benzene yield higher for all catalysts under microwave
- Likely due to reduction in formation of deactivating carbon deposits on catalyst surface
- Post-reaction TPO supports this conclusion

Condition	Value
Mass catalyst, g	1.0
Methane flow rate, sccm	50
Temperature, °C	700
Pressure, atm	1.0
MW power, W	300
MW frequency, GHz	2.45
MW pulse, ms on/off	500

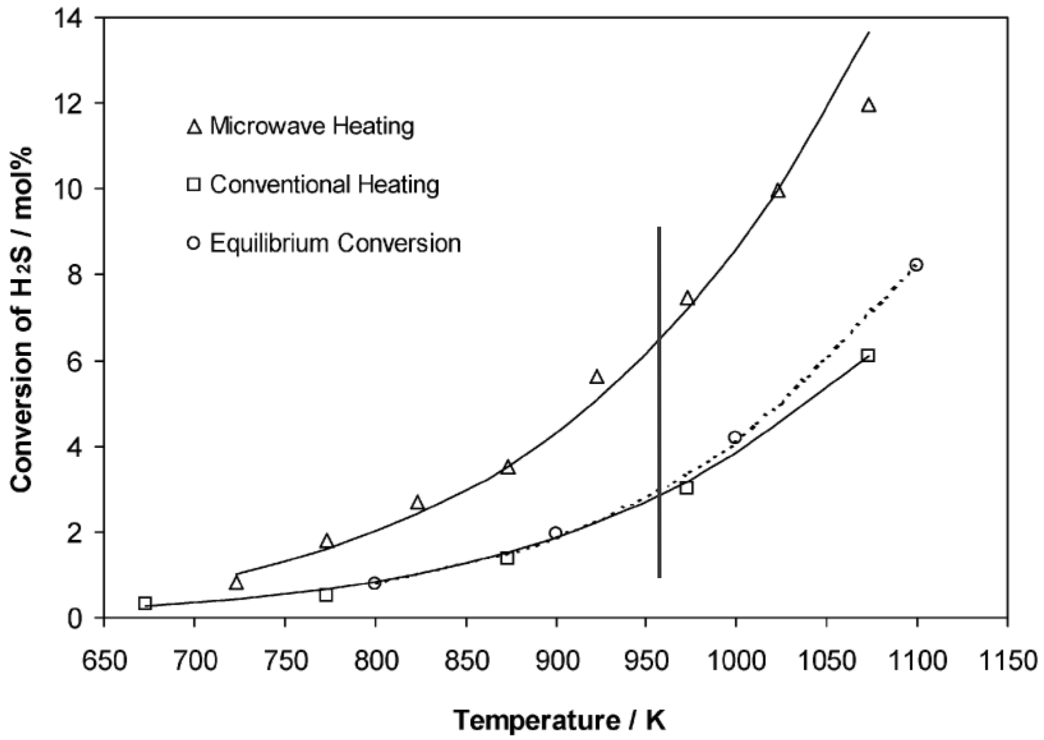
Microwave-Assisted Reactions

Improve conversion and selectivity

Microwave Enhanced Boudouard Reaction



$H_2S \rightarrow H_2 + S$

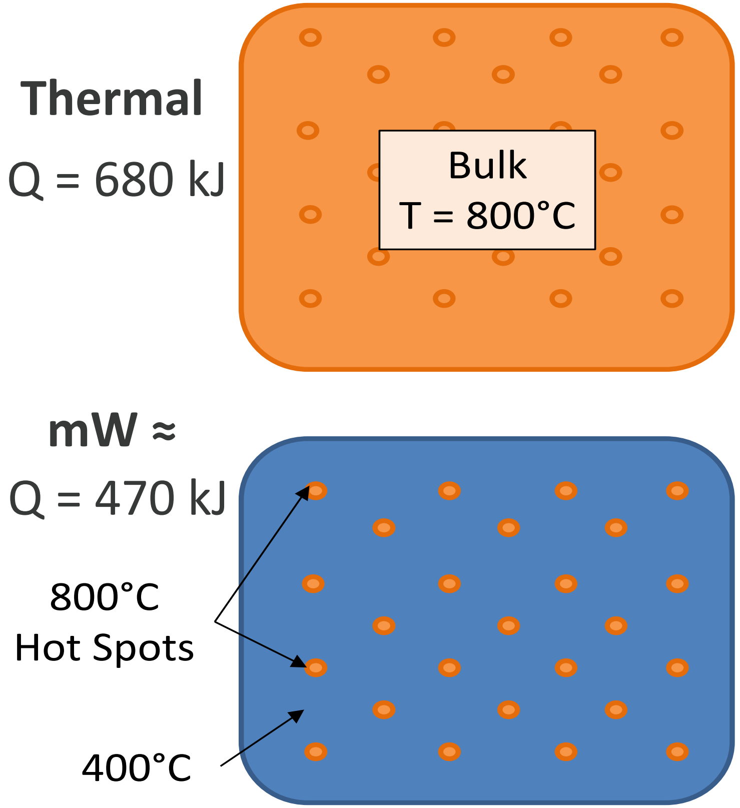


- MWs, plasmas, etc deposit energy in "non-thermal" manner
- Product streams deviate from thermodynamic predictions & traditional thermal reactors

A.E. Steigman et al. (2013) J. Phys. Chem. C, 26871-26880.

X. Zhang et al., (2003) Catal. Lett. 88 (1-2), 129.

What about efficiency?



Assumptions:

C_p = 880 J/kg-K (alumina)

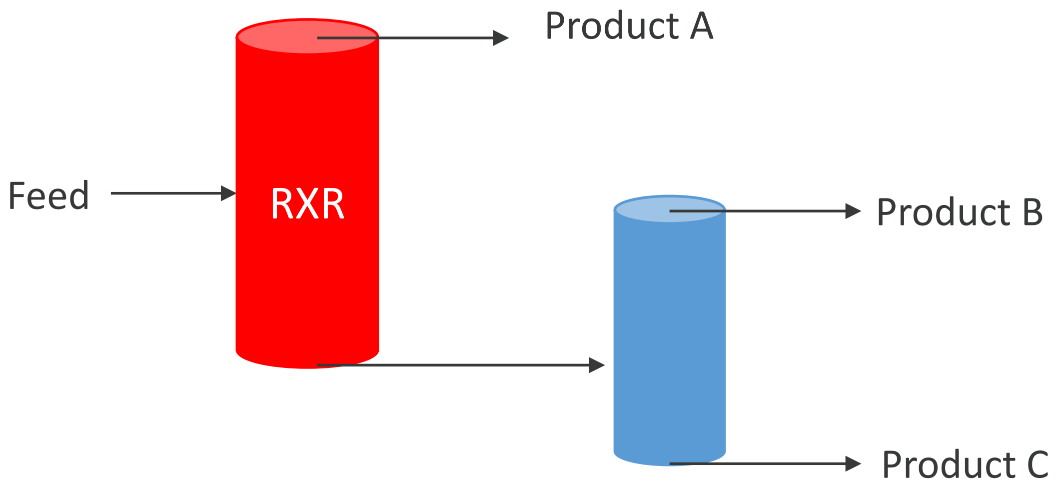
Fluid phase & rxn negligible

Heat losses negligible

1 wt% Active Phase

Frequency = 2.45 GHz

Reflected power negligible



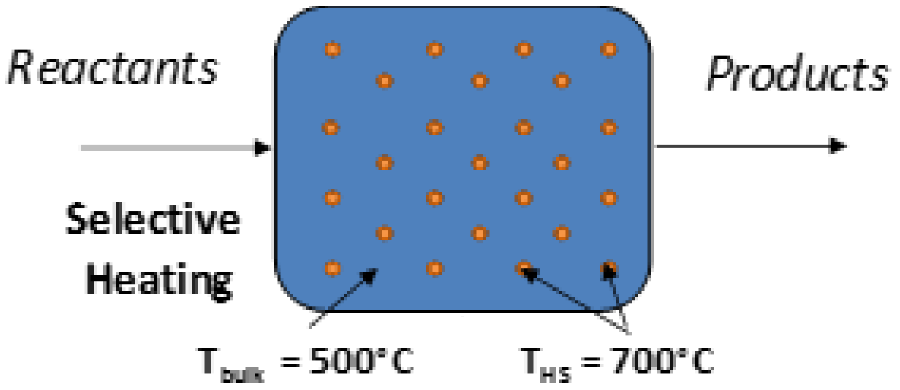
U.S. DEPARTMENT OF ENERGY

Selective Pulsing of Microwaves

Additional approach to Selective Heating

Reaction:

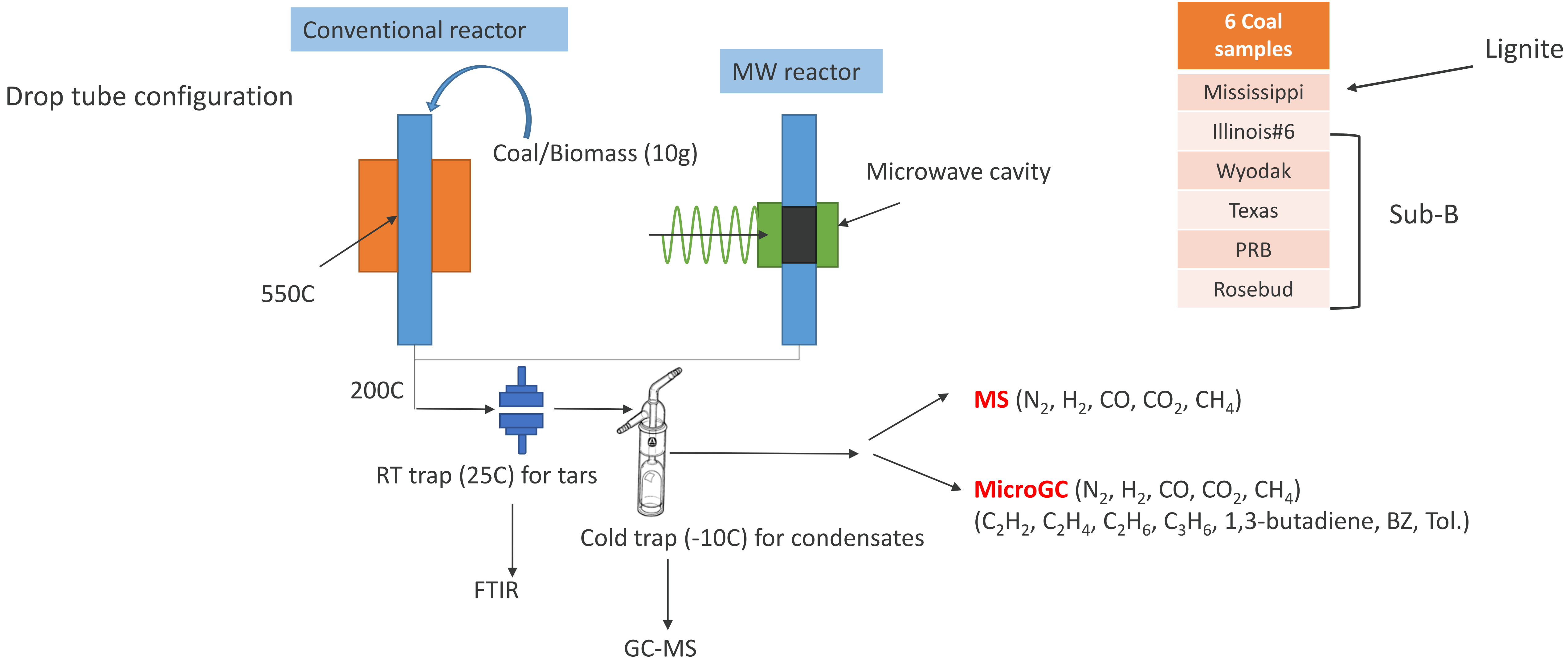
xA → B + C	Desired	ΔH > 0	Endothermic
yB → D	Undesired	ΔH < 0	Exothermic



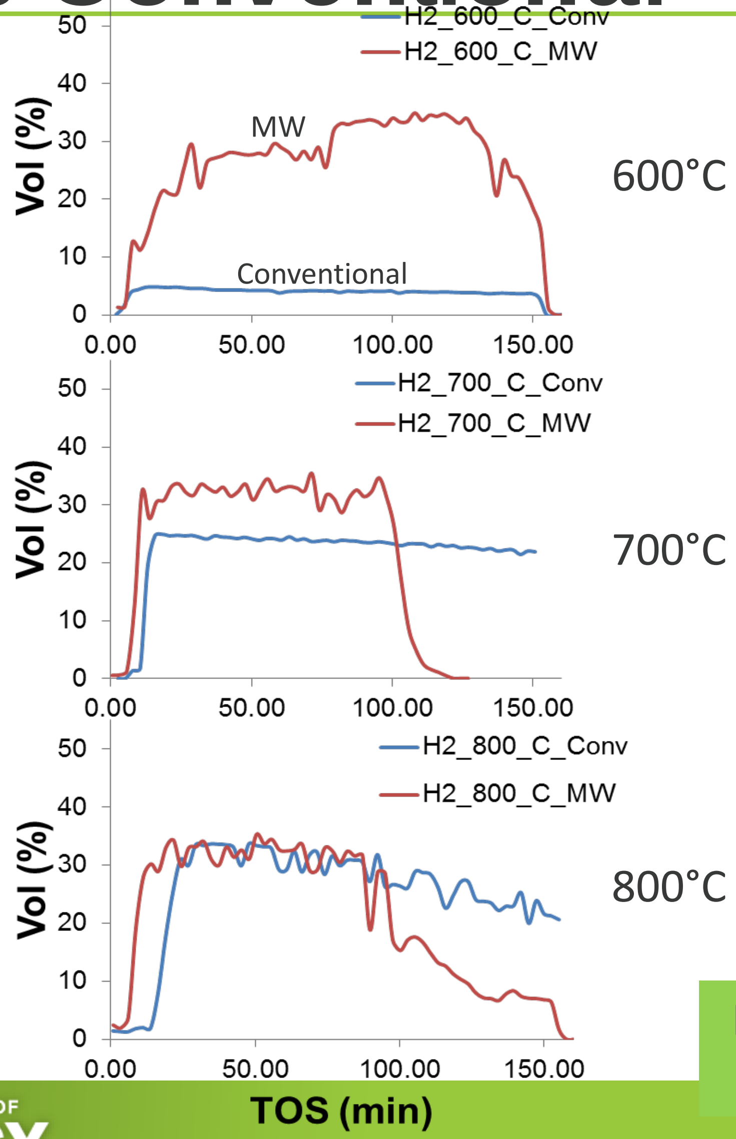
- MW addition will have greater effect on endothermic reactions than exothermic
- Selective heating promotes desired reaction on catalytic sites instead of on bulk support or in the gas phase

Analytical Setup

Microwave and Conventional Reactor



Coal Gasification
MW vs Conventional

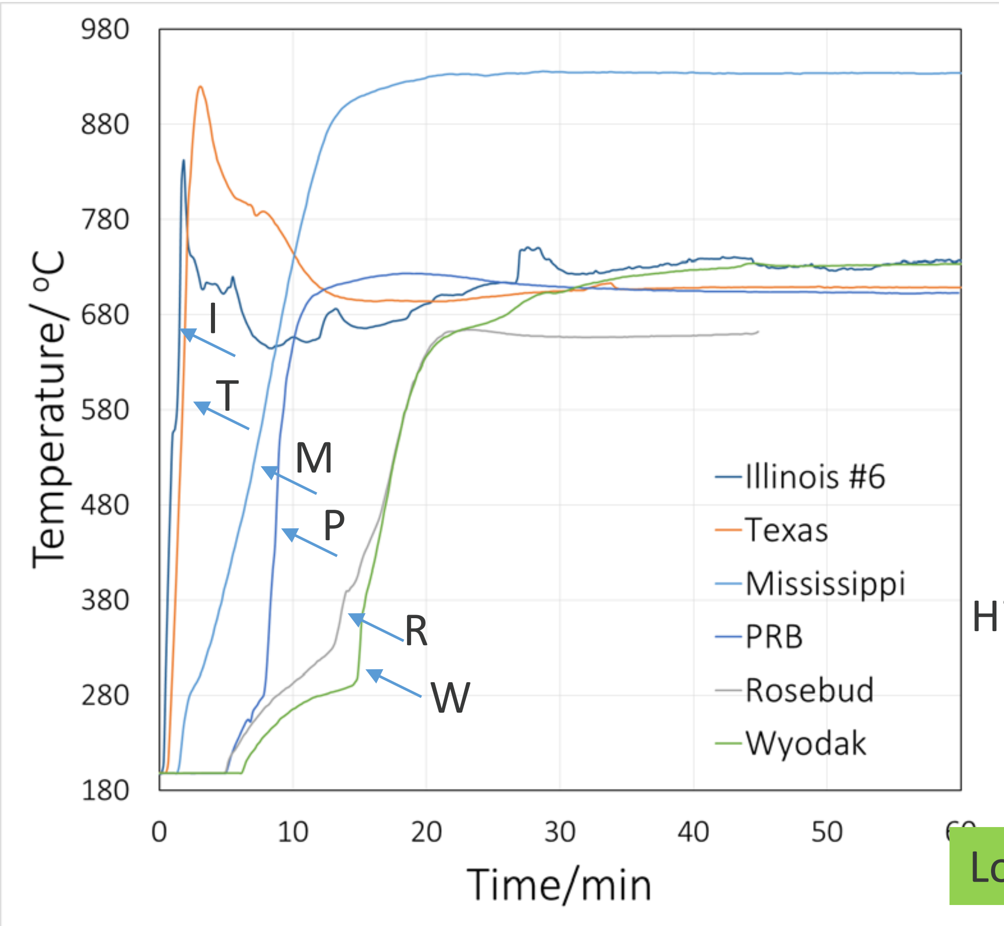


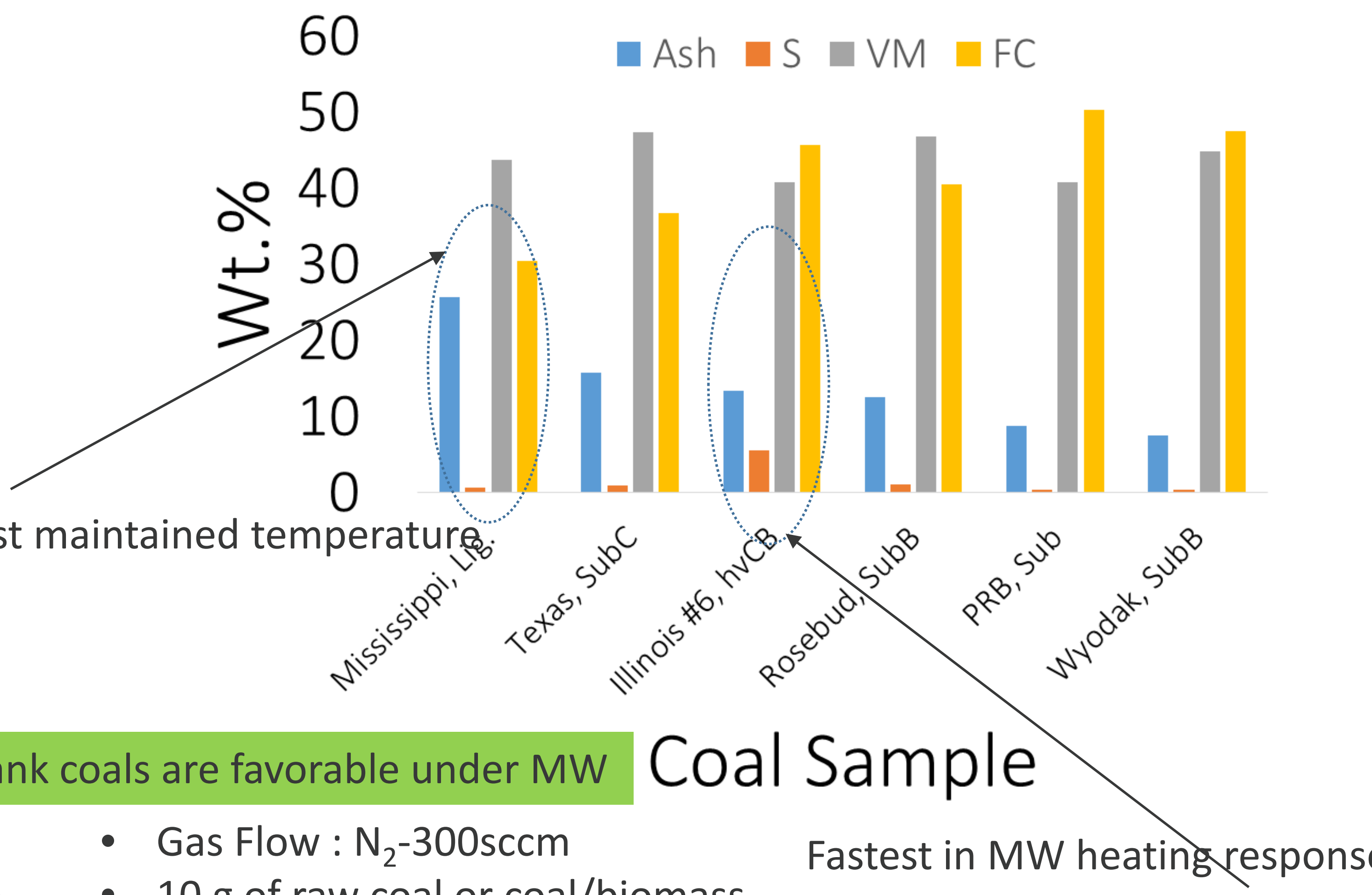
- Experimental Conditions:
  - Mass of Coal sample: 10 g
  - Steam flow rate: 165 sccm
  - Pressure: atmospheric
  - Forward MW Power: 100-300 W
  - MW pulse width: 500 ms on/off
  - Frequency: 2.45 GHz

- MW enhanced the formation of H_2 at low gasification temperature compared to conventional operation
- Concentration of H_2 produced is almost the same under MW at all temperatures

Higher gasification rates observed in the presence of MW even at low temperatures

Pyrolysis of Different Coal Types



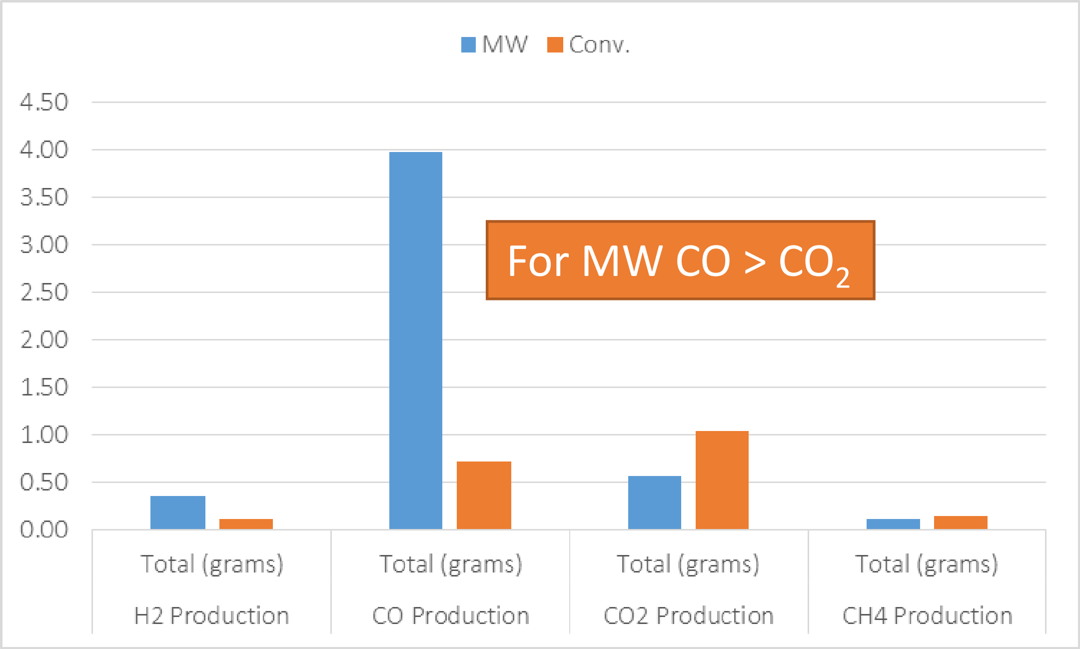


Low rank coals are favorable under MW

- Two MW active sites could be responsible during pyrolysis:
  - Organic active MW sites (VM, heteroaromatic species containing S, …)
  - Inorganic active MW sites (moisture, MO, …)

- Gas Flow : N_2-300sccm
- 10 g of raw coal or coal/biomass
- MW Power : 500 W
- Pressure: 0.1 MPa

MW vs Conventional pyrolysis: Mississippi coal



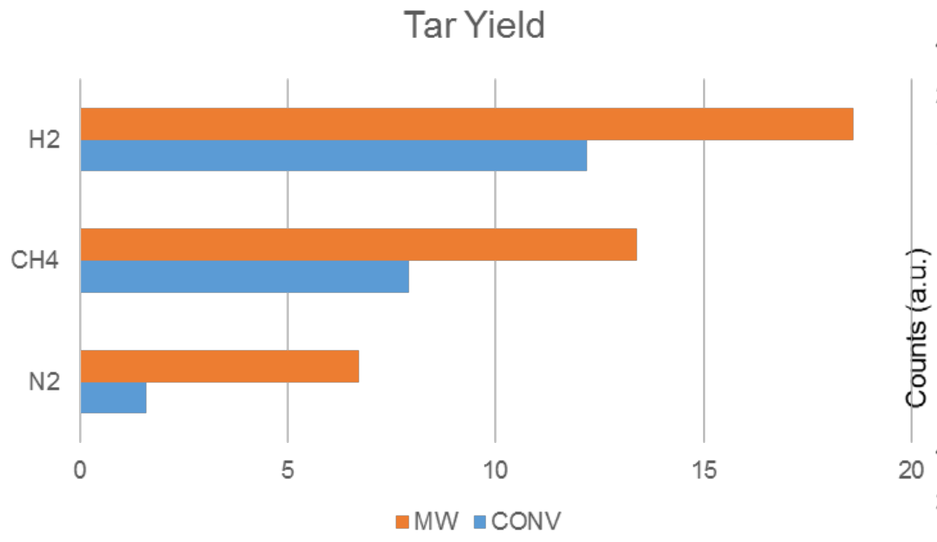
	CO/H2
MW	11.34
CONV.	6.85

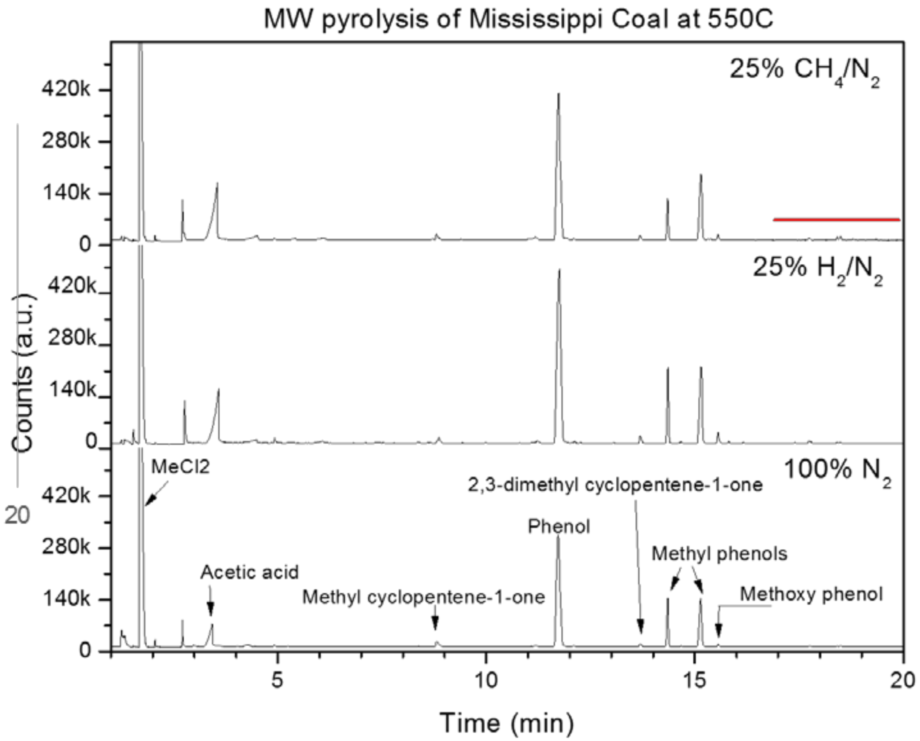
- Gas Flow : N_2-300sccm
- 10 g of raw coal or coal/biomass
- MW Power : 500 W
- Pressure: 0.1 MPa
- Reaction Time : 120min

Could it be the heating rate or MW enhancement effect ?

Effect of H_2 and CH_4 during pyrolysis under MW conditions

NATIONAL ENERGY TECHNOLOGY LABORATORY



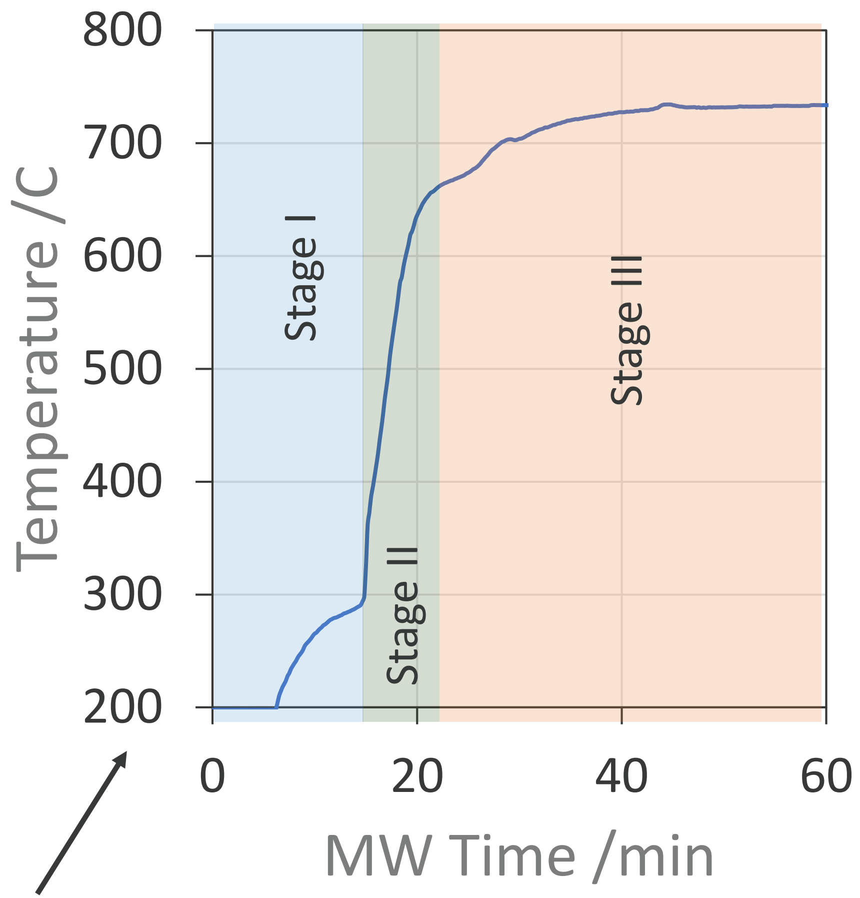


- Significant amount of hydrocarbons produced at low temperature, particularly in the presence of H_2 or CH_4 in feed
- The product distribution is wider and tends to shift to higher molecular weight compounds under conventional heating

MW enhanced the liquid yields particularly in the presence of a hydrogenating compound in the feed

MW heating stages

Temperature profile during Wyodak coal MW pyrolysis



Pyrometer temperature range (200-1000 °C)

Goal - Study the interaction of coal with MW

Stage I

- Slow heating rate
- How long it takes for coal to start heating up rapidly

Stage II

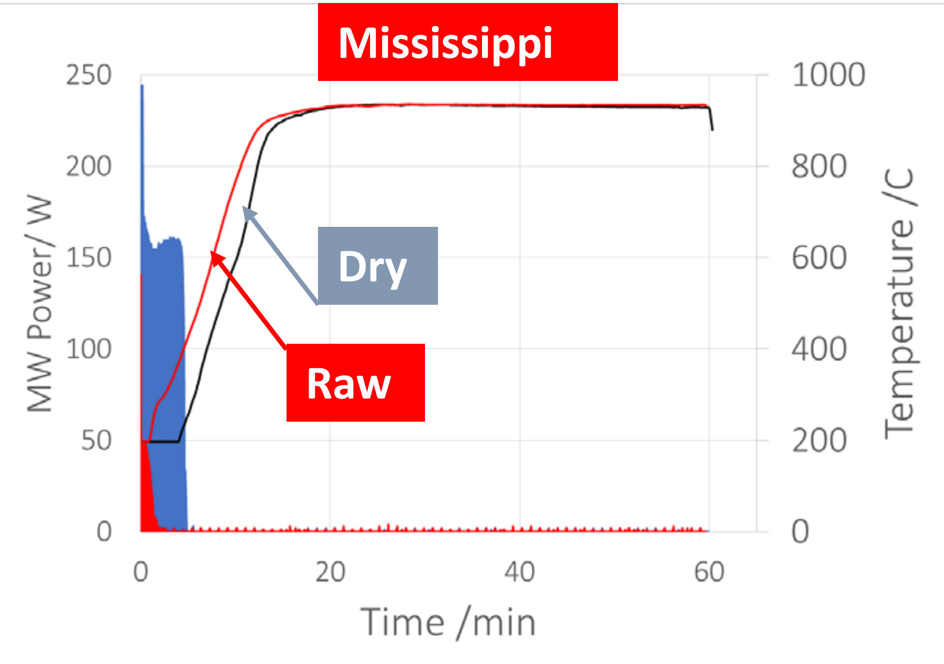
- Fast heating rate
- How high the pyrolysis temperature can go to

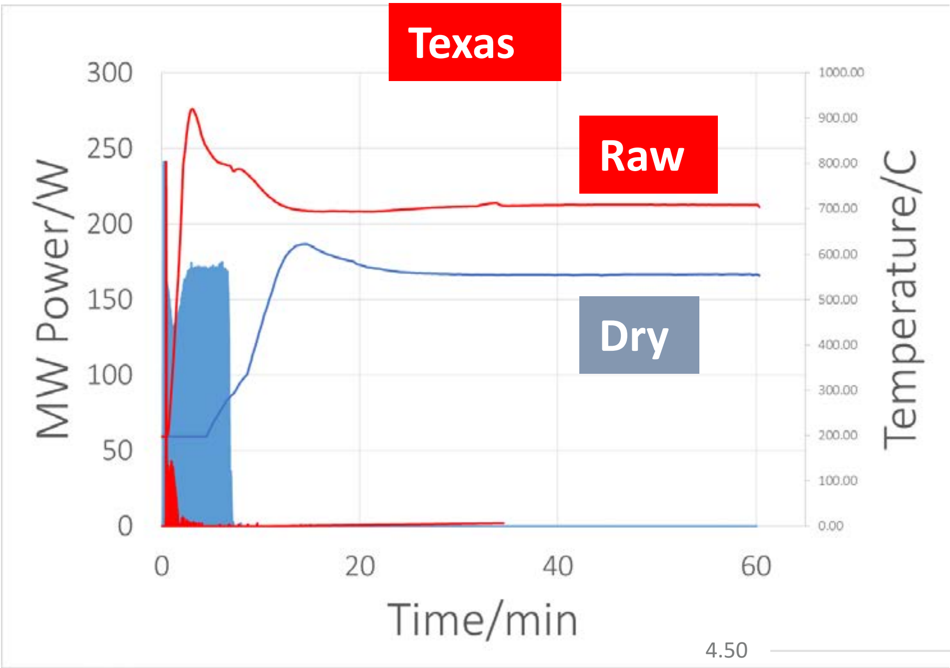
Stage III

- How stable is the pyrolysis temperature

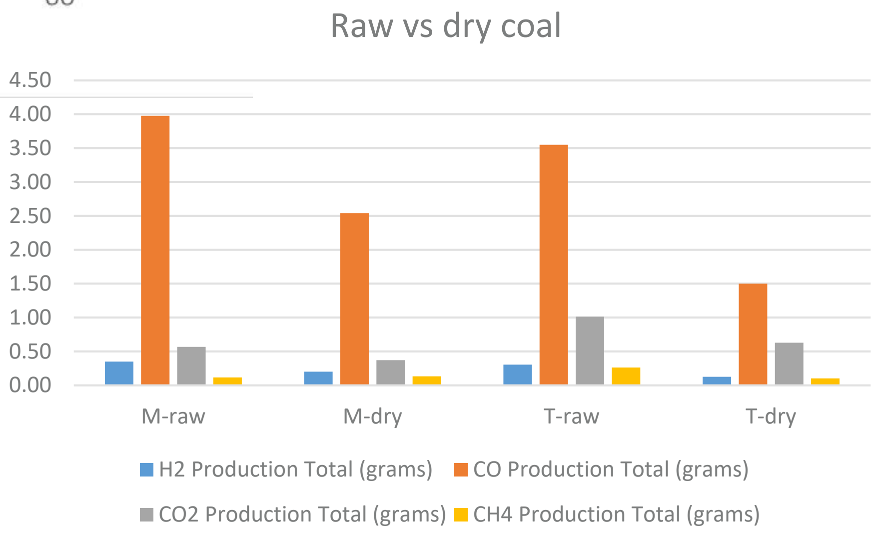
Effect of moisture

NATIONAL ENERGY TECHNOLOGY LABORATORY





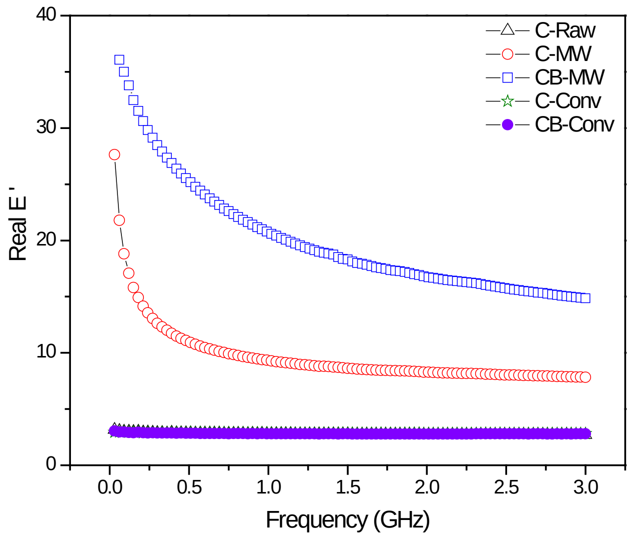
More gases were produced in presence of moisture than when it was dried for both coal samples M and T

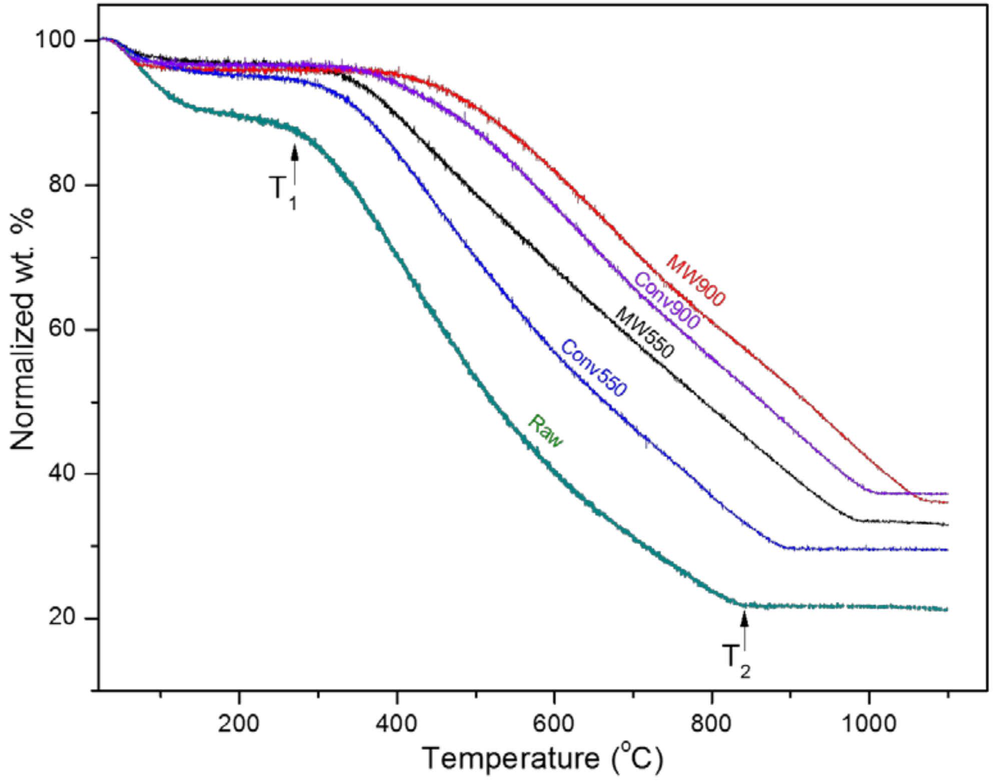


- Presence of moisture helped in reducing the reflected MW power and shortened the first heating stage
- Moisture could play a role in heating up the coal faster during the first stage enough to a temperature where the dielectric loss tangent increased drastically leading to zero MW power reflection

MW Pyrolysis of Coal: Properties of Chars

NATIONAL ENERGY TECHNOLOGY LABORATORY





- MW generated chars has higher permittivity which could be due to higher electron conductivity compared to conventional chars
- Addition of biomass increased the permittivity of MW chars which could indicate that the graphitic nature has increased upon biomass addition

TG curves of the raw coal and generated chars prepared at 550 and 900 oC under the microwave and conventional pyrolysis methods

Microwave-Enhanced Reactions

Target desired steps in mechanism

Series Reaction:	Example – MDA:
$xA \rightarrow B \rightarrow C$ B – desired product C – undesired	$6CH_4 \rightarrow C_6H_6 + H_2 \rightarrow \text{Coke}$
Parallel Reaction:	**Example – Methane decomposition:**
$xA \rightarrow B\ (\Delta H > 0)$ $yA \rightarrow C\ (\Delta H < 0)$	$CH_4 \rightarrow C_{(s)} + 2H_2$

Reaction	Equation	Endo/Exothermic
Non-oxidative methane dehydroaromatization	$6\ CH_4 \leftrightarrow C_6H_6 + 9\ H_2$	Endo (ΔH = 596 kJ/mol)
Non-oxidative coupling of methane	$2\ CH_4 \rightarrow C_2H_4 + 2H_2$	Endo (ΔH = 202 kJ/mol)
Oxidative coupling of methane	$2\ CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	Exo (ΔH = -455 kJ/mol)
Fischer-Tropsch	$nCO + 2n\ H_2 \rightarrow C_nH_{2n} + n\ H_2O$	Exo (ΔH = - 165 kJ/mol)
Methane dry reforming	$CH_4 + CO_2 \leftrightarrow 2\ CO + 2\ H_2$	Endo (ΔH = 247 kJ/mol)
Methane steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3\ H_2$	Endo (ΔH = 226 kJ/mol)

Catalytic MW Selective Pulsing: Concept

Matching pulse time to individual steps in reaction mechanism

Reaction:

$xA \rightarrow B + C$	Desired	t_1
$yB \rightarrow D$	Undesired	$t_2 > t_1$

Methane dehydroaromatization:

$6\ CH_4 \leftrightarrow C_6H_6 + 9H_2$ ***Eq. Yield at 700°C ≈ 10-12%***

$$2CH_4 = C_2H_4 + 2H_2 \qquad \Delta H^0_{298.15} = 202.0 kJ/mol$$
$$3C_2H_4 = C_6H_6 + 3H_2 \qquad \Delta H^0_{298.15} = -74.0 kJ/mol$$
$$C_6H_6 + 2C_2H_4 = C_{10}H_8 + 3H_2 \qquad \Delta H^0_{298.15} = -39.5 kJ/mol$$

Note: Need to consider parallel side reactions as well!

$$6CH_4 = C_6H_6 + 9H_2$$
$$CH_4 = C + 2H_2$$