Microwave-Enhanced Coal Gasification

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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

Traditional Thermal Approach

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

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
\( \nu = 2.45 \text{ GHz} \)
\( \lambda = 12.25 \text{ cm} \)
\( E = 0.098 \text{ cm}^{-1} (0.978 \text{ J/mol}) \)

A material’s ability to absorb microwave depends on:
- Dielectric properties
- Frequency of microwave energy
- Temperature of material

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

Permittivity

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)
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
NETL MW Capabilities

Reactors

- 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

- Dual E-Band Applicator

- Fixed bid

- Slotted window

- 8mm window for IR Pyrometer

- Water cooling

- Interchangeable chimneys

- Quartz tube

- Mass Flow Controller
  - Air, H2, CO2

- Glan Slab Porcelain

- Microwave Power Supply

- Sliding Short

- Unique position for each frequency

- Standing Wave applicator

- Maxima at load

- Downstream source section
Multi-scale FDTD Simulations of Microwave Interactions

Macroscopic Electromagnetic Waveguide Interaction

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

Microscopic Electromagnetic Material Interaction

Prediction of Local Heat Flux and Energy Deposition
Complex Material Characterization

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

- 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

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

MW conditions produced higher CO/CO₂ ratio attributed to CO₂ gasification of carbon

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$_6$H$_6$ products that increased with time and leveled off at 2 hrs
- Ethylene production trended the same as benzene

**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.

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>N2 flow: 100 (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Carbon black 300-600 micron</td>
</tr>
<tr>
<td>Applicator</td>
<td>Frequency (fixed) Sweep Time MW Power</td>
</tr>
<tr>
<td>Large applicator /low range</td>
<td>2.4-3.95 GHz 155 min (10 min/100MHz) Repeat the sweep at 100, 200, 300 W and 400 W (if applicable)**</td>
</tr>
<tr>
<td>Mid range</td>
<td>3.95-5.85 GHz 190 min (10 min/100MHz) Same as **</td>
</tr>
<tr>
<td>Small applicator/ High range</td>
<td>5.85-8 GHz Same as **</td>
</tr>
<tr>
<td>Temperature limit</td>
<td>Not to exceed 1000 C For either the reactor or catalyst surface temperatures</td>
</tr>
<tr>
<td>MW Power steps</td>
<td>100 W steps up to 400W* *Middle band can go up to 400W</td>
</tr>
</tbody>
</table>

**Repeat sweep at 100, 200, 300 W and 400 W (if applicable)**
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

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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

Microwave-Assisted Reactions

Improve conversion and selectivity

\[ \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S} \]

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

Oxidative Coupling of Methane

Methane Dehydroaromatization

\[ 6 \text{CH}_4 \leftrightarrow \text{C}_6\text{H}_6 + 9 \text{H}_2 \]

- 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

Selective Conversion

Example: Methane to Benzene

$$\text{CH}_4 \xrightarrow{[\text{MoC}_x]} \text{C}_2\text{H}_4 \xrightarrow{[\text{H}^+]} \text{C}_{6}\text{H}_6$$

Product Desorption

Temperature

Time (microseconds)

$\text{CH}_4 \rightarrow \text{C(s)} + 2\text{H}_2$

$\text{xCH}_4 \rightarrow \text{xCH}_2\cdot + \text{H}_2$

$\text{xCH}_4 \rightarrow \text{xCH}_2\cdot + \text{H}_2$

$\text{CH}_2=\text{CH}_2\cdot \rightarrow \text{C}_6\text{H}_6$

$\text{CH}_2=\text{CH}_2\cdot + \text{C}_6\text{H}_6 \rightarrow \text{Coke}$

Microwave Effect:
- Intended to promote or prevent the endothermic steps of the overall reaction mechanism, depending on the desired products.
Methane Dehydroaromatization

**CH₄** → **[MoCₓ]** → **C₂H₄** → **[H⁺]** → **[H⁺]** → Benzene

- 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

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass catalyst, g</td>
<td>1.0</td>
</tr>
<tr>
<td>Methane flow rate, sccm</td>
<td>50</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>700</td>
</tr>
<tr>
<td>Pressure, atm</td>
<td>1.0</td>
</tr>
<tr>
<td>MW power, W</td>
<td>300</td>
</tr>
<tr>
<td>MW frequency, GHz</td>
<td>2.45</td>
</tr>
<tr>
<td>MW pulse, ms on/off</td>
<td>500</td>
</tr>
</tbody>
</table>
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

What about efficiency?

**Assumptions:**
- $C_p = 880 \text{ J/kg-K} \text{ (alumina)}$
- Fluid phase & rxn negligible
- Heat losses negligible
- 1 wt% Active Phase
- Frequency = 2.45 GHz
- Reflected power negligible

**Thermal**
- $Q = 680 \text{ kJ}$
- $T = 800^\circ \text{C}$

**mW ≈**
- $Q = 470 \text{ kJ}$
- $800^\circ \text{C}$
- 400°C

**Hot Spots**

**RXR**
- Feed
- Product A
- Product B
- Product C
Selective Pulsing of Microwaves
Additional approach to Selective Heating

Reaction:

\[ xA \rightarrow B + C \] Desired $\Delta H > 0$ Endothermic
\[ yB \rightarrow D \] Undesired $\Delta H < 0$ 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

Drop tube configuration

Conventional reactor

MW reactor

550°C

50°C

Coal/Biomass (10 g)

Microwave cavity

MS (N₂, H₂, CO, CO₂, CH₄)

MicroGC (N₂, H₂, CO, CO₂, CH₄)

(C₂H₂, C₂H₄, C₂H₆, C₃H₆, 1,3-butadiene, BZ, Tol.)

6 Coal samples
Mississippi
Illinois#6
Wyodak
Texas
PRB
Rosebud

Lignite
Sub-B

MTL

FTIR

Cold trap (-10°C) for condensates

GC-MS
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 H₂ at low gasification temperature compared to conventional operation
- Concentration of H₂ produced is almost the same under MW at all temperatures

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

**Graphs:**
- Graphs showing gasification rates at 600°C, 700°C, and 800°C for MW and conventional operation.
Pyrolysis of Different Coal Types

- 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: N₂-300sccm
- 10 g of raw coal or coal/biomass
- MW Power: 500 W
- Pressure: 0.1 MPa
MW vs Conventional pyrolysis: Mississippi coal

For MW CO > CO₂

- Gas Flow: N₂-300 sccm
- 10 g of raw coal or coal/biomass
- MW Power: 500 W
- Pressure: 0.1 MPa
- Reaction Time: 120 min

Could it be the heating rate or MW enhancement effect?
Effect of H₂ and CH₄ during pyrolysis under MW conditions

- Significant amount of hydrocarbons produced at low temperature, particularly in the presence of H₂ or CH₄ 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
**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

- 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.

More gases were produced in presence of moisture than when it was dried for both coal samples M and T.
MW Pyrolysis of Coal: Properties ofChars

- 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 °C under the microwave and conventional pyrolysis methods.
Microwave-Enhanced Reactions

Target desired steps in mechanism

Series Reaction:

\[ xA \rightarrow B \rightarrow C \]

- B – desired product
- C – undesired

Parallel Reaction:

\[ xA \rightarrow B \ (\Delta H > 0) \]
\[ yA \rightarrow C \ (\Delta H < 0) \]

Example – Methane decomposition:

\[ CH_4 \rightarrow C_{(s)} + 2H_2 \]

Example – MDA:

\[ 6CH_4 \rightarrow C_6H_6 + H_2 \rightarrow \text{Coke} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Endo/Exothermic</th>
</tr>
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<tbody>
<tr>
<td>Non-oxidative methane dehydroaromatization</td>
<td>[ 6 \text{CH}_4 \leftrightarrow \text{C}_6\text{H}_6 + 9 \text{H}_2 ]</td>
<td>Endo ((\Delta H = 596 \text{kJ/mol}))</td>
</tr>
<tr>
<td>Non-oxidative coupling of methane</td>
<td>[ 2 \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2 ]</td>
<td>Endo ((\Delta H = 202 \text{kJ/mol}))</td>
</tr>
<tr>
<td>Oxidative coupling of methane</td>
<td>[ 2 \text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} ]</td>
<td>Exo ((\Delta H = -455 \text{kJ/mol}))</td>
</tr>
<tr>
<td>Fischer-Tropsch</td>
<td>[ n\text{CO} + 2n \text{H}_2 \rightarrow \text{C}<em>n\text{H}</em>{2n} + n \text{H}_2\text{O} ]</td>
<td>Exo ((\Delta H = -165 \text{kJ/mol}))</td>
</tr>
<tr>
<td>Methane dry reforming</td>
<td>[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2 \text{CO} + 2 \text{H}_2 ]</td>
<td>Endo ((\Delta H = 247 \text{kJ/mol}))</td>
</tr>
<tr>
<td>Methane steam reforming</td>
<td>[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2 ]</td>
<td>Endo ((\Delta H = 226 \text{kJ/mol}))</td>
</tr>
</tbody>
</table>
Catalytic MW Selective Pulsing: Concept

Matching pulse time to individual steps in reaction mechanism

Reaction:

\[ xA \rightarrow B + C \quad \text{Desired} \quad t_1 \]
\[ yB \rightarrow D \quad \text{Undesired} \quad t_2 > t_1 \]

Methane dehydroaromatization:

\[ 6 \text{CH}_4 \leftrightarrow \text{C}_6\text{H}_6 + 9\text{H}_2 \quad \text{Eq. Yield at 700°C} \approx 10\text{-}12\% \]

\[ 2\text{CH}_4 = \text{C}_2\text{H}_4 + 2\text{H}_2 \quad \Delta H_{298.15}^0 = 202.0\text{kJ/mol} \]
\[ 3\text{C}_2\text{H}_4 = \text{C}_6\text{H}_6 + 3\text{H}_2 \quad \Delta H_{298.15}^0 = -74.0\text{kJ/mol} \]
\[ \text{C}_6\text{H}_6 + 2\text{C}_2\text{H}_4 = \text{C}_{10}\text{H}_8 + 3\text{H}_2 \quad \Delta H_{298.15}^0 = -39.5\text{kJ/mol} \]

Note: Need to consider parallel side reactions as well!