Microwave Effects in Heterogenous Materials: A Study on Catalysis

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NATIONAL ENERGY TECHNOLOGY LABORATORY

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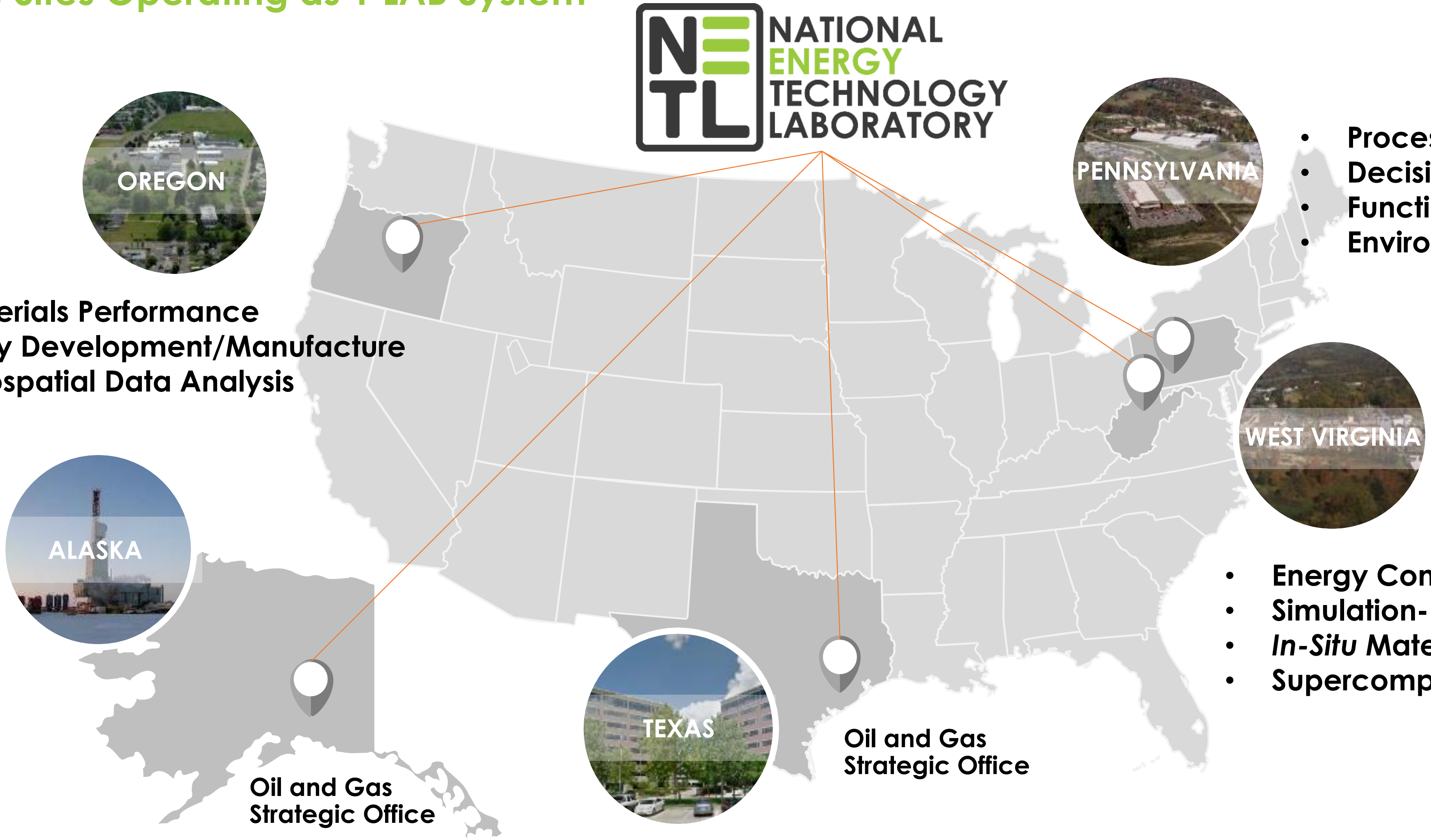
Presentation Outline

- **NETL Reaction Engineering Team Introduction**
  - Mission Statement
- **Microwave Catalysis - Background**
- **Experimental Capabilities**
- **Case Study – Ammonia Synthesis**
  - Support material
  - Active Site Loading
  - Microwave Variables
- **Future Work**

NETL Structure

Multiple Sites Operating as 1 LAB System



Oregon

- Materials Performance
- Alloy Development/Manufacture
- Geospatial Data Analysis

Pennsylvania

- Process Systems Engineering
- Decision Science
- Functional Materials
- Environmental Sciences

West Virginia

- Energy Conversion Devices
- Simulation-Based Engineering
- *In-Situ* Materials Characterization
- Supercomputer Infrastructure

NETL R&IC Core Competencies

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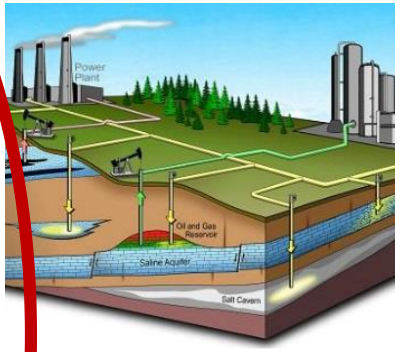
Materials Engineering & Manufacturing

- Structural & Functional
- Design, Synthesis, & Performance

Energy Conversion Engineering

- Component & Device
- Design & Validation

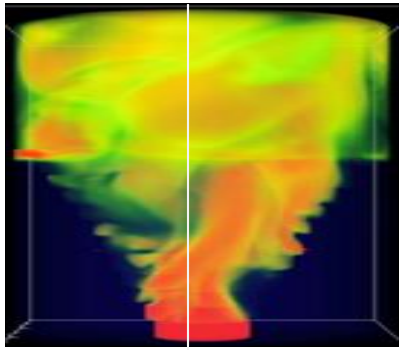


Geological & Environmental Systems

- Air, Water & Geology
- Understanding & Mitigation

Systems Engineering & Analysis

- Process & System
- Optimization, Validation, & Economics



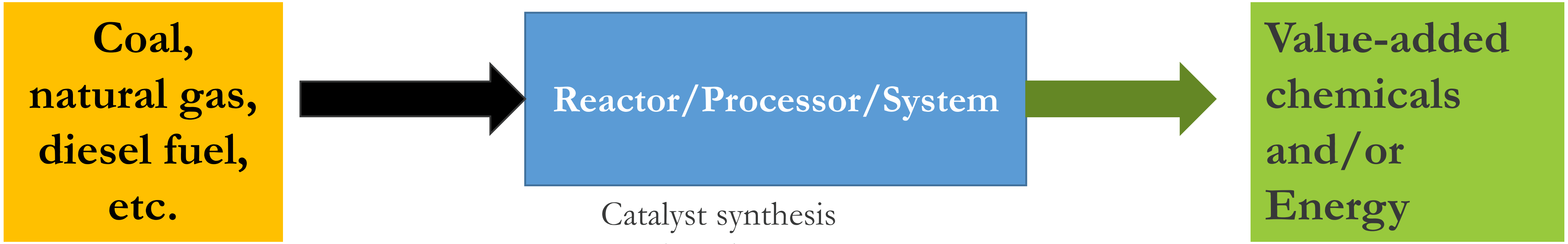
Computational Science & Engineering

- High Performance Computing
- Data Analytics

Effective Resource Development • Efficient Energy Conversion • Environmental Sustainability

Reaction Engineering Team

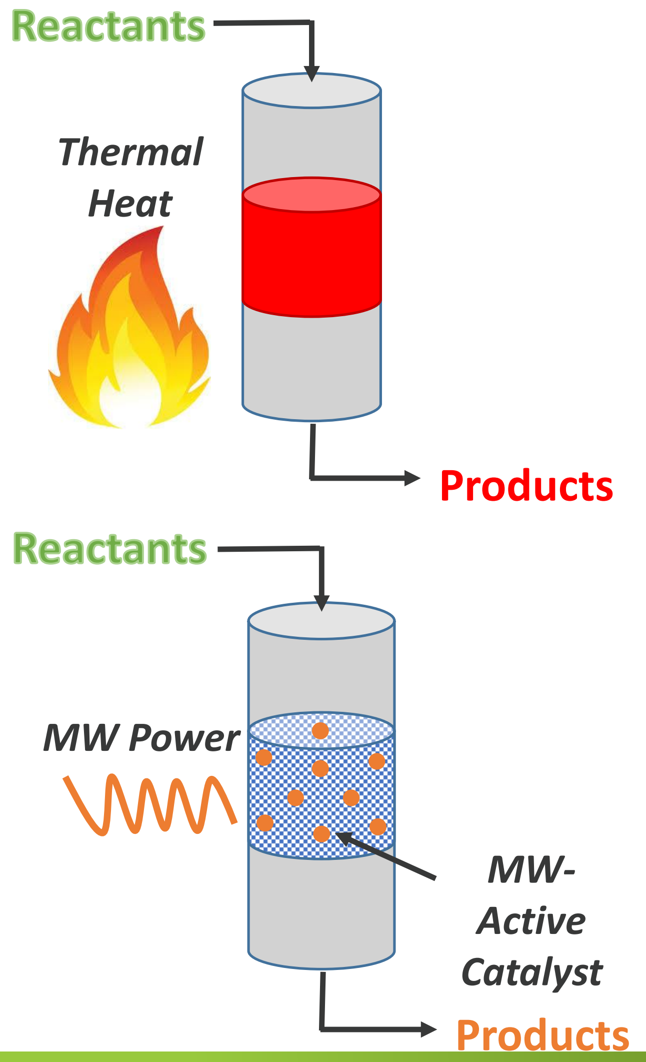
- Evaluate and develop electromagnetic energetic systems (microwave, plasma, etc.) for conversion of materials into energy and/or value-added products.



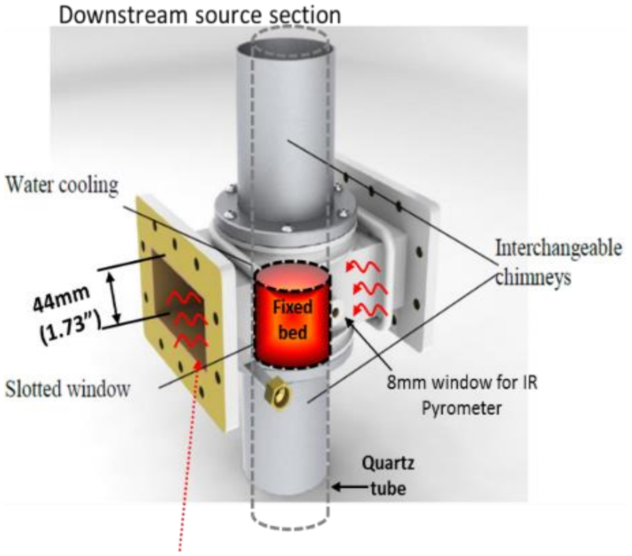
Catalyst synthesis
Catalyst characterization
Reaction Mechanism
Kinetics
Thermodynamics
Catalyst testing

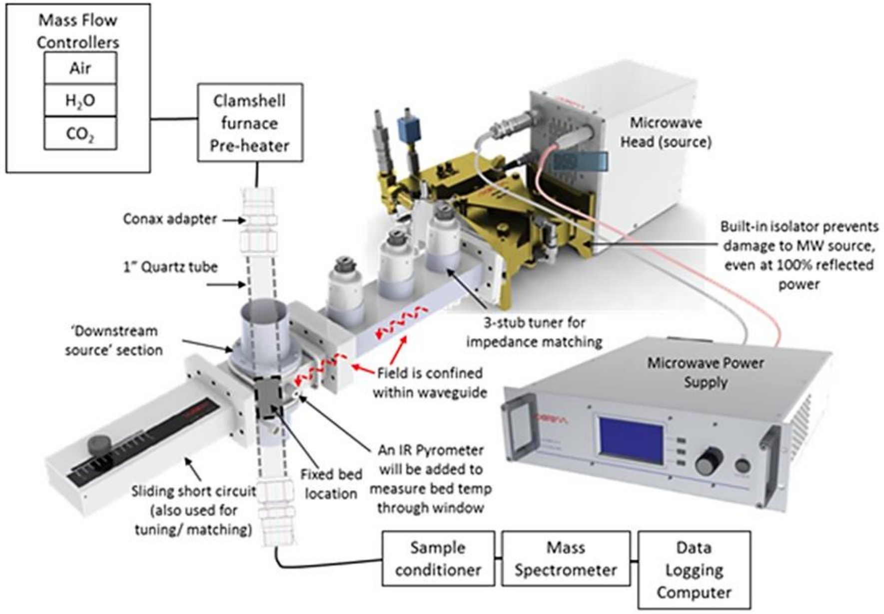
Advantages of Microwaves in Catalysis

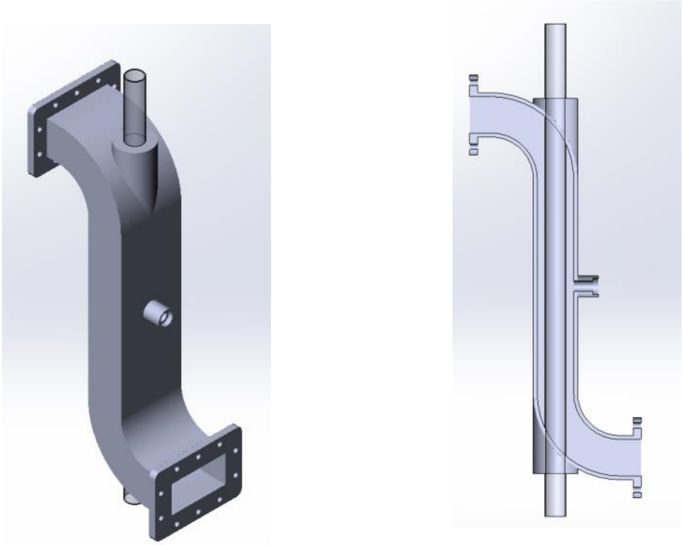
- **Heterogeneous Catalysis at NETL**
  - Heterogenous material
  - Gas/Solid interaction
- **Benefits include:**
  - Selective heating
  - Volumetric heating (efficiency savings)
  - Product selectivity
  - Lower bulk temperatures for reactions
  - Lower activation energy
  - Mechanistic changes not available with conventional thermal reactors



NETL MW Capabilities
Reactors and Characterization







Variable Frequency Vertical Configuration

- **Reactor Systems**
  - **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 and vertical
  - **High Pressure Flow Through Reactor (2020)**

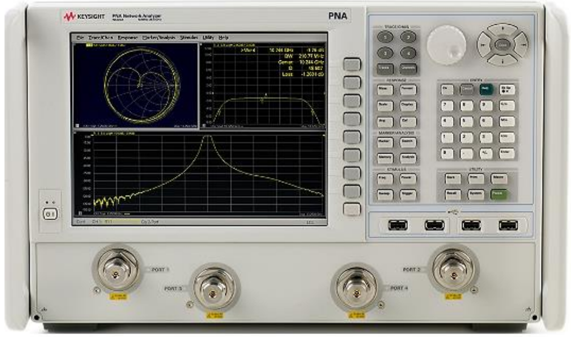
NETL MW Capabilities
Reactors and Characterization

OceanOptics Spectrometer

Cell for EM measurement

IR Camera - FLIR

- **Microwave Characterization**
  - Vector Network Analyzers (Keysight N5231A PNA-L & N5222A PNA)
    - To measure electromagnetic (EM) properties of materials
  - Developing a cell to measure the electromagnetic properties up to 500° C
  - Optical Spectrometers
  - FLIR IR Camera 400-1500°C



Vector Network Analyzers

Case Study – Ammonia Synthesis

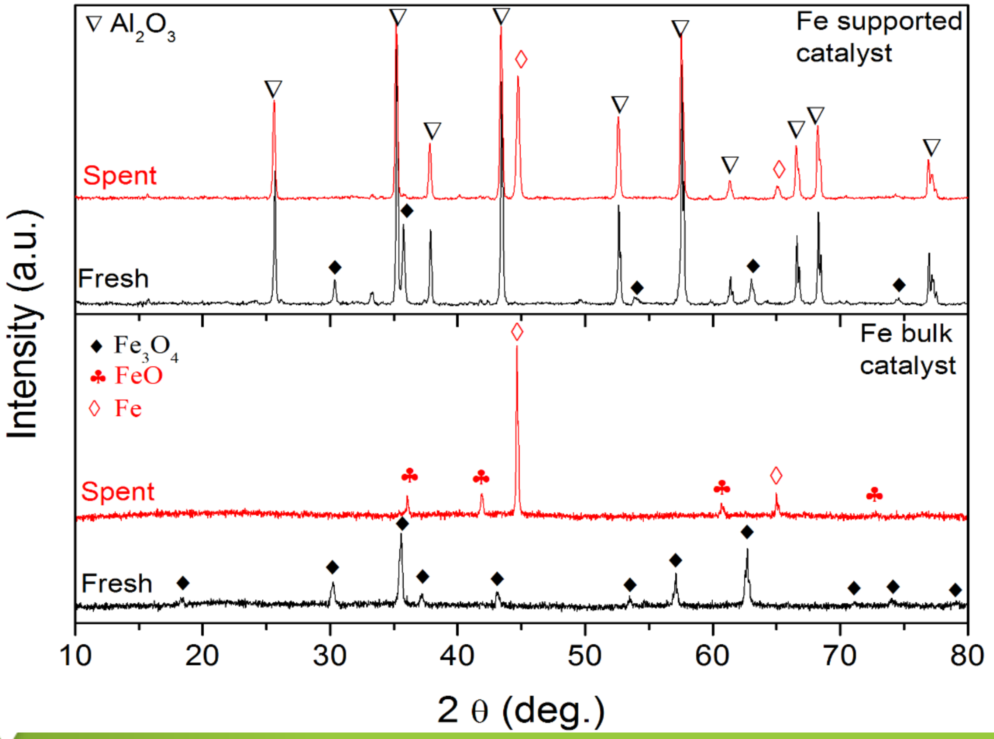
- **Transform High Pressure/High Temperature Process to Atmospheric Pressure/Low Temperature**

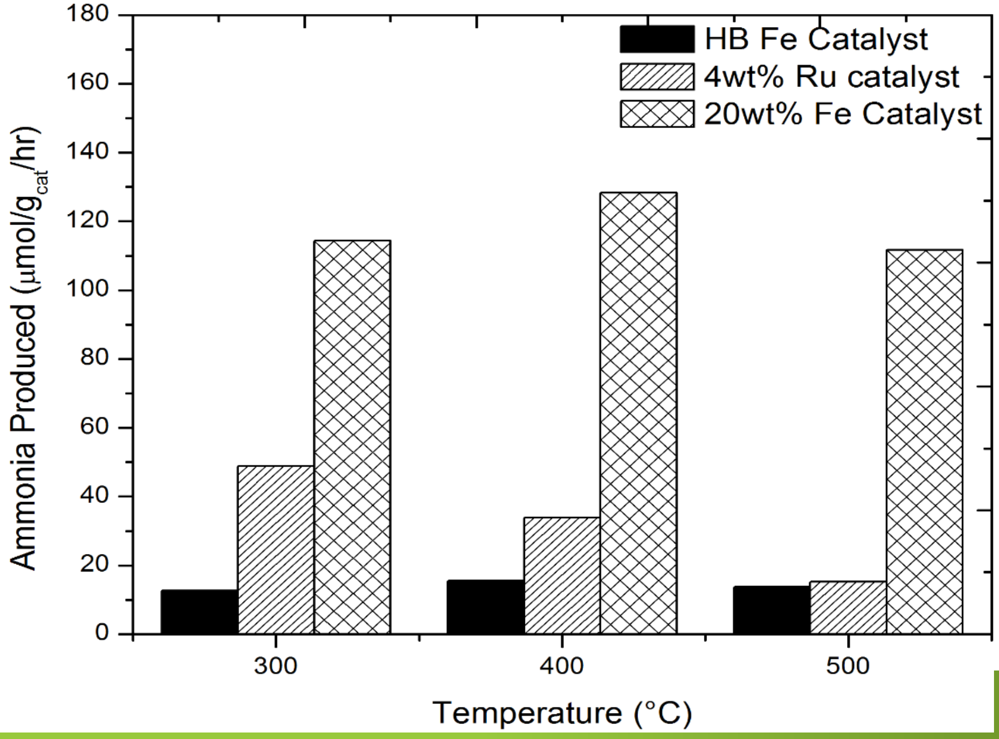
$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

- **No By-Products**
- **High activation energy needed for dissociative adsorption of Nitrogen**
- **Long history of catalytic data for tradition thermal reaction**
  - Iron and Ruthenium most commonly used

Importance of Heterogeneous Catalyst

- Commercial Haber-Bosch catalyst > 90% Fe based
- HB catalyst had very low activity in MW
- Activity greatly improved by separating active sites





Catalyst Formulation Variables

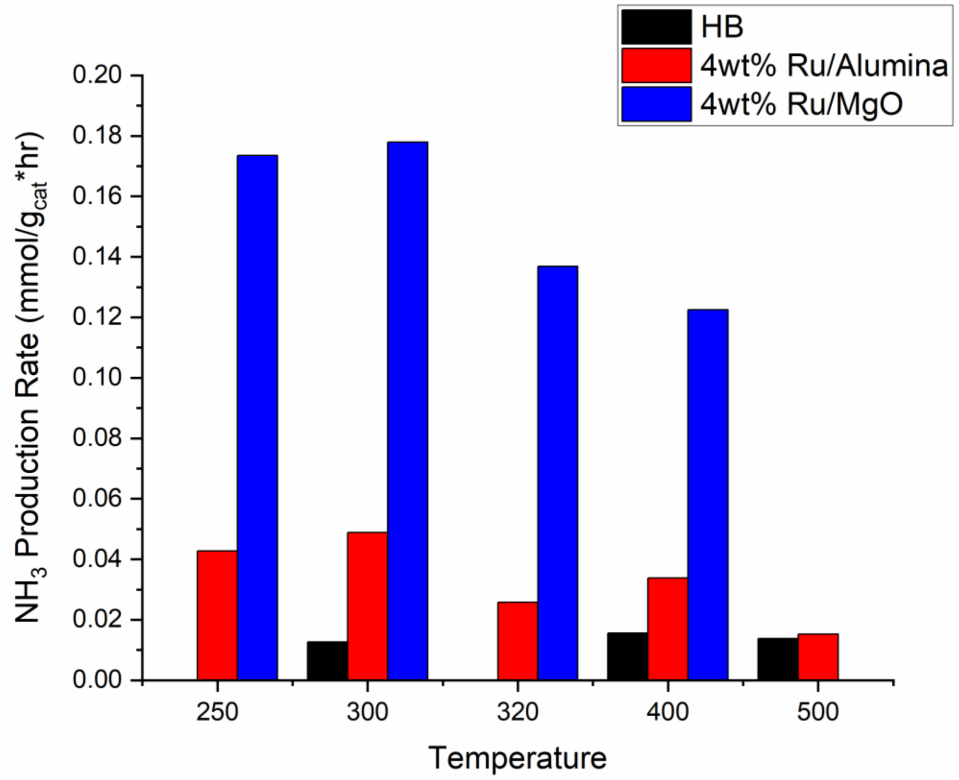
- **Support Material**
  - High porosity, acidic sites – traditional catalysis
  - Microwave absorptive
- **Active sites**
  - Type of metal (Iron vs Ruthenium)
  - Volume loading
  - Size of metallic sites

Catalyst Support

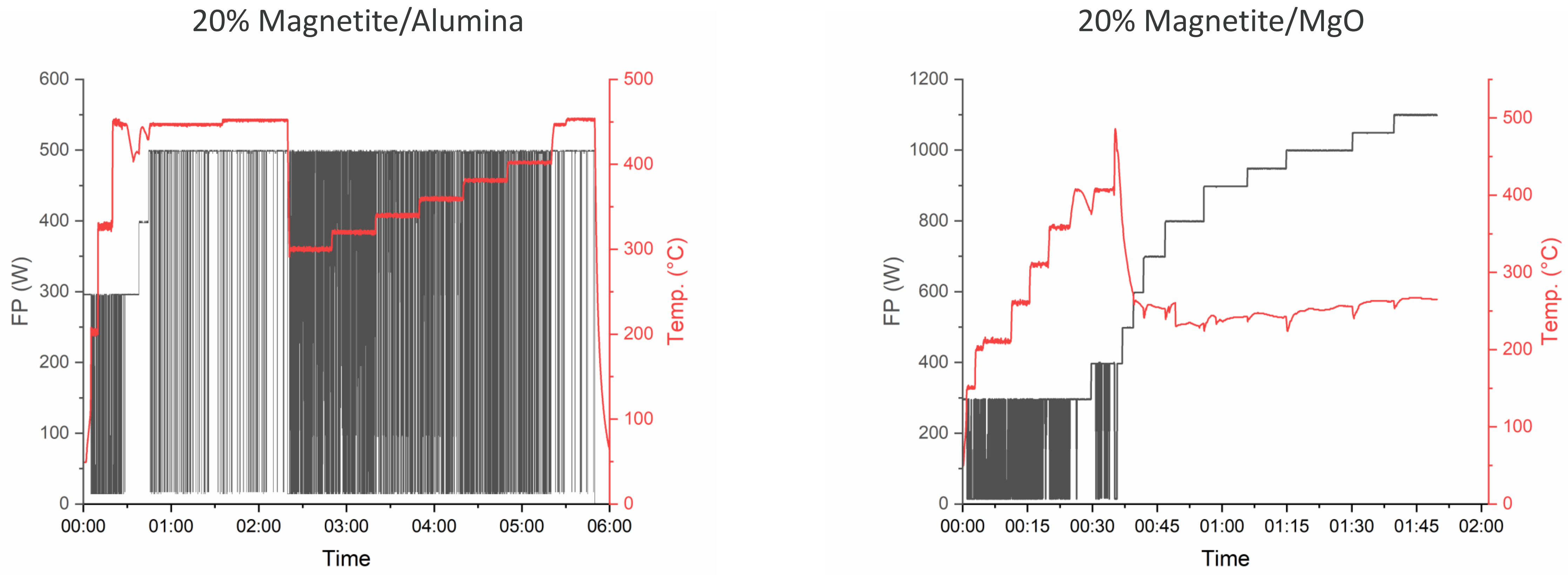
- **Catalytic activity was highly dependent on support**
  - Support needed to be "inert" in MW field
  - Optimal support dependent on metal site used
    - MgO – Ru
    - Alumina – Fe
  - Balance between catalytic activity and efficiency of system

Catalyst Support- Activity Testing

- **Tested Ru based catalysts with multiple supports**
  - Alumina
  - MgO
  - Carbon
  - Silica
- **Carbon supports created Methane**
- **Silica was non-responsive to MW**



Catalyst Support – Dependency of Active Site



- 20% Magnetite/Alumina active and able to achieve reaction temperatures of 500^{o}C
- MgO support lost ability to heat once reduction temperatures for Magnetite was reached
- Fe was ruled out as an active site candidate

Catalyst Support – System Efficiency

- **How is efficiency defined? Applied Power or Absorbed Power**
  - MgO support had highest activity
  - Highest efficiency depends on definition of Power

Catalyst Type	250°C		300°C		400°C	
	Applied	Absorbed	Applied	Absorbed	Applied	Absorbed
Alumina Support	300	97.5	300	87.7	300	103.4
MgO Support	400	34	400	37.53	500	63.98

Effect of Active Site Loading

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- **Increasing active sites:**
  - Increased Activity
  - Lowered absorbed power/site
  - Decreased Sintering of Catalyst

Effect of Metal Loading on Power and Activity

	Avg. Power Absorbed (W)	Avg. Power Absorbed/gram metal (W/g)	Avg. Ammonia (g_{amm}/g_{cat}/day)
4 wt% Ru/MgO	59	737.5	0.1
10 wt% Ru/MgO	64	320	0.25

Effect of Metal Loading on Surface Area

Catalyst		S_{BET} (m^2/g)
4wt% Ru/MgO	Fresh	71.5
	Spent	53.7
10wt% Ru/MgO	Fresh	61.0
	Spent	57.8

Microwave Variables

- **What is the mechanism driving the reaction?**
  - Hot Spots
  - Electric Field Generation

- **Does frequency have an effect?**

Microwave Variables – Hot Spots

- Comsol modeling – relate to BET data

Effect of Power

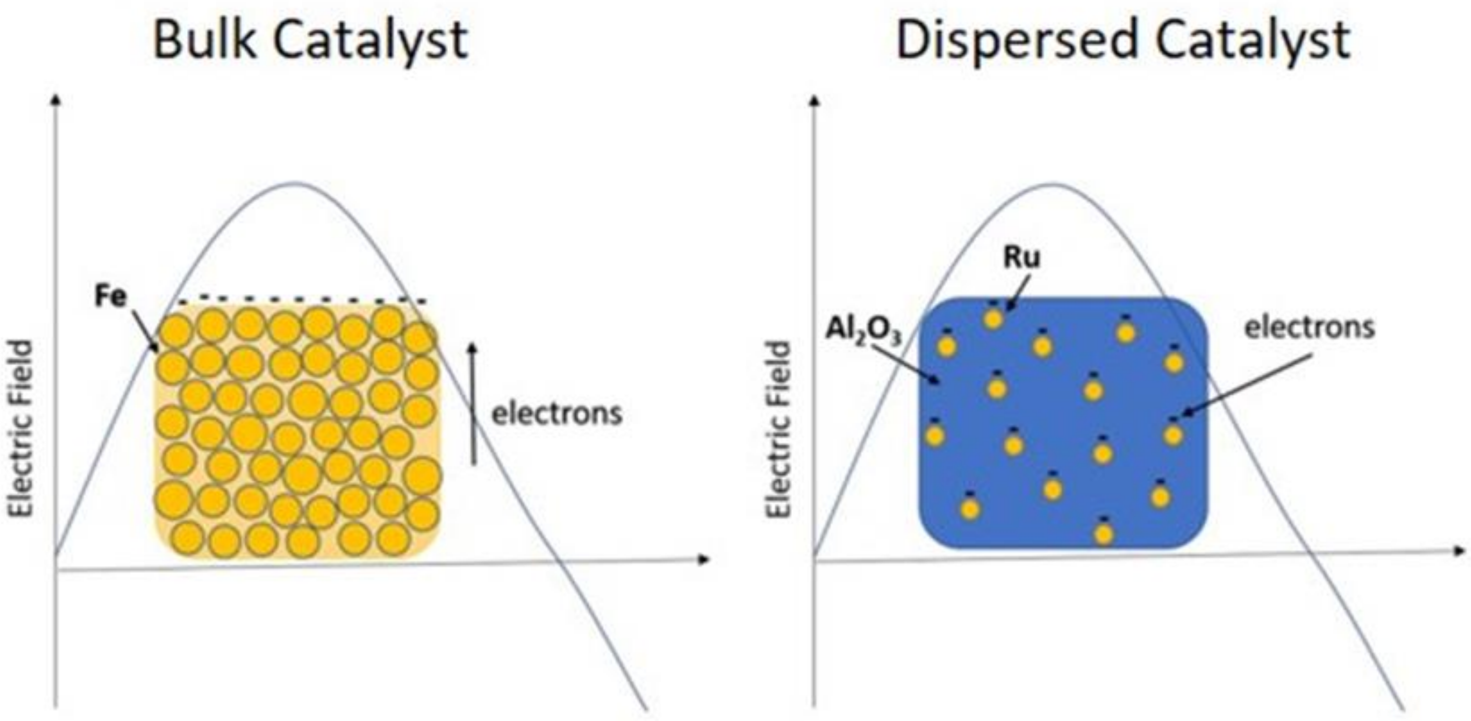
- Total ammonia produced was affected by power applied at a given temperature
- Increasing power from 300W to 500W doubled ammonia produced
- More than likely due to fields generated between particles

Electric Fields generated by MW can be used to increase ammonia production

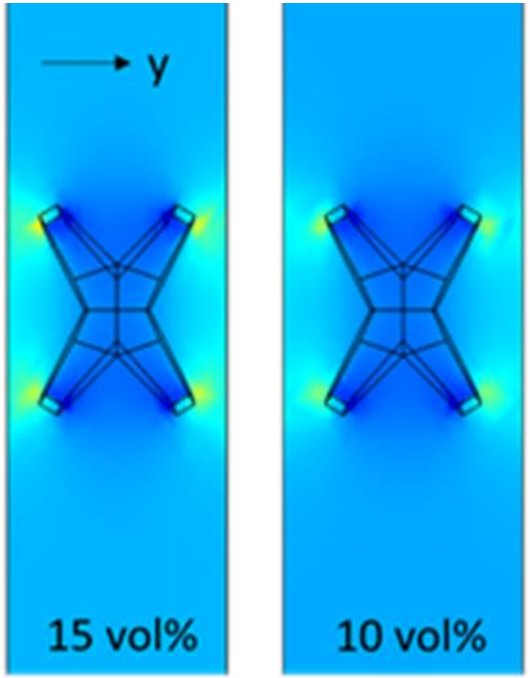
	Total ppm	250°C	300°C	400°C	500°C
4wt% Ru/Al_2O_3	300W	8633.5	10157.3	6635.4	1448.5
	500W	14590.9	16166.8	7371.9	3315.4

Microwave Variables – Electric Field

- **Power dependent activity – not explained by hot spots**



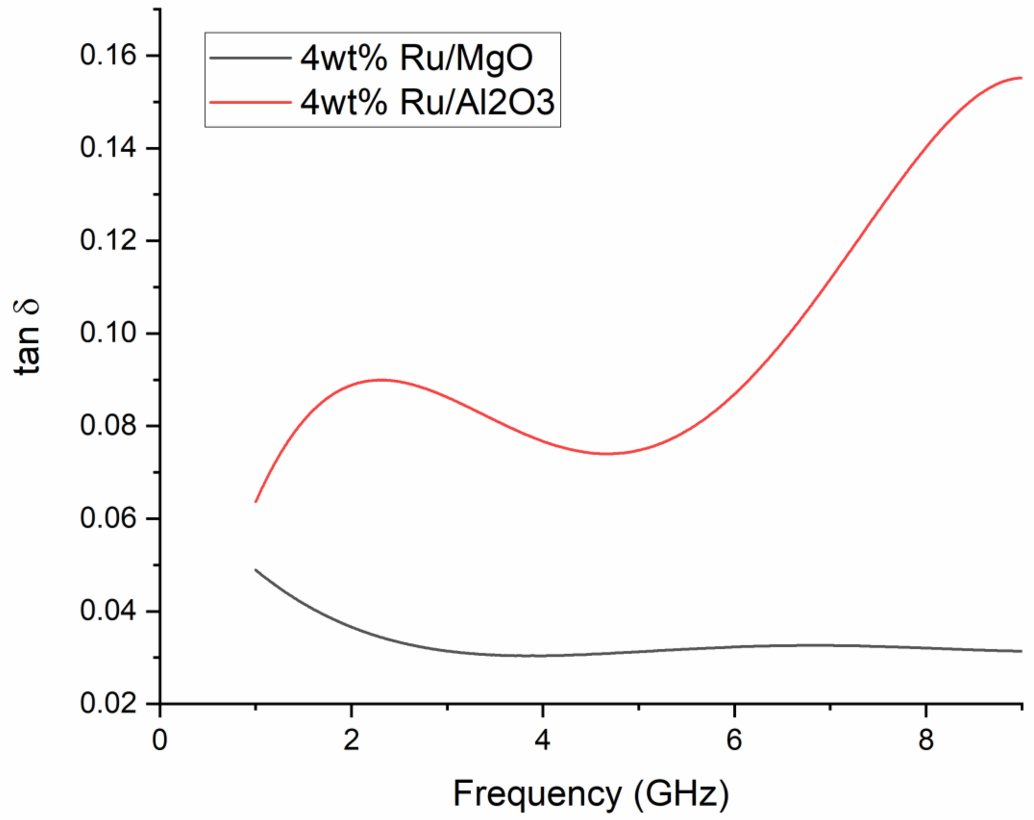
Electron movement within catalyst critical to activity



Electric field intensifies at edges of particles

Microwave Variables – Frequency Testing

- **Dielectric testing of catalysts**
  - MgO catalyst not frequency dependent
  - Alumina seems optimal at frequencies above 7 GHz



Microwave Variables - Frequency Testing

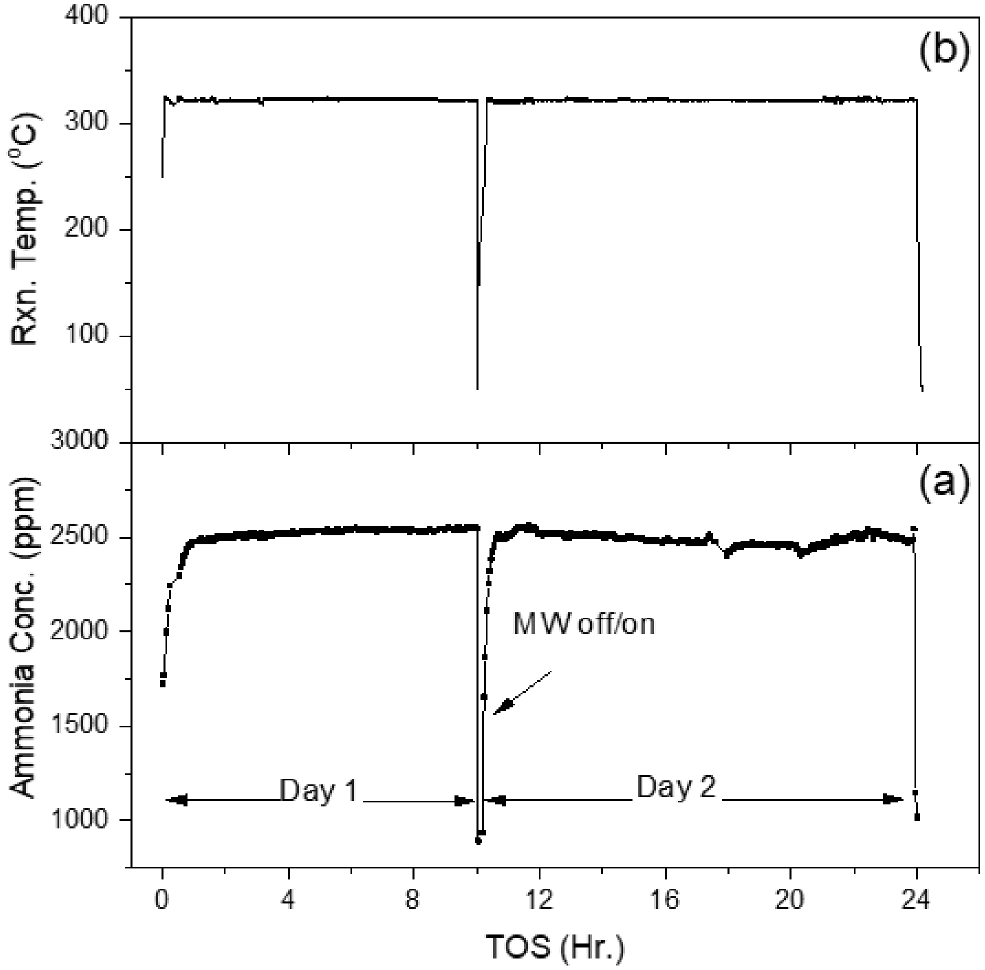
- Alumina and MgO catalyst were tested from 2.2-8 GHz
- Frequency had effect on ammonia production rate and overall efficiency
- The optimal frequency was unique for each catalyst
- Trends didn't follow dielectric testing results

Frequency response of Ru/Alumina

Frequency (GHz)	Ammonia Rate (μmol/g_{cat}/hr)	Power Absorbed (W)
4.1	0.29081	140.77
4.2	0.69086	114.7
4.65	0.70371	108.3
4.75	0.69467	121.1
5.7	0.64021	58.2
6.35	0.78094	110
7.4	1.0119	146
8	0.46875	84.4

MW Durability Testing

- First durability test was 24hr with one shutdown
- Microwave reactors allow for intermittent power shutdowns associated with renewable energy sources
- No loss of efficiency



Conclusions

- Microwave reactors can be efficiently used to scale down industrial processes
- Relationship between catalyst support, active sites, and processing parameters are very complex
- Optimization for efficiency will need to be done on a case-by-case basis

Future Plans

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- **Ammonia Synthesis**
    - Phase II includes increasing overall reactor efficiencies – sensitivity analysis
    - Adding pressure testing
    - Demo semi-pilot scale reactor
- **Reaction Engineering Team**
    - Adding characterization tools to understand fundamentals of MW-material interactions
    - Using heterogeneous material insights to understand reactions of complex structures like coal

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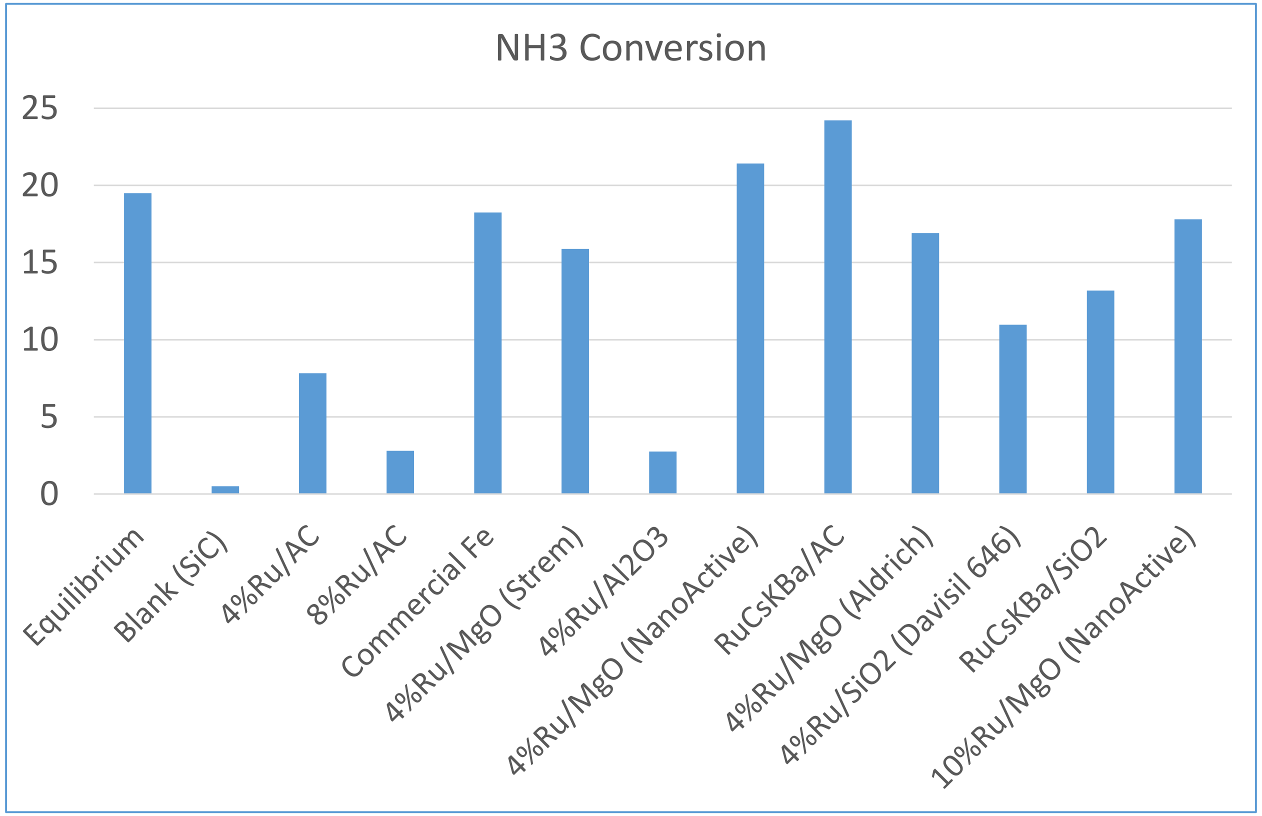
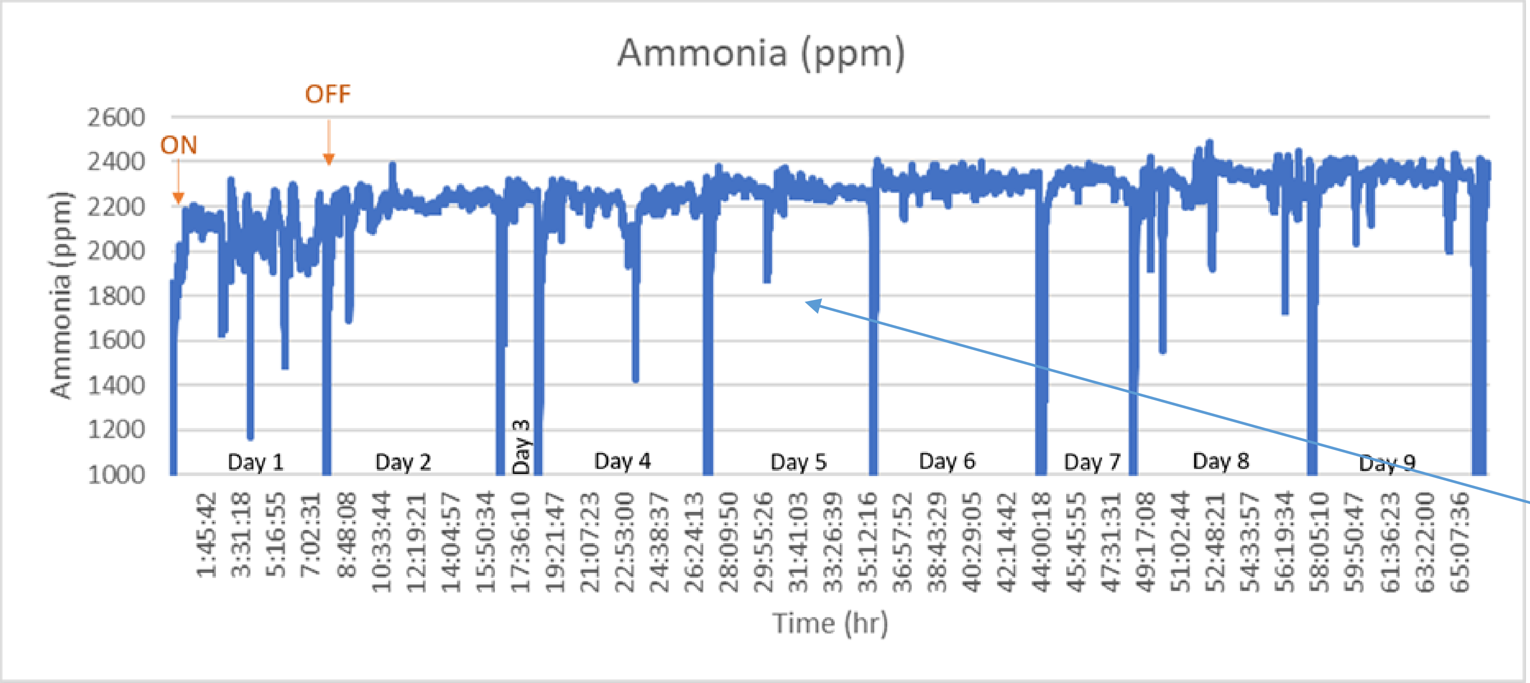
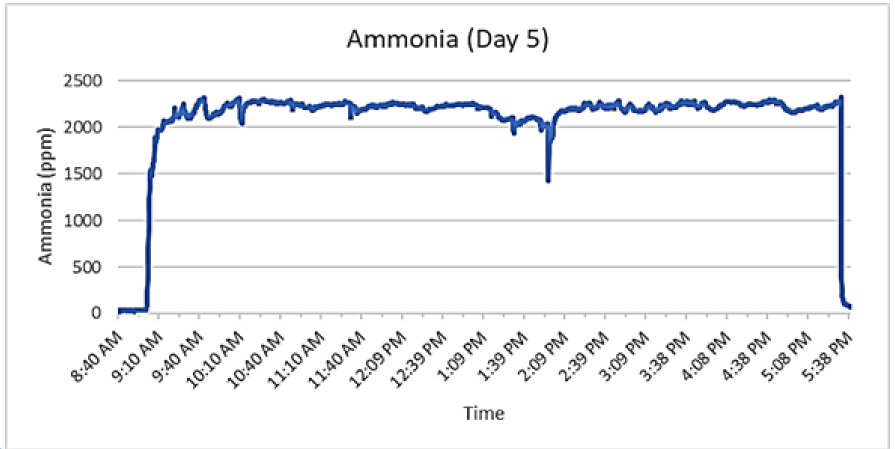
Questions?

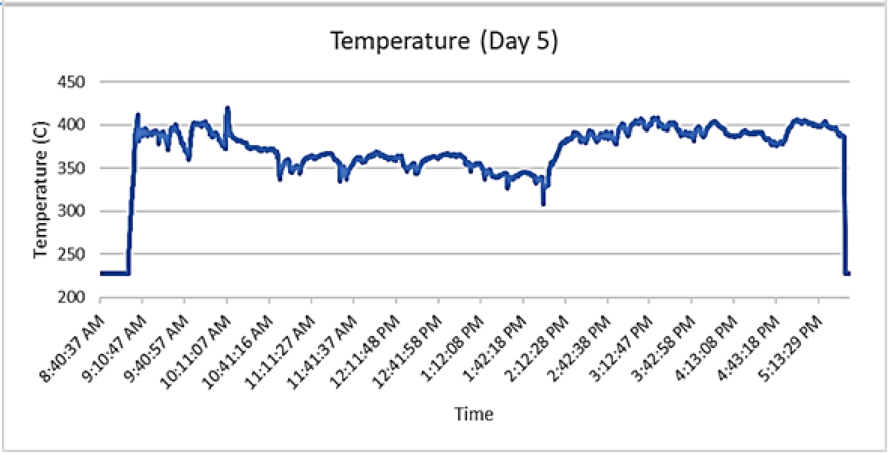
HB Ammonia Synthesis



70 hour durability testing







- MgO system used for long term durability test
- 9 days of testing with shutdown every night
- Temperature and reaction stabilized within 20 min
- Reaction temperature of 400ºC at 7350 MHz