Microwave Catalysis for Ammonia Synthesis under Mild Reaction Conditions

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Background of the Research

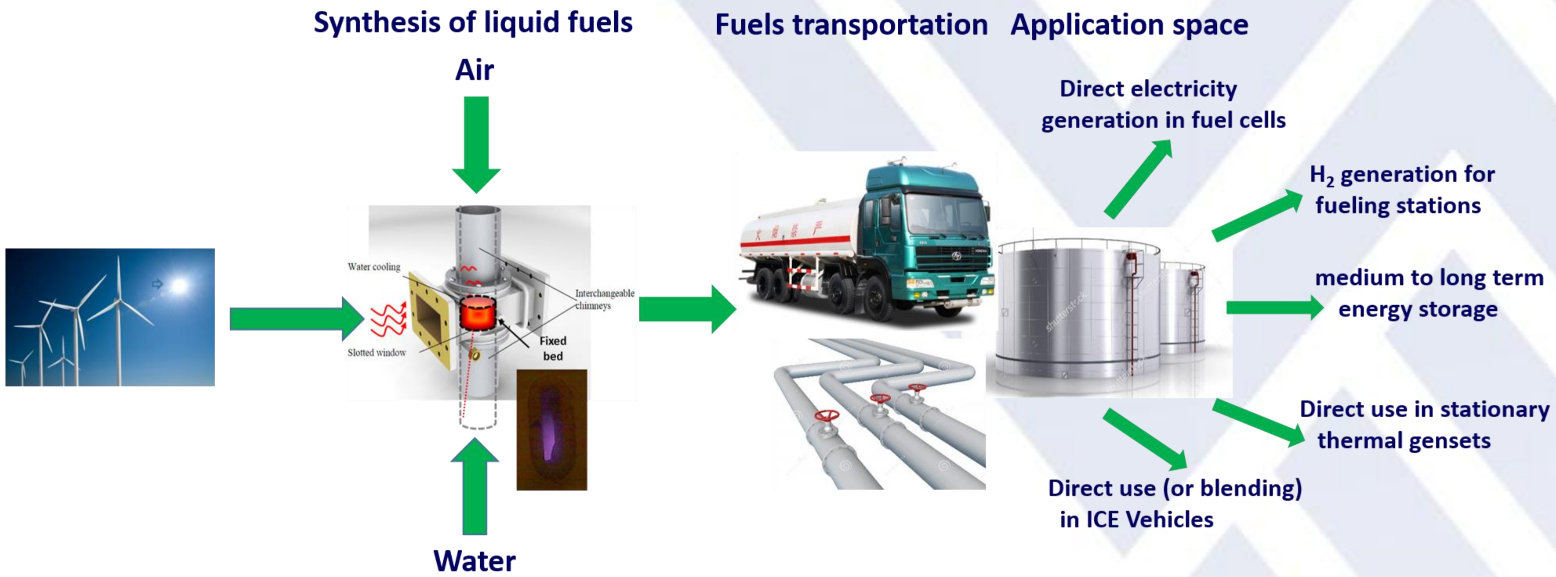


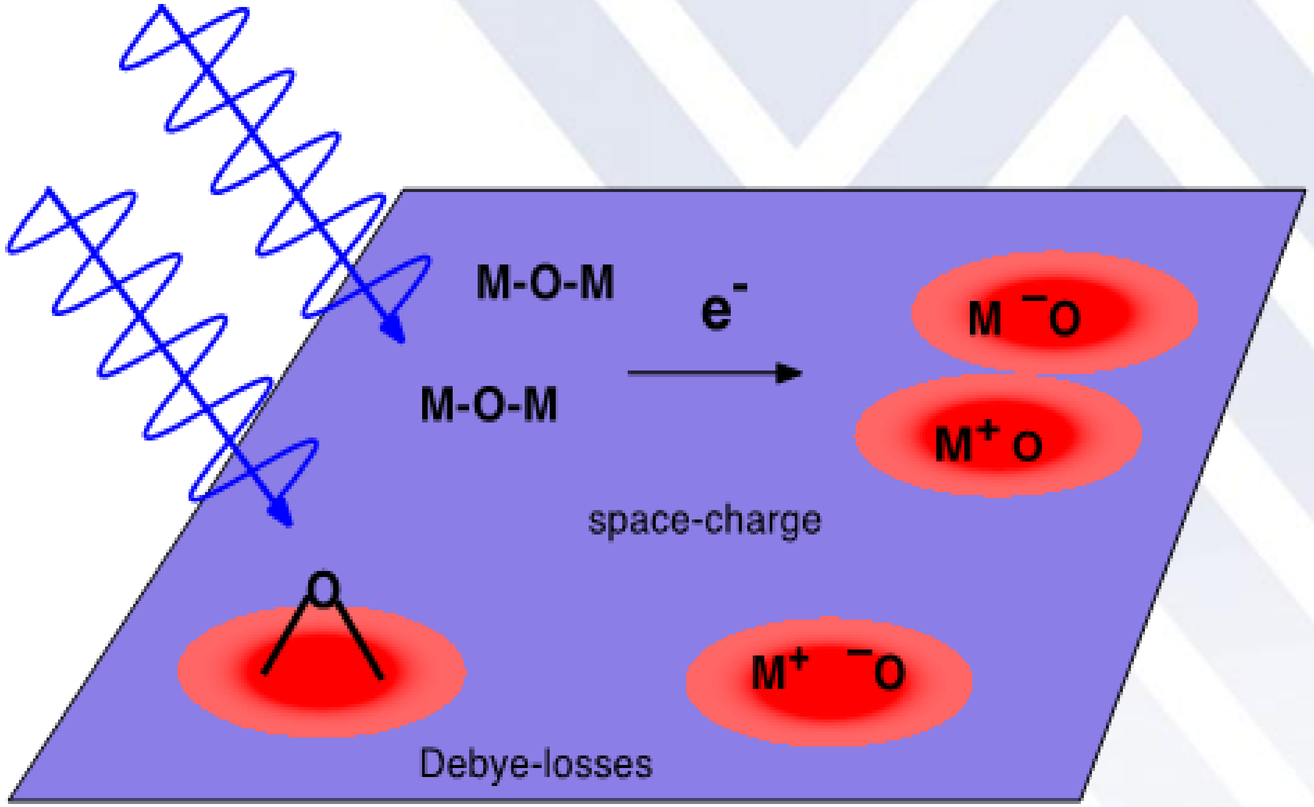
Figure 1. The production, transport and use of carbon-neutral liquid fuels (NH_3) for energy delivery

Haber-Bosch Process: the challenge of scaling down economically.

The technology is fundamentally different from H-B process, having cost advantages at small scale (~100-150MW input, 25-100tpd) comparable with large scale H-B process (~1000tpd). It can be tolerant to intermittent energy supply, therefore effectively operated at variable rates of production

Microwave Catalysis-Theory

Space-charge and Debye dielectric loss mechanisms for microwaves interacting with a catalyst surface for selective bond activation of reactant molecules

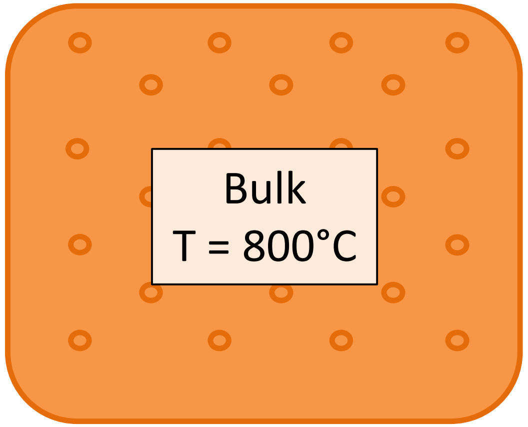


Thermal vs. Microwave Conversion

The myth of MW inefficiency

Thermal

Q = 682 kJ



Assumptions:

C_p = 880 J/kg-K (alumina)

Fluid phase & rxn negligible

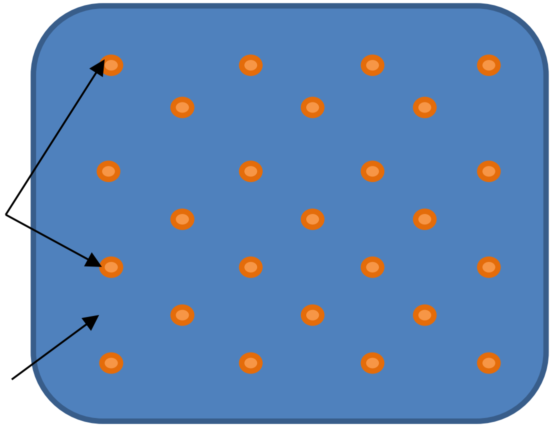
Heat losses negligible

Heater Eff ≈ 100%

mW ≈

Q = 473 kJ

800°C Hot Spots



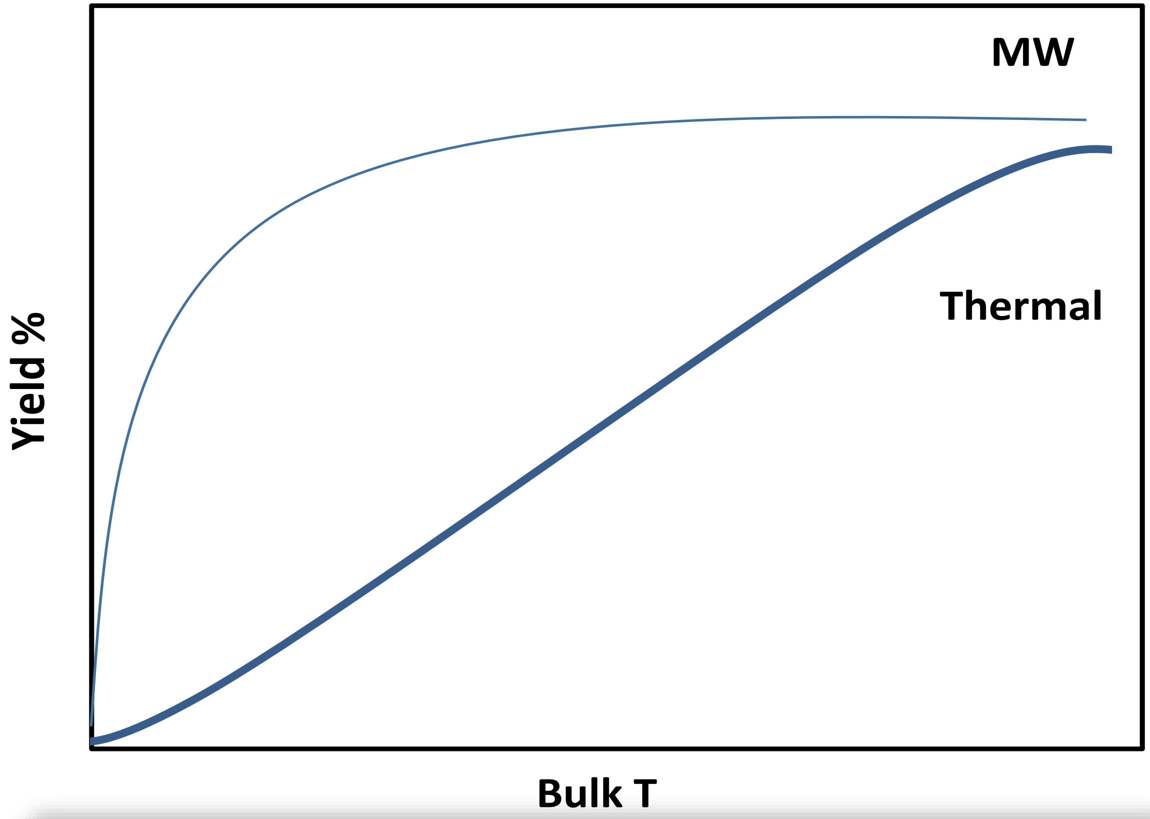
400°C

1 wt% Active Phase

Frequency = 2.45 GHz

Reflected power negligible

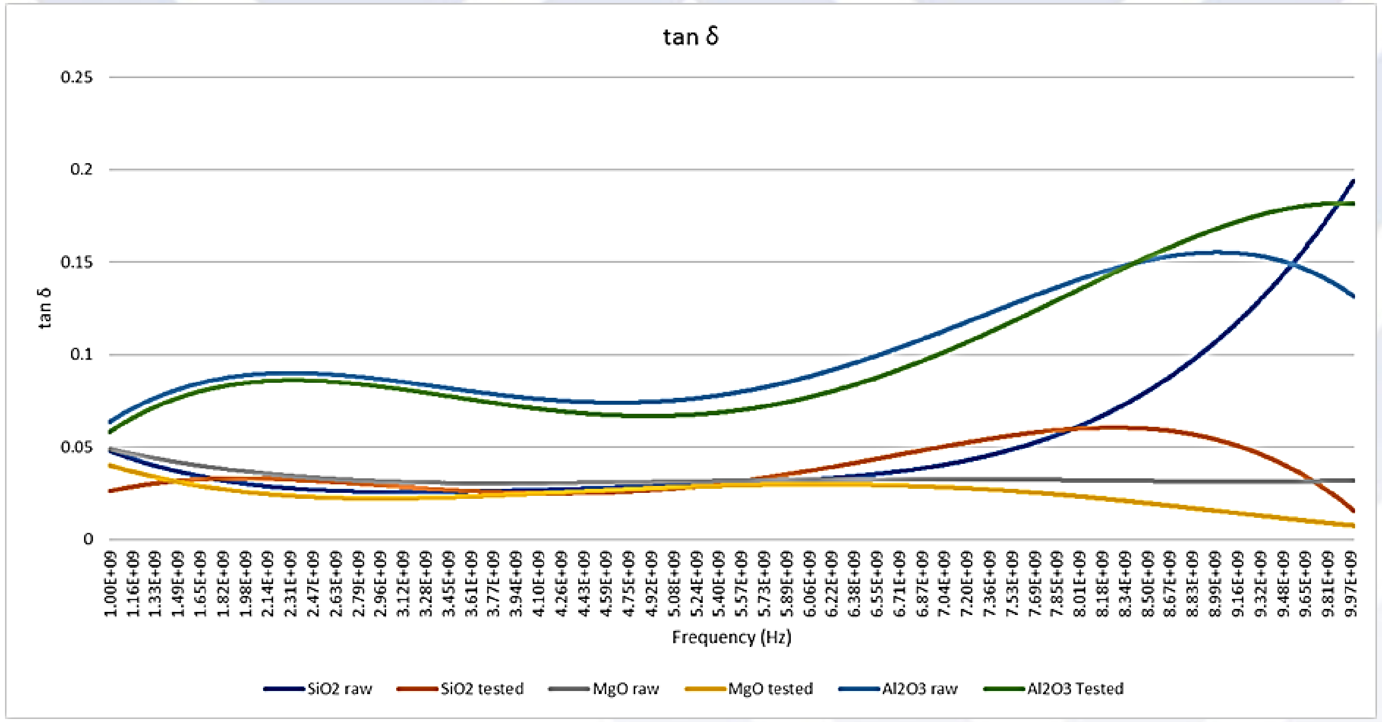
Magnetron Eff = 70%



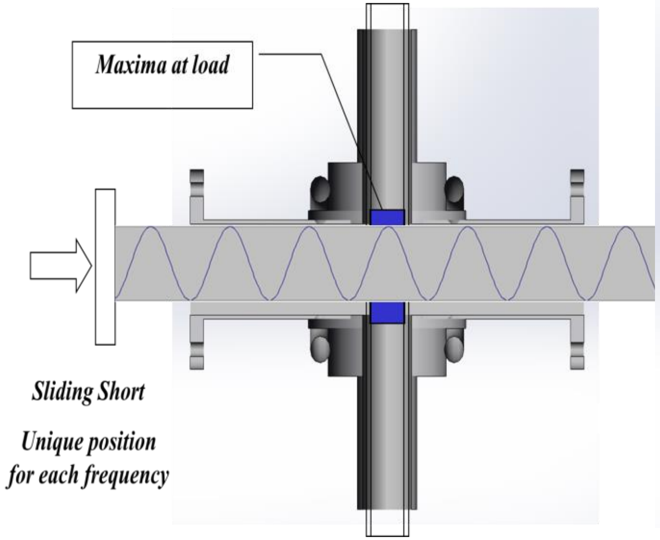
MWs allows for *selective heating* of reacting species/sites, which can lower bulk T…can result in higher product yields for reactions that favor lower equilibrium temperatures

Variable Frequency Testing

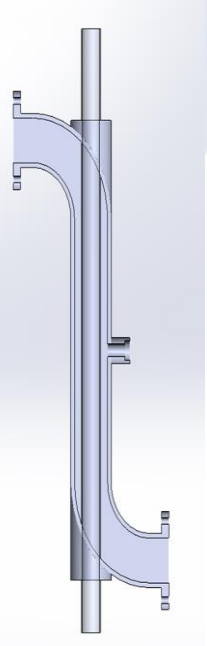
- Using Dielectric testing to find optimal frequencies for catalyst systems
- Substrate material largely defines effect of frequency



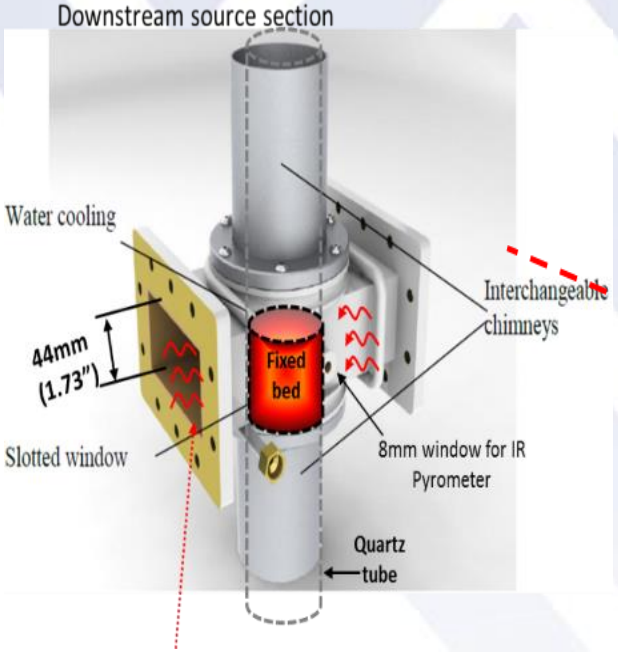
Microwave Reactor Systems

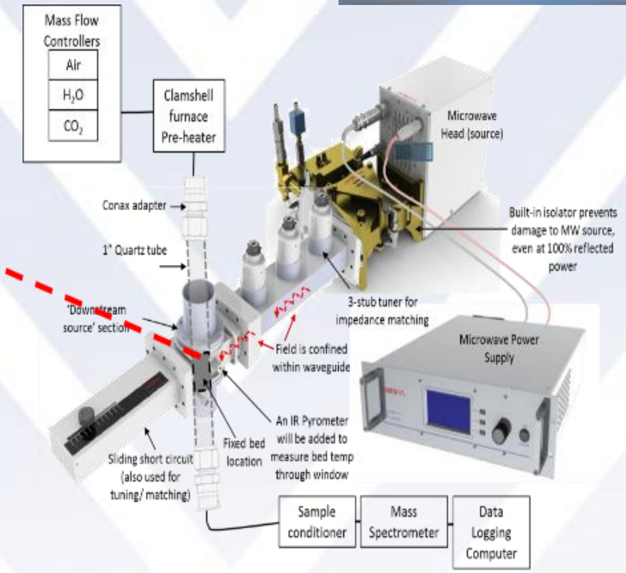


Standing Wave applicator



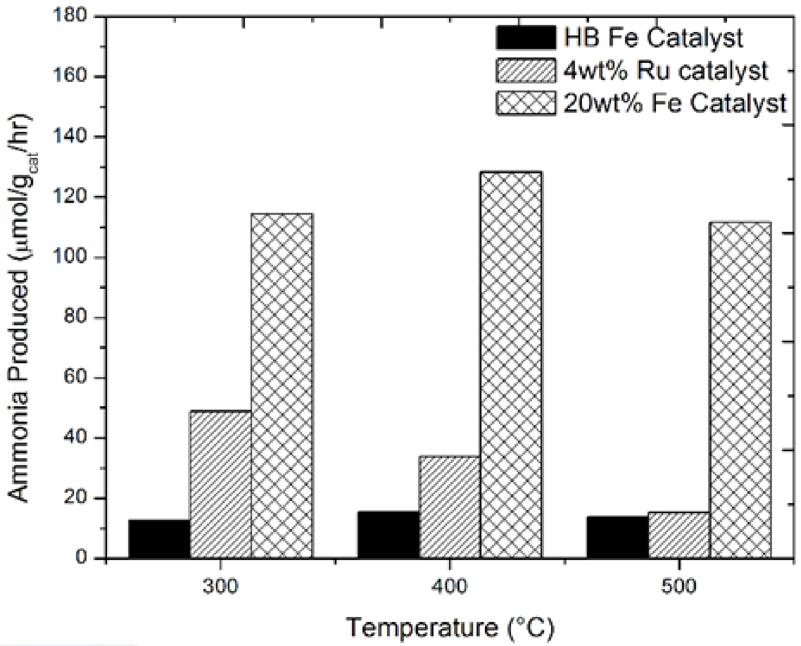
Dual E-Band Applicator

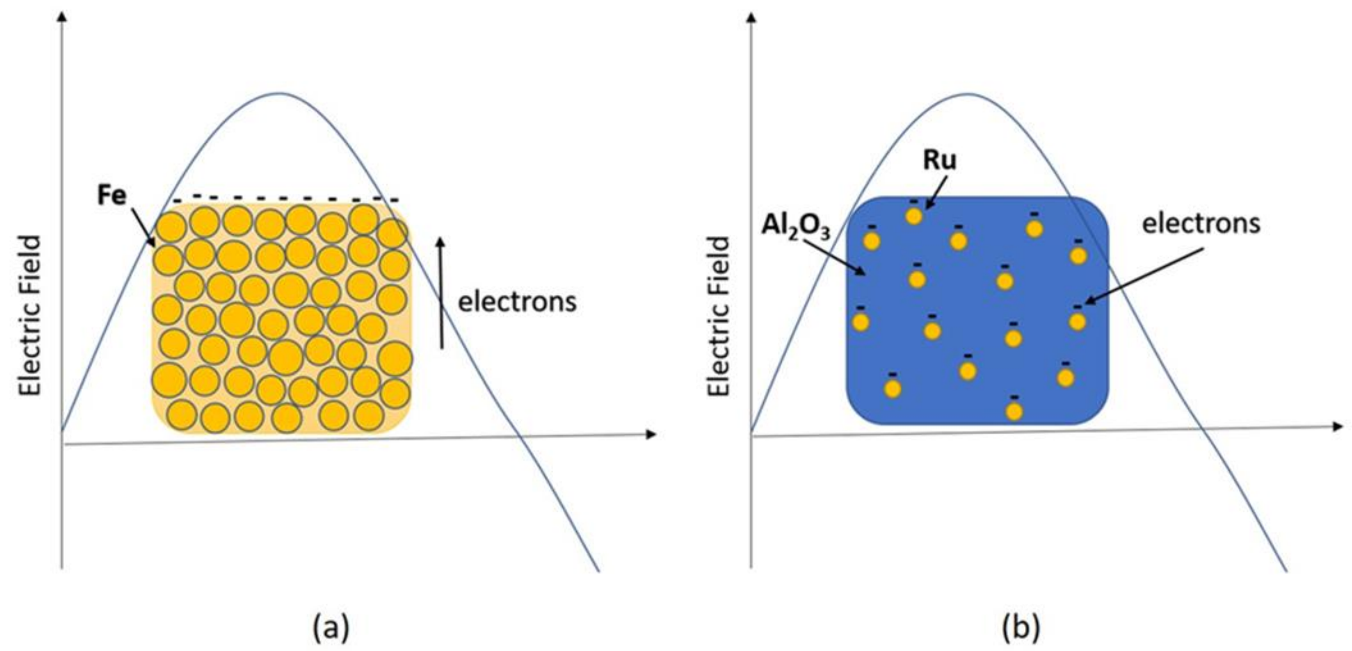




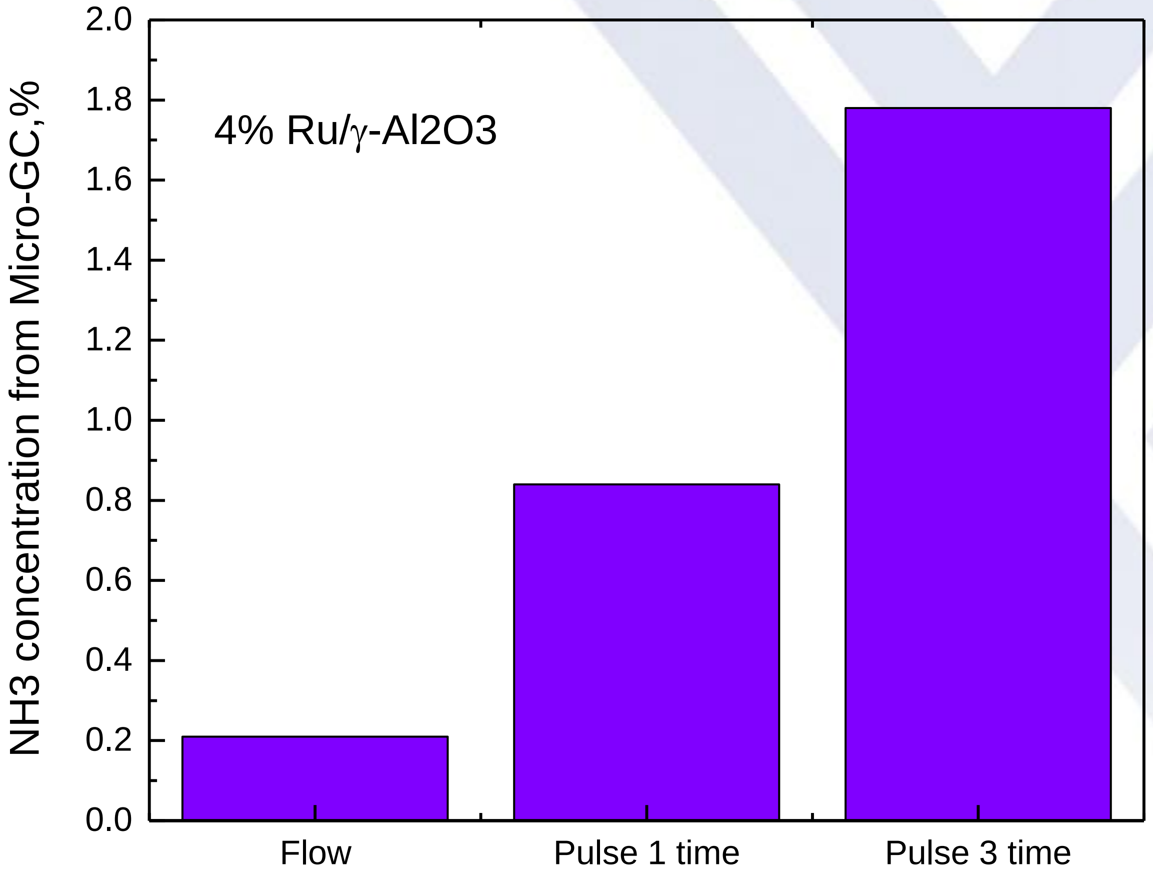
Distributed Iron Catalyst

- Catalyst design is very important for MW reactor
- By separating Fe active sites, performance increased 10X
- Electrons flow in “bulk” catalyst which hinders performance
  - Active site(metal site) size and spacing very important in MW field

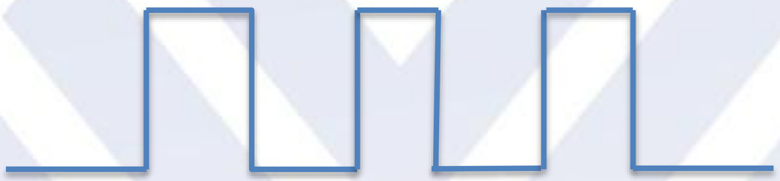




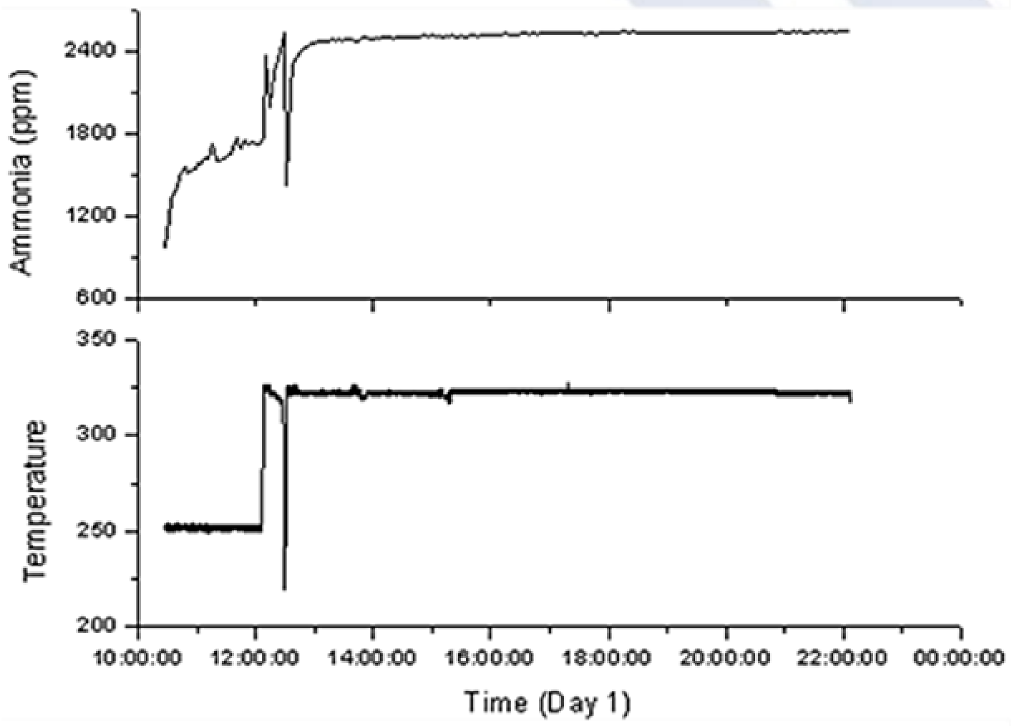
Effect of Microwave Pulsing

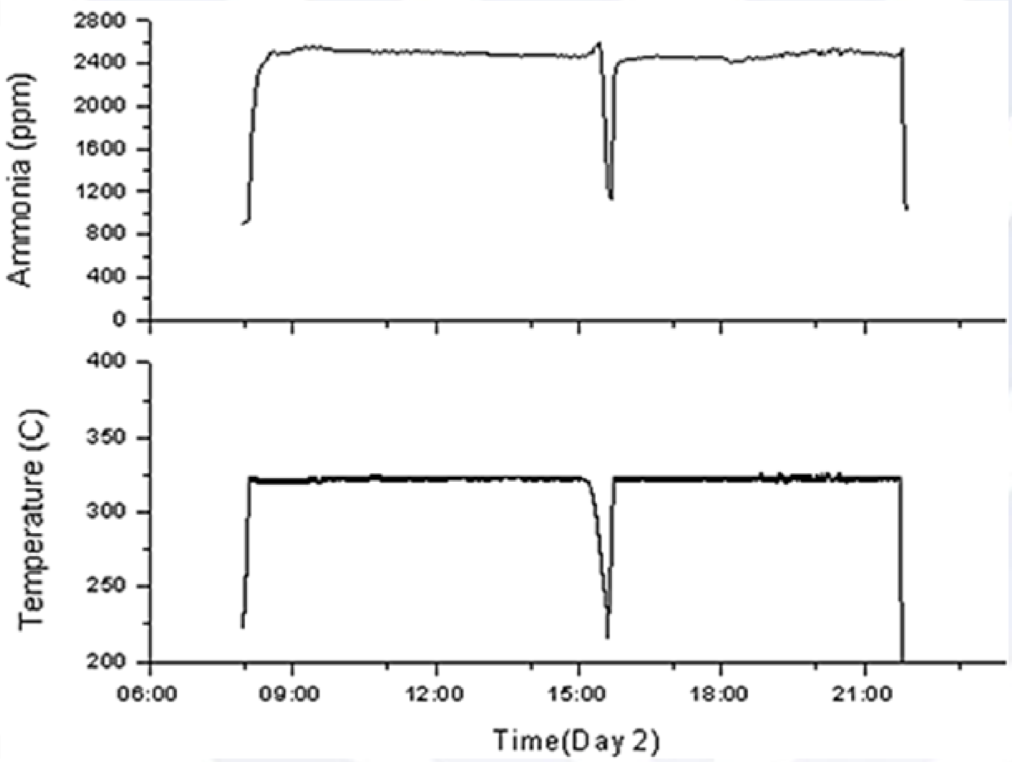


(280^{o}C, 1 atm)



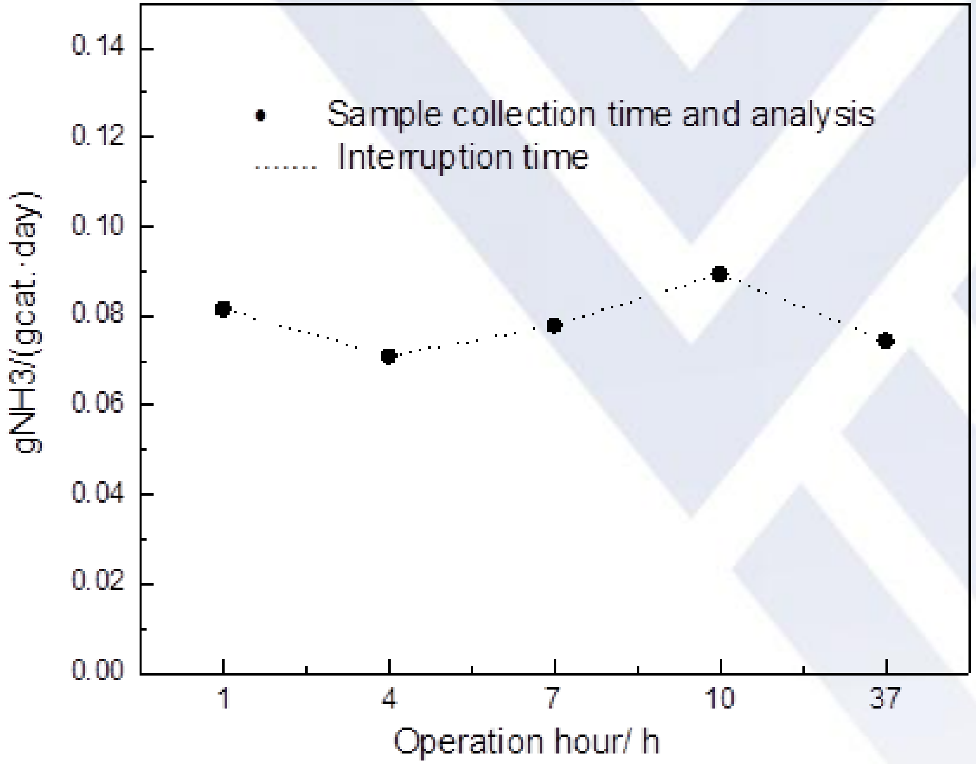
Durability Testing





Micorwoave allows for shutdown/restarts in production without deactivation

Tolerance of Intermittent Power Supply



Microwave catalytic ammonia synthesis under intermittent power supply (280°C, 1 atm, GHSV=5000 h^{-1}, each cycle consists of one hour operation, 2 hour shutdown, 5 cycles)

TEA Results: CAPEX for Ammonia Synthesis

60,000 tons NH_3/year scale

	Benchmark H-B	Base Case	Worst Case	Best Case
H_2 Treatment	5.21	2.15	2.15	2.15
NH_3 Synthesis Unit	6.19	2.95	16.99	2.35
NH_3 Recovery	5.73	16.58	28.25	16.58
NH_3 Compressors	11.2	8.13	14.48	8.13
OSBL	7.36	2.62	2.93	2.62
Total, $ million	35.70	32.43	63.91	31.84

Japan: microwave chemical plant, 10 ton/day

World’s first large-scale microwave chemical plant

http://mwcc.jp/en/service_technology/platform03.html

- Implication: Microwave ammonia synthesis-engineering scale-up risk is low