Process Intensification by a One-Step, Plasma-Assisted Synthesis of Liquid Chemicals from Light Hydrocarbons

DE-FE0031862

Jason C. Hicks (PI), David Go (co-PI), Casey O'Brien (co-PI), and William F. Schneider (co-PI)

University of Notre Dame

U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
October 25 - 27, 2022

Project Overview: DE-FE0031862

Funding (DoE and Cost Share)

	Spend Plan by Fiscal Year Format							
	FY 2020		FY 2021		FY 2022		Total	
	DOE Funds	Cost Share	DOE Funds	Cost Share	DOE Funds	Cost Share	DOE Funds	Cost Share
Applicant	$331,464	$91,535	$331,318	$ 82,265	$ 337,172	$ 76,244	$999,954	$250,044
Total ($)	$331,464	$ 91,535	$331,318	$ 82,265	$ 337,172	$ 76,244	$999,954	$250,044
Total Cost Share %	21.64%		19.89%		18.44%		20.00%	

Total: $1,249,998

DoE: $999,954
Cost Share: $250,044

Overall Project Performance Dates

03/01/2020 – 02/28/2023

Project: DE-FE0031862

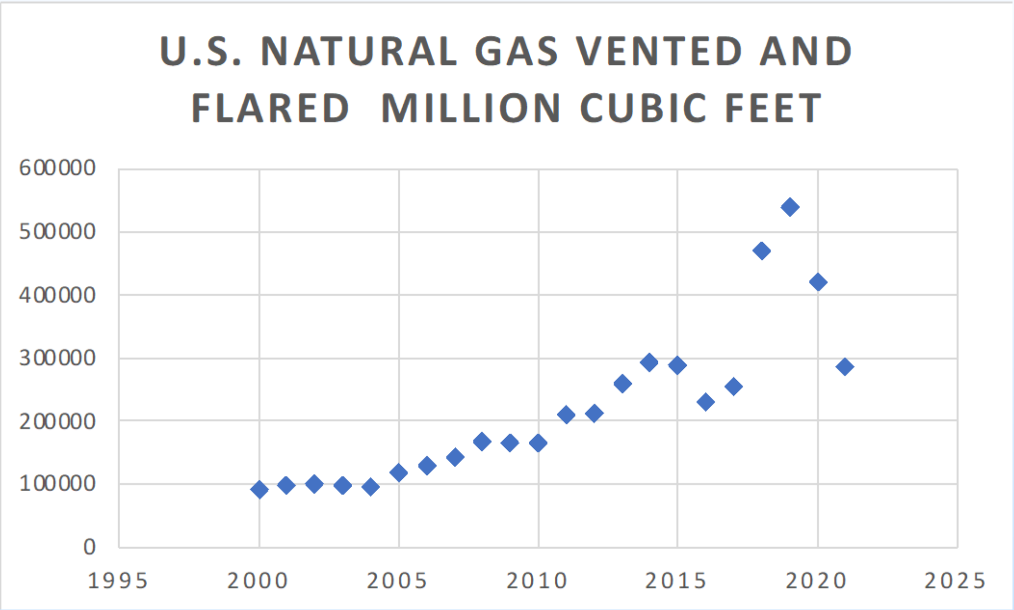
Project Participants (U. of Notre Dame)

Jason Hicks (PI), Professor, Chemical & Biomolecular Engineering
David Go (co-PI), Professor, Aerospace & Mechanical Engineering
Casey O'Brien (co-PI), Assistant Professor, Chemical & Biomolecular Engineering
William Schneider (co-PI), Professor, Chemical & Biomolecular Engineering

Overall Project Objectives:

(1) Develop plasma/catalyst reactor that will convert methane (and/or ethane) and N_2 as feedstocks and produce liquid chemicals containing C-N bonds
(2) Observe, quantify, model, and predict dependence of product yield and selectivity on plasma, catalyst and reactor characteristics.

Research Challenges and Technology/Knowledge Advances



Venting and flaring data from 1990 to 2021. (U.S Energy Information Administration)

Opportunity: Alternative, one-pot process to synthesize (N-containing) liquids from natural gas resources.

Target: Cleavage of C-H and N_2 followed by selective coupling under mild conditions via a catalytic process.

Process/Chemistry Challenges:

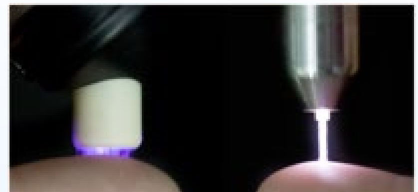
- C-H bond (>415 kJ/mol) and N_2 triple bond are stable (~940 kJ/mol)
- Poor selectivity
- Catalyst identification

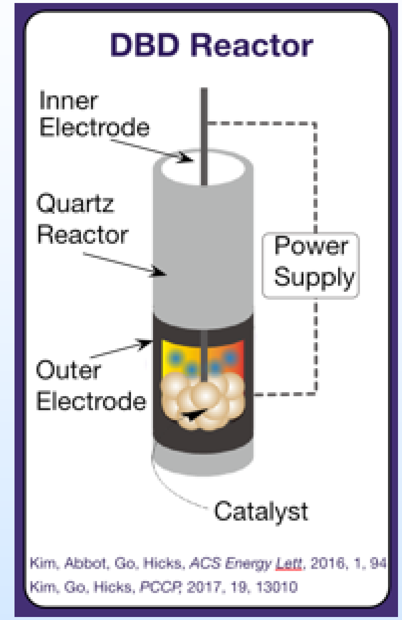
Background: Non-Thermal Plasmas

- Ionized gas (e.g. by electric discharge)
- Comprised of reactive intermediates: electronically and vibrationally excited species, ions, radicals

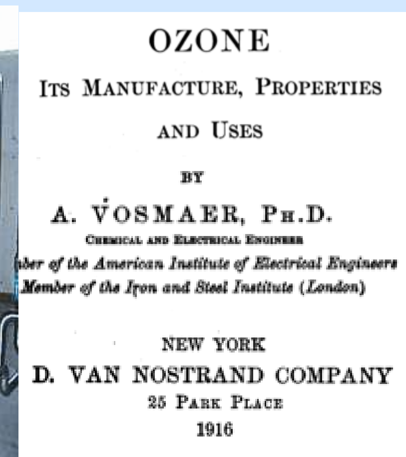
Non-thermal plasma

- Electrons much "hotter" (10000 K) than gas (near-ambient)
- $T_{elect} > T_{vib} > T_{rot} = T_{trans}$
- e.g., ozone generation ("cold" plasma)


Plasma Phys. Control. Fusion 59 (2017) 014031



Kim, Abbot, Go, Hicks, *ACS Energy Lett.* 2016, 1, 94
Kim, Go, Hicks, *PCCP* 2017, 19, 13010


OZONE
ITS MANUFACTURE, PROPERTIES AND USES
BY
A. VOSMAER, PH.D.
CHEMICAL AND ELECTRICAL ENGINEER
ber of the American Institute of Electrical Engineers
Member of the Iron and Steel Institute (London)
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25 PARK PLACE
1916

Technology Background

Chemical advantages

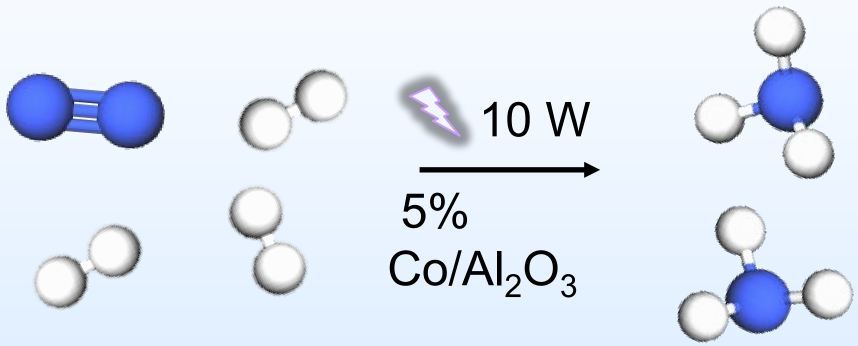
- Reactions proceed at conditions (*P*, *T*) inaccessible thermally
- Product slate (selectivity) often different from thermal
- Different optimal catalyst design space

Practical advantages

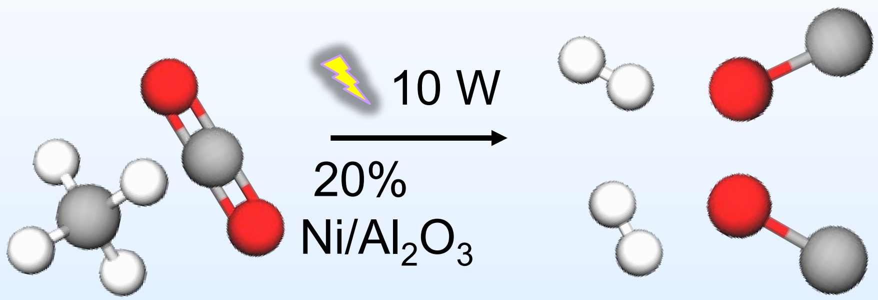
- Low temperature (as low as ambient)
- Compact and distributed/mobile systems
- Rapid start-up/shutdown

Technology Background

$N_2 + 3\,H_2 \rightarrow 2\,NH_3$



$CH_4 + CO_2 \rightarrow 2\,H_2 + 2\,CO$



1. Mehta, P.; Barboun, P.; Engelmann, Y.; Go, D.B.; Bogaerts, A.; Schneider, W.F.*, and Hicks, J.C.*, *ACS Catalysis,* **2020**, 10, 12, 6726–6734.
2. Barboun, P.; Mehta, P.; Go, D.B.; Schneider, W.F.; and Hicks, J.C.*, *ACS Sustainable Chemistry & Engineering,* **2019**, 798621-8630.
3. Mehta, P.; Barboun, P.; Herrera, F.A.; Kim, J.; Rumbach, P.; Go, D.B.*; Hicks, J.C.*; and Schneider, W.F.*, ACS Energy Letters, **2019**, 4 (5), 1115-1133.
4. Mehta, P.; Barboun, P.; Herrera, F.A.; Kim, J.; Rumbach, P.; Go, D.B.*; Hicks, J.C.*; and Schneider, W.F.*, Nature Catalysis, **2018**, 1, 269.

1. Geng, F; Haribal, V; Hicks, J.C.*, Applied Catalysis A: General, **2022**, in press.
2. Herrera, F.; Brown, G.; Barboun, P.; Turan, N.; Mehta, P.; Schneider, W.; Hicks , J.; Go, D.*, Journal of Physics D: Applied Physics, **2019**, 52 224002
3. Kim, J.; Go, D.B.; Hicks, J.C.*, Phys. Chem. Chem. Phys., **2017**, 19, 13010-13021
4. Kim, J.; Abbott, M.S.; Go, D.B.; Hicks, J.C.*, ACS Energy Letters, **2016**, 1, 94–99

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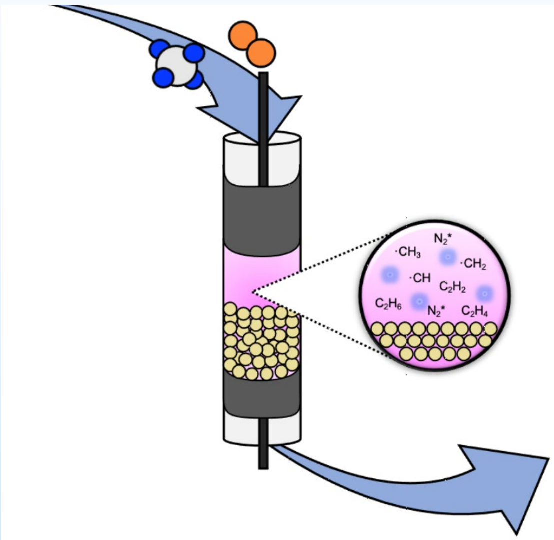
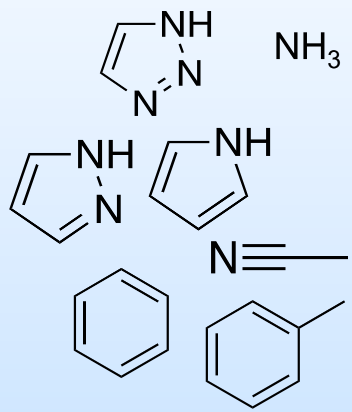
Hydrocarbon Liquefaction in a Plasma-Catalytic System



Hydrocarbon and Nitrogen-Containing Liquid Products



Potential Uses and Applications

Liquid Chemicals

Goals/Objectives:

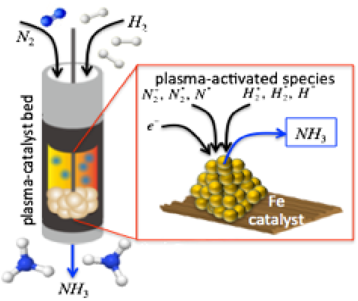
(1) Develop plasma/catalyst reactor that will convert methane (and/or ethane) and N_2 as feedstocks and produce liquid chemicals containing C-N bonds

(2) Observe, quantify, model, and predict dependence of product yield and selectivity on plasma, catalyst and reactor characteristics

Project Approach: DE-FE0031862

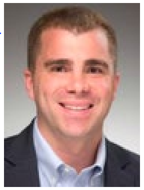
Catalyst Synthesis and Performance Measurements

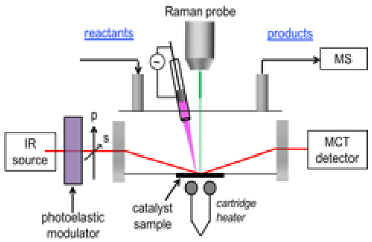
Prof. Jason Hicks (PI)



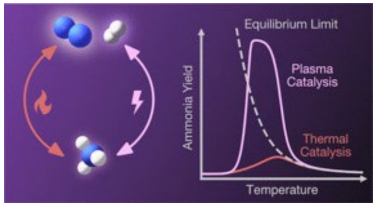
In situ/operando Spectroscopy

Prof. Casey O'Brien (co-PI)



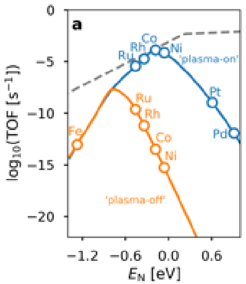


Plasma Catalysis



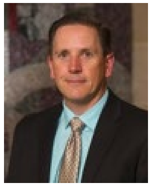
Plasma Physics/ Characterization

Prof. David Go (co-PI)



Theory and Simulation

Prof. Bill Schneider (co-PI)



Project Schedule/Scope: DE-FE0031862

Subtask	Milestone Title & Description	Planned Completion Date
5.1, 5.2, 5.3	Selective N-C forming catalysts experimentally identified by evaluating the selectivity to products of zeolite and metal-based catalysts	08/31/2022
5.5	Chemistry-specific model is developed and predicts changes in selectivity with changes in material. Model evaluated through comparison of predicted and observed responses to changes in material.	11/30/2022
5.4	Spectroscopic identification of plasma-surface interactions for N-C formation	02/28/2023
4.3	Operation of alternative plasma reactor configuration and characterization of power consumption and electrical characteristics (current and voltage) under different flow and temperature conditions	11/30/2022
6.1, 6.2	Optimal plasma reactor configuration identified and demonstrated through the operation of ~1 scfm (TRL 4) plasma/reactor system	02/28/2023

Status of Planned Activities

Identification of catalyst compositions capable of facilitating liquid production. Completed

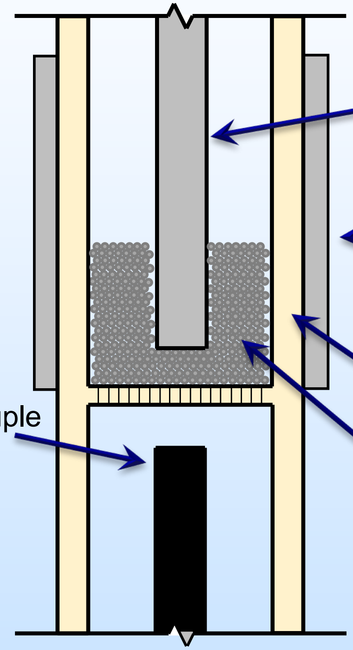
Predictions of surface species across a series of metals has been completed and correlates with experimental results. Completed.

In situ/operando spectroscopy results show evidence of surface species from plasma stimulation. Identification of these species is ongoing. No concerns for completion.

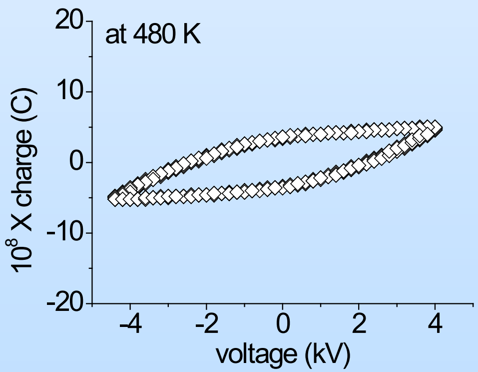
A gliding arc plasma reactor has been constructed and tested. No concerns for completion.

Experiments to-date provide regions for operating a DBD plasma reactor based on composition, power, residence time, and temperature. No concerns for completion.

Approach: Non-Thermal Plasma Reactor



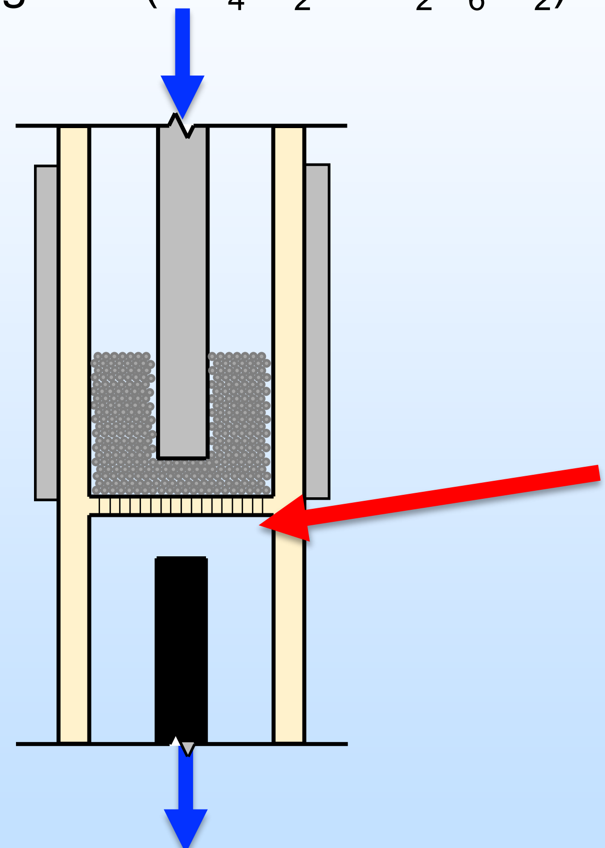
Reactor: 0.5 cm (I.D.), 0.7 cm (O.D.)
Discharge distance: ~1.75 mm
Plasma zone volume: 1.07 cm^3



Kim, Abbott, Go, Hicks, *ACS Energy Letters,* **2016**, 524, 85-93.

Approach: Reactor Construction (Subtask 2.1)

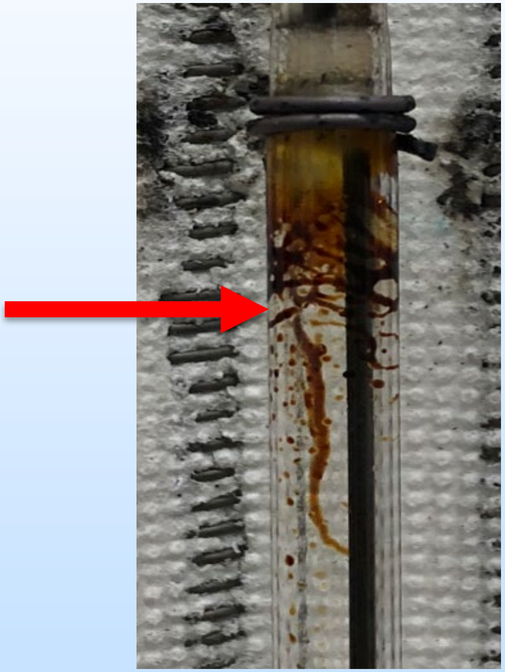
Feed gases (CH_4/N_2 or C_2H_6/N_2)



Effluent gases (out) to GC and MS

Liquids form and condense on walls of reactor.

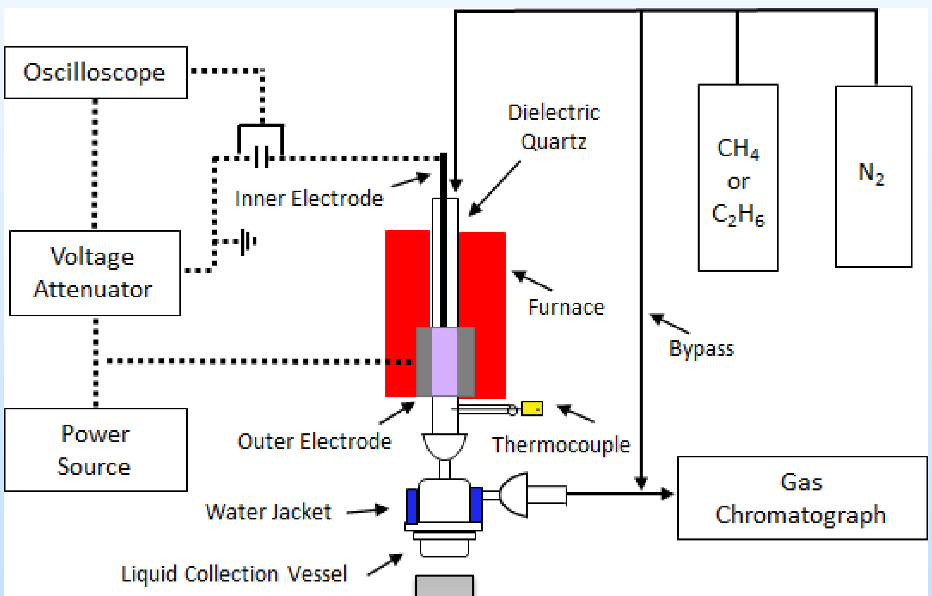
Difficult to collect, quantify, analyze…

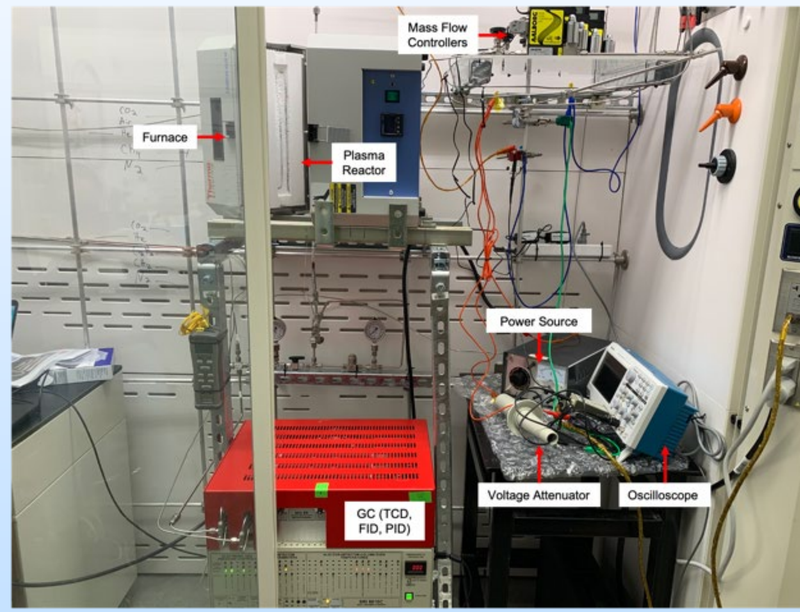


Year 1 Goal: Design new reactor to improve liquid collection.

Approach: Reactor Construction (Subtask 2.1)

New Reactor Designed and Constructed to Enhance Liquid Recovery (Subtask 2.1)

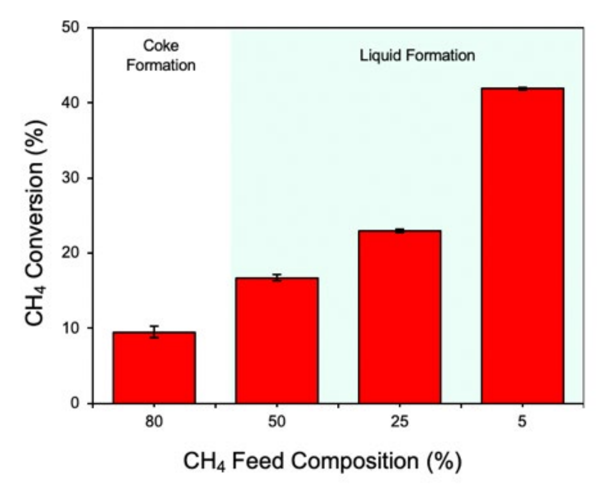


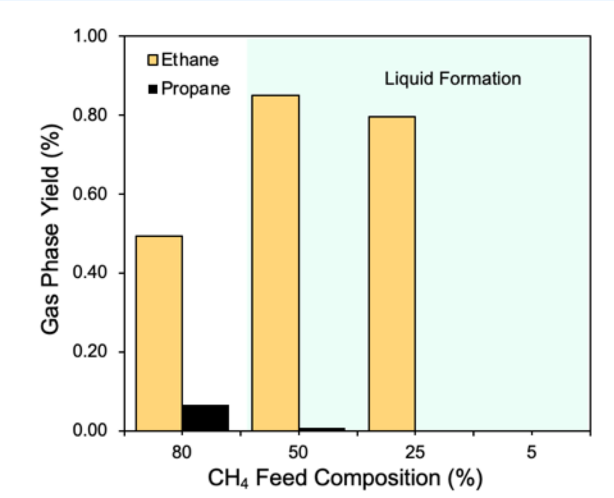


Approach: Reactor Performance Evaluation (Subtasks 2.1, 2.2, 3.1, and 3.2)

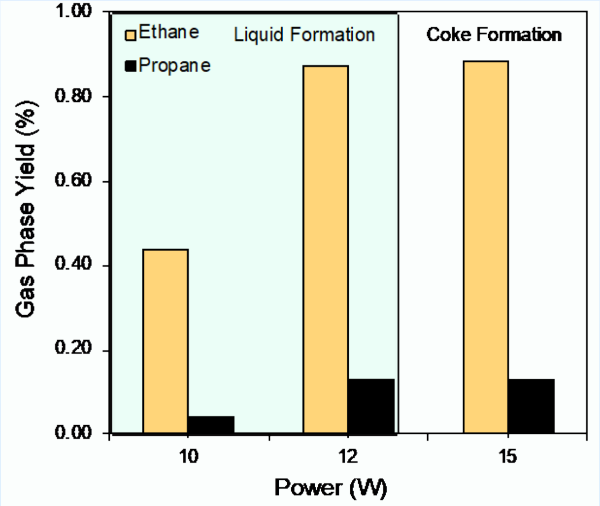
We are able to characterize the products from plasma stimulated hydrocarbon/N_2 feeds and determine stable species formed in the gas phase and conditions that favor desired product formation.

<u>*Feed Composition*</u>



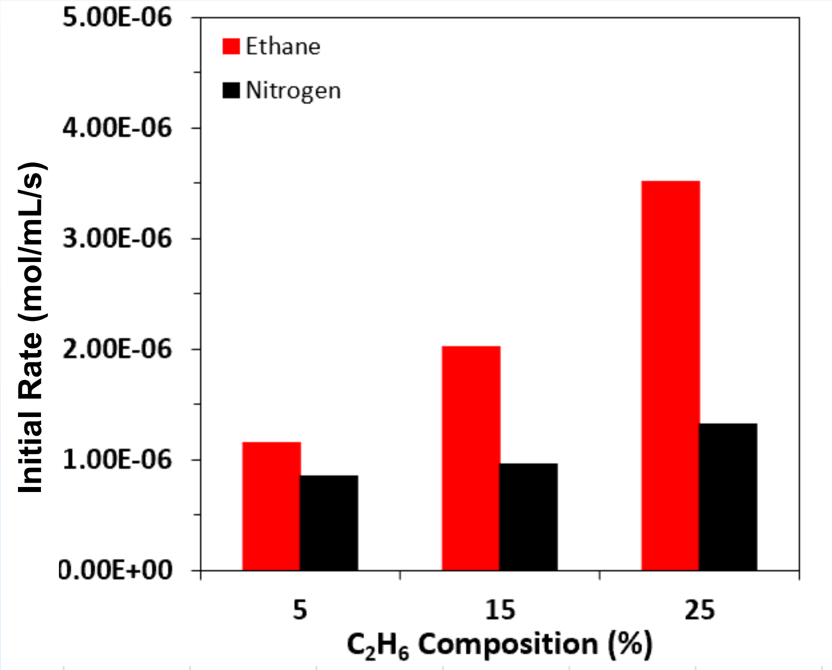


<u>*Input Power*</u>

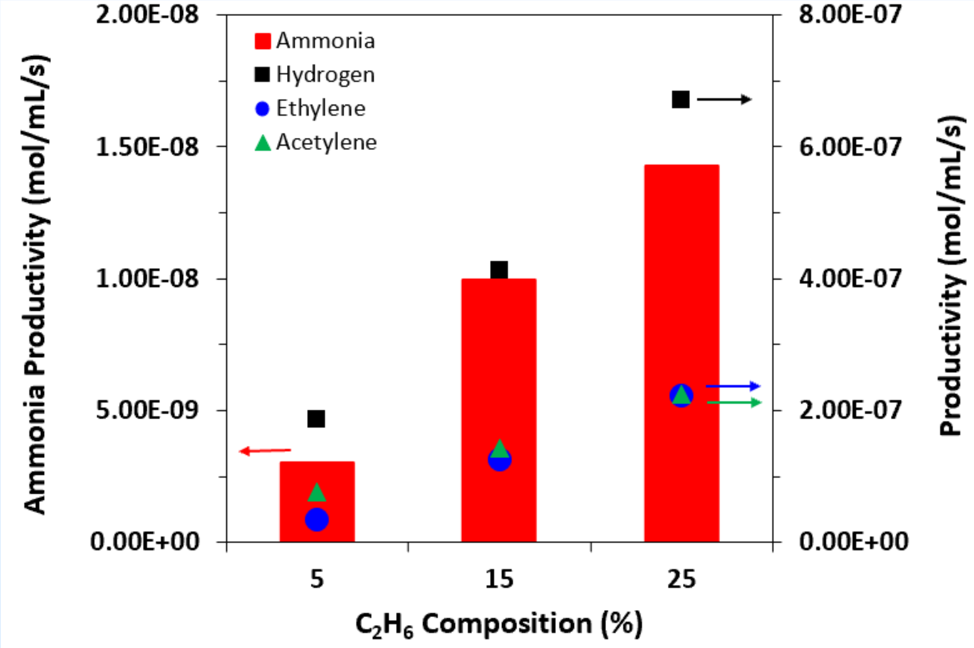


Approach: Reactor Performance Evaluation (Subtasks 2.1, 2.2, 3.1, and 3.2)

Feed composition effects on initial consumption rates



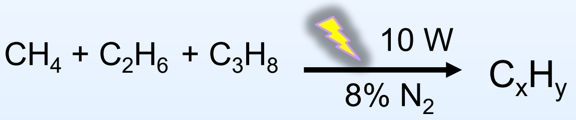
Feed composition effects on ammonia production rates

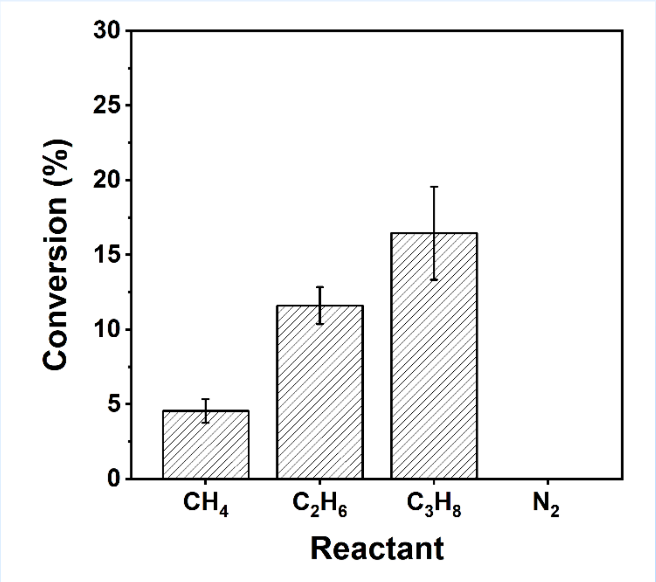


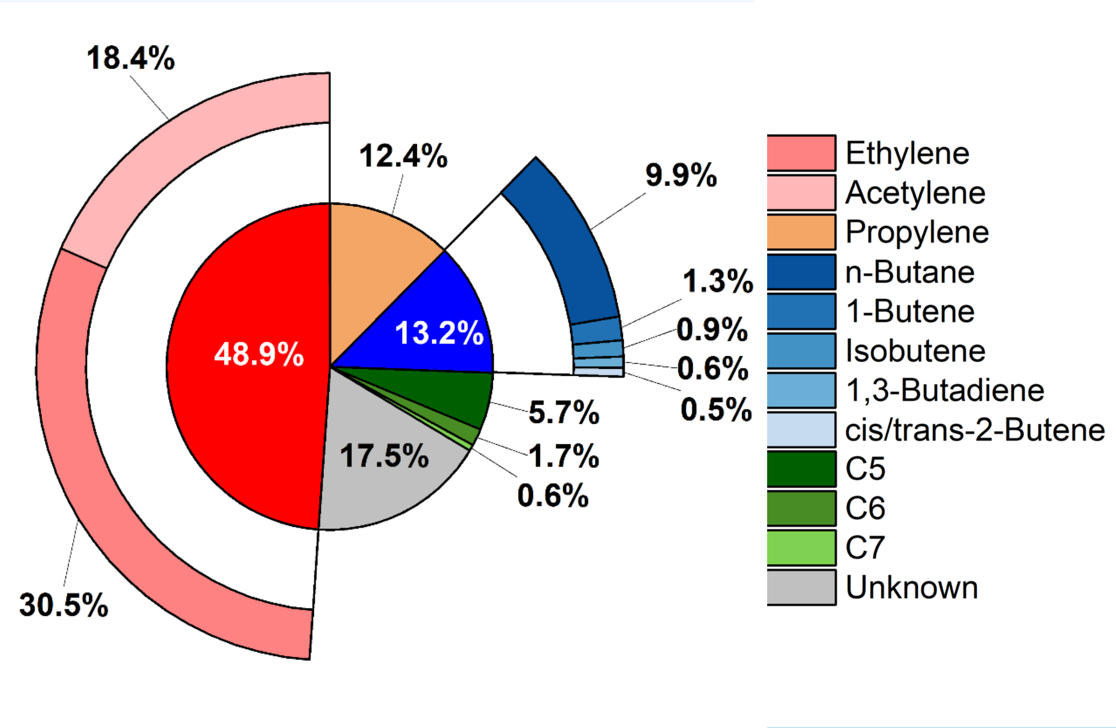
*Hydrogen is not directly observed. It is determined from ethylene and acetylene formation.

Approach: Reactor Performance Evaluation (Subtasks 2.1, 2.2, 3.1, and 3.2)

We are able to characterize the products from plasma stimulated hydrocarbon/N_2 feeds and determine stable species formed in the gas phase and conditions that favor desired product formation.





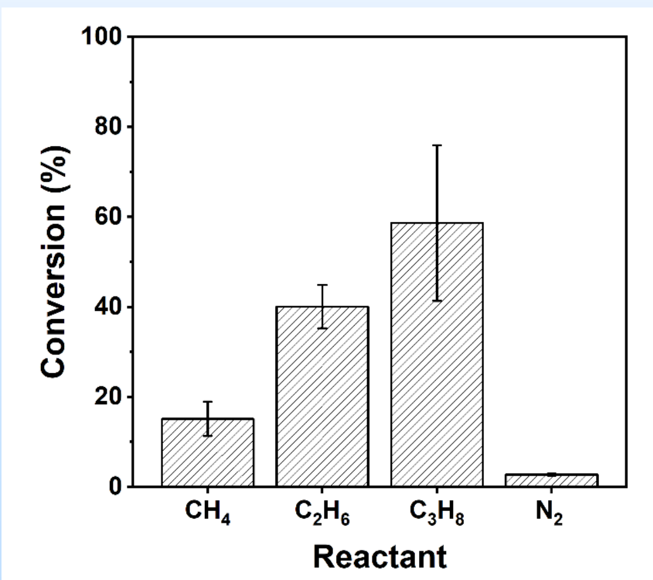


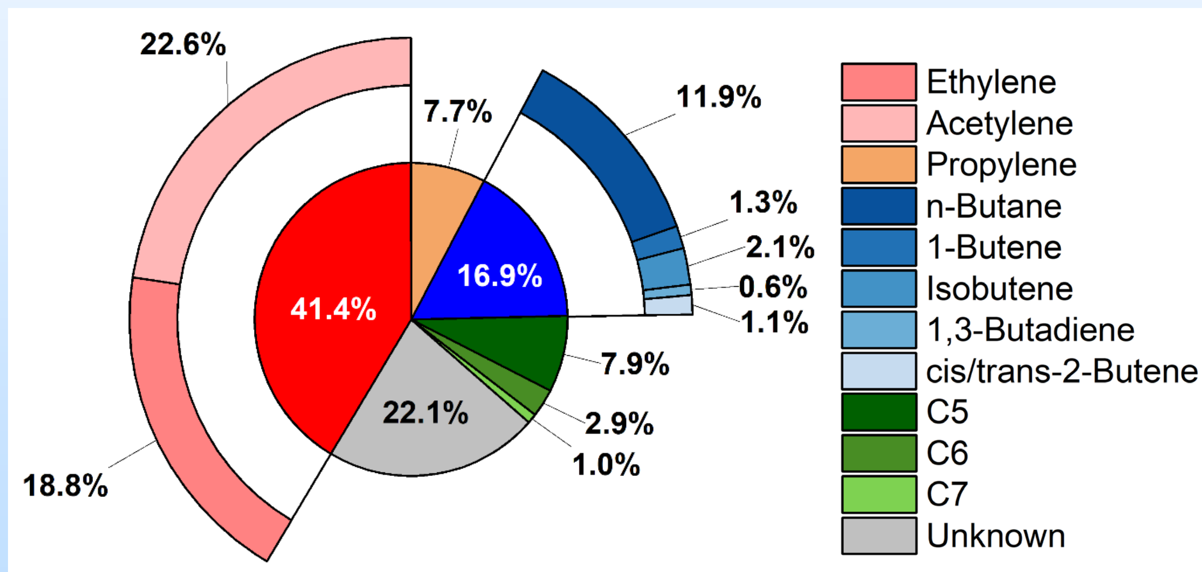
- Selective to C2 products
- Observation of C-C bond forming pathways

Approach: Reactor Performance Evaluation (Subtasks 2.1, 2.2, 3.1, and 3.2)

We are able to characterize the products from plasma stimulated hydrocarbon/N_2 feeds and determine stable species formed in the gas phase and conditions that favor desired product formation.

$$CH_4 + C_2H_6 + C_3H_8 \xrightarrow[90\%\ N_2]{10\ W} C_xH_y,\ C_xH_yN_z$$

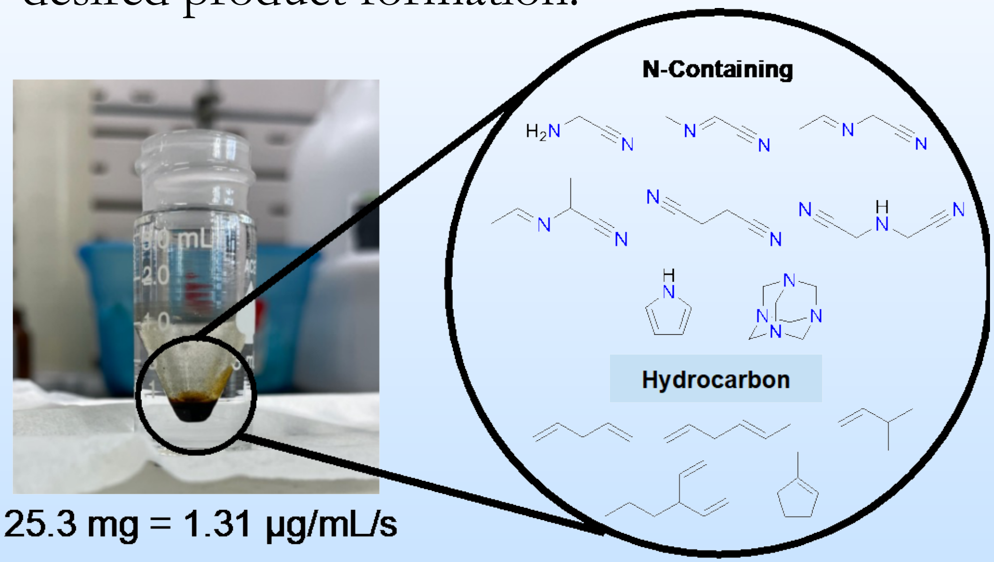




- C4+ selectivity has increased
- N-containing liquids collected

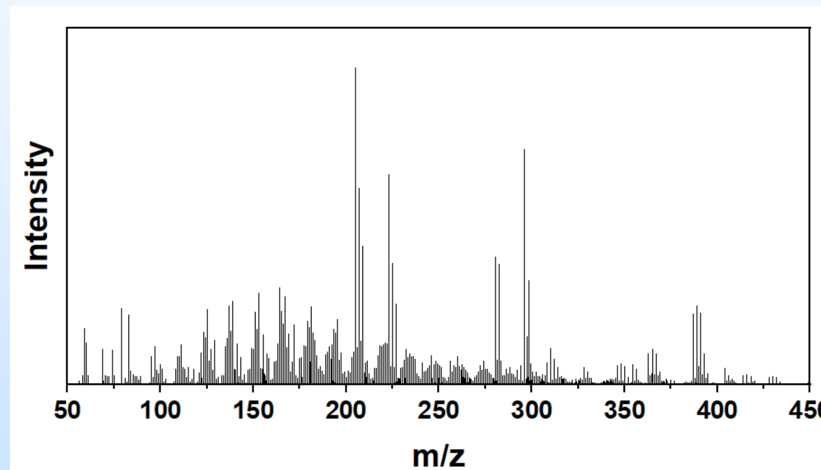
Approach: Reactor Performance Evaluation (Subtasks 2.1, 2.2, 3.1, and 3.2)

We are able to characterize the products from plasma stimulated hydrocarbon/N_2 feeds and determine stable species formed in the gas phase and conditions that favor desired product formation.



25.3 mg = 1.31 μg/mL/s

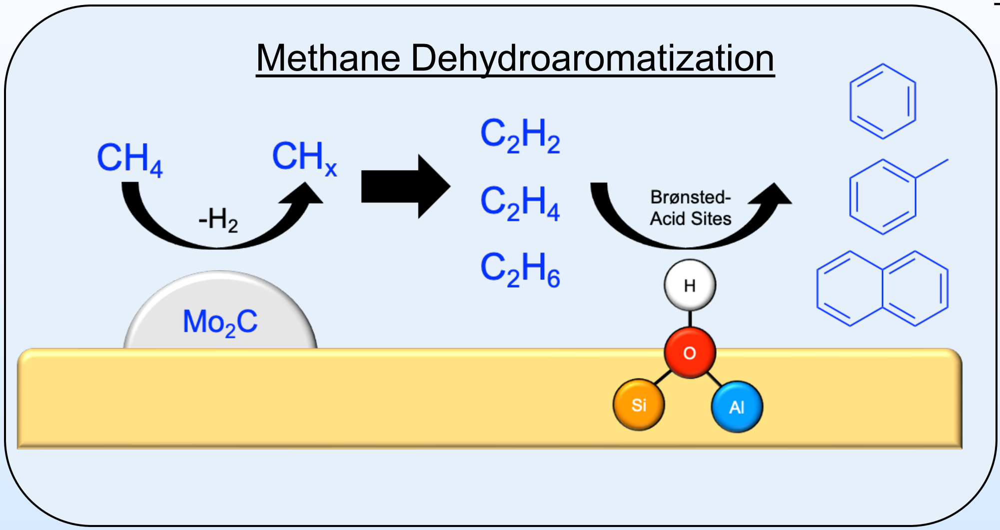
N/C = 0.35



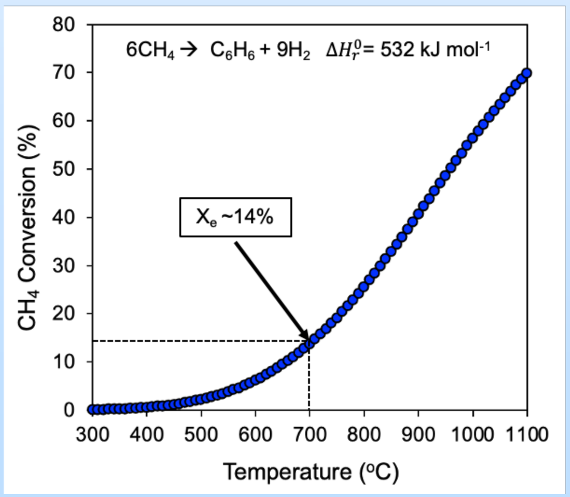
<u>Characterization of the liquid phase and quantifying N incorporation</u>

- Wide range of products with varying degree of N-incorporation into the molecule.
- N content of the liquid phase is invariant for the different feed compositions.
- Liquid production rates are similar for all plasma phase reactions.

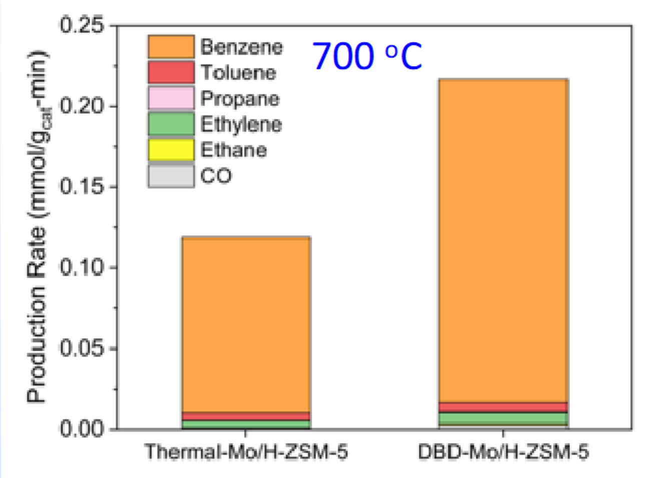
Approach: Improving Selectivity via Plasma-Assisted Catalysis (Subtasks 5.1 and 5.2)

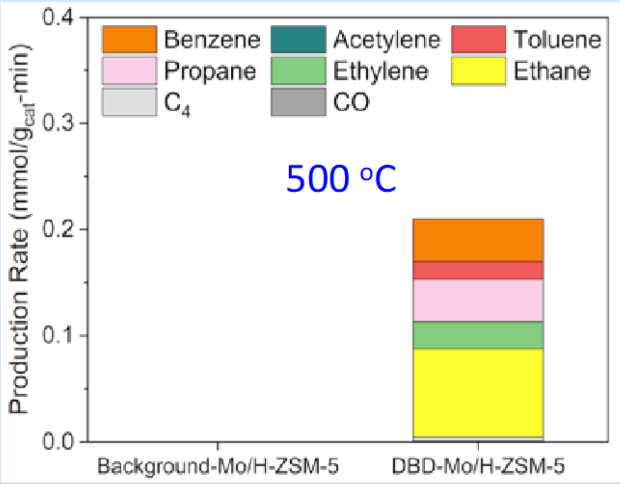


Highly endothermic reaction, elevated temperatures required to achieve significant methane conversions and benzene yields.

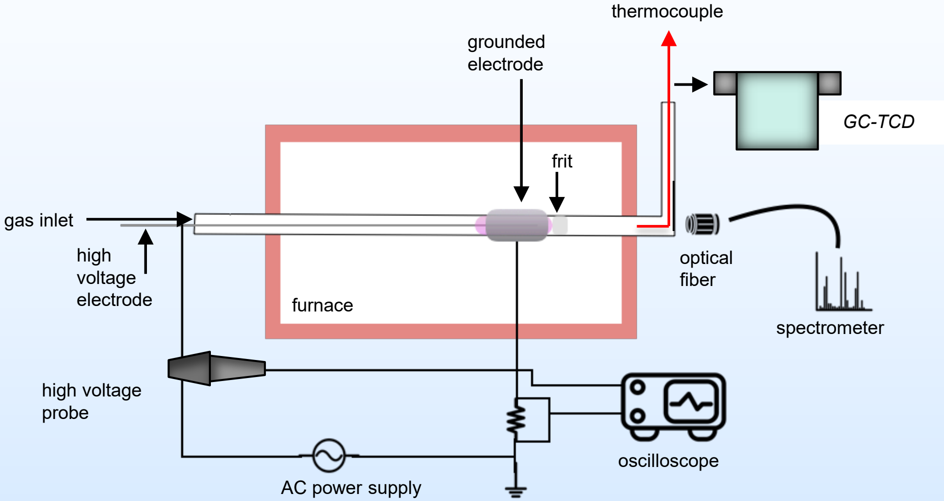


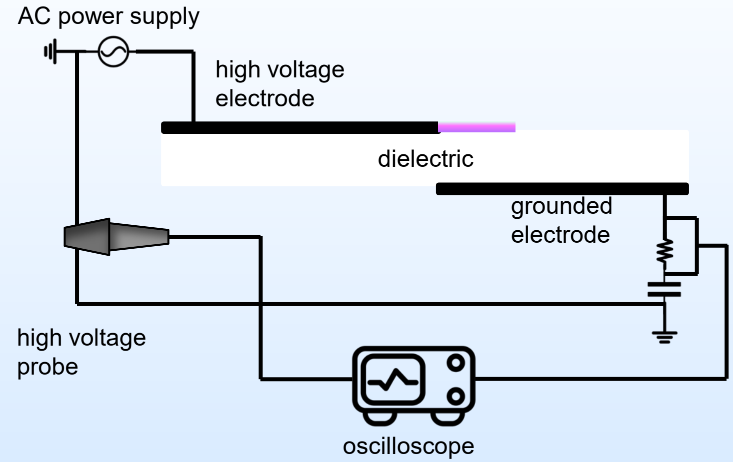
Comparing Thermal and Plasma-Assisted Catalytic Dehydroaromatization





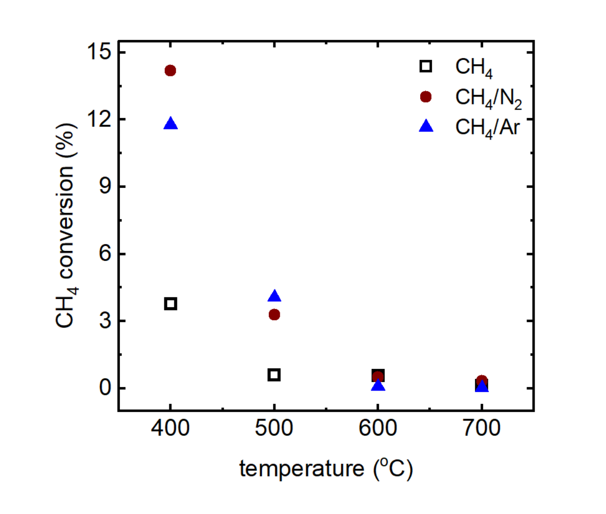
Approach: Characterization of the Plasma (Subtasks 2.3, 4.1, and 4.2)

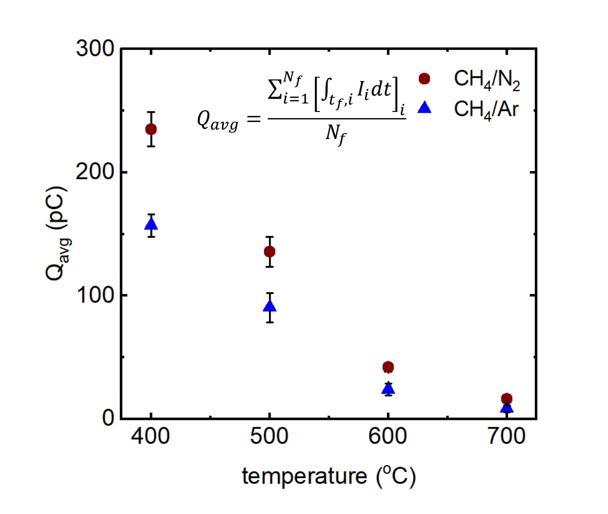


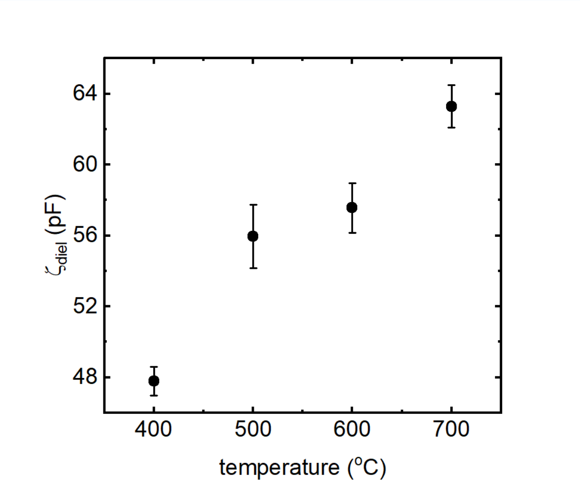


- Left schematic shows a DBD plasma system used to investigate how changes in temperature affect reactions and plasma properties
- Right schematic shows a simple surface DBD to investigate how changing permittivity affects plasma properties when temperature and power are held constant
- We hypothesize an increase in temperature leads to an increase in permittivity which causes changes to plasma properties and subsequent reactivity

Approach: Characterization of the Plasma (Subtasks 2.3, 4.1, and 4.2)

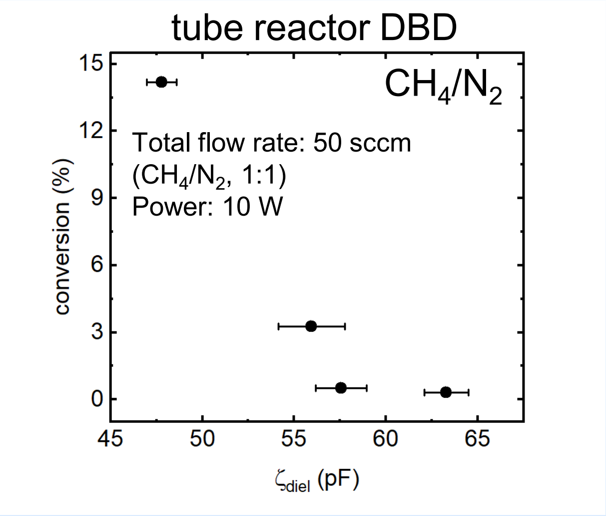


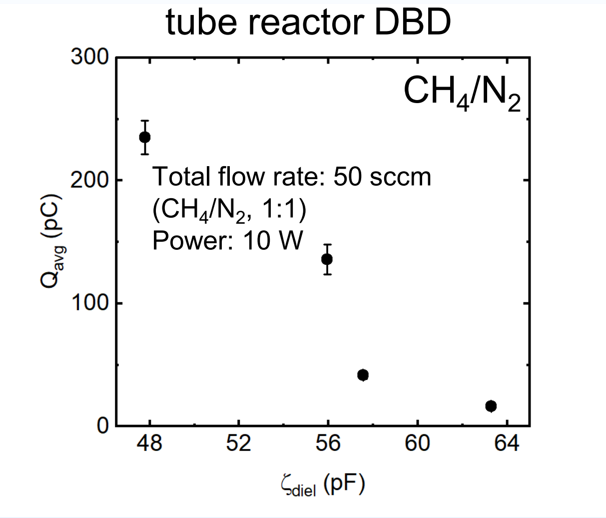


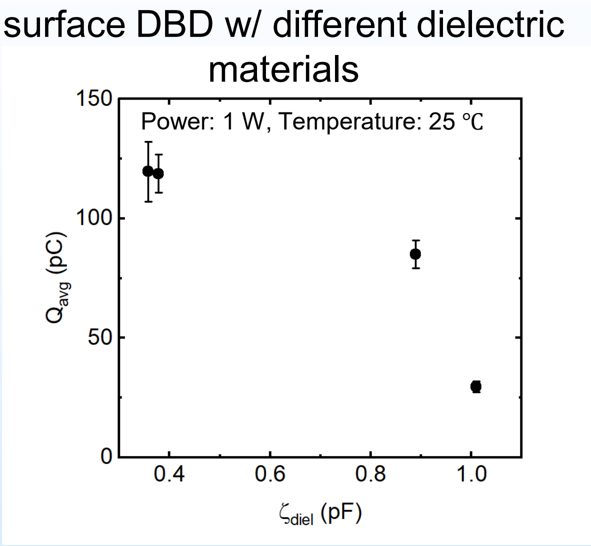


- Increasing temperature reduces methane conversion regardless of the presence of an additive gas or the type of additive gas
- Increasing temperature also has an inverse relationship with the average charge per filament of the DBD plasma
- Effective capacitance during discharge, ζ_{diel}, shows the permittivity of the dielectric material increases with temperature

Approach: Characterization of the Plasma (Subtasks 2.3, 4.1, and 4.2)

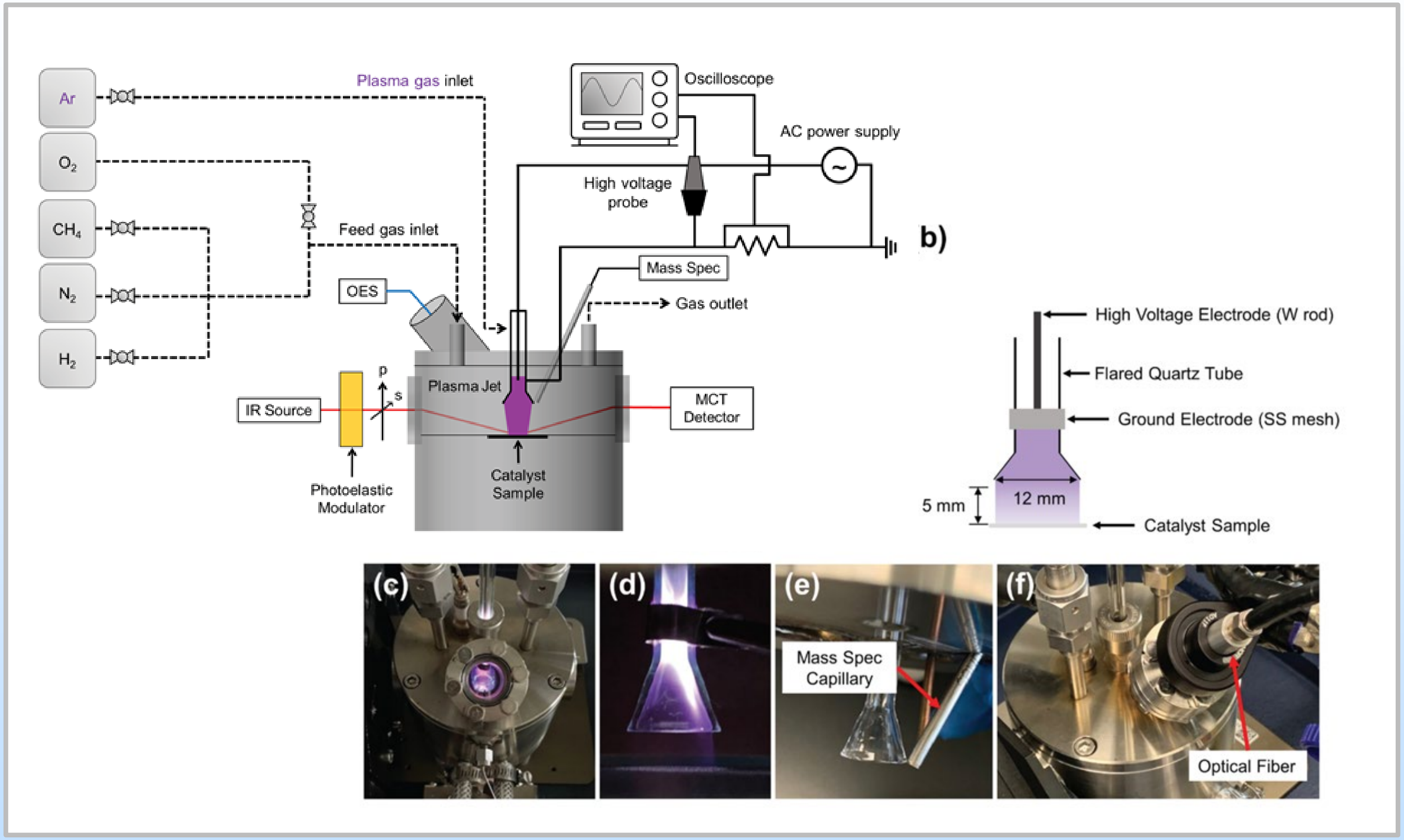






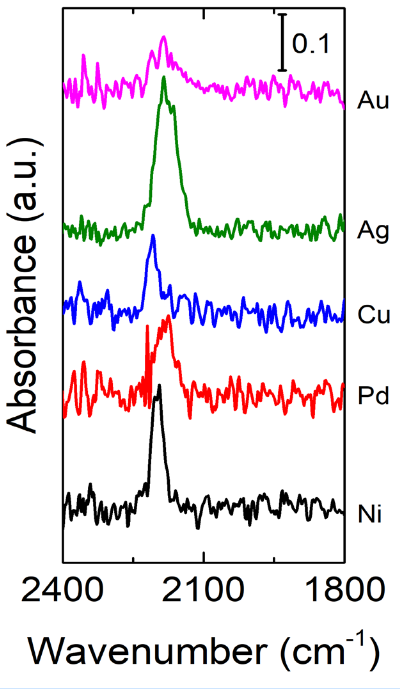
- Tube reactor results suggest a correlation between increasing reactor permittivity at higher temperatures and decreased conversion
- Surface DBD measurements using dielectrics with different permittivities show an increase in permittivity has an inverse relationship with the average charge per filament of the plasma – consistent with tube reactor findings
- A change in permittivity causes changes to the reduced electric field, E/N, which changes the energy distribution of electrons in the plasma and subsequent electron reactions
- Further study is required to fully understand relationship between plasma properties and potential other temperature related effects on methane conversion

Approach: In Situ Observation of Plasma-Surface Interactions (Subtasks 2.4 and 3.5)



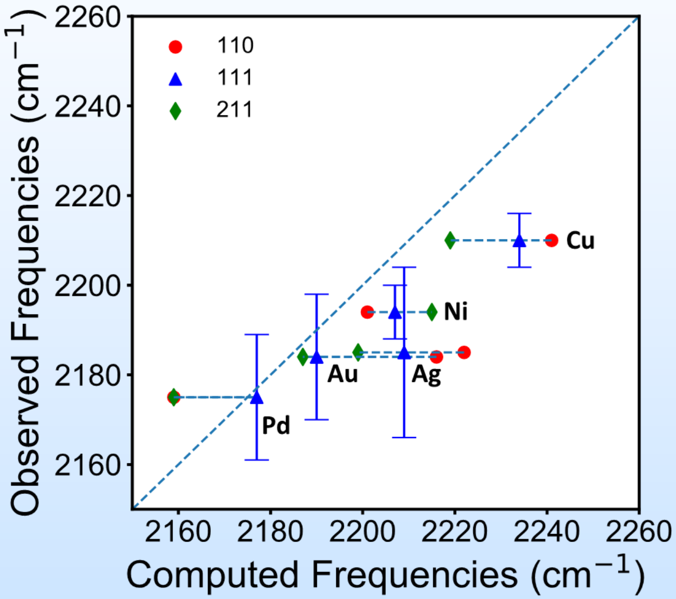
"Direct Observation of Plasma-Stimulated Activation of Surface Species using Multi-Modal In-Situ/Operando Spectroscopy Combining Polarization-Modulation Infrared Reflection-Absorption Spectroscopy, Optical Emission Spectroscopy, and Mass Spectrometry" Garam Lee, David B. Go, Casey P. O'Brien
ACS Sustainable Chemistry & Engineering, 2021.

Approach: In Situ Observation of Plasma-Surface Interactions (Subtasks 2.4 and 3.5)



Surface adsorbed nitrogen species (~2200 cm^{-1}) on Ni and Cu group metals observed under room temperature plasma exposure

Good agreement between theory and experiment for N_3 adsorption

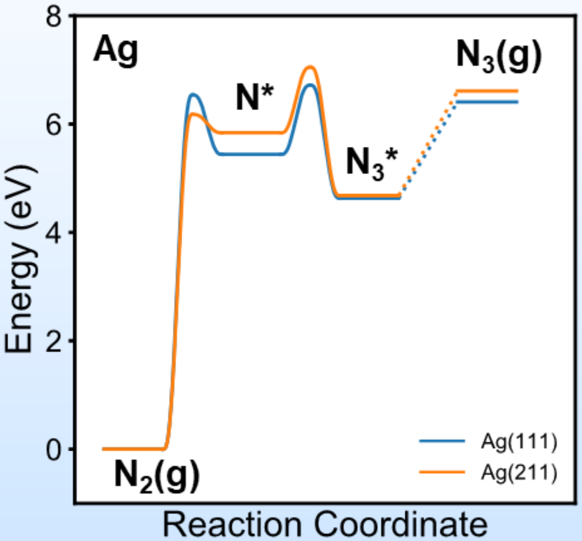


- N_3 binds on every metal surfaces tested
- Good agreement between experimental and computational vibrational frequencies

Two-step surface N_3 formation

(1) $N_2(g) + e^- \rightarrow 2N(a)$

(2) $N(a) + N_2(v) \rightarrow N_3(a)$



Potential energy surfaces (PES) based on DFT calculations were constructed and show that (1) two-step N_3 formation and (2) surface N_3 is kinetically trapped in a local energy minimum

Plans for future testing/development/ commercialization

Provisional patent applications have been filed.

- 63/367,649 Plasma-Assisted Process for the Production of Liquids from Methane, 7/5/2022
- 63/367,646 Process to Synthesize Nitrogen-Containing Liquids and Higher Molecular Weight Hydrocarbons from Shale Gas/N_2 Feeds 7/5/2022

Seeking new funding to continue research (DoE, DoD, NSF)

Working with ND IDEA center to identify additional funding opportunities (e.g., industry, start-ups, ...).

Workforce Development Efforts

Training/Professional Development

- 7 students and 1 postdoc supported by this grant, students trained on campus facilities (e.g., NMR, CHN analysis, reactor design/development, plasma systems, mass spectrometry, IR…),
- Student attended a machine learning workshop
- Students have attended AIChE 2020, AICHE 2021, AIChE 2022, AVS Conferences (2022) and Gaseous Electronics Conference 2021 meetings
- Deanna Poirier (Hicks group) awarded 2022 Eilers Graduate Student Fellowship for Energy Related Research

Summary Slide

Project Approach:

– Develop a plasma-assisted process to facilitate C-N coupling and liquid production by combining reaction performance results, in situ/operando characterization, and predictive modeling

Key Findings:

– Liquid production and N-incorporation strongly depend on gas concentration
  - Higher N_2 concentrations facilitate liquid formation and N-incorporation.

– Liquid production depends on plasma input power.
  - Higher plasma powers often resulted in an increase in coke due to over reaction of the hydrocarbon.

– Plasma-assisted aromatization can minimize the bulk temperature requirement and improve product selectivity.

– Identification of N_3 surface intermediates that could facilitate C-N formation.

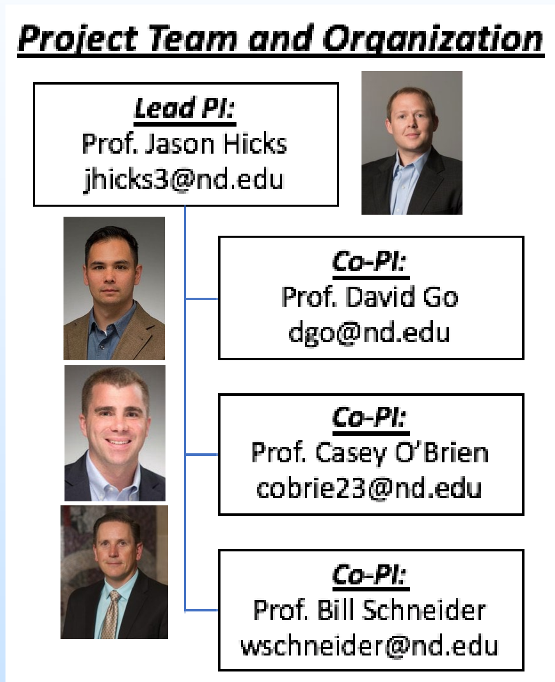
Opportunities:

– Designing plasma (e.g., gliding arc) and catalyst combination to enhance liquid production rates.

Appendix

– These slides will not be discussed during the presentation but are mandatory.

Organization Chart



Plasma Catalysis, Catalyst Synthesis, and Kinetics

Plasma Physics, Plasma Catalysis, and Characterization

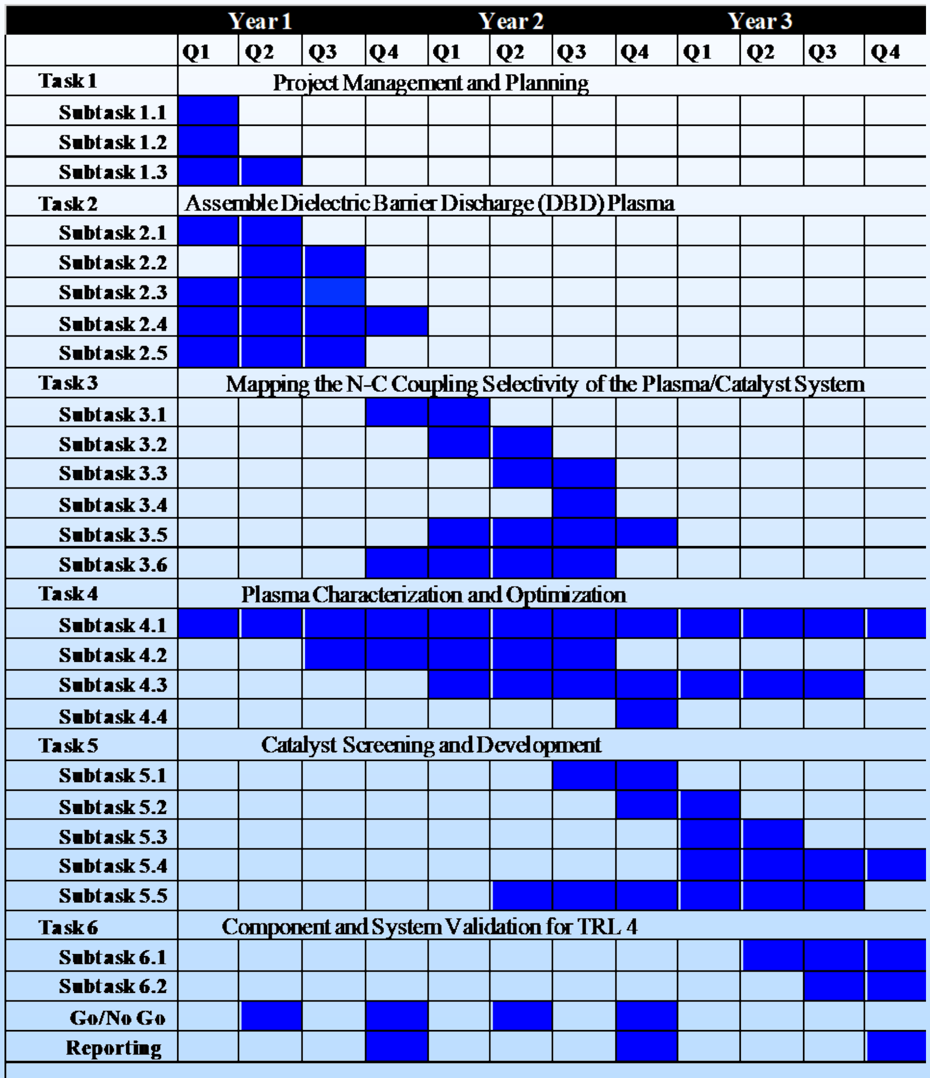
Interfacial Science and Spectroscopy

Theory and Simulations

Graduate and Postdoctoral Researchers

Gerardo Rivera-Castro (4th year), Deanna Poirier (4th year), Russell Clarke (3rd year), Feiyang Geng (graduated), Garam Lee (4th year), Amanda Brown (graduated), Ibukunoluwa Akintola (4th year), Hanyu Ma (former postdoc)

Gantt Chart



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