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

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U.S. Department of Energy

National Energy Technology Laboratory

2021 Carbon Management and Oil and Gas Research Project Review Meeting

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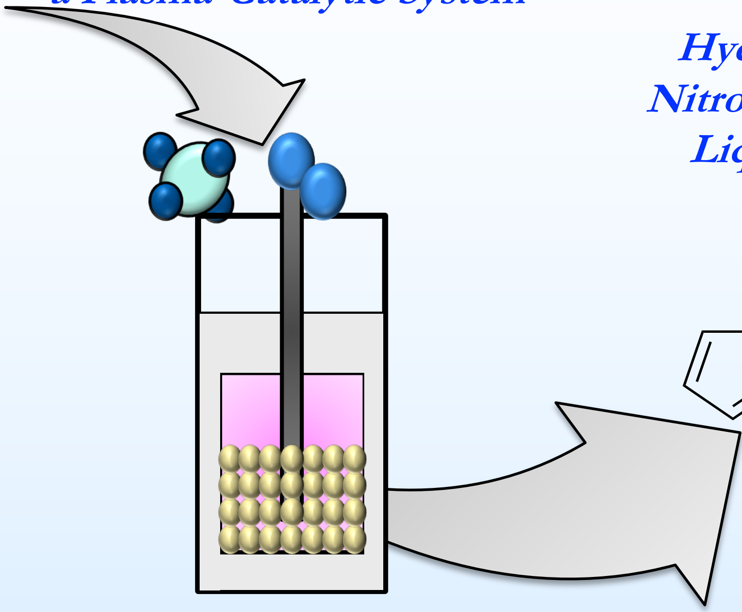
Presentation Outline

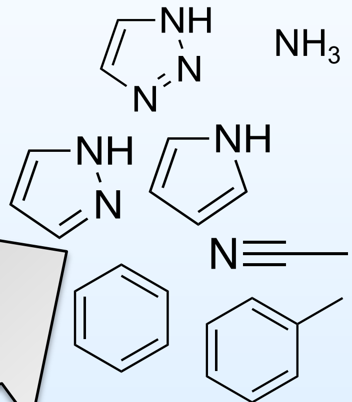
- Project Background/Motivation
- Technical Approach and Project Status
- Accomplishments to date
- Lessons Learned
- Synergy Opportunities
- Project Summary
- Appendix

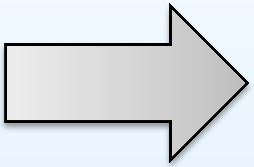
Process Intensification by a One-Step, Plasma-Assisted Synthesis of Liquid Chemicals from Light Hydrocarbons

Hydrocarbon Liquefaction in a Plasma-Catalytic System



Hydrocarbon and Nitrogen-Containing Liquid Products





Potential Uses and Applications

Liquid Chemicals

Goals/Objectives:

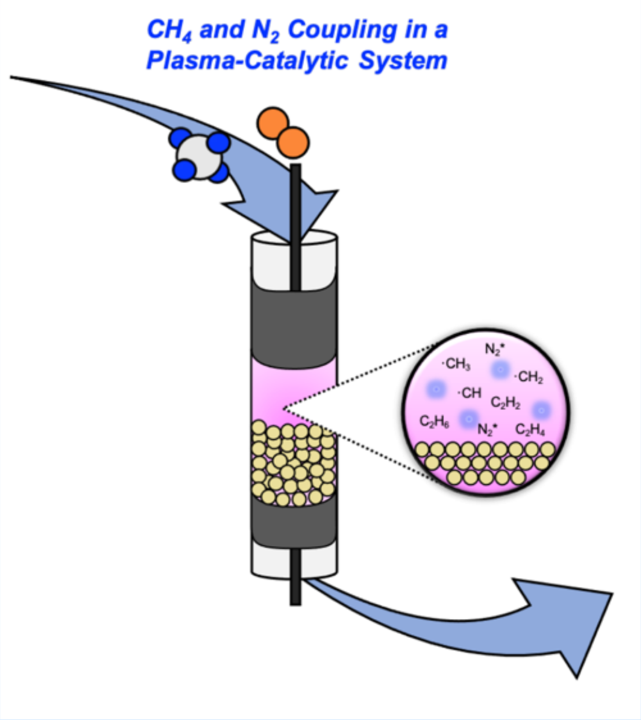
(1) Develop plasma/catalyst reactor that will convert methane (and/or ethane) and N_2 as feedstocks and produce liquid chemicals containing C-N bonds

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

Research Challenges and Technology/Knowledge Advances

Opportunity: Alternative, one-pot process to synthesis of N-containing liquids from natural gas resources. Industrial processes require furan and ammonia (pyrrole) or acetaldehyde, ammonia, and formaldehyde (pyridines) at >400 ^{o}C.

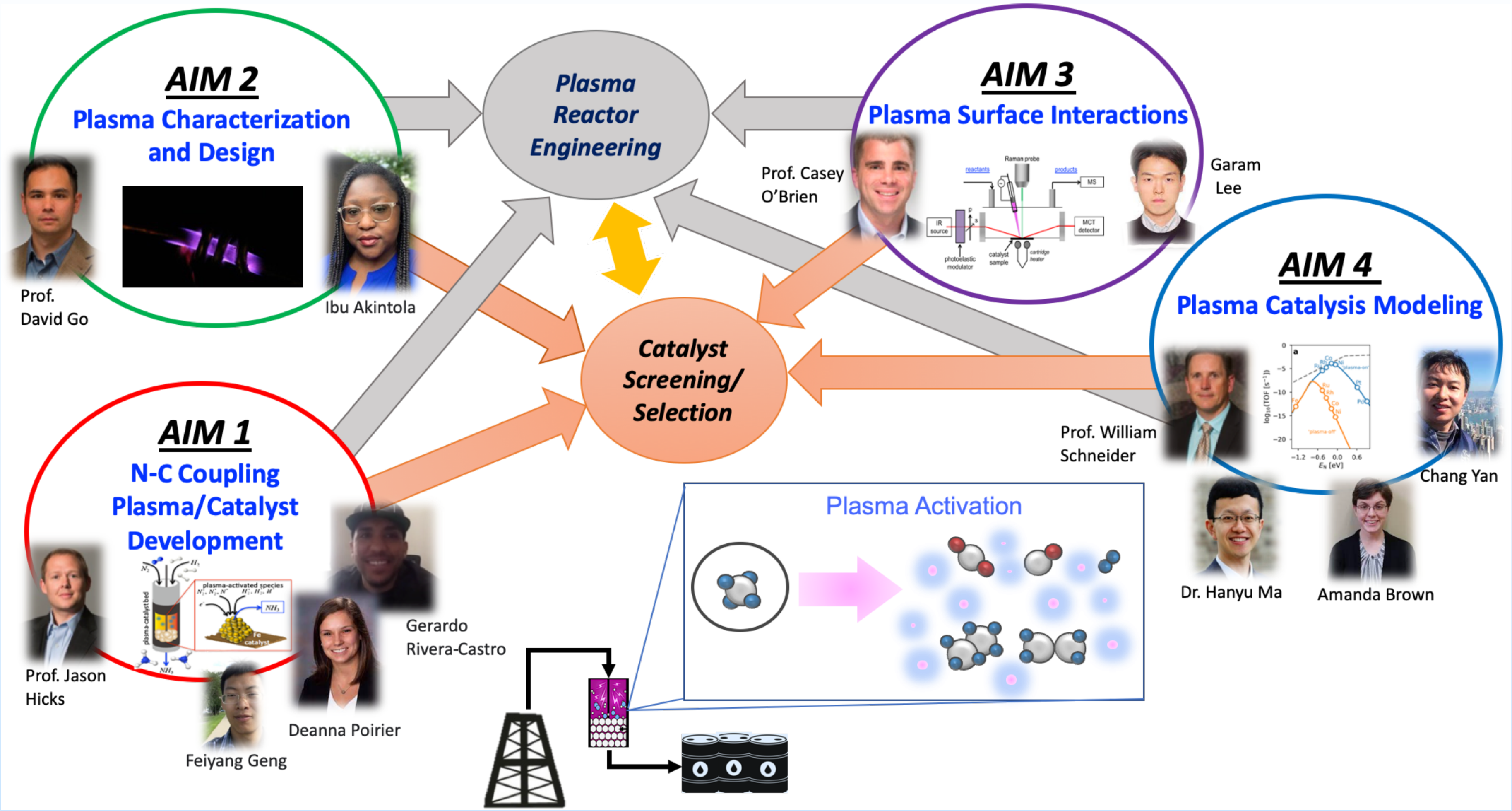
Target: Cleavage of C-H and N_2 followed by selective coupling under mild conditions via a catalytic process.



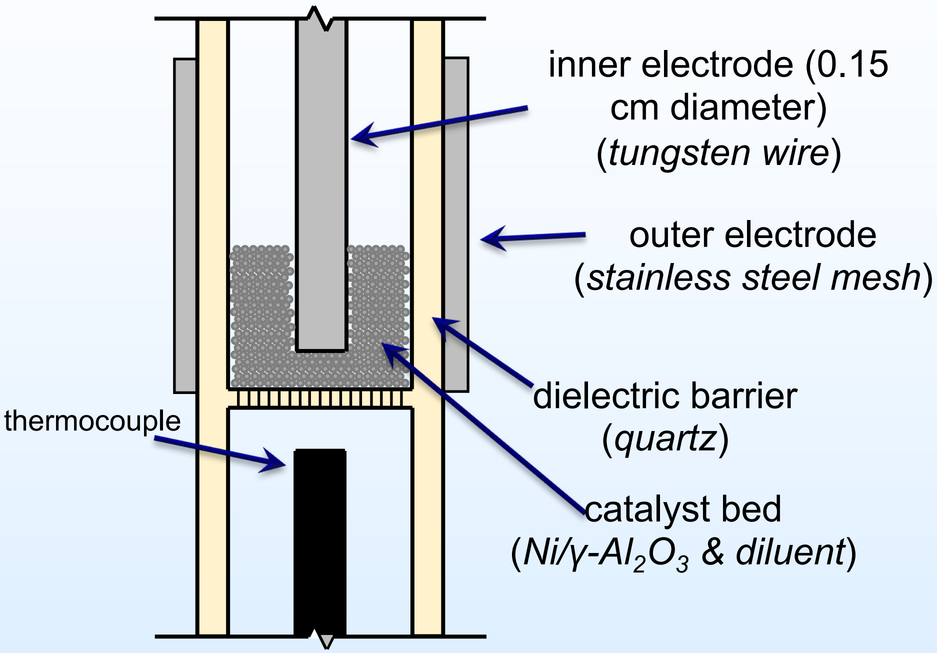
Process/Chemistry Challenges:

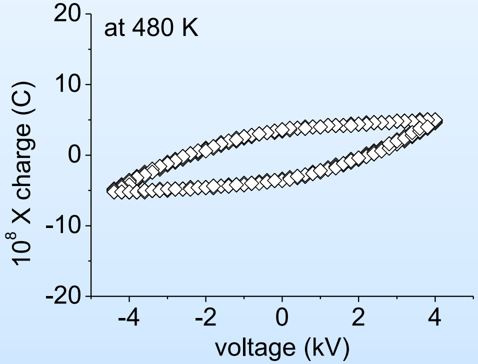
- C-H bond (>415 kJ/mol) and N_2 triple bond are stable (~940 kJ/mol)
- Poor selectivity
- Catalyst identification

Project Team and Connectivity



Approach: Plasma Reactor



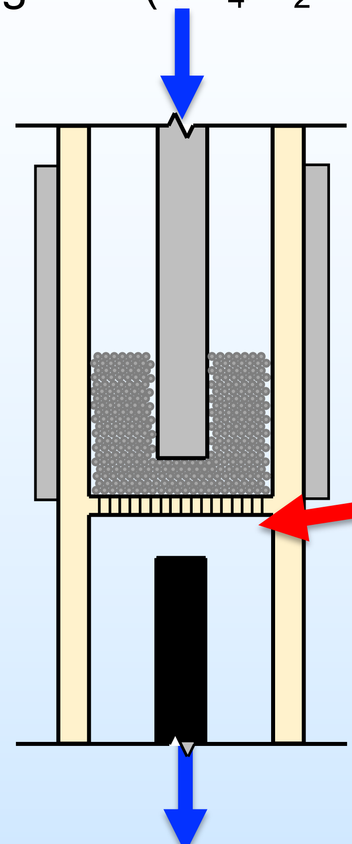


Reactor: 0.5 cm (I.D.), 0.7 cm (O.D.)
Discharge distance: ~1.75 mm
Plasma zone volume: 1.07 cm^3

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

Approach: Reactor Construction (Subtask 2.1)

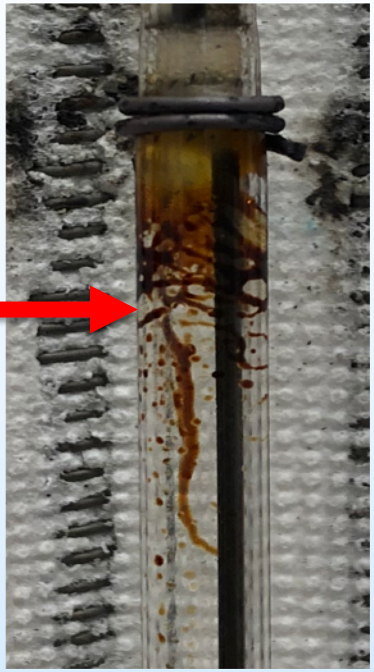
Feed gases (CH_4/N_2 or C_2H_6/N_2)



Effluent gases (out) to GC and MS

Liquids form and condense on walls of reactor.

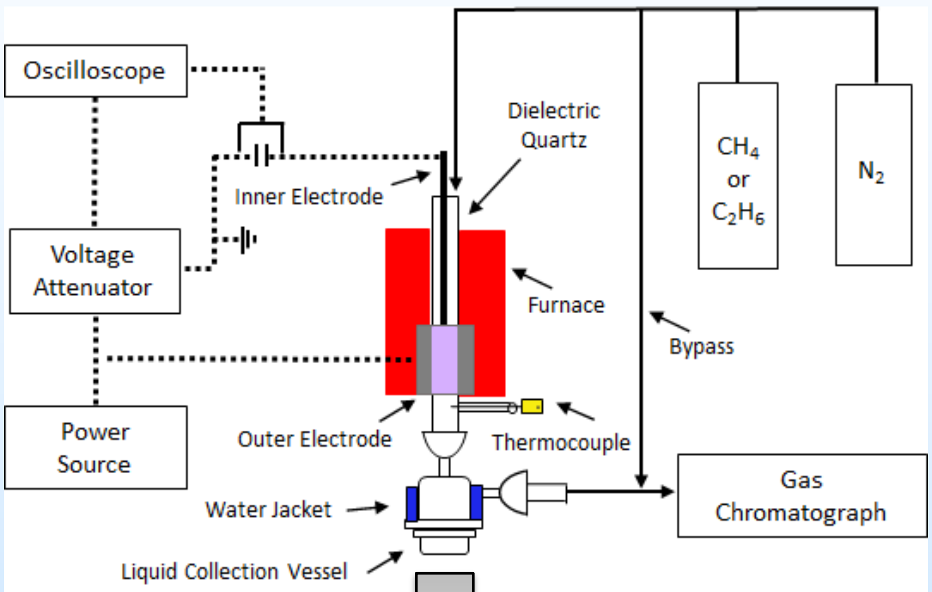
Difficult to collect, quantify, analyze…

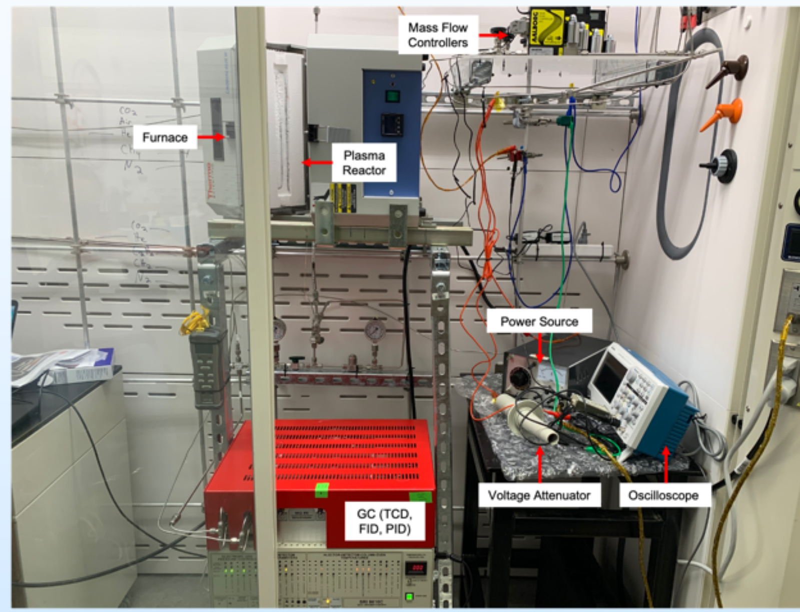


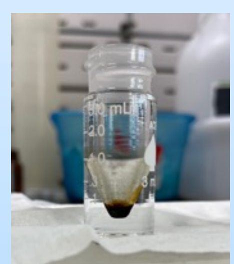
Year 1 Goal: Design new reactor to improve liquid collection.

Approach: Reactor Construction (Subtask 2.1)

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



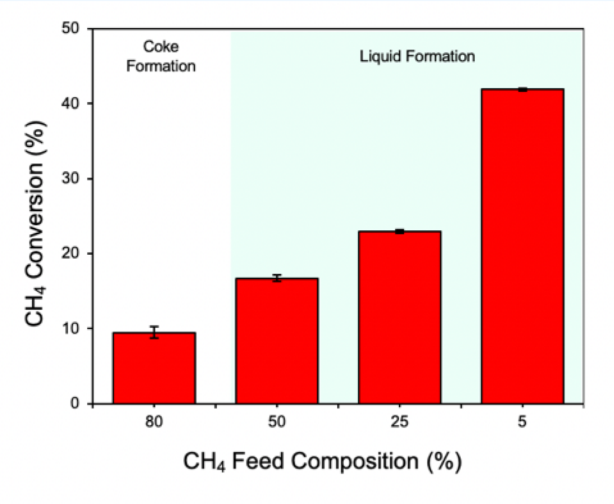


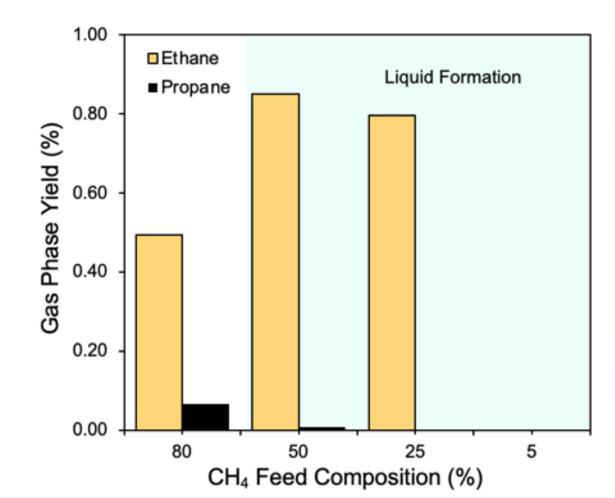


Approach: Reactor Performance Evaluation (Subtasks 2.1, 2.2, 3.1, and 3.2)

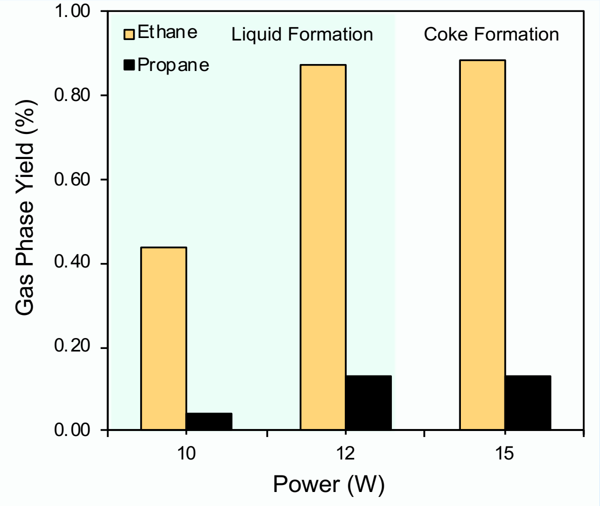
We are able to characterize the products from plasma stimulated hydrocarbon/N_2 feeds and determine stable species formed in the gas phase and conditions that favor desired product formation.

Feed Composition



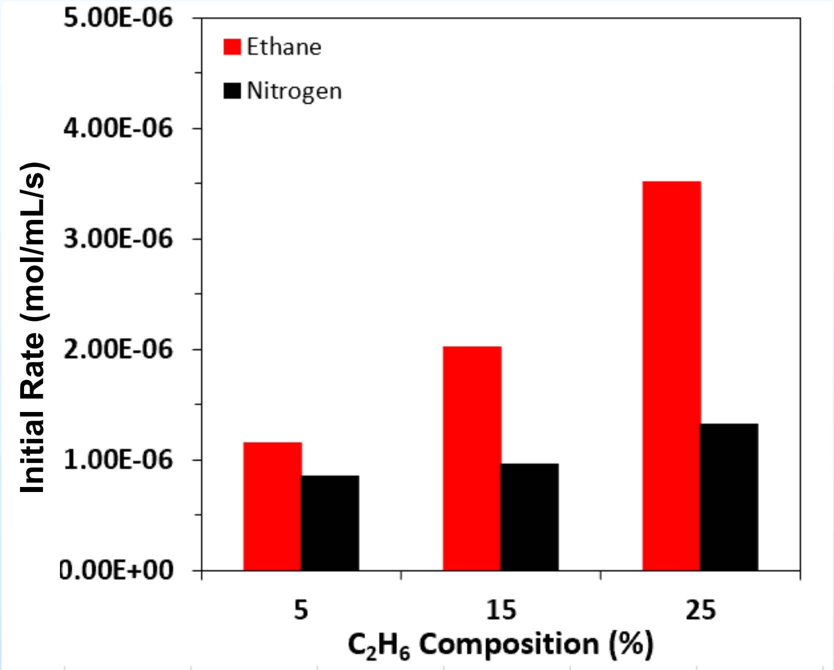


Input Power

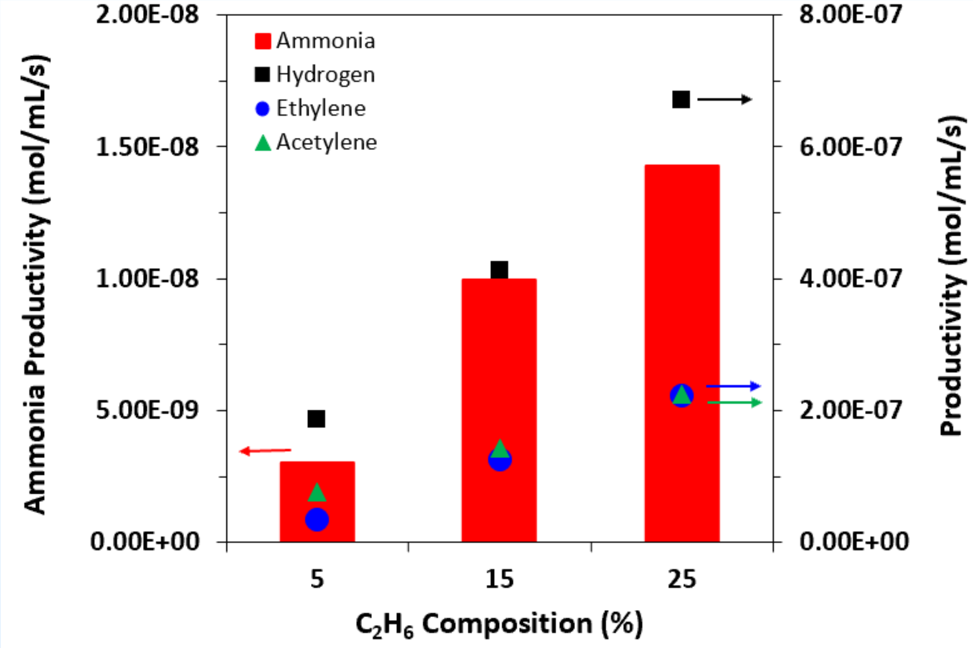


Approach: Reactor Performance Evaluation (Subtasks 2.1, 2.2, 3.1, and 3.2)

Feed composition effects on initial consumption rates

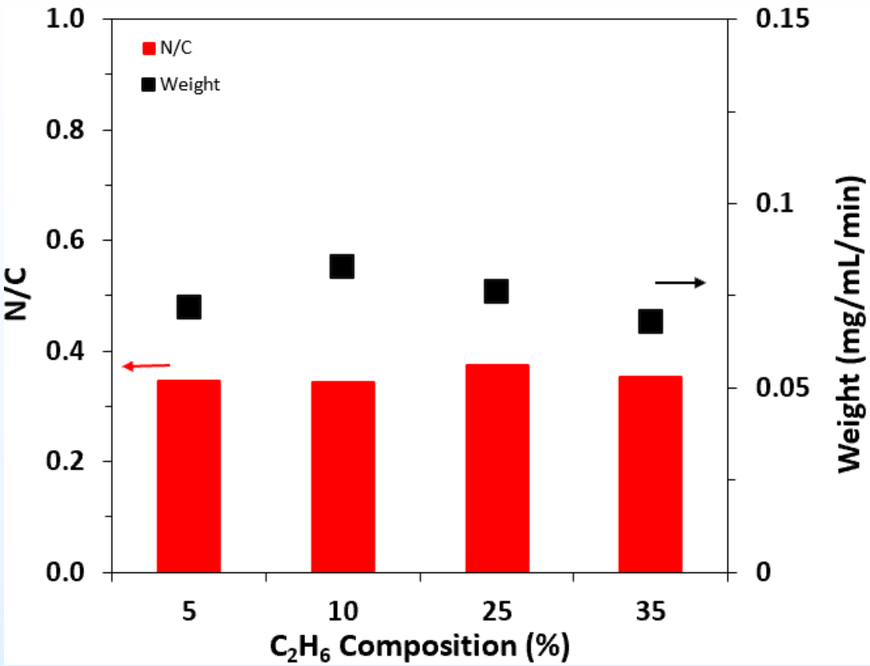


Feed composition effects on ammonia production rates



*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)

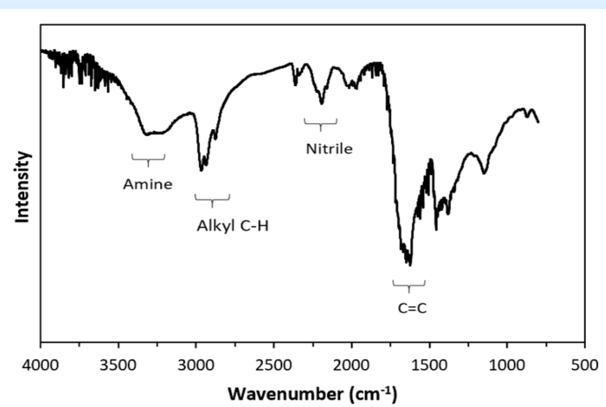


Characterization of the liquid phase and quantifying N incorporation

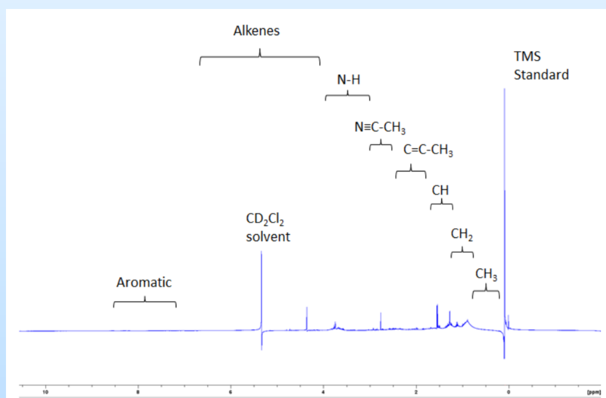
N content of the liquid phase is invariant for the different feed compositions.

Liquid production rates are similar for all plasma phase reactions.

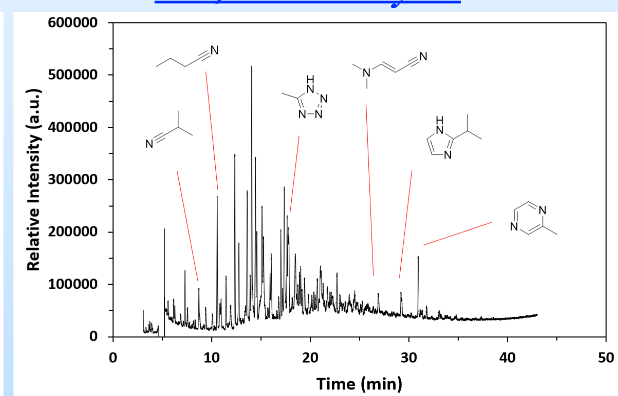
FT-IR Characterization



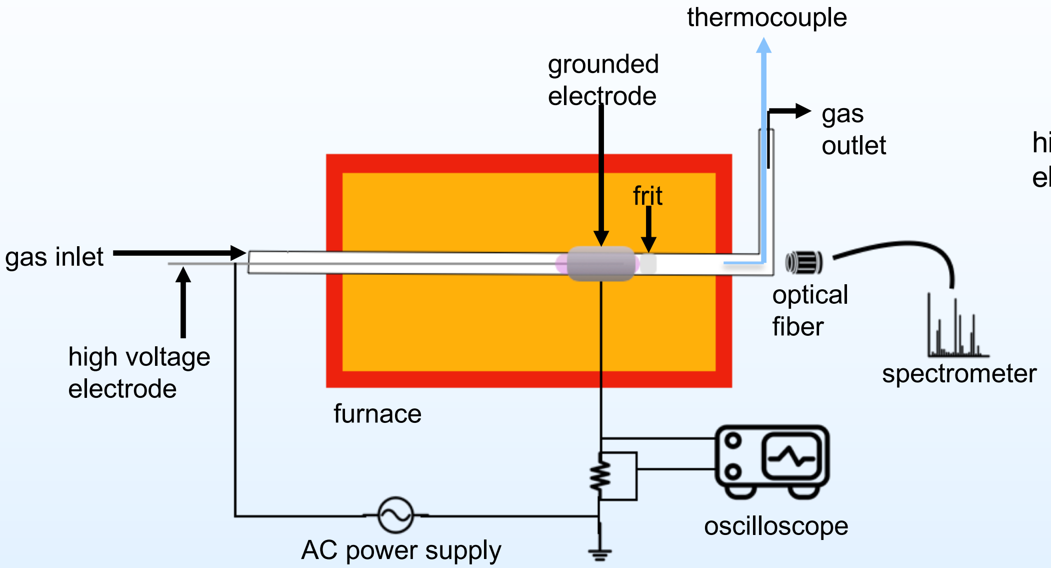
1H NMR Characterization

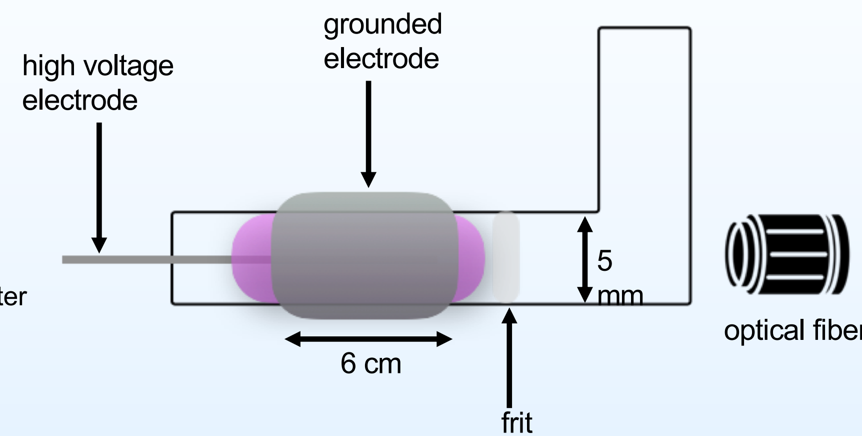


GC/MS Analysis

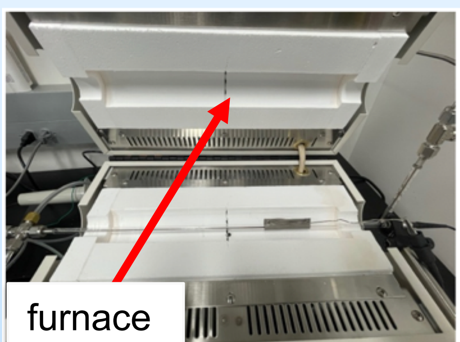


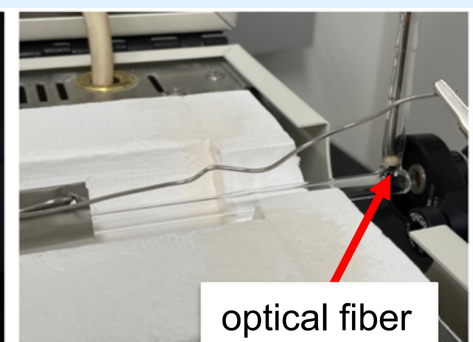
Approach: Characterization of the Plasma (Subtasks 2.3, 4.1, and 4.2)





Images depicting the setup required for optical characterization of plasmas using optical emission spectroscopy (OES) and for electrical characterization of the DBD reactor plasma.

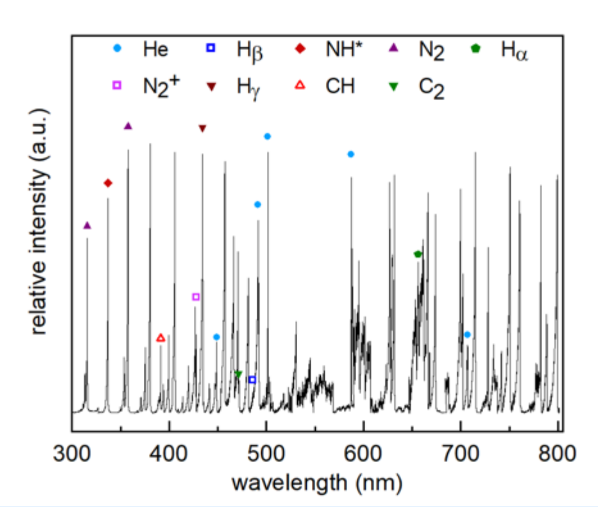




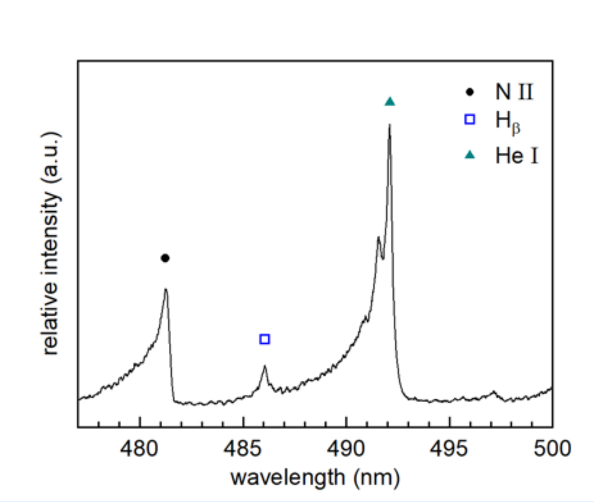
Approach: Characterization of the Plasma (Subtasks 2.3, 4.1, and 4.2)

We are able to optically characterize the DBD reactor plasma with high resolution images and determine species being formed in the gas phase as well as extract key plasma parameters.

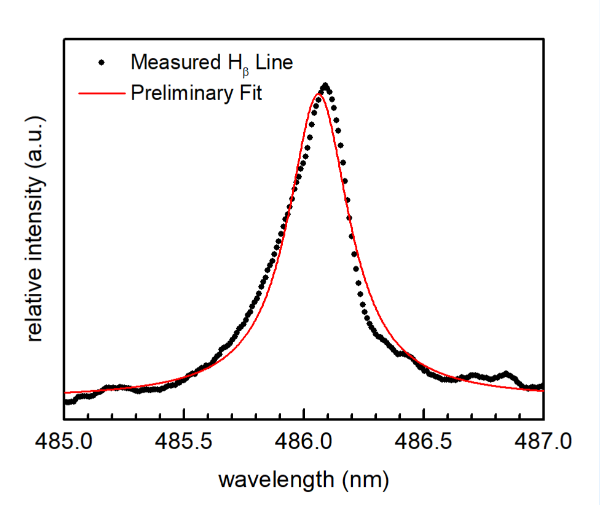
Optical Emission Spectroscopy (OES)



Close-up View of Key Gas Phase Species

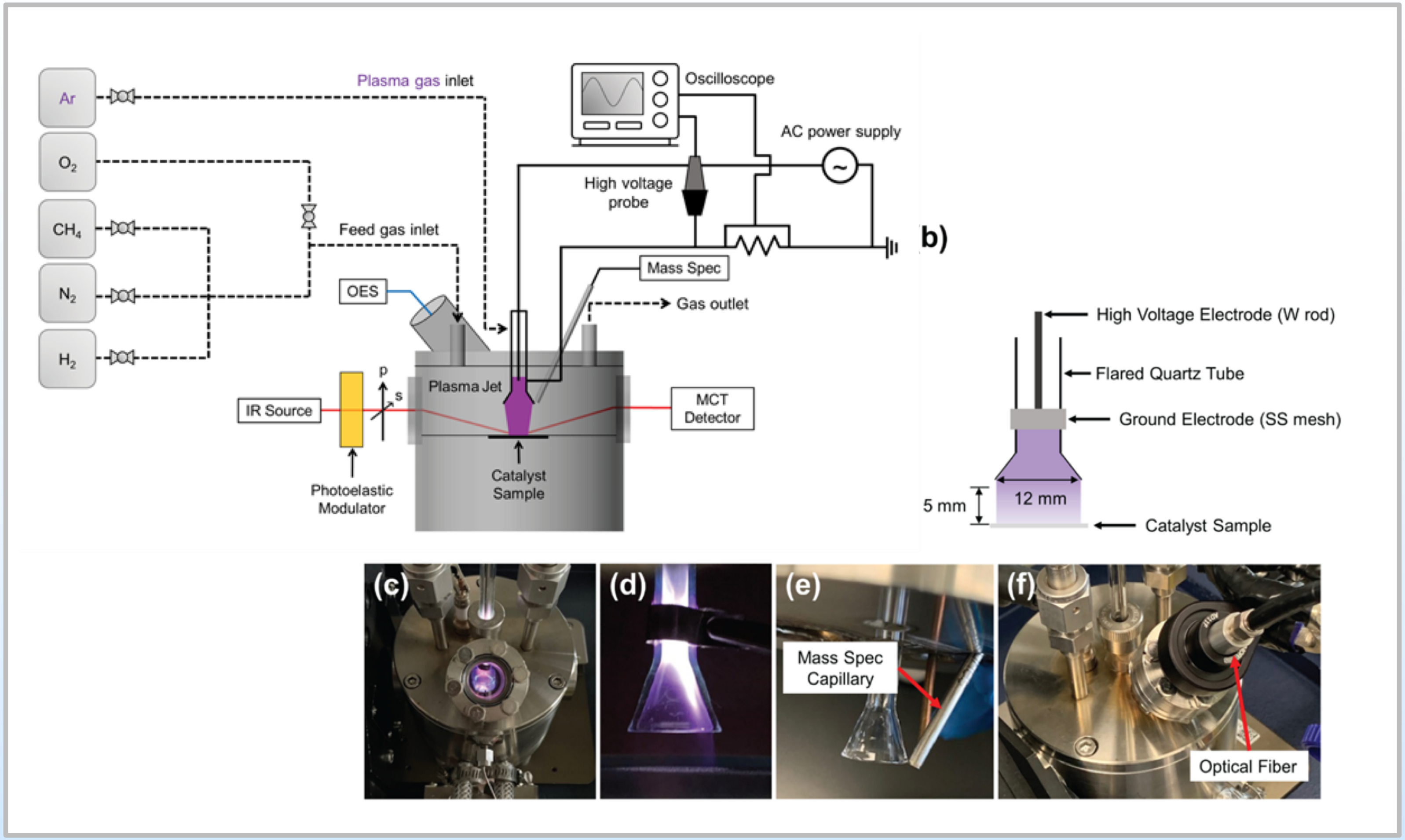


Stark Broadening Curve Fit of H_β Line to Extract Electron Density



Flow rate: N_2 (37.5 mL/min)/CH_4 (12.5 mL/min)/He (5 mL/min), **Surface Temperature:** 25 °C, **Plasma:** ~24 kHz, 9.75 kV (pk-to-pk)

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



This work is currently under review at *JACS*:

"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

University of Notre Dame

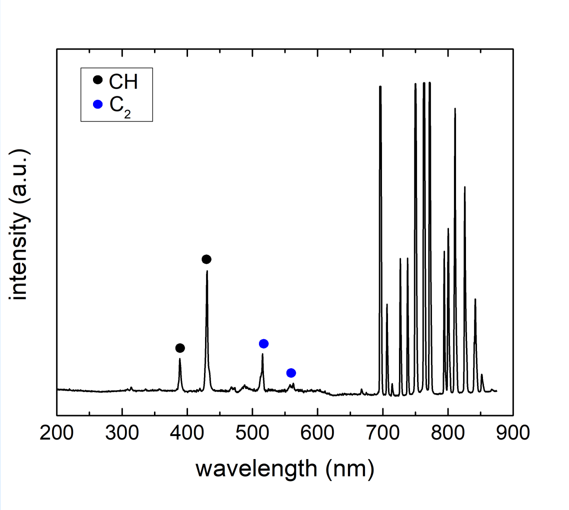
Approach: In Situ Observation of Plasma-Surface Interactions (Subtasks 2.4 and 3.5)

The new tool can correlate plasma-phase species to surface-adsorbed species and final gas-phase products, all measured simultaneously on the same sample (Ni) under plasma jet irradiation.

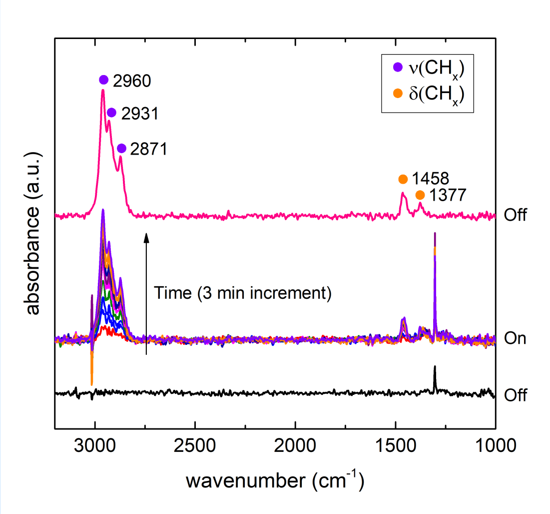
Plasma-phase species (OES) — *Surface-adsorbed species (PM-IRAS)* — *Gas-phase products (MS)*

$$CH_4 \rightarrow CH + C_2 + e^- \rightarrow (CH_2)_x(CH_3)_y \rightarrow C_2H_2 + C_2H_4 + C_2H_6 + C_3H_8$$

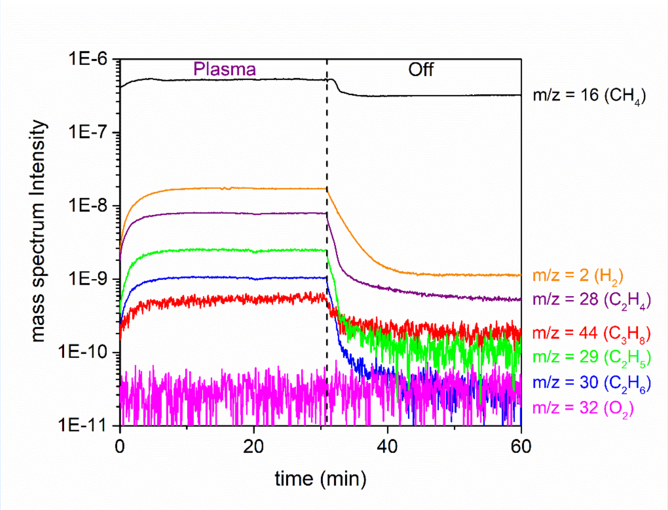
Optical Emission Spectroscopy (OES)



Polarization-Modulation Infrared-Reflection Absorption Spectroscopy (PM-IRAS)



Mass Spectrometry (MS)



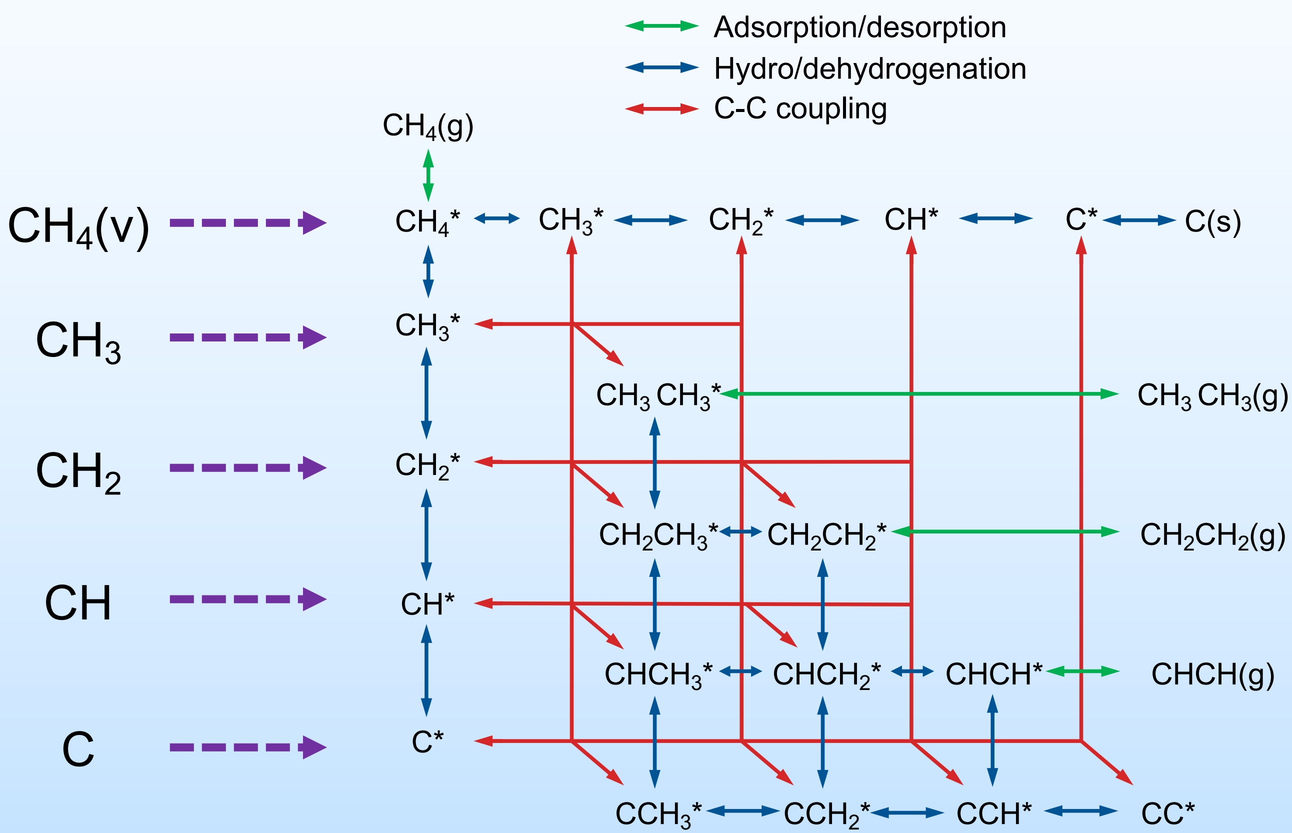
Flow rate: Ar (60 mL/min)/CH_4 (10 mL/min), **Surface Temperature:** 25 °C, **Plasma:** ~20 kHz, 6 kV (pk-to-pk)

Approach: Predictive Modeling (Subtasks 2.5 and 3.6)

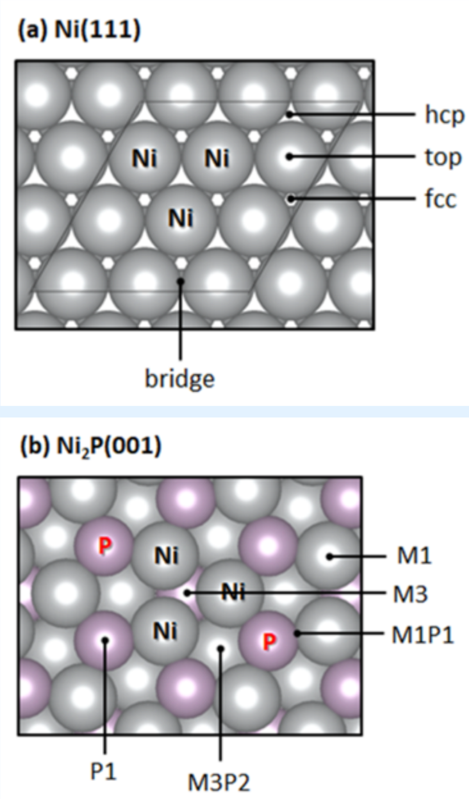
Microkinetic modeling of catalytic C-C/C-N bond formation with plasma excitation

Adsorption of plasma species

C-C bond formation over a catalyst

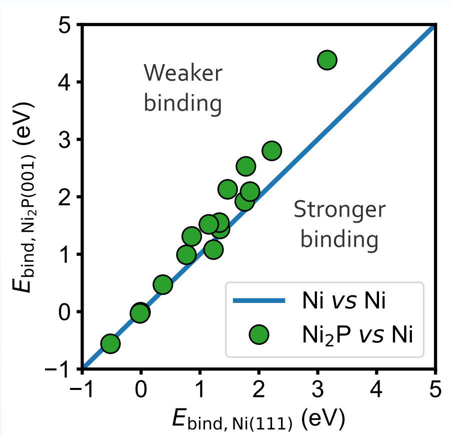


Comparison between metals and metal phosphides

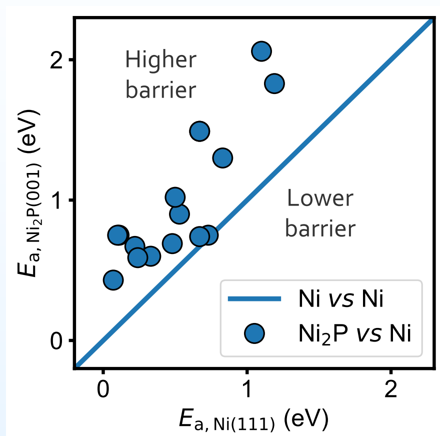


Approach: Predictive Modeling (Subtasks 2.5 and 3.6)

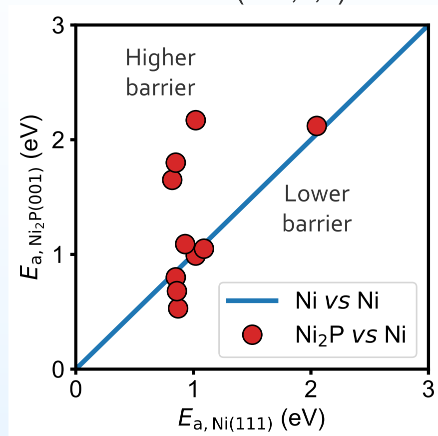
Binding strength



Dehydrogenation barriers



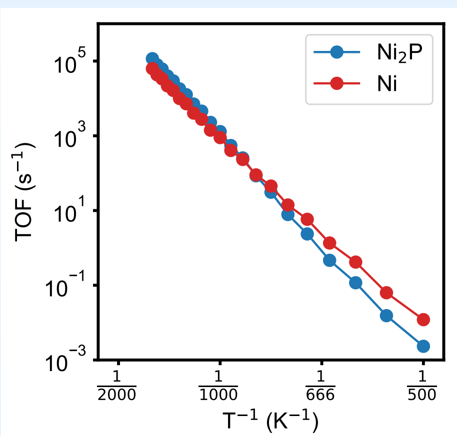
CH_x-CH_x formation barriers (x=0,1,2)



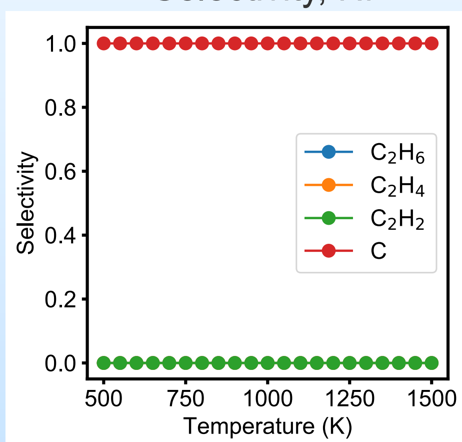
DFT calculations:

- Ni binds species stronger than Ni_2P
- Ni_2P shows higher E_a for C-H breaking
- Ni_2P shows higher E_a for coke formation

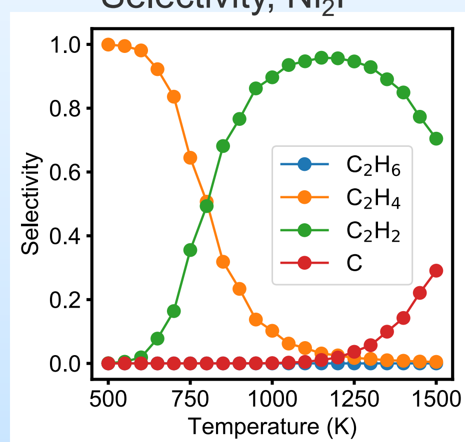
Rate



Selectivity, Ni



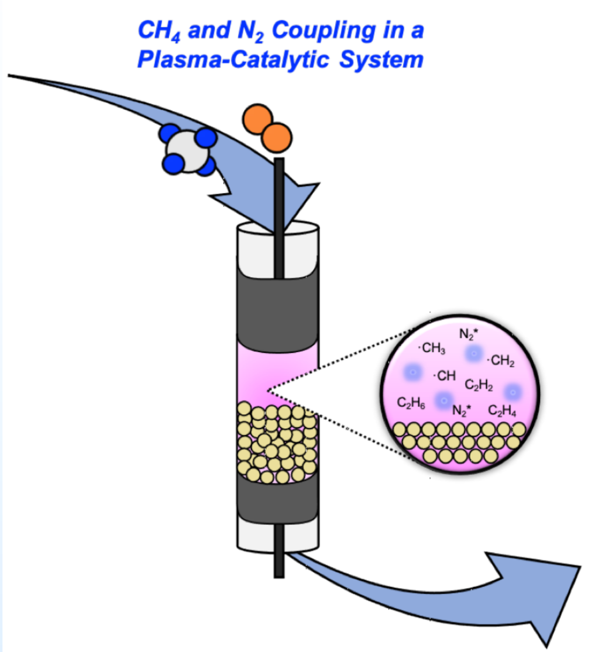
Selectivity, Ni_2P



Microkinetic modeling:

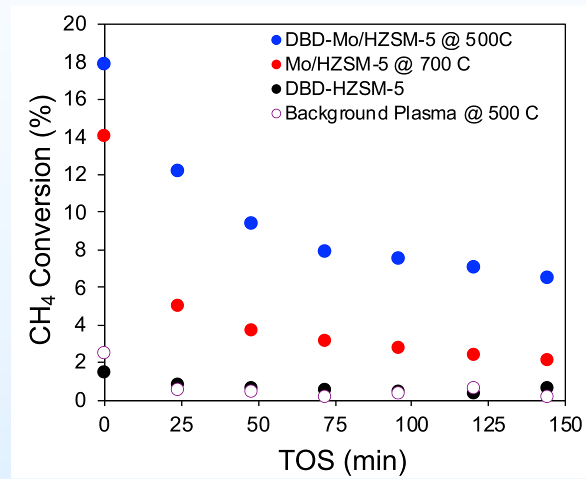
- Comparable rates in CH_4 transformation
- Coke formation over Ni
- C2 product formation over Ni_2P

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

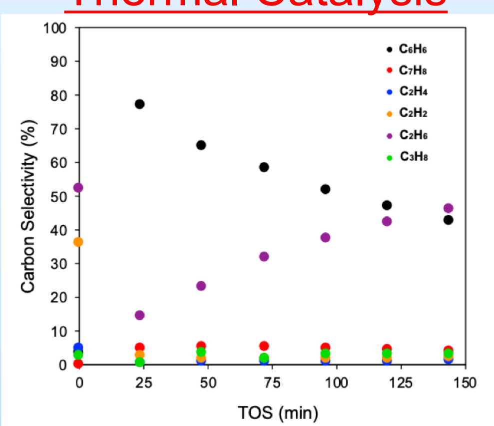


Comparing Thermal and Plasma-Assisted Catalytic Dehydroaromatization

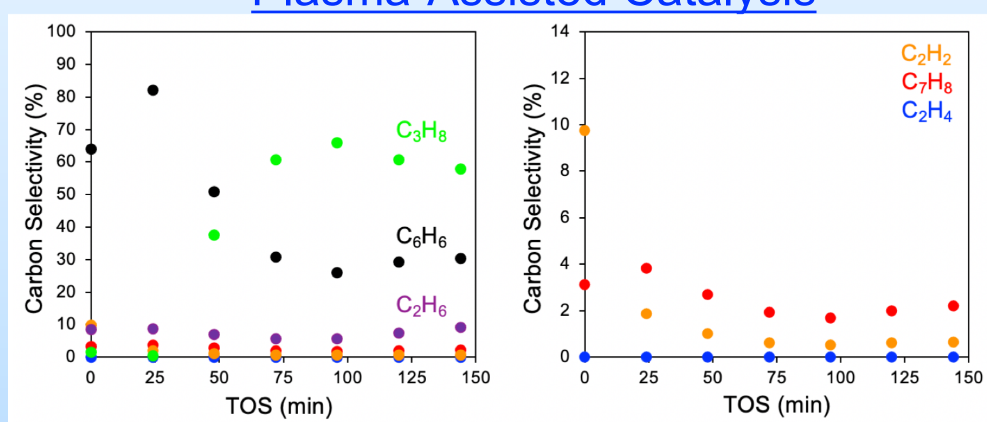
(2 % Mo/HZSM-5 (Si/Al = 11.5)



Thermal Catalysis



Plasma-Assisted Catalysis



Accomplishments to Date

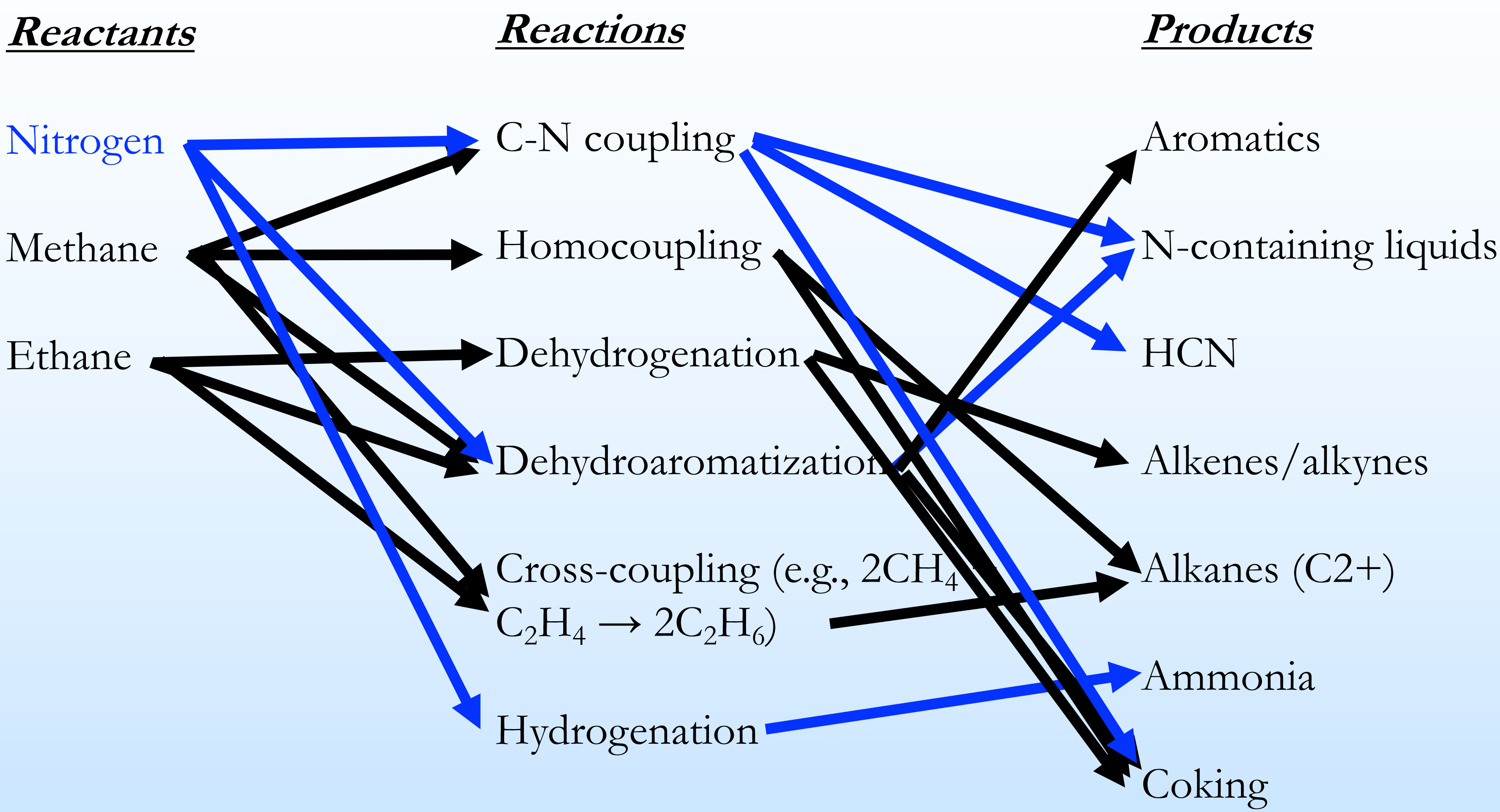
- Design, construction, and safe operation of three plasma-stimulated reactor systems operated with reproducible experimental data collection.
- Validation and demonstration of hydrocarbon – N_2 coupling under plasma stimulation, liquid production, and product identification.
- Identification of surface-adsorbed intermediates from plasma stimulation using the in-situ/operando spectroscopy plasma reactor.
- Experimental evidence of product selectivity control via plasma-simulated catalysis at lower bulk temperatures than thermal catalysis.
- Publications/Intellectual Property:

• Bogaerts, A., Tu, X., Whitehead, J.C., Centi, G., Lefferts, L., Guaitella, O., Azzolina-Jury, F., Kim, H.-H., Murphy, A.B., Schneider, W.F., Nozaki, T., Hicks, J.C., Rousseau, A., Thevenet, F., Khacef, A., Carreon, M., 2020. The Plasma Catalysis Roadmap. Journal of Physics D: Applied Physics, 53, 44, 443001. https://doi.org/10.1088/1361-6463/ab9048.

• Lee, G., Go, D.B., and O'Brien, C.P. 2021. 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. Submitted - under review.

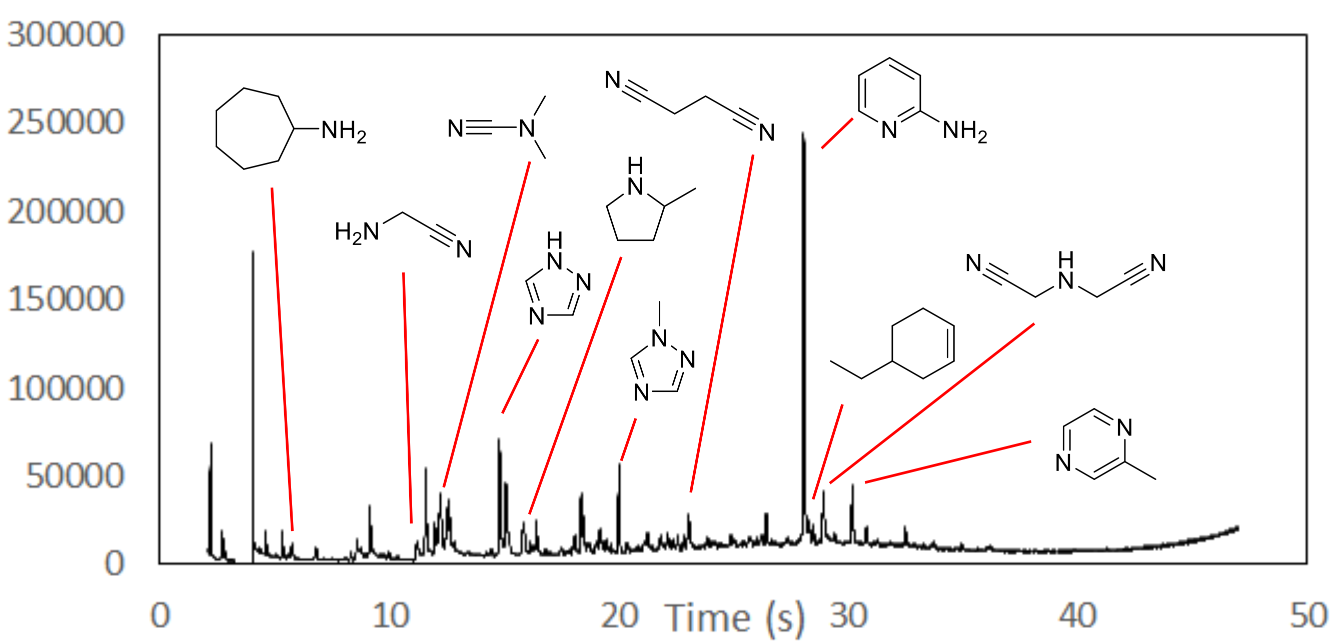
• Hicks, J.C., Barboun, P., Poirier, D., Rivera-Castro, G.; Production of Nitrogen-Containing Liquids from Hydrocarbon and N_2 Feeds. File Date: 4/3/2020. Application #: 63/004,676.

Lessons Learned: Research Challenges - Reaction Complexity



Lessons Learned: Research Challenges - Reaction Complexity

- Difficult quantifying each individual species due to the non-selective plasma-phase reactions.
- Development of selective catalysts to facilitate N-C formation are underway.



Synergy Opportunities

- Exploring alternative plasma approaches to form carbon nanomaterials (John Hu, WVU; …)

- Exploring oxidative plasma environments/processes to increase liquid production (Fangxing Li, NC State; Andreas Heyden, U. South Carolina; …)

- Exploring alternative catalytic materials for liquids production under plasma stimulation (Dongxia Liu, U. Maryland College Park; Andreas Heyden, U. South Carolina; …)

Project Summary

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.
  - From elemental analyses of the liquid phase, N is incorporated.

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

Next Steps:

– Determine appropriate catalyst to facilitate C-N coupling and liquid production by combining reaction performance results, in situ/operando characterization, and predictive modeling

– Evaluate alternative plasmas (e.g., gliding arc) to enhance liquid production rates.

Appendix

Benefit to the Program

- ***Program Goals Addressed:*** A plasma-assisted catalytic process has high promise to minimize the flaring of light hydrocarbons for a variety of reasons: (1) plasma processing is applicable to a wide range of feedstocks, (2) potential for increased catalyst lifetimes through plasma-driven removal of impurities, (3) capability to enhance reaction kinetics at ambient temperatures, (4) fast response for immediate startup and shutdown, and (5) opportunities to build delocalized, small-scale processing plants powered by renewable energy sources for decarbonization (e.g., solar or stranded wind energy).
- ***Project Benefits Statement:*** In the proposed project, the Recipients will design, develop, and test a process for direct light hydrocarbons-to-liquids conversion via plasma-assisted, catalytic chemistry. The project outcomes will enable atom-efficient transformations (such as hydrocarbon activation) through the combination of a reactive plasma and well-defined catalysts that together selectively and efficiently direct catalytic reactions that are otherwise inaccessible. This project will also lead to the development of new catalytic materials designed specifically for operation under plasma stimulation.
- The proposed research is directly in line with the goals and approach of the FOA (DoE/NETL).

Project Overview

Goals and Objectives

The overarching objective of this project is to use plasma stimulation of a light hydrocarbon resource to synthesize value-added liquid chemicals to relieve the strain associated with gas separations at the well and to evaluate the hypothesis that the plasma will serve multiple roles in this transformative chemistry including:

(1) activate Carbon - Hydrogen (C-H) bonds at low bulk gas temperature and pressure,

(2) provide a fast response for immediate startup and shutdown,

(3) enhance the lifetime of the catalyst through plasma-assisted removal of surface impurities, and

(4) provide a means to activate Nitrogen (N_2) to allow for the direct formation of chemicals containing Nitrogen – Carbon (N-C) bonds.

Project Overview
Success Criteria (Year 2 to Year 3)

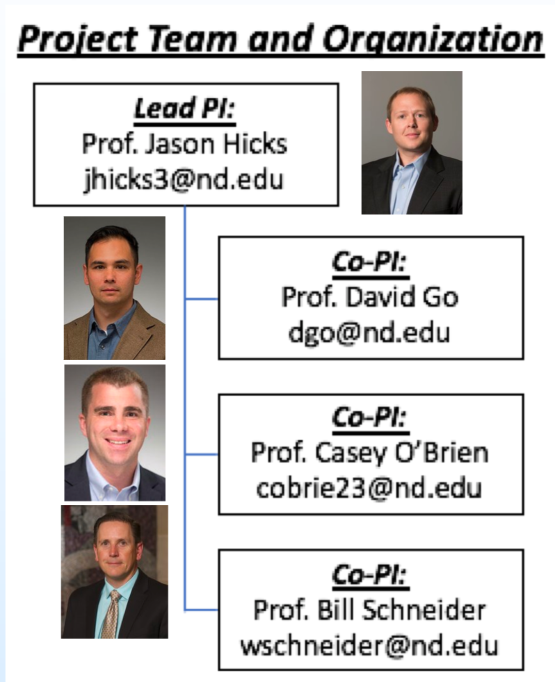
- Experimental sensitivity analysis through the correlation of feed inputs and reaction results (representative data plots) and analysis of results to identify favorable (and unfavorable) reaction conditions of plasma-assisted N-C coupling chemistry under plasma power inputs (1-15 W), hydrocarbon:N_2 ratio ($P_{hydrocarbon}/P_{N2} = 0.05 – 10$), and a simulated shale gas stream (80% CH_4, 20% C_2H_6) by the end of the fourth quarter in year 2. **75% complete**

- Reproducibly collected and literature benchmarked, optical spectroscopic identification of plasma-activated gas phase species and spectroscopic identification of surface-adsorbed C-H features and NH* features formed in $P_{hydrocarbon}/P_{N2} = 0.05 – 10$ environments and plasma power inputs (1-15 W) by the end of the fourth quarter in year 2. **60% complete**

- Identification of surface-adsorbed intermediates from plasma stimulation using the in-situ/operando spectroscopy plasma reactor with a hydrocarbon:N_2 ratio ($P_{hydrocarbon}/P_{N2} = 0.05$ – 10) and plasma power inputs (1-5 W) by the end of the fourth quarter in year 2. **85% complete**

- Correlative models developed and evaluated for ability to predict changes in performance (conversion, selectivity) with changes in operating parameters (power, temperature, residence time) and in changes in catalytic materials. Models exercised to direct system/material modifications towards improved reactor performance. **35% complete**

Organization Chart



Plasma Catalysis, Catalyst Synthesis, and Kinetics

Plasma Physics, Plasma Catalysis, and Characterization

Interfacial Science and Spectroscopy

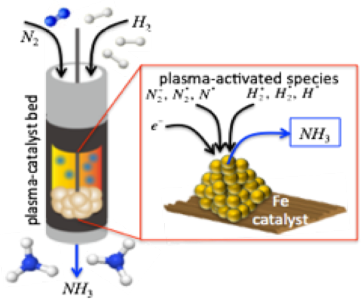
Theory and Simulations

Graduate and Postdoctoral Researchers

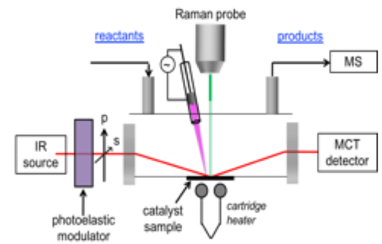
Gerardo Rivera-Castro (2nd year), Deanna Poirier (2nd year), Feiyang Geng (4th year), Garam Lee (2nd year), Amanda Brown (2nd year), Ibukunoluwa Akintola (2nd year), Hanyu Ma (postdoc)

Project Team/Approach: DE-FE0031862

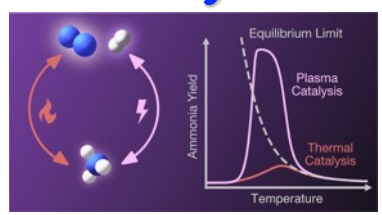
Catalyst Synthesis and Performance Measurements
Prof. Jason Hicks (PI)



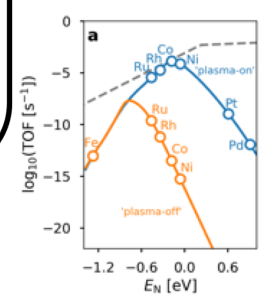
In situ/operando Spectroscopy
Prof. Casey O'Brien (co-PI)



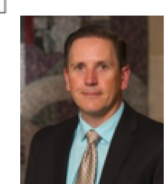
Plasma Catalysis



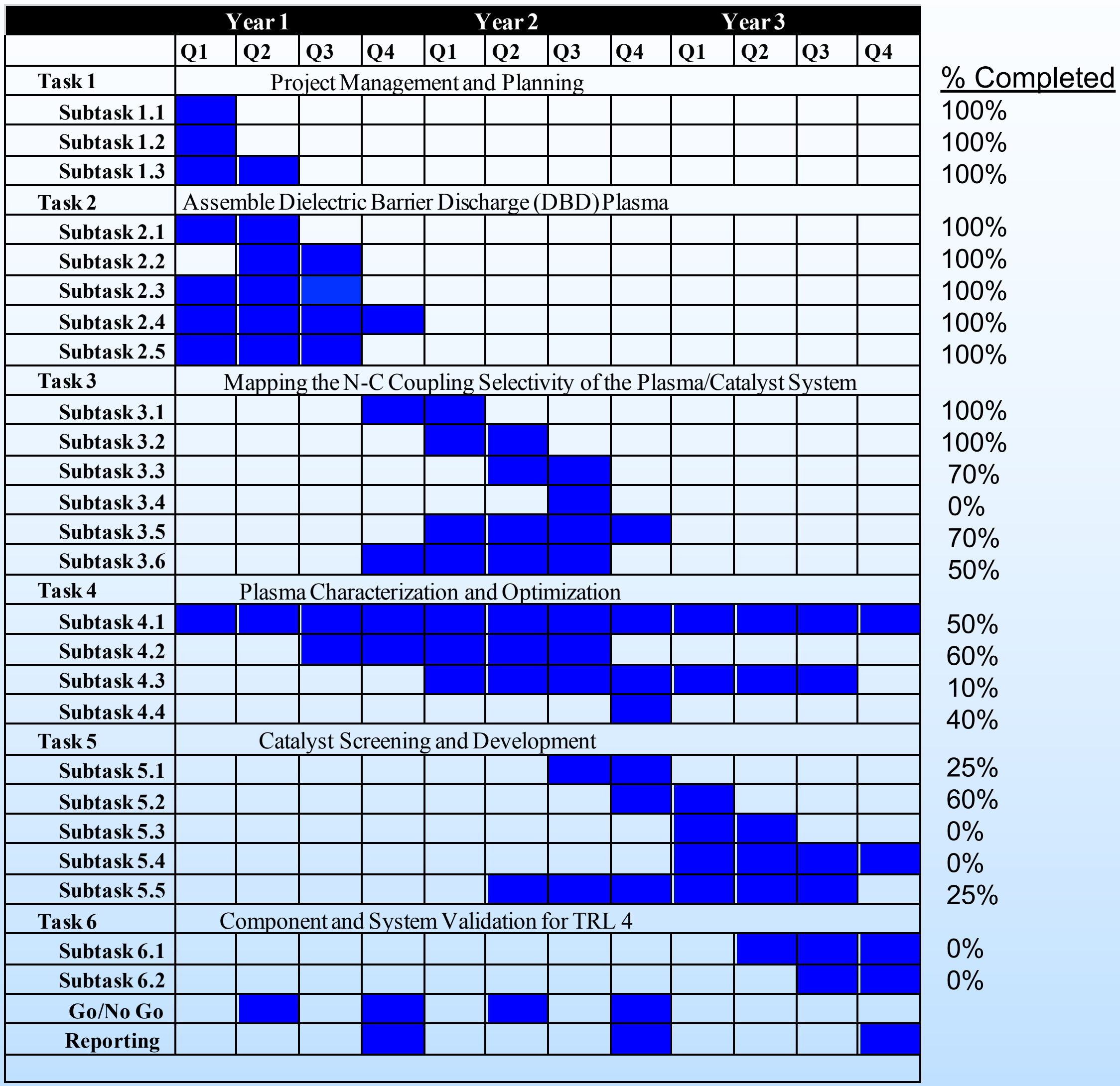
Plasma Physics/ Characterization
Prof. David Go (co-PI)



Theory and Simulation
Prof. Bill Schneider (co-PI)



Gantt Chart


Year 1
Year 2
Year 3
Q1
Q2
Q3
Q4
% Completed
Task 1
Project Management and Planning
Subtask 1.1
100%
Subtask 1.2
100%
Subtask 1.3
100%
Task 2
Assemble Dielectric Barrier Discharge (DBD) Plasma
Subtask 2.1
100%
Subtask 2.2
100%
Subtask 2.3
100%
Subtask 2.4
100%
Subtask 2.5
100%
Task 3
Mapping the N-C Coupling Selectivity of the Plasma/Catalyst System
Subtask 3.1
100%
Subtask 3.2
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Subtask 3.3
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Subtask 3.4
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Subtask 3.6
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Task 4
Plasma Characterization and Optimization
Subtask 4.1
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Subtask 4.2
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Subtask 4.4
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Task 5
Catalyst Screening and Development
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Task 6
Component and System Validation for TRL 4
Subtask 6.1
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Subtask 6.2
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Go/No Go
Reporting

Bibliography

- Bogaerts, A., Tu, X., Whitehead, J.C., Centi, G., Lefferts, L., Guaitella, O., Azzolina-Jury, F., Kim, H.-H., Murphy, A.B., Schneider, W.F., Nozaki, T., Hicks, J.C., Rousseau, A., Thevenet, F., Khacef, A., Carreon, M., 2020. The Plasma Catalysis Roadmap. Journal of Physics D: Applied Physics, 53, 44, 443001. https://doi.org/10.1088/1361-6463/ab9048.
- Lee, G., Go, D.B., and O'Brien, C.P. 2021. 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. Submitted - under review.