EILERS GRADUATE STUDENT FELLOWSHIP
FINAL REPORT

EILERS FELLOW:	Deanna Poirier
FACULTY ADVISOR:	Jason Hicks
REPORT PERIOD:	2022
PROJECT TITLE:	Plasma-Assisted Catalysis for Upgrading Ethane to Valuable Liquid Products through Carbon-Nitrogen Coupling
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**(x) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **( ) Transformation Solar** **(x) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS:
List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Design of a new reactor system able to handle complex product slate	Developed a method to increase the number of gas phase products analyzed from 4 to 13. Modified the plasma reactor to be able to handle collection of liquid products.	100
Characterization of the liquid products from mixed feed reaction	Identified hydrocarbon compounds, nitrogen-containing compounds with nitrile, amine, and imine functional groups, and polymeric compounds.	90
Incorporation of a catalyst into the system to direct aromatic formation from ethane	Al_2O_3 and ZSM-5 catalysts promoted aromatic formation. Future work will be focused on studying the addition of a metal to these catalysts with the goal of nitrogen incorporation into aromatics products.	25

RESEARCH OUTPUT:
Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	
EXTERNAL AWARDS	
JOURNAL ARTICLES	
BOOKS AND CHAPTERS	
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	Presentations: Catalysis Club of Chicago 2023 Young Scientist Symposium, Plasma-Assisted Approaches for the Direct Conversion of Natural Gas to Liquid Products, January 13, 2023, Virtual American Chemical Society Fall 2022, Direct Conversion of Plasma-Stimulated Natural Gas Streams to Value-Added Products, August 25, 2022, Chicago, IL 27th North American Catalysis Society Meeting, Plasma-Assisted Approaches for the Direct Production of Liquid Products from Shale Gas, May 26, 2022, New York, NY Posters: Chemical and Biomolecular Engineering Graduate Research Symposium, Plasma-Assisted Approaches for the Direct Conversion of Natural Gas to Value-Added Products, September 23, 2022, South Bend, IN Gordon Research Conference: Plasma Processing Science, Plasma-Assisted Approaches for the Direct Conversion of Natural Gas to Value-Added Products, July 27, 2022, Andover, NH
AWARDS, PRIZES, RECOGNITIONS	Graduate Student Professional Development Award, March 2022

	Graduate Student Government Conference Presentation Grant, March 2022
INTERNAL COLLABORATIONS FOSTERED	Ibu Akintola, Aerospace and Mechanical Engineering, University of Notre Dame, Provided electrical characterization of the plasma in order to help understand the product distribution
EXTERNAL COLLABORATIONS FOSTERED	
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	Invention Disclosure D-0450, 2022; submitted

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

We began by studying the non-catalytic plasma reaction of methane, ethane, propane, and nitrogen, a feed that is similar to natural gas. With this complex feed, we needed to improve our gas phase analysis. A method was developed to analyze the products on two gas chromatographs in order to increase the number of products we could identify and quantify. With our improved gas phase analysis, we were able to analyze products containing 2-7 carbons (i.e., C_2H_4, C_3H_6, etc.). Interestingly, we observed the formation of a dark, viscous liquid after reaction. With the original reaction design, it was challenging to collect this product. The reactor was modified to have a liquid collection vessel that allowed the liquid product to accumulate and be more easily analyzed after reaction.

A variety of techniques were used to characterize the liquid product. A N/C molar ratio of 0.35 was determined through elemental analysis, indicating that nitrogen was being incorporated into the liquid. 1D (^{1}H, ^{13}C) Nuclear Magnetic Resonance (NMR), 2D (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC) NMR, X-ray Photoelectron Spectroscopy (XPS), and Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) identified nitrile, amine, imine, and alkene functional groups. Gas Chromatography Mass Spectrometry (GC-MS) was used to identify possible products in the liquid, and the products contained the functional groups identified by the previous techniques (Figure 1). Molecular weights ranging from 50-750 g/mol were detected by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS) for the individual products within the liquid (figure 2). Evidence of polymerization of -CH_2- and -HCN-, as well as various levels of hydrogen saturation for the individual products was also observed, and these results were corroborated through Electrospray Ionization Mass Spectrometry (ESI-MS).

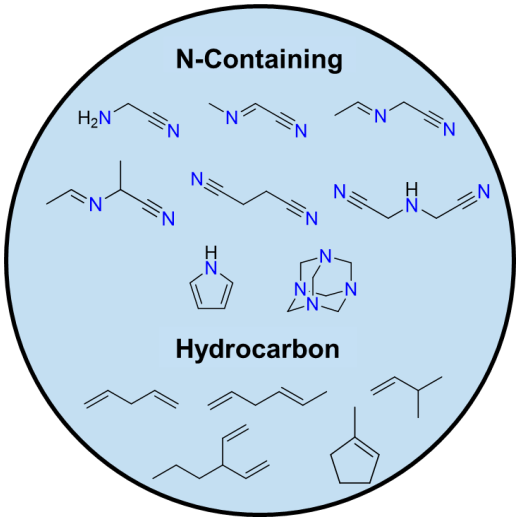

Figure 1. Liquid products identified by GC-MS show evidence of nitrile, amine, imine, and alkene function groups.

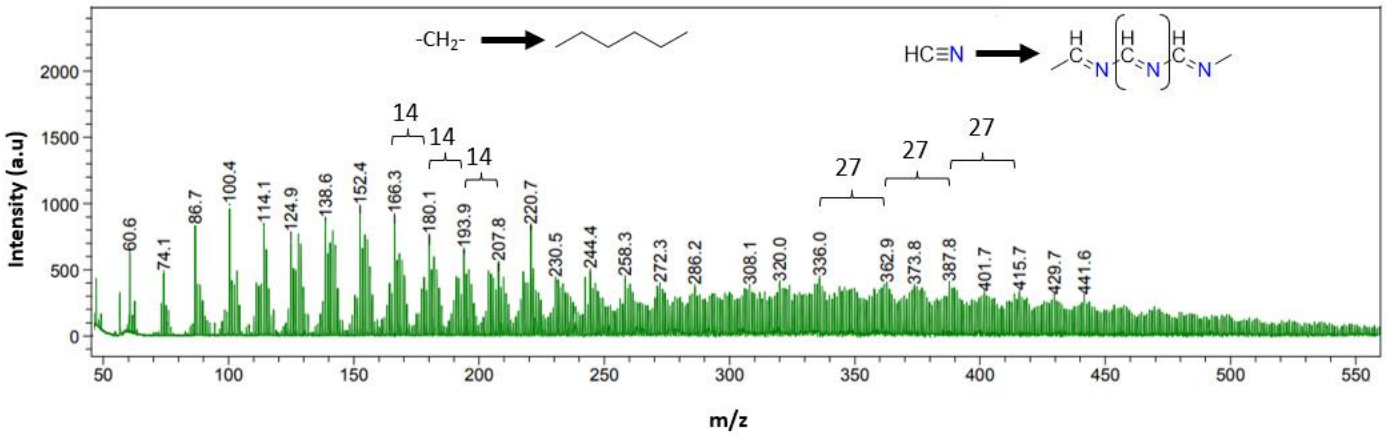

Figure 2. MALDI-TOF-MS of the liquid product shows evidence of polymerization.

The final goal of this project was to incorporate a catalyst into the plasma system in order to shift the selectivity of the reaction towards nitrogen-containing aromatics. We have begun this study using ethane rather than the more complex mixed feed. Al_2O_3 and ZSM-5 based catalysts were chosen in order to enhance aromatic production, which was not seen for the previously discussed non-catalytic reactions. Initial results show the formation of benzene and toluene for these catalysts. Future work will explore the addition of a metal to these catalysts, with the aim of promoting carbon-nitrogen coupling to drive formation of nitrogen-containing aromatics.