A SURP Proposal titled

Structured Carbon Synthesis through Plasma-based Decomposition of Natural Gas

Abstract:
The proposed research explores plasma-based natural gas (NG) decomposition to produce structured carbon materials and hydrogen. This new approach to utilizing NG as a material synthesis technique is potentially more profitable than the traditional use of NG for energy production and thus provides an economic driving force to shift NG-based energy production to renewable sources. Despite previous demonstrations of the decomposition concept using hydrocarbons of high purity, the associated high costs and stringent operation conditions prevent this technique from being employed on a large scale. In this research, NG will be tested as reactant in a microwave plasma reactor to generate structured carbon and hydrogen. In particular, the impact of NG composition variation and hydrogen addition on the yield and quality of final carbon products will be investigated. Testing of NG/hydrogen blends is particularly relevant to the regional initiative of blending hydrogen to existing NG pipelines in Southern California [1]. Proposed research activities include 1) microwave plasma reactor design and construction, 2) experiments and data/sample collection, and 3) carbon materials characterization using electron microscopy (EM) techniques.

Background:
A large share of global CO_2 emissions is caused by electricity production and the associated natural gas usage. While renewable energy technologies have made tremendous progress in the past two decades, natural gas remains to be technologically and economically advantageous, impeding the transition to a zero-carbon emission future. An effective approach to mitigating the use of natural gas and its emissions is to develop methods that are able to transform natural gas into profitable products and provide an economic incentive to shift energy production to renewable sources.

Plasma-based decomposition of hydrocarbons is one promising technique that could provide a new technological home to natural gas: solid carbon materials of high value, such as graphene or carbon nanotubes, can be synthesized from feeding hydrocarbon through microwave plasmas [2]. In addition, auxiliary hydrogen will be produced through the process and can be used for zero-emission energy production. There are several advantages of the plasma-based approach in comparison to other existing carbon-synthesis techniques such as Chemical Vapor Decomposition (CVD) and reduction of graphene oxide [3]: First, plasma synthesis of structured carbon is not sensitive to specific hydrocarbon species and has been successfully performed using a variety of hydrocarbons from alkanes to alcohols. Second, the process is entirely gas-phase and does not require a substrate for the synthesis to occur, reducing the system design complexity and cost. Lastly, the synthesis process is able to run continuously without the need to frequently stop the reaction for reasons such as removing built-up carbon from some filter or membrane. Figure 1 showcases some carbon samples generated from a microwave plasma fed with alcohols such as ethanol [4].

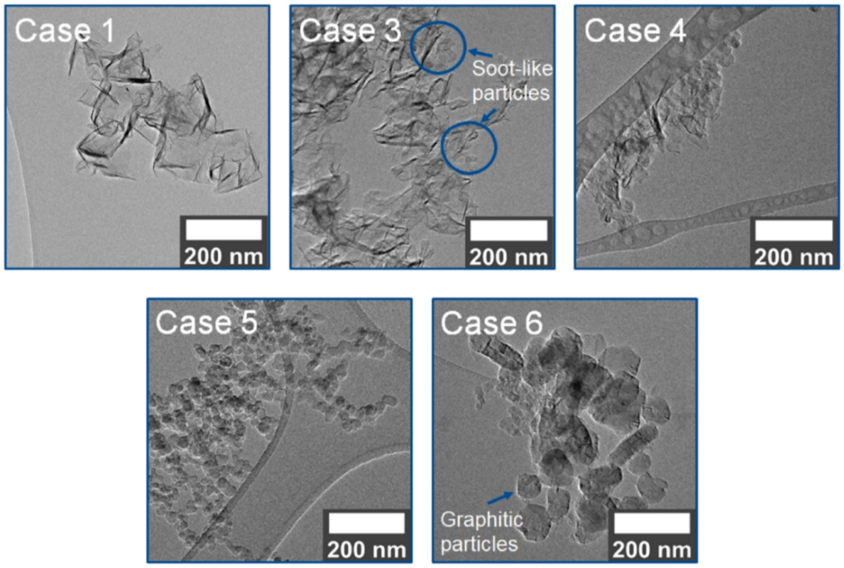

Figure 1: Solid carbon produced from alcohols [4].

As the major component in natural gas, methane (CH_4) has been studied in the past for its carbon-synthesis potential. There is a significant amount of research regarding the thermocatalytic decomposition of methane, a traditional method in which heated methane is decomposed into solid carbon and hydrogen gas, sometimes with assistance of a carbon- or metal-based catalyst. While the majority of research into this topic utilizes furnaces or ovens as a heat source, it has been successfully demonstrated that methane can decompose into hydrogen gas and structured carbons by plasma without the use of a catalyst [5, 6]. Figure 2 depicts a scanning electron microscope (SEM) image of the carbon materials produced in such an experiment. To date, all the experiments performed so far used high-purity research-grade methane, whose high costs could prevent the process from scaling up. Large-scale implementation of this process will become possible if the reactants require little to no pretreatment and are easily accessible, making natural gas the ideal candidate reactant. If natural gas that is currently used in energy production is able to produce a sufficient amount of both structured carbons and hydrogen gas, there is great potential for plasma-based decomposition of natural gas to disrupt the current energy generation and material production industries and reduce greenhouse gas emissions.

The proposed research explores the use of natural gas as the hydrocarbon feed to microwave plasma to synthesize structured carbon and hydrogen. Different from previous work, this study focuses on examining the composition effect of natural gas on the final carbon product quality and quantity. Recent studies have shown that the large number of components in natural gas and other fossil fuels render these compounds more resistant to composition variations, in contrast to pure hydrocarbons subject to impurities [7]. Therefore, it's not unreasonable to expect that natural gas is a better reactant choice than methane for microwave plasma sythesis. Moreover, hydrogen added to the hydrocarbon feed has shown to shift carbon products to more structured forms [4]. Hydrogen blending into natural gas, being currently implemented to the local NG pipeline network in the Los Angeles basin, provides an additional opportunity to examine this technique as a "plug-in" technology suitable for near-future NG infrastructures.

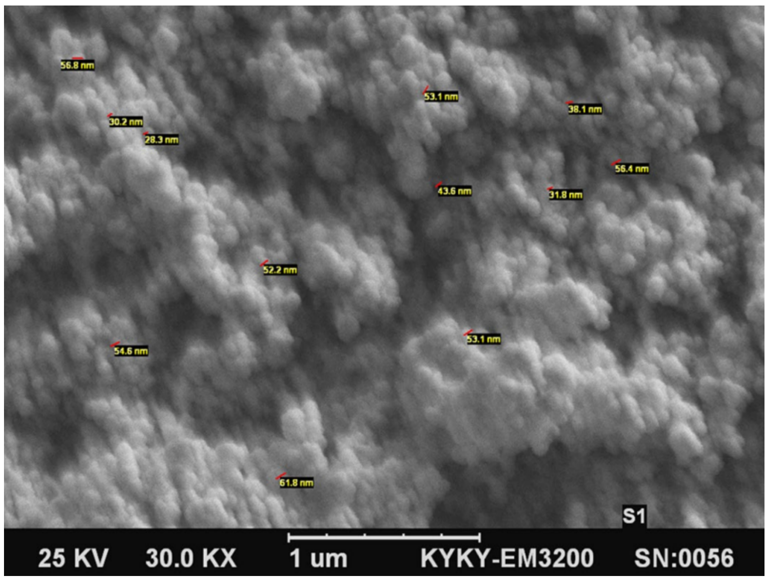

Figure 2: The length of solid carbons produced from methane [3].

Objective:

The objectives of this research are to:

1) construct a gas-phase microwave-plasma reactor,

2) evaluate the potential of using natural gas to synthesize structured carbon and hydrogen, and

3) identify key parameters that control yield, structure, and quality of the carbon product.

Approach:

First, I will conduct a literature review in order to determine the range of operating parameters for decomposition reactions of various hydrocarbons. These could include but are not limited to temperature, pressure, flow velocity, or reactor type. Then, a lab-scale miscrovae plastma reactor will be constructed that will be utilized to perform the plasma synthesis process. Control conditions for a control group will be determined through further reviewing the literature, performing preliminary experiments, or a combination of both. Finally, decomposition of natural gas will be performed using the plasma reactor under various conditions in order to analyze how the different parameters affect hydrogen and solid carbon production.

When analyzing the results of the experiments, there are a few key metrics that will be focused on. First is the structure of the carbon materials produced by the decomposition reaction, since it is one of our primary goals to produce structured solid carbon material. This could be done via scanning or transmission electron microscopy (SEM and TEM), and the data from various conditions can be plotted and compared. We will also analyze the contents and purity of the hydrogen gas, which could be accomplished using a gas chromatograph. The overall efficiencies of both hydrogen gas and solid carbon will also be calculated in order to assess the overall performance of the plasma-based decomposition and to consider whether this process could occur on a much larger scale. Finally, the operating costs will be compared to the current costs of energy production to assess the feasibility of plasma-based decomposition from an economic standpoint.

Student's Specific Responsibilities:
The student will work with a faculty advisor in all aspects of planning, designing, executing, and analyzing the experiment. Regarding planning, the student will research the devices needed in order for the reaction to fit our overall requirements (i.e. plasma reactor), as well as more background information about the reaction itself. For designing, the student will work with their faculty advisor in order to design a plasma reactor system that can decompose natural gas and capture the produced hydrogen gas and solid carbon. Furthermore, the student will work with their faculty advisor in ordering or designing the necessary components and getting them running. Finally, after the experiments are completed, the student will work with their faculty advisor to analyze the data and come to a conclusion. If time permits, the student will help write a research paper and help in submitting it to research journals for publication.

Timeline:

Time	**Tasks**	**Deliverables**
Before 1st Week	● Literature review of existing experimental setups ● Literature review of operating parameters for different hydrocarbon species ● Identify operating and design requirements for using natural gas as reactant	Preliminary design of the plasma reactor
Weeks 1-3	● Finalize the plasma reactor design ● Finalize bill of materials and order devices, such as the plasma reactor, microwave generator, and piping system ● Get trained for operating SEM and TEM	Reactor components; ability to operate SEM and/or TEM
Weeks 4-6	● Set up the reactor system	Preliminary results

	• Perform baseline experiments using research-grade methane • Perform preliminary tests using NG	using methane and natural gas
Weeks 7-10	• Perform parametric studies using natural gas and identify optimal operation conditions for carbon yield and quality • Perform data analysis • Brainstorm a paper outline if possible	Optimal operation conditions identified for NG plasma decomposition

References:

1. SoCalGas Among First in the Nation to Test Hydrogen Blending in Real-World Infrastructure and Appliances in Closed Loop System, Southern California Gas Company Newsroom, Sept. 30, 2021.

2. Pasquali, M., & Mesters, C. (2021). We can use carbon to decarbonize—and get hydrogen for free. *Proceedings of the National Academy of Sciences of the United States of America, 118*(31).

3. Dato, A. (2019). Graphene synthesized in atmospheric plasmas—A review. *Journal of Materials Research, 34(1)*, 214-230.

4. Fortugno, P., Musikhin, S., Shi, X., Wang, Hai., Wiggers, H., & Schulz, C. (2021). Synthesis of freestanding few-layer graphene in microwave plasma: The role of oxygen. *Carbon, 186*, 560-573.

5. Kheirollahivash, M., Rashidi, F. & Moshrefi, M.M. (2019). Hydrogen Production from Methane Decomposition Using a Mobile and Elongating Arc Plasma Reactor. *Plasma Chem Plasma Process, 39*, 445–459.

6. Keipi, T., Tolvanen, K. E. S., Tolvanen, H., & Konttinen, J. (2016). Thermo-catalytic decomposition of methane: The effect of reaction parameters on process design and the utilization possibilities of the produced carbon. *Energy Conversion and Management, 126*, 923-934.

7. Crane, J., Shi, X., Xu, R., & Wang, H. (2022). Natural gas versus methane: Ignition kinetics and detonation limit behavior in small tubes. *Combustion and Flame, 237*, 111719.