



**U.S. Department of Energy
Advanced Research Projects Agency – Energy
Request for Information (RFI)
DE-FOA-0001936
on
Upgrading Carbon Derived From Methane Pyrolysis**

Objective:

The Advanced Research Projects Agency –Energy (ARPA-E) in the US Department of Energy is seeking information concerning technologies to produce hydrogen and elemental carbon from the thermal decomposition of methane (also known as methane pyrolysis, methane cracking, or methane splitting). Recognizing that the value of the carbon product would be a key factor in the economic feasibility of such processes, ARPA-E seeks input from experts in the fields of materials science (including advanced carbon fiber synthesis), process engineering, methane pyrolysis, plasma chemistry, and chemical engineering regarding potential mechanisms for the bulk conversion of carbon materials, specifically from less valuable forms (e.g. amorphous carbon) or mixtures, to more valuable single allotropes or controlled mixtures of high-value carbon structures. Consistent with the agency’s mission, ARPA-E is seeking insights on clearly disruptive, novel technologies for such conversions, early in the R&D cycle, and not integration strategies for existing technologies.

Please carefully review the REQUEST FOR INFORMATION GUIDELINES below. Please note, in particular, that the information you provide will be used by ARPA-E solely for program planning, without attribution. **THIS IS A REQUEST FOR INFORMATION ONLY. THIS NOTICE DOES NOT CONSTITUTE A FUNDING OPPORTUNITY ANNOUNCEMENT (FOA). NO FOA EXISTS AT THIS TIME. Respondents shall not include any information in their response to this RFI that might be considered proprietary or confidential.**

Background:

The United States produces ~10 million tons of hydrogen annually, primarily for use on-site at petroleum refineries, and for the production of ammonia or methanol. However, the opportunity for hydrogen utilization in the future is vast, with potential applications in electricity production, transportation, and novel chemical processes. Already, hydrogen use in the transportation sector has seen rapid growth with 500 megawatts of fuel cells shipped worldwide in 2016.¹ Today, the vast preponderance of hydrogen produced in the US is derived from natural gas in a reforming reaction that produces hydrogen and carbon dioxide. Options for producing hydrogen without the release of carbon dioxide include reforming with carbon capture and sequestration, electrolysis of water to hydrogen and oxygen, and methane pyrolysis to hydrogen and elemental carbon.

ARPA-E is interested in transformative technologies for methane pyrolysis. Processes capable of methane pyrolysis include (but are not limited to) the following: thermal decomposition (both catalytic and non-catalytic, including solar thermal), non-thermal plasma, fluidized catalyst and molten metals. Carbon products produced via methane pyrolysis include metallurgical coke, carbon black, graphite, carbon nanotubes, and carbon fiber.²

The economics for methane pyrolysis are made more favorable when the carbon byproduct is valuable.³



However, processes that are optimized for hydrogen production may not produce valuable carbon products directly. Optimizing processes for both hydrogen and valuable carbon products is a daunting challenge. Technology that can economically convert less valuable forms of carbon to more valuable forms, either in-situ during the pyrolysis process or in a subsequent step, could enable large-scale hydrogen production from methane without the release of carbon dioxide.

In this RFI, ARPA-E is specifically interested in the conversion of existing carbon materials (which may be derived from the pyrolysis of methane) into higher value carbon materials.

In the context of hydrogen production from methane on an energy-relevant scale, it is important to recognize that the volumes of co-produced carbon would be very large. For example, the amount of hydrogen required to produce 1 quadrillion BTU (quad) of energy would be associated with over 22 million tonnes of co-produced carbon. Therefore, potential applications for the resulting carbon products have to be on a correspondingly large scale, e.g., on the scale of the construction sector or large-scale manufacturing industries. These applications will require the carbon materials to have useful macroscopic properties with regard to thermal, electrical and/or mechanical performance. The functional performance of the carbon materials will be determined by the molecular structure of the carbon, as well as by the arrangement and alignment of substructures at the nano- or meso-scale. Processes capable of changing the molecular structure, e.g. via rearrangement of carbon-carbon bonds, or of changing the solid phases (i.e. crystal structure or molecular ordering) may have the potential to convert a lower value carbon into a higher value carbon product. Examples include, respectively, conversion of amorphous carbon to carbon nanotubes or graphene, or the dispersion of carbon nanotubes and subsequent spinning to carbon fiber like materials.⁴

Purpose and Need for Information:

The purpose of this RFI is solely to solicit input for ARPA-E consideration, to inform the possible formulation of future programs intended to help create transformative technology for producing valuable carbon materials from less valuable forms of carbon. ARPA-E will not provide funding or compensation for any information submitted in response to this RFI, and ARPA-E may use information submitted to this RFI without any attribution to the source. This RFI provides the broad research community with an opportunity to contribute views and opinions regarding the interconversion of carbon forms.

REQUEST FOR INFORMATION GUIDELINES:

No material submitted for review will be returned and there will be no formal or informal debriefing concerning the review of any submitted material. ARPA-E may contact respondents to request clarification or seek additional information relevant to this RFI. All responses provided will be considered, but ARPA-E will not respond to individual submissions or publish publicly a compendium of responses. **Respondents shall not include any information in the response to this RFI that might be considered proprietary or confidential.**

Responses to this RFI should be submitted in PDF format to the email address ARPA-E-RFI@hq.doe.gov by **5:00 PM Eastern Time on June 4th, 2018**. Emails should conform to the following guidelines:

- Please insert "Responses for Upgrading Carbon Derived from Methane Pyrolysis" in the subject line of your email, and include your name, title, organization, type of organization (e.g. university, non-governmental organization, small business, large business, federally funded research and development center (FFRDC), government-owned/government-operated (GOGO), etc.), email address, telephone number, and area of expertise in the body of your email.



- Responses to this RFI are limited to no more than 10 pages in length (12 point font size).
- Responders are strongly encouraged to include preliminary results, data, and figures that describe their potential methodologies.

Questions: ARPA-E encourages responses that address any subset of the following questions and encourages the inclusion of references to important supplementary information.

1) Macroscopic properties of elemental carbon products:

What are recent developments in understanding and characterization of the required molecular, micro- and meso-scale properties of carbon materials for desired thermal, mechanical, or electrical performance in high-performance, high-value carbon materials?

2) Carbon-carbon bond rearrangements in elemental carbon:

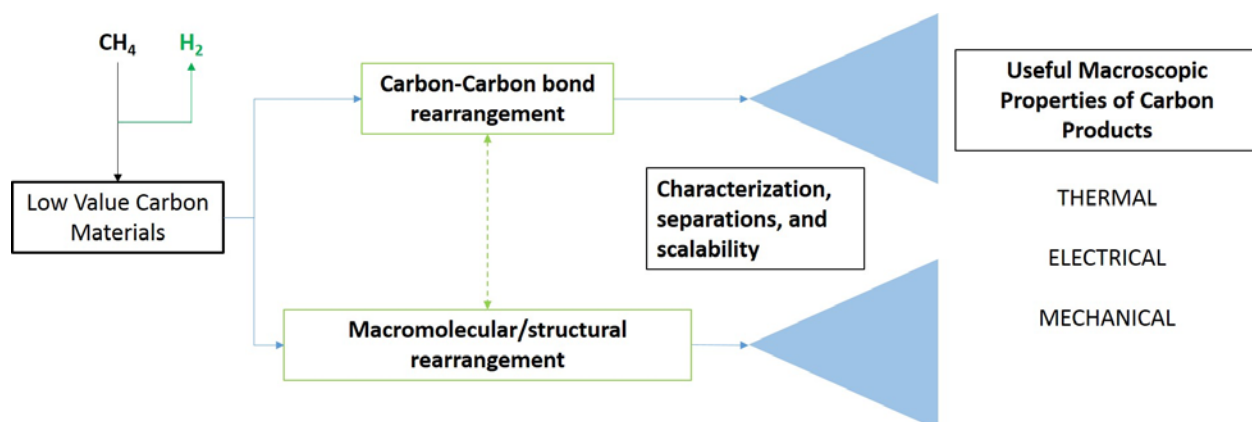
- a) To what extent is the fundamental chemistry of carbon-carbon bond rearrangements understood? This includes thermodynamics, mechanisms, and catalysis.
- b) What is the state of the art in bulk-scale molecular transformations of elemental carbon species (single carbon allotropes or mixtures)?

3) Macromolecular/structural rearrangement and separation:

- a) To what extent is intermolecular carbon aggregation and/or realignment understood? This may range from changes in crystal structure to spinning of fibers.
- b) What processes are known to modify carbon aggregation, crystal structure or alignment of carbon particles? Are the outcomes of these processes predictable?
- c) What is the state of the art in bulk separations of different carbon structures?
- d) What is the current understanding of the scalability of the possible transformation and separation processes?

4) Characterization:

- a) What are recent advances in characterizing bulk samples of different carbon species, especially mixed samples with regard to their molecular and structural composition?
- b) What new methods or approaches need to be developed to better characterize carbon rearrangement products and to improve the underlying processes?





Topics not of interest:

ARPA-E is not interested in approaches that use carbon materials primarily as filler in composites where the performance properties of the composite are defined primarily by the binder and not the carbon filler.

References:

1. Department of Energy Office of Energy Efficiency and Renewable Energy. Fuel Cell Technologies Market Report 2016.
[https://www.energy.gov/sites/prod/files/2017/10/f37/fcto_2016_market_report.pdf]
2. Department of Energy Office of Energy Efficiency and Renewable Energy. R&D Opportunities for Development of Natural Gas Conversion Technologies.
[https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-26726.pdf]
3. Keipi, T., Hankalin, V., Nummelin, and Raiko, R., *Techno-economic analysis of four concepts for thermal decomposition of methane: Reduction of CO2 emissions in natural gas combustion*. Energy Conversion and Management, 2016. **110**: p 1-12.
4. Behabtu, N., et al., Strong, Light, Multifunctional Fibers of Carbon Nanotubes with Ultrahigh Conductivity. Science, 2013. **339**: p 182-186.