R&D Opportunities for Development of Natural Gas Conversion Technologies

for Co-Production of Hydrogen and Value-Added Solid Carbon Products

November 2017

Argonne is a multi-program national laboratory operated for the U.S. Department of Energy Office of Science by UChicago Argonne, LLC, under contract DE-AC02-06CH11357

ANL-17/11

PNNL is a multi-program national laboratory Operated for the U.S. Department of Energy Office of Science by Battelle, under contract DE-AC05-76RL01830.

PNNL-26726

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

An Overview of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products

This report was prepared in response, in part, to the U.S. Department of Energy Fuel Cell Technologies Office's fiscal year 2017 Congressional direction[1] to support research on carbon dioxide-free production of hydrogen using new chemical synthesis methods that break apart natural gas to solid carbon and hydrogen.

R Dagle[2]
V Dagle[2]
M Bearden[2]
J Holladay[2]
T Krause[3]
S Ahmed[3]

November 2017

Operated for the U.S. Department of Energy Office of Science by UChicago Argonne, LLC, under contract DE-AC02-06CH11357

Operated for the U.S. Department of Energy Office of Science by Battelle, under contract DE-AC05-76RL01830.

---

[1] https://www.congress.gov/114/crpt/srpt236/CRPT-114srpt236.pdf, p. 65
[2] Pacific Northwest National Laboratory
[3] Argonne National Laboratory

Executive Summary

This report was prepared, in part, in response to the U.S. Department of Energy Fuel Cell Technologies Office fiscal year 2017 Congressional direction to support research on carbon dioxide-free production of hydrogen using new chemical processes that use natural gas to produce solid carbon and hydrogen. The purpose of this report is to provide an overview of the status in the field and help guide activities, including additional research and development (R&D) areas required for technical and commercial viability.

The United States produces approximately 10 million metric tons of hydrogen annually and more than 95% of the hydrogen is produced by steam-methane reforming (SMR) of natural gas. SMR is attractive because of its high hydrogen yield, but it also converts the carbon to carbon dioxide (CO_2). Methane pyrolysis, the non-oxidative thermal decomposition of methane to carbon and hydrogen, is an alternative to SMR and produces CO_2-free hydrogen. The produced carbon can be sold as a co-product, thus providing an economic credit that reduces the delivered net cost of hydrogen. The combination of producing hydrogen with potentially valuable carbon byproducts has market value because it allows greater flexibility to match the market prices of hydrogen and carbon. That is, the higher value product can subsidize the other in pricing decisions.

Thermal decomposition of natural gas is currently used in the carbon black industry to produce carbon black for use in tires and electrical equipment, but natural gas as the feedstock has been largely replaced by heavy oil fractions from crude oil processing. The high reaction temperature ($>1000^{o}$C) required for methane conversion contributes greatly to process inefficiencies, limits the choice of materials of construction, adversely impacts catalyst life, and exacerbates heat losses. Catalytic thermal decomposition has been extensively researched at the laboratory scale with the primary purpose of decreasing the temperature required for conversion. However, steam pressure buildup and loss of catalytic active sites due to carbon fouling are problematic. Non-thermal plasma processes for producing carbon and hydrogen have been reported as alternatives, but they require a significant amount of electric power. Molten-metal technology has been reported to have a major benefit from the relative ease of solid carbon separation from the molten metal due to density differences; however, a high conversion temperature is still required. Solar thermochemical processes leverage the use of inexpensive solar heat, but non-catalytic processes require high temperature (e.g., 1600°C), and the high conversion temperature requires the use of expensive construction materials. Catalytic processes drive down operating temperature requirements, but solid carbon handling is still an issue.

Solid carbon separation and high energetic requirements (e.g., high temperature or electrical requirements) are key challenges for methane pyrolysis. Additionally, while hydrogen production is relatively easy with the high effective temperatures in pyrolysis processes, and cleanup/purification is manageable with pressure-swing adsorption, the steps of hydrogen compression and delivery can significantly increase cost. High-value byproducts, including different solid carbon products produced through pyrolysis, can offset this cost. Examples of existing high-value carbon markets are listed below.

- Graphite is a high-value product used in lithium-ion batteries.
- Carbon fiber is a premium product used in carbon-reinforced composite materials.
- Nanotube carbons are high-value products used in polymers, plastics, and batteries.
- Needle coke is used in graphite electrodes for electric arc steel furnaces.

Suitable technologies optimized to produce both hydrogen and valuable carbon byproducts must be developed, as no known commercial process produces both carbon and hydrogen as commercial products.

Commercial processes for producing carbon black typically burn the hydrogen to generate process heat with a portion of the heat used for the reaction process and remainder used at the plant or sold to nearby facilities. Commercial processes also exist for producing fuel cell-quality hydrogen, but carbon is not recovered. Instead, carbon is burned to regenerate the catalyst and to provide process heat.

Techno-economic analysis performed in this study suggests that the production and sale of solid carbon byproducts can significantly reduce the hydrogen net cost. For example, based on ASPEN modeling of a small-scale plasma system the cost of hydrogen was estimated at \$7.0/kg for a natural gas price of \$5/MMBtu without carbon credit, and decreased to \$2.5/kg when selling carbon black at \$1.35/kg. For comparison the cost of hydrogen produced by conventional SMR is < \$2.0/kg at comparable natural gas pricing. Nevertheless, this analysis demonstrates the potential for significant reduction in hydrogen cost in emerging technologies with the sale of valuable carbon byproducts— yet the carbon selling price is a critical factor and needs to be high in order for such technologies to compete today with the incumbent SMR technology. Further development of natural gas pyrolysis methods that yield high-value forms of carbon, such as carbon fiber or carbon nanotube is critical for successful commercial implementation.

Key attributes for methane decomposition are that the gaseous product stream contains a very high concentration of hydrogen, the relatively low heat of reaction, and production of a solid carbon that can be sequestered or sold as a commodity byproduct. Table ES.1 highlights different types of potential valuable carbon products, their applications in industry, and market pricing, size, and relevance. Potential carbon products are varied and include carbon black, carbon nanotubes, carbon nanofibers, carbon fibers, graphene, and needle coke. Carbon product pricing can vary tremendously and depends on product characteristics and purity. Carbon black is the oldest and most mature market for carbon. In Section 4.0, we provide additional details for these carbon markets, including both current and potential new market opportunities. It should be noted that solid carbon as a byproduct can reduce the cost of the methane decomposition reaction only if sufficiently large markets for the carbon products are found. Some of the carbon markets shown in Table ES.1, with the possible exception of carbon black and needle coke, would be saturated before a fraction of the overall hydrogen market demand is met.

In this report, we highlight the relevant technologies reported in the literature—primarily thermochemical and plasma conversion processes—and recent research progress and commercial activities. Longstanding technical challenges include the high energetic requirements (e.g., high temperatures and/or electricity requirements) necessary for methane activation and, for some catalytic processes, the separation of solid carbon product from the spent catalyst. We assess current and new carbon product markets that could be served given technological advances, and we discuss technical barriers and potential areas of research to address these needs. We provide preliminary economic analysis for these processes and compare them to conventional (e.g., SMR) processes for hydrogen production. The overarching conclusion of this study is that the cost of pyrolytically produced CO_2-free hydrogen can be potentially reduced to levels < \$2/kg target with the co-production and sale of sufficiently high-value carbon products. Technological advances are required to understand the reaction conditions, design reactor systems that can achieve high yields of the selected carbon products, segregate or separate the high-value carbon products, and optimize the production process for both hydrogen and carbon.

Additionally, the report identifies key areas for further R&D in the CH_4 pyrolysis technical space including:

- Improved fundamental understanding of the conditions at which the different grades of carbon will be formed during the decomposition process, since production of high-value carbon byproduct is desirable to help to offset the cost of hydrogen production.

- Innovation/ breakthroughs in technology to overcome the thermodynamic limitations that restrict the high yields of H_2 and carbon under high-pressure and low-temperature operating conditions which would allow dramatic reductions in the cost of the products.

- Further catalyst development. Despite the availability of well-established catalysts for natural gas reforming and pyrolysis, further catalyst material development is needed to better address ongoing challenges associated with extensive catalyst recycling (i.e., carbon deposition/carbon removal). Catalyst mechanical stability remains an issue because the process of carbon deposition on catalysts surfaces can lead to catalyst detachment from the support.

- Innovation to resolve fundamental issues associated with solid carbon separation and process challenges associated with solid carbon management.

Suitable technologies optimized for producing both H_2 and valuable carbon byproduct must be developed. Solid carbon as a byproduct could reduce costs only if sufficiently large markets for the carbon products are found. One alternative to the production of solid carbon is the production of hydrocarbons such as BTX that have large global market demand of ~100 million tons/yr. Challenges in this area include low conversion levels and catalyst stability, which are key technological barriers to commercial implementation.

Table ES.1. Market Analysis for Potential Carbon Products (K = thousand, M = million, MT = metric ton)

Type of Carbon	Types of Applications	Expected Price for Carbon	Size of the Market (current/ projected)	Corresponding Hydrogen Production[(a)]
Carbon black [1] [2] [3]	Tires, printing inks, high-performance coatings and plastics	\$0.4–2+ /kg depending on product requirements	U.S. market • ~ 2M MT (2017) Global market • 12M MT (2014) • 16.4M MT (2022)	U.S. market • 0.67M MT Global market • 4M MT (2014) • 5.4M MT (2022)
Graphite [4]	Lithium-ion batteries	\$10+/kg	Global market • 80K MT (2015) • 250K MT (2020)	Global market • 27K MT (2015) • 83K MT (2020)
Carbon fiber [5] [6] [7]	Aerospace, automobiles, sports and leisure, construction, wind turbines, carbon-reinforced composite materials, and textiles	\$25–113/kg depending on product requirements	Global market • 70K MT (2016) • 100K MT (2020)	Global market • 23.3K MT (2016) • 33.3K MT (2020)
Carbon nanotubes [8] [9]	Polymers, plastics, electronics, lithium-ion batteries	\$0.10–600.00 per gram depending on application requirements	Global market • 5K MT (2014) • 20K MT (2022)	Global market • 1.7K MT (2014) • 6.7K MT (2022)
Needle coke [10]	Graphite electrodes for electric arc steel furnaces	~\$1.5/kg	Global market • ~1.5M MT (2014)	Global market • ~0.50M MT (2014)

(a) Based on stoichiometric ratio of carbon to hydrogen present in methane. Does not take into account process efficiency or use of hydrogen to provide process heat or loss of hydrogen during hydrogen recovery.

Acknowledgments

The authors thank the U.S. Department of Energy Fuel Cell Technologies Office within the Office of Energy Efficiency & Renewable Energy for funding the authoring of this report. We also thank the staff from that office for technical assistance, including Maxim Lyubovsky, Eric Miller, Richard Farmer, and Sunita Satyapal. Thanks also to Cary Counts and Susan Ennor from Pacific Northwest National Laboratory for their technical editing support.

This report was peer reviewed by Professor John Hu from West Virginia University, Drs. Christopher Matranga and Peter Balash from the U.S. Department of Energy's National Energy Technology Laboratory, Dr. Marc Von Keitz from the U.S. Department of Energy's Advanced Research Projects Agency-Energy, as well as Joe Cresko and Rudy Kashar from the U.S. Department of Energy's Advanced Manufacturing Office.

Acronyms and Abbreviations

AC	alternating current
ANL	Argonne National Laboratory
ASTM	American Society for Testing and Materials
BTU	British thermal unit
BTX	benzene, toluene, and xylene
CAC	CO_2 Avoidance Cost
CCS	carbon capture and storage
CH_4	methane
CNT	carbon nanotube
CO	carbon monoxide
CO_2	carbon dioxide
DC	direct current
DOE	U.S. Department of Energy
FBR	fluidized bed reactor
FCTO	Fuel Cell Technology Office
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (Model)
IEA	International Energy Agency
LCOH	levelized cost of hydrogen production
LHV	lower heating value
mcf	million cubic feet
mmBTU	a million BTUs
MT	metric tons
MWCNT	multi-walled carbon nanotube
Nm^3/hr	normal cubic meter per hour
PAN	polyacrylontitrile
PBR	packed-bed reactor
PEP	Process Economics Program
PSA	pressure-swing adsorption
R&D	research and development
RF	radio frequency
SLPM	standard liter per minute
SMR	steam-methane reforming
SWCNT	single-walled carbon nanotube
tcf	trillion cubic feet
WGS	water-gas shift

Contents

Figures

Tables

1.0 Introduction

Use of abundant natural gas and its efficient conversion to fuels and chemicals has been an important area of research. In addition to energy independence, development of new technologies that produce no emissions and carbon dioxide (CO_2)-free energy and fuels has also received significant interest in recent decades [11]. Hydrogen (H_2) in particular has received substantial attention in part because it can be produced from diverse domestic resources, used in multiple applications across sectors, and its use in fuel cell applications is completely pollution-free. Furthermore, because fuel cells convert H_2 and oxygen directly to electricity more efficiently than internal combustion engines, they can reduce systemic energy losses. The ability to produce H_2 cost effectively will be a major determining factor for future implementation of this energy resource [12]. Natural gas is an abundant resource in the United States, and coupled with its available and growing infrastructure, it offers a pathway to building H_2 infrastructure. Today, 95% of the H_2 produced in the United States is made by natural gas reforming in large central plants. This is an important technology pathway for near-term H_2 production [13]. This report will first cover the conventional process of SMR, followed by an assessment of natural gas to solid carbon and H_2 processes.

1.1 Steam-Methane Reforming

SMR is a mature production process in which high-temperature steam (700°C–1000°C) is used to produce H_2 from a methane (CH_4) source, such as natural gas. In SMR, CH_4 reacts with steam under 3–25 bar pressure in the presence of a catalyst to produce H_2, carbon monoxide (CO), and a relatively small amount of CO_2. Steam reforming is endothermic—that is, heat must be supplied to the process for the reaction to proceed (Equation SMR (1.1)). Subsequently, in what is called the water-gas shift (WGS) reaction, the CO and steam are reacted using a catalyst to produce CO_2 and more H_2 (Equation WGS (1.2)). Combining the SMR and WGS reactions results in primary products H_2 and CO_2 (Equation Net Reaction (1.3)) [13]. In a final process step called pressure-swing adsorption (PSA), CO_2 and other impurities are removed from the gas stream, leaving essentially pure H_2. Steam reforming can also be used to produce H_2 from other fuels, such as ethanol, propane, or even gasoline.

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H^o = 206 \text{ kJ/mol} \qquad \text{SMR (1.1)}$$

$$CO + H_2O = CO_2 + H_2 \quad \Delta H^o = -41 \text{ kJ/mol} \qquad \text{WGS (1.2)}$$

Combining Equations SMR (1.1) and WGS (1.2), the net reaction is:

$$CH_4 + 2H_2O = CO_2 + 4H_2 \quad \Delta H^o = 165 \text{ kJ/mol} \qquad \text{Net Reaction (1.3)}$$

Currently, SMR is the technology with the greatest advantage in terms of the lowest cost and highest energy efficiency and is the preferred choice of industry today. SMR is used industrially to produce ~95% of the H_2 consumed in the United States [11]. However, the process generates significant quantities of CO_2. The reaction stoichiometry (Equation Net Reaction (1.3)) suggests 5.5 kg_{CO2}/kg_{H2} is produced, but the quantity is much higher in practice. Being a strongly endothermic process, it requires additional energy that results in the release of additional CO_2. Depending on the energy sources used and efficiency of the process, SMR generates 9–14 kg_{CO2}/kg_{H2}. Based on low-cost shale gas, the cost of H_2 production from SMR can be less than $2/kg. If CO_2 capture is considered as part of a SMR technology option, this presents additional cost.

1.2 Steam-Methane Reforming with Carbon Capture

To understand the cost of deploying a CO_2 capture system in a H_2 production plant, the International Energy Agency (IEA) Greenhouse Gas R&D Program commissioned Amec Foster Wheeler to undertake a study, which resulted in a report entitled, *Techno-Economic Evaluation of Hydrogen Production with CO_2 Capture* [14]. The primary purpose of the study was to evaluate the performance and cost of a greenfield modern SMR plant producing 100,000 Nm^3/h of H_2 from natural gas as feedstock/fuel operating in merchant plant mode. (Note that 100,000 Nm^3/h of H_2 corresponds to 216 tons per day production; for comparison, the Air Products' Port Arthur II plant has capacity of 265 tons per day). The IEA study focused on the economic evaluation of five different options to capture CO_2 from SMR, and these include the following cases:

- Base Case: Modern SMR Plant with feedstock pre-treatment, pre-reforming, high-temperature WGS, and PSA
- Case 1A: SMR with capture of CO_2 from the shifted syngas using methyl diethanolamine
- Case 1B: SMR with burners firing H_2-rich fuel and capture of CO_2 from the shifted syngas using methyl diethanolamine
- Case 2A: SMR with capture of CO_2 from the PSA tail gas using methyl diethanolamine
- Case 2B: SMR with capture of CO_2 from the PSA tail gas using cryogenic and membrane separation
- Case 3: SMR with capture of CO_2 from the flue gas using monoethanolamine.

For this study, the price of natural gas was assumed to be 6€/GJ (LHV) (~ $7/MMBtu) and the price of electricity 80€/MWh (~$0.09/kWh; 1€ = 1.1$ is assumed for cost conversion throughout the report). The levelized cost of H_2 production (LCOH) was calculated for these six cases, and results are shown in Figure 1.1. Some export of electricity takes place in the base case (from excess steam fed to a steam turbine), thus lowering the LCOH, but this accounts for only a small fraction of the overall H_2 cost. The cost of natural gas is the major fraction in the LCOH.

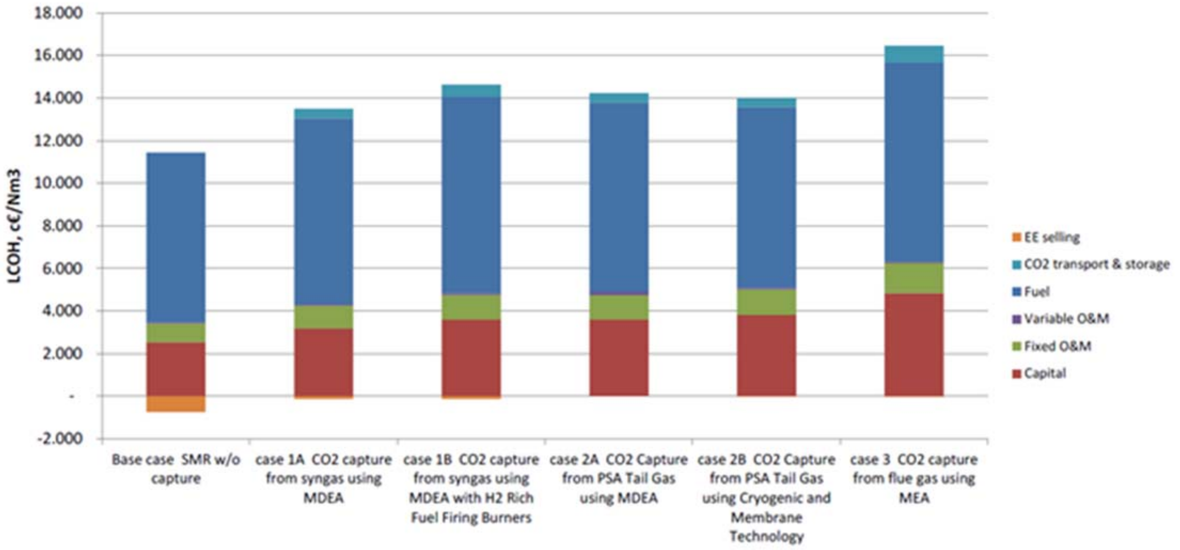


Figure 1.1. LCOHs for the Six Cases Taken from Figure 8 in Reference [14]

Costs of CO_2 avoidance (CAC) were calculated by comparing the CO_2 emissions per Nm^3 H_2 and the LCOH of plants with capture and a reference plant without capture:

$$CO_2 \text{ Avoidance Cost (CAC)} = (LCOH_{CCS} - LCOH_{Ref}) / (CO_2Emissions_{Ref} - CO_2Emissions_{CCS}) \quad (1.4)$$

where CAC is expressed in € per tonne (metric ton) of CO_2 (or in \$/tonne), LCOH is expressed in € per Nm^3/h H_2 (or in \$/kg), and CO_2 emission is expressed in tonnes of CO_2 per Nm^3/h H_2 (or in tonnes CO_2 per kg H_2). The notation CCS stands for carbon capture and storage.

Table 1.1 summarizes data for the LCOH, CO_2 emissions, and CAC. It can be seen that it would require a cost of €76.8/tonne of CO_2 emissions to make the higher capture rate option (Case 3) more attractive than the base case.

Table 1.1. Summary of Data for LCOH, CO_2 Emissions, and CO_2 Avoidance Cost [14]

Case	CO_2 Emissions	CO_2 Avoided	LCOH		Cost of Avoided CO_2	
	kg_CO_2/ kg H_2	%	€c/Nm^3	\$/kg	€/tonne	\$/tonne
Base Case	9.0		11.4	1.39		
Case 1A	4.1	54.2	13.5	1.65	47.1	51.8
Case 1B	3.2	63.9	14.6	1.78	62	68.2
Case 2A	4.3	52.2	14.2	1.74	66.3	72.9
Case 2B	4.2	53.4	14	1.71	59.5	65.5
Case 3	1.0	89.0	16.5	2.02	69.8	76.8

H_2 production cost when coupling SMR with CO_2 capture can be compared to renewable or pyrolytic H_2 production processes which do not produce CO_2. Equation (1.4), which defines the CAC for the cases with CCS relative to the base case SMR, can be used to compare the cost of H_2 produced from renewable sources or through NG decomposition (with no CO_2 emissions) to the cost of H_2 from SMR. The CAC is assumed to be \$80/tonne (as for Case 3, where 90% of CO_2 emissions is avoided), and CO_2 emissions from the average SMR plant are assumed to be 10 kg CO_2/kg H_2. Note that the base case in this study uses 9 kg/kg, but this is apparently a more efficient plant model than most commercial SMR plants. By comparison, SMR GREET Model suggests greenhouse gas emissions to be 11 kg/kg. Substituting these values in Equation (1.4) results in the following price difference [14]:

$$H_{2\ renew} - H_{2\ SMR} = 0.8 \text{ \$/kg} \quad (1.5)$$

A \$1.4/kg hydrogen cost in the base case SMR suggests that the cost of pyrolytic H_2 should be below \$2.2/kg to compete with the SMR-CCS strategy. Sales of carbon co-produced with pyrolytic H_2 can help offset the prosecution price and reach the CO_2 free hydrogen price point that is competitive with the SMR-CCS.

1.3 Methane Pyrolysis

The prevalence of fracking has revolutionized the U.S. natural gas industry, making it economically competitive to recover large reserves of natural gas that were previously considered uneconomical to recover and leading to an unprecedented increase in natural gas production coupled with a drop in the price of natural gas to historical lows. As such, there is considerable interest in developing new process technologies that use natural gas for producing fuels and chemicals, including H_2. One potential technology is the thermal decomposition of natural gas. Methane can be decomposed into carbon (C) and H_2 according to the following endothermic reaction:

$$CH_4 \rightarrow C(s) + 2H_2 \quad \Delta H^o = 74.8 \text{ kJ/mol} \tag{1.6}$$

The reaction stoichiometry suggests that the molar ratio of H_2 and carbon to the feedstock CH_4 as 2 and 1, respectively. Actual processes will yield less because of the production of byproducts (e.g., olefins, aromatics) and the need to oxidize part of the feedstock to generate the heat for the process. Muradov estimates the H_2/CH_4 molar ratio from a process to be 1.7 [15]. Assuming the carbon-containing products will be sequestered or sold as carbon black, the efficiency of producing H_2 via decomposition using a molar yield of 1.7 translates to (1.7 × LHV of H_2/LHV of CH_4) = 51%.

For the pyrolysis reaction above, each mol of CH_4 can yield a mass-balanced maximum of 12 g of carbon and 4 g of H_2. This 3:1 mass ratio (2:1 molar ratio) is skewed in practice by the formation of byproducts and the process energy required. The heat of formation of CH_4 is 74.8 kJ, i.e., the energy required to decompose a mol of CH_4. If the energy for the decomposition is derived by combustion of CH_4, then that requires another 0.093 mol of CH_4. Thus, the mass and energy balanced maximum yields for H_2 and carbon are reduced to 10.98 g of carbon and 3.66 g of H_2 per mol of CH_4. Stated in terms of energy, the minimum energy that will be consumed for the production of the H_2 and carbon via CH_4 decomposition are 240 kJ/gH_2 (66.7 kWh/kgH_2, 5.96 kWh/m^3_{H2}) and 73 kJ/g_{carbon} (20.3 kWh/kg_{carbon}), respectively. The yield of practical systems will necessarily require more energy as a result of inefficiencies that include incomplete CH_4 conversion, loss of products (H_2, C), formation of byproducts, heat transfer limitations, energy recovery, heat loss, etc.

The pyrolysis process does not produce CO or CO_2 as byproducts, and thus the need for WGS or CO_2 removal is eliminated [11]. Without inclusion of the WGS and preferential oxidation of CO reactions, processing for CH_4 decomposition is greatly simplified relative to steam reforming [16]. Thus, the energy requirement for CH_4 catalytic cracking is nearly half of that required for steam reforming on a per mole CH_4 decomposed basis [16]. One study reports that per mol of H_2 produced, the energy requirement is 37.4 kJ/mol for CH_4 decomposition, compared to 63.3 kJ/mol for steam reforming [16]. However, about half of the amount of H_2 per mol CH_4 is produced.

CH_4 decomposition is an endothermic reaction, and because of the strong carbon-to-hydrogen (C-H) bonds, non-catalytic thermal cracking of CH_4 requires a temperature >1200°C to obtain a reasonable yield. By using a catalyst, the temperature can be significantly reduced [11]. Thermodynamically, breaking all four C-H bonds of CH_4, such as with steam reforming CH_4, into synthesis gas or CH_4 decomposition into C and H, is much easier than breaking only one or two of the C-H bonds, under either oxidative or non-oxidative conditions [12]. Direct conversion of CH_4 with the assistance of oxidants is thermodynamically more favorable than under non-oxidation conditions, and thus has received much more attention [12]. However, there are potential benefits for non-oxidative conversion. At high temperatures of between 1300 and 1600°C, CH_4 and other hydrocarbons present in natural gas decompose to yield H_2 and solid carbon in an inert atmosphere. Compared to SMR, the reaction is less endothermic and produces no CO_2 emissions if the produced carbon is not burned in subsequent processes. Furthermore, there is the potential for a considerable reduction in capital and operating costs compared to

SMR. This is because the gas stream exiting the reactor in the thermal decomposition process has a considerably higher H_2 concentration and does not contain CO_2 or CO, compared to the composition of the gas stream existing the steam reformer. Therefore, the gas stream should require considerably less downstream processing to produce commercial-grade H_2 compared to SMR. In addition, sale of the carbon product (i.e., carbon black, carbon fibers, etc.) can be used to offset the cost of the H_2.

Commercially, the thermal decomposition of natural gas has been employed in the carbon black industry since the 1920s to produce selected grades of carbon for use in manufacturing tires and electrical components [17]. The H_2 could, in theory, be recovered and sold as merchant H_2, but in practice, the carbon black industry uses a portion of the H_2 to provide the required process heat, and the remainder of the H_2 is used to generate process heat for the facility or nearby facilities adjacent to the fence line. The ability to offset the cost of producing H_2 by the sale of carbon is a promising scenario. To the best of our knowledge, there is no commercial process based on producing both carbon and H_2 for the carbon black and H_2 markets, respectively.

A number of excellent recent articles provide reviews of CH_4 decomposition. These include discussion of catalysts and reaction mechanisms and kinetics [11, 18, 19], technologies that use renewable energy options for producing H_2 by thermal decomposition [20], and engineering design considerations [19]. For example, an in-depth review by Amin et al. [16] discusses the catalytic cracking of CH_4 for H_2 production and reports on the thermodynamics, catalysts and supports used, catalyst deactivation and regeneration, the growth of carbon product particles, and the cracking reaction mechanism with inclusion of kinetic models. Additionally, the cost of H_2 production is reported for a number of different pathways. Abbas and Wan Daud [11] also review decomposition processes and discuss insights about heating sources, reactor types, catalysts employed, catalyst regeneration, and the quality of the carbon produced. The effects of temperature and flow rate on the product distribution, the energy sources, the reactors and their operating condition, and catalysts are also reported.

1.4 Report Objectives

Given the opportunity to develop the thermal decomposition of natural gas that can take advantage of low-cost natural gas for producing H_2 and carbon for commercial sale, the purposes of this report are to:

1. Evaluate the thermodynamics and processing requirement and discuss the different thermal and non-thermal (e.g., plasma) approaches to CH_4 pyrolysis.
2. Identify and describe specific technologies—both commercial and those under research and development (R&D)—for decomposition of natural gas to produce carbon and/or H_2.
3. Identify specific carbon market opportunities and synergies for producing both carbon and H_2 for merchant sale.
4. Provide a techno-economic analysis that provides the cost of producing H_2 and quantifies the energy demand to provide the basis for comparing it to alternative technologies for producing H_2, as well as to identify where R&D is needed to lower cost and increase energy efficiency.
5. Identify barriers to market adaption and potential R&D opportunities for producing both valuable solid carbon product and H_2.

2.0 Engineering Review

In this section we report in broad terms the thermodynamic and processing requirements for each of the classes of process technologies (e.g., thermal, catalytic, plasma). In Section 3.0 we report on specific processes that have been reported in the literature—both commercial and those under R&D—that use different approaches to tackle the issues described above.

2.1 Reactants, Products, and Energy

Several approaches to supplying heat for the highly endothermic CH_4 pyrolysis reaction have been proposed. These include direct heating of the reaction zone, externally heated catalyst particles used as the heat carrier, similar to fluidized bed reactors (FBRs), and addition of a small amount of oxygen to generate the necessary heat, which is an autothermal pyrolysis type process [21]. Fluidized bed and fixed bed reactors are the most commonly used reactors for CH_4 decomposition.

The endothermic heat of reaction and sensible heat requirements have also led to some processes in which air or oxygen are co-injected to generate the heat and thus lead to other byproducts that require separations downstream. Depending on the source of heat for the reaction, the process may be termed *autothermal*—in which the heat of reaction is generated by oxidation of the CH_4 or other hydrocarbons present in the natural gas, or *allothermal*—in which the energy is supplied from an external source and transferred via a heated surface or transmitted with waves, or electric power. These reactions may be conducted with or without catalysts; the catalysts offer the benefits of faster kinetics at lower temperature and may improve the selectivity of the product streams.

Because the main products of CH_4 decomposition are solid carbon and H_2 gas, the problem with FBRs is carbon deposition on the catalyst particles [11]. As the reaction proceeds, carbon will deposit on the catalyst surface, blocking the pores and the interparticle spaces. Because of this pore-blocking process, the pressure drop through the bed will rise as the gas flow is impeded [11]. Thus, the deposited carbon must be removed periodically. Muradov studied different types of reactors and concluded that FBRs were the most promising type of reactor for large-scale operations because it provides a constant flow of solids through the reaction zone, making it suitable for continuous addition and withdrawal of catalyst from the reactor and catalyst regeneration [11, 22].

There are many reports about the use of an electric furnace as a heating source for the high energetics needed to drive CH_4 decomposition. Other reports focus on the use of plasma, concentrated solar energy, and a molten-metal bath as alternative means of supplying the required energy. The ensuing sections provide brief overview descriptions of various means of providing the reactor energetics and the various reactor technologies as reported in the open and closed literature.

2.2 Thermal (Non-Catalytic) Reactions

Thermal cracking of CH_4 removes and separates carbon in a single step [23]. A major drawback of this technique is that non-catalytic cracking is very slow for practical applications below 1000°C, while catalytic cracking of CH_4 can be conducted at temperatures as low as 500°C [16]. The function of the catalyst is to reduce the activation energy required for CH_4 decomposition, thereby leading to lower operating temperatures. In this section we focus our attention on thermal approaches.

Thermal decomposition of CH_4 at temperatures above 1000°C will yield H_2 gas and soot or coke (carbon-rich species) with higher temperatures, favoring faster and higher conversion. The combination of higher temperature and longer residence times favors the production of H_2 and carbon [24-26]. The product distribution favors more gaseous products with higher yields of olefins and aromatics at lower temperatures in short contact time reactors. Low pressure favors higher conversion of CH_4, but also tends to produce more olefins. The olefins decompose to carbon and H_2 with increasing residence time. The morphology of the solid carbon is affected by the prevailing decomposition mechanism, which in turn is determined by the combination of temperature, pressure, catalyst, and residence time. Figure 2.1 shows a conceptual representation of the conversion of CH_4 during the decomposition process as a function of the operating conditions. The intermediates, olefins and aromatics, are initially formed and then decompose further to "carbon" and H_2. The soot part of "carbon" is essentially a C-H molecule where the C/H ratio is near 1 at low temperatures and increases with residence time at high temperatures [27]. The soot particles are considered to be aggregates formed from smaller spherical primary particles.

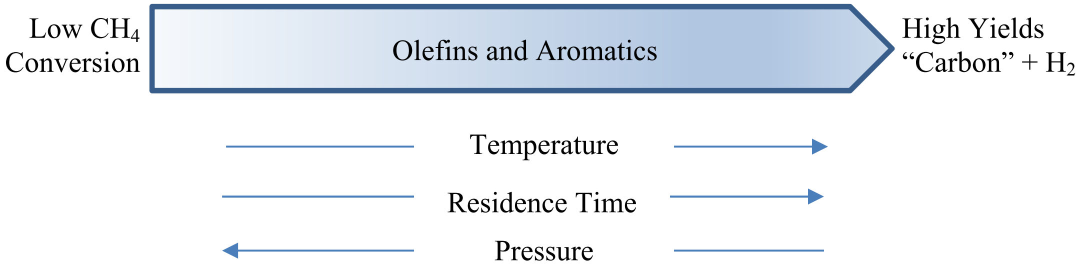


Figure 2.1. Conceptual Representation of Conversion and Yields as a Function of Reactor Conditions. "Carbon" represents particles of soot and graphite.

Holmen et al. [26, 28] studied the conversion of CH_4 in high-temperature processes and reported on the yields of products that include carbon, H_2, and olefins, with mechanisms and reaction kinetics.

Equilibrium product distributions of CH_4, H_2, and carbon (typically graphite) can be derived from calculations using correlations for the equilibrium constants or Gibbs free energy minimization [16]. Snoeck [29] provides experimental results and correlations for catalytic cracking on nickel (Ni).

Figure 2.2 shows the equilibrium yields from the decomposition of CH_4 in the temperature range of 25 to 1000°C at a pressure of 1 atm [30]. The dominant products are CH_4, carbon, and H_2. A small amount (less than 2 × 10-5 mol/mol-CH_4) of ethane is formed and peaks at 500°C. Small amounts of ethylene and acetylene are also predicted at temperatures above 500°C and 1300°C, respectively. The effect of pressure can be seen in Figure 2.3, where the higher pressure shifts the conversion of CH_4 and yields of carbon and H_2 toward a higher temperature.

2.3 Catalytic Reactions

2.3.1 Catalytic Reactors Types

The choice of reactor type is an important consideration in the design of an economically viable process. Packed-bed reactors (PBRs) and FBRs are the most commonly used reactors for CH_4 decomposition. The review by Abbas and Wan Daud [11] discusses different reactor technologies evaluated and reported upon in the literature. The in-depth review by Amin et al. [16] also specifically describes the reaction kinetics and models available for predicting reaction rates. Here we discuss the highlights for the various reactor approaches reported in the literature, as well as the means for separation of the carbon product from the process.

FBRs offer advantages that include the ability to continuously add catalyst particles and withdraw the carbonaceous solid products, avoidance of reactor clogging due to carbon deposits, uniform temperature distribution, and good mass and heat transfer. Challenges include the need to capture the fine particles and large gas flows required to maintain fluidization and the particle size reduction by attrition.

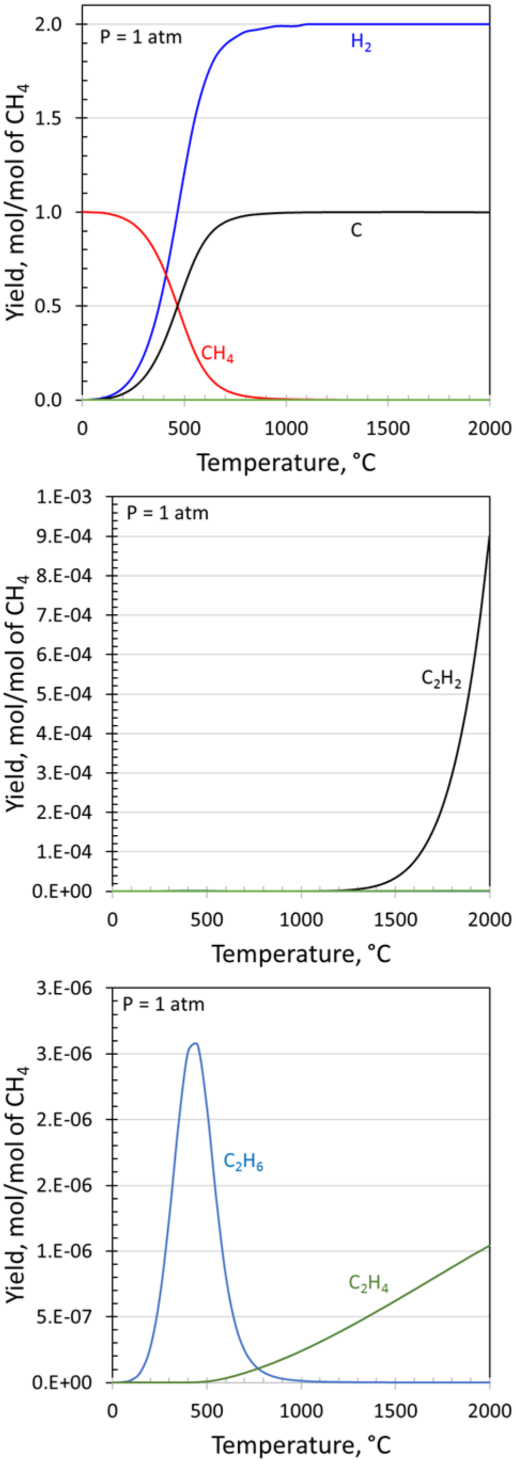


Figure 2.2. Equilibrium Yields of Methane and Products as a Function of Temperature at P = 1 Atm during Methane Pyrolysis

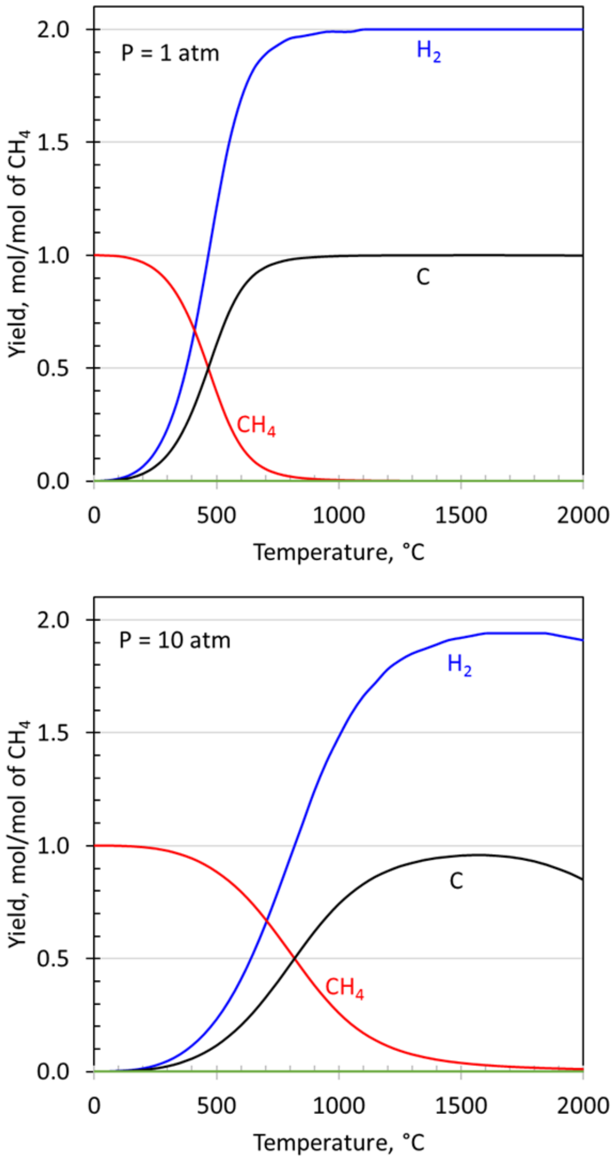


Figure 2.3. Effect of Pressure and Temperature on the Equilibrium Yields of Methane and Products during Methane Pyrolysis

PBRs are simple in design; they require only the CH_4 reactant to flow through the reactor. The reactor may or may not contain catalysts, but the design demands a temperature profile conducive to fast conversion and effective removal of the carbon products.

A rotary bed reactor is designed like a rotary kiln. The CH_4 flows through an inclined tube that moves the catalyst layer forward as the bed rotates. The carbon forms on the catalysts and the carbon and catalysts are withdrawn at the bottom of the tube. Energy to drive the reaction can be provided by heating sources either outside or inside the tube wall. Figure 2.4 shows a schematic of a rotary bed. This design allows a continuous withdrawal of the solid products and possible regeneration of the catalyst [31, 32].

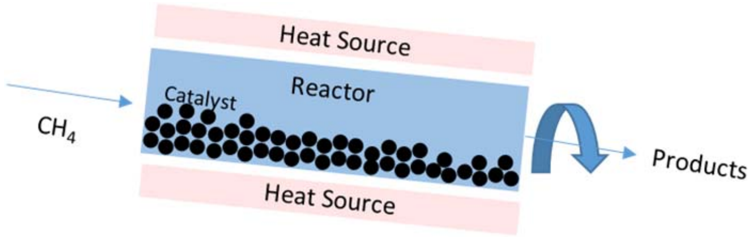


Figure 2.4. Simplified Rotary Bed Reactor Process Flow Diagram

Plasma reactors, described in more detail below, use gas and electrical energy to create a strong electromagnetic field to generate a gaseous mixture of electrons and highly charged positive ions. A plasma torch increases the temperature of the CH_4 to very high temperatures (~2000°C), causing its decomposition [26, 33-36].

2.3.2 Catalysts

Muradov [37] summarizes published data available on the conversion of CH_4 to carbon products as shown in Figure 2.5. Ni- and iron (Fe)-based catalysts operate in the 500 to 700°C and 700 to 950°C ranges, respectively, and produce carbon filaments (including carbon nanotubes [CNTs]). Carbon-based catalysts operated in the 850 to 950°C range produce both carbon filaments and turbostratic carbon. Graphitic and turbostratic carbon are formed in the 700 to 1000°C range using a variety of catalysts. Amorphous carbon is produced non-catalytically at operating temperatures >1150°C [15]. Amorphous carbon includes carbon black and thermal black. Here we highlight the key attributes reported for both metallic and carbon types of catalysts and the nature of carbon produced from each.

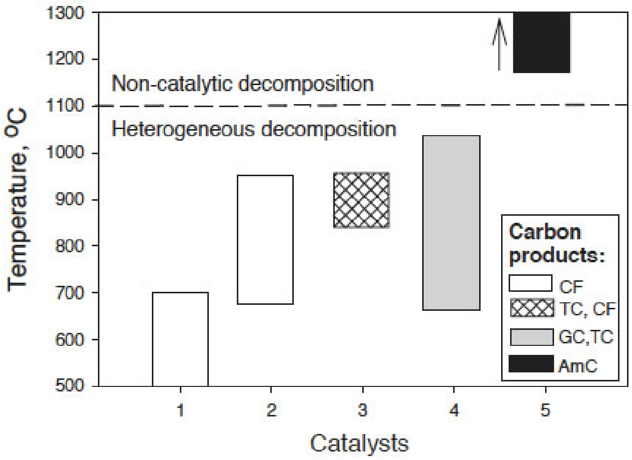


Figure 2.5. Summary of Published Data on Catalysts, Temperature, and Carbon Products from Methane Decomposition. Catalysts: 1–Ni-based, 2–Fe-based, 3–carbon-based, 4–Co, Ni, Pd, Pt, Cr, Ru, Mo, and W catalysts, 5–non-catalytic decomposition. Carbon products: CF–carbon filaments, TC–turbostratic carbon, GC–graphitic carbon, AmC–amorphous carbon [15]. (Reproduced with permission from Elsevier.)

Deactivation of the catalyst by coke formation is seen as the most important problem with CH_4 pyrolysis. The capacity of the catalyst to accumulate a significant amount of carbon filaments limits its time on stream or the residence time required. Two main types of catalysts—metallic and carbonaceous—have been the focus of most investigations [38]. In their comprehensive review, Abbas and Wan Daud [11] go into more detail on the various catalysts reported and discuss catalyst deactivation and regeneration.

2.3.2.1 Metal Catalysts

Numerous metal-based catalysts have been studied for CH_4 decomposition. Their practical application requires development to increase their specific activities and lifetimes. It has been reported that the rate of CH_4 decomposition activity of the metals follows the order: Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe, Mo [11]. However, much attention has been given to Ni- and Fe- based catalysts [11].

The effectiveness of a catalyst should be based on its activity, and given the large amount of carbon produced during conversion, its operating lifetime. A key finding regarding catalyst deactivation pertains to the mechanism by which carbon dissolution occurs on the metal surface and diffuses through the particle. The carbon then precipitates at the metal-support interface, detaching the metal particle from the support and forming a carbon filament with an exposed metal particle at its tip. This mode of carbon accumulation allows the catalyst to maintain its activity for an extended period of time without deactivation. It has been shown that thousands of carbon atoms can be deposited on the catalyst by surface nickel atoms. However, eventually the catalyst is deactivated as access to active site becomes limited [11]. Regardless of the catalyst activity and lifetime, two overarching problems with the use of a metal catalyst are regeneration and practical separation of the produced carbon.

The operating conditions and kinetic results for metal catalysts, as reported from reference [11], are as follows:

- Reaction Order: 1 [29]
- Activation Energy (kJ/mol): 29.5 to 46 [39]
- Temperature (°C): 500 to 1000
- Space Velocity (per hr): 50 to 50,000
- Sustainability Factor (ratio of the reaction rate after 1 hour time on stream divided by the initial reaction rate): 0.14 to 1.

Reaction Mechanisms. Various reaction mechanisms have been developed by different groups and can be summarized as follows [16]:

- Non-dissociative adsorption of CH_4
  - CH_4 + I (Vacant site) = CH_4 (ad)
  - CH_4 (ad) = CH_3 (ad) + H (ad)
  - CH_3 (ad) = CH_2 (ad) + H (ad)
  - CH_2 (ad) = CH (ad) + H (ad)
  - CH (ad) = C (ad) + H (ad)
  - C (ad) = C (dissolved)
  - 2H (ad) = H_2 + 2I.
- Dissociative adsorption of CH_4
  - CH_4 + I (Vacant site) = CH_3 (ad) + H (ad)
  - CH_3 (ad) = CH_2 (ad) + H (ad)
  - CH_2 (ad) = CH (ad) + H (ad)
  - CH (ad) = C (ad) + H (ad)
  - C (ad) = C (dissolved)
  - 2H (ad) = H_2 + 2I.

Holmen et al. [26] reviews and summarizes the conversion of CH_4 to carbon, H_2, olefins, and aromatics, and presents values for the reaction rate parameters. Considerable mechanistic and kinetic information is available from the work on CH_4 coupling reactions [40].

2.3.2.2 Carbon Catalysts

Industrial catalysts typically consist of metals supported on appropriate catalyst supports. Alumina, silica, and carbon are the most widely used industrial supports [11]. One strategy for CH_4 decomposition is to use carbon as not only a support, but as the catalyst itself [11, 41]. The separation of carbon product from the carbon catalyst itself is thus not necessary. Also, the process can be autocatalytic with the carbon produced serving as the catalyst for further reaction [11, 15]. Additional benefits reported for using carbon include its relatively low cost, high-temperature resistance, and tolerance to sulfur and other contaminants found in the feedstock [11].

Several types of carbon materials have been evaluated for catalyzing CH_4 decomposition: activated carbon, carbon black, glassy carbon, acetylene black, graphite, diamond powder, CNTs, and fullerenes [42]. Among these materials, most studies have focused on activated carbon because of its activity, good stability, and availability. The catalytic activity of carbon forms for CH_4 decomposition has been reported to vary according to the ordered nature of carbon as follows: amorphous > turbostratic > graphite [11]. With all carbon types, deactivation occurs through deposition of carbon on the catalyst surface that blocks active sites and reduces the catalyst surface area. The deposit has lower surface area and activity compared to the original carbon catalyst [11]. Physical attributes of the carbon, such as surface area, pore volume, and particle size, are important characteristics that affect deactivation. In addition, at higher temperatures (e.g., >850°C), carbon catalysts tend to deactivate at a slower rate. The reason is that at higher temperatures, the rate of diffusion and deposition increases inside the pores where the majority of the surface area is located [11].

Operating conditions and results have been summarized for carbon catalysts as follows [11]:

- Reaction order: 0.4 (activated carbon); 2 (carbon black) [43, 44]
- Activation energy (kJ/mol): 138 (activated carbon); 236 (carbon black) [37, 43]
- Temperature (°C): 750 to 1500
- Space Velocity (per hr): 360 to 36,000.

2.3.3 Catalyst Regeneration

The regeneration of deactivated catalysts is usually done by burning off the carbon with air or steam, both of which lead to CO_2 production in amounts nearly comparable to the quantity of CO_2 produced in the SMR process [11]. Regeneration by oxidation generates high temperatures on the catalyst surface, which leads to sintering and loss of active area. Regenerating with CO_2 has also been reported, but doing so produces CO [38]. Thus, carbon oxides are produced regardless which process is used. Other researchers have also evaluated catalyst regeneration via physical removal of carbon deposits on the catalyst surface by attrition [11]. However, these results have been mixed in that only the carbon deposited on the external surface of the catalyst particle can be removed, and this carbon represents only a fraction of the total carbon produced by decomposition [11]. Therefore, not all solid carbon product is separated, and this carbon will need to be removed from the catalyst surface by the methods described previously, which results in the production of carbon oxides.

2.4 Plasma Reactions

Plasma processes can be classified as either thermal plasmas (hot plasma, usually greater than ~700ºC) or non-equilibrium plasmas (cold plasma, less than ~700ºC). Thermal plasmas include direct current (DC) arch torch, alternating current (AC), radio frequency (RF) inductively coupled torch, and high-frequency capacitive torch. Non-equilibrium plasma (cold plasma) includes microwave, corona discharge plasma, dielectric barrier discharge plasma, atmospheric pressure glow discharge plasma, and gliding arc discharge. Generally, thermal plasmas achieve higher CH_4 conversions than non-thermal plasmas. Operating under plasma conditions requires the use of electric power, temperatures in the range of 700 to 5500°C (for thermal plasma) [45-48], pressures close to atmospheric [45, 48-50], and the use of a plasma gas (e.g., nitrogen, argon, helium, H_2, CO) [48]. Plasma-assisted CH_4 conversion can be carried out with or without catalysts. Two types of catalysts that have been evaluated for CH_4 dissociation with plasma include metal-based catalysts (e.g., Ni, Co, La, Fe/Si, Pd, and Pt) [45, 51-54] and carbon-based catalysts [55]. Catalysts have not been reported to enhance CH_4 conversion significantly [53, 54], although in one study conducted with a microwave plasma-catalytic system, CH_4 conversion was reported to be improved by about one order of magnitude with the use of Pd and Pt catalysts [52]. Cold plasmas are inhomogeneous in discharge space, which results in a limited reaction region and restricted conversion [56]. However, in one case, Longmier et al. [57] developed an RF non-thermal plasma reaction chamber that was efficient for fully decomposing CH_4 into H_2 and carbon graphite. Thermal plasma processes enable high CH_4 conversion (>80%) with H_2 as a major product [48, 49, 58, 59]. Other products may include carbon, acetylene, benzene, and ethane [58].

Plasma technologies for converting CH_4 into H_2 and carbon present several advantages. High yields of H_2 and carbon (100% carbon yield) can be obtained. The size of plasma reactors is an order of magnitude smaller in comparison to traditional reactors [57, 60]. A large range of feedstocks can be used in the plasma process, thereby making the process flexible. Also, the use of non-thermal plasmas, for example, have been reported to work at temperatures in the 850 to 900°C range, which is approximately 500°C lower than temperatures used for non-catalytic CH_4 decomposition [55]. Thus, there are many benefits to using plasma to provide the high energetics required for the process.

Overall, the following advantages of microwave energy over conventional thermochemical processes have been summarized by Abbas and Wan Daud [11]:

- Noncontact heating.
- Energy transfer without heat transfer.
- Rapid heating.
- Quick startup and shutdown.
- Volumetric heating, which can be more uniform throughout the material body.
- Higher level of safety and automation.
- Microwave energy can be transported from the source through a waveguide (a hollow, nonmagnetic metal tube) to the applicator (where the electromagnetic energy interacts with the material), which can be designed to optimize absorbed energy.
- At higher temperatures, different grades of product carbon can be made [49].

Disadvantages of plasma processes relate to the energy requirements and the fact that energy is provided by externally supplied electricity. A study by Longmier et al. [57] indicates that the energy required per kilogram of H_2 produced is 37 times higher than that required for steam reforming of CH_4, but the energy comparison does not include the energy required to sequester the emitted CO_2 during SMR. Nonetheless, the high energy requirements for plasma processing have been a distinct drawback of this approach. Another potential issue with plasma processes is low solid carbon product yield. In the decomposition process, a relatively high fraction of methyl radical enables the formation of stable hydrocarbons and polymeric species, and a significant amount of energy is needed to crack CH_4 all the way to solid carbon [61]. However, as discussed above, some plasma processes provide sufficient energy to achieve complete decomposition.

2.5 Separations Required

A major challenge for the continuous catalytic CH_4 pyrolysis process is separation of the solid carbon product and regeneration of the spent catalyst (if used), which are critical in the overall economics of the process [16]. Some have also described the aggregation of carbon deposits in the reactor as a main obstacle; one report describes it as the main technological "show stopper" [18]. In a PBR, carbon buildup will eventually cause pressure increases and ultimately block process flow through the reactor. To maintain catalytic activity and to avoid plugging of the reactor, the deposited carbon reactant must be periodically removed. In a review, Muradov [62] evaluated various reactor types (e.g., PBR, FBR, free-volume reactor, spouted-bed reactor, and tubular reactor) and concluded that the FBR is the most promising reactor for large-scale application because it provides a constant flow of solids through the reaction zone, making it suitable for continuous addition and withdrawal of catalyst particles from the reactor. Fluidization of catalyst particles also increases heat and mass transfer rates [11].

Different methods have also been used to separate the carbon byproduct from the H_2 stream. For example, bag filters have been used to remove carbon elutriates [11]. Bag filters also have been employed in plasma processes. Economic analysis for CH_4 pyrolysis technology employing this separation method needs to be evaluated. Also, the use of a molten-metal reactor makes it possible to skim carbon from the top of the metal surface because of its density difference. While this may offer one solution to the issue of solid carbon separation, relatively high temperatures are still required (as with non-catalytic thermal pyrolysis). Geisler et al. [63] report liquid metal temperatures in the range of 930 to 1175^{o}C are required. This technology, being pursued by Arenius Systems, is discussed in the next section.

The conversion of CH_4 to carbon and H_2 would ideally not include any other chemical species in the reactor stream. However, natural gas contains impurities (moisture, air, sulfur species, etc.) and requires separations in the process. If the pyrolysis process is conducted at elevated pressures, then PSA is an effective solution for extracting the product H_2. For low pressure pyrolysis, alternative gas separation techniques must be adopted.

3.0 Process Technologies

In Section 2.0, we report in broad terms the thermodynamic and processing requirements for each of the classes of process technologies (e.g., thermal, catalytic, plasma). Here we report on specific technologies that have been reported in the literature— at various stages of commercialization —that use different approaches to tackle the issues described above. Methane decomposition processes considered in this study are summarized in Table 3.1. More detail is provided for each process, as classified within thermal, plasma, microwave, and hybrid technology classes.

Table 3.1. Summary of Methane Decomposition Processes

Wulff [64]	• Thermal cracking • Intermittent: Natural gas combustion followed by cracking • Packed media: carborundum • 1200–1650°C • Desired product: olefins • Research & development phase
HYPRO [65]	• Solid recirculating catalyst • Methane thermal cracking • Carbon deposited on catalyst burned to regenerate the catalyst • Pilot scale
Fluidized Bed [66, 67]	• Activated carbon catalyst • Electrical heating or by alternately switching between combustion and catalytic cracking • Research & development phase
EGT Enterprises [68]	• Methane pyrolysis reactor • 2000°C • Energy demand 14 kJ/g_C and 43 kJ/g_{H2} • Research & development phase
Institut Francais du Petrole [69]	• Combustion followed by CH_4 pyrolysis on ceramic honeycomb • 1200°C • Pilot-scale demonstration • Desired product: olefins • Research & development phase
Steinberg and Arenius Systems [70, 71]	• Methane decomposition in molten metal (tin, 232°C or copper, 1083°C) • Methane bubbled through bath, carbon floats to the surface, gas is mainly H_2 • H_2 purified by PSA • Pilot scale
BASF [72-74]	• Methane pyrolysis, 1200–1400°C, produces carbon and H_2 • H_2 reacted with CO_2 from external process to produce syngas • Fluidized bed with support materials and carbonaceous granules • Research & development phase
Monolith Materials [75, 76]	• Plasma reactor • Produces carbon black and H_2 • H_2 combustion to produce steam (replacing coal-fired boiler) • Commercial (early stage)

Kvaerner [34, 77]	- Plasma torch decomposes CH_4 to form carbon - H_2 is the plasma gas - 1000–2000°C - Research & development phase
GasPlas [78]	- Co-axial vortex flow reactor - Microwave induced plasma - Research & development phase
Remarks on Plasma Processes	- Use of inert gases such as argon. - Electrical power is a premium, available from the grid at efficiencies of less than 40%.

3.1 Thermal Catalytic Processes

One of the earlier technologies for the thermal cracking of CH_4 to produce useful products is the Wulff process [64], which uses high-temperature steam to crack natural gas to acetylene, producing significant byproducts of H_2 and carbon. It is an intermittent process that begins with natural gas combustion to heat the chamber and the packed media made of carborundum crystals. In subsequent steps, the combustion air is stopped, and the CH_4 cracks in contact with the heated surfaces of the chamber and the particles, which can be at temperatures as high as 1650°C (3000°F). This process continues until the temperature cools down to 1200°C. The products are primarily H_2, acetylene, ethylene, carbon oxides in the gas stream, and solid carbon deposited on the media. The valued gas products need to be subsequently separated from the small amounts of nitrogen, oxygen, and unreacted CH_4.

Another pioneering process for producing H_2 by thermal decomposition of CH_4 is the HYPRO [65] process, which was demonstrated by UOP in McCook, Illinois. A solid recirculating catalyst was used. The process employed a Ni-based catalyst to lower the decomposition temperature and two FBRs with a solids-circulation system. The carbon deposited on the catalyst was burned to regenerate the catalyst and provide process heat. This process was not CO_2-free.

Muradov [79] compared the thermodynamically predicted yield of H_2 as a function of temperature to experimental yields observed using several different catalysts. Iron oxide was shown to achieve equilibrium-predicted H_2 yields at 900°C. Carbon in the form of graphite crystallites was observed on the catalyst based on X-ray diffraction. A later patent and progress report [66, 67] proposed the use of activated carbon or carbon as the catalyst in an FBR. The fluidized bed could be heated using either electrical heaters or by using a dual bed reactor system where one of the reactors is decomposing CH_4, while the other is being regenerated and heated by combustion [80].

EGT Enterprises developed a pyrolysis reactor using a series of heating zones with an electric resistance heating screen capable of operating up to 2000°C [68]. One configuration showed the process operating at a feed rate of 4600 ft^3/hr at a temperature of 1370°C and producing 9180 ft^3/hr of product gas containing 97% H_2 with the balance being mainly unreacted CH_4. The 97% H_2 in the product corresponds to 94% CH_4 conversion. The energy demand for the process was 260 kW, which is 128% more than the required heat of reaction (i.e., the process has an efficiency of 44%) equivalent to 14 kJ/g of carbon and 43 kJ/g of H_2.

Weill et al. [69] used a ceramic honeycomb pyrolysis reactor in which combustion gas was used to heat the CH_4 to be pyrolyzed at 1200°C. When demonstrated at the pilot scale, the process showed yields of ethylene, acetylene, benzene, coke, and tars.

BASF, Linde Group, and ThyssenKrupp [72] have developed a pyrolysis-based process for producing syngas and solid carbon. The H_2 produced by this pyrolysis process is reacted with CO_2 (captured elsewhere) to produce syngas via the reverse WGS reaction. The pyrolysis reaction occurs in a FBR containing support materials and carbonaceous granules and operating at 1200 to 1400°C.

Steinberg [70] proposed a molten metal-based CH_4 decomposition process that bubbles CH_4 through a molten-tin (melting point of 232°C) or copper (1083°C) bath. Because of its lower density, the carbon floats to the surface of the bath, which facilitates its recovery. The gas stream contains primarily H_2 with lesser amounts of unreacted CH_4 and other byproducts. Arenius Systems is developing such a process at a pilot scale to provide H_2 for fuel cells with carbon black as a byproduct [71].

3.2 Concentrated Solar Power

Concentrated solar power is a renewable source of high-temperature process heat, and direct solar irradiation of the reactants provides for a very efficient heat transfer directly to the reaction site [81]. A recent review article by Steinfeld discusses several solar natural gas conversion approaches and provides a comparative analysis for the different approaches in terms of exergy efficiency, which was reported to be about 30% for solar cracking of CH_4 [82]. Hirsch and Steinfeld also report the design of a solar chemical reactor that uses a cavity-receiver that directly irradiated a vortex flow of natural gas premixed with carbon particles, which serves as both a radiant absorber and as a catalyst [83]. After exiting the reactor, the products are cooled and the solid products are collected in filters. A continuous mode of operation was demonstrated at the 5 kW scale with 67% CH_4 conversion at 1600K and 1 bar. The carbon formed was filamentary in nature [83].

In a different study by Steinfeld, a sun-tracking heliostat and stationary parabolic concentrators were used to supply to a small-scale FBR [81]. The direct irradiation of a Ni/Al_2O_3 catalyst provided effective heat transfer to the reaction site. Methane underwent pyrolysis at 850K with the conversion decreasing with time on stream as the carbon product accumulated, which caused the catalyst to deactivate. Yields of 200 g carbon/g catalyst were reported.

Generally, catalytic-based solar thermochemical applications have issues similar to other catalytic-based thermochemical conversion processes, such as recovery of the carbon from the catalyst and regenerating the catalyst. One disadvantage with using solar power specifically is difficulty in maintaining stable heat flux. However, there is great potential benefit in utilizing solar for supplying the energy for highly endothermic reactions.

3.3 Plasma Processes

Fulcheri et al. [49] extensively studied CH_4 conversion to H_2 and carbon. They developed a plasma reactor with three electrodes, creating a compound arc by applying an AC current to the electrodes [45, 47-49]. The major advantage of this process is the total conversion of the hydrocarbon into carbon (100% carbon yield) and pure H_2. This process allows the production of different carbon materials with defined nanostructures (e.g., carbon black, fullerenes, and nanotubes) by controlling the operating conditions [45, 48]. In addition, the feedstock may contain or consist of CH_4, acetylene, propylene, C_4 hydrocarbons, light or heavy oil, waste oil, and pyrolysis fuel oil [48]. The feedstock can also comprise solid carbon material (e.g., carbon black, acetylene) for production of CNTs [45].

Recently, Monolith Materials partnered with Fulcheri and Schwob's group and Aker Solutions to build a pilot plant, located in Redwood City, California. The plant uses a plasma-based process for converting natural gas into H_2 and carbon black [75]. Monolith is building a production-scale plant in Hallam, Nebraska, expected to be online in 2018, that will sell the H_2 to an adjacent power plant to produce CO_2-free electricity [76].

Kim et al. [35] studied the thermal decomposition of CH_4 by using a DC-RF hybrid thermal plasma to demonstrate the production of H_2, a small amount of olefins, and 20 to 50 nm carbon particles. Their design simulation estimates a total power requirement of 40 kW to produce 10 Nm^3/hr (0.89 kg/hr) of H_2 and 2.5 kg/hr of carbon black, assuming 60% thermal efficiency of the DC-RF torch (see Table 3.2). Their simulated process uses 83.5 SLPM of CH_4 with a LHV of 49.8 kW. Considering only the 40 kW of plasma power for the process, the specific energy demands are 161 kJ/g_{H2} and 57.6 kJ/g_{Carbon}, or cumulatively 42 kJ/$g_{Carbon+H2}$ products. Comparing this to an SMR process operating with 70% efficiency (LHV of H_2 as a percentage of LHV of the CH_4 feed), the specific energy demand is 172 kJ/g_{H2}, which compares favorably with the plasma process. However, if we include the LHV of the CH_4 in the energy input to the plasma process, then the specific energy demands for that process increase by a factor of 2+ to 362 kJ/g_{H2}, 129 kJ/g_{Carbon}, and 95 kJ/$g_{Carbon+H2}$.

Table 3.2. Hydrogen from Thermal Plasma Decomposition of Methane (100% conversion assumed) [61]

Argon/CH_4 Ratio	Ar Flow	CH_4 Flow	Plasma Power	Total Input Power	H_2 Output
2	167 SLPM	83.5 SLPM	24 kW	40 kW	10 Nm^3/hr

Moshrefi et al. [84] reported on CH_4 conversion using a DC spark discharge plasma experiment designed to produce olefins, where the gaseous products included acetylene, ethylene, and ethane accompanied by the formation of solid carbon. With a conversion percentage of 45% and assuming all H_2 in the converted CH_4 is available, the process efficiency based on the LHV of H_2 only is 16% (Figure 3.1). Extrapolating to 100% conversion, the efficiency would increase to 35%. From a H_2-only perspective, the process energy efficiency is low; however, if the carbon can be sold as a commodity, the process may be economically attractive. The plasma was generated using argon gas, which is likely to pose an economical challenge to scale up.

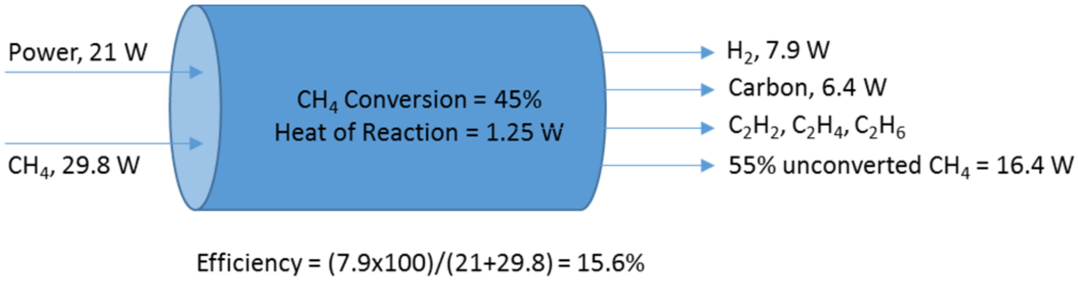


Figure 3.1. Direct Current Spark Discharge Plasma Experiments Produced Hydrogen and Carbon [84]

Kvaerner [34, 77] developed the Carbon Black and Hydrogen Process using a plasma torch for CH_4 pyrolysis to produce H_2 and carbon black. H_2 is used as the plasma gas. A commercial plant was built and operated in Canada between 1999 and 2004. The reactor temperatures vary between 700°C at the primary gas inlet and reach a high of up to 2000°C. A secondary stream of CH_4 is then decomposed by contacting the hot gases.

GasPlas uses a microwave, non-thermal plasma to produce H_2 and carbon [78]. Its noted features include an ambient pressure process, use of a highly non-equilibrium plasma, scalability, and ability to control the carbon formation and collection. One set of experimental results showed that a stream of CH_4 (3 L/min) mixed with Ni (17 L/min) when subjected to 1900 W of microwave power converted 53.9% of the CH_4 [85].

3.4 Chemical Processes for Decomposing Methane

ETCH, LLC is developing a low-temperature, quasi-catalytic process for producing carbon and H_2 from natural gas based on a process invented by Professor Jonah Erlebacher at Johns Hopkins University under a U.S. Department of Energy (DOE) Advanced Research Projects Agency-Energy (ARPA-E) grant [86]. The process is based on the reaction of hydrocarbons, such as CH_4, with anhydrous nickel chloride to form nickel metal, carbon, and HCl at a temperature of ~800°C. Lowering the temperature results in a back reaction between the nickel metal and HCl to regenerate nickel chloride and release H_2 gas. The carbon is separated from the nickel chloride by sublimation. The reaction is tolerant to impurities found in natural gas, such as sulfur, water, and other hydrocarbons. The process requires no water and uses substantially less energy than SMR making it attractive for deployment in regions where process water is not readily available. Initial estimates indicate that the process could produce 4.7 kg of carbon for every kilogram of H_2, with a projected H_2 production cost competitive with SMR [87].

4.0 Market – Current and New Opportunities

The United States produces about 10 million metric tons of H_2 annually, and SMR accounts for more than 95% of this production. New markets for H_2 such as fuel cell-powered vehicles are projected to significantly increase the demand for H_2 in the coming decades. A key challenge for fuel cell cars is the ability to produce H_2 at a cost that is competitive with the cost of producing gasoline on an equivalent energy basis. The ability to monetize the carbon produced during the thermal decomposition of natural gas offers the potential to reduce production costs of H_2 compared to those of SMR. In a 1987 study, Steinberg et al. [88] compared the production cost of H_2 by several pathways, including CH_4 cracking, and estimated a cost of $5.10 per kilogram after taking credit for carbon black, exceeding SMR. To the best of our knowledge, there are still no viable commercial processes based on producing both carbon and H_2 for the carbon black and H_2 markets, respectively. This highlights the need for continued cost reductions through research and development, and through creative market strategies.

Carbon is marketed in a number of different forms including carbon black, CNTs, carbon nanofibers, carbon fibers, graphene, and needle coke. Carbon black is the oldest and most mature market for carbon. Table ES.1 summarizes the market potential for the different types of carbons. More details for each of the markets are included in this section.

4.1 Current Markets

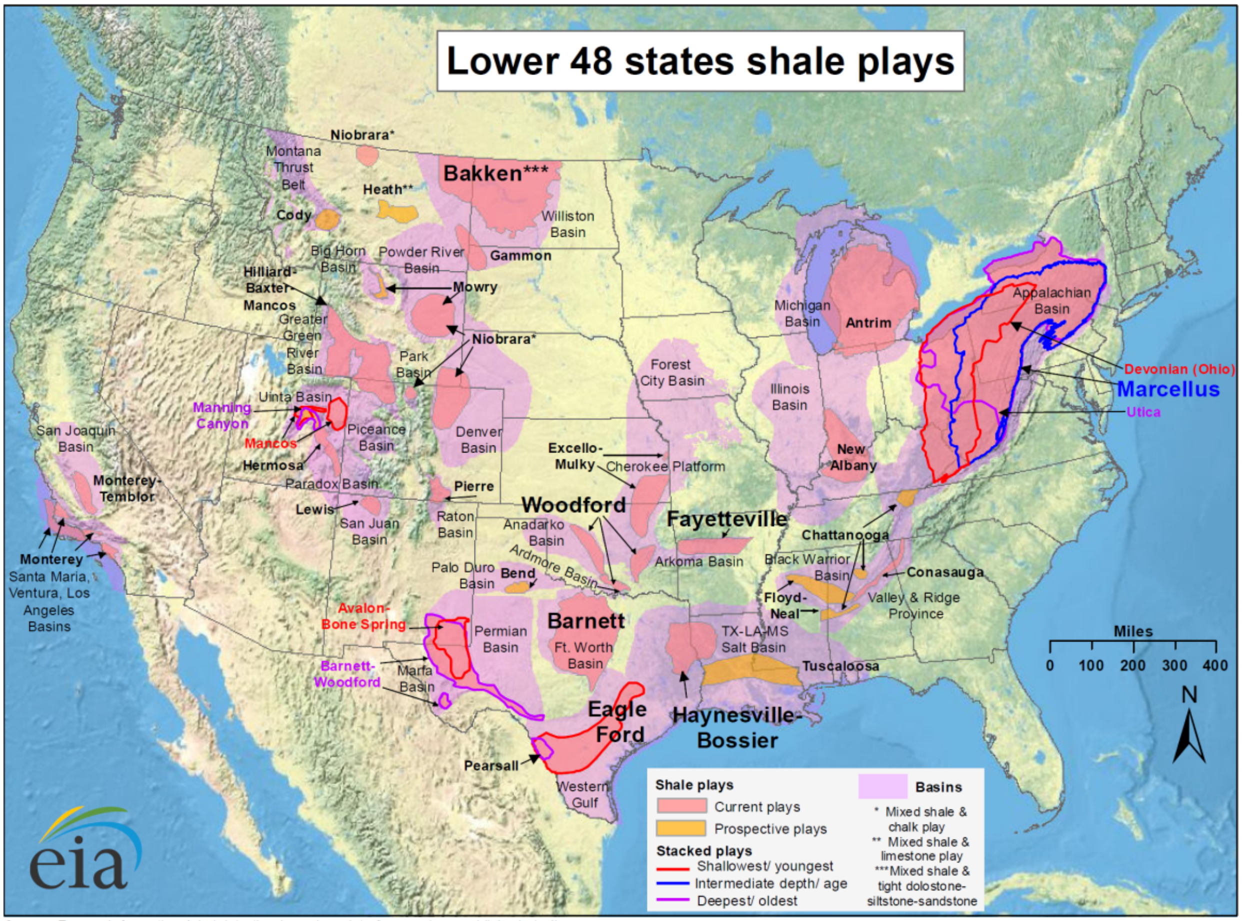
4.1.1 Natural Gas

The development of hydraulic fracking and horizontal drilling has enabled the ability to recover natural gas from shale and tight formations at cost-competitive prices resulting in significant growth in the natural gas supply while leading to lower prices. For example, U.S. natural gas production rose from 23.7 trillion cubic feet (tcf) in 2005 to 32.6 tcf in 2016; consumption rose from 21.7 tcf in 2005 to 27.5 tcf in 2016; and prices dropped from $8.12 per million cubic feet (mcf) to $2.35 /mcf. U.S. natural gas reserves have increased from 213.3 tcf in 2005 to 307.7 tcf in 2015 [89]. Figure 4.1 shows the location and reserve potential for the major shale gas basins in the United States.

According to the Energy Information Administration *Annual Energy Outlook (AEO) 2017* [90], natural gas prices are projected to increase its Reference Case, rising modestly through 2030 to $5.00 to $6.00/mmBTU[4] as the use of natural gas for electric power generation increases. Prices projected to remain relatively flat after 2030 as technology improvements keep pace with the rising demand (Figure 4.2). Under its High Oil and Gas Resource and Technology scenario, prices are projected to remain relatively low at $3.00 to $4.00/mmBTU due to lower production costs and higher resource availability. Under its Low Oil and Gas Resource and Technology case, prices are projected to approach $10.00/mmBTU, driving down domestic production and consumption. U.S. natural gas production is projected to grow at an annual growth rate of around 4% between 2016 and 2020 spurred by large, capital-intensive projects such as new liquefaction export terminals and petrochemical plants built in response to the low natural gas prices (Figure 4.3). Beyond 2020, natural gas consumption is expected to grow at a rate of about 1% annually as export growth moderates and domestic use becomes more efficient, causing prices to rise more slowly. Natural gas from shale gas and tight oil is projected to account for nearly two-thirds of U.S. production by 2040 (Figure 4.4).

---

[4] The unit mmBTU is a thousand-thousand, or million BTUs.



Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

Figure 4.1. Location and Projected Reserves for Major U.S. Shale Gas Basins in the United States [91]

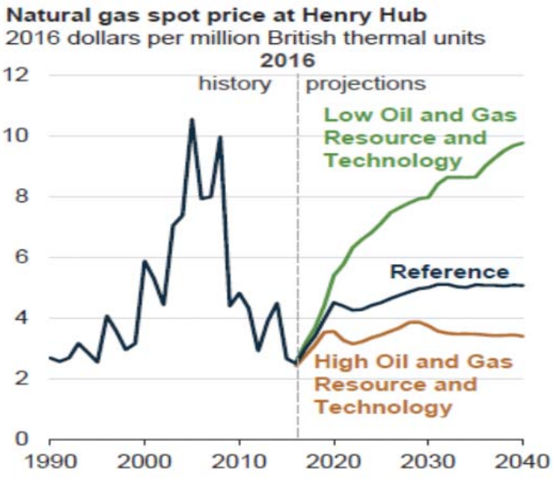


Figure 4.2. Historical and Projected Price of Natural Gas from 1990 through 2040 [90]

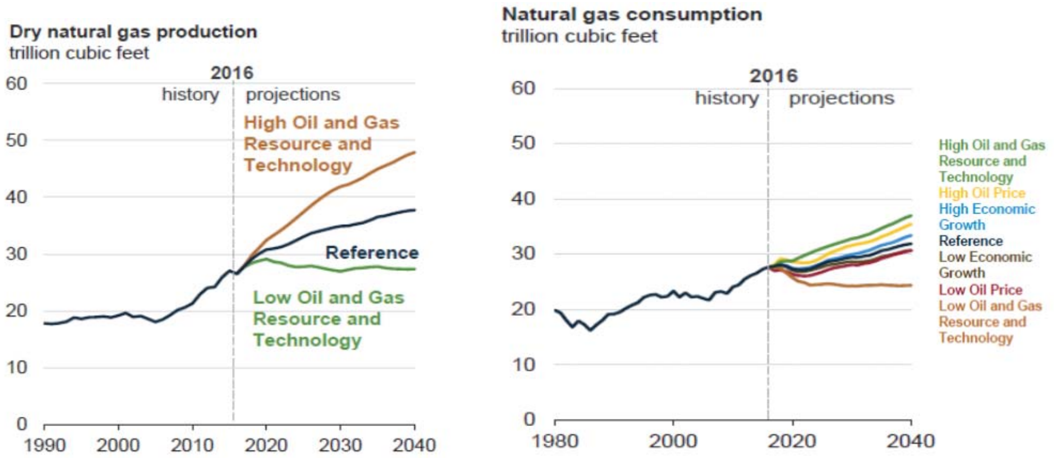


Figure 4.3. Total U.S. Natural Gas Production and Consumption from 1990 through 2040 [90]

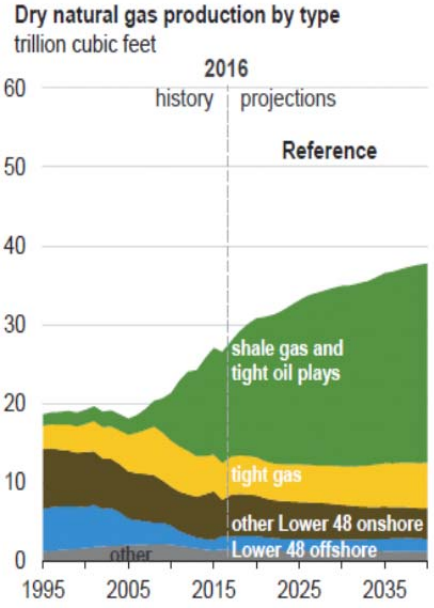


Figure 4.4. Historic and Projected Growth in the Production of Natural Gas from Shale Basins and Tight Oil between 1995 and 2040 [90]

4.1.2 Hydrogen

The United States produces about 10 million metric tons of H_2 annually and SMR accounts for 95% of the H_2 produced. The major consumers of H_2 are petroleum refining (47%) and fertilizer production (45%). Methanol production consumes about 4% of the H_2 produced and the electronics, metals, and food industries combined consume the remaining 3% [92].The U.S. demand for H_2 by industry was 13.8 million metric tons in 2015 and the demand in oil refining accounted for 10.5 million metric tons, which is equivalent to 76% of the total demand [93]. The industrial demand is met by either on-purpose production or the recovery of byproduct H_2. On-purpose H_2 is produced by both the consuming industry, referred to as captive production, and by merchant gas companies. In 2015, approximately 10 million tons of H_2 was produced; 6.4 million tons were produced by captive production, and 3.6 million tons were produced by merchant gas companies. Approximately 5.8 million metric tons of byproduct H_2 was recovered by the oil refining industry and from multiple other processes. Of this amount, approximately

3.8 million metric tons of H_2 were recovered for self-use or for sale to merchant gas companies and the remaining 2.0 million metric tons were combusted for process heat. Merchant gas companies recovered 0.29 million metric tons of H_2 (including ethylene, chlor-alkali, styrene, acetylene, and propylene) from a number of industries, and another 0.10 million metric tons were recovered from other unidentified sources. In terms of production cost, the price of H_2 is tied to the price of natural gas given that SMR accounts for more than 90% of the H_2 produced in the United States. As a "rule of thumb," the cost of H_2 produced by SMR is approximately three times the cost of natural gas per unit of energy produced [94]. Given the current cost of natural gas of about \$3.00/mmBTU, the production cost of H_2 equates to \$9.00/mmBTU or approximately \$1.00/kg based on the LHV of H_2.

Demand for H_2 in the United States and globally is dominated by the oil refining, ammonia, and methanol industries [95]. In the United States, captive H_2 production accounts for nearly all the H_2 used in ammonia and methanol production. Growth in these markets appears promising with the price of natural gas in the United States likely to be competitive with world prices over the next decade. In oil refining, slightly more than half of the H_2 demand is met by recovering byproduct H_2 from catalytic reforming units with the remaining H_2 demand met by captive production and merchant supply. While captive production has increased substantially over the past 25 years, merchant supply has increased from nearly nothing to 15% over the same period. Growth in demand in the methanol industry is due to a fourfold increase in methanol production since 1990. In oil refining, the growth in demand is due to stricter limits on the sulfur content in gasoline and diesel fuel resulting in an increase H_2 demand for hydrodesulfurization and the increasing need for H_2 for hydroprocessing heavier crudes to favor distillates over residuals. Growth in the merchant supply market has been driven by the increasing demand of oil refineries with more than 90% of U.S. merchant H_2 production being delivered to oil refineries [96]. Long-term growth in the demand for H_2 for oil refining is uncertain given the projected flat or decreasing demand for petroleum products in the transportation sector in the coming decades due to increasing penetration of electric vehicles into the light-duty vehicle market coupled with projections that U.S. petroleum consumption peaked in 2006 and that annual miles driven is expected to peak in 2018 [90].

Globally, the demand and supply of H_2 was estimated to be 87 million metric tons in 2015 with captive production accounting for more than 60 million metric tons. Ammonia production accounted for about 30 million metric tons or nearly 50% of the captive H_2 production with methanol production and oil refining each accounting for approximately 25% of the total production. Merchant supply of H_2 accounted for less than 10% of the total demand; however, it is the fast growing market, growing at an annual rate of 15.3% since 1990 [97].The global market for H_2 is projected to grow from an estimated \$115.25B in 2017 to \$154.74B by 2022, at a compound annual growth rate of 6.07% [98]. The growing demand for H_2 is due to: 1) an increasing demand in oil refining to further reduce the sulfur content of gasoline and diesel and an increasing demand for a lighter mix of products (i.e., a higher percentage of distillates and a lower percentage of residual products); and 2) an increasing demand for methanol for use as a transportation fuel and as a feedstock for producing olefins [95]. Fuel cell-powered vehicles represent a potential disruptive technology that could have a significant impact on the world demand for H_2. With about one billion light-duty vehicles on the road globally, the potential demand for H_2, assuming all vehicles are fuel cell-powered, is estimated to be around 150 million metric tons (based on 10,000 miles driven annually and a fuel economy of 67 miles per kilogram).

4.1.3 Carbon

Carbon black is essentially pure carbon, typically 97% or greater by weight, in the form of colloidal particles formed by the thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions[47]. Because the thermal decomposition of CH_4 is endothermic, some processes add some oxygen to the feed resulting in the partial oxidation of CH_4 to accelerate the reaction. Carbon black is distinct from soot or black carbon, which typically contains less than 60% carbon and as much as 50% ash by weight. Carbon black is used as filler and a strengthening/reinforcing agent in the manufacture of tires and other rubber and plastic products. It is used in printing inks to enhance formulations and in high-performance coatings to provide pigmentation, conductivity, and protection from ultraviolet light. Certain grades of carbon black are approved by the U.S. Food and Drug Administration for use in items such as coffee mugs, food trays, and cutlery [99]. Approximately 90% of the carbon black produced is used in rubber applications, primarily tires, 9% as a pigment, and the remaining 1% in a number of diverse applications [47].

Carbon black can be produced by a number of processes including the furnace black or oil-furnace process, the thermal black process, and the acetylene black process. In the furnace black process, heavy aromatic oils are atomized and injected into a natural gas-heated furnace under controlled conditions [100]. The oils are partially combusted or undergo thermal decomposed at temperatures ranging from 1600 to 1800°C to form microscopic carbon particles. The exhaust gas containing the carbon particles is cooled using water quenches and heat exchangers. The carbon is separated from the cooled gas stream using water sprays and a fabric filter. The recovered carbon is densified and processed into pellets of various grades and sizes. Yields range from 35 to 65% depending on the composition of the grade of carbon black produced. The residual gas contains a variety of compounds, including H_2 and CO, and is used without further purification to produce heat, steam, or electric power.

In the thermal black process, natural gas is thermally cracked to produce carbon black [100]. Two furnaces are used in the process and natural gas undergoes thermal cracking in the first furnace. Similar to the furnace black process, the exhaust from the first furnace is cooled and the carbon is filtered out. The exhaust gas, which contained upwards of 90% H_2 and a balance of CH_4 and other light hydrocarbons, is burned to heat the second furnace. When the temperature of the first furnace becomes too low to promote cracking, the order of the furnaces is reversed. Typically about 15 to 20% of the exhaust gas is used to heat the furnace, and the remaining gas is used without further processing to produce heat, steam, or electric power.

In the acetylene black process, acetylene is used instead of natural gas [101]. Whereas the thermal black process is endothermic, the acetylene process is highly exothermic. Because of the higher purity of the feedstock and exothermic nature of the process compared to the thermal black process, the acetylene process produces a very pure carbon black that has a greater degree of crystallinity than that produced by the other methods.

Each process produces different grades of carbon black that have unique physical properties (e.g., particle size, agglomerate size, surface area, structure/void volume, color, etc.). Rubber-grade carbon black is classified as either ASTM or Specialty Grade, and each classification contains a large number of grades based on physical properties such as particle size and structure [102, 103]. Today more than 95% of the carbon black produced in the United States is produced using the furnace black process, because it can produce nearly all of the different grades by carefully controlling the process conditions [104].

The price of carbon black depends on the product specifications (i.e., the grade and volume purchased). Prices can range from $400 to over $1000 per ton for ASTM-grade carbon black for use in tires to over $2000 per ton for specialty grade carbon black based on a survey of commercial price lists [1]. Given that the vast majority of carbon black produced worldwide is produced from oil, the price of crude oil has an overriding influence on the carbon black market [105].

The United States currently produces about 2 million metric tons of carbon black annually with a projected 4.2% annual growth rate through 2022 (Figure 4.5) [2]. Producers headquartered in the United States include Cabot Corporation (Boston, MA), Continental Carbon Company (Houston, TX), and Sid Richardson Carbon & Energy Co (Fort Worth, TX). The two other major industrial manufacturers are Birla Carbon, headquartered in India, and Orion Engineered Carbon, headquartered in Luxembourg [104]. Given favorable market factors, new companies such as Monolith are entering the market [99]. Monolith's plant located in Redwood City, California, is the first carbon black manufacturing facility built and licensed in the United States in the last 30 years.

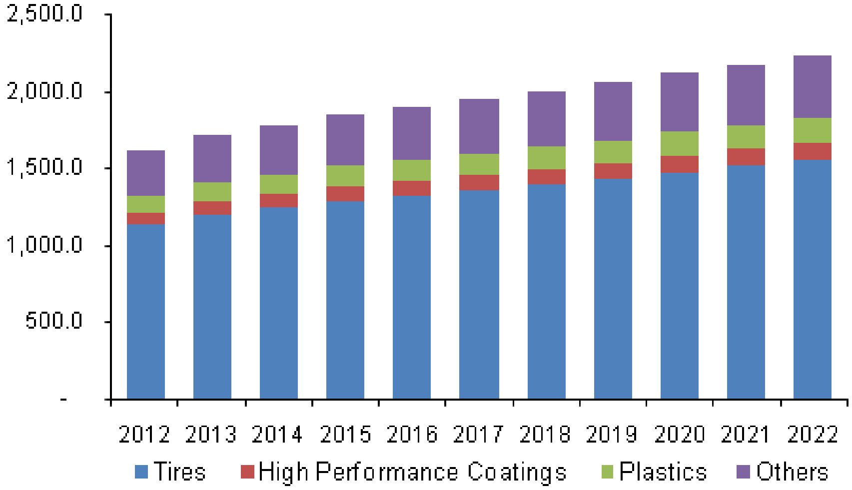


Figure 4.5. U.S. Carbon Black Market Volume by Application from 2012 Projected through 2022. Volume is in kilotons [2]. (Reproduced with permission from Grand View Research.)

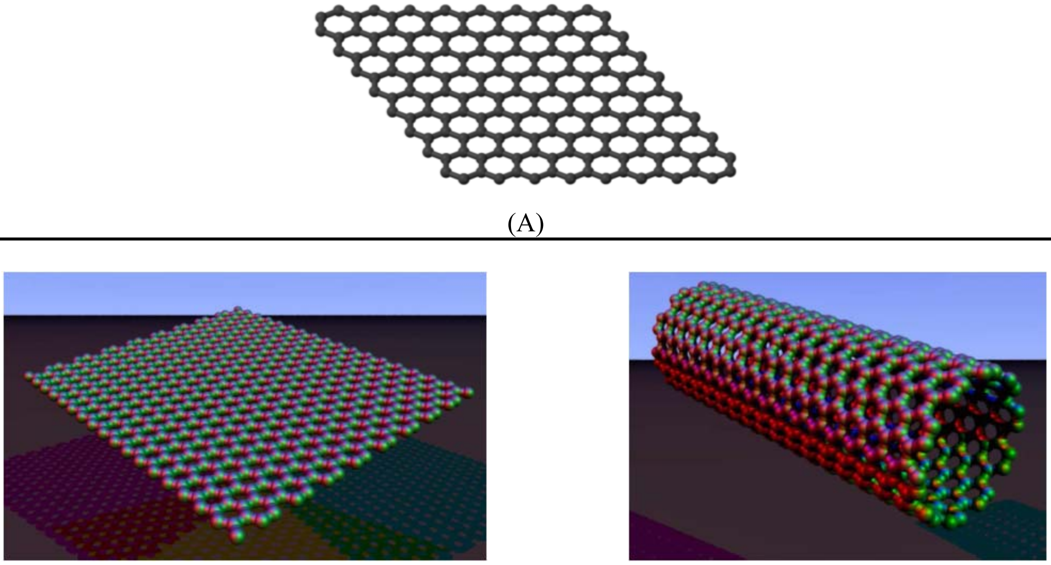
The global demand for carbon black was nearly 12 million metric tons in 2014. Global demand is projected to increase to 16.4 million metric tons by 2022, representing a market value of $28B dollars, with most of the growth in demand occurring in China and India [3]. Global demand is being spurred by the increasing demand for automobiles in the Asian market that will drive tire sales. Analysts predict that U.S. tire manufacturers will face a shortfall in the availability of carbon black manufactured in the United States beginning in 2020 due to the projected global growth in the demand for tires worldwide. Specialty carbon black for use in plastics and lightweight automotive components is expected to be the fastest growing market segment [106].

4.2 New Market Opportunities for Methane Conversion to Carbon and Hydrogen

Other forms of carbon besides carbon black may be considered as products. Examples for carbon include graphite/graphene, carbon fiber precursors, CNTs, and needle coke. We also discuss hydrocarbons in the form of aromatics that can be produced from CH_4 pyrolysis. Each of these forms of carbon is discussed below.

4.2.1 Graphite/Graphene

Graphite/graphene materials are all nearly 100% carbon and differ primarily in topology (Figure 4.6). Graphite is the naturally occurring material. It has a layered, planar structure. The individual layered sheets are called graphene. In each layer, the carbon atoms are arranged in a honeycomb lattice with a separation of 0.142 nm, and the distance between planes is 0.335 nm [9]. Atoms in the plane are bonded covalently, with only three of the four potential bonding sites being satisfied. The fourth electron is free to migrate in the plane, making graphite electrically conductive. However, it does not conduct in a direction at right angles to the plane. Bonding between layers is via weak van der Waals bonds, which allows layers of graphite to be easily separated or to slide past each other. A rolled up layer is a CNT.



(A)

(B)

(C)

Figure 4.6. Comparison of the Structure of (A) Graphite, (B) Graphene, and (C) a Single-Walled Carbon Nanotube [107]

Demand for natural graphite is 1 to 1.2 million tons per year and consists of several different forms of graphite—flake, amorphous, and lump. Historical applications primarily use amorphous and lump graphite, while most newly emerging technologies and applications use flake graphite. Of the up to 1.2 million tons of graphite that are processed each year, just 40% is the flake form. Historically, China was responsible for the large decline in graphite prices in the 1990s as product was dumped on the market to earn foreign exchange. Much like rare earths, this essentially killed the industry in the West, making the United States highly dependent on supply from China. It is unlikely China can do the same thing again. The majority of Chinese graphite mines are small, many are seasonal, and labor and environmental standards are poor. Easily mined surface oxide deposits are being depleted and mining is now moving into deeper and higher cost deposits [108].

Graphite is used in electronic applications such as for Li-ion batteries where the market in 2015 was 80,000 tons/yr [4]. Additionally, the U.S. Geological Survey states that large-scale fuel cell applications being developed today could consume as much graphite as all other uses combined. But even if only half of the U.S. Geological Survey demand is realized, graphite use is going to explode just because of fuel cells, let alone other known demand drivers and new applications [109]. Thus, the natural graphite market is currently small, but it possibly will be very important for new fuel cell applications and/or batteries.

Graphene is a special form of graphite that is 100% carbon and only one layer or at most a few layers thick. It potentially has all of the application space that graphite has but currently has little production. The global market for graphene reached $9 million by 2012, with most sales in the semiconductor, electronics, battery energy, and composites industries [110]. The market is projected to grow from 80,000 metric tons produced in 2015 to 250,000 metric tons by 2020 [4]. Generation as a co-product with H_2 could be a potential benefit, but the current market would soon be saturated unless demand increases.

There is little reason to believe a priori that carbon produced from a pyrolysis process would be well ordered. However, one study has reported formation of well-ordered pyrolytic graphite structures as well as fibrous carbon on transition metals. The pyrolytic carbon was reported to be of equal quality to recrystallized graphite normally produced at much higher temperatures. Results appeared to be repeatable [111]. However, the value of the carbon will depend heavily on the treatment of the feed gas. Carbon black furnace processes operate by injecting a heated aromatic liquid hydrocarbon into the combustion zone of furnace fired by natural gas, where the hydrocarbon is decomposed to form carbon black at temperatures on the order of 1320 to 1540°C. Depending on the feed composition and the grade of black produced, process carbon black yields have ranged from 35 to 65% [100].

4.2.2 Carbon Fibers

Carbon fibers are polycrystalline, two-dimensional planar hexagonal networks of carbon containing between 92 to 100% carbon by weight formed by heating carbon-containing precursors at temperatures ranging from 1000 to 1500°C [112]. If the fibers are heated above 2000°C, the hexagonal carbon network undergoes conversion to graphene with yields in excess of 99%. These fibers are referred to as "graphite fibers."

Carbon fibers have a number of favorable mechanical and chemical properties, such as high tensile strength and stiffness, low density, dimensional stability, low coefficient of thermal expansion, fatigue resistance, and chemical inertness and biological compatibility [112]. Carbon fibers are finding increasing use in a variety of applications such as aerospace, automobiles, sports and leisure, the chemical industry, wind turbines, carbon-reinforced composite materials, and textiles [6, 7, 112-114]. The physical properties (primarily tensile strength and modulus, as well as others) determine the proper utilization of produced carbon fibers [115].

Carbon fibers are manufactured from precursor fibers using a combination of heat and stretching treatments. The most common precursors are polyacrylonitrile (PAN) and pitch, which is a complex blend of polyaromatic and heterocylcic compounds. Other linear and cyclic precursors include phenolic polymers, polyacenephthalene, polyamide, polyphenylene, poly-p-phenylene, benzobisthiazole, polybenzoxazole, polybenzimidazole, polyvinyl alcohol, and polyvinylidene chloride, and polystyrene. [116]. Currently PAN is used to produce 95% of the carbon fibers worldwide, and pitch is used for the remaining 5%. Precursors, namely PAN, account for approximately 51% of the manufacturing cost of carbon fibers, and their high price is one of the barriers to their widespread use [115]. Additionally, the current methods for manufacturing carbon fibers are slow and energy-intensive. Thus, both alternative methods of manufacturing and use of cheaper precursors are under exploration.

Alternative precursors to PAN under investigation include biomass precursors such as lignin, glycerol, and lignocellulosic sugars [115]. There has been a particular interest in using lignin as a precursor because of its availability, low cost relative to other precursors, and enhanced structural properties. However, it has been reported that no biomass-based carbon fiber has been developed with the necessary structural properties to be used in the major carbon fiber applications (e.g., aerospace, wind, and automotive. For more information the report authored by Milbrandt and Samuel Broth provides both technical and market information about each bio-based carbon fiber precursor [115]. Also, the report authored by Baker et al. provides a comprehensive review of carbon fiber manufacture specifically from lignin, which includes a cost comparison of potentially low-cost carbon fibers [117].

The process for producing carbon fibers depends on the precursor and the desired physical properties. For PAN, the process starts by polymerizing the PAN-based precursor, which is then spun into fibers. The fibers are then treated using an air-based oxidation process at temperatures between 200 and 400°C to stabilize the fiber. The stabilized fibers are heat treated in the absence of oxygen at temperatures ranging from 800 to 1600°C to remove non-carbon impurities such as H_2, oxygen, and nitrogen and to induce carbonization. Next, a surface treatment is used to improve the mechanical properties of the carbon fiber. Finally, the fiber is washed, dried, and sized [112, 116]. For pitch, the process starts by melting pitch so that it can be extruded and drawn into fibers. Similar to the PAN-based process, the fibers are air-treated to stabilize the fiber; they then undergo a higher temperature heat treatment to induce carbonization [116]. Pitch has the advantage of lower cost and producing a higher char yield than PAN, but the processing costs are higher to achieve carbon fibers of similar performance to PAN [116].

An alternative to the PAN- and pitch-based processes is the “vapor-grown” production process. The process involves exposing light-hydrocarbon gases [112, 118], such as CH_4 [119], acetylene, or ethylene or coal-gas [120], to a solid catalyst, such as Co, Fe, or Ni, to form carbon filaments with diameters as small as 0.1 µm as precursors for carbon fiber growth. The filaments consist of graphitizable carbon that is transformed into larger diameter graphite fibers by heat treatment at temperatures above 250°C. Exposing these carbon filaments to subsequent chemical vapor deposition using the same carbonaceous gases causes the filaments to grow in diameter ranging from 60 to 200 nm and approximately 100 µm in length, yielding vapor-grown carbon fibers or gas-phase-grown carbon fibers [112]. Compared to the complex PAN-based process, the manufacturing process for vapor-grown carbon fibers is simpler, faster, and cheaper and could provide an innovative approach for fabricating high-performance fibers at lower costs.

The global market demand for carbon fibers in 2016 was 70,000 metric tons [6]. The market is projected to grow at an annual growth rate of 10 to 13% through 2020 with the market demand expected to exceed 100,000 metric tons in 2020 [7]. The global market value was approximately $2.15B in 2015 [7], which is projected to grow to $4.2B by 2022. Combined, the aerospace industry including defense, the automotive industry, and wind turbine manufacturing in the energy sector accounted for between 35,000 to 45,000 metric tons, and continuing growth in these industries is expected to support the high projected annual growth rate. Although worldwide demand for carbon fibers has increased significantly over the past decade, the high production costs have limited wider spread use of carbon fibers [112]. Owing to the complex and multistage manufacturing processes required to produce carbon fibers, only a limited number of companies are engaged in the mass production of carbon fibers. These companies include Toray (including its purchase of Zoltek), Toho Tenax, Mitsubishi Chemical, Formosa Plastics, SGL, Hexcel, DOW, and Kemrock [112, 121].

Analysts believe there is an excellent potential market opportunity for the use of carbon fibers in the construction industry [6, 113, 114]. An increasing demand for fiber-reinforced plastic bathtubs, doors, windows, and panels is being spurred on by the continual growth in the U.S. housing market [114]. Another application is concrete reinforced with carbon fibers (i.e., “carbon concrete”), which is increasingly being used to repair bridges and other aging structures [113]. Using carbon concrete to repair bridges that are in unsatisfactory condition is considered a major market opportunity. For example, more than 150,000 of the 600,000 bridges in the United States are considered unsuitable for the current or projected traffic demands, primarily because of corrosion of the steel reinforcement [122]. Germany is projected to invest up to €16B to €17B to repair or replace bridges by 2030 [113]. Although the cost of carbon-reinforced concrete is higher than steel-reinforced concrete, the higher cost is counterbalanced by its high specific properties such as lower weight relative to a steel-reinforced concrete deck (which reduces the load demand on the supporting structure), better corrosion resistance, better seismic protection, and lower erection and maintenance costs [122]. Worldwide demand for carbon concrete in 2013 was 2300 metric tons, representing revenues totaling $590M. An annual growth rate of 6 to 9% is projected through 2020, and revenues are projected to exceed $1B by 2022. Lowering the cost of carbon concrete is considered key to more rapidly increasing its use in the construction industry. Finding additional applications for carbon fiber and associated composites are also desired.

The Institute for Advanced Composites Manufacturing Innovation (IACMI) is working to advance the composite industry, developing new manufacturing techniques and identifying potential new markets. One project is aimed at optimizing vinyl ester resins and fiber sizings for the fabrication of carbon fiber composites. Advancements will increase scrap and material costs and applications within the automotive industry has been identified [123].

4.2.3 Carbon Nanotubes

CNTs, including single-walled carbon nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs), are used in polymers, electronics, plastics, and energy storage. The major application for CNTs is in composite fibers in polymers to improve thermal, electrical, and mechanical properties. This application accounted for over 60% of the market share in 2014. The high molecular complexity of graphene in MWCNTs increases their tensile strength. MWCNTs are increasingly being used in engineered polymers including polyetherimide, polycarbonate, and polyetheretherketone. The growing demand for polymers for use in the automotive and construction industries, particularly in China, India, Brazil, and the Middle East, is expected to spur market growth [9]. CNTs also are increasingly being used in the production of lithium-ion batteries for which their use can increase battery efficiency by a factor of 10. The application growth in lithium-ion batteries for use in grid and renewable energy storage is expected to increase the demand for CNTs for these applications.

The global CNT market demand for CNTs was slightly over ~5000 tons in 2014 and is projected to grow to over 20,000 tons by 2022 (Figure 4.7) [9]. This is orders of magnitude lower than for other carbon products such as carbon black (12 million tons per year). Estimates of market value range from $3.4B (2022) [9] to $5.6B in (2020) [124]. MWCNTs are the largest production segment given that their manufacturing cost is significantly lower than that of SWCNTs. Selling prices range from $50/lb (MWCNT at Hyperion Catalysis) to $600 per gram (SWCNT in defense and niche markets) [8].

The Asia Pacific region is the fastest growing market due to increasing domestic demand coupled with lower manufacturing costs compared to the United States and Europe. Among the major manufacturers of CNTs are Arkema S.A. (France), Arry International Group LTD. (China), Carbon Solutions Inc. (United States), Cheap Tubes Inc. (United States), CNano Technology LTD. (United States), CNT Company Ltd. (Korea), Continental Carbon Company (United States), Hanwha Chemical Co. Ltd. (Korea), Hyperion Catalysis international Inc. (United States), KLEAN CARBON Inc. (Canada), Kumho Petrochemical Company LTD. (South Korea), Nano-C Inc. (United States), Nanocyl S.A. (Belgium), NanoIntegris Inc. (United States), NanoLab, Inc. (United States), Nanoshel LLC (United States), Nanothinx S.A. (Greece), Showa Denko K.K. (Japan), SouthWest NanoTechnologies Inc. (United States), Thomas Swan and Co. Ltd. (United Kingdom), and Toray Industries, Inc. (Japan).

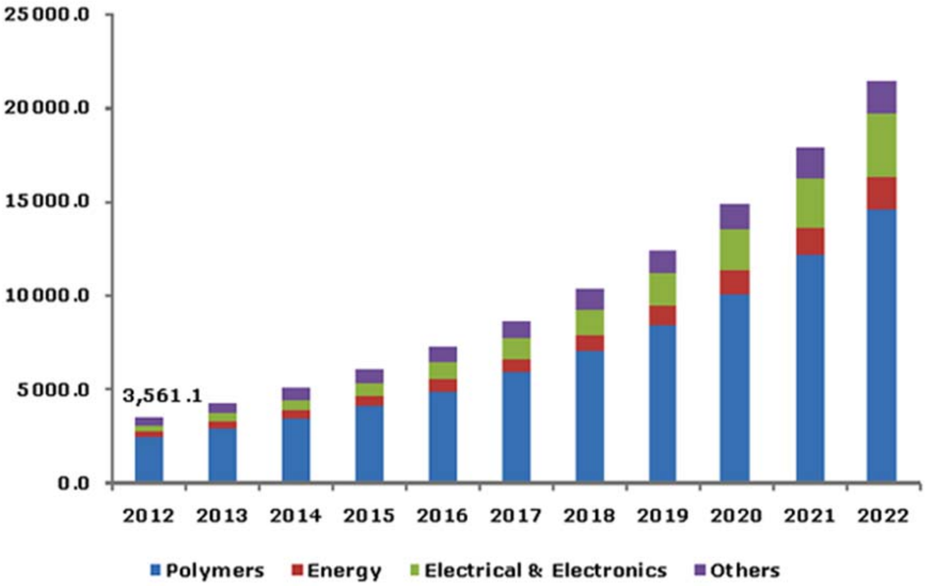


Figure 4.7. Global CNT Market Estimates and Forecast by Application from 2012 through 2022. Volume is in tons [9]. (Reproduced with permission from Grand View Research.)

4.2.4 Needle Coke

Needle coke is a premium grade, high-value petroleum coke used in the manufacturing of graphite electrodes for electric arc furnaces in the steel industry. The main differences between needle coke and ordinary coke are their structural characteristics, coefficients of thermal expansion, electrical conductivity, and oxidizability [125]. Needle coke has a high level of graphite resulting from its microcrystalline structure. A high level of anisotropy, large crystalline size, and large crystal areas must be achieved to obtain good quality needle coke [10]. The term “needle” is used to describe the acicular morphology of the coke; it tends to form oriented needle-like structures that are visible to the naked eye. The coefficient of thermal expansion is one of the most important characteristics of petroleum coke in evaluating the feasibility of using a particular coke in the production of graphitized items that have a high resistance to shock [125]. Put simply, carbon with a low coefficient of thermal expansion can dissipate thermal energy without cracking [10].

Needle coke is typically produced by delayed coking of the heavies remaining after catalytic cracking in a refinery. Delayed coking is a process for producing coke by transforming a complex mixture of aromatics to solid carbon [10]. It provides thermal energy to form the mesophase of the precursor during carbonization. To achieve excellent quality needle coke, two major steps are needed: first, coalescence of the mesophase to its formation and second, rearrangement of the mesophase in the solidification stage. Different starting materials will have different chemical make-ups, thus requiring different operating conditions. These conditions, particularly temperature and pressure, need to be optimized to achieve quality needle coke. Calcined needle coke is typically higher in carbon and lower in ash constituents, such as sulfur and metals, than standard calcined petroleum coke. A calcined form of needle coke is the raw material to produce graphite electrodes used in electric arc steel furnaces. The global market demand for needle coke is currently approximately 1.5M tons/yr. It has been reported that demand has increased in recent years and that this trend will continue.

4.2.5 Aromatics from Natural Gas

Solid carbon as a byproduct can reduce the cost of the CH_4 decomposition reaction only if sufficiently large markets for the carbon products are found. Muradov et al. [20] pointed out that if 100 million tons of H_2 were produced from CH_4 decomposition, approximately 300 million tons of byproduct carbon would be produced. However, annual worldwide consumption of all solid carbon products amounts to only 15 to 20 million tons, and it is unlikely that there will be any dramatic increase in carbon use in the near future (additional markets would need to be developed) [20].

An alternative to producing solid carbon product is the conversion of CH_4 into hydrocarbons such as ethylene and/or aromatics such as benzene, in addition to H_2. Ethylene and aromatics are commodity chemicals whose market sizes are greater than existing markets for elemental carbon. Ethylene is widely used in the chemical industry and had a worldwide production of over 150 million tons in 2016. It is used primarily to produce polyethylene, a widely used polymer. Ethylene is currently produced by the petrochemical industry by steam cracking heavier molecular weight hydrocarbons into smaller ones, which introduces unsaturation. This requires heating to high temperatures of 750 to 950^{o}C. This process is considered to be one of the most energy-intensive processes used by the chemical industry [126]. Aromatics such as benzene can also be produced via the aromatization reaction; ethylene is considered to be an intermediate product [127, 128]. Single-ring aromatics, including mixtures of benzene, toluene, and xylene (known as “BTX”), are generally produced primarily from two sources: refinery catalytic reforming and pyrolysis gasoline cracking from olefin production. BTX has a large global market demand of ~100 MT/year. Conventional feedstocks for BTX are currently being reduced because lighter feedstocks derived from U.S. natural gas availability are reducing the pyrolysis gasoline supply and gasoline production is declining [129]. A further supply reduction should occur as alternative fuel vehicles displace internal combustion engine (ICE) vehicles. Thus, there is some incentive to find alternative feedstocks for BTX in order to fulfill the potential demand. Additionally, the historical price differential between natural gas and petroleum is an economic incentive to examine aromatics from natural gas. Stoichiometrically, a majority of the H_2 in natural gas would be a byproduct of aromatics production, as illustrated in Table 4.1.

Table 4.1. Relative Hydrogen Production on Basis of Stoichiometry and Co-Product Values for Carbon, Benzene, and Ethylene Product Routes

Reaction	Hydrogen Molar Production Relative to C Co-Product Case (%)	Co-Product	Value, Co-Product (2014)[130]
$CH_4 \rightarrow C + 2H_2$	100.0	Carbon Black	58 ¢/lb
$CH_4 \rightarrow 1/6\ C_6H_6 + 9/6\ H_2$	75.0	Benzene	290 ¢/gal
$CH_4 \rightarrow ½\ C_2H_4 + H_2$	50.0	Ethylene	52.7 ¢/lb

We note that direct conversion of natural gas into hydrocarbon fuels and chemicals—not producing intermediate syngas—has been a long researched field. However, no direct CH_4 conversion processes have progressed to the commercial stage because technical challenges persist [131, 132]. For example, the yield to useful product and severe catalyst deactivation via formation of carbonaceous deposits (coking) and metal sintering are problematic [132, 133]. For non-oxidative catalytic CH_4 coupling to produce olefins or BTX directly, the use of high reaction temperatures (~ 1100°C) [127] or catalytic membranes to reduce the reaction temperatures (<900°C) by separating the H_2 from the carbon products [134] to achieve economically viable yields has met with limited success and faces a number of major technical challenges including catalyst stability, long-term durability of the ceramic membranes, and cost-effective methods for recovering the H_2. Furthermore, oxidative approaches often over-oxidize products (e.g., CO_2 formation) and often require costly separations [131]. Nonetheless, if these longstanding challenges could be overcome pyrolysis of CH_4 into hydrocarbons and hydrogen holds promise.

4.3 Techno-Economic Assessment

Commercial production of H_2 and a carbon product from the decomposition of natural gas will ultimately depend on the process economics. Capital investment and operating costs will vary with the technology choice and scale of operations, but it is possible to set some target prices based on information known at this time. The DOE Fuel Cell Technology Office (DOE-FCTO) has set the cost of H_2 dispensed and delivered at $4/gge (~$4/kg). The economic analysis presented below assumes the following simplifying assumptions:

- The selling price of H_2 is $4/kg
- The cost of CH_4 (as the raw material) represents a certain percentage, *x*, of the total sales revenue. The value of *x* will increase as the production process technology matures. That is, higher yield to desired products will lead to improvements in energy efficiency and lower capital investments. Larger plants will also improve the economics due to economies of scale. The product yields of H_2 and carbon are the same and proportional to their ratio in the CH_4 (i.e., 2 moles of H_2 per g-atom of carbon, or 4 g of H_2 per 12 g of carbon).

These assumptions allow one to set the lowest possible price for the carbon product at which the process can be economically viable. Figure 4.8 shows the relationship between the break-even price of the carbon product and the cost of CH_4 in the plant as a percentage of the revenue from selling the H_2 and carbon products for three different prices of natural gas. For example, with $x = 50\%$ and a natural gas price of $2.95 per million BTU (MBtu), the carbon product price needs to be greater than $6.53/kg.

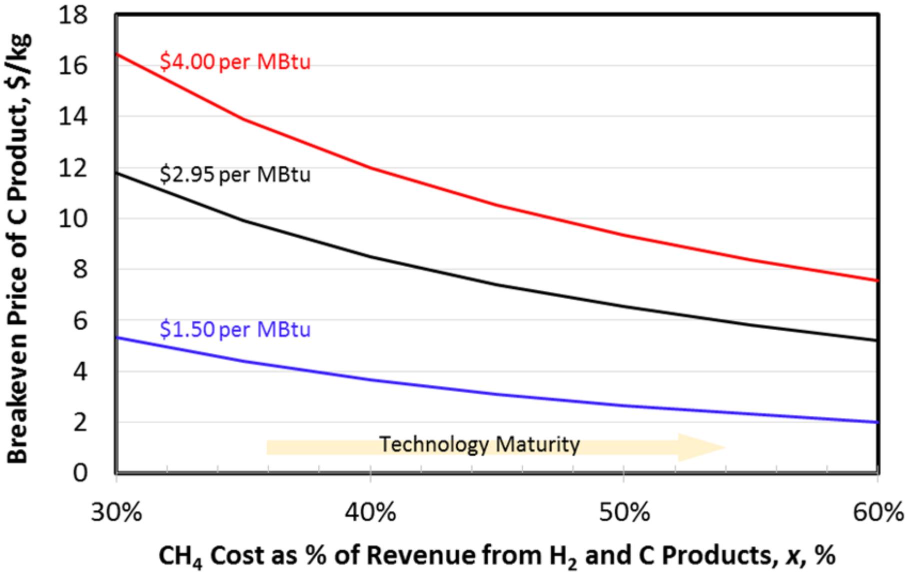


Figure 4.8. Break-Even Price of Carbon Products vs. the Cost of Methane as a Percentage of the Revenue from the Sale of Hydrogen and Carbon Products, as Functions of the Price of Methane. Price of H_2 = $4/kg.

It was found with this analysis that at less than a $1/kg, carbon black is not a viable final product. However, higher value products such as graphite, graphene, nanocarbons, and/or needle coke would enable the decomposition process to be economically viable.

With this high level pricing analysis in place, a separate set of process economics were evaluated in more detail for low-temperature plasma conversion of CH_4 using ASPEN modeling. The low-temperature plasma conversion was modeled at the small scale of 1900 kg H_2/day. Conversion at 700°C with a 100°C approach to equilibrium was used to determine the reaction products. An ASPEN Plus® simulation was used to determine the material and energy balance and operating costs. The ASPEN Process Economic Analyzer® was used to assess capital cost. The capital cost and unit ratio information was then transferred to an H2A spreadsheet for this process for economic evaluation.

The bottom-line energy requirements, CAPEX, byproduct production, and resulting H_2 cost summary is presented in 2007 U.S. dollars in Table 4.2. As expected it was found that the production and sale of carbon black in the plasma process reduces the net cost of H_2. However, it should be noted that the price assigned to the carbon black byproduct greatly affects the resulting H_2 cost, as illustrated in the sensitivity analysis shown in Figure 4.9 for the small-scale plasma case. In Table 4.2, we assume a carbon black selling price of $1.35/kg, resulting in an H_2 cost reduction from $7/kg down to $2.5/kg due to the byproduct credit. For comparison, the current cost of H_2 from steam methane reforming of natural gas is less than $2/kg over a wide range of natural gas prices and for different production volumes [135]. Nonetheless, these process economic results demonstrate how the cost of H_2 can be substantially driven down in emerging technologies such as plasma NG pyrolysis by the sale of valuable carbon byproduct- and the carbon selling price is a critical factor. Ongoing research and development is needed to further reduce the costs of such emerging technologies.

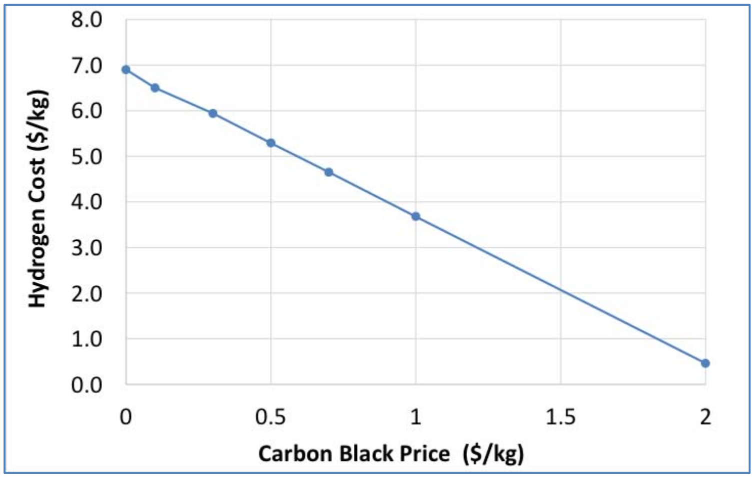


Figure 4.9. Sensitivity of Carbon Black Selling Price on Net Hydrogen Cost for the Small-Scale Plasma Case Study

Table 4.2. Hydrogen Cost, Requirements, and Byproduct Production Summary for the Techno-Economic Cases Analyzed in this Study. (Assumptions: hydrogen cost before compression and delivery; electricity price = \$0.056/kWh; natural gas price = \$5/MMBTU; carbon black selling price = \$1.35/kg.)

Technology	H_2 Production Scale (kg/day)	Electric Power Requirement (kWh/kgH_2)	Natural Gas Requirement (MMBtu/kgH_2)	CAPEX (MM\$)	Carbon Black Byproduct (kg/kgH_2)	H_2 Cost (\$/kg)
Plasma (Small Scale without Byproduct Credit)	1,914	16.1	0.26	11.4	3.1	7.0
Plasma (Small Scale with Byproduct Credit)	1,914	16.1	0.26	11.4	3.1	2.5

5.0 Technology Barriers to Commercial Implementation and R&D Opportunities

In Table 5.1, we summarize potential carbon products and provide an assessment of the status of natural gas conversion technology, major barriers to commercial implementation, and R&D needed to overcome these barriers. We focus here on solid carbon versus hydrocarbon (e.g., aromatic) products.

Table 5.1. Summary of Carbon Products and Natural Gas Conversion Technology Status, Major Barriers to Commercial Implementation, and R&D Needs to Overcome Barriers

Type of Carbon	Technology Status	Major Barriers in Technology Applications and Scaling Up	R&D Needed to Overcome Barriers
Carbon black, thermal	Commercialized	• Ability to produce multiple grades of carbon black using natural gas as a feedstock to provide greater flexibility to meet to market demand • Lack of downstream processes to recover and produce industrial-grade high-purity H_2 • Impact of producing industrial-grade high-purity H_2 on the overall process efficiency and production costs of carbon black • Production cost of H_2 needs to be competitive with H_2 produced by SMR	• Reaction studies to define operating parameters and reactor designs for producing different grades of carbon black • Separations and recovery process technology development to produce industrial-grade high-purity H_2 at a cost-competitive price • Demonstrate an integrated process for producing carbon black and recovering industrial-grade high-purity H_2 that maximizes overall product yields of carbon black and H_2 and produces both products at market-competitive prices • Techno-economic analysis to determine the cost of recovering H_2 and its impact on producing H_2 and carbon black at market-competitive prices at various production capacities

Type of Carbon	Technology Status	Major Barriers in Technology Applications and Scaling Up	R&D Needed to Overcome Barriers
Carbon black, plasma	Pilot-scale tests demonstrated, first commercial plant expected to be operational in 2018	• Ability to produce multiple grades of carbon black using natural gas as a feedstock to provide greater flexibility to meet to market demand • Lack of downstream processes to recover and produce industrial-grade high-purity H_2 • Impact of producing industrial-grade high-purity H_2 on the overall process efficiency and production costs of carbon black • Production cost of H_2 needs to be competitive with H_2 produced by SMR	• Reaction studies to define operating parameters and reactor designs for producing different grades of carbon black • Separations and recovery process technology development to produce industrial-grade high-purity H_2 at a cost-competitive price • Demonstrate an integrated process to produce carbon black and recover industrial-grade high-purity H_2 that maximizes overall product yields of carbon black and H_2 and produces both products at market-competitive prices • Techno-economic analysis to determine the cost of recovering H_2 and its impact on producing H_2 and carbon black at market-competitive prices at various production capacities
Carbon fiber	Commercialized	• Lower production capacity of the vapor-grown carbon nanofiber process compared to PAN- and pitch-based processes • Downstream processing to recover and produce industrial-grade high-purity H_2 • Impact of producing industrial-grade high-purity H_2 on the overall process efficiency and production costs of carbon fibers • Production cost of H_2 needs to be competitive with H_2 produced by SMR	• Process development to increase production capacity to allow vapor-grown carbon fibers process to compete with PAN- and pitch-based processes • Separations and recovery process development to recover industrial-grade high-purity H_2 • Demonstrate an integrated process to produce carbon fibers and recover industrial-grade high-purity H_2 that maximizes overall product yields of carbon fibers and H_2 and produces both products at market-competitive prices • Techno-economic analysis to determine the cost of recovering H_2 and its impact on producing H_2 and carbon fibers at market-competitive prices

Type of Carbon	Technology Status	Major Barriers in Technology Applications and Scaling Up	R&D Needed to Overcome Barriers
Carbon nanotubes	Commercialized	• Low production capacity of vapor-grown carbon nanotubes process • Downstream processing to recover and produce industrial-grade high-purity H_2 • Impact of producing industrial-grade high-purity H_2 on the overall process efficiency and production costs of carbon nanotubes • Production cost of H_2 needs to be competitive with H_2 produced by SMR	• Process development to increase production capacity of carbon nanotubes • Separations and recovery process development to recover industrial-grade high-purity H_2 • Demonstrate an integrated process to produce carbon nanotubes and recover industrial-grade high-purity H_2 that maximizes overall product yields of carbon nanotubes and H_2 and produces both products at market-competitive prices • Techno-economic analysis to determine the cost of recovering H_2 and its impact on producing H_2 and carbon nanotubes at market-competitive prices
Needle Coke	Commercialized	• Ability to produce highly crystalline needle coke from natural gas is not well understood • Downstream processing to recover and produce industrial-grade high-purity H_2 • Production cost of H_2 needs to be competitive with H_2 produced by SMR	• Process development aimed at producing needle coke needed • Understand quality of crystalline carbon formation and evaluate suitability as a needle coke precursor • Separations and recovery process development to recover industrial-grade high-purity H_2 • Techno-economic analysis to determine cost of recovering H_2 and its impact on producing H_2 and needle coke at market-competitive prices

6.0 Conclusions

The major findings and conclusions from this study are outlined below:

- Processes for decomposing natural gas to generate carbon and H_2 are attractive because of the current low cost of natural gas and the available infrastructure for delivery of natural gas to the conversion plant, which allows for flexibility in plant location. Production costs and demand for carbon and H_2 will be key factors in determining the optimal production capacity and location of these plants.
- Non-catalytic thermal decomposition of natural gas is currently used in the carbon black industry to produce carbon black for use in tires and electrical equipment, but natural gas as the feedstock has been largely replaced by heavy oil fractions from crude oil processing. H_2 is burned to provide process heat. Because these processes operate at high temperatures, off-gas treatment that significantly increases the capital cost is required to reduce nitrogen oxides and other emissions. Additionally, the high reaction temperatures required for CH_4 conversion contributes greatly to process inefficiencies. The high reaction temperatures also limit the choice of materials of construction, adversely impact catalyst life, and exacerbate heat losses.
  - Despite historically low natural gas prices, it is not clear whether existing oil-furnace process facilities can be retrofitted to burn natural gas (as is done in the power industry).
  - Emissions control, particularly of nitrogen oxides, is a major issue with many of the major U.S. carbon black producers that have been fined by the U.S. Environmental Protection Agency in recent years and have had to install expensive gas cleanup systems. This could be a major technical issue for a small-scale distributed facility.
  - The purity of the H_2 is not known because it is burned to provide process heat. Cleanup will be necessary to produce fuel-cell-quality H_2.
- Catalytic thermal decomposition has been extensively researched at the laboratory scale, primarily to reduce the temperature required for conversion. A wide range of metal and carbon-based catalysts have been reported in the literature. Nickle, cobalt, and iron are the most studied metal catalysts, and they produce both amorphous and structured carbons. Amorphous carbons such as activated carbon and carbon black are more active than structured carbons such as graphite and diamond. Data from the literature do not delineate the effect of catalysts and process conditions on the quality/morphology of the carbon product. Reactors have been demonstrated or proposed with intermittent fixed beds or fluidized beds.
  - At least one potentially commercial process, UOP's HYPRO™ process, was developed in the late 1960s, but it was not cost-competitive with SMR. Carbon was burned during the catalyst regeneration stage to generate process heat.
  - The National Aeronautics and Space Administration, the U.S. Department of Defense, and the DOE have funded a number of pilot-scale demonstrations for producing fuel-cell-quality H_2 in which the carbon is burned to regenerate the catalyst.
  - Although several highly-active catalyst material formulations have been employed, further catalyst material development is needed, since any process will require extensive recycling of the catalyst (i.e., carbon deposition/carbon removal). Catalyst mechanical stability will be an issue because the process of carbon deposition on catalysts surface leads to detaching the catalyst from the support as the carbon is deposited. Separation of the catalyst and the carbon byproduct remains a challenge.

  - Cost-competitive and process-effective technologies for recovering the carbon (separating the carbon from the catalyst) will require further R&D. It is not clear whether carbon can be recovered without having to burn a portion of it to fully regenerate the catalyst. Retention of a portion of the catalyst, particularly Ni-based catalysts, in the carbon product could be a regulatory problem.
  - It is not clear what effect catalysts have on the grade of carbon produced and how much this can be controlled by the catalyst. Optimizing the catalyst/process to produce the desired grade of carbon represents an R&D opportunity. Preventing the gas-deposition of carbon during a catalytic process could be a major issue depending on the grade of carbon being produced and product specifications.
  - Optimizing the process to produce both the desired grade of carbon and fuel cell-grade H_2, particularly if a carbon with very tight product specification is being produced, could be a major challenge. It may require less than ~100% single-pass CH_4 conversion, which increases the complexity with added separations and recycle burdens. Current processes for producing carbon are not overly concerned with the H_2 purity because the hydrogen is combusted to provide heat. It will be a major challenge for processes targeting high-value carbons, such as nanofibers, to achieve high-quality product carbon and H_2 products.
- Plasma processes for producing carbon and H_2 require electric power (expensive and produced with low efficiencies) and plasma gas.
  - Non-thermal equilibrium plasmas are not considered energetic enough to produce carbon and H_2 at the production scales required.
  - Studies have suggested that DC plasma processes could be economically competitive for producing H_2 with alternative processes. DC plasma processes operate at extremely high temperatures and producing large reaction volumes with DC plasma is an issue.
  - The AC three-phase plasma process is being commercialized by Monolith Materials in Hallam, Nebraska. The technology has been demonstrated at various pilot scales in Europe.
- Molten-metal technology has been reported and a major benefit is its relative ease of solid carbon separation from the molten metal. Density differences make separation of carbon from molten metal easier. However, high temperature for conversion still is required.
- Solar thermochemical processes rely on solar augmentation for heating. However, non-catalytic processes require high temperature (e.g., 1600°C) and this makes the use of costly materials of construction. Catalytic processes would drive down operating temperature requirements, but solid carbon handling remains an issue. Finally, the cost of a "solar" plant is an issue.
- Our techno-economic analysis suggests that the net cost of H_2 can be drastically reduced to below the $2/kg - the Office of Energy Efficiency & Renewable Energy H_2 cost target (before compression and delivery) when the carbon is sold as byproduct. However, the economics are largely driven by the value and quality of the carbon byproduct.
- No known commercial process produces both carbon and H_2 (fuel cell quality) as commercial products. There are commercial processes for producing carbon that burn some of the H_2 to provide process heat for the reaction and burn the rest to provide process heat to the facility or nearby facilities. There are also commercial processes for producing fuel-cell-quality H_2, but carbon is not recovered. Carbon is burned to regenerate the catalyst and to provide process heat.

Areas of opportunity for R&D in the CH_4 pyrolysis technical space include the following:

- The natural gas infrastructure allows for setting up a distributed H_2-refueling network and distributed fuel cell power networks. Producing H_2 is also achievable using SMR or water electrolysis using wind (or other renewable) energy. These processes also produce pressurized H_2. The natural gas decomposition process will have to compete with the above alternatives to produce a higher value product—derivable from the carbon combined with any environmental credit for not producing CO_2.
- High-pressure, low-temperature decomposition would reduce the cost of the product. Innovation/breakthroughs in technology will be required to overcome the thermodynamic limitations that restrict the high yields of H_2 and carbon at these conditions.
- Solid carbon separation, classification by value, and handling are key challenges. H_2 production is relatively easy because all of these processes use high temperatures. Even cleanup/purification is manageable with PSA. The next steps of compression and delivery drive up the cost of H_2. Therefore, a high-value byproduct is needed to offset this cost.
- High-value carbon markets do exist. For example, graphite is a high-value product used in lithium-ion batteries. Nanotube carbons also are high-value products (20 kilotons/yr by 2022). However, suitable technologies optimized for producing both H_2 and valuable carbon byproduct must be developed. Furthermore, solid carbon as a byproduct could reduce costs only if sufficiently large markets for the carbon products are found. One alternative to the production of solid carbon is the production of hydrocarbons such as BTX that have a large global market demand of ~100 million tons/yr. Challenges include low conversion levels and catalyst stability, which are key technological barriers to commercial implementation.
- The overarching challenges for producing these high-value carbon products are 1) identification of the conditions at which the different grades of carbon will be formed during the decomposition process, 2) separation of the different grades of carbon, and 3) competition from alternative feedstock sources. For example, petcoke from refineries is cheap and can be processed to produce graphite.

7.0 References

[1] Alibaba.com, "Market price for carbon black," https://www.alibaba.com/showroom/market-price-for-carbon-black.html, Accessed August 14, 2017.

[2] Grand View Research, "Carbon black market analysis by application (tires, high performance coatings, plastics) and segment forecasts to 2022," http://www.grandviewresearch.com/industry-analysis/carbon-black-market, Accessed August 14, 2017.

[3] Grand View Research, "Carbon black market size to reach USD 28.05 billion by 2022," http://www.grandviewresearch.com/press-release/global-carbon-black-market, Accessed August 14, 2017.

[4] Benchmark Mineral Intelligence, "Graphite demand from lithium ion batteries to more than treble in 4 years" http://benchmarkminerals.com/graphite-demand-from-lithium-ion-batteries-to-more-than-treble-in-4-years/, Accessed on August 14, 2017.

[5] S. Das, J. Warren, D. West, S.M. Schexnayder, *Global carbon fiber composites supply chain competitiveness analysis*, Technical Report ORNL/SR-2016/100 | NREL/TP-6A50-66071 Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2016. (https://www.nrel.gov/docs/fy16osti/66071.pdf, Accessed August 14, 2017)

[6] 2017 State of the Industry Report, "Composites Manufacturing," 2017, 22-27. (http://compositesmanufacturingmagazine.com/2017/01/composites-industry-report-2017/, Accessed August 14, 2017)

[7] T. Elmar Witten, Kraus, Michael Kuhnel, "Composites Market Report 2016 – Market developments, trends, outlook and challenges, 2016." (http://www.eucia.eu/userfiles/files/20161128_market_report_2016_english.pdf, Accessed August 14, 2017)

[8] Plastics Technology, "Carbon Nanotubes Lots of Potential – If the Price is Right," http://www.ptonline.com/articles/carbon-nanotubes-lots-of-potentialif-the-price-is-right, Accessed August 14, 2017.

[9] Grand View Research, "Carbon Nanotubes (CNT) Market Analysis By Product (Single Walled Carbon Nanotubes (SWCNT), Multi Walled Carbon Nanotubes (MWCNT)), By Application (Polymers, Energy, Electrical & Electronics) And Segment Forecasts To 2022," http://www.grandviewresearch.com/industry-analysis/carbon-nanotubes-cnt-market, Accessed August 14, 2017.

[10] H.P. Halim, J.S. Im, C.W. Lee, "Preparation of needle coke from petroleum by-products," *Carbon Lett.*, 14 (2013) 152-161.

[11] H.F. Abbas, W.M.A. Wan Daud, "Hydrogen production by methane decomposition: A review," *Int. J. of Hydrogen Energ.*, 35 (2010) 1160-1190.

[12] Y. Xu, X. Bao, L. Lin, "Direct conversion of methane under nonoxidative conditions," *J. Catal.*, 216 (2003) 386-395.

[13] J.R. Rostrup-Nielsen, J. Sehested, J.K. Nørskov, "Hydrogen and synthesis gas by steam and $C0_2$ reforming," *Adv. Catal.*, 47 (2002) 65-139.

[14] "Techno-Economic Evaluation of SME Based Standalone (Merchant) Hydrogen Plants with CCS," in *IEAGHG Technical Report*, I.E. Agency (Ed.), February 2017.

[15] N.Z. Muradov, T.N. Veziroğlu, "From hydrocarbon to hydrogen–carbon to hydrogen economy," Int. *J. Hydrogen Energ.*, 30 (2005) 225-237.

[16] A.M. Amin, E. Croiset, W. Epling, "Review of methane catalytic cracking for hydrogen production, Int. J. of Hydrogen Energ., 36 (2011) 2904-2935.

[17] M-J Wang, S.A. Reznek, K Mahmud, Y Kutsovsky, "Carbon Black," *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2003.

[18] A. Abánades, E. Ruiz, E.M. Ferruelo, F. Hernández, A. Cabanillas, J.M. Martínez-Val, J.A. Rubio, C. López, R. Gavela, G. Barrera, C. Rubbia, D. Salmieri, E. Rodilla, D. Gutiérrez, "Experimental analysis of direct thermal methane cracking," *Int. J. Hydrogen Energ.*, 36 (2011) 12877-12886.

[19] M.C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R.M. Navarro, J.L.G. Fierro, "Direct methane conversion routes to chemicals and fuels," *Catal. Today*, 171 (2011) 15-23.

[20] N.Z. Muradov, T.N. Veziroğlu, “Green” path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies, " *Int. J. of Hydrogen Energ.*, 33 (2008) 6804-6839.

[21] N.Z. Muradov, "Hydrogen production via catalytic reformation of fossil and renewable feedstock," Florida Solar Energy Center, 2005.

[22] N.Z. Muradov, Thermocatalytic CO2-free production of hydrogen from hydrocarbon fuels. , Proceedings of the 2002 U.S. DOE Hydrogen Program Review, 2002.

[23] S. Ahmed, A. Aitani, F. Rahman, A. Al-Dawood, F. Al-Muhaish, "Decomposition of hydrocarbons to hydrogen and carbon," *Appl. Catal. A: Gen.*, 359 (2009) 1-24.

[24] R.V. Wheeler, W.L. Wood, "The pyrolysis of methane," *Fuel*, 7 (1928) 535-539.

[25] F. Fischer, H. Pichler, Uber die Thermische Zersetzung von Methan. Brennst- Chem., 13 (1932) 381-383.

[26] A. Holmen, O. Olsvik, O.A. Rokstad, "Pyrolysis of natural gas: chemistry and process concepts," *Fuel Process. Technol.*, 42 (1995) 249-267.

[27] H. Blanquart, H. Pitsch, "Analyzing the effects of temperature on soot formation with a joint volume-surface-hydrogen model," *Combust. Flame*, 156 (2009) 1614-1626.

[28] A. Holmen, O.A. Rokstad, A. Solbakken, "High-Temperature Pyrolysis of Hydrocarbons. I. Methane to Acetylene," *Ind. Eng. Chem., Proc. D.D.*, 15 (1976) 439-444.

[29] J.W. Snoeck, G.F. Froment, M. Fowles, "Kinetic study of the carbon filament formation by methane cracking on a nickel catalyst," *J. Catal.*, 169 (1997) 250-262.

[30] Outotec Pori Research Center, "Outokumpu HSC Chemistry 5, "Pori, Finland, 2002, https://www.scribd.com/document/81923599/00-HSC-Chemistry-5.

[31] J.L. Pinilla, R. Utrilla, M.J. Lazaro, I. Suelves, R. Moliner, J.M. Palacios, "A novel rotary reactor configuration for simultaneous production of hydrogen and carbon nanofibers," I*nt. J. Hydrogen Energ.*, 34 (2009) 8016-8022.

[32] V.V. Chesnokov, A.S. Chichkan, "Production of hydrogen by methane catalytic decomposition over Ni–Cu–Fe/Al2O3 catalyst," *Int. J. Hydrogen Energ.*, 34 (2009) 2979-2985.

[33] L. Fulcheri, Y. Schwob, "From methane to hydrogen, carbon black and water," *Int. J. Hydrogen Energ.*, 20 (1995) 197-202.

[34] S. Lynum, K. Haugsten, K. Hox, J. Hugdahl, N. Myklebust, "A method for decomposition of hydrocarbons," European Patent Application EP0616599, February 28, 1996.

[35] R.F. Fincke, R.P. Anderson, T.A. Hyde, B.A. Detering, "Plasma Pyrolysis of Methane to Hydrogen and Carbon Black," *Ind. Eng. Chem. Res.*, 41 (2002) 1425-1535.

[36] H. Jabs, D. Westerheim, B. Hennings, D. Soekamto, S. Shandy, Z. Minevski, A.J. Cisar, "Hydrogen production using plasma-based reformation," U.S. Patent Application No. US20070267289, November 22, 2007.

[37] N. Muradov, Z. Chen, F. Smith, "Fossil hydrogen with reducedCO_2 emission: Modeling thermocatalytic decomposition of methane in a fluidized bed of carbon particles," *Int. J. Hydrogen Energ.*, 30 (2005) 1149-1158.

[38] A. Abánades, C. Rubbia, D. Salmieri, "Technological challenges for industrial development of hydrogen production based on methane cracking," *Energy*, 46 (2012) 359-363.

[39] S. Fukuda, N. Nakamura, J. Monden, M. Nishikawa, "Experimental study of cracking methane by Ni/SiO_2 catalyst," *J. Nucl. Mater.*, 329-333 (2004) 1365-1369.

[40] O. Olsvik, F. Billaud, "Thermal coupling of methane. A comparison between kinetic model data and experimental data," *Thermochim. Acta*, 232 (1994) 155-169.

[41] F. Rodríguez-Reinoso, "The role of carbon materials in heterogeneous catalysis," *Carbon*, 36 (1998) 159-175.

[42] N. Muradov, F. Smith, A. T-Raissi, "Catalytic activity of carbons for methane decomposition reaction, *Catal. Today*, 102–103 (2005) 225-233.

[43] J.L. Pinilla, I. Suelves, M.J. Lazaro, R. Moliner, "Kinetic study of the thermal decomposition of methane using carbonaceous catalysts," *Chem. Eng. J.*, 138 (2008) 301-306.

[44] F.A. Abbas, W.M.A. Wan Daud, "Hydrogen production by thermocatalytic decomposition of methane using a fixed bed activated carbon in a pilot scale unit: Apparent kinetic, deactivation and diffusional limitation studies," *Int. J. Hydrogen Energ.*, 35 (2010) 12268-12276.

[45] J.-C. Charlier, F. Fabry, G. Flamant, L. Fulcheri, J. Gonzalez, E. Grivei, T.-M. Gruenberger, H. Okuno, N. Probst, *Carbon nanostructures and process for the production of carbon-based nanotubes, nanofibres and nanostructures*, Armines Association Pour la Recherche et le Development des Methodes et Processis Industriels, Paris (France); Timcal SA, Bodio (Chile), 2007.

[46] L. Fulcheri, Y. Schwob, "From methane to hydrogen, carbon black, and water," *Int. J. Hydrogen Energ.*, 20 (1995) 197-202.

[47] Y. Schwob, F. Fischer, L. Fulcheri, P. Willemez, *Conversion of carbon or carbon-containing compounds in a plasma*, Armines, Paris, France; Timcal Ltd., Bodio, Switzerland, 2000.

[48] F. Fabry, E. Grivei, L. Fulcheri, P. Leroux, N. Probst, N. Smet, J.-Y. Peroy, G. Flamant, F. Fischer, "Device and method for converting carbon containing feedstock into carbon containing materials having a defined structure," U.S. Patent Application US20090142250 A1, Published June 4, 2009.

[49] L. Fulcheri, N. Probst, G. Flamant, F. Fabry, E. Grivei, X. Bourrat, "Plasma processing: A step towards the production of new grades of carbon black," *Carbon*, 40 (2002) 169-176.

[50] M. Dors, H. Nowakowska, M. Jasinski, J. Mizeraczyk, "Chemical kinetics of methane pyrolysis in microwave plasma at atmospheric pressure," *Plasma Chem. Plasma P.*, 34 (2014) 313-326.

[51] K. Konno, K. Onoe, Y. Takiguchi, T. Yamaguchi, "Direct preparation of hydrogen and carbon nanotubes by microwave plasma decomposition of methane over Fe/Si activated by biased hydrogen plasma," *Green and Sustainable Chemistry*, 3 (2013) 19-25.

[52] W. Cho, S.-H. Lee, W.-S. Ju, Y. Baek, J.K. Lee, "Conversion of natural gas to hydrogen and carbon black by plasma and application of plasma carbon black," *Catal. Today*, 98 (2004) 633-638.

[53] B. Wang, G. Xu, "Conversion of methane to C–2 hydrocarbons via cold plasma reactions," *J. Natural Gas Chem.*, 12 (2003) 178-182.

[54] A. Indarto, J.-W. Choi, H. Lee, H.K. Song, "Methane conversion using dielectric barrier discharge: comparison with thermal process and catalyst effects," *J. Nat. Gas Chem.*, 15 (2006) 87-92.

[55] N. Muradov, F. Smith, G. Bockerman, K. Scammon, "Thermocatalytic decomposition of natural gas over plasma-generated carbon aerosols for sustainable production of hydrogen and carbon," *Appl. Catal. A: Gen.*, 365 (2009) 292-300.

[56] X. Tao, M. Bai, X. Li, H. Long, S. Shang, Y. Yin, X. Dai, "CH_4–CO_2 reforming by plasma – challenges and opportunities," *Prog. Energ. Combust.*, 37 (2011) 113-124.

[57] B. Longmier, A. Gallimore, N. Hershkowitz, "Hydrogen production from methane using an RF plasma source in total nonambipolar flow," *Plasma Sources Sci. T.*, 21 (2012) 8pp.

[58] J.R. Fincke, R.P. Anderson, T.A. Hyde, B.A. Detering, "Plasma pyrolysis of methane to hydrogen and carbon black," *Ind. Eng. Chem. R.*, 41 (2002) 1425-1435.

[59] C.-H. Tsai, K.-T. Chen, "Production of hydrogen and nano carbon powders from direct plasmalysis of methane," *Int. J. Hydrogen Energ.*, 34 (2009) 833-838.

[60] V. Vinokurov, R. Sharafutdinov, Y. Tychkov, "Plasma-chemical processing of natural gas," *Chemsitry and Technology of Fuels and Oils*, 41 (2005) 112-115.

[61] S.K. Kim, J.H. Seo, J.S. Nam, W.T. Ju, S.H. Hong, "Production of hydrogen and carbon black by methane decomposition using DC-RF hybrid thermal plasmas," I*EEE T. Plasma Sci.*, 33 (2005) 813.

[62] N. Muradov, "Thermocatalytic CO_2-free production of hydrogen from hydrocarbon fuels," *Proceedings of the 2002 U.S. Department of Energy Hydrogen Review*, 2002, pp. 227, Washington, D.C.

[63] T. Geibler, A. Abánades, A. Heinzel, K. Mehravaran, G. Müller, R.K. Rathnam, C. Rubbia, D. Salmieri, L. Stoppel, S. Stückrad, A. Weisenburger, H. Wenninger, T. Wetzel, "Hydrogen production via methane pyrolysis in a liquid metal bubble column reactor with a packed bed," *Chem. Eng. J.*, 299 (2016) 192-200.

[64] R.G. Wulff, "Process of producing acetylene gas," U.S. Patent No. 2037056, April 14,1936.

[65] "UOP Process cleaves hydrogen from hydrocarbons," *Chem. Eng.*, 69 (1962) 90.

[66] N.Z. Muradov, *Thermocatalytic process for CO_2-free production of hydrogen and carbon from hydrocarbons, Final Report*, United States Department of Energy Under Cooperative Agreement: No. DE-FC36-99GO10456 08/01/1999 - 08/31/2003 (https://www.osti.gov/scitech/servlets/purl/828215, Accessed August 14, 2017.

[67] N.Z. Muradov, "CO_2-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuel," *Energ. Fuel*, 12 (1998) 41-48.

[68] B.P. Ennis, "Electric reaction technology for fuels processing," U.S. Patent No. 7563525, July 21, 2009.

[69] J. Weill, C.J. Cameron, C. Raimbult, "IFP processes for the direct conversion of methane into higher hydrocarbons," Presented at The European Oil and Gas Conference: a multidisciplinary approach in exploration and production R&D, Kluwer Academic Publishers Group, Norwell MA 02061 USA, Palermo, Italy, 1990, pp. 544.

[70] M. Steinberg, "Fossil fuel decarbonization technology for mitigating global warming," *Int. J. Hydrogen Energ.*, 24 (1999) 771.

[71] http://www.arenius.systems, Accessed August 14, 2017.

[72] A. Bode, D.W. Agar, K. Buker, V. Goke, M. Hensmann, U. Janhsen, D. Klingler, J. Schlichting, S.A. Schunk, "Research cooperation develops innovative technology for environmentally sustainable syngas production from carbon dioxide and hydrogen," Presented at the 20th World Hydrogen Energy Conference, Gwangju Metroplolitan City, Korea, June 16-21,2014.

[73] M. Kern, F. Glenk, D. Klingler, A. Bode, G. Kolios, S. Schunk, G. Wasserschaff, J. Bernnat, B. Zoels, S. Schmidt, R. Koenig, "Parallel preparation of hydrogen, carbon monoxide, and a carbon-comprising product, U.S. Patent Application No. 20150336795, November 26,2015.

[74] H.-J. Maass, V. Goeke, O. Machhammer, M. Guzmann, C. Schneider, W.A. Hormuth, A. Bode, D. Klingler, M. Kern, G. Kolios, "Method for the parallel production of hydrogen and carbon-containing products," U.S. Patent No. 9359200, June 7, 2016.

[75] Monolith, "Olive Creek Plant," http://monolithmaterials.com/olive-creek/, Accessed August 14, 2017.

[76] Monolith, "Nebraska Project Updates," http://monolithmaterials.com/olive-creek/project-update-details/, Accessed August 14, 2017.

[77] S. Lynum, N. Myklebust, K. Hox, "Decomposition of hydrocarbon to carbon black," U.S. Patent 6 068 827, May 30, 2000.

[78] GlassPlas, The plasma revolution," http://www.gasplas.com/resources/upload/news/160_110608_GasPlas_Presentation_UEA-email%201.pdf, Accessed August 14, 2017.

[79] N.Z. Muradov, "How to produce hydrogen from fossil fuels without CO_2 emissions," *Int. J. Hydrogen Energ.*, 18 (1993) 211-215.

[80] N.Z. Muradov, T.N. Veziroglu, "From hydrocarbon to hydrogen–carbon to hydrogen economy," I*nt. J. Hydrogen Energ.*, 30 (2005) 225-237.

[81] A. Steinfeld, V. Kirillov, G. Kuvshinov, Y. Mogilnykh, A. Reller, "Production of filamentous carbon and hydrogen by solarthermal catalytic cracking of methane," *Chem. Eng. Sci.*, 52 (1997) 3599-3603.

[82] A. Steinfeld, "Solar thermochemical production of hydrogen—A review," *Sol. Energy*, 78 (2005) 603-615.

[83] D. Hirsch, A. Steinfeld, "Solar hydrogen production by thermal decomposition of natural gas using a vortex-flow reactor," *Int. J. Hydrogen Energ.*, 29 (2004) 47-55.

[84] M.M. Moshrefi, F. Rashidi, H.R. Bozorgzadeh, S.M. Zekordi, "Methane conversion to hydrogen and carbon black by DC-spark discharge," *Plasma Chem. Plasma P.*, 32 (2012) 1157-1168.

[85] J.P. Risby, D. Pennington, "Method for processing a gas an device for performing the method," U.S. Patent Application 14/180981, 2014.

[86] J. Erlebacher, B. Gaskey, "Method of carbon dioxide-free hydrogen production from hydrocarbon decomposition over metal salts, U.S. Patent Application 20170240421.

[87] J. Erlebacher to T. Krause (Private Communication), June 15, 2017.

[88] M. Steinberg, H.C. Cheng, "Modern and prospective technologies for hydrogen production from fossil fuels," *Int. J. Hydrogen Energ.*, 14 (1989) 797-820.

[89] U.S. Department of Energy Energy Information Administration, "Natural gas," https://www.eia.gov/naturalgas/data.php, Accessed August 14, 2017.

[90] U.S. Department of Energy Energy Information Administration, *Annual Energy Outlook 2017* (Available online at https://www.eia.gov/outlooks/aeo/pdf/0383(2017).pdf).

[91] U.S. Department of Energy Energy Information Administration, "North American shale plays." https://www.eia.gov/oil_gas/rpd/northamer_gas.pdf, Accessed August 14, 2017.

[92] D. Brown, "U.S. and World Hydrogen Production – 2014," *CryoGas International*, March 2016, 32-33.

[93] D. Brown, "U.S. Hydrogen Production – 2015, " *CryoGas International*, July 2016, 22-23.

[94] Florida Solar Energy Center, "Hydrogen production – Basics," http://www.fsec.ucf.edu/en/consumer/hydrogen/basics/production.htm, Accessed August 14, 2017.

[95] D. Brown, "Hydrogen supply and demand – Past, present, and future," *Gasworld*, April 2016, 37-40.

[96] D. Brown, "Hydrogen production and consumption in the U.S. – The last 25 years, *CryoGas International*, September 2015, 38-39.

[97] R. Cockerill, "Supply and demand – Start-ups signal a shift in future hydrogen supply," *Gasworld*, October 2016.

[98] Markets and Markets, Hydrogen generation market worth 154.74 billion USD by 2022, http://www.marketsandmarkets.com/PressReleases/hydrogen.asp, Accessed August 14, 2017.

[99] Monolith, "Fact sheet," http://monolithmaterials.com/wp-content/uploads/2016/09/Monolith-Fact-Sheet-2016.pdf, Last accessed March 1, 2017.

[100] U.S.E.P. Agency, AP 42, *Fifth Edition Compilation of Air Pollutant Emission Factors*, Chapter 6 Organic Chemical Process Industry (Available online at https://www3.epa.gov/ttnchie1/ap42/ch06/final/c06s01.pdf) Accessed August 14, 2017.

[101] G. Kühner, M. Voll, *Carbon black: Science and technology*, Marcel Dekker, New York, 1993.

[102] ASTM, Designation D1765-16, "Standard Classification System for Carbon Blacks Used in Rubber Products," (https://compass.astm.org/EDIT/html_annot.cgi?D1765+17), Accessed August 14, 2017.

[103] Sid Richardson Carbon & Energy Co., "Carbon Black 101," (http://www.sidrich.com/products-and-pricing/education/how-carbon-black-is-made/), Accessed August 14, 2017.

[104] Sid Richardson Carbon & Energy Co., "2015 NFTA Carbon Black Industry Report – A Year Later, (Available online at http://www.sidrich.com/files/1614/2904/5204/A-Year-Later_SidRich.pdf), Accessed August 14, 2017.

[105] Carbon Black Sales, "Carbon black – World sales," http://carbonblacksales.com/carbon-black-reinforcing-agent/, Accessed August 14, 2017.

[106] Cision, "Growth opportunities in the United States carbon black market 2016-2021: Trends, forecast, and opportunity analysis, August 2016," https://www.prnewswire.com/news-releases/growth-opportunities-in-the-united-states-carbon-black-market-2016-2021-trends-forecast-and-opportunity-analysis-august-2016-300391570.html, Accessed on 2017.

[107] Wikipedia, "Carbon nanotube," https://en.wikipedia.org/wiki/Carbon_nanotube, Accessed August 21, 2017.

[108] Northern Graphite, "The graphite supply problem," http://northerngraphite.com/the-graphite-supply-problem/, Accessed August 14, 2017.

[109] Mining Feeds, "Graphite: Supply and Demand," http://www.miningfeeds.com/2012/02/14/graphite-supply-and-demand, Accessed August 14, 2017.

[110] Wikipedia, "Graphene," https://en.wikipedia.org/wiki/Graphene#Production, Accessed August 14, 207.

[111] S.D. Robertson, "Carbon formation from methane pyrolysis over some transition metal surfaces – I. Nature and properties of the carbons formed," *Carbon*, 8 (1970) 395-400.

[112] S.-J.P.a.S.-Y. Lee, "History and Structure of Carbon Fibers," In S.-J. Parks (Ed.) *Carbon Fibers*, Springer Series in Materials Science 2010, Springer, 2015.

[113] M.K. Thomas Kraus, "Global carbon fibre market remains on upward trend," REINFORCEDplastics, (2014) 38-45.

[114] S. Mazumdar, "Annual State of the Composites Industry Report," Composites Manufacturing (2016) 19-23.

[115] A. Milbrandt, S. Booth, "Carbon fiber from biomass," Clean Energy Manufacturing Analysis Center (CEMAC), https://www.nrel.gov/docs/fy16osti/66386.pdf, Accessed October 31, 2017.

[116] G.-Y.H. Soo-Jin Park, "Precursors and manufacturing of carbon fibers," In S.-J. Park (Ed), *Carbon Fibers*, Springer Series in Materials Science 210, 2015.

[117] D.A. Baker, T.G. Rials, "Recent advances in low-cost carbon fiber manufacture from lignin," *J. Appl. Polym. Sci.*, 130 (2013) 713-728.

[118] M. Endo, M. Dresselhaus, "Carbon Fibers and Carbon Nanotubes, "Science unpublished, 2003 (Available online at http://web.mit.edu/tinytech/Nanostructures/Spring2003/MDresselhaus/i789.pdf, Accessed August 14, 2017).

[119] G. Tibbets, "Carbon fibers produced by pyrolysis of natural gas in stainless steel tubes," *Appl. Phys. Lett.*, 42 (1983) 666-668.

[120] D.B. R. Alig, E. Kennel, M Lake, *Final Report: Development of pilot plant for the production of vapor grown carbon fiber from Ohio coal*, November 2000 (https://www.osti.gov/scitech/servlets/purl/1185202/, Accessed August 14, 2017).

[121] S. Das, J. Warrin, S. M. Schexnayder, *Global carbon fiber composites supply chain competitiveness analysis*, Technical Report ORNL/SR-2016/100 | NREL/TP-6A50-66071, Oak Ridge National Laboratory, Oak Ridge, TN, 2016.

[122] H.E. Brent Kawahara, Luke S. Lee, "Life-cycle cost comparison for steel reinforced concrete and fiber reinforced polymer bridge decks," In: R.J.a.L. Lee (Ed.) *Fiber Reinforced Polymer (FRP) Composites for Infrastructure Applications*, Springer, 2012.

[123] IACMI, https://iacmi.org/2017/06/21/iacmi-the-composites-institute-and-material-innovation-technologies-partner-on-carbon-fiber-project/, Accessed August 14, 2017.

[124] Markets and Markets, http://www.marketsandmarkets.com/PressReleases/carbon-nanotubes.asp), Accessed August 14, 2017.

[125] V.V. Fryazinov, B.M. Ezhov, V.S. Goryunov, R.N. Gimaev, R.K. Sadykov, M.M. Akhmetov, S.M. Slutskaya, A.A. Abrosimov, V.P. Zaporin, "Production of needle coke," *Chem. Tech. Fuels Oil*, 16 (1980) 163-165.

[126] E. Worrell, D. Phylipsen, D. Einstein, N. Martin, "Energy use and energy intensity of the U.S. chemical industry," In E.A. Department (Ed.) Ernest Orlando Lawrence Berkeley National Laboratory, 2000.

[127] X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wei, D. Tan, R. Si, S. Zhang, J. Li, L. Sun, Z. Tang, X. Pan, X. Bao, "Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen," *Science*, 344 (2014) 616-619.

[128] Y. Liu, D. Li, T. Wang, Y. Liu, T. Xu, Y. Zhang, "Efficient conversion of methane to aromatics by coupling methylation reaction," *ACS Catalysis*, 6 (2016) 5366-5370.

[129] E.V. Makshina, M. Dusselier, W. Janssens, J. Degreve, P.A. Jacobs, B.F. Sels, "Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene," *Chem. Soc. Rev.*, 43 (2014) 7917-7953.

[130] ICIS Chemical Pricing (2014), icis.com, 2014.

[131] J.H. Lunsford, "Catalytic conversion of methane to more useful chemicals and fuels: A challenge for the 21st century," *Catal. Today*, 63 (2000) 165-174.

[132] A. Holmen, "Direct conversion of methane to fuels and chemicals," *Catal. Today*, 142 (2009) 2-8.

[133] J. Gao, Y.T. Zheng, J.M. Jehng, Y.D. Tang, I.E. Wachs, S.G. Podkolzin, "Identification of molybdenum oxide nanostructures on zeolites for natural gas conversion," *Science*, 348 (2015) 686-690.

[134] L. Li, R.W. Borry, E. Iglesia, "Design and optimization of catalysts and membrane reactors for the non-oxidative conversion of methane," *Chem. Eng. Sci.*, 57 (2002) 4595-4604.

[135] DOE Hydrogen and Fuel Cells Program Record #12024: Hydrogen Production Cost Using Low-Cost Natural Gas, https://www.hydrogen.energy.gov/pdfs/12024_h2_production_cost_natural_gas.pdf, Accessed on September 13, 2017.

R&D Opportunities For Development of Natural Gas Conversion Technologies

For Co-Production of Hydrogen and Value-Added Solid Carbon Products

Argonne NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY

ANL-17/11; PNNL-26726 • November 2017