

GAS-TO-LIQUIDS RESEARCH PROGRAM OF THE U.S. DEPARTMENT OF ENERGY  
A PROGRAMMATIC OVERVIEW

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ABSTRACT

Commercially viable technology development for converting light hydrocarbon gases to value-added fuel forms and chemicals is of strategic and scientific importance for responding to the growing needs for energy security, environmentally superior liquid fuels, and economic stimulation from introducing new technologies in the market place. To assist the development of technologies, the United States Department of Energy (USDOE) established the Gas-to-Liquids Research Program. This paper describes the Gas-to-Liquids technology development projects sponsored by the Pittsburgh Energy Technology Center (PETC) of the USDOE.

INTRODUCTION

Current proven world reserves of natural gas are estimated at around 4500 trillion cubic feet (TCF), approximately half of which is in remote areas (1, 2). Additionally, 400 TCF are occluded as coal bed methane in the U.S.(3). A potentially huge source of natural gas as gas hydrates has also been reported in the literature (4). Flaring of associated (oil field) gas in some regions of the world and venting of coal bed methane contribute to greenhouse effects. In energy equivalence terms, natural gas production has been predicted to grow faster than oil, but technology growth areas are not yet identified except for the electric utility sector (5). However, at identical capacity factors, it costs more to generate electricity by burning natural gas than coal. Monetization of natural gas by upgrading to value-added products, such as environmentally superior transportation fuels that will exceed requirements of the 1990 Clean Air Act Amendments (CAAA), is an attractive option. For effective utilization, natural gas reserves in remote areas will have to be converted to liquid hydrocarbon products on site and then transported to the marketplace. The increase in the Federal Energy Resources budget over the fiscal year 1994 appropriation shows government encouragement to develop natural gas utilization technologies.

In 1991, the Pittsburgh Energy Technology Center (PETC) of the United States Department of Energy (USDOE) issued a Program Research and Development Announcement (PRDA) inviting proposals for the development and demonstration of technologies for economical conversion of methane and other light hydrocarbon gases to transportation fuels and chemicals. The seven selected awards represented an optimal mix of projects believed to maximize the probability of achieving USDOE's overall objectives.

Methane conversion technologies will allow efficient utilization of our Nation's abundant supply of natural gas to manufacture the cleanest burning fuels, and the new technologies can be easily integrated into the existing refinery and distribution system. USDOE supported gas-to-liquids program to conserve natural gas will help the agency deliver its role in implementing the Climate Change Action Plan aimed at reducing carbon dioxide emissions.

HISTORY

Natural gas was first used as a fuel by the Chinese for lighting, circa 250 A.D., by piping it through bamboo tubes. In the United States, natural gas was first discovered in Fredonia, New York, in 1821 but was not considered a fuel source (4). After World War II, natural gas was recognized as a fuel commodity.

During the 1950s, natural gas dominated the market of fuel-gas industries. Gas pipelines were installed countrywide, reaching from gas fields to homes and factories. Natural gas not only became a predominating fuel gas, it also qualified as an important feedstock for synthesis of various liquid fuels, chemicals, and intermediates.

In the early 1950s, a commercial natural gas-to-liquid fuels plant was built by the Carthage Hydrocol Company in Brownsville, Texas. However, due to the availability of cheap Middle Eastern petroleum, the operation was not economical, and thus the plant was shut down. A 14,500 barrel-per-day natural gas-to-gasoline plant started operating in New Zealand in 1985 and was on stream producing 87 octane unleaded gasoline until recently. In this process, natural gas was first converted to methanol via synthesis gas, followed by conversion of methanol to gasoline using a novel catalyst developed by Mobil in the 1970s. A portion of Mobil's development efforts was funded by the Fossil Energy Program of the USDOE. In April 1993, Exxon announced its AGC-21 Advanced Gas Conversion Technology for converting natural gas to high quality refinery feedstock (6). Olefin-based transportation fuels from natural gas is produced in the Mossgas plant in South Africa (7). Recently, Shell Gas B.V. built a 12,000 barrels per day natural gas-to-middle distillate plant in Malaysia (8).

#### GAS-TO-LIQUIDS CONVERSION TECHNOLOGIES

Coupling of two methane molecules to higher hydrocarbons is not thermodynamically feasible because the energy of formation is not favorable. However, in the presence of a co-reactant, such as oxygen, the reaction path can be altered, and methane conversion reactions can be successfully carried out. Natural gas (primarily methane) can be upgraded to higher hydrocarbons either by direct conversion routes (single-step or staged), or via synthesis gas (a mixture of carbon monoxide and hydrogen). In this paper, the synthesis gas based process is termed the indirect process. A discussion of terminology classifying methane conversion processes can be found in the literature (9). The important process considerations for commercially viable natural gas upgrading operations are methane conversion rate and selectivity to preferred products.

Based on chemistry, the processes for natural gas upgrading include 1) partial oxidation to oxygenates, such as methanol, 2) oxidative coupling to higher hydrocarbons, such as ethylene, 3) derivatization, such as oxyhydrochlorination to chlorinated hydrocarbons, which are subsequently converted to higher hydrocarbons, and 4) pyrolysis to aromatic and/or higher hydrocarbons.

In the indirect process, natural gas is first converted to synthesis gas, followed by catalytic hydrogenation of the carbon monoxide in a synthesis reactor to a variety of higher hydrocarbon fuels. Fischer-Tropsch (FT) synthesis and its variants are important synthesis reactions, involving low-pressure conversion of synthesis gas to gasoline, diesel fuel, wax, and oxygenates. The products of reaction depend on the temperature, pressure, and catalyst used in the synthesis reactor.

#### PETC'S GAS-TO-LIQUIDS PROGRAM

The goals of PETC's Gas-to-Liquids program can be summarized as follows:

- Discover new chemistry and catalysts for the conversion of methane and other light hydrocarbon gases to value-added, easily transportable fuels and chemicals.
- Obtain necessary design and engineering information to develop prototype technologies for demonstration and commercial deployment.
- Pursue cost-shared, risk-shared, industry-driven R&D, demonstration, and technology transfer to ensure pay-off of Federal R&D investments.
- Contribute to energy policy goals by selecting investments consistent with the four major policy thrusts:
  - Energy security

- Economic growth
- Environmental quality improvement
- Enhancing scientific foundations.

PETC's program consists of R&D activities in several natural gas conversion chemistries. They will be discussed in the following groups (10):

- Partial Oxidation
- Oxidative Coupling
- Pyrolysis
- Derivatization

#### PARTIAL OXIDATION

Partial oxidation of methane refers to the selective oxidation of methane to oxygenates, such as methanol, or to synthesis gas. In either technology, control of the extent of gas phase oxidation to prevent the formation of complete oxidation products is extremely important. For both technologies, oxygen must be separated from air, which is capital and energy intensive. PETC is managing three projects in this area of technology.

1) PETC is sponsoring a Cooperative Research and Development Agreement (CRADA) between Amoco Chemical Company and USDOE's Argonne National Laboratory (ANL). The research is focusing on the development of oxygen-specific, dense-phase ceramic membranes for the conversion of methane to synthesis gas or methanol. These oxygen specific membranes permit the transport of oxygen through the membrane while totally excluding nitrogen. Research and development efforts are focused on producing membranes that have sufficient strength and mechanical integrity to withstand the harsh reaction environment of a commercial reactor. Such membranes will permit the use of air instead of purified oxygen for the oxidation reactions, thereby substantially improving the economics of both existing synthesis gas production technologies, as well as direct conversion technologies for methanol. Also, by using the ceramic membranes as a means of regulating the contact between oxygen and methane, and as a support for catalytic materials, achieving highly selective yields of tailored products may be possible. The project is examining the applicability of the membranes for partial oxidation of methane to both synthesis gas and methanol.

The Amoco/ANL team has developed novel, non-perovskite membrane materials for separation of oxygen from air, and conversion of methane into value-added, easily transportable liquid hydrocarbons. These proprietary membrane materials exhibited more than adequate oxygen separation capacity and thermal stability during a demonstration run. A pilot-scale demonstration is under active study, and the Amoco/ANL team has proposed several unique, conceptual process designs for the development of a commercial process.

2) Sandia National Laboratory (SNL) is developing catalysts for the low-temperature conversion of methane to methanol by simulating biological mechanisms using computer-aided molecular design techniques. SNL has tested several halogenated iron porphyrin catalysts for isopentane oxidation, and have gleaned mechanistic information for developing methane oxidation catalysts.

3) AMAX Research and Development has developed techniques for the synthesis and activation of vanadium phosphate catalysts from precursors to form the required active phase for the conversion of methane to methanol. The Colorado School of Mines will continue this activity.

#### OXIDATIVE COUPLING

Oxidative coupling refers to the chemistry of reacting methane with oxygen to form C<sub>2</sub> hydrocarbons as intermediate reactive feedstocks for subsequent conversion to preferred products.

Worcester Polytechnic Institute (WPI) is investigating the use of high-temperature inorganic membranes that are specific for oxygen diffusion to achieve the oxidative coupling of methane. By incorporating a suitable oxidative coupling catalyst into the membrane system and controlling the flow of oxygen across the membrane, the coupling reaction may be favored over other methane

oxidation reactions, thereby minimizing the production of carbon dioxide.

WPI is currently working to select suitable membrane material that will not undergo phase change at reaction conditions while providing optimal oxygen flux. Various perovskite type catalysts are being tested in suitable membrane reactors of various configurations.

#### PYROLYSIS

Pyrolysis refers to thermal decomposition of methane in the absence of any oxidant. Theoretically methane can be pyrolyzed to higher hydrocarbons by successive dehydrogenation and radical recombination, and to aromatics by cyclization of radical fragments. However, the pyrolysis must be controlled at a certain time-temperature condition to maximize yields of low molecular weight products and prevent coke formation. SRI International and Altamira Instruments are the two participants in this category of research.

1) SRI International is attempting to develop a process for the direct conversion of methane to higher hydrocarbons under controlled thermal and catalytic conditions using Fullerene-based catalysts. SRI has prepared metallized Fullerene catalysts and these catalysts have been shown to be effective in stabilizing methyl radicals. Preliminary methane conversion tests using Fullerene containing soot in the presence of an inert diluent gave high selectivity to preferred higher hydrocarbons at lower activation temperature.

2) Altamira Instruments is investigating a catalytic and/or free radical-induced pyrolysis route for converting methane to higher unsaturated hydrocarbons or aromatics.

The thermal decomposition of methane shows potential as a process for the production of higher unsaturated and aromatic hydrocarbons when the extent of reaction is limited. Preliminary experiments have shown that cooling the products and reacting gases as the reaction proceeds can significantly reduce or eliminate the formation of solid carbon and  $C_{10}+$  products. Optimizing the quenching process is one of the goals of the program. Another objective is to reduce the temperature of the pyrolysis reaction by using free-radical generators and catalysts.

Altamira has completed construction of a rapid-quench reactor to limit the extent of reaction and minimize coke formation. A thermodynamic simulation was used to determine yields of various pyrolysis products as a function of the time-temperature history in the reaction environment. Baseline runs in the absence of quench gave 31-48 mol% methane conversion, with the major detectable product being benzene. In the rapid-quenched mode operation, a conversion of 33 mol% was obtained with over 15 mol% selectivity to benzene, and at least a 20 mol% selectivity to  $C_6$  hydrocarbons. Product distribution shifted to lower hydrocarbon products as a result of quenching. Operating temperature was 900-1100 °C at ambient pressures. A 1100 °C quenched-mode run at a specific operating condition and methane feed rate gave 38 mol% methane conversion with 45 mol% selectivity to benzene.

The project was selected for economic and engineering analysis. The purpose of the analysis was to determine product and yield targets for commercial viability of the process and to estimate capital requirements. It is believed that systematic feedback of information from engineering analysis to the researchers would result in a parallel evolution of both an engineering and a scientific knowledge base for advancing the state-of-the-art needed for commercial demonstration.

#### DERIVATIZATION

Derivatization, in this paper, refers to a two-step process where methane is first converted to a reactive, but stable, intermediate followed by subsequent conversion of the intermediate product to desired higher hydrocarbons or value-added chemicals. The participants in this category of research are Dow Corning Corporation, Massachusetts Institute of Technology (MIT), Institute of Gas Technology (IGT), and the USDOE's Pittsburgh Energy Technology Center.

1) A multi-step approach involving oxyhydrochlorination was developed by in-house researchers at PETC for converting methane to gasoline using several new and better catalyst formulations. Dow Corning Corporation, the largest manufacturer of silicone products in the United States, is attempting to improve the PETC process by developing a direct methane to methyl chloride conversion route. Because large quantities of methanol for methyl chloride production are imported, replacing it with domestic natural gas will ensure a stable source and price. The cost of a methyl group from methane is significantly lower than that of a methanol-derived methyl group at current pricing.

Dow Corning successfully developed a highly selective Cu-based catalyst and a separation unit to recover methyl chloride from unreacted non-condensable effluent streams. Construction of a bench-scale reactor for optimization of catalyst and process condition studies is nearing completion. This project is an example of government-industry collaboration on technology development. PETC will provide catalyst expertise, while Dow will provide engineering experience in commercialization of technology. Dow will have a cost-effective process for producing methyl chloride for its silicone business, and PETC will have an improved first step in its methane to gasoline process. Such industrial cost participation promotes technology or technical know-how transfer to target segments of industry and enhances U.S. competitiveness.

2) The objective of the MIT project is to develop a process for converting methane to solid metal carbides that can be easily stored, transported, and hydrolyzed to acetylene or methyl acetylene, which are reactive precursors to higher hydrocarbons. MIT researchers are investigating the use of a thermal plasma reactor to cause decomposition of methane into an ionized, electrically conducting plasma followed by energetic reaction with alkaline metal oxides, such as calcium or magnesium oxides, to form corresponding carbides. Stoichiometrically, these reactions are net hydrogen producers.

MIT performed a thermodynamic simulation study to determine equilibrium compositions for the Ca-C-H-O and Mg-C-H-O systems. It was observed that a significant driving force exists for converting methane to carbides at 2100 K. Although energy intensive, such a process will be useful for on-site upgrading of remote natural gas.

3) IGT is investigating the catalytic reaction of methane with hydrogen sulfide to carbon disulfide, followed by subsequent conversion of the carbon disulfide to gasoline range hydrocarbons. The second step is the MOBIL process. Reaction of methane with sulfur to make carbon disulfide is known. The novelty of this process, however, is the reaction with hydrogen sulfide (instead of sulfur), which results in the net production of hydrogen for use in the second step. In the second step, carbon disulfide is reacted with hydrogen, regenerating hydrogen sulfide for recycle to the first step.

IGT prepared several proprietary transition metal sulfide catalysts for the methane/hydrogen sulfide reaction. These catalysts have been used to investigate the decomposition of hydrogen sulfide. Hydrogen sulfide decomposition is one of the mechanisms postulated to occur in the first step of the proposed process. At 600-1100 °C, and ambient pressure, one catalyst gave hydrogen sulfide decomposition close to values predicted by equilibrium. However, the thermal background, if any, has not yet been determined for this reaction.

4) PETC in-house methane conversion research has evolved from chemical to photochemical reaction systems. Currently, the researchers are investigating the production of methanol from the photochemical reaction of methane and water. This project combines interesting chemistries from several different technology areas and could result in a commercially viable process.

#### CONCLUSION

The USDOE Gas-to-Liquids R&D portfolio considers technical and policy objectives, and identifies key energy policy goals in the implementation of the program. The energy policy goals are based on balancing the economic, environmental, and energy security

objectives. The major policy thrusts for evaluating investments in the natural gas conversion/upgrading technology projects are energy security, economic growth, environmental quality improvement, and fortifying scientific foundations. The criteria for evaluating investments are based on how potential R&D activities can assure a secure, fuel-diverse, and environmentally sensitive energy sector.

Technological advances are critical to achieving the Nation's energy, economic, and environmental objectives and maintaining U.S. competitiveness in a rapidly advancing global economy. Growth in economic productivity arises principally from the introduction of new technology into the market place. The PETC Gas-to-Liquids conversion R&D program is based upon these convictions.

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