

Natural Gas to Liquids: An Overview

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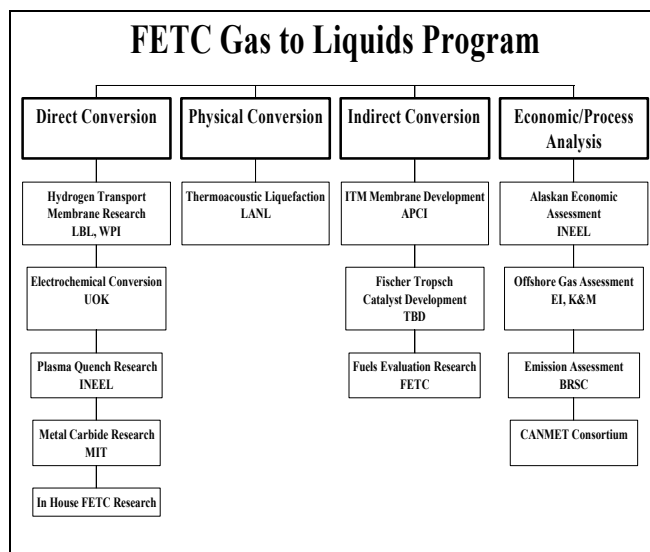
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Introduction

Natural gas, which is comprised primarily of methane, is one of our most abundant natural resources, both domestic and abroad. Unfortunately, many of the natural gas reservoirs are located in relatively remote areas, or offshore, and high transportation costs tend to prohibit extensive use of this potentially valuable resource. To overcome this limitation, the Department of Energy's Federal Energy Technology Center (FETC) has developed a highly diversified research program to evaluate, promote and develop processes that convert natural gas, methane, into higher value products (*i.e.*, liquid fuels) which will offset the high transportation costs and allow use of this untapped, environmentally friendly resource.

By advancing technologies to convert unmarketable gas resources into valuable products, cooperative efforts between DOE and industry could yield the following benefits by 2010.

(1) Our domestic production of oil will be increased through the supply of 200,000 to 500,000 barrels per day of high quality liquid transportation fuel made from Alaska's North Slope gas resources; (2) Advanced gas-to-liquids conversion technology that yields ultra clean burning diesel fuels that meet the most stringent emissions requirements, at costs below those of comparable fuels made from crude oils, will be utilized; and (3) Small-scale gas-to-liquids technology for both natural gas liquefaction and chemical conversion to higher hydrocarbon liquids will enable economic and environmentally sound usage of remote offshore oil reservoirs with associated gas, and also onshore gas reservoirs without pipeline access.

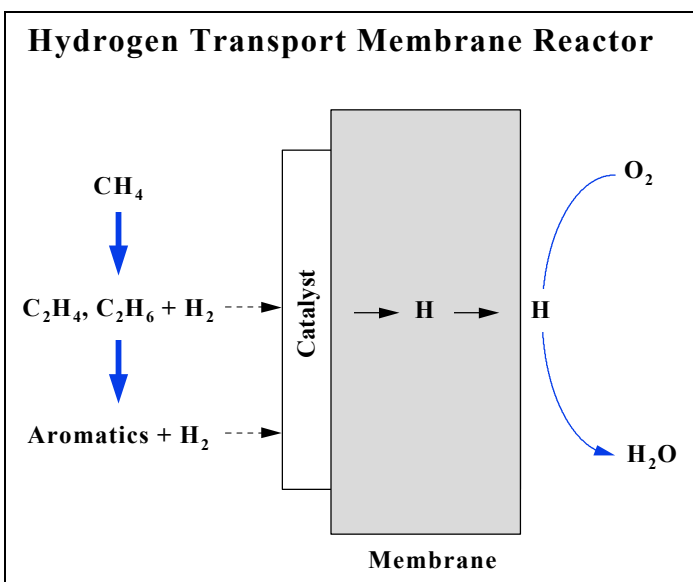


Three potential routes for the conversion of natural gas have emerged: direct, indirect and physical conversion. Direct conversion focuses on the chemical transformation of natural gas to ethane, ethylene, acetylene or methanol. Indirect conversion methods concentrate on the production of syngas (CO and

H₂), which is subsequently converted to liquid fuels. Physical conversion techniques center on the conversion of natural gas to liquefied natural gas (LNG). All three approaches are currently under investigation under the gas-to-liquids conversion program at FETC. In addition, the economics of gas-to-liquids conversion is continually evaluated. An overview of the entire program is presented in Figure 1.

Direct Conversion

The direct conversion of methane to higher hydrocarbons has been extensively investigated in the past 15 years. Unfortunately, employing conventional catalytic systems, yields have remained low. In the case of C₂ production, yields have been limited to 30% or less. Yields of oxygenated hydrocarbons (*i.e.*, methanol and formaldehyde) have remained even lower, on the order of 5 - 6%. In order to overcome these limitations, FETC has attempted to fund relatively novel research projects.



Approaches include the use of electric fields, plasma torches and hydrogen transport membranes. As an example, the hydrogen transport membrane approach is presented in more detail.

A schematic of the overall process is presented in Figure 2. Methane is allowed to react in the absence of oxygen (pyrolytically), over a catalyst, on one side of the membrane. Conversion to higher hydrocarbons, in particular C₂ is highly equilibrium limited. However, hydrogen produced during the reactions is selectively removed via transport through the

membrane. Removal of hydrogen allows the reaction to proceed further, thus removing the equilibrium constraints. On the other side of the membrane oxygen is present. The transported hydrogen can further react with the oxygen to produce water. Overall the reaction can be written as: $2 \text{CH}_4 + \text{O}_2 = \text{C}_2\text{H}_4 + 2 \text{H}_2\text{O}$, which is simply the oxidative coupling of methane. Results of this work are anticipated in the coming year.

Physical Conversion

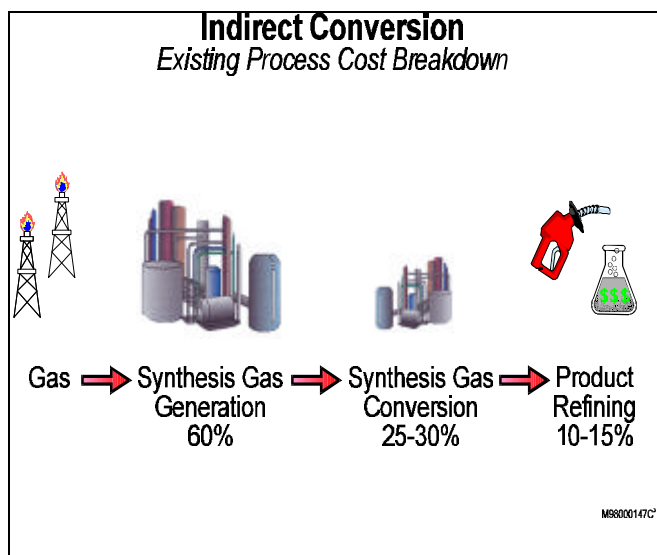
In addition to chemical conversion, physical conversion of methane to liquefied natural gas (LNG) has shown promise. In this work, natural gas is liquefied employing Thermoacoustically Driven Orifice Pulse Tube Refrigeration (TADOPTTR). This technology has the unique capability of producing refrigeration power at cryogenic temperatures with no moving parts. The technology is well suited for liquefaction capacities in the range of roughly 500 to 10,000 gallons per day. The research is being carried out under a Cooperative Research and Development Agreement (CRADA) between Los Alamos National Laboratory (LANL) and Cryenco, a small business located in Denver, Colorado. During 1997, the

TADOPTR demonstrated production of 100 gallons per day of liquefied natural gas. The system is currently being scaled up to demonstrate production of 500 gallons per day of liquefied natural gas in early 1998.

Indirect Conversion

Indirect methane conversion requires the production of synthesis gas (CO and H₂) which is subsequently to higher hydrocarbons and liquid fuels. Synthesis gas production requires either steam (steam

reforming) or oxygen (partial oxidation) as a co-reactant. In either case, generation of these reactants is extremely energy and capital intensive and, as a result, the major cost of converting natural gas to liquid fuels lies in the initial synthesis gas production step. The cost breakdown for the individual steps in the overall process is depicted in Figure 3. Clearly, over half of the process cost, approximately 60%, is associated with synthesis gas generation.

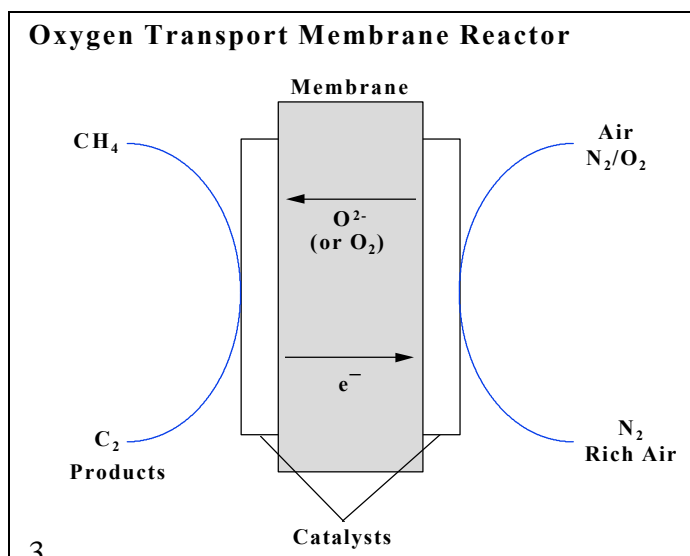


Considering the partial oxidation route to synthesis gas, any reduction in the cost of oxygen production would translate into a reduction in the overall cost of liquid fuels production. One technology which shows considerable promise is the use of ceramic membranes for oxygen

production. Briefly, air (80% nitrogen, 20% oxygen) is allowed to pass on the outside of the membrane.

The membrane is a highly dense, non-porous ceramic material capable of withstanding high temperatures. Due to 1) an oxygen partial pressure differential across the membrane and 2) the nature of the ceramic material, oxygen is selectively removed from the air and transported across the membrane as an oxide ion (O²⁻). The process is illustrated in Figure 4. It is important to note that oxygen separation has been achieved without the use of relatively expensive cryogenics or compression.

In addition to functioning as an oxygen separation unit, the membrane also serves as the synthesis gas reactor. As shown in the Figure, methane (natural gas) is passed through the inside of the membrane. Oxygen diffusing through the membrane further reacts with the methane resulting in the formation of synthesis gas. By utilizing the above approach, it is anticipated that both capital and operating costs can be substantially reduced and provide an alternate, cost competitive route for the production of liquid fuels.

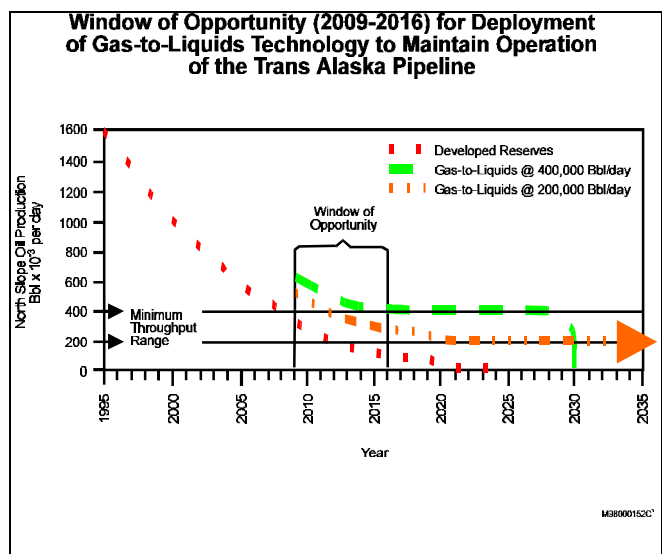


Currently, several new downstream research activities are being initiated. This includes the development of Fischer-Tropsch catalysts for the production of liquid fuels and testing of these materials for their performance and emission characteristics.

Economic/Process Analysis

It is imperative that the current status of all issues concerning the conversion of natural gas to liquid fuels be continually monitored and updated. Therefore, continued economic and process analysis of existing and potential natural gas conversion technologies is a necessary and integral part of the gas to liquids program. Recent studies include: 1) the potential and economics for offshore gas to liquids conversion

and 2) an economic assessment of Alaskan North Slope gas utilization options. Of particular importance in the latter work was the identification of the window of opportunity to extend the lifetime of the Trans Alaskan Pipeline System (TAPS). The result is illustrated in Figure 5. Identification of a viable technology to convert gas to pipeline quality liquids by 2009 - 2016 could extend the lifetime of TAPS by some 20+ years. Continued operation of TAPS is vitally important to Alaska's economy; therefore, this provides considerable incentive to develop and commercialize new gas to liquids conversion technologies, capable of 200,000 - 500,00 bbl/day production, early in the 21st century.



The primary focus of the gas to liquids program is on the conversion and utilization of domestic natural gas supplies. However, it is important to remain active in world wide gas activities. Participation in the CANMET Consortium allows interaction with an international group of oil, gas, utilities and chemical companies.

Summary

The overall objective of the gas to liquids program is: "In partnership with industry, develop and demonstrate advanced technologies and processes for the economical conversion of methane to liquids that can be used as fuels". FETC's gas to liquids research program provides a unique opportunity for industrial partnerships and rapid technology transfer in an effort to achieve this goal.