NATURAL GAS TO LIQUIDS CONVERSION PROGRAM DISCUSSION

by
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Abstract

In conversion of natural gas to liquids, the promising prospect is a simple one- or two-step process carried out under mild temperature and pressure conditions and yields high conversions and selectivity of the gasoline and/or distillate fuels. Both catalytic and non-catalytic methods are being explored along with other unique methods, such as biological techniques. Some high potential catalytic methods are in the conceptual stage and need further exploration.

Non-catalytic methods are being explored as potential means to initiate desired reactions. Biological methods are in their infancy but could develop into a promising approach, while possibly shedding light on catalytic improvements. In all processes, yield and selectivity trade-offs must be considered. There is a need for new and improved separation techniques to remove desired products from unconverted feed and undesirable products. Techniques such as membrane, liquid membrane, or improved fractionation and absorption techniques should be studied toward reducing costs. Recycling of unconverted feedstock and undesired product is also costly. Methods to reduce these costs are being investigated.

Natural Gas to Liquids Program

The natural gas to liquids conversion research is a multidisciplinary effort focused on the development of an economic one, step process which will convert natural gas to gasoline or distillates. This research effort is anticipated to provide process technology to convert natural gas to higher value uses and to provide a means of transporting natural gas from remote locations to the marketplace. One of the most promising options is to convert the gas to liquid fuels such as methanol or gasoline. Conventional technology using steam reforming is economically unfeasible. Other techniques, such as direct catalytic oxidative coupling, have potential for significant cost reduction. Therefore, this research effort has been initiated to develop new or improved techniques specifically related to rate and efficiency of conversion. In order to accomplish this research, two broad goals have been defined: (1) develop a method for conversion of natural gas to liquid fuels with acceptable conversion rates and selectivity to desired products and (2) assess several catalytic and noncatalytic techniques through laboratory experiments, theoretical analyses, and systems analyses.

In pursuit of these goals/objectives, the approach to natural gas to liquids conversion research is as follows:

- Development of a major cost reduction through the exploration of new concepts to simplify the process, improve yields and selectivity, and improve separation and recovery of the product. The long-term research approach is to seek the ultimate one step conversion process with high yield, high selectivity, and a high separation/recovery efficiency. The achievement of these goals will result in a competitive process on both large and small scales.

- Achievement of the major cost reduction through the development of catalytic, noncatalytic, and biologic processes, as well as trade-off evaluations of separation and recycle facilities for conversion and selectivity.

The natural gas to liquids conversion (NGTL) research project contains each of the elements indicated above plus a project management function. The latter is a DOE function of planning, execution control, and technical integration of the subprogram. Specific research activities are described below:

- Efforts underway in new catalysts research include efforts to assess several catalytic techniques through laboratory experiments, theoretical analysis, and systems analyses, in order to select the most promising methods for further development. The major part of the effort will be devoted to laboratory investigation of simplified catalytic conversion methods for production of ethylene and/or other intermediates that might be further converted to gasoline or other "end use" fuels.

- Efforts underway in noncatalytic processes research include efforts to develop an understanding of the fundamental chemistry necessary to develop a process to effect the partial oxidation of methane to methanol by some form of exothermic reaction such as a plasma source, electromagnetic radiation or other thermal initiation technique.
- Activities have been initiated to conduct and evaluate the use of biomimetic methods which use the desirable aspects of bio-conversion but avoid negative aspects such as slow reactions, large reactors, and product separation problems.

- Preliminary efforts are planned to evaluate the development and enhancement of facilities for the separation, recycling and collection of gas in disadvantaged areas of natural gas production. These facilities will be an integrated part of mobile conversion units.

- Future plans will include preliminary activities to investigate the potential of converting natural gas into some form of high density fuel. The focus of the work is to enhance the development of cost-effective, high density, and advanced fossil fuels for military and commercial applications. The categories of research will include the development of high density diesal fuel, advanced

industrial/aviation turbine fuels, and advanced high-energy endothermic aviation fuel.

Accomplishments in FY 90

- Tests were conducted that provided preliminary information that could allow investigators to determine the influence of the reactor to conversion chemistry and aid in the evaluation of simulation and/or analytical models currently being developed.

- Studies have been preformed which stabilize sodium pyrophosphate and allow the substitution of perovskite type oxides for the normal cation. This substitution provides what appears to be a superior catalysts. Work will continue to study this catalyst to determine it value for natural gas conversion processes.

Natural Gas to Liquid Fuels

-- Program Discussion --

Natural Gas to Liquids Conversion Project Focus

- Development of cost reduction through
  - Simplified process
  - Improved yields and selectivity
  - Improved separation and recovery of product
- Achievement of cost reduction through
  - Development of new catalysts
  - Development of noncatalytic processes
  - Development of biological processes
  - Evaluation of engineering trade-offs in conversion processes and facilities

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Natural Gas to Liquids Research

Performer	Activity
METC	Selection and evaluation of catalysts for the conversion of methane to Ethylene/Gasoline distillates
LLNL*	Development of catalysts using silica-based aerogels
Lehigh U #	Development and evaluation of dual redox catalysts for methane conversion
TBD	Development and evaluation of a catalytic membrane reactor/separator
LANL	Development of a model for the thermal conversion of methane to higher value hydrocarbons
SUN*	Development and evaluation of catalysts which mimic the behavior of biological enzymes
METC	Development and assessment of conversion process economics and system analyses

* Cost shared research

Non-cost shared with industry involvement

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Questions/Data Needs on Adv. Conversion Technology

- Are economics favorable at "best" conditions?
- What are technical requirements for "good" economics?
- What are best product/byproduct separation and recycle techniques?
- What are "real" conversion characteristics?
  - Conversion/selectivity
  - Byproducts
  - Catalyst regeneration requirements
  - Poisoning/enhancement effects
- Can conversion/selectivity be significantly improved?
- What is best oxidant (air, O_2, oxygen donor)?
- Does methanol make sense as final product?
- Can "dual function" catalysts be found to make gasoline/ distillate directly in one stage?

Natural Gas to Liquids Conversions

Noncatalytic Process Research

- Provide fundamental chemical kinetics, investigations, gas phase chemistry, surface chemistry, and thermal characteristics for conversion processes

- Develop partial oxidation technique for methane to methanol

- Develop comprehensive simulation model and validate usefulness of model

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Methane To Methanol Conversion

- Objective
  - To develop a novel process utilizing a form of thermal initiation to effect partial oxidation
- Goals
  - Determine fundamental kinetics as a function of experimental parameters
  - Demonstrate the feasibility of methanol production in a small reactor cell

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Methane To Methanol Conversion

- Status
  - Studies have been completed in both static and flow cells
    - The static cell proved to be unsuitable due to lack of temperature control
    - The flow cell surface reactions quenched production of free radicals
- Accomplishments
  - Demonstrated the significance of mass effects which quench free radicals
  - Demonstrated the use and application of low-pressure

Natural Gas to Liquids Conversion

Catalytic Process Research

- Research efforts to assess new catalytic techniques through laboratory experiments, theoretical analysis, and systems analysis

- Selection of most promising methods for development to olefins or other "end use" fuels

Methane Oxidation
Dual Redox Catalysts

- Objective
  - To investigate dual Redox-Lewis base acid systems doped into oxide and silicate matrices for selective oxidation of methane to C2 hydrocarbons and methanol
- Goals
  - Investigate the dual Redox systems using copper and stannosilicates in ZSM- 5 and SAPO zeolite
  - Investigate the dual Redox systems in zinc oxide matrices

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Methane Oxidation
Dual Redox Catalysts

- Status
  - Metal oxide silicate matrix catalysts have been prepared for testing
- Accomplishments
  - Dual Redox doped zinc oxide, ZSM-5 zeolite, and paladium-silicated catalysts have been tested
  - Copper, tin, and zinc catalysts exhibit a reaction for selective oxidation of methane
  - Preliminary tests indicate the paladium catalysts

Methane To Higher Hydrocarbons
Oxidative Coupling

- Objective
  - To develop a novel concept for conversion of methane to liquid hydrocarbons through the use of chemical catalysts
- Goals
  - Discover the basic chemistry that converts methane to higher hydrocarbons and develop a process using that chemistry
  - To develop a process that operates economically at low temperatures and pressures

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Methane To Higher Hydrocarbons
Oxidative Coupling

- Status
  - Preliminary metal-silica gel catalysts have been synthetically developed and are being tested
- Accomplishments
  - The testing has included both techniques for partial oxidation and oxidative coupling
  - A model for the aerogel conversion process has been developed and is being tested
  - Oxidative coupling appears to have a barrier that cannot

Catalyst Characterization
Carbonaceous Materials

- Objective
  - To analyze the effect preparation of catalysts has on the gasification of various carbonaceous materials
- Goals
  - Perform characterization of mixed solid-state catalysts
  - Emphasize reaction parameters and effect on final products
  - Approaches include thermal and salt decomposition, low-/high-temperature cycling, and grinding

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Natural Gas to Liquids Conversion

Biological Research

- Evaluation of conversion through the use of bacteria such as methanotropic bacteria

- Development of a new biological enzyme that will convert natural gas to selected liquid products

- Development of a catalyst which mimics favorable aspects of biological systems

Catalyst Evaluation and Analysis
Biological Catalysts

- Objective
  - To develop a process that mimics biological enzymes in conversion of natural gas to higher hydrocarbons
- Goals
  - To identify and analyze the biological enzymes responsible for converting gases to hydrocarbons
  - Develop catalysts that mimic the biological process for commercial application

Catalyst Evaluation and Analysis
Biological Catalysts

- Status
  - Work has been proceeding on the identification of the biological catalysts and testing has been initiated
- Accomplishments
  - Preliminary studies indicate that iron porphyrin complexes appear to catalyze isobutane using molecular oxygen at room temperatures
  - The most active of these catalytic complexes appears to enhance catalytic activity when the electron withdraws

Catalytic Membrane Reactor

- Objective
  - To evaluate the effectiveness of a ceramic membrane reactor combined with catalyst to selectively form methanol by partial oxidation of methane
- Goals
  - Measure the rates of diffusion and reaction for the development of a process
  - Develop a model that will predict reactions in various forms of membrane reactors

Natural Gas to Liquids Conversion

Systems Analysis

- Evaluate various technology options for gas to liquids conversion
  - Technical achievement potential
  - Economical achievement potential

- Identify systems integration issues
  - Selectivity/conversion tradeoffs
  - Product/by-product separation and recovery systems

Natural Gas To Liquids

Economics and Systems Analysis

- Objective
  - To analyze technical and economical conversion processes of natural gas to olefins, gasoline, and distillates
- Goals
  - Identify and evaluate supply, market, processes, environmental, economics, and regulatory issues for liquid fuels strategies
  - Identify alternative pathways and chemistry for gas to liquid conversion and yield improvement

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