NATURAL GAS TO LIQUIDS CONVERSION TECHNOLOGY STATUS - AN OVERVIEW -

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EXECUTIVE SUMMARY

The United States has substantial uncommitted reserves of natural gas and large quantities of undiscovered conventional resources. Most of the uncommitted gas is on Alaska's North Slope. There are also large "unconventional" resources in tight sands, coalbed methane, and Devonian shales, some of which are not accessible by available pipelines. Conversion of gas to liquid fuels could unlock these resources, reduce the need for imported fuels, and provide a secure supply of liquid fuels in geographically distributed areas. Such chemical conversion technology could also be used to produce cheaper chemical feedstocks for industry.

In 1984, DOE initiated a program for expanding the knowledge base and for developing concepts, methods, and processes to convert natural gas to liquid fuels. The initial research activities focused on developing a comprehensive understanding of the fundamental mechanisms and kinetics when partially oxidating methane directly to methanol as the basis for designing a process. The goal is to achieve a sufficiently high yield that an operable and economically viable process can be applied to converting remote natural gas to liquids for transportation to U.S. markets. This research project is ongoing and has progressed to include research in catalytic, noncatalytic, and biological conversion processes.

In the conversion of gas to liquids, the promising prospect is a simple one- or two-step process conducted under mild temperature and pressure conditions that yields high conversions and selectivity to gasoline and/or distillate fuels. Both catalytic and noncatalytic methods should be explored in addition to other unique methods, such as biological or "biomimetic" routes that use some of the biological systems' capabilities. Some high-potential catalytic methods are in the conceptual stage and need further exploration.

Noncatalytic 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. New and improved separation techniques are needed to remove desired products from unconverted feed and undesirable products. Techniques such as membrane, liquid membrane, or improved fractionation and absorption should be studied to reduce costs. Methods to reduce costly recycling of unconverted feedstock and undesired products also need to be investigated.

1.0 INTRODUCTION

1.1 Background

Natural gas, consisting largely of methane with smaller amounts of ethane, propane, and other hydrocarbons, is a plentiful domestic resource in the U.S. Contaminants are also present in varying amounts that may include some or all of the following: nitrogen, carbon dioxide, hydrogen sulfide, and helium. Since price deregulation began, the supplies of natural gas "in the pipeline" at competitive prices have increased considerably. DOE's assessment shows that a technically recoverable reserve and resource base of 1,059 trillion cubic feet (Tcf) of natural gas exists in the lower 48 States. This resource base is made up of proved reserves, inferred reserves, and resources. The latter requires discovery and development, some using improved understanding of reservoir frameworks that must be more fully developed and applied. Of that, 800 Tcf exists or is estimated to exist in conventional reservoirs. More than half of the total resource evaluated in the lower 48 States, or 583 Tcf of gas, is judged economically recoverable (including finding costs) at less than $3.00 per Mcf (wellhead price, 1987 dollars). However, some of the potentially producible resources of natural gas are not accessible to markets because there are few pipelines from these resource areas. These unaccessible resources generally fall into two categories: large resources intruly remote locations where new pipelines would be expensive, and small- or medium-sized resources in areas where no pipelines presently exist. In order to improve the marketability of natural gas, especially those resources located in remote areas, a research effort to convert natural gas to "higher-value" fuels was conceived.

The Alternative Fuels Act of 1988 states that the development of alternative fuels is a must for the U.S. This act provides for developing dual-use vehicles and, therefore, requires developing alcohol fuels, such as methanol and ethanol, as well as higher density fuels. The ability to convert natural gas cheaply and efficiently into a transportable fuel, such as gasoline, would not only open new markets for presently "usable" gas but would also contribute to reducing petroleum imports to the U.S. Achieving these desirable uses for natural gas is contingent on the availability of a conversion process that produces a high yield of a transportable liquid fuel, which has favorable energy density, combustion, and environmental characteristics.

The natural gas-to-liquids conversion research is a multidisciplinary effort focusing on developing an economic process that will convert natural gas to gasoline, distillates, or other liquid fuels. This research effort is expected 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. Some of the promising options are to convert the gas to liquid fuels, such as methanol, gasoline, or distillates. Conventional technology using steam reforming is expensive under current conditions. Other techniques, such as direct, catalytic-oxidative coupling, may reduce costs. Therefore, this research effort has been initiated to develop new or improved techniques specifically related to rate and efficiency of conversion. The goal for accomplishing this research has been defined: develop a method for conversion of natural gas to liquid fuels with acceptable conversion rates (~ 10 to 20 percent per pass) and selectivity to desired products (~ 80 percent or greater). This will be achieved by assessing several catalytic and noncatalytic techniques through laboratory experiments, theoretical analyses, and systems analyses.

This research could have a significant impact on the energy fuels market with the recognition that natural gas may well be an important fuel in meeting the problems of liquid fuel shortages. Natural gas can be used for industrial and power plant energy needs by displacing residual fuel, distillates, and other liquids, or by conversion to meet transportation fuel demands (Figure 1). By substituting gas for oil, some 2 million barrels per day (MM bbl/d) of oil imports can be eliminated. Both methanol and ethanol are technically viable options to displace crude oil imports.

1.2 DOE Mission

Fossil Energy's basic strategy is to identify research opportunities and conduct research (and transfer the results of such research to the user community) in extracting, processing, and utilizing domestic fossil fuel resources. An important element of this strategy is related to promoting a balanced- and mixed-energy supply that can be used to significantly expand the nation's fuel supply.

DOE, through the Office of Fossil Energy (FE), has developed a program for the research and development (R&D) of gas-to-liquids conversion. This program encourages research efforts to extend the fundamental scientific and engineering knowledge base to provide advanced concepts and innovative ideas for conversion of gas to liquids, in particular, and gas utilization, in general. Investigations should result in increased gas reserves by providing new, higher-value market outlets and increased, domestic liquid-fuel supplies. These results will be obtained by developing new concepts to simplify conversion processes and to improve yields and selectivity as well as separation and recovery of the end-use product. For example, the application of a low-cost, one-step, gas-to-liquids conversion process could lead to increased utilization of natural gas from such remote areas as Alaska's North Slope without the enormous costs associated with constructing a Trans-Alaskan natural gas pipeline.

Within the context of the DOE/FE mission, DOE sponsors activities for the R&D of gas-to-liquid conversion. The major goals of the program's focus on the conversion of natural gas to liquids are

- To develop a major cost reduction by exploring 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. Achieving these goals will result in a competitive process on both large and small scales, and

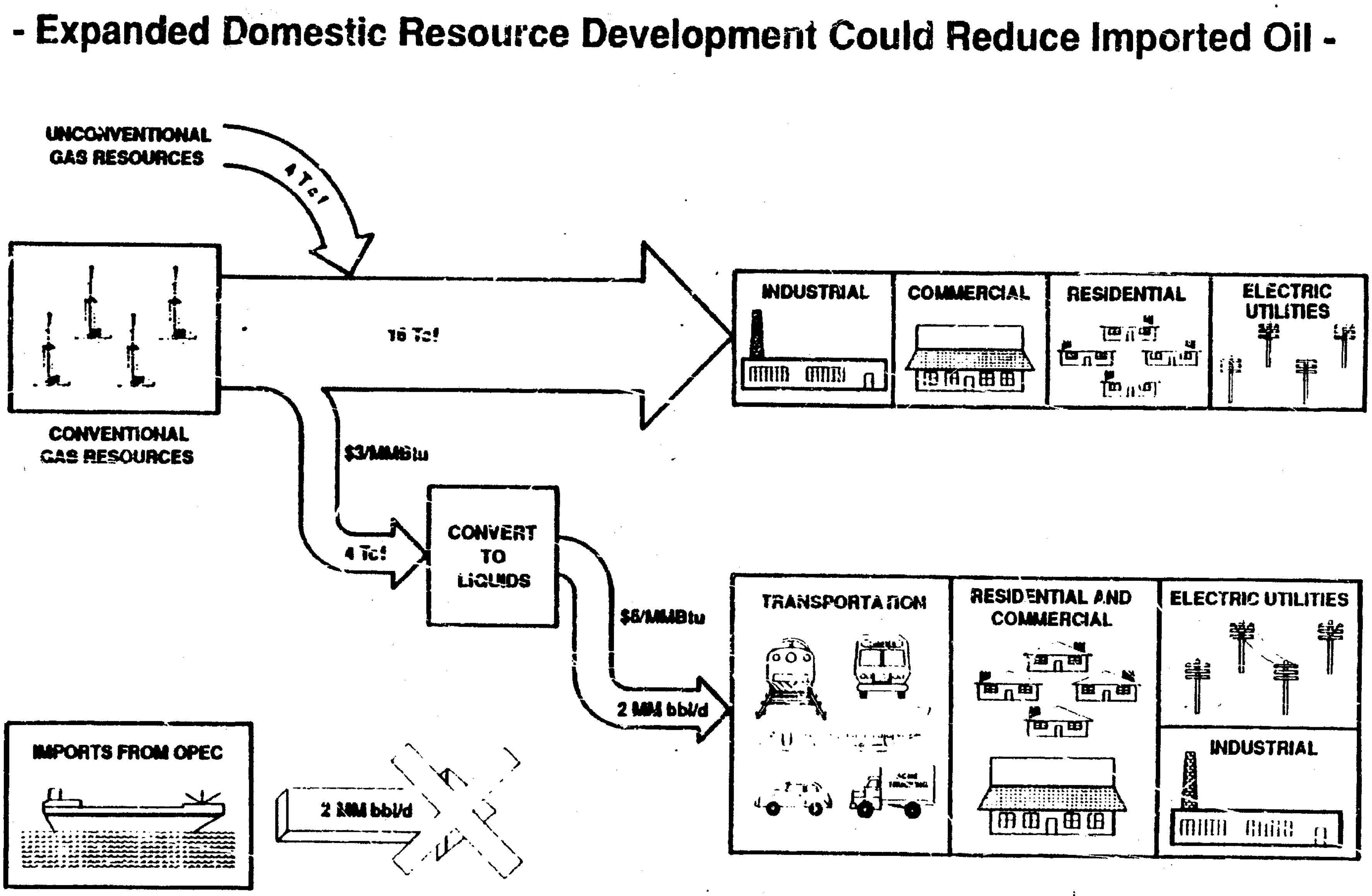

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Figure 1. Changing the Energy Equation

- To achieve major cost reductions by developing catalytic, noncatalytic, and biologic processes as well as trade-off evaluations of separation and recycle facilities for conversion and selectivity.

With significant potential to decrease the transportation market areas and to expand the utilization of natural gas from distant and remote areas, development of gas-to-liquid fuel conversion methods and processing concepts depends upon innovative and novel approaches. These broad issues and possible solutions require multidisciplinary R&D expertise. The expertise of several organizational entities may be required. The research areas of interest are summarized into five categories:

- Determining and developing new or modified catalysts for conversion of natural gas to liquids;
- Developing noncatalytic techniques for gas-to-liquid conversion;
- Determining and developing biological-to-biomimetic techniques for conversion of natural gas to liquids;
- Evaluating the processes for novel concepts/innovations on separation and recycling facilities with respect to conversion and selectivity during the conversion process; and
- Performing systems analysis on new and existing processes to determine areas of cost reduction and to evaluate the economics of potential market areas.

Research efforts in these areas are necessary to expand the understanding of the basic phenomena of conversion chemistry and potential processes, to assess novel and innovative concepts, and to provide technical and economic solutions to the natural gas conversion issue. Table 1 identifies the research efforts being funded through the Morgantown Energy Technology Center (METC) on the Natural Gas-to-Liquids Conversion program.

2.0 RELATED RESEARCH

2.1 Fossil Energy Programs

METC interest in producing and utilizing methane has been supplemented by the fuel cells program, where natural gas is a primary fuel, and the surface gasification program, where methane is either the sought-after product, as in high-Btu coal gas, or a fixed-bed gasifier by-product that must be further converted to syngas (H_2 and CO) for subsequent processing to liquids. DOE's fuel cells program, with industrial groups that are heavily involved, is aimed at developing more efficient and cheaper fuel cells using coal-derived, natural gas to produce electricity. In addition to work on relatively conventional, phosphoric acid fuel cells, the DOE research effort focuses on developing molten carbonate and solid oxide fuel cells and exploring novel types of cells that may have even higher efficiency. While the direct

Table 1. Natural Gas-to-Liquids Research and Participants

Technical Activity	Participants
Catalytic Research	
• Catalytic Selection and Evaluation	METC
• Development of Synthetic Catalysts	LLNL[1]
• Analysis of Dual Redox Catalysts for Methane Oxidation Conversion	Lehigh University
• Evaluation of New Concepts/Processes Based on Biologic Structures	TBD[2]
Noncatalytic Research	
• Proof of Concept Experiments for Thermally Induced Conversion	LANL[3]
Utilization Technology	
• Evaluation of Conversion Economics	METC

[1] Lawrence Livermore
[2] To be determined
[3] Los Alamos National Laboratory

feedstock to the cell is usually assumed to be hydrogen, some effort is being expended to allow the cells to use methane directly by means of "internal reforming," a catalytic breakdown of methane occurring at the surface of the cell electrode. A cell using methane directly would have significant economic advantages over those requiring separate steam reformers to produce fuel. The surface gasification program sponsors work on all three major types of gasifiers (fixed bed, fluidized bed, and entrained) to produce gas for a variety of applications, including combined cycle power production, synthesis of fuels and chemicals, and industrial heat. Figure 2 indicates a schematic blending of various DOE/FE programs into a natural gas research effort.

2.2 Basic Energy Sciences Program

DOE's Office of Basic Energy Sciences sponsors fundamental investigations of catalyst activity and structure through its programs in Chemical Sciences and Materials Sciences (Summary Report 1987). Approximate[illegible] 70 projects in this area are supported primarily at universities. While m[illegible]y of these projects relate directly to methane activation or conversion, [illegible]er projects undoubtedly contribute to a better understanding of catal[illegible] mechanisms and, thus, indirectly support chemical gas conversion effort[illegible]

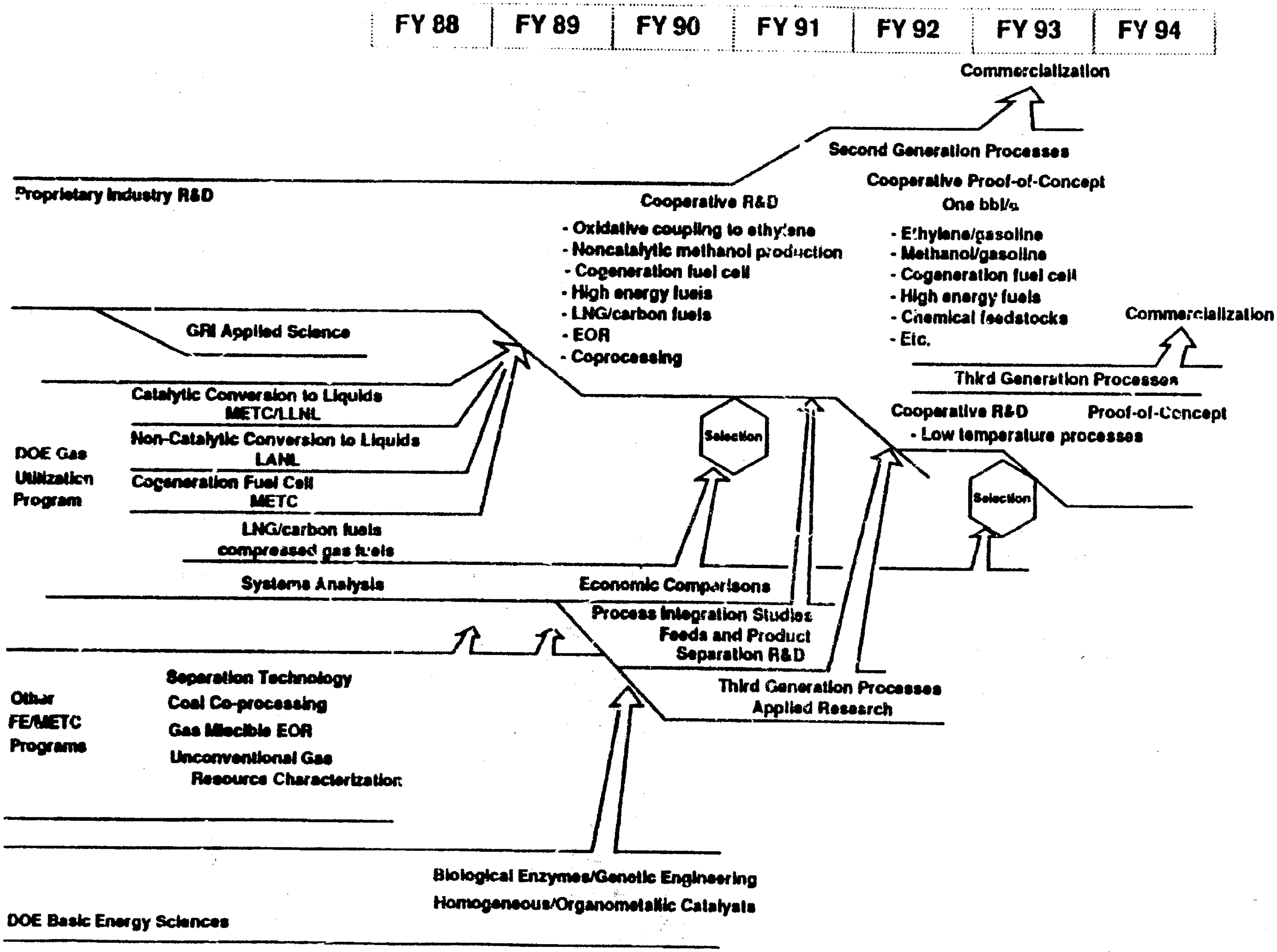

Figure 2. Natural Gas Utilization Strategy

FE's program on indirect liquefaction (IL) of coal is managed by the Pittsburgh Energy Technology Center (PETC), the other major DOE Fossil Energy Center (Proceedings 1988).

The IL program sponsors studies of synthesis gas conversion to liquid hydrocarbons (through the Fischer-Tropsch process) and oxygenates as well as work on upgrading Fischer-Tropsch liquids. Syngas conversion studies are not listed in Table 1 since they are beyond the scope of this report. However, some syngases produced from coal gasification contain considerable amounts of methane, and research studies have been sponsored on conversion of syngas (methane and other light alkanes) to higher hydrocarbons and alcohols.

Union Carbide Corporation, under PETC funding, is investigating catalytic processes for conversion of methane to ethylene, which is a useful chemical feedstock for their product line. PETC is also currently involved in a research effort using halogens as possible catalysts. The effort has been titled "Oxyhydrochlorination."

2.3 Gas Research Institute Program

Gas Research Institute (GRI) supports research on gas conversion primarily through the methane reaction science program, which is funded both by the regular program and an industrial associates program, and sponsors related work through its advanced gas separation science and technology program (Gas Research Institute 1988). The objective of the methane reaction science activity is to identify and characterize new chemical and biological concepts for the conversion of methane, or for modifications of its physical form that could lead to new or improved services for the gas consumer. The methane reaction science activity sponsors work in six areas: chemical reactions, biochemical reactions, natural gas as a chemical feedstock, metal oxide reduction chemistry, methane chlorination, and technical evaluation of chemical processes. The objective of the gas separation activity is to provide a scientific basis for improving existing technology and developing new concepts for separating gas mixtures and for converting methane into higher form-value products.

2.4 Industrial Programs

While much industrial research is proprietary to protect competitive positions in technology, many organizations have interests and active research in natural gas conversion. Several groups are participating as members of GRI's Industrial Associates Program, and DOE has had discussions on sponsored research with several companies. Union Carbide has published data on oxide catalysts for oxidative coupling of methane, as have Atlantic Richfield (ARCO) and Phillips. Exxon has patented processes for conversion of methane to olefins and aromatics. BP America (formerly SOHIO) has obtained patents on catalytic and noncatalytic processes for converting methane to aromatic hydrocarbons. A number of other U.S. companies are known to have active research programs.

3.0 STATE OF TECHNOLOGY

The overall focus of this research area is expanding the technology base on converting gas to liquids (1) through theoretical and experimental investigations into areas of technical uncertainty, and (2) assessments of innovative concepts for improving process performance. Exploratory research to investigate the technical feasibility of new ideas is a key element of this advanced research and development program. The areas of investigation are discussed in the following sections.

3.1 Catalytic Technologies for Conversion of Natural Gas to Liquids

Existing commercial catalytic technology for conversion of natural gas is typified by the New Zealand plant, which uses steam reforming to produce a hydrogen/carbon monoxide mixture (called synthesis gas), followed by a methanol synthesis step and the well-known Mobil-M process for conversion of methanol to gasoline. Several studies have indicated that such a process is not, at this time, economically competitive with either refinery production of gasoline from crude oil or anticipated world crude oil prices, and that the New Zealand plant requires government subsidies. Preliminary systems studies at METC have indicated that capital costs of such plants will increase drastically when they are sited in remote locations such as North Alaska, and economic competitiveness of the product fuel at market locations will be correspondingly poorer. Although variations and incremental improvements in the basic process are possible, they are unlikely to lead to major cost reductions since the steam reformer stage of the current process, the highest cost section, represents a relatively mature technology. Improvements in the methanol synthesis and Mobil-M steps have little leverage on the overall cost.

While no commercially available technology exists to convert natural gas to gasoline or an equivalent "high-value" fuel at competitive costs, a METC feasibility evaluation indicates that a new process could be developed that would be less complex, require fewer conversion steps, and possibly be cheaper. Other recent review articles validate these conclusions. Laboratory research has shown that direct, catalytic, partial oxidation of methane (reacting methane with oxygen over a catalyst) can produce methanol or an ethylene/ethane mixture, depending on process conditions. Effective catalysts include a wide range of metal oxides, and the presence of non-methane hydrocarbons appears to enhance conversion in some cases. Either of these products can be further reacted to make gasoline in a separate catalytic step. Since bench- or larger-scale data are not available on such a methodology, the economics are speculative, but preliminary estimates indicate significant cost reductions based on the simplicity of the process. However, the percentage of methane converted (called conversion) and the percentage of "desirable" product from the total product mix (called selectivity) achieved in selected lab tests may not be high enough for commercial viability, and the factors controlling these parameters are not well understood. Factors that affect results include catalyst type (metal oxides, zeolites, and natural materials), oxidant (oxygen, air, and oxygen-donor in the catalyst), gas composition (ratio of methane to other hydrocarbons), and product separation and recycle techniques. While the simplified two-step process appears to be promising, the "ultimate" could be a conceptual one-step, "combined catalyst" process that might convert methane (and other associated gas constituents) directly to gasoline-range compounds. Figure 3 shows a simple schematic of various routes available thro conversion processes. Such a process has not been found even on laboratory scale, but a possible approach is suggested by experiments that produce ethylene, a very reactive compound, which might be made to polymerize (react with itself) to form larger hydrocarbons. An alternative to the "pure" one-step process might be one in which "intermediates," such as ethylene, would pass into a second catalyst bed without an intervening separation/recycle step.

The previously described catalysts fall into the heterogeneous classification. Recent advances in organometallic chemistry have resulted in developing combined metal-hydrocarbon complexes that activate the hard-to-react methane molecule at much lower temperatures than do the presently known heterogeneous catalysts. These developments might lead to a new class of homogeneous catalysts for natural gas conversion.

The overall research objectives for catalytic technologies relative to natural gas-to-liquids conversion are

- To derive fundamental information and concepts about chemistry reactions achieved during conversion phases,
- To enhance the conversion rate and selectivity percentage through the use of catalysts, where feasible in the processing cycles, and
- To obtain high conversion/high selectivity percentages in an "ultimate" low-cost, one-step conversion process.

3.2 Noncatalytic Techniques for Natural Gas-to-Liquid Conversion

While temperatures in the range of 1,000°C and above are known to partially decompose methane, processes based strictly on pyrolysis are not believed to be promising because of the high temperatures and low selectivity for desirable products. Some noncatalytic methods attempt to circumvent the extreme thermal stability of the methane molecule by utilizing other forms of energy as an "initiator" to activate methane and form a more active precursor that will then undergo gas-phase reactions to form desirable products. LANL is investigating the use of plasma formed by a laser to provide this initiation step. Other schemes are possible, and these could include photochemical reactions, electrolytic reactions, chemical initiators, and conceivably other types of radiation fields and/or particle bombardment. Some potential schemes rely on gas-phase reactions for selectivity of products, and there is some concern that the potential of such methods may be more limited than those using catalysts.

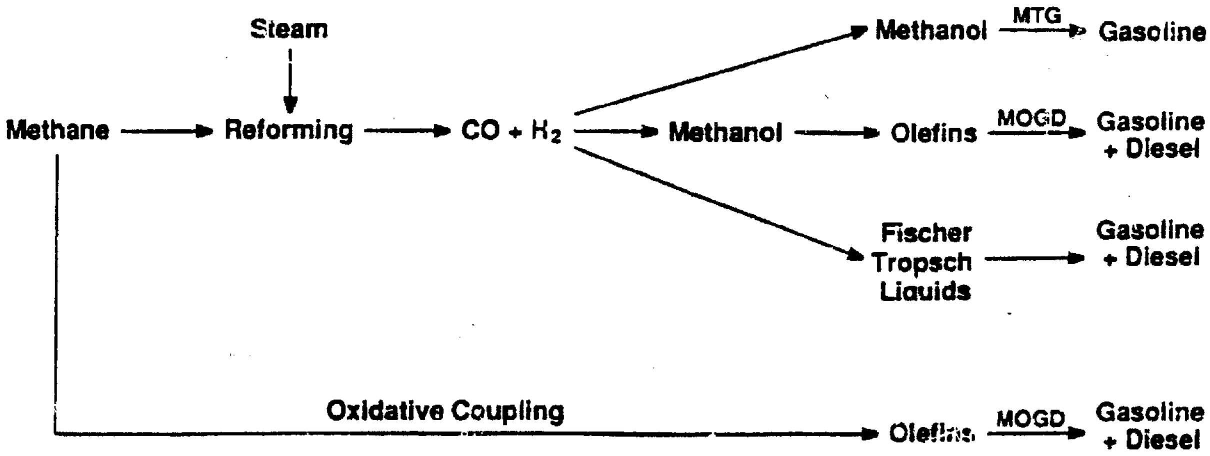

Figure 3. Conversion Routes for Liquid Hydrogen From Methane

The overall research objectives for noncatalytic techniques for the conversion of natural gas to liquids are

- To extend the current knowledge base of conversion processes and reaction engineering to systems that have significant potential to achieve conversion without the use of catalytic agents, and
- To conduct laboratory-scale experiments to study plasma-, electrolytic-, or electron-initiated conversion technologies.

3.3 Biological Techniques for Natural Gas-to-Liquid Conversion

While biologists have long known that certain bacteria can utilize methane as a "food" by transforming it into complex compounds, the chemical bases for such reactions are not well understood. When a better understanding of the biochemistry of such bacteria is achieved, it may be possible through genetic manipulation to develop bacteria that would produce hydrocarbon fuels rather than proteins. Alternatively, it might be possible to isolate a "methane-activating" chemical from the bacteria and mass-produce such a chemical synthetically to be used as a homogeneous catalyst in natural gas conversion.

The overall research objectives for biological techniques on natural gas-to-liquids conversion are

- To evaluate the current knowledge base on biological engineering and its potential for converting natural gas to higher hydrocarbons (liquid phase),
- To conduct laboratory-scale experiments to study bio-controlled conversion techniques on conversion potential, selectivity potential, and by-products produced, and
- To conduct investigations that use biomimetic methods. which use the desirable aspects of bio-conversion but avoid negative aspects, such as slow reactions, large reactors, and product separation problems.

3.4 Novel Concepts/Innovations for Separation and Recycling Facilities

Separating desirable products and recycling feed gases are likely to be necessary in any process on conversion of natural gas to a liquid fuel. For example, assume that methane is first converted to methanol by an oxidation catalyst, and methanol is then converted to gasoline in a second stage. A typical methane conversion might be 20 percent for a single pass, so most of the feed gas must be recycled a number of times to reduce unconverted methane to a low value. Methanol would likely be separated by selective condensation from unconverted feed gas and other gaseous products such as CO_2. Other potential intermediate products (such as ethylene) might require more exotic separation techniques. The nature and difficulty of separation and recycle methods are clearly linked to the type(s) of products, the conversion rates and selectivities, the operating conditions, and the number of conversion stages. In addition, they may be affected by economic factors, such as the cost of feedstock and the potential nonprocess uses for unconverted gas. Separation and recycle concepts must clearly be considered in a systems context in addition to the basic conversion technologies.

The overall research objectives for novel concepts/innovations on separation and recycle facilities are

- To evaluate the current knowledge base on separation/recycle facilities applicable to natural gas-to-liquids conversion processes,
- To expand the understanding of reaction or interactions between the conversion process and its reactor vessel/facility, and
- To evaluate novel/innovative concepts for developing low-cost, mobile conversion facilities that use remote areas of gas production.

3.5 Utilization Technology/Systems Analyses

The research necessary within utilization technology/systems analyses is to evaluate the current systems for economics relative to converting natural gas to liquids and to identify those areas where technology advancement could reduce the costs related to the conversion process. The overall research objectives are

- To provide a preliminary estimate of gas transportation cost from remote areas such as Alaska,

- To determine the economics relative to current and potential conversion process systems, and

- To identify areas where technology research and development could reduce conversion costs to commercial compatibility.

These activities encourage advanced research efforts to extend the fundamental scientific and engineering knowledge base to provide advanced concepts and innovative ideas on conversion of gas to liquids, in particular, and gas utilization, in general. These investigations should result in increased gas reserves by providing new, higher-value market outlets and increased, domestic liquid-fuel supplies by developing new concepts to simplify conversion processes and to improve yields and selectivities as well as separation and recovery of the end-use product. While yields of 28 to 30 percent are being sought, the important factor is high selectivity. (See Figure 4.) For example, the application of a small-scale, low-cost, one-step gas-to-liquids conversion process could lead to increased utilization of natural gas from such remote areas as Alaska's North Slope without the enormous prohibitive costs associated with constructing a Trans-Alaskan natural gas pipeline. These research activities encompass several R&D areas.

Since the overall objective of this gas-to-liquid research effort is to develop a low-cost, one-step conversion process for natural gas to liquids, it will be necessary to evaluate each of the research efforts for both technical and economic feasibility. Furthermore, it is important that by-products of each research effort be thoroughly studied and evaluated.

4.0 CURRENT RESEARCH

4.1 Status of Chemical Conversion

4.1.1 Methane Conversion to Syngas Followed by Methanol Synthesis or Fischer-Tropsch Conversion to Hydrocarbons

As far as the natural gas-to-liquids research program is concerned, the Fischer-Tropsch process is considered "conventional" technology. However, incremental improvements are being made in several aspects of this route.

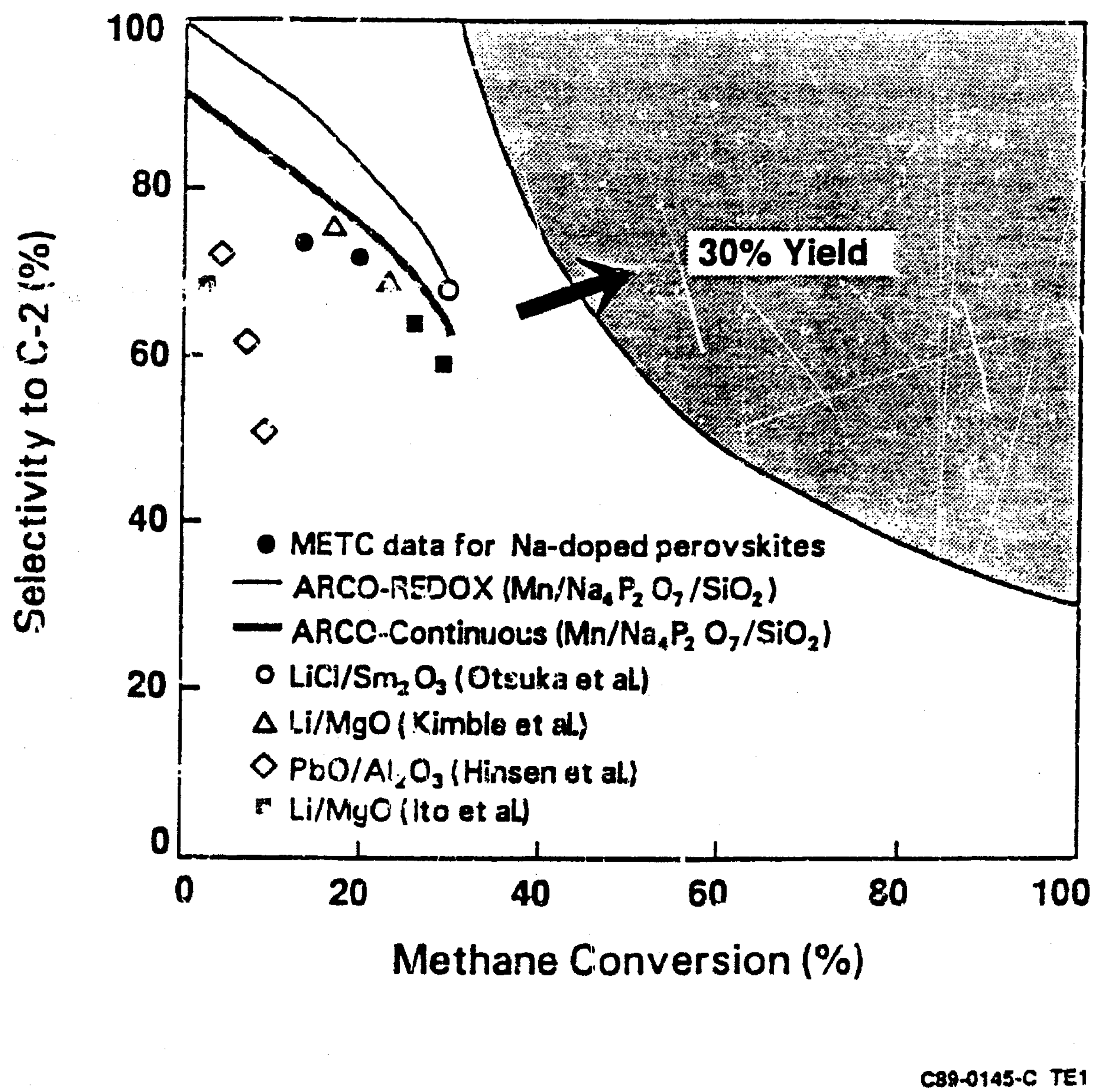

Figure 4. Selectivity-Conversion Relationships for Methane Conversion to Ethylene/Ethane

Brookhaven National Lab, under DOE funding, has developed a liquid-phase methanol synthesis reactor, which can utilize syngas made from methane by partial oxidation with air rather than oxygen (O'Hare et al. 1986). Methanol is synthesized in a catalytic solution that converts syngas to methanol at > 90 percent conversion in one pass, obviating the need for recycling gas. In a parallel development, Air Products and Chemicals and Chem Systems, Inc., under DOE sponsorship, are developing a liquid-phase methanol synthesis process that allows easy removal of reaction heat and is particularly suited for high CO content gases (Studer et al. 1986). This process has been tested at a process development unit (PDU) scale in Laporte, Texas. These and other developments could improve the economics of the conventional steam reformer-based processes, which are not presently favorable in the U.S.

4.1.2 Direct Partial Oxidation to Methanol

Both catalytic and noncatalytic processes have been investigated for producing methanol from natural gas. Only processes that use oxygen or air as an oxidant will be discussed, since use of other oxidants, such as nitrous oxide or halogens, would be prohibitively expensive unless the reagents are recycled. These processes, based on direct, partial oxidation, offer relative simplicity and relatively low heat transfer requirements, but economically promising conversion rates and selectivities have not been proven in large-scale equipment.

Noncatalytic conversion, sometimes called "cool flame oxidation," takes advantage of high-temperature chemical equilibria, which favor methanol formation. Temperatures in the range of 350 to 500°C are needed for the process to be effective, and high pressure (> 40 atm) also favors methanol formation. Short residence times and rapidly quenching products improve methanol selectivity. Formaldehyde is usually produced in addition to methanol. As with most methane conversion processes, conditions that favor high selectivity (> 50 percent) to desirable products usually favor low conversion of methane per pass through the reactor (< 5 percent). Promising results on this process, indicating > 80 percent selectivity to methanol with conversion per pass approaching 10 percent, and negligible formaldehyde have been obtained at the University of Manitoba but have not been verified elsewhere.

In 1984, METC initiated funding of a project at LANL to investigate the potential for high-temperature plasma technology on conversion of natural gas to methanol. This project has continued and evolved into a modelling and laboratory study of the kinetics of gas-phase methane chemistry, which serves as the basis for noncatalytic thermal conversion technology. LANL has developed a comprehensive model for methane gas-phase reactions, verified the model by extensive comparisons with literature data, and used the model to predict conditions that should give favorable conversion in thermal reactors. The modelling results indicate that high temperatures (500 to 800°C) and high pressures (50 atm) will be necessary to achieve economically favorable results in noncatalytic systems. A proof-of-concept experiment is being planned to validate the theoretical predictions.

Proposed catalytic processes for direct, partial oxidation to methanol typically use metal oxide catalysts and operate in similar temperature and pressure ranges as the noncatalytic processes, but offer promise of higher conversion efficiency. While publications are numerous, no one has achieved and confirmed usefully high yields with only oxygen or air as an oxidant. Recent research has neglected this approach in comparison with work on forming C_2 hydrocarbons, but the lower temperatures necessary for methanol formation, the increasing interest in the U.S. in methanol fuels, and the ability to easily convert methanol into other products may lead to a resurgence of interest. Using zeolite catalysts to convert methane to methanol is being explored by Lehigh University as a promising route to reduce temperature requirements while achieving good yields of product. In fiscal year 1989, METC initiated funding to Lehigh University to pursue research in this area.

4.1.3 Oxidative Coupling to Olefins

In a process called "oxidative coupling," oxygen can be reacted with methane over an oxide catalyst to "activate" methane and form hydrocarbons containing two or more carbon atoms, typically ethylene and ethane. These reactions occur at 1 atm pressure, but typically require temperatures in the 600 to 800°C range. A similar process uses a metal oxide as an "oxygen donor" to perform the methane activation, thus requiring no oxygen addition to the methane stream, but requiring a separate step to regenerate the catalyst in a stream of air. Once light olefins, such as ethylene, are formed, they can be used as feedstock for producing gasoline or chemicals in separate process steps using known technology. Some investigators have considered combining several process steps into a "combined-function" catalyst to produce gasoline-range hydrocarbons directly from methane. Several laboratories are investigating the basic chemistry of these reactions and testing various types of catalysts.

As far as is known from published data, no group has yet achieved a selectivity/conversion comparable to an overall yield of 30 percent, estimated by different groups to be necessary for a commercially successful process. By comparing partial oxidation to methanol, oxidative coupling to olefins has two disadvantages: (1) light olefins, such as ethylene, are more difficult to separate from the unreacted methane and reaction by-products, such as carbon oxides, so gas recycle can be accomplished, and (2) heat transfer requirements are more complex possibly leading to increased heat exchange duties and costs.

In a project that is co-funded by METC and GRI, LLNL is investigating potential benefits of silicon oxide-based material, with a high surface area, as a support for metal atoms that provide catalytic sites for methane activation. This is a new project, just beginning to achieve significant results.

METC has an in-house activity to screen promising catalysts for conversion activity, investigate the mechanisms of oxide catalysts for partial oxidation and oxidative coupling, and evaluate novel concepts. A new series of mixed, metal-oxide catalysts has been developed that gives C_2 yields (the product of conversion and selectivity) in the 19-percent range.

4.1.4 Monoxygen Reagents

As previously noted, routes using oxidants or reagents other than oxygen or air must allow for recycling of expensive reagents to be economic. PETC has developed a process based on conversion of methane to chloromethane by oxyhydrochlorination, followed by conversion of chloromethane to gasoline in a zeolite catalysis step (Taylor et al. 1987). Similar processes have been reported by British Petroleum and Mobil. The process shows favorable conversion rates and operates at lower temperatures (~ 350°C) than the partial oxidation-based processes. Potential problems with the corrosion of recycled hydrogen chloride and the formation of undesirable by-products require further investigation.

4.2 Long-Range Research

At present, two other promising options exist that might, in the long range, lead to a true breakthrough in natural gas conversion. Recent advances in organometallic chemistry sponsored by DOE Basic Energy Sciences have resulted in developing combined metal-hydrocarbon "complexes" that activate the hard-to-react methane molecule at much lower temperatures than do presently known catalysts. Among others, Lawrence Berkeley Laboratory and Yale University are conducting work in this area. Significant laboratory research is still required on the synthesis and properties of these special chemical complexes before process conditions, products, and yields can be defined even on a laboratory scale.

Another option, and perhaps the most promising, is a process based on biological activation of methane. While biologists have known for a long time that certain bacteria can utilize methane by transforming it into complex compounds, the chemical bases and mechanisms for such reactions are not well understood. When a better understanding of such microorganisms and their biochemistry is achieved, it may be possible through genetic manipulation to develop bacteria that would produce hydrocarbon fuels or methanol effectively. Alternatively, it might be possible to duplicate the essential functions of the bacterial enzymes in a chemical that could be used as a heterogeneous or homogeneous catalyst. This technique is called biomimetic. With internal funding, LLNL is evaluating possible routes for duplicating the critical functions of methane-metabolizing bacteria to heterogeneous or homogeneous catalysts for methane conversion to methanol. Others are investigating biological activity in connection with conversion processes. Sandia National Laboratory (SNL) is using fundamental, molecular-modelling techniques to investigate methane interactions with catalysts based on biological porphyrin structures. The University of Warwick and Celgene Corporation are studying methanotrophic bacteria to assess whether key functions could be duplicated in useful catalysts.

4.3 Economics of Chemical Gas Conversion

Conventional technology on conversion of natural gas to liquid fuels, such as methanol and/or gasoline-range hydrocarbons, uses steam reforming to produce syngas (carbon monoxide and hydrogen), followed by catalytic conversion of syngas to methanol and conversion of methanol to gasoline by Mobil technology, as exemplified by the New Zealand project. This technology is too expensive to be used in the U.S., considering the cost of feedstock. Table 2

Table 2. Comparison of Conventional and Advanced Processes for Conversion of Natural Gas to Liquid Fuels

Basis: Zero-Cost Gas Feed

	Conventional Steam Reforming		Advanced Process Partial Oxidation or Oxidative Coupling	
	Gasoline Price $/bbl	Equivalent Crude Price $/bbl	Gasoline Price $/bbl	Equivalent Crude Price $/bbl
Gulf Coast (Fluor)	31	25	25	19
Alaska's North Slope (METC)	61	47	47	36

illustrates this point with cost estimates made by METC and Fluor-Daniel Corporation in a study for GRI (Green 1988). For no-cost gas, this technology at a U.S. Gulf Coast location can produce gasoline at a cost competitive to gasoline made from crude oil at a crude price of $25/billion barrels (Bbbl). However, gas at this location would cost > $2/Mcf ($71/Mcm), raising the crude oil break-even price to > $40/Bbbl. At an Arctic location, plant costs will increase because of higher construction costs, resulting in an estimated crude oil break-even price of $47/Bbbl, assuming zero cost gas. Costs would also be added for moving product gasoline through the existing pipeline, shipping it to the lower 48 ports, and recovering gasoline from the crude oil mix in the pipeline. New developments in steam reforming and methanol conversion technology may reduce these costs somewhat in the future.

Cost estimates for new technologies, such as oxidative coupling and partial oxidation, can only be preliminary since laboratory data must be extrapolated with the attendant lack of accuracy. Recognizing this caveat, Table 2 compares Fluor and METC estimates for the break-even crude oil price of a conceptual process based on partial oxidation to that of conventional, steam reforming technology as previously described. Costs for processes based on oxidative coupling should be similar. Although there is a cost reduction compared to steam reforming, it is not clear that the improvement is substantial enough to justify construction of such a plant at today's oil prices, unless a favorable combination of low gas cost and low construction cost can be found. Simulation of mass and energy balances for plants based on partial oxidation and oxidative coupling indicates that partial oxidation to methanol is more promising in terms of simplicity and heat transfer requirements than oxidative coupling to olefins, while both new processes offer efficiency improvements relative to steam reforming (Kuo 1987). The goal for R&D is to reduce costs further by improved efficiency and simplification.

METC, as lead center for gas supply and utilization, has been involved in research and technology development necessary for the conversion of natural gas to liquids and/or higher-value hydrocarbons. These advanced research and technology activities have been developed to conduct (1) enhanced research in the areas of catalytic, noncatalytic, and biologic processes, (2) novel or innovative process concepts, and (3) assessment and evaluation of concepts for developing a low-cost, one-step process on the conversion of natural gas to liquids (Figure 5). In order to comply with the FE program mission, METC has worked closely with industry and GRI so that research efforts at METC are compatible with those research efforts in industry (Figure 2).

METC is interested in extending the scientific and technology base on conversion of gas-to-liquids processes. This advanced research and technology development program intends to conduct fundamental research in the areas of (1) catalytic, noncatalytic, and biologic processes, (2) novel or innovative process concepts, and (3) assessment and evaluation of concepts for developing a low-cost, one-step process for the conversion of gas to liquids.

METC's research activities focus on

- <u>Catalytic Processes Research</u> -- Includes efforts to assess new catalytic techniques through laboratory experiments, theoretical analyses, and systems analyses, in order to select the most promising methods for further development to olefins or other "end-use" fuels;

- <u>Noncatalytic Processes Research</u> -- Includes fundamental chemical kinetics, investigations, gas phase and surface chemistry, partial oxidation of methane to methanol, developing and validating a comprehensive model;

- <u>Biologic Research Efforts</u> -- Includes an investigation to determine the potential for developing a gas-to-liquids conversion process based on catalytic structures that mimic favorable aspects of biological systems, such as methanotropic bacteria;

- <u>Separation/Recycle Systems Research</u> -- Includes the research necessary to improve separating end products from the input train and to reduce the number of conversion cycles that the gas train undergoes in the reactor system; and

- <u>Utilization Technology/Systems Analysis</u> -- Includes efforts to comparatively evaluate various technological options and to identify systems integration issues, such as selectivity/conversion trade-offs and separation technology.

4.4 Future R&D Needs

As research continues in the conversion of natural gas to higher-value fuels, several research areas will need to be analyzed. These include (1) improved selectivity (the percentage of "desirable" product out of the total product mix) for both noncatalytic and catalytic conversion to methanol or olefins, while retaining good conversion (the percentage of methane