Conversion of Natural Gas to Liquids
- An Overview -

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Abstract

Natural gas to liquids conversion research is a multidisciplinary effort focused on the development of an economic process which 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, especially natural gas from remote locations. 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 uneconomic under current conditions. 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. The goal for accomplishing this research has been defined as follows: develop an economically acceptable method for conversion of natural gas to liquid fuels with acceptable conversion rates (~ 10 to 20 percent per pass) and selectivity to desi ed products (~ 80 percent or greater). This will be achieved through the assessment of several catalytic and noncatalytic techniques through laboratory experiments, theoretical analyses, and systems analyses.

Background

Natural gas, consisting largely of methane with smaller amounts of ethane, propane, and other hydrocarbons, is a plentiful domestic resource in the United States and is widely available at competitive prices. U.S. proved reserves of natural gas are estimated at 159 Tcf (4.5 Tcm) by the DOE. Uncommitted reserves are approximately 37 Tcf (1.1 Tcm) including those in Alaska, while undeveloped conventional resources may be as much as 650 Tcf (18.4 Tcm), much of it available at a cost of less than $3/Mcf ($106/Mcm). Unconventional resources (low permeability reservoirs, coalbed methane, and shale gas) in the "lower 48" states are estimated to be at least 258 Tcf (7.3 Tcm), and may be as much as 2000 Tcf (57 Tcm) or more if gas hydrates and other unconventional resources are included. However, much of the potentially producible resources of natural gas are not accessible to markets because of the lack of pipelines from these resource areas. These unavailable resources generally fall into two categories: large resources in truly remote locations where new pipelines would be very expensive, and small or medium sized resources in areas where no pipelines presently exist.

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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 greatly contribute to reduction of petroleum imports to the United States (Figure 1). Achievement of these desirable uses for natural gas is contingent on the availability of a conversion process which produces a high yield of a transportable liquid fuel which has favorable energy density, combustion, and environmental characteristics. There are two possible classes of products: methanol and gasoline/distillate fuels. Gasoline/distillate fuels are most desirable for several reasons. They would be immediately marketable through an existing infrastructure, and (for the Alaskan case) they could be transported from the North Slope to the year-round ports through the existing petroleum pipeline. Markets for methanol as a motor fuel are uncertain and speculative, and methanol is probably incompatible with the existing Alaskan pipeline because of moisture equilibrium, corrosion and other concerns.

Existing commercial 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 economically competitive with refinery production of gasoline from crude oil at present or anticipated world prices and that the New Zealand plant requires government subsidies. Preliminary system studies at METC have indicated that capital costs of such plants will increase drastically when they are sited in remote locations such as the North Slope of 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 reformer, the highest cost section, represents a relatively mature technology. Improvements in the methanol, synthesis and Mobil-M steps have little leverage on the overall costs.

Conversion of gas to liquids is an exciting research area and is just now beginning to have an impact with the recognition that natural gas may well be our most important fuel in meeting the problems of liquid fuel shortages. Use of natural gas for industrial and power plant energy needs can displace residual fuel, distillates, and other liquids which can then be used as such, or can be readily converted to meet transportation fuel demands. By substituting gas for oil some 2 million barrels per day of oil imports can be eliminated. Both methanol and ethanol are technically viable options to displace crude oil imports.

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 the extraction, processing, and utilization of domestic fossil fuel resources. An important element of this strategy is related to promoting a balanced and mixed energy supply which can be used to significantly expand the Nation's indigenous supply of fuels.

Within the context of the DOE/Fossil Energy Mission, the DOE sponsors activities for the research and development of gas to liquid conversion. The following are the major goals of the program focused on the conversion of natural gas to liquids:

- 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 development 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 new catalysts, noncatalytic processes, biological methods, and trade-off evaluations of separation and recycle facilities for conversion and selectivity.

These activities encourage advanced 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. These investigations are projected to result in increased gas reserves by providing new higher value market outlets and increased domestic liquid fuel supplies through the development of new concepts to simplify conversion processes and to improve yields and selectivities as well as separation and recovery of the end-use product. For example, the application of a small-scale, low-cost, one-step gas to liquids conversion process could lead to the increased utilization of natural gas from such remote areas as Alaska's North Slope without the prohibitive costs associated with construction of a Trans-Alaskan natural gas pipeline. These research activities encompass several research and development areas.

Research Focus

Research needs include: improved selectivity for both catalytic and non-catalytic conversion to methanol or olefins while retaining good conversion per pass through the reactor, reduction in temperatures required for conversion, improved methods for separation of products from unreacted materials that must be recycled, improved methods for oxidant production and separation of methane from contaminated or dilute feedstocks, and better knowledge of catalyst life and rejuvenation requirements.

Government funded programs in gas conversion are managed by DOE. Process research and applied science, including technology transfer to industry, are funded by the Fossil Energy programs, while basic science of methane reactions and other C_1 chemistry is funded by the Office of Energy Research's Basic Energy Science program. The Gas Research Institute (GRI) plans, manages, and develops financing for a cooperative R&D program in supply, transport, storage, and end use of gaseous fuels for the mutual benefit of the gas industry and its present and future customers. Funding for the overall GRI program is derived primarily through regulated natural gas sales or transportation services.

The Morgantown Energy Technology Center (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 activities include research in the development of catalytic, noncatalytic and biologic processes; novel or innovative process concepts; and separation and recycling concepts (Figure 2). A primary focus in this program is the assessment and evaluation of concepts for development of a low-cost, one-step process for the conversion of natural gas to liquids. The Pittsburgh Energy Technology Center (PETC) is currently pursuing research in a program called Indirect Liquefaction. This program is focused on the conversion of solids (coal) to liquid fuels and is complimentary to the METC natural gas to liquid fuels program. In order to comply with the FE program mission, METC and PETC have worked closely with industry and the Gas Research Institute (GRI) so that research efforts at METC and PETC are compatible with those research efforts in industry.

METC's research activities are focused on the following research areas:

- <u>Catalytic processes research</u> includes efforts to assess new catalytic techniques through laboratory experiments, theoretical analysis, 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, gas phase and surface chemistry, and partial oxidation of methane to methanol, development of a comprehensive model, and validation of the model.

- <u>Biologic research</u> efforts include an investigation to determine the potential for development of a gas to liquids conversion process based on catalytic structures which mimic favorable aspects of biological systems such as methanotropic bacteria.

- <u>Utilization Technology</u>

  - <u>Process Evaluation</u> includes the determination and development of improved methods for separation of products from unreacted materials that must be recycled, and improved methods for the separation of methane from contaminated or dilute feedstocks.

  - <u>Systems analysis</u> includes efforts to comparatively evaluate various technology options and to identify systems integration issues, such as selectivity/conversion tradeoffs and separation technology.

In pursuit of the identified project activities; Table 1 and Table 2 identify the project research efforts, associated participants, and the currently established schedules for milestone completion.

Table 1: Natural Gas to Liquids Research and Participants

Technical Activity	Participants
Catalytic Research	
o Catalyst selection and evaluation	METC
o Development of synthetic catalysts	LLNL
o Analysis of dual redox catalysts for methane oxidation conversion	Lehigh University
Non-catalytic Research	
o Proof of concept experiments for thermally induced conversion	LANL
Biologic Research	
o Evaluation of new concepts/processes based on biologic structures	TBD
Utilization Technology	
o Evaluation of conversion economics	METC

Table 2: Project Elements and Schedule

	1989			
	1st	2nd	3rd	4th
Phase 1				
Systems Analyses				1
In-House Laboratory				2
Noncatalytic Study			3	
Synthetic Catalysts		4		
Dual Redox Studies	5			6
Innovative Concepts		7		

1. Provide analyses of the process systems currently utilized in the conversion research efforts.
2. Provide test results on both gas phase reaction and surface reaction chemistry.
3. Provide results of low temperature simulation model.
4. Provide test results on the comparison of LLNL/LANL computer simulation models.
5. Initiate research effort.
6. Provide initial results for studies of methane oxidation performed over doped Copper/Metal oxides.
7. Initiate research effort.

Research Discussion

The following discussion describes research activities relative to the Natural Gas to Liquids Program at METC, as well as work being undertaken by PETC's Indirect Liquefaction Program and GRI's Methane Activitation Program.

Direct partial oxidation to methanol -- Both catalytic and non-catalytic processes have been investigated for production of methanol from natural gas. These have been extensively reviewed and will only be briefly summarized here. Only processes that use oxygen or air as an oxidant will be discussed, since use of other oxidants such as nitrous oxide or halogens require the recycling of reagents for economic operation. 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.

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

METC initiated funding of a project at Los Alamos National Laboratory (LANL) in 1984 to investigate the potential for high temperature plasma technology in conversion of methane 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 non-catalytic 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 (500-800 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 temperature and pressure ranges similar to the noncatalytic processes but offer promise of higher conversion efficiency. While publications are numerous on the use of oxygen or air as an oxidant, no one appears to have achieved and confirmed usefully high yields with this process. Recent research appears to have neglected this approach in comparison with work on formation of C_2 hydrocarbons, but the lower temperatures necessary for methanol formation, 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. Use of 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. METC initiated funding in FY1989 to Lehigh University to pursue research in this area.

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 600-800 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 production of gasoline or chemicals in separate process steps using known technology. Some investigators have speculated on 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.

METC has an inhouse activity to screen promising catalysts for conversion activity, to investigate the mechanisms of oxide catalysts for partial oxidation and oxidative coupling, and to 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% range.

In a project that is co-funded by METC and GRI, Lawrence Livermore National Laboratory (LLNL) is investigating potential benefits of new silica based materials, as a support for metal atoms which provide catalytic sites for methane activation. This is a relatively new project and significant results are just beginning to be achieved.

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 bacteria and their biochemistry is achieved, it may be possible through genetic manipulation to develop bacteria which would produce hydrocarbon fuels or methanol effectively. Alternatively, it might be possible to duplicate the essential functions of the bacterial enzymes in a manufactured catalyst which could be used as a heterogeneous or homogeneous catalyst. LLNL is evaluating under internal funding possible routes for duplicating the critical functions of methane-metabolizing bacteria to heterogeneous or homogeneous catalysts for methane conversion to methanol. There are others currently 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 in a study sponsored by PETC. The University of Warwick and Celgene Corp. are studying methanotrophic bacteria to assess whether key functions could be duplicated in useful catalysts in studies funded by GRI.

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 non-catalytic and catalytic conversion to methanol or olefins while retaining good conversion (the percentage of methane converted per pass through the reactor), (2) reduction in temperatures required for conversion, (3) improved methods for separation of products from unreacted materials that must be recycled, (4) improved methods for oxidant production and separation of methane from contaminated or dilute feedstocks, and (5) better knowledge of catalyst life and rejuvenation requirements.

Both for direct partial oxidation to methanol and oxidative coupling to olefins, some groups have shown promising results in the laboratory, but the conversion and selectivity achieved in these lab tests must be validated and improved, and the factors that control these parameters must be better understood before large-scale process development work can be undertaken. Other process parameters that need to be understood include the effects of catalyst type and oxidant.

Reduction in temperatures from the high values currently required for some reactions (600-800 C. for oxidative coupling, up to 1000 C. for noncatalytic conversion) would reduce the need for special materials of construction. The optimum temperature may not, however, be the lowest temperature, since most oxidative processes are exothermic, and excess heat at low temperatures is not as useful as high temperature heat. A balance between this consideration and the materials requirement may dictate the optimum temperature for the process.

Byproducts from partial oxidation reactions include carbon dioxide, carbon monoxide, and water, as well as other minor or trace species. For best process efficiency, methane will have to be separated from these byproducts and the major products and recycled. If methanol is the product, separation is relatively easy, but if ethylene has to be separated at an intermediate stage of the process so that it can be passed on to other process stages, cryogenic separation would be required. For this reason, some approaches envision coupling a second stage conversion of light olefins to heavier hydrocarbons directly to the first stage without a separation step, or possibly with only water and carbon dioxide removal steps between stages. In any case, advanced separation processes are likely to be useful as part of any new conversion system developed. Since some processes require oxygen as oxidant, any advances in air separation technology, such as new membrane-based processes, are likely to improve the economics of conversion technology.

It is more and more being recognized that the U.S. and the world, have more gas resources than oil. Conversion of gas to liquids may well be our most promising long-term source for synthetic fuels. As with all synthetic fuels, the challenge in converting gas to liquids is to do it on a cost competitive basis. Mobil Oil is doing it in New Zealand with its commercial plant -- converting natural gas to a mixture of CO and hydrogen, converting that "synthesis gas" to methanol and converting the methanol to gasoline. The thrust of DOE's Fossil Energy through both METC's and PETC's companion research programs is to find ways to convert natural gas or coal directly or indirectly to liquids. There is a long way to go, but the opportunity is exciting.

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Gas to Liquids

— Changing the Energy Equation —

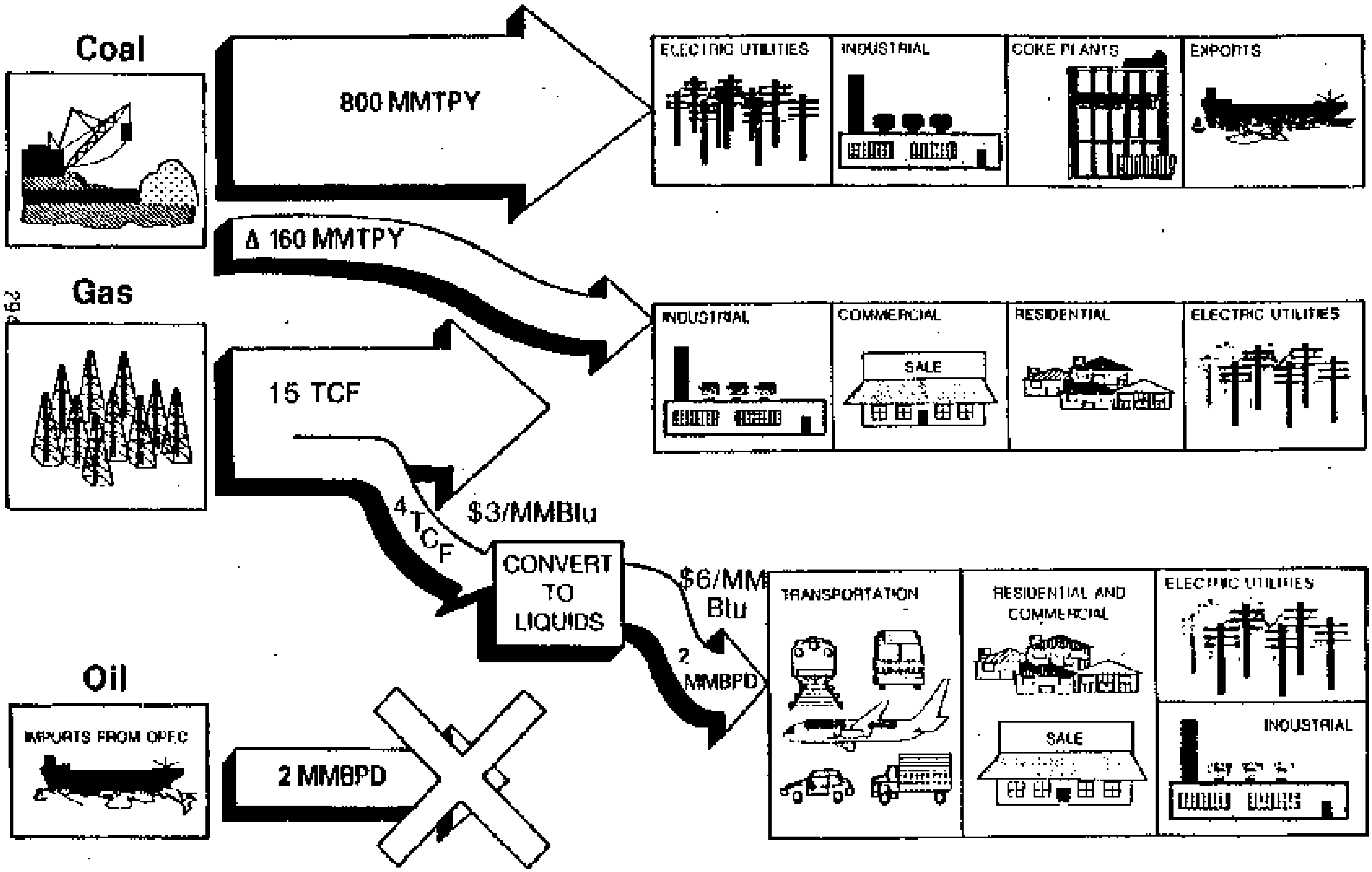

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FIG

Conversion of Natural Gas to Liquids

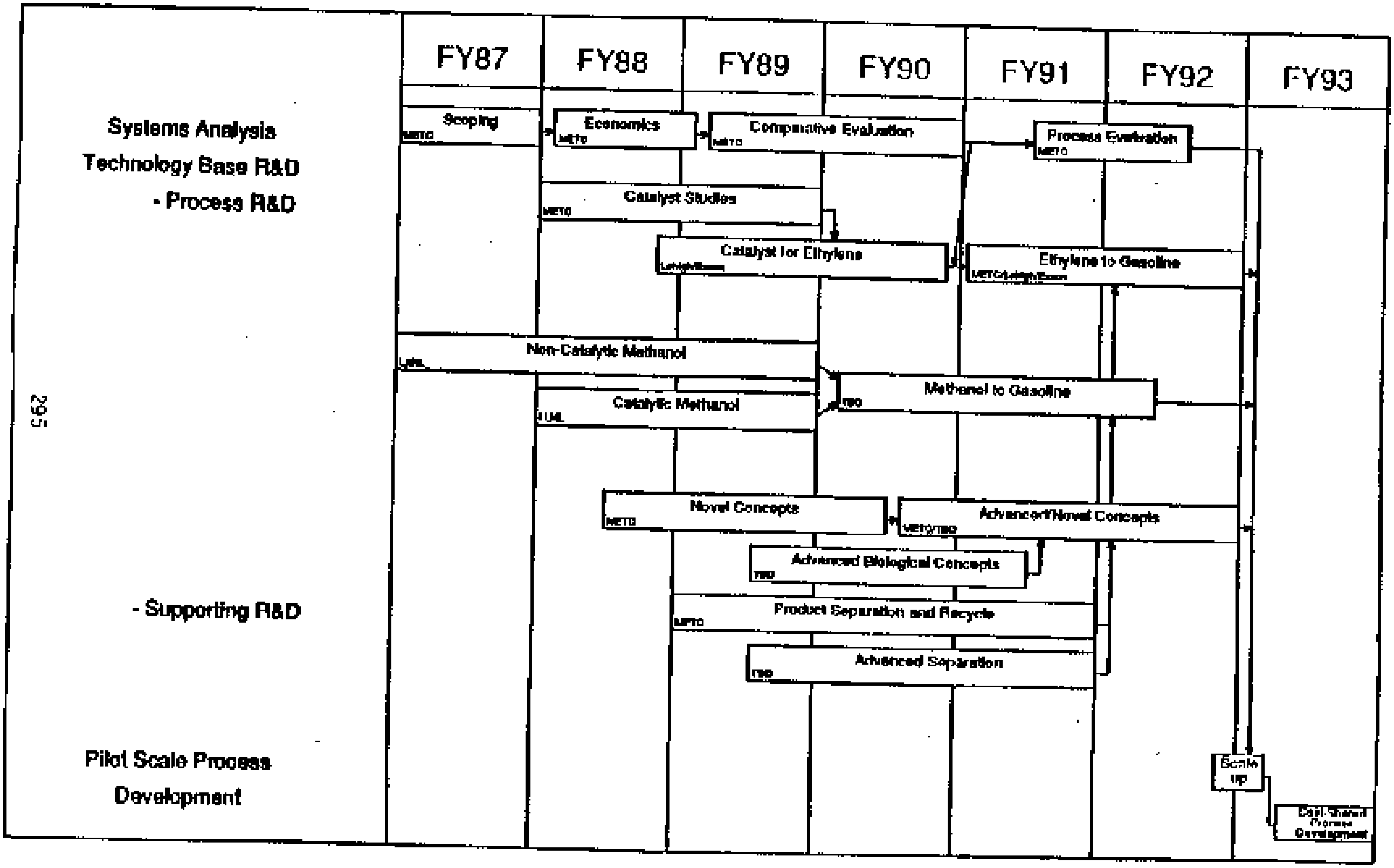


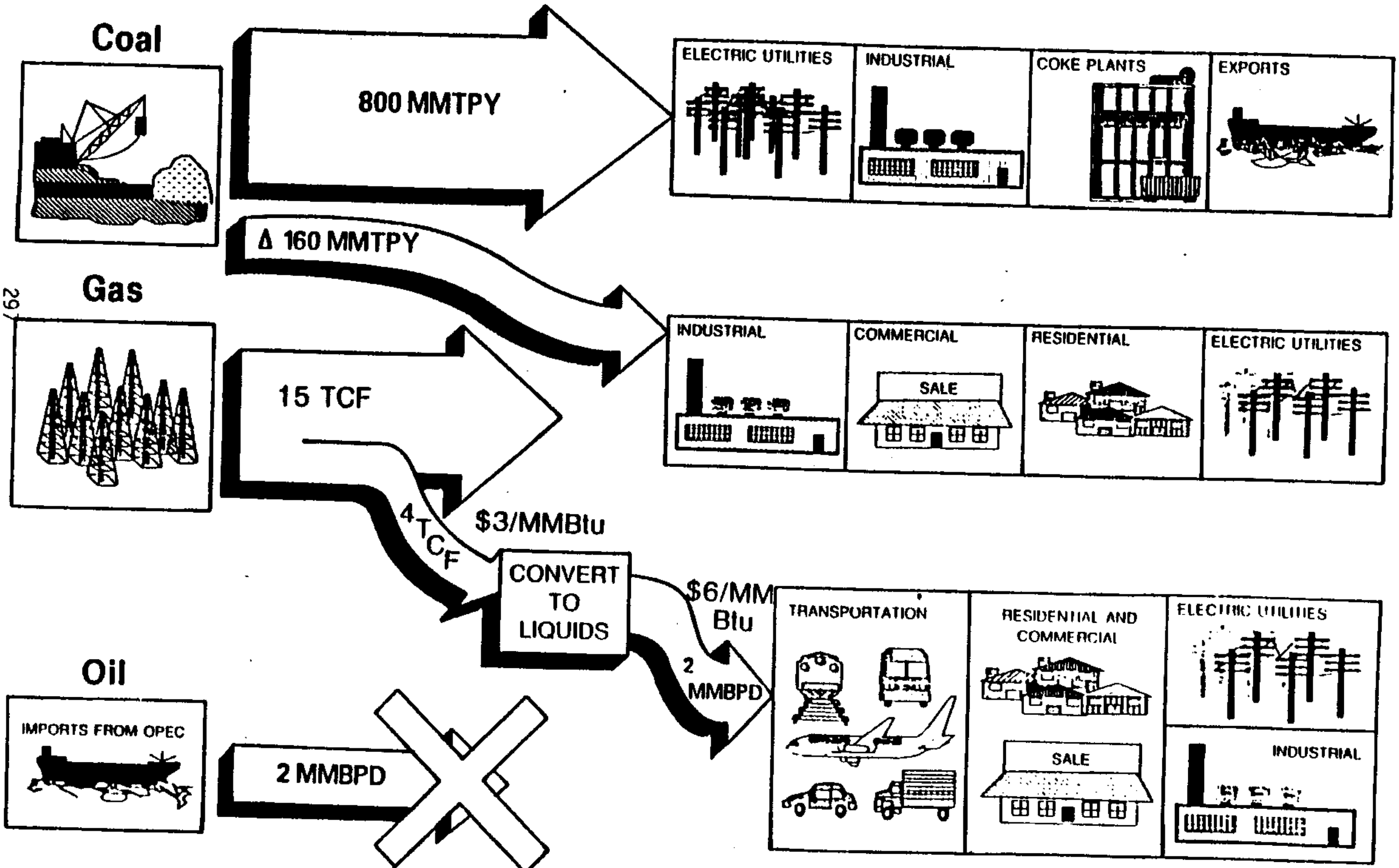
FIGURE 2

Natural Gas to Liquid Fuels

-- An Overview --

Gas to Liquids

— Changing the Energy Equation —



Insights To New Trends In Transportation

- Shift to alternative fuels in transportation within 10 years
  - Environmentally driven
  - Legislation enacted

- Alternative Motor Fuels Act of 1988
  - Encourages widespread development of:
    - Methanol
    - Ethanol
    - Compressed natural gas

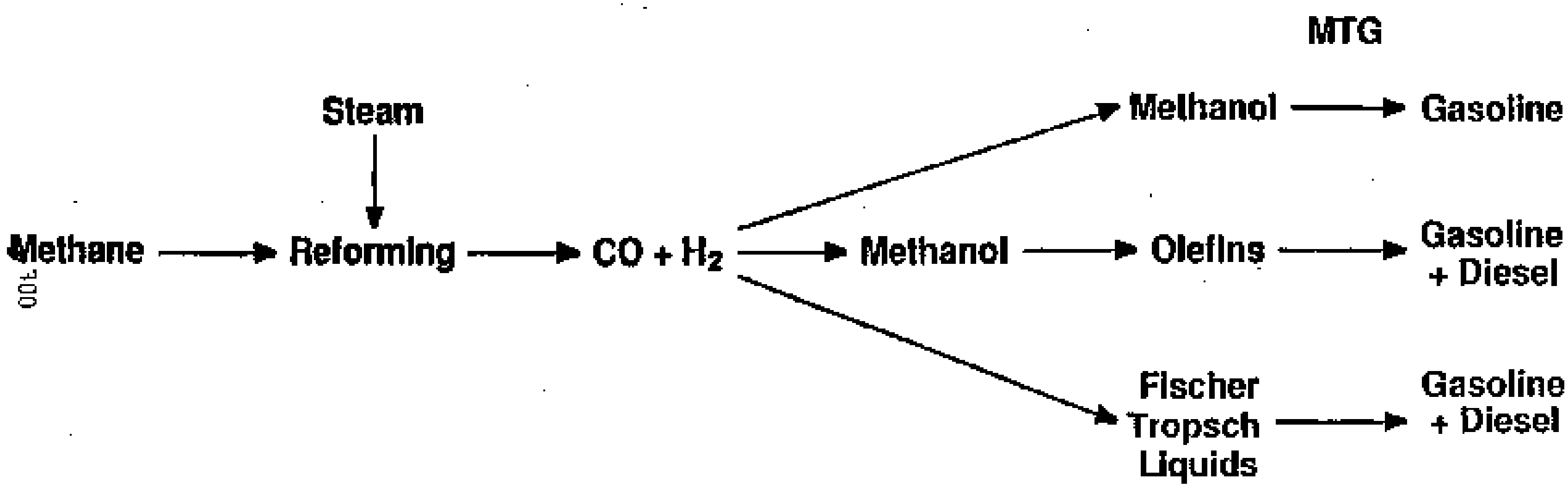
  - Encourages the production of vehicles that use them
    - Dual fuel
    - Fleet/personal

Methanol

- "Wood" alcohol --CH_3OH
- Heating value as fuel ~ 1.8 gallon methanol= 1 gallon gasoline
- Principal current market
  - Feedstock to make Methyl Tertiary Butyl Ether (MTBE) used as Octane Enhancer for gasoline (20 percent of market)
- Current U.S. consumption -- 1.3 billion gallons/year
- Current U.S. gasoline consumption -- 122 billion gallons/year

Equivalent to 220 billion gallons/year methanol fuel

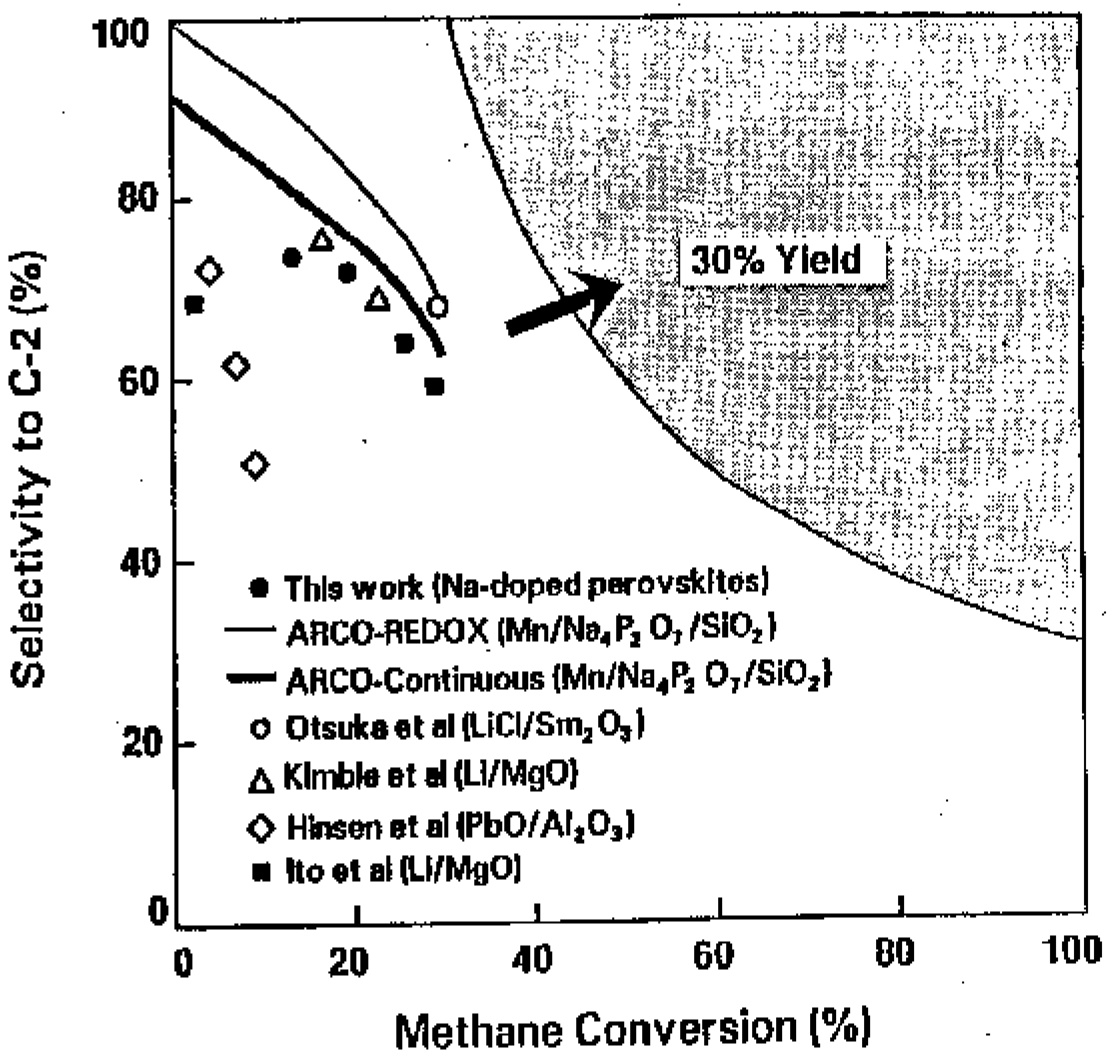
Available Routes to Liquid Hydrocarbon from Methane



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

Selectivity-Conversion Relationships for Methane Conversion to Ethylene/Ethane



Technology Options for Conversion of Natural Gas to Liquids

Novel Concepts

Homogeneous Catalysis

- Liquid Phase
- Low temperature operation
- Organometallics

- Theoretical concept
- Methane "activation" demonstrated, but no "process" identified
- Excellent long-range potential

Biological Oxidation

- Organisms convert methane to methanol
- Room temperature operation

- Organisms being studied
- Isolation and production of active enzyme are key factors
- Scale-up and product separation are major problems
- Good long-range potential

Non-Catalytic Methods

- Thermal reactors
- Laser/plasma dissociation

- Simple system which does not require catalyst
- Very high temperatures normally required
- Potential depends on non-obvious chemistry

Data Needs on Advanced Conversion

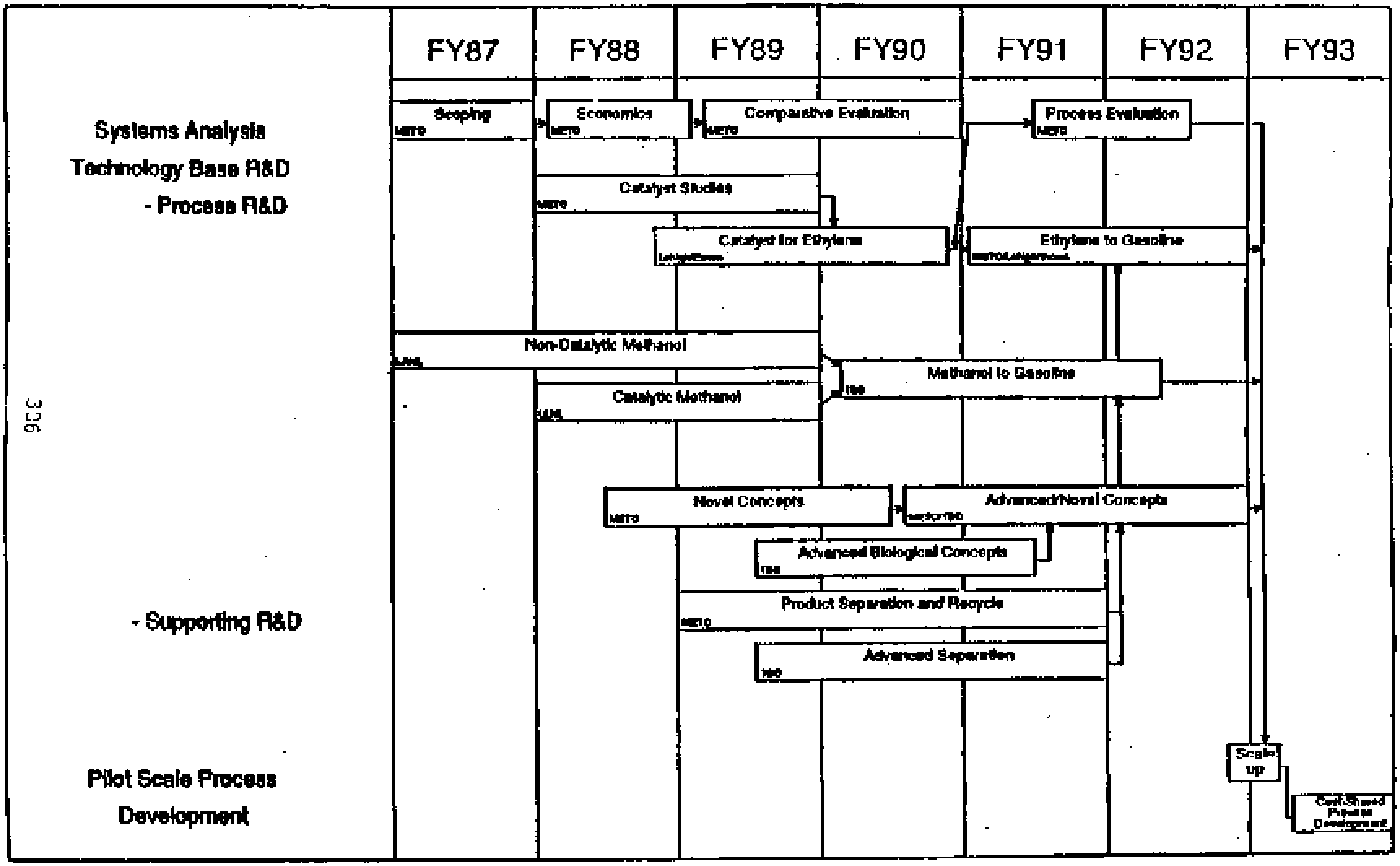
- Are economics favorable at "best" conditions?
- What are technical requirements for "good" economics?
- What are best product/byproduct separation and recycle techniques?
- What are "real" conversion characteristics?
  - Conversion/selectivity
  - Byproducts
  - Catalyst regeneration requirements
  - 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

Major Research Areas

- Catalytic processes
- Noncatalytic processes
- Biological processes
- Systems analysis

Conversion of Natural Gas to Liquids



Naturals Gas to Liquids Conversion

Current Research Activities and Participants

- Catalytic research
  - Catalytic selection and evaluation, METC
  - Development of synthetic catalysts, LLNL
  - Analysis of dual redox catalysts, Lehigh Univ.
- Noncatalytic research
  - Development of thermally induced conversion, LANL
- Biological catalyst research
  - Evaluation of new concepts/processes, TBD
- Systems analysis
  - Evaluation of conversion economics, METC

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

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

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

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

Conversion of Natural Gas to Liquids

Significant Accomplishments

- Developed a 93-reaction simulation model
- Low pressure kinetic model indicates selectivity at 70%
- A flow reactor developed for screening catalyst performance
- Demonstrated formation of methanol by laser irradiation
- A variety of metallic oxides and silica-based materials used for catalyst synthesis
- Lightweight metallic oxide suitable for chemical catalyst