

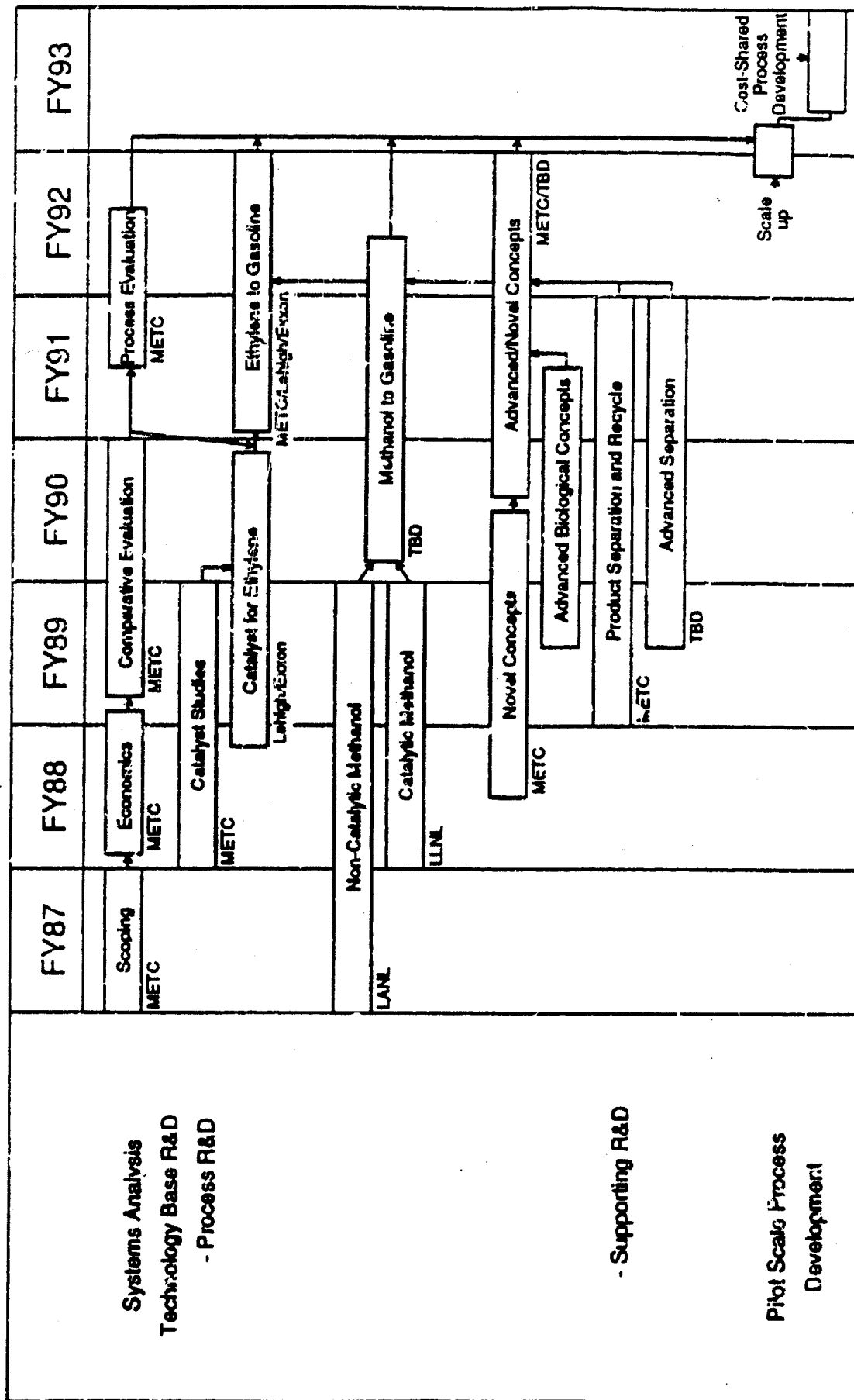


Figure 5. Research Plan for Conversion of Natural Gas to Liquids

V89-0145-E TE2

converted per pass through the reactor), (2) reduction in temperatures required for conversion, (3) improved methods for separating 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.

Some groups, both for direct partial oxidation to methanol and oxidative coupling to olefins, have shown promising results in the laboratory, but the conversion and selectivity achieved in these lab tests must be validated and improved. The factors controlling 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 required for some reactions (600 to 800°C for oxidative coupling, up to 1,000°C for noncatalytic conversion) would reduce the need for special materials of construction. However, the optimum temperature may not 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 requirement and the materials requirement may dictate the optimum temperature for the process.

By-products 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 both these by-products 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 the 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 being recognized more and more 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 FE programs, 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, bypassing the reforming step.

## 5.0 ACRONYMS AND ABBREVIATIONS

|         |                                        |
|---------|----------------------------------------|
| ARCO    | Atlantic Richfield Company             |
| atm     | atmosphere                             |
| B       | billion                                |
| bbl     | barrels                                |
| Btu     | British thermal unit                   |
| DOE     | Department of Energy                   |
| EOR     | enhanced oil recovery                  |
| FE      | fossil energy                          |
| FY      | fiscal year                            |
| GRI     | Gas Research Institute                 |
| IL      | indirect liquefaction                  |
| LANL    | Los Alamos National Laboratory         |
| LNL     | Lawrence Livermore National Laboratory |
| LNG     | liquefied natural gas                  |
| Mcf     | thousand cubic feet                    |
| Mcm     | thousand cubic meters                  |
| NETC    | Morgantown Energy Technology Center    |
| m bbl/d | million barrels per day                |
| MMBtu   | million British thermal units          |
| PETC    | Pittsburgh Energy Technology Center    |
| PDU     | process development unit               |
| R&D     | research and development               |
| SOHIO   | Standard Oil of Ohio                   |
| SNL     | Sandia National Laboratory             |
| TBD     | to be determined                       |
| Tcf     | trillion cubic feet                    |
| Tcm     | trillion cubic meters                  |

## 6.0 REFERENCES

- Gas Research Institute. April 1988. 1989-1993 Research and Development Plan and 1989 Research and Development Program.
- Green, W., et al., "Conversion of Natural Gas to Transport Fuels," AICHE Symposium of Fuels and Chemicals from Natural Gas, Louisiana, March 6-10, 1988.
- Kuo, J.C. August 1987. Evaluation of Direct Methane Conversion to Higher Hydrocarbons and Oxygenates: Final Report. 218p. DOE/PC/90009-3. NTIS/88003812.
- O'Hare, T.E., R.S. Sapienza, D. Mahajan, and G.T. Skaperdas. 1986. Low Temperature Methanol Process. Paper presented at Industrial and Engineering Chemistry Division Symposium, June 15, at American Chemical Society, Marco Island, Florida.

Proceedings of the Indirect Liquefaction Contractors' Review Meeting. 1988. December 8-9, 1988, Pittsburgh, Pennsylvania.

Studer, D.W., et al. 1986. An Update of the LaPorte Liquid Phase Methanol Program. Catalysis Reviews. -- Science and Engineering, 28(1), 13-88.

Summary Report. 1987. Sixth DOE Catalysis and Surface Chemistry Research Conference, October 14-16, 1987, Gaithersburg, Maryland. CONF-8710136.

Taylor, C.E., and R.P. Noceti. 1987. Conversion of Methane to Gasoline-Range Hydrocarbons. Paper presented at the Symposium on Hydrocarbon Oxidation, American Chemical Society, August 31-September 4, 1987, New Orleans, Louisiana.

## 7.0 BIBLIOGRAPHY

Danen, W.C. 1986. Plasma Chemistry Initiation. Catalysis Reviews. -- Science and Engineering. 28(1): 13-88.

JE Office of Policy, Planning, and Analysis. May 1988. An Assessment of the Natural Gas Resource Base of the United States. 202 p., DOE/W/31109-H1, NTIS/DE89010612.

France, J.E., A. Shamsi, L.C. Headley, and M.Q. Ahsan. 1988. Oxidative Coupling Catalyst Research for the Conversion of Natural Gas to Liquid Fuels. Energy Progress. 8(4): 185-188.

Guthrie, H., and J. Batchelor. 1988. Chemical Conversion of Natural Gas in the United States. Paper presented at the International Energy Agency Meeting on Chemical Gas Conversion, Oslo, Norway.

Hunter, N.R., H.D. Gesser, L.A. Morton, P.S. Yarlagadda, and D.P.C. Fung. 1987. The Catalyzed Conversion of Methane to Methanol at High Pressure. Paper presented at the American Chemical Society Symposium on Hydrocarbon Oxidation, August 31-September 4, 1987. New Orleans, Louisiana.

Klier, K., and R. Pitchai. 1986. Partial Oxidation of Methane. Catalysis Reviews. -- Science and Engineering. 28(1): 13-88.

# **Natural Gas to Liquid Fuels**

## **-- An Overview --**

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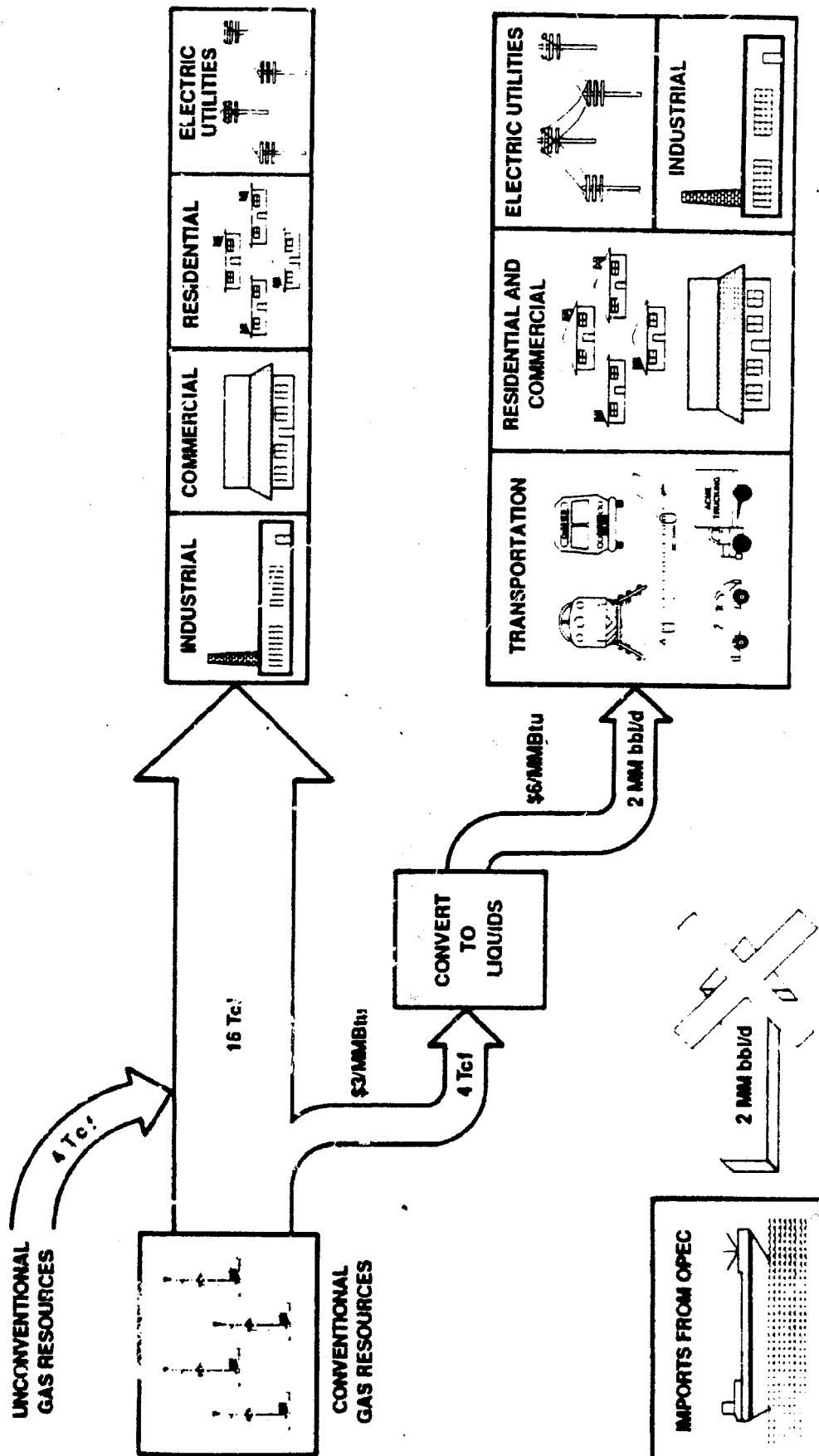
## Insights To New Trends In Transportation

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- 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

# Natural Gas to Liquids

- Expanded Domestic Resource Development Could Reduce Imported Oil -



METC

189-1115-B TE6

## Gasoline/Distillates are Most Desirable Conversion Products

| Product Options      | Advantages                                                                                                                                          | Disadvantages                                                                                                                                                                                      |
|----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Methanol             | <ul style="list-style-type: none"> <li>● Good turbine fuel</li> <li>● Low emissions</li> <li>● High production efficiency</li> </ul>                | <ul style="list-style-type: none"> <li>● Uncertain transportation market</li> <li>● Cannot Co-pipeline with oil</li> <li>● Low energy density</li> <li>● Toxicity/lack of visible flame</li> </ul> |
| Gasoline/distillates | <ul style="list-style-type: none"> <li>● Compatible with present supply/marketing systems</li> <li>● Miscible with crude oil in pipeline</li> </ul> | <ul style="list-style-type: none"> <li>● More complex process required</li> <li>● Lower production efficiency</li> </ul>                                                                           |
| Chemical Feedstocks  | <ul style="list-style-type: none"> <li>● More marketing and process options</li> <li>● Potential high value products</li> </ul>                     | <ul style="list-style-type: none"> <li>● Incompatible with Alaskan situation</li> </ul>                                                                                                            |



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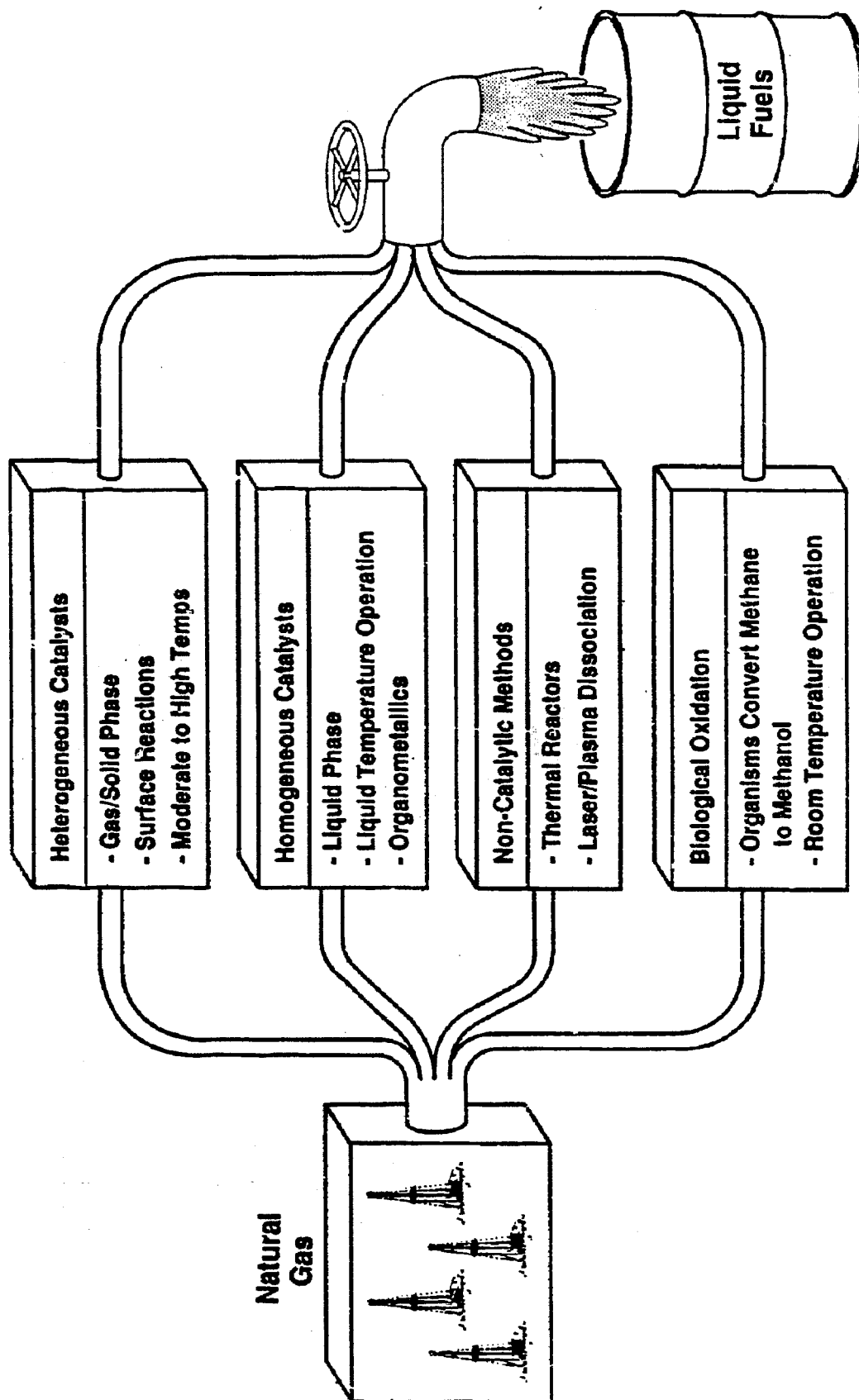
## Data Needs on Advanced Conversion

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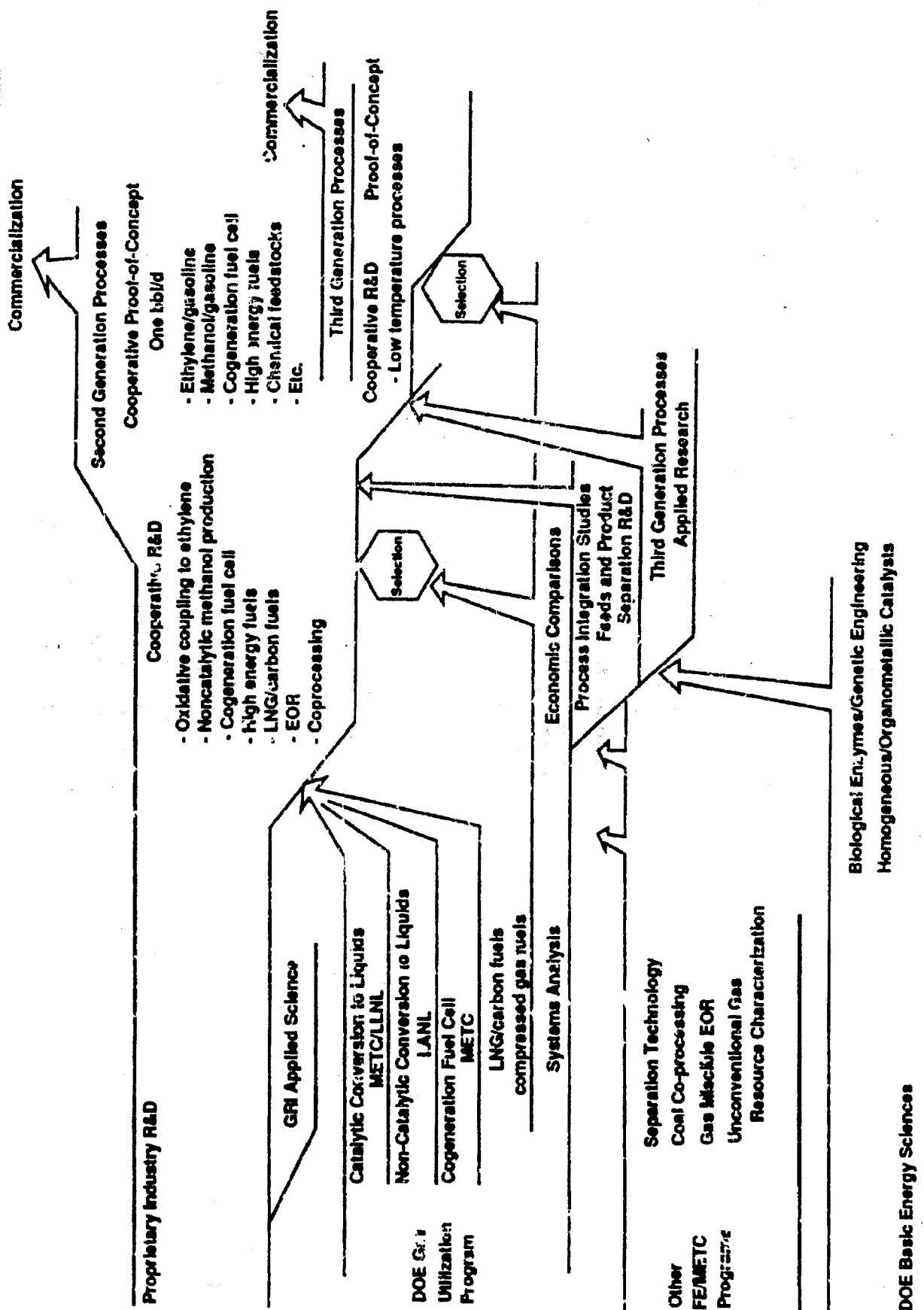
- Are economics favorable at "best" conditions?
- What are technical requirements for "good" economics?
- What are best product/byproduct separation and recycle techniques?
- What are "real" conversion characteristics?
  - Conversion/selectivity
  - Byproducts
  - Catalyst regeneration requirements
  - Poisoning/enhancement effects
- Can conversion/selectivity be significantly improved?
- What is best oxidant (air, O<sub>2</sub>, 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

- Technology Research to Accelerate the Conversion Process -



|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| FY 88 | FY 89 | FY 90 | FY 91 | FY 92 | FY 93 | FY 94 |
|-------|-------|-------|-------|-------|-------|-------|



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## Laboratory Research Needs

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- Investigate improved catalytic techniques
  - Emphasize ethylene-type commands
  - Flow reactions and surface mechanistic studies
  - Possible methanol studies
  - Determine yield, selectivity, byproducts, mechanisms
- Study potential synergistic or poisoning mechanisms
  - Non-methane compounds in natural gas
  - Reaction shifts due to recycle gas composition
- Assess "second-stage" catalysts for ethylene→gasoline conversion
- Explore advanced "dual function" catalysts
  - Single stage conversion to gasoline/distillates
- Assess organometallic chemistry for potential applications
- Investigate non-catalytic conversion (lasers/plasmas)

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# Naturals Gas to Liquids Conversion

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## 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

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## Thermally Initiated Noncatalytic Conversion

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### Description of work:

- Evaluate the potential of laser photolysis to initiate reaction
- Determine potential of selectivity from gas-phase chemistry
- Develop simulation model of conversion process and reactor chemistry

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# Silica-Based Catalytic Conversion

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## Description of work:

- Evaluate the potential use as conversion catalysts of metal doped silica-based materials
- Characterize the reactions and develop simulation of the reactor and the catalytic behavior
- Evaluate the potential use of biologic catalysts

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## Methane Oxidation of Dual Redox Catalysts

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### Description of Work

- Perform a series of experiments at both Lehigh University Laboratories and Exxon Research and Development Center
- Experiments will include a system of combined reduction and oxidation (REDOX) reactions in base and acid solutions
- The purpose is to evaluate the potential for selective oxidation of methane to C<sub>2</sub> hydrocarbons and methanol



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## Innovative Concepts

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### Description of work:

- To develop a simple, efficient process for the direct conversion of light alkane gases to liquid transportation fuels
- Design and synthesize a catalyst for the direct air-oxidation of light alkanes to alcohols
- Provide a catalyst design which will mimic biological enzymes, but will avoid problems associated with biological reactors

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## Methane to Olefins Conversion

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### Description of work:

- Develop and test improved partial oxidation catalysts to convert methane to intermediate olefin products
- Screen catalyst performance; investigate active sites and mechanisms; and investigate novel concepts such as combined function catalysts

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# Systems and Economic Evaluation

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## Description of work:

- Provide a preliminary estimate of transportation cost of gas from remote areas such as Alaska
- Determine the economics relative to the current and potential conversion process systems
- Identify areas where technology research and development could reduce conversion costs to commercial compatibility

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# Conversion of Natural Gas to Liquids

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## 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