

Department of Energy

Summary of published papers by the United States Department of Energy, Natural Gas-to-Liquids

1. Venkataraman, V.K., et al., "Natural Gas-To-Liquids: Solution for the Next Millennium, U. S. Department of Energy", Gas-To-Liquids Processing 99 Conference, Texas, 1999.

Describes the Department of Energy's RD&D program in Gas to liquids and the interesting opportunities for utilizing Fischer-Tropsch technology to extend the North Slope reserves and a rapid way to utilize the associated gas in the Gulf of Mexico.

2. Goguen, Stephen, "DOE Program on New Fuels and Diesel Technology: Performance, Emissions, and Durability Issues of New Diesel Fuels for Heavy Vehicles", Office of Heavy Vehicle Technologies, U.S. Department of Energy.

Presentation on DOE's tests and market potential for F-T diesel and discussion on what makes F-T diesel a good fuel.

3. Venkataraman, V. K., et al., "Overview of U.S. DOE's Natural Gas-to-Liquids RD&D Program and Commercialization Strategy", U. S. Department of Energy.

Describes how GTL allows use of North Slope and Gulf of Mexico gas reserves, and the benefits of the diesel fuels made from GTL have significant environmental and efficiency benefits over petroleum-derived diesel.

4. Singh, Gurpreet, "Alternative Fuels In Heavy Duty Vehicles Identifying Technologies and Markets for New Fuels", Office of Heavy Vehicle Technologies, U. S. Department of Energy, Gas-to-Liquids: Clean Fuels Strategy Conference, London, 1998.

Describes the DOE testing program for heavy duty vehicles and the results of testing showing the significant environmental improvements that operating these vehicles with Fischer-Tropsch diesel produces. Then goes on to describe the factors that make Fischer-Tropsch diesel a good fuel.

5. Belcher, Jack "DOE Sees GTL as Solution for Stranded Gas, Global Warming" Gas-to-Liquids News, February 1999.

The interview with Department of Energy officials explains that Department of Energy sees Gas-to-Liquids as a solution for stranded gas in Alaska and the Gulf of Mexico. In addition the Fischer-Tropsch diesel has significant environmental benefits and DOE sees it as offering a significant contribution to the reduction in carbon dioxide in the fight against global warming.

6. Vertin, Keith, "Gas-to-Liquid Fuels for On-highway Truck & Bus Engines" The National Renewable Energy Laboratory, A Department of Energy National Laboratory, Energy Frontiers International Conference, Arizona, 1999.

The National Renewable Energy Laboratory (NREL) discusses the use of gas-to-liquids products and how they could be exceptional future fuels because of the step change in emissions that result from its use in heavy trucks. The NREL has tested the Fischer-Tropsch diesel in unmodified engines and trucks and the results show significant reductions in all pollutants and no performance degradation.

Natural Gas-To-Liquids: Solution for the Next Millenium

- presented by -

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NATURAL GAS-TO-LIQUIDS: SOLUTION FOR THE NEXT MILLENNIUM

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Natural gas, which is comprised primarily of methane, is one of our most abundant energy resources, both domestically and abroad. Development of commercially viable technology for converting natural gas into transportation fuels and value added chemicals is of strategic and scientific importance. Unfortunately, many natural gas reservoirs are located in remote areas or offshore, and high transportation costs limit the use of this valuable resource. To overcome this limitation, the Department of Energy's Federal Energy Technology Center (FETC) has developed a highly diversified gas-to-liquids research program (Figure 1) to evaluate, promote, and develop processes that convert natural gas into products, whose higher value will offset the high transportation costs and allow use of this largely untapped, environmentally friendly resource (1,2). (Since methane has a relatively high hydrogen to carbon ratio, its use results in less carbon dioxide generation than with other fossil fuels.)

Three routes for the conversion of natural gas to transportation fuels and chemicals have emerged: direct conversion, indirect conversion, and physical conversion. In direct conversion processes, the methane in natural gas is directly converted into desired end products, such as ethane, ethylene, acetylene, or methanol. During indirect conversion, the natural gas is first converted into synthesis gas (a mixture of carbon monoxide and hydrogen) which is then converted into the desired end product, such as Fischer-Tropsch (F-T) liquids, methanol, MTBE, or mixed alcohols. In physical conversion, the physical state of the natural gas is changed, such as converting it to liquefied natural gas (LNG). All three approaches are currently under investigation as part of the gas-to-liquids conversion program at FETC. Equally as important as technology development is the economics of the conversion processes. Even the most innovative technology will not be used if it is not economically competitive. Therefore, the FETC program also involves continual economic evaluation of the processes under development.

Physical Conversion

Physical conversion is the simplest of the gas-to-liquids concepts, involving only changing the physical state of the natural gas. This usually means converting the natural gas to a liquid to form LNG. LNG occupies a much smaller volume than the original gas and can be maintained at ambient pressure, although it does have to be kept at cryogenic temperatures. One difficulty with LNG has been the cost of liquefaction. One novel approach being explored is known as Thermoacoustically Driven Orifice Pulse Tube Refrigeration (TADOPT). This technology, which is well suited for liquefaction capacities in the range of 500-10,000 gallons per day, has the unique capability of producing refrigeration at

cryogenic temperatures with no moving parts. Research on this concept is being carried out under a Cooperative Research and Development Agreement (CRADA) between Los Alamos National Laboratory (LANL) and Cryenco, a small business located in Denver, CO. TADOPTR has already been demonstrated at a production rate of 100 gal/day, and scale up to 500 gal/day is underway.

Direct Conversion

The direct conversion of methane to higher hydrocarbons has been extensively investigated over the past 15 years (3). However, the inherent stability of methane makes its direct conversion difficult, since most of the desired products are more reactive than methane itself and, once formed, tend to react further to undesirable by-products (CO and CO₂). With conventional catalytic systems, yields have remained low. In the case of C₂ production, yields have been limited to 30% or less. Yields of oxygenated products, such as methanol and formaldehyde, have been even lower, on the order of 5-6%. To overcome these limitations, FETC has funded relatively novel research projects, including the use of electric fields, plasma torches, and hydrogen transport membranes.

As an example of this approach, hydrogen transport membrane technology operates as follows. Methane is allowed to react in the absence of oxygen (pyrolytically) over a catalyst on one side of the membrane. Although conversion to higher hydrocarbons, in particular C₂, is highly equilibrium limited, the hydrogen produced during the reaction is selectively removed via transport through the membrane, thus removing the equilibrium constraint and allowing the reaction to proceed further. On the other side of the membrane, pure hydrogen can be recovered or the hydrogen can react with oxygen to produce water and generate heat needed for the pyrolysis reaction. In this latter case, the overall reaction is: $2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$, which is simply the oxidative coupling of methane.

Indirect Conversion

Indirect conversion of natural gas requires the intermediate production of synthesis gas (syngas) which is then converted into the desired end product. Syngas can be produced by a variety of processes, two of the most important being steam reforming and partial oxidation. In steam reforming, the hydrocarbons in the natural gas react with steam at high temperature to form a mixture of CO and H₂. In partial oxidation, the natural gas reacts with a mixture of oxygen and steam to form syngas. The H₂/CO ratio is higher from steam reforming than from partial oxidation. Both of these processes are energy and capital intensive, and syngas production remains the most expensive step in the indirect conversion of natural gas.

Since so much of the cost of indirect conversion is associated with syngas production, any improvement which reduces this cost will have a significant beneficial effect on indirect conversion economics. In turn, any reduction in the cost of oxygen manufacture would translate into a reduction in the cost of syngas by partial oxidation. One technology which shows considerable promise is the use of ceramic membranes for oxygen production. Air is passed over the outside of the membrane, which is a dense, nonporous ceramic material capable of withstanding high temperatures. Because of the nature of the ceramic material, the oxygen partial pressure differential across the membrane causes oxygen from the air to

diffuse through the membrane in the form of oxide ions (O^{2-}). Thus, air separation is achieved without the use of relatively expensive cryogenics or compression.

In addition to functioning as an oxygen separation unit, the membrane can also serve as the synthesis gas reactor. The process is depicted in Figure 2. If natural gas is passed over the inside of the membrane, it will react with the oxygen diffusing through the membrane, resulting in the formation of synthesis gas. When fully developed, this approach should substantially reduce both capital and operating costs for syngas production, thus allowing indirect conversion of natural gas to become an alternative, cost-effective source of liquid fuels and value added chemicals.

As an added benefit, recent studies have indicated that F-T fuels are considerably cleaner burning than conventional liquid fuels. The reductions in emissions are summarized in Figure 3. Obviously, reductions of this order provides considerable incentive to further develop and commercialize these fuels.

Economic and Process Analysis

It is imperative that the current status of all activities concerning the conversion of natural gas to liquid fuels be continually monitored and updated. Therefore, continued economic and process analysis of existing and potential natural gas conversion technologies is a necessary and integral part of the gas-to-liquids program. Recent studies include the potential and economics for offshore gas-to-liquids conversion and an economic assessment of Alaskan North Slope gas utilization options. Of particular importance in the latter work was the identification of the window of opportunity (Figure 4) to extend the life of the Trans Alaskan Pipeline System (TAPS) (4). Identification of a viable technology to convert gas to pipeline quality liquids by 2009-2016 could extend the life of TAPS by 20 or more years. Continued operation of TAPS is vitally important to Alaska's economy; therefore, there is considerable incentive to develop and commercialize new gas-to-liquids conversion technologies, capable of a 200,000-500,000 bbl/day production rate (either in a single unit or using multiple units), by early in the 21st century.

Because of the increasing interest in F-T, based on syngas from natural gas, as a potential source of high quality liquid transportation fuels, considerable effort has been expended on developing the economics of the F-T process. Recently, Bechtel conducted an economic study of a full scale F-T facility, using both natural gas and coal as feed stocks (5). In general, a F-T facility consists of three major sections - syngas production, F-T synthesis, and product upgrading, although the details within the sections will vary depending upon the type of feed, the syngas production technology used, the desired F-T product slate, and the degree of product upgrading (Figure 5). Reactor sizing is based on a slurry-bed reactor model developed from input from several sources (6).

Estimated total capital cost for a plant feeding 410 million SCFD of natural gas and producing about 45,000 BPD of F-T liquid products is \$1,840 million. At a southern Illinois location, the estimated Crude Oil Equivalent (COE) price is \$32.8/bbl (1994 dollars) if natural gas costs \$2/million Btu (Figure 6) (7). However, the COE price is strongly dependent on gas cost. If natural gas is available at \$0.50/million Btu, the COE price drops to \$19.7/bbl (Figure

7). From this analysis, it is clear that a low natural gas cost is necessary if F-T technology is to be competitive domestically. One place with potentially low cost natural gas is the North Slope of Alaska. The low value of North Slope natural gas is dictated by the high infrastructure cost required to bring this gas to market. However, if the gas were first liquefied using F-T technology, the F-T liquids could be blended in with North Slope crude and transported through TAPS, not only potentially extending the life of the existing pipeline but also avoiding the cost of a new natural gas pipeline. This scenario appears to offer a significant incentive for utilizing F-T technology on the North Slope.

If a F-T facility were to be built on the North Slope, its configuration would probably be somewhat different from that in Bechtel's baseline design. It is very unlikely that finished products would be produced on the North Slope. Rather, a so-called syncrude would be produced, which would consist essentially of the C_3+ product directly from the F-T reactors. Therefore, the product upgrading section of the baseline plant would be eliminated, thus reducing capital costs by 10-15%. However, construction costs will be higher on the North Slope than in the lower 48 states, and this may offset the savings from eliminating product upgrading. If some of the improvements discussed above, such as use of membranes for syngas production, can be incorporated, F-T technology for conversion of remote gas could be very attractive.

Recently, Energy International Corporation completed a DOE funded study evaluating the conversion of associated natural gas to liquid hydrocarbons (8). Of particular interest was their analysis of the potential of employing F-T conversion as a means of utilizing offshore associated gas. The report indicated that an offshore F-T could best be accommodated by a Floating Production, Storage, Offloading vessel (FPSO) based on a converted surplus tanker, such as have been frequently used around the world recently. Other structure types used in deep water (platforms) are more expensive and cannot handle the required load. The following conclusions were specified:

- In many water based locations such as, but not limited to, the Gulf of Mexico converted tankers offer an attractive "platform" for combining production operations with Fischer-Tropsch conversion of natural gas.
- At pipeline distances of greater than 200 miles, or with difficult ocean bottom conditions, Fischer-Tropsch conversion of remote natural gas may provide superior economics to pipeline delivery of natural gas.
- Given the availability of a ship mounted production/Fischer-Tropsch facility, one could get an early start on producing a new discovery, *i.e.*, otherwise marginal competitive economics could be made attractive from cash flow considerations.
- A floating Fischer-Tropsch plant is moveable/usable for a series of short life projects.

Conclusions

FETC has a comprehensive, balanced natural gas-to-liquids RD&D program, covering direct, indirect, and physical conversion of natural gas to transportation fuels and value added chemicals. This program includes continued economic and systems analysis of the technologies under development. Of particular interest is the development of new technology for producing LNG and development of membranes for both direct conversion processes and

syngas manufacture. A very interesting opportunity exists for utilizing F-T technology to convert remote North Slope natural gas to syncrude which would be shipped through TAPS, thus extending the life of that facility. The recent Energy International/DOE supported study indicates that there is a need for a more economical and/or a more rapid way of utilizing associated gas in the offshore Gulf of Mexico in the deep water provinces currently being actively explored and developed. Although not specifically addressed in this article, another potential source of natural gas for conversion to liquids is gas hydrates. DOE/FETC's research program on gas hydrates is now being initiated and has the potential to significantly expand in the future (9).

Acknowledgments

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References

1. Venkataraman, V.K. and Driscoll, D.J., "Natural Gas to Liquids: An Overview", Proceedings of the 1997 Coal Liquefaction & Solid Fuels Contractors Review Conference, Pittsburgh, PA, September 1997.
2. Venkataraman, V.K., Driscoll, D.J., H.D. Guthrie and R.A. Avellanet, "DOE Overview of Development Needs for GTL", Presented at Monetizing Gas Reserves Conference, organized by Zeus Development Corporation, Houston, TX, December 1997.
3. Driscoll, D.J., "Direct Methane Conversion", Proceedings of Gas Conversion: Strategies, Technologies & Activities, Energy Frontiers International, Girdwood, AK, July, 1997.
4. Final Report, "Economics of Alaskan North Slope Gas Utilization Options", Contract No. DE-AC07-94ID13223, August 1996.
5. Topical Report VI, Natural Gas Fischer-Tropsch Case, Volume II, Plant Design and Aspen Process Simulation Model, Baseline Design/Economics for Advanced Fischer-Tropsch Technology, Contract No. DE-AC22-91PC90027, August 1996.
6. Final Report, "An Innovative Catalyst System for Slurry-Phase Fischer-Tropsch Synthesis: Cobalt Plus a Water-Gas Shift Catalyst", Contract No. DE-AC22-87PC79816, July 1991.
7. Choi, G.N., Kramer, S.J., Tam, S.S., Srivastava, R.D., and Stiegel, G.J., "Natural Gas Based Fischer-Tropsch to Liquid Fuels: Economics," Society of Petroleum Engineers 66th Western Regional Meeting, Anchorage, Alaska, May 22-24, 1996.

8. Singleton, A.H. and Cooper, P.G. (Energy International Corporation), Final Report, "Conversion of Associated Natural Gas to Liquid Hydrocarbons", Contract No. DE-AC21-95MC32079, November 1997.
9. "A Strategy for Methane Hydrates Research and Development", Report No. DOE/FE-0378, U.S. Department of Energy, Office of Fossil Energy, August 1998.

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FETC Gas to Liquids Program

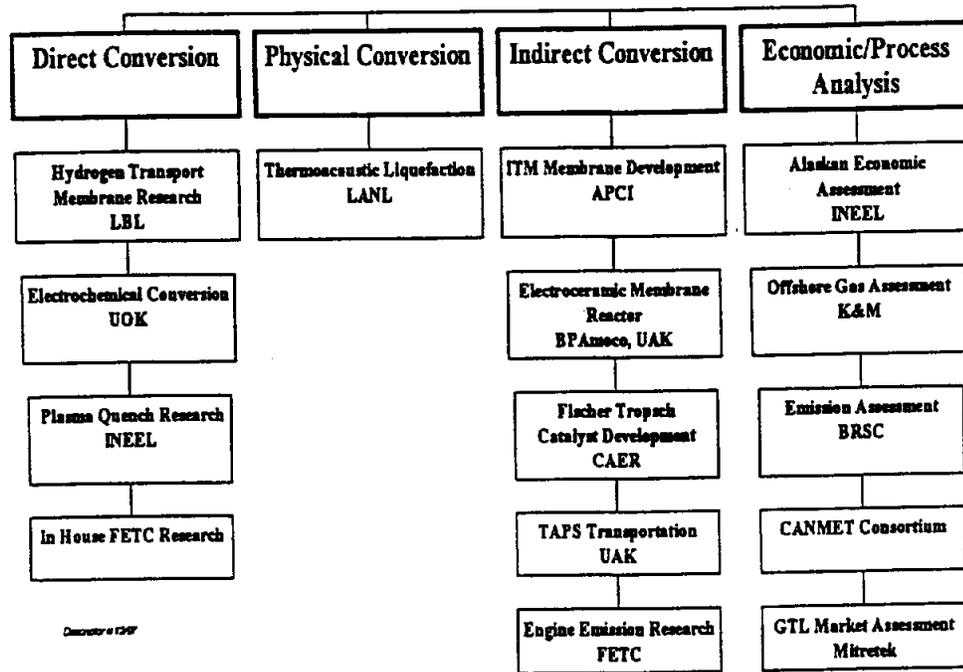


Figure 1

Oxygen Transport Membrane Reactor

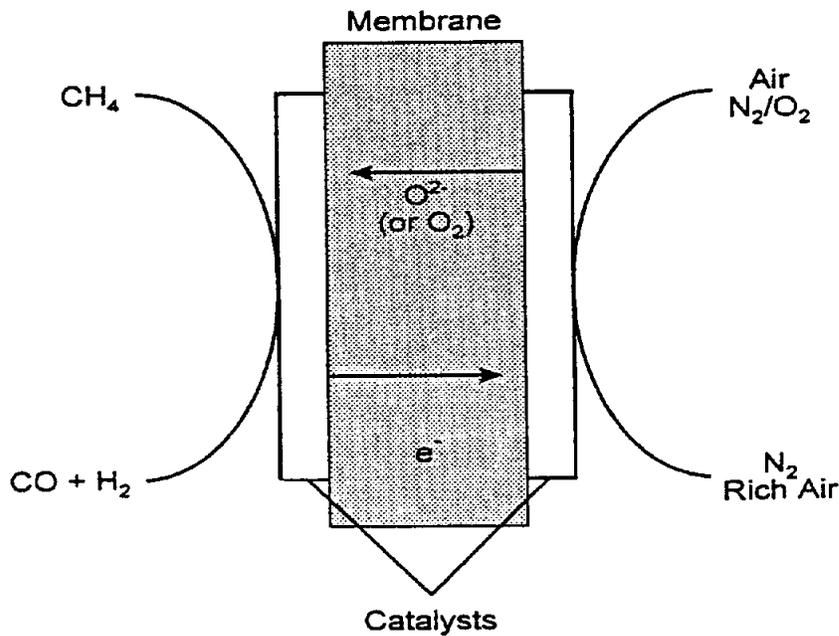


Figure 2

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Emissions Performance of Synthesis Gas-Derived Diesel Fuels Is Superior to Petroleum Diesel Fuels

Emissions Reduction Relative to Low Sulfur Petroleum Diesel

| | |
|--------------|--------|
| Hydrocarbons | 41-46% |
| CO | 45-47% |
| NOx | 9% |
| Particulates | 27-32% |

Emissions Reduction Relative to Low Sulfur/Low Aromatics Petroleum Diesel

| | |
|--------------|--------|
| Hydrocarbons | 25-31% |
| CO | 34-38% |
| NOx | 5% |
| Particulates | 23-29% |



Results are Independent of feedstock origin

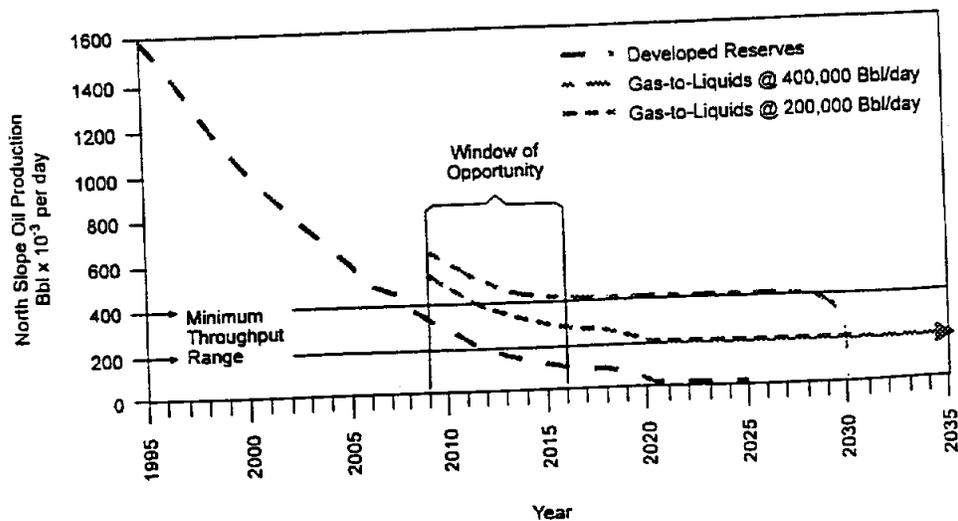


*Ranges based on three fuels, i.e., summer, winter, and California formulations, produced from natural gas and coal feedstocks.

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Figure 3

Window of Opportunity (2009-2016) for Deployment of Gas-to-Liquids Technology to Maintain Operation of the Trans Alaska Pipeline



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Figure 4

Natural Gas Fischer - Tropsch Study Overall Process Configuration

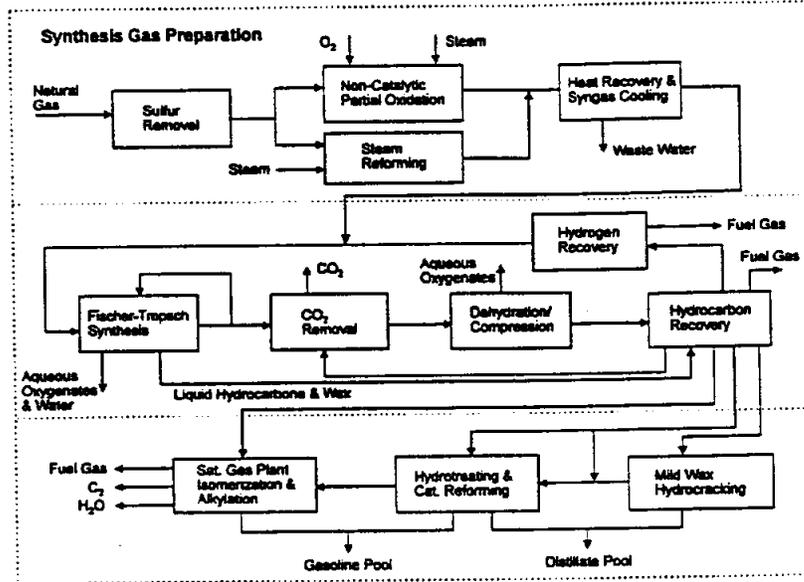


Figure 5

0.2
~~1.5~~
 \$ 28,000 / DAY
 AIR
 JS \$ 3,300 / DAY
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COE Cost Distribution @ 2.00 \$/MMBtu Gas COE = 32.80 \$/Bbl at Southern Illinois

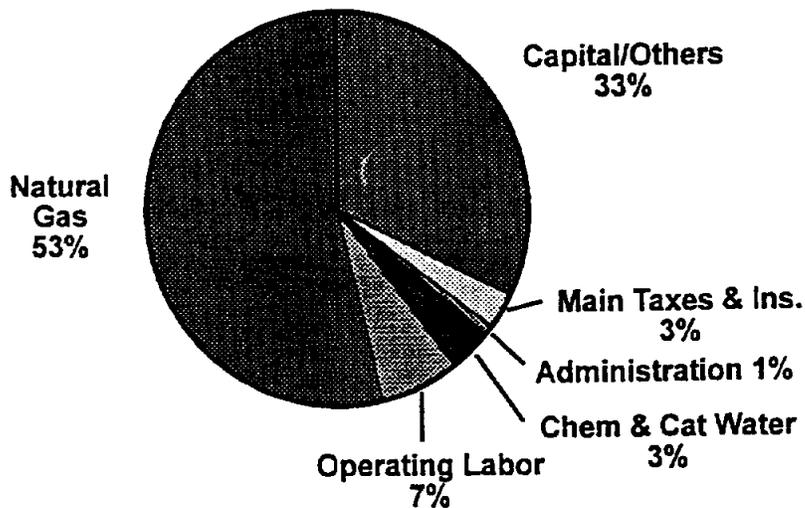
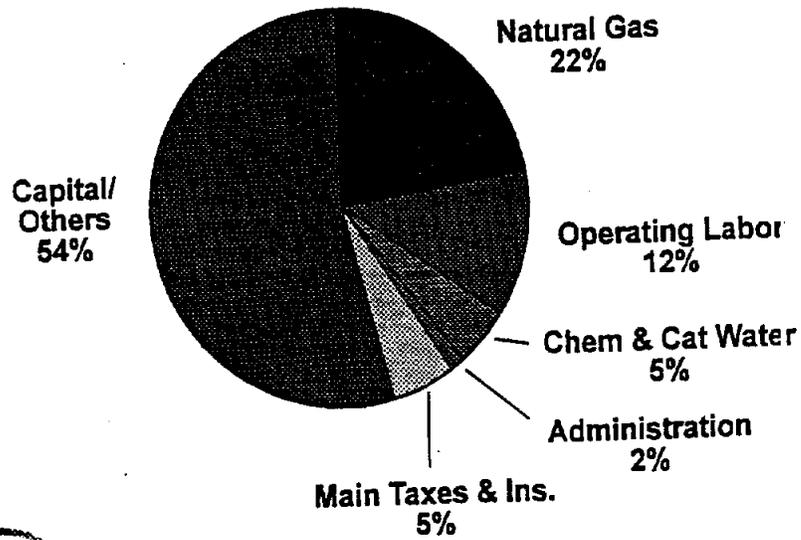


Figure 6

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COE Cost Distribution @ 0.50 \$/MMBtu Gas
COE = 19.70 \$/Bbl at Southern Illinois



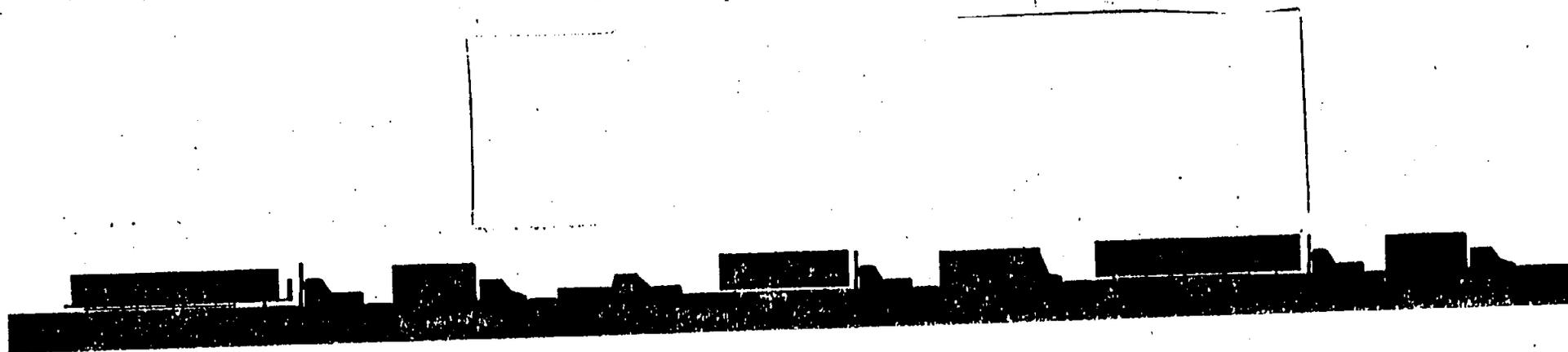
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Figure 7

DOE Program on New Fuels and Diesel Technology: Performance, Emissions, and Durability Issues of New Diesel Fuels for Heavy Vehicles



Stephen Goguen
Office of Heavy Vehicle Technologies
U.S. Department of Energy



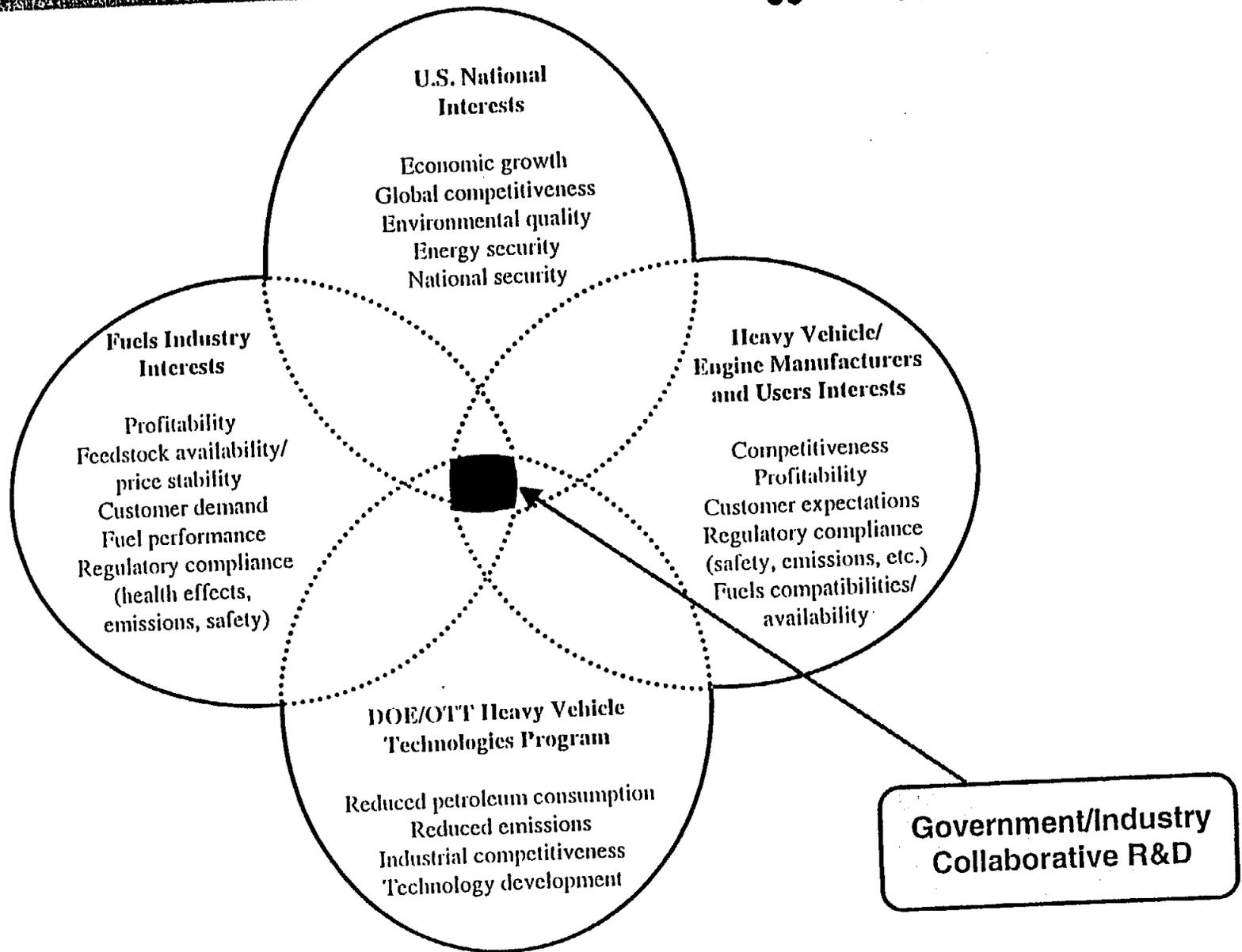
New Diesel Cycle Fuels Program



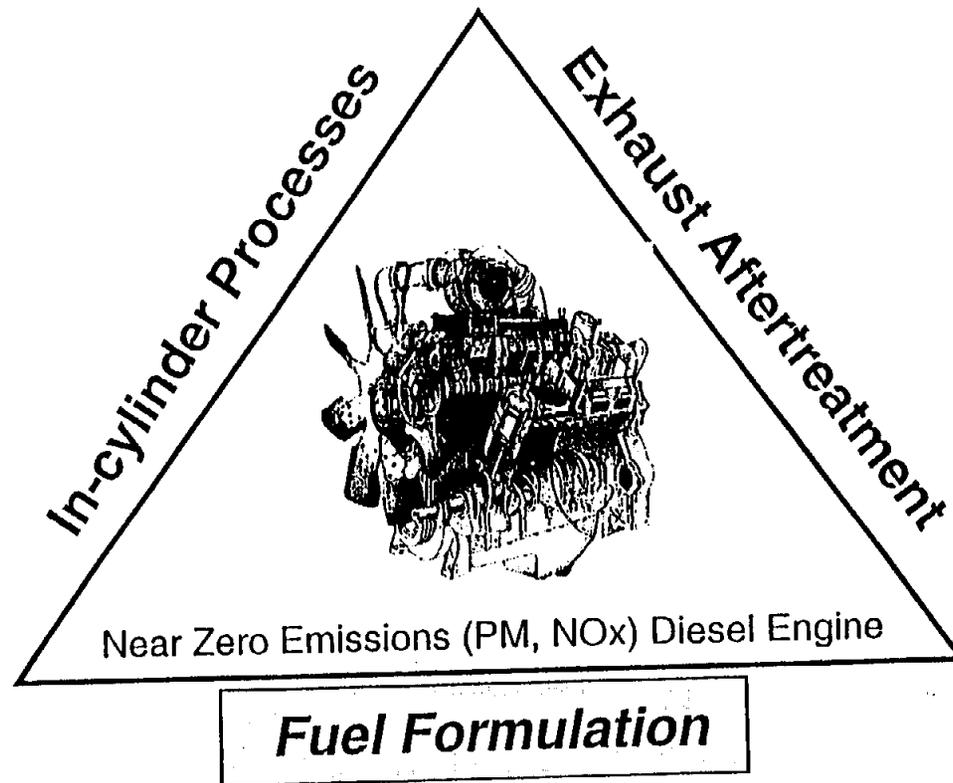
DOE's Role

Catalyze collaboration between engine manufacturers and fuel companies to develop performance, emissions and durability data on likely future diesel fuels

DOE/Industry Collaborative Efforts Target Common Interests



Diesel Cycle Engine Emissions Control Strategy



Three-pronged systems approach appears necessary to meet very low emissions without sacrificing engine efficiency

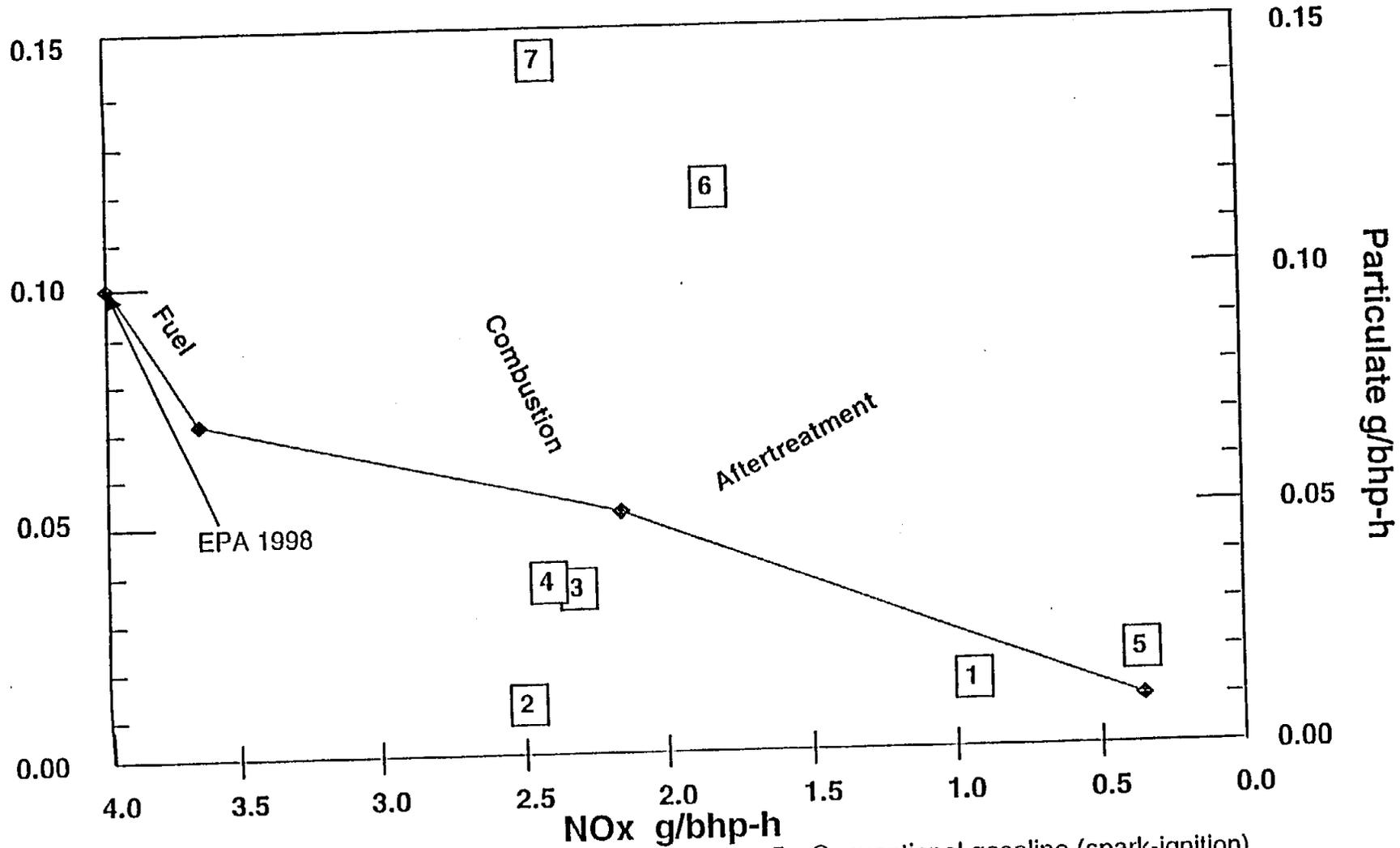
Alternative Fuels for Heavy Vehicles



In a systems approach, alternative fuels could:

- ◆ Shift the tradeoffs among NO_x, particulate matter, and engine efficiency;
- ◆ Shift the balance between engine technologies and aftertreatment; and
- ◆ Make certain aftertreatment technologies technically- and cost-competitive.

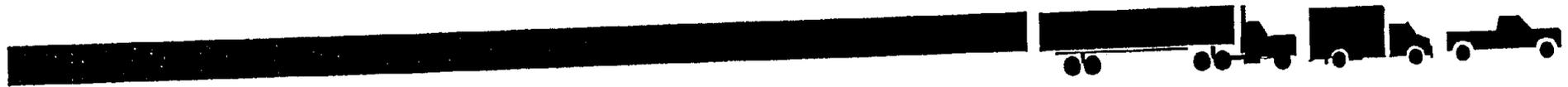
Very Low Diesel Emissions Technically Possible



1. DME/SCTE, turbo + EGR
2. Natural gas/Cummins C8.3-250 G with catalyst
3. Natural gas/Cummins L10-300 G with catalyst
4. DME/Navistar Diesel Engine (without EGR)

5. Conventional gasoline (spark-ignition)
6. Gasoline direct injection (GDI)
7. VW TDI (turbocharged direct injection diesel)

Advanced Heavy Vehicle Technologies R&D



Strategy for Future Fuels

- ◆ **Focus on the requirements of the Diesel cycle engine**
 - ◆ high cetane number for compression ignitability
 - ◆ low sulfur and low aromatics for clean emissions
 - ◆ lubrication requirements
 - ◆ additive requirements, e.g., fuel injector detergents
 - ◆ chemical compatibility, e.g., fuel solubility characteristics
- ◆ **Use existing liquid diesel fuel infrastructure**
- ◆ **Use domestic resources**
- ◆ **Use diverse feedstocks**

New Diesel Cycle Fuels Program



Status

- ◆ Conducted workshop (San Antonio, TX, January 15, 1998) to elicit input from engine manufacturers and fuel producers on New Diesel Cycle Fuels Program
- ◆ Program Objective:
 - ◆ To evaluate emissions, performance, and durability of advanced Diesel cycle engines running on potential future neat and blended liquid diesel fuels from alternative feedstocks (natural gas, biomass, coal, and petroleum).

Proposed Program Management Structure



Steering Committee

- Fuel Companies
- Engine Manufacturers
- Government

Advisory Board

- Academics
- Economists

R&D Program

- Sandia National Laboratories (Combustion Research Facility)
- Fuel Companies
- Engine Companies
- DOE 2000

Test Program

- Independent Test Facility
- West Virginia University (Mobile Emissions Lab)
- Sandia National Laboratories
- Federal Energy Technology Center

Status (continued)

- 
- ◆ Initiated screening test of Fischer-Tropsch diesel fuels in trucks and buses in service.
 - › Both current and emerging Diesel cycle engines used.
 - › Fleet testing of fuels in trucks and buses in service.
 - › Both chassis dynamometer and engine dynamometer tests will be conducted.
 - › Conventional diesel, 100 percent F-T diesel, and 50/50 blend to be used.
 - › To test trucks with Caterpillar dual-fuel (diesel fueled/natural gas using F-T diesel as pilot injection fuel)

1998 Screening Test of Fischer-Tropsch Diesel



Chassis Dynamometer Test Plan

| Vehicle | Engine | Fuel | Number of Vehicles |
|-------------------------|---------------------------------|-------------------------------------|--------------------|
| Transit Bus | DDC 6V92 | Conventional #2 Diesel | 5 |
| | | 100% F-T Diesel | 5 |
| | | 50% F-T Diesel | 5 |
| Class 8 Tractor | Cat 3176B Diesel Engine | Conventional #2 Diesel | 3 |
| | | 100% F-T Diesel | 3 |
| | | 50% F-T Diesel | 3 |
| | Cat 3176B Dual-Fuel Natural Gas | #2 Diesel Pilot F-T Diesel Pilot | 5 5 |
| Total Tests = 34 | | | |

5-mile route and new "City-Suburban Heavy Truck Route" will be used for emissions characterization.

What Makes Fischer-Tropsch Diesel a Good Fuel?

- 
- ◆ High Cetane Number of 76
(compared to 48-50 for conventional diesel)
 - ◆ No sulfur
 - ◆ No aromatics
 - ◆ Low cloud point (-10° C)
 - ◆ Low emissions (compared to U.S. average Diesel fuel, based on Southwest Research Institute study)
 - ◆ 8% less NO_x
 - ◆ 30% less PM
 - ◆ 38% less HC
 - ◆ 46% less CO
 - ◆ Even lower emissions possible in engines optimized for Fischer-Tropsch

U.S. Sources of Feedstocks for Fischer-Tropsch Fuels

Near term

- ◆ 37 tcf reinjected natural gas in North Slope of Alaska (would produce about 3.7 billion barrels of F-T diesel)

Mid term

- ◆ 246 tcf of sub-quality gas in lower 48 states [GRI 1993] could produce about 24 billion barrels of F-T diesel (more than twice the original Prudhoe Bay oil discovery)
- ◆ Combination of coal or biomass gasification plus use of lower 48 sub-quality gas (to furnish supplemental H₂) could lead to very large quantities of FT products.

Long term

- ◆ Virtually inexhaustible (1000's of Quads) supplies of methane tied up in methane hydrate off U.S. coastline

OVERVIEW of U.S. DOE's Natural Gas-to-Liquids RD&D Program and Commercialization Strategy

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R.A. Avellanet*

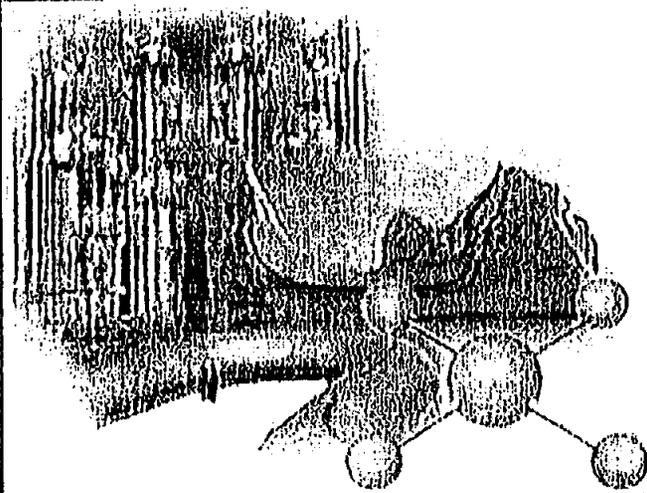
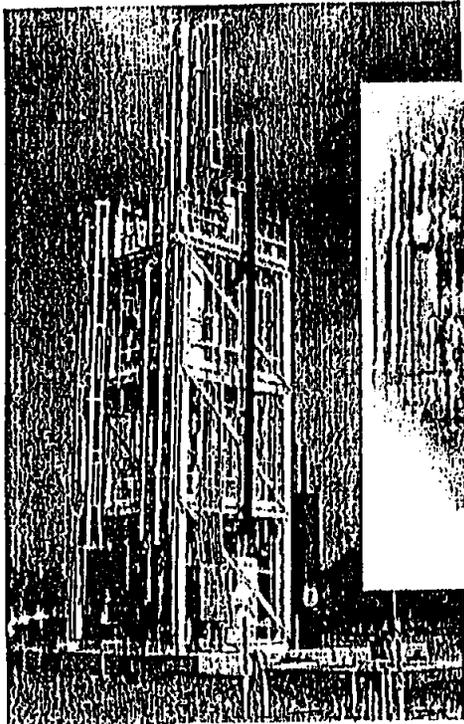
D.J. Driscoll

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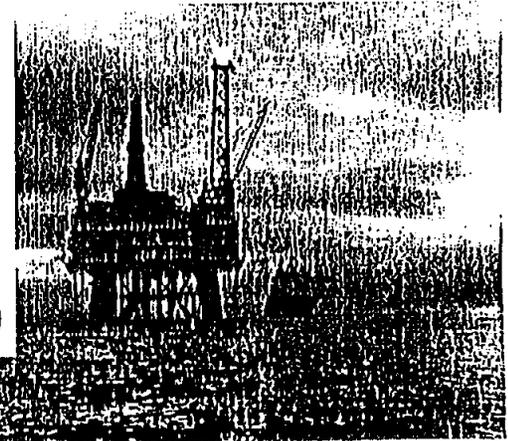
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Oil and Gas Programs**



Emerging Processing Technology Applications



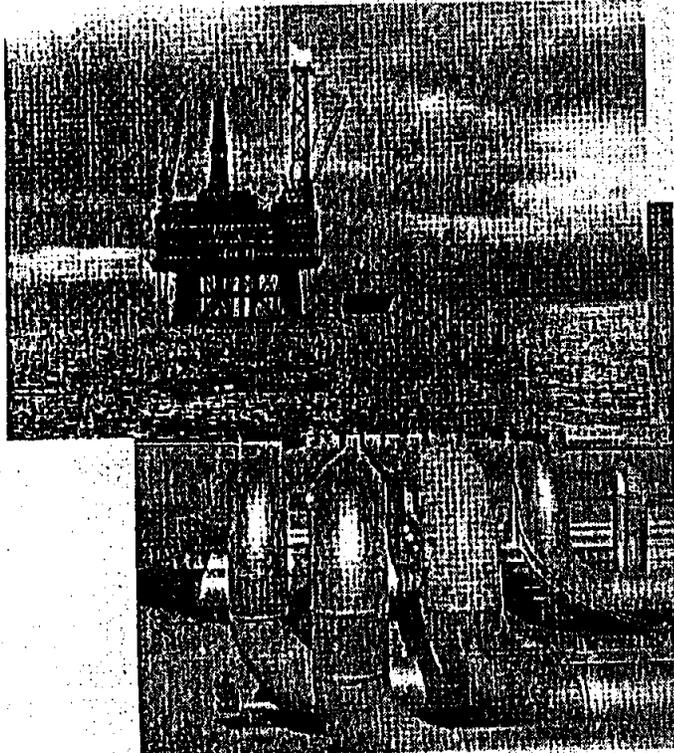
Venkat Venkataraman
Product Manager



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 FETC

Why Gas-to Liquids?



- **GTL option allows use, and extends life, of existing Trans-Alaska oil pipeline -- leading to additional North Slope oil production**
- **Advanced GTL technologies will allow remote and deep gas to be converted to transportable liquid fuels and petrochemicals**
- **Diesel fuels made with gas-to-liquids technology have environmental and efficiency benefits over petroleum-derived diesel**

Program Objectives

In partnership with industry, develop and demonstrate advanced technologies and processes for the economical conversion of natural gas to liquids that can be used for transportation fuels



Natural Gas Processing

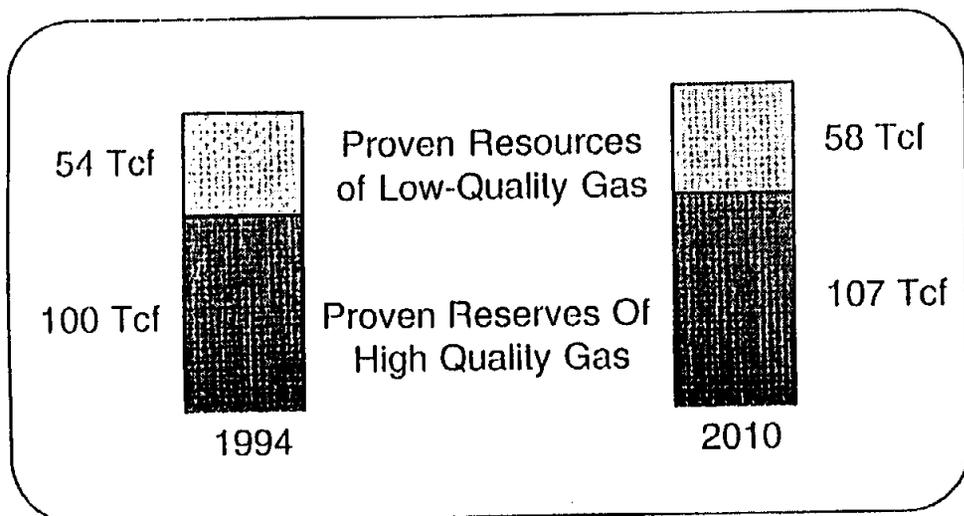
Program Drivers

Federal Government Role:

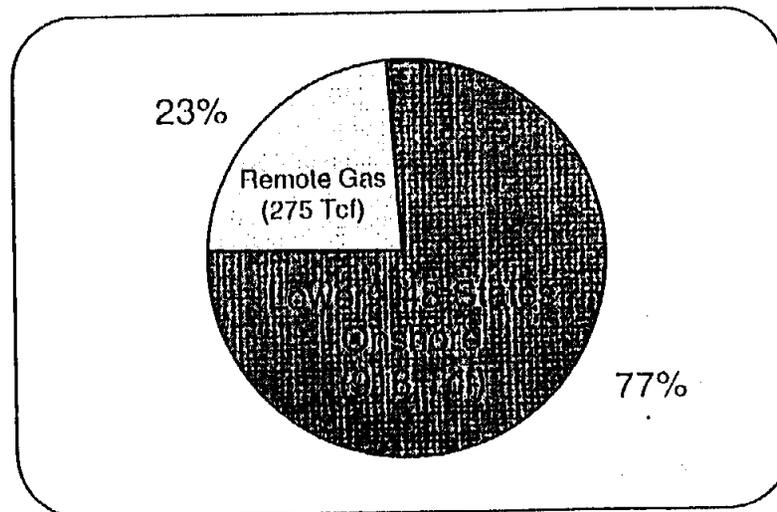
- Ensure reliable supply of pipeline quality natural gas
- Provide science and technology leadership

Develop advanced technology for economic conversion of remote gas to easily transportable and clean liquids - liquified natural gas, petrochemicals, fuels

Challenge: Convert unmarketable low-quality and remote gas resources into valuable gas and oil products



35% of Lower - 48 gas reserves do not meet pipeline specifications



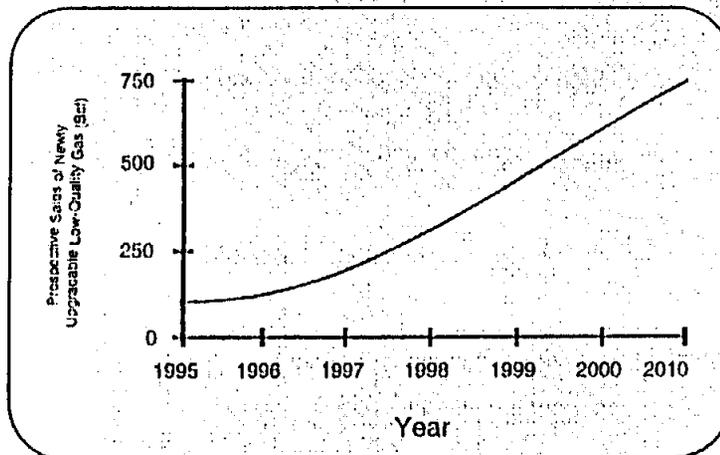
23 % of gas resources are in remote locations (Alaska and Deep Offshore Gulf of Mexico)



Natural Gas Processing

Impact of Technology

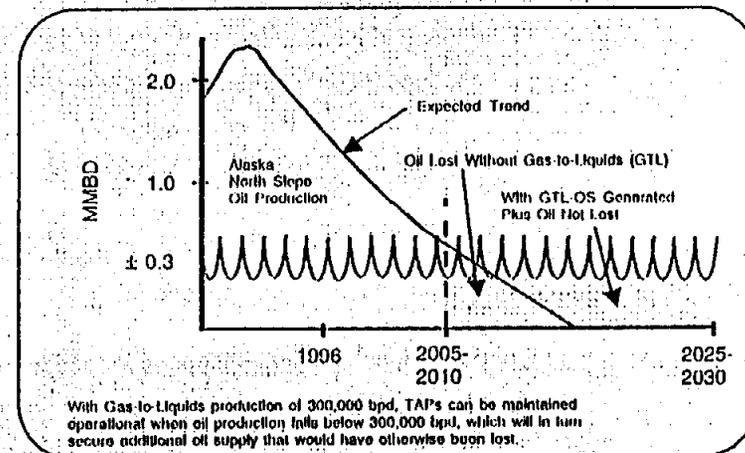
Advanced separation technologies will increase marketability of low quality gas...



- High efficiency gas separation processes can reduce the cost of upgrading low quality gas (average for N₂ removal \$0.50 - 1.00/Mcf) to pipeline heating and purity levels
- 25-50% reduction in nitrogen removal cost (\$0.15 - 0.30/Mcf reduction) will increase marketability for 15% of total U.S. gas resource

M990571 PPT

... advanced gas-to-liquids (GTL) technologies will allow conversion of remote gas to transportable fuels and petrochemicals



- Advances in separation technologies promise 25+% cost reduction breakthroughs for GTL conversion (from current technology \$26-28/bbl to \$18 - 22/bbl)
- Small-scale technologies of both LNG manufacture and GTL conversion can meet space and size limitations of remote offshore platforms and isolated, small gas deposits

FETC

Emerging Processing Technology Applications

Major Program Thrusts

■ ITM Ceramic Membrane (Air Products)

- Development of a novel ion/electron transport membrane which will reduce gas-to-liquids production costs 25-30%
- \$86MM effort, cost shared 35%DOE/65% Participant, DOE share split 75% FE/25% EE, complete repayment of DOE share by Participant in 20 years

■ Thermoacoustic Natural Gas Liquefier (LANL)

- Built and demonstrated a unique technology to convert natural gas to LNG (100 gallons per day)



DOE Gas-to-Liquids Program

DOE TECHLINE

DOE Selects Winner for Project To Make Liquids From Natural Gas

The U.S. Department of Energy has selected a team headed by Air Products and Chemicals, Inc., to scale-up the ceramic membrane technology for the production of synthetic liquid fuels from natural gas.

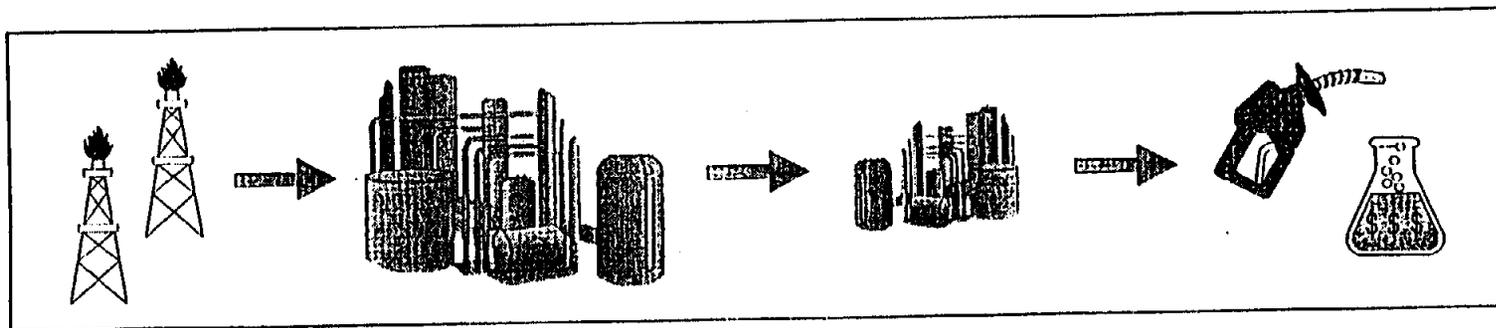
The team will develop a process for producing synthetic liquid fuels from natural gas. The process will be based on the use of a ceramic membrane reactor. The reactor will convert natural gas into a mixture of hydrogen and carbon monoxide. This mixture will then be reacted with carbon dioxide to produce synthetic liquid fuels.



Air Products and Chemicals Gas-to-Liquids Project

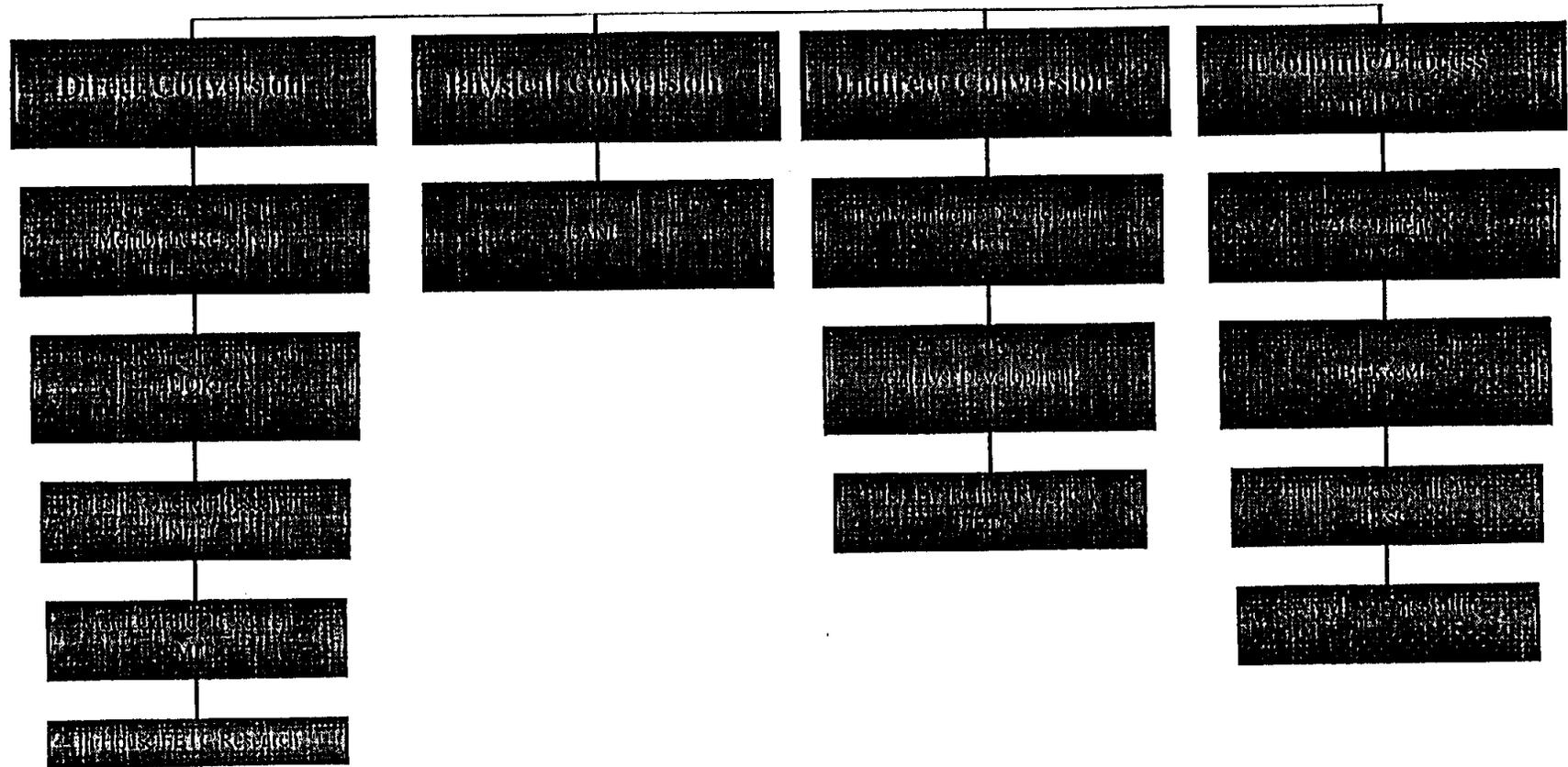
- On May 20, 1997, DOE announced the selection of a team headed by Air Products and Chemicals, Inc., to scale-up the ceramic membrane technology.
- Eight-year, \$85 million, cost-shared project
 - DOE: \$30 million
 - Industry Team: \$55 million
- Phase I (2 years): Membrane Development
Phase II (3.5 years): Technology Scaleup
 - Process Development Unit: 12 Mcf/day (2 bbls/d)
 - Sub-scale Prototype Unit: 500 Mcf/day (60 bbls/d)Phase III (2.5 years): Final Development
 - Pre-Commercial Plant: 15 MMcf/day (2,000 bbls/d)

Gas-to-Liquids Opportunities



- Production of environmentally superior transportation fuels.
- Production of high-value chemicals.
- Production of low-cost, high-volume hydrogen.

FETC Gas to Liquids Program

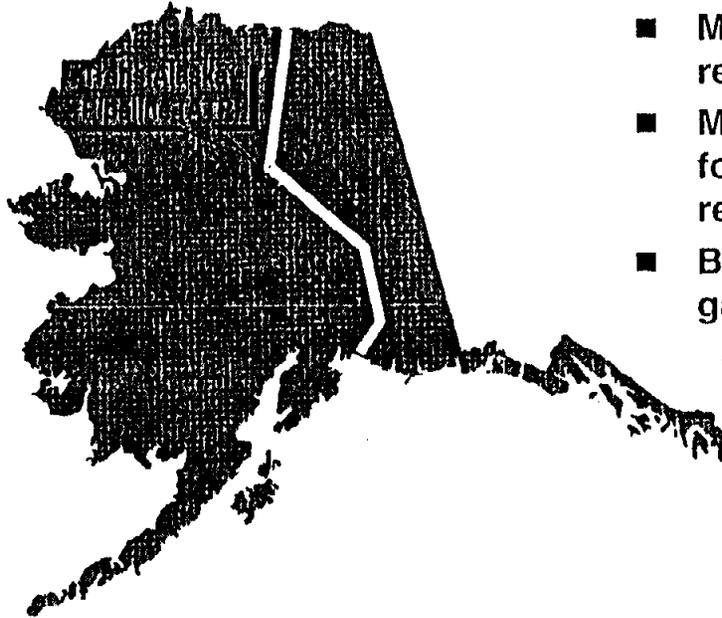


Methane Conversion

- **Direct Conversion**
Initial Conversion to Higher Hydrocarbons
(C₂ and oxygenates)
- **Indirect Conversion**
Synthesis Gas Production
- **Physical Conversion**
LNG Production



Alaskan North Slope Natural Gas Economic Opportunities



- Known and recoverable resource is 40 trillion cubic feet (TCF)
- Most likely undiscovered and recoverable resource estimated at 64 TCF
- Majority of gas currently reinjected to reservoir for interim enhanced oil recovery as remaining recoverable oil diminishes
- Building an 800-mile Trans Alaska Pipeline for gas transport would cost \$14 billion
 - Converting known developed reserve to liquid fuel could extend use of TAP by 25 years or longer while concurrently recovering an additional 1 billion barrels of oil

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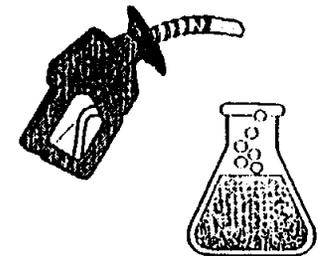
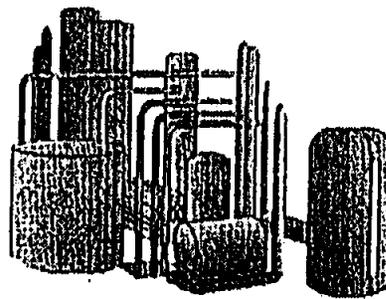
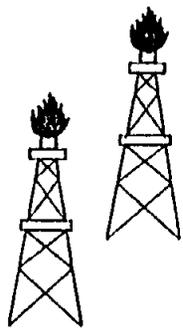


Program Benefits

- Enhanced utilization of on/offshore natural gas resources (1200 Tcf).
- Utilization of 100 Tcf natural gas resources in Alaska.
- Continued operation of TAP transporting both petroleum and gas-derived fuels for at least 25 years.
- Continued operation will result in recovery of an additional 1 billion barrels of petroleum.
- Increase of domestic natural gas production by 1 Tcf per year for each 172 million barrels of fuel produced (Btu exchange basis).

Indirect Conversion

Existing Process Cost Breakdown



Gas



Synthesis Gas
Generation

60%



Synthesis Gas
Conversion

25-30%



Product
Refining

10-15%



**Engineering Development of Ceramic Membrane
Reactor Systems for Converting Natural Gas to
Hydrogen and Synthesis Gas for Liquid
Transportation Fuels**

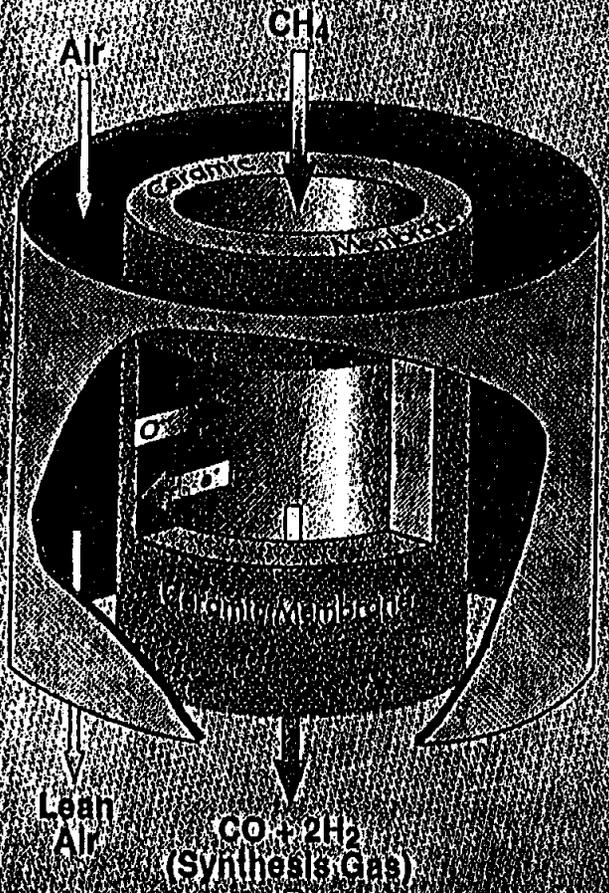
Air Products, *et al.*

Project Objectives

**To develop and commercialize novel oxygen
ion/electron conducting ceramic membranes
for the conversion of natural gas to syngas**



Breakthrough Technologies



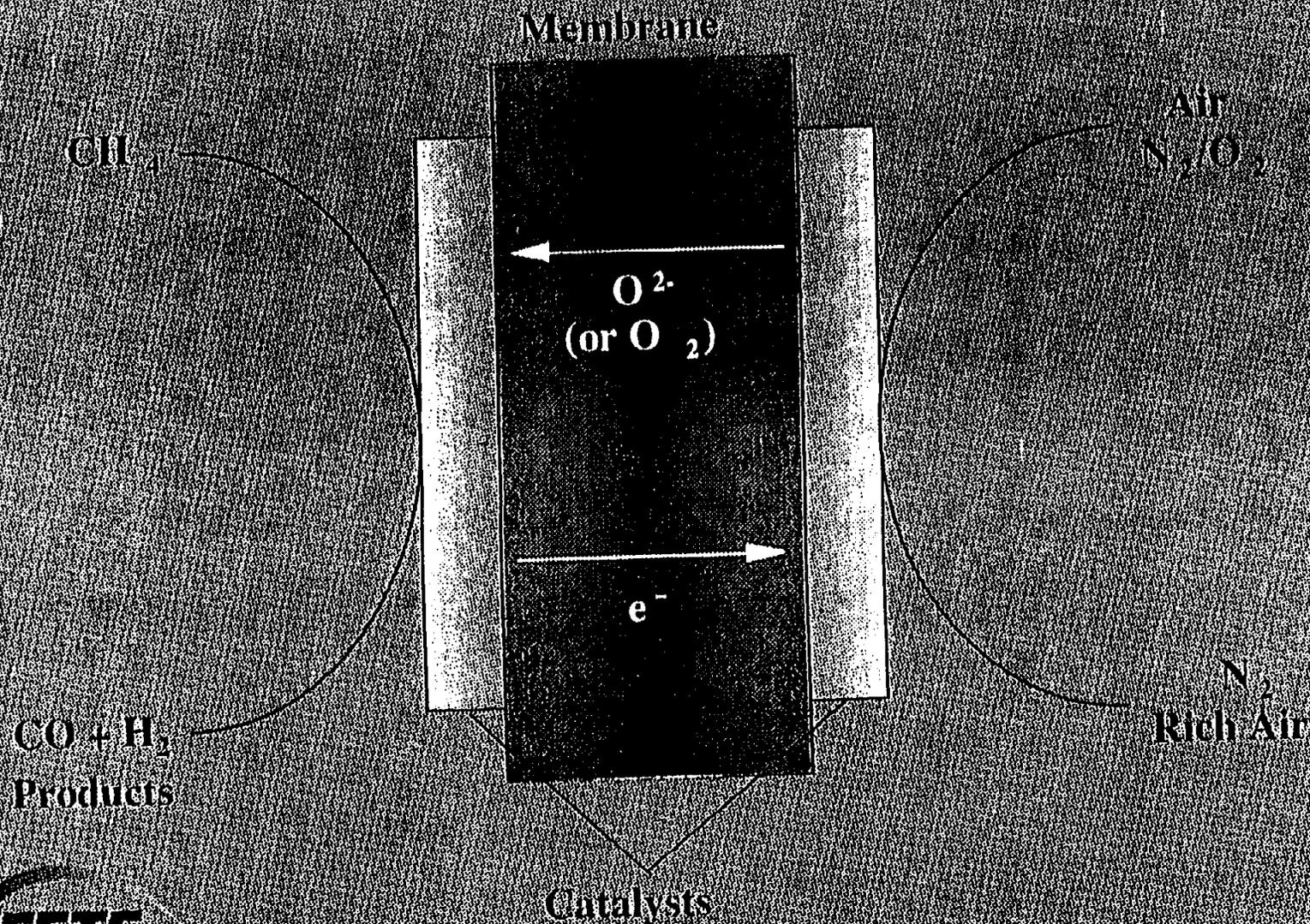
Mixed-Conducting Membrane

- 25% reduction in capital and operating costs
- Opens cost-effective routes to high quality transportation fuels and chemicals
- Target estimated cost \$15 per barrel by 2005.

High quality
Transportation Fuels and
Premium Chemicals

Hydrogen Production

Oxygen Transport Membrane Reactor



Major Research Issues

- **Oxygen flux**
- **Membrane thickness**
- **Ceramic stability**
- **Seals**
- **Reaction temperature**
- **Catalyst deposition/Thermal Compatibility**



Thermoacoustic Natural Gas Liquefier

Los Alamos National Laboratory

Project Objectives

**To develop and demonstrate the ThermoAcoustically
Driven Orifice Pulse-Tube Refrigerator (TADOPTR)
as an economically viable alternative to produce
liquefied natural gas (LNG) from natural gas**



Project Status

- No moving parts in the liquefier unit
- Achieved LNG production rates of 100 gallons/day
- CRADA developed with Cryenco
- Presently scaling up to 500 gallon/day production



Feasibility Study to Evaluate Plasma Quench Technology for Natural Gas Conversion

**Idaho National Engineering and
Environmental Laboratory**

Project Objectives

**To determine engineering and economic
feasibility of plasma quench technology
and**

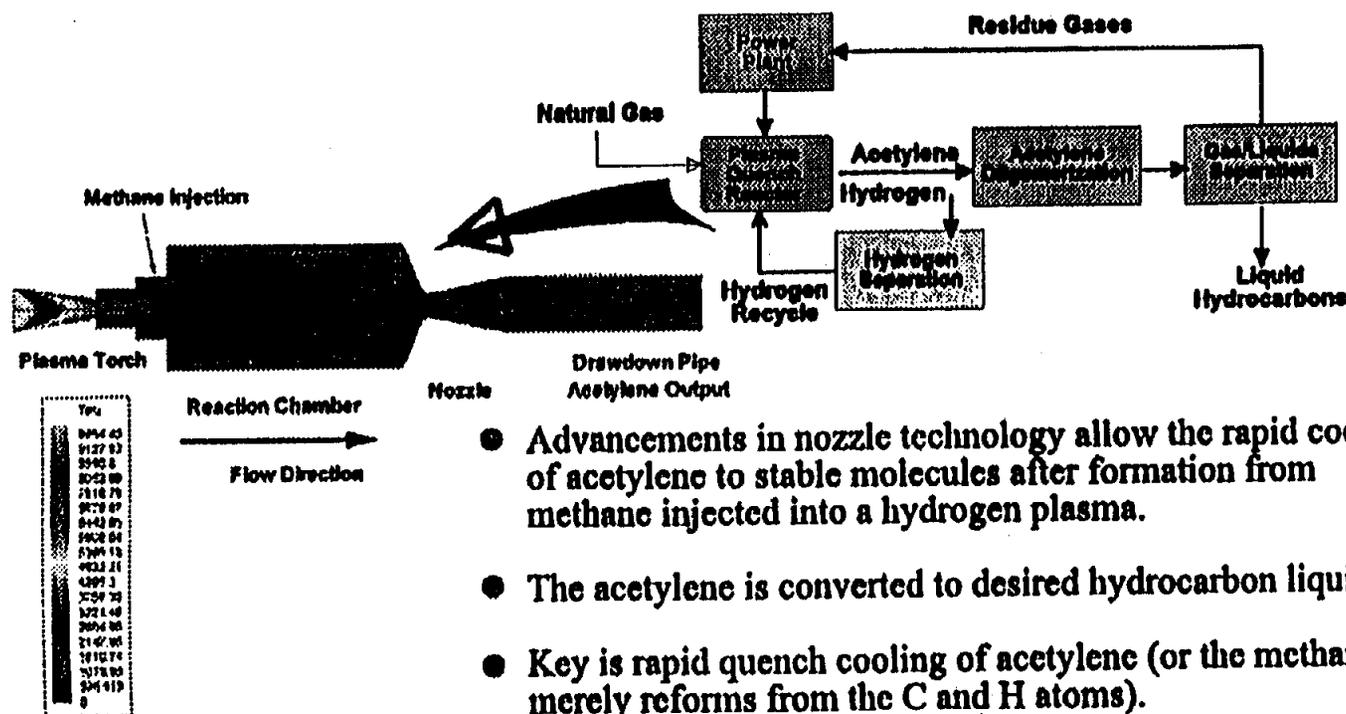
**To develop the plasma quench technology
process for the conversion of natural gas to
acetylene and liquid hydrocarbons**





DOE Gas-to-Liquids Program

An Alternative Gas-to-Liquids Approach Plasma Quench Process



- Advancements in nozzle technology allow the rapid cooling of acetylene to stable molecules after formation from methane injected into a hydrogen plasma.
- The acetylene is converted to desired hydrocarbon liquids.
- Key is rapid quench cooling of acetylene (or the methane merely reforms from the C and H atoms).

Project Status

- Three reactors currently being tested: tungsten, copper and high carbon steel
- Acetylene yields of >90% achieved at 75kWhr power ($2 \text{ CH}_4 = \text{C}_2\text{H}_2 + \text{H}_2$)
- Carbon deposition issues (15% at times)
- Demonstration planned in 1998



Special Washington Report:

DOE Sees GTL as Solution for Stranded Gas, Global Warming

In funding numerous R&D projects on gas-to-liquids technology, the U.S. Department of Energy is seeking to find a way to foster utilization of the stranded gas reserves of Alaska and the Gulf of Mexico, according to two officials with DOE.

"Our focus is the gas we have in the Alaska North Slope that is removed from the market and gas in the deepwater Gulf of Mexico that is far from pipelines," said Ralph Avellanet, program manager, gas processing, DOE.

DOE, in working with other federal agencies like the Environmental Protection Agency, also sees natural gas and gas-to-liquids as a part of the solution to reducing motor vehicle emissions that can pollute the air. "It generates far less CO₂ than coal or oil," said Sandra Waisley, DOE associate deputy assistant secretary for the Office of Natural Gas and Petroleum Technology in the Office of Fossil Energy. "So we can use it as a transition fuel. And that's why we have expanded and accelerated this program."

Potential remote U.S. gas reserves makes GTL a very attractive transportation fuel option for the future, the DOE officials noted. "We know from what has been identified and made public for Prudhoe Bay and other North Slope reservoirs, that there are well over 25 Tcf of gas that you could actually sell. And there may be two or three times as much up there," said Avellanet.

Further, those numbers could get much larger when you look at all of the methane hydrates—methane trapped in cages of ice and sediment on the ocean floor and also inland. "The potential resource in the Arctic, East Coast, West Coast and Gulf of

Mexico is tremendous," said Waisley, who noted that a U.S. Geological Survey report estimated that there is a 200,000 Tcf resource offshore. "Our program is seeking to delineate that resource base and its producibility. But this is a 15-year program," she said.

Agency Role

DOE's gas-to-liquids programs attempt to work with the private sector to make sure commercially viable GTL processes are available for when those domestic resources can be accessed. Prudhoe Bay gas will not be available until the reservoirs' oil is largely recovered eight to 10 or more years from now.

"Our job is basically to define the realistic GTL options for this and other remote gas. We want to make sure that the technology is there in the future, especially in light of significant decreases in oil and gas R&D spending in the private sector," said Avellanet.

In providing assistance to the private sector, DOE is producing an advanced process database that will be available to anyone seeking GTL development in the U.S. "It is important to give the decision makers in the private and public sectors information they can use to work out the best deals for the U.S., the states involved and the developers themselves," he said.

DOE sees itself as partial financiers in important GTL research projects advancing technology. Such projects are cost-shared. An example is the ionic transport

membrane (ITM) syngas project, directed to the development of a 1-step, air-oxygen separator and syngas generator.

It will be done in three phases, with DOE funding about 35% of the project.

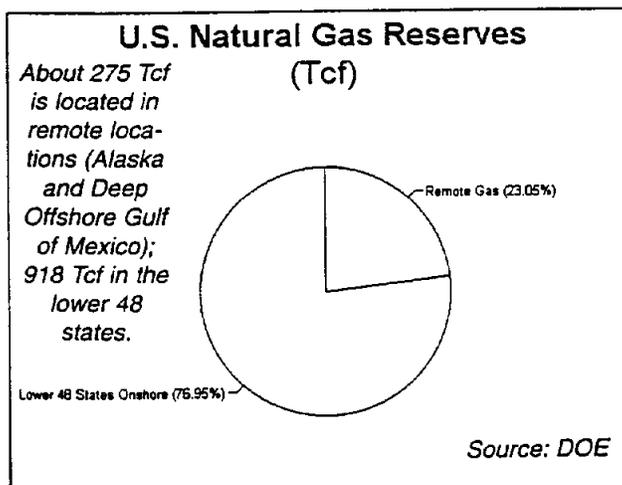
"We can play a leadership role here, providing greater cost-sharing at the higher-risk, scaled-up on to the last stage--precommercial sized operations," said Avellanet.

And in this case, the project also has a recapture arrangement whereby, if the technology becomes profitable, the government gets its money back through a percentage of the profits.

Some of DOE's GTL projects have several participants from the private sector. For example, there are two groups working with DOE on ceramic membrane technology for syngas generation.

The ITM-Syngas group is led by Air Products & Chemicals and includes ARCO, Chevron, McDermott Technology Inc. and Norsk Hydro. Another group called the Alliance includes BP-Amoco, Phillips, Praxair, Sasol and Statoil. Other projects include only one or two participants.

In addition, the GTL program sup-



Special Report:**DOE Sees GTL as Solution ... (from p5)**

ports joint efforts of mutual interest with DOE's coal liquids program, and also joint efforts with the fuels utilization R&D element of DOE's transportation technologies research effort. Similarly, DOE's hydrogen program is partially funding the \$86 million ITM-Syngas project, noted Avellanet.

Some of the biggest breakthroughs in GTL R&D in DOE programs have taken place in the area of ceramic membranes. "That one can selectively pull oxygen through a ceramic membrane from the air side to the reaction side where you're making the syngas by controlled, partial burning of the methane--that's pretty impressive and I think the industry realizes that," said Avellanet.

But there are many complexities in making this technology work, such as connecting a metal tube to the ceramics to take the gas away without burning it up in the associated 1,000C temperatures. However, he noted that progress is being made and he remains optimistic that the ITM-Syngas program could exceed expectations.

Plasma quench technology is another focus of DOE funding, though still more in the exploratory stages. There are some big questions regarding both its workability and its economics. "Basically you are injecting methane into a hydrogen plasma forming acetylene. The problem is what do you do with the acetylene?," asked Avellanet.

"Yes, it may be a chemical building block, but more for aromatic compounds rather than for straight-chain paraffinic compounds sought for advanced fuels."

But the quench could be operated using excess power from GTL production in places like the Alaskan North Slope that don't have much of a mar-

ket for power. And some companies believe that they can make syngas of any composition using a plasma quench.

New technology is also being focused on the cost-effective, small-scale manufacture of LNG.

One DOE-funded project is seeking to develop a thermoacoustic liquefier for LNG production (*see story, p11*). "We are using sound waves to put in a pulse using helium as a medium to effectively run a sterling engine for a refrigeration cycle to allow really small levels of LNG manufacture at acceptable efficiency," Avellanet said. The project is taking place with DOE's Los Alamos National Laboratory with Denver-based Cryenco. "That project is very intriguing," he said, noting that it could be used for the stranded gas in offshore locations.

Moving Target

While reaching commercialization in GTL is not an easy task, "every plant is going to have a different situation," said Avellanet.

For instance, North Slope and Qatar construction costs are going to be high, but in Qatar, you are right on the harbor so costs might be less, plus you might be able to sell the power easily, he said.

Another consideration is how cheap is the gas? "If you have a 50,000 to 100,000 barrel per day plant with free gas then you probably can make it pay, even today, depending upon how isolated you are." But how many producers are ready to give away a lot of gas, he added.

Another factor that will affect commercialization is worldwide environmental statutes, said Waisley. "We have restrictions on flaring in the U.S. and the whole world is tightening such

restrictions," she said (*see story, p.7*). Also the Administration is trying to encourage the world to comply with Kyoto, she noted. While utilizing remote gas resources is the primary driver behind DOE's GTL program, environmental factors are the second driver. "The U.S. is moving forward with its environmental movement—I don't think that is going to stop."

When asked what DOE would like to see in GTL 10 years down the road, Avellanet answered, "I'd like to see a commercial scale operation in Alaska." But he noted that he expects LNG production to become more economic by that time as well and both may very well be forthcoming for North Slope gas.

"We have a strong interest in providing development options in Alaska. Prudhoe Bay has 25 to 30 Tcf of gas that needs a market," he said, noting that future projects like those to take place at Alpine, Point Thompson, the National Petroleum Reserve-Alaska and other places will increase the known gas reserves in the region.

And with oil depletion lessening the amount of oil shipped through the TransAlaska Pipeline, new shippable liquid products need to be developed to keep the pipes economic.

While Avellanet does not foresee GTL products being able to handle the entire U.S. transportation fleet or even a major fraction, he does see them making a contribution. And it may be something other than FT distillates—perhaps a new form of additive. "We will probably participate with our allied coal liquids people, searching out whether there are some new fuels we can focus on, before we can get completely wedded to FT diesel products."

--Jack Belcher

Gas-to-Liquid Fuels for On-Highway Truck & Bus Engines

Energy Frontiers International Conference
Tucson, AZ - January 18-20, 1999

Prepared by: Keith Vertin, (303)275-4422



The National Renewable Energy Laboratory
A Department of Energy National Laboratory

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The Use of "Gas-to-Liquids" for Transportation Fuels

- Gas-to-Liquid blendstocks can be used to upgrade crude-derived diesel fuels
 - zero sulfur & high cetane products such as Fischer-Tropsch have been used for producing "California" diesel
 - oxygenates such as DMM reduce soot formation
- Synthetic fuels may find applications in niche markets
 - urban fleets
 - underground mines, etc.
- Gas-to-Liquids could be exceptional future fuels
 - step-change reductions in engine-out emissions possible
 - enables the use of sulfur-intolerant aftertreatment technologies

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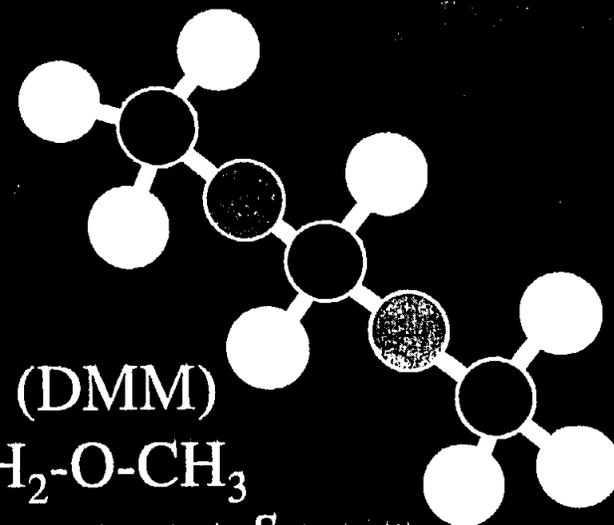
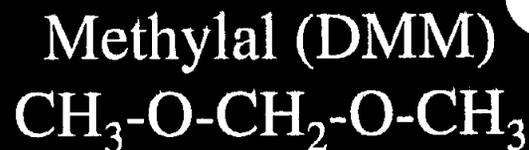


GTL Research Highlights from the DOE/NREL Fuels Utilization Program

- Research of DMM and DMM-diesel blends in the laboratory
- Fischer-Tropsch diesel fuel evaluation in Class 8 on-highway trucks

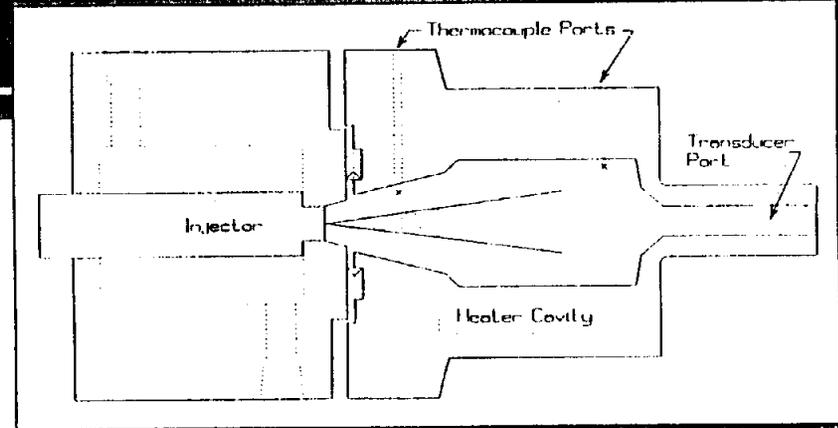
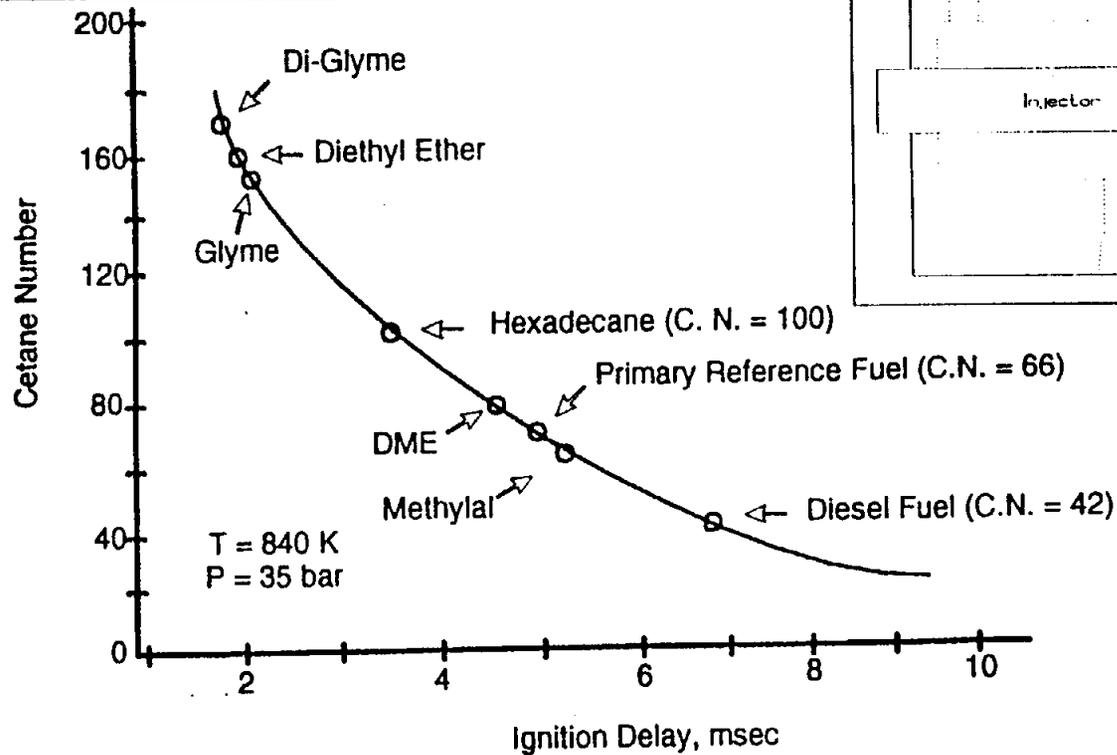
Dimethoxymethane (DMM) Attributes

- Colorless liquid at ambient conditions
- Boiling point of 42°C
- Lower Heating Value of 20.2 MJ/litre (has about 0.55 of the energy density of diesel fuel)
- Good autoignition characteristics for CI engines
- No carbon-carbon bonds and relatively high H/C ratio, correlates with very low soot formation in diffusion flame
- 42% oxygen by weight
- Soluble in diesel fuel
- Gas-to-liquids production economics are becoming more favorable



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DMM Cetane Number from Combustion Bomb Apparatus



Source:
Bradley Edgar
PhD Dissertation,
U.C. Berkeley, 1997

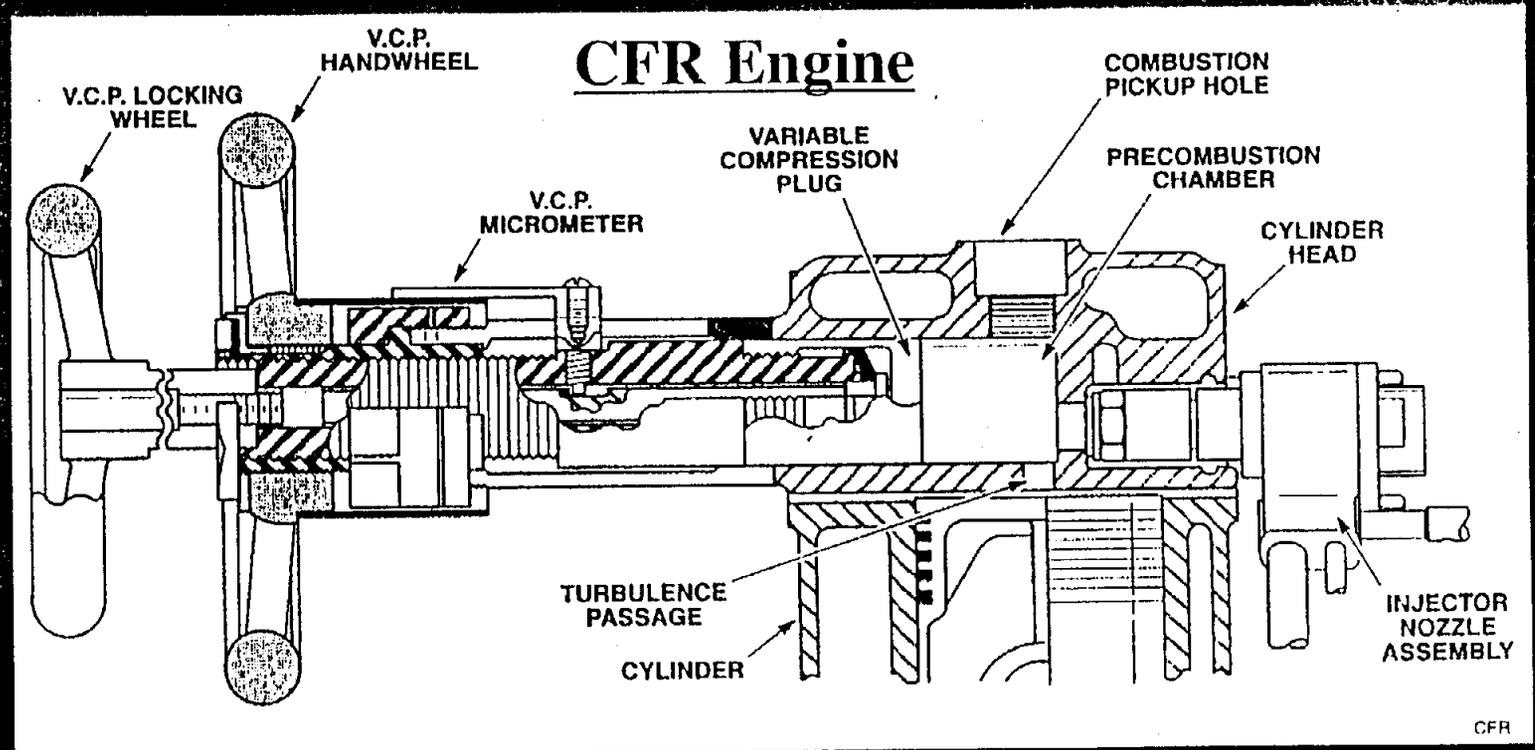
- Ignition delay correlation used to estimate cetane number
- Various reports of cetane number for neat DMM (99+% purity) have ranged from 29 to 57

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Cetane Test Engine for ASTM D 613

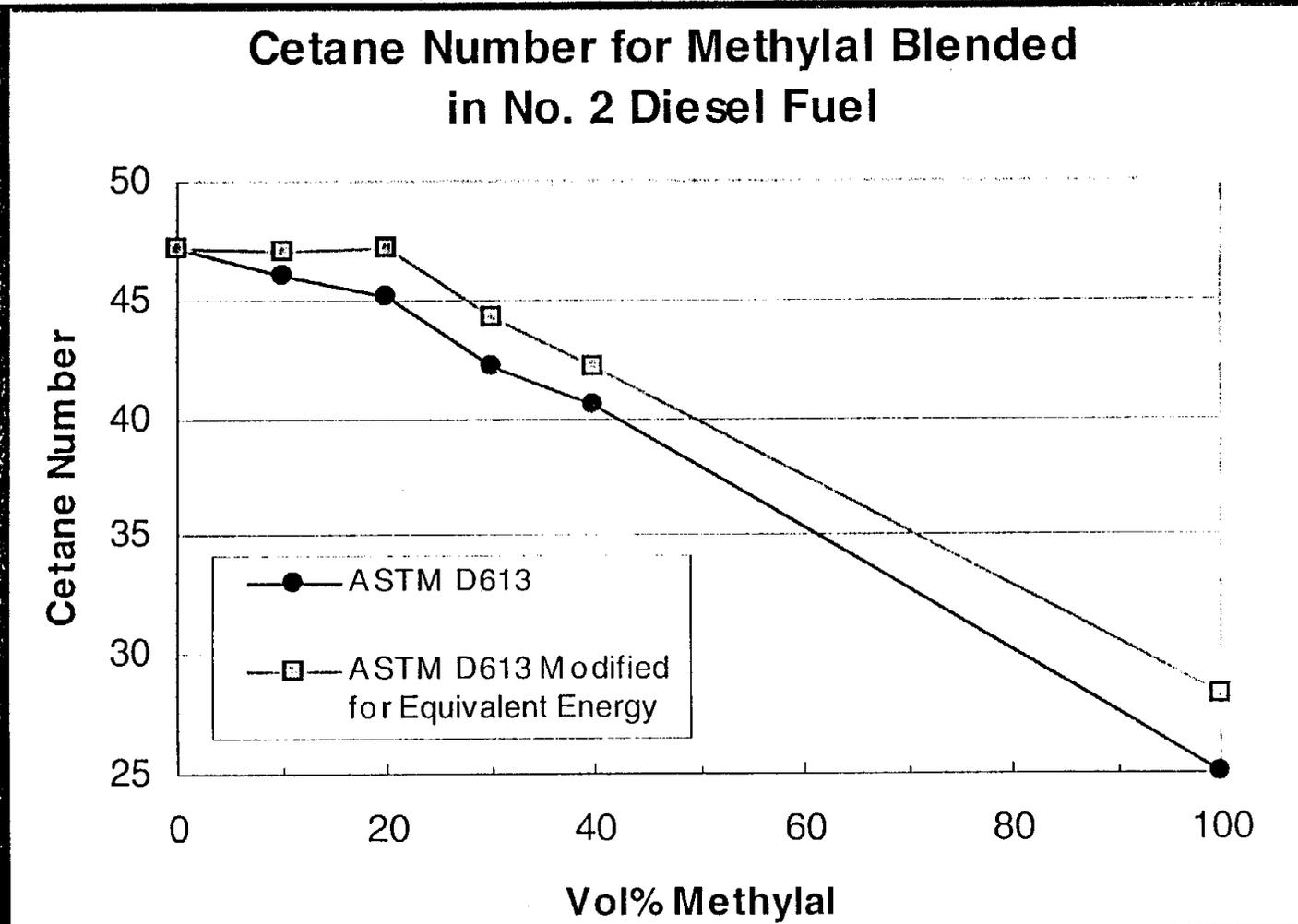
“This test may be used for unconventional fuels such as synthetics....However, the relationship to the performance in full scale engines is not completely understood.”

Source: ASTM D 613



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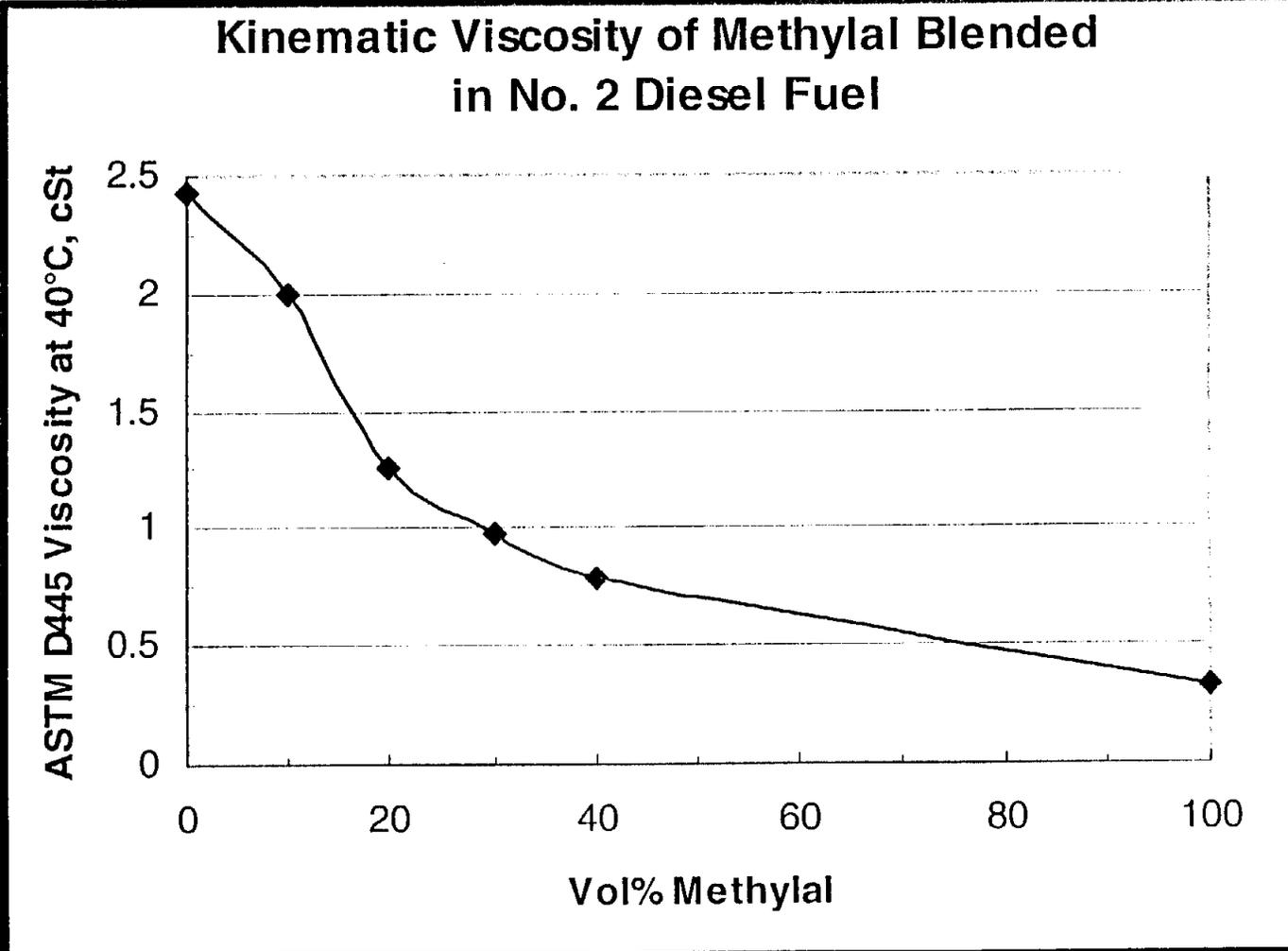
Cetane Number of DMM from ASTM D613



Source: NREL S/C ACI-8-18096 in progress (Southwest Research Institute)

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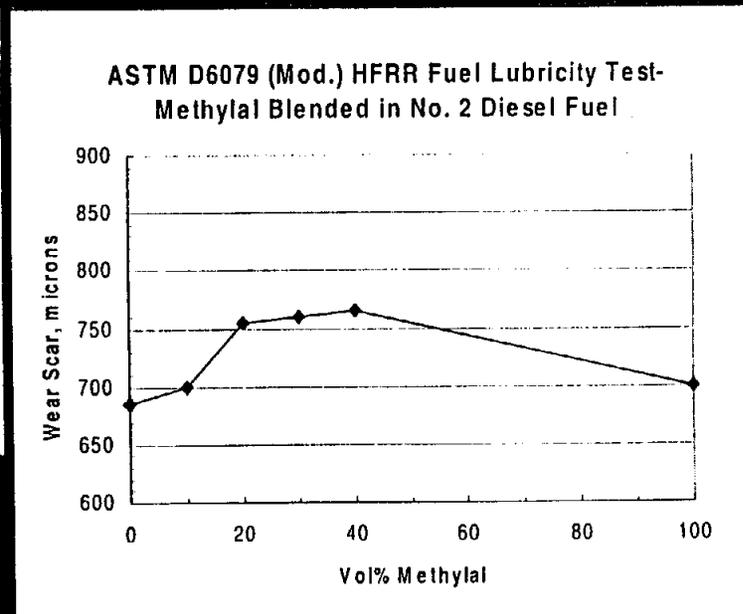
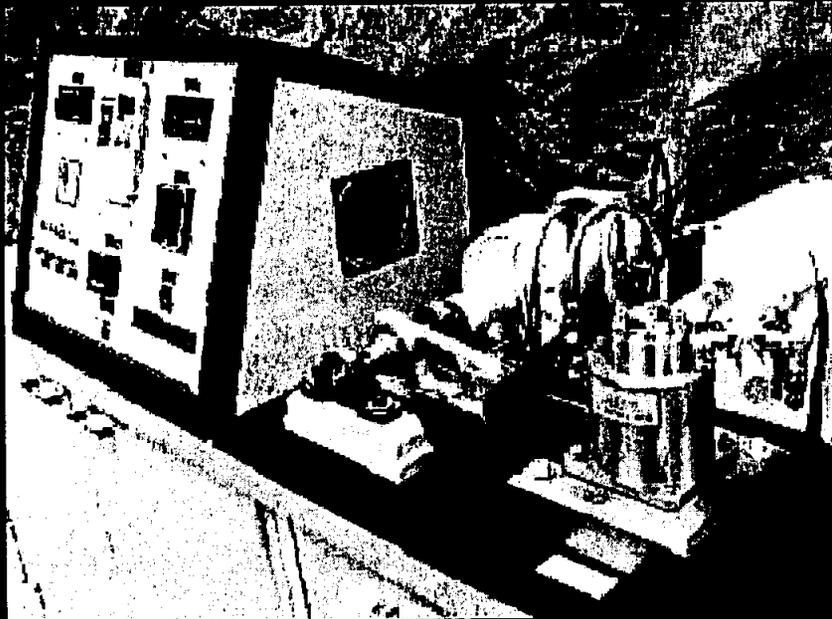
Kinematic Viscosity of DMM



Source: NREL S/C ACI-8-18096 in progress (Southwest Research Institute)
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Lubricity of DMM

- SwRI/DOE/OAAT/NREL collaborated to develop “High Temperature Pressurized High Frequency Reciprocating Rig”
- Preliminary tests indicated DMM lubricity is similar to a 10% aromatic certification fuel



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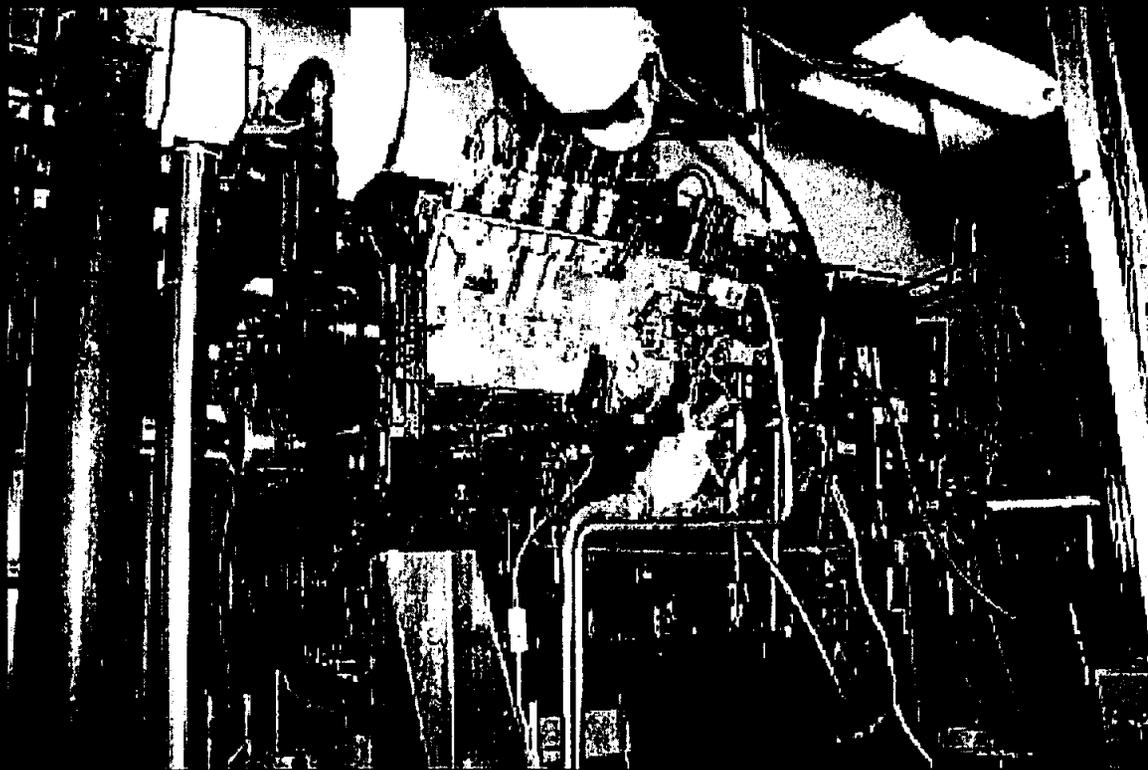


Design Issues for DMM-Diesel Fuel Blends

- New fuel tank and fuel delivery system designs required
 - DMM is volatile, boiling point = 42°C, RVP=0.86 bar
 - For a 20:80% DMM-diesel blend,
Upper Temperature Limit of Flammability = 6°C
 - Sealed fuel tank required to contain vapors
- DMM-diesel blends have been successfully run in unmodified engines, but
 - Seal compatibility unknown, study underway
 - Some fuel injection system modifications may be necessary to increase injection volumes

DMM-Diesel Blended Fuels Testing in an Unmodified Diesel Engine

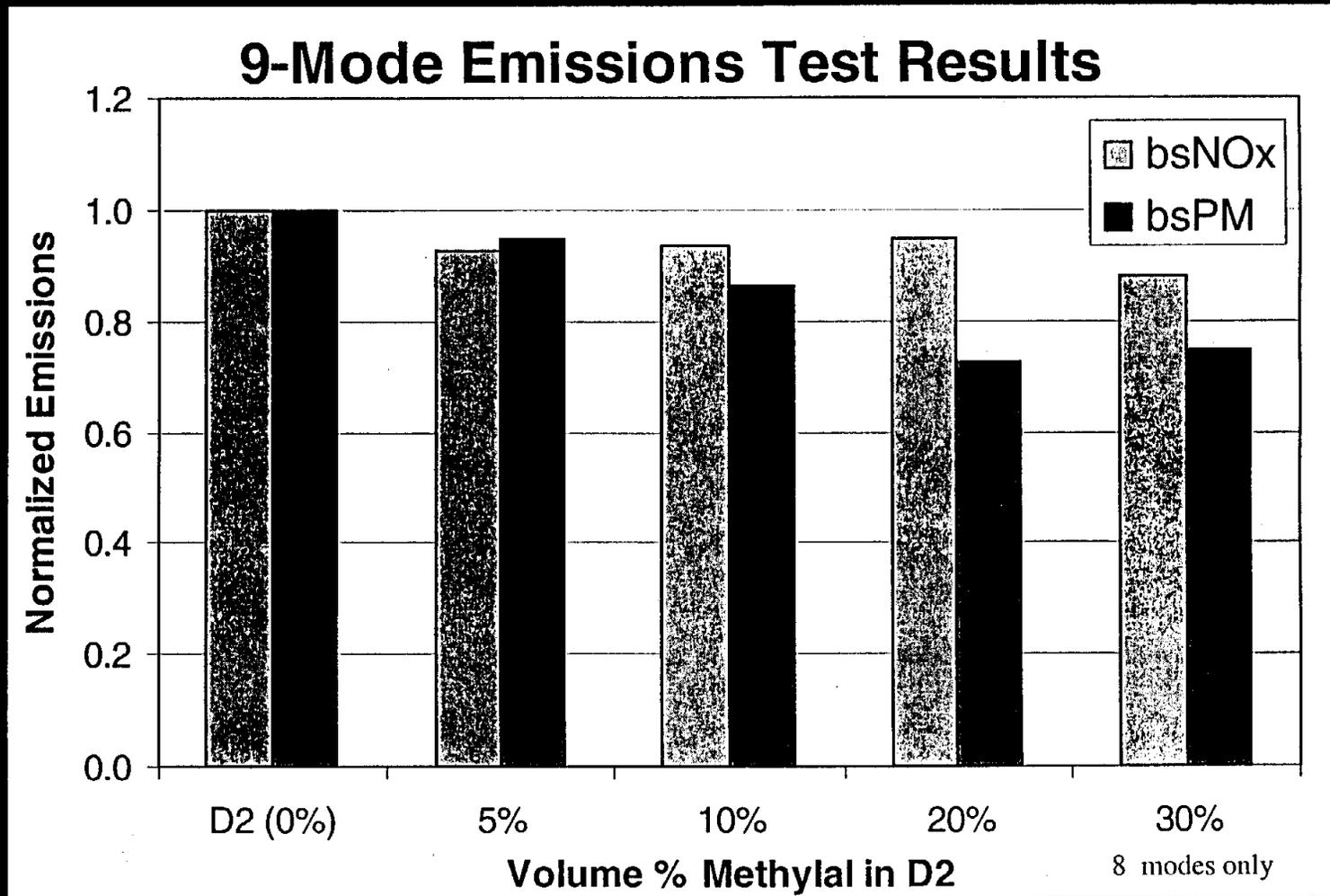
- University of California at Berkeley performing fuels tests at nine steady state modes
- 5%, 10%, 20% and 30% DMM blends in Diesel No. 2



1993 Cummins B5.9 Series Engine, Bosch P7100 Fuel Pump

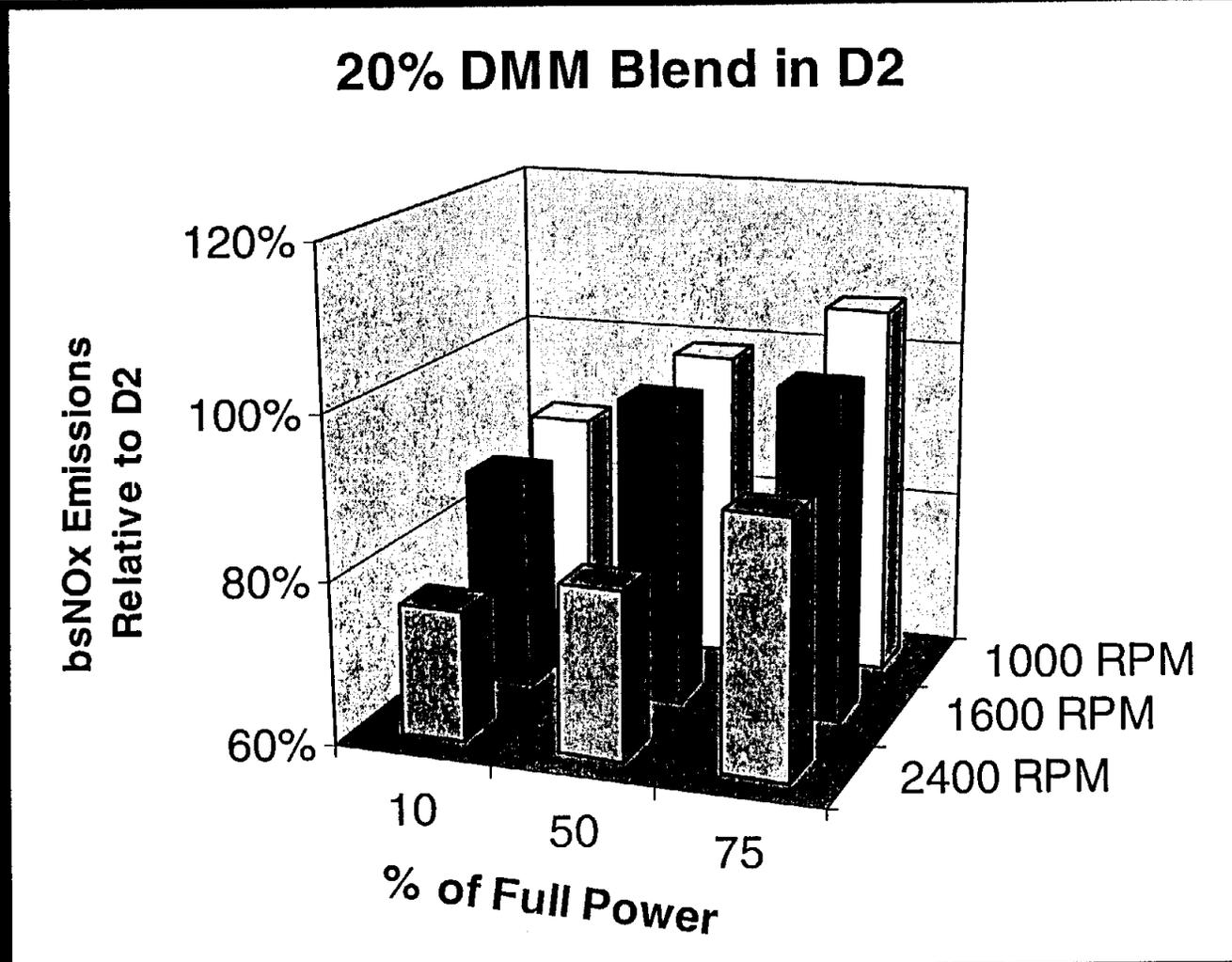
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DMM-Diesel Blended Fuels Testing in an Unmodified Diesel Engine, cont.



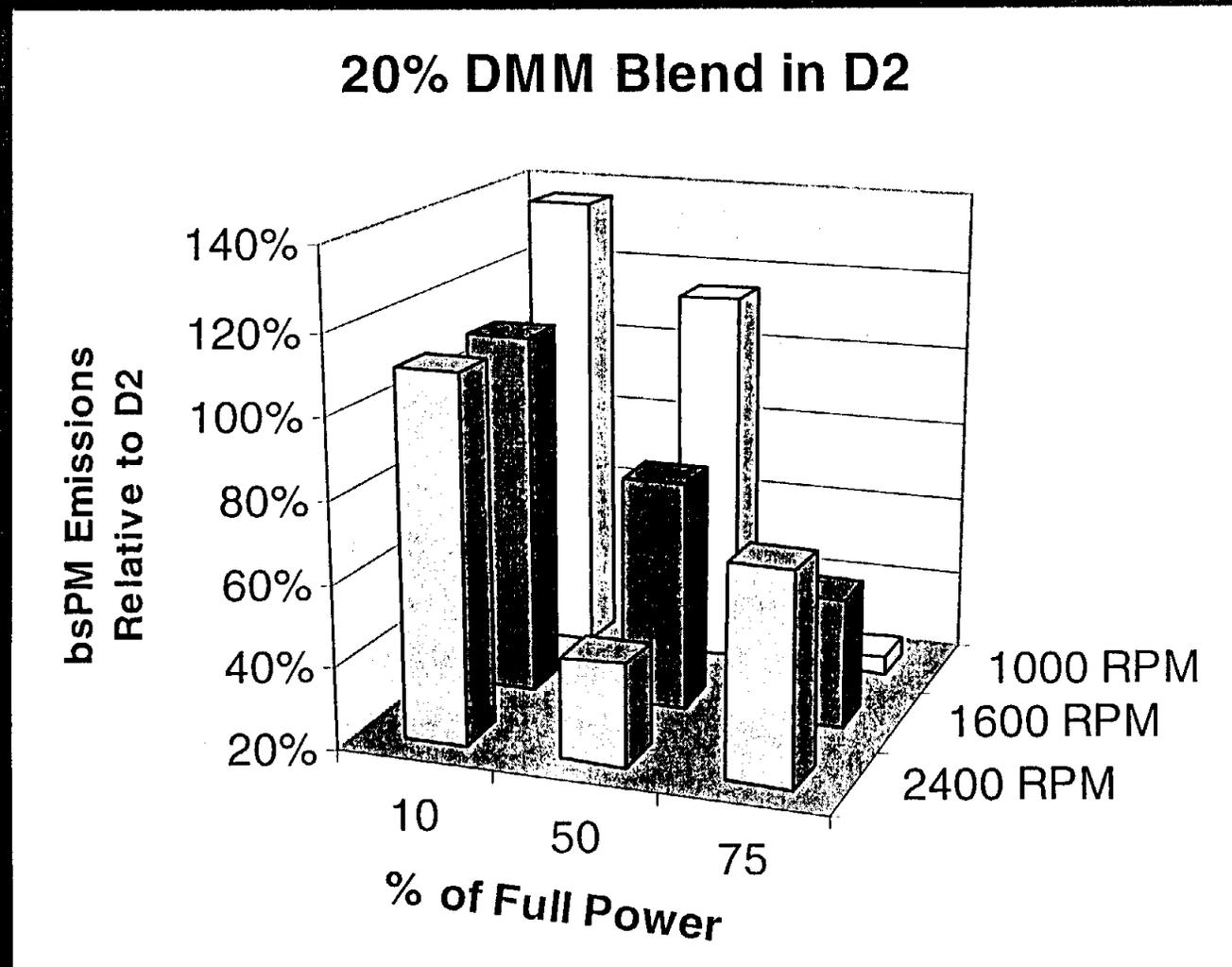
Source: NREL S/C XCV-7-16620 in progress (U. California at Berkeley)
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Oxygenated Fuels Testing in an Unmodified Diesel Engine



Source: NREL S/C XCV-7-16620 in progress (U. California at Berkeley)
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Oxygenated Fuels Testing in an Unmodified Diesel Engine, cont.



Source: NREL S/C XCV-7-16620 in progress (U. California at Berkeley)
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Conclusions about DMM to date

- DMM is not a cetane enhancer, but could still be an effective blendstock because it does not reduce the cetane number of diesel fuel until blend levels exceed about 25% by volume
- Substantial particulate matter (PM) emission reductions have been demonstrated for 10-30% DMM blends in diesel fuel, using a variety of unmodified diesel engine models
- No increases in NO_x emissions were apparent for 10-30% DMM-diesel blends
- Further research is planned to evaluate DMM for use as a blendstock for diesel fuel, and to assess its potential as a “future fuel”



GTL Research Highlights from the DOE/NREL Fuels Utilization Program

- Research of DMM and DMM-diesel blends in the laboratory
- **Fischer-Tropsch diesel fuel evaluation in Class 8 on-highway trucks**

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Attributes of Fischer-Tropsch Diesel

- Can be synthesized from natural gas, coal and biomass feedstocks
- Liquid phase at ambient conditions
- Miscible in conventional crude-derived diesel
- Good autoignition characteristics (cetane number of 50-75 typically)
- Zero sulfur
- Very low aromatics (less than 3 vol% possible)
- Energy density only ~3% less than crude-derived diesel
- Fuel tank flammability similar to crude-derived diesel
- Suitable for use in unmodified diesel engines
- Transportable as a liquid in existing petroleum infrastructure

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Test Vehicles and Procedures

- Fischer-Tropsch diesel and California diesel fuels were tested “back-to-back” in seven White/GMC Class 8 tractors equipped with Caterpillar 3176B engines
- Vehicle emissions tests were performed using West Virginia University’s transportable chassis dynamometer
- 5 mile drive cycle



Source: SAE Paper 982526

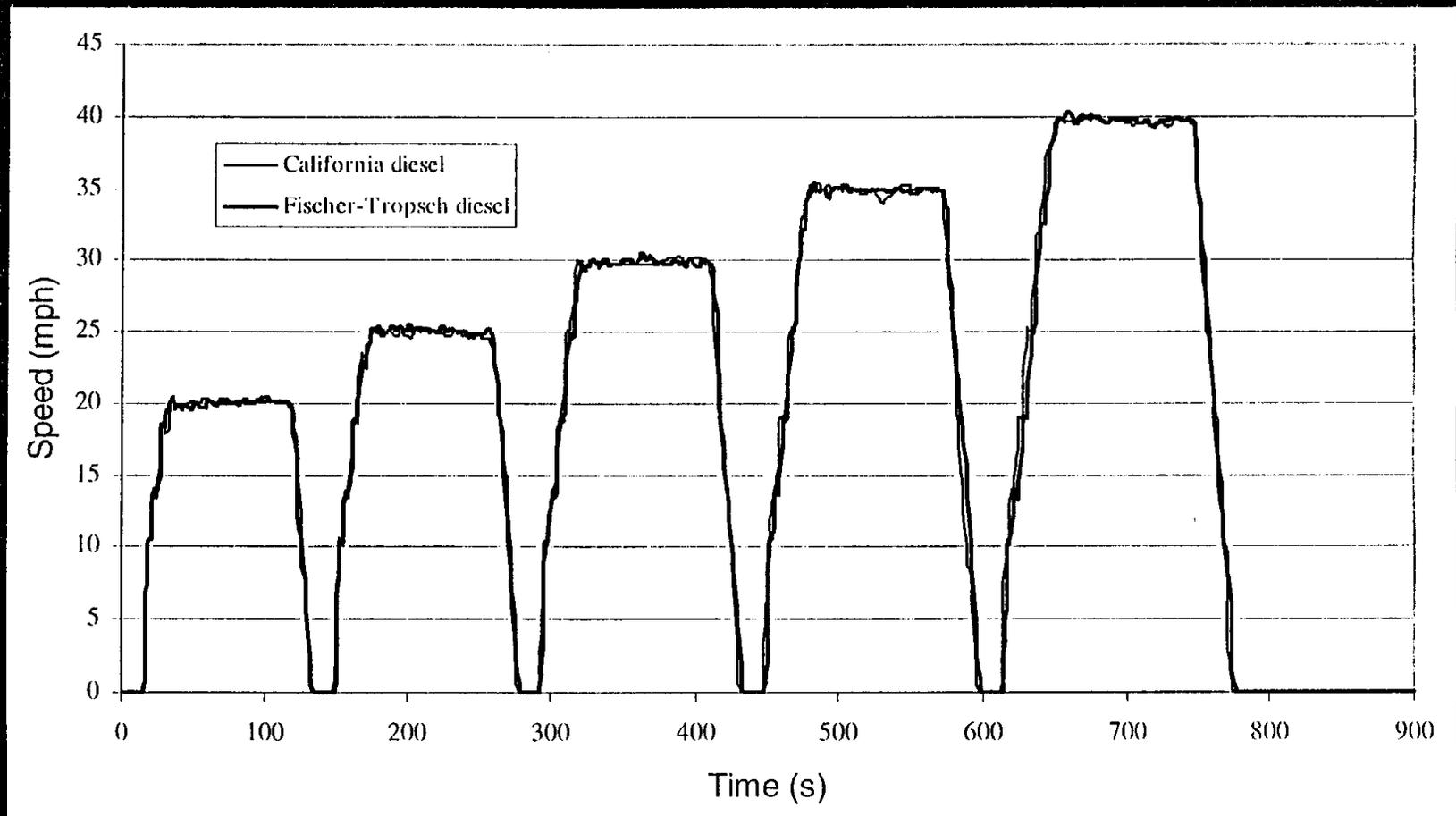
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Test Fuels

- California Diesel Fuel
 - Cetane index = 54
 - 100 ppm sulfur
 - 18% aromatics
 - Net heat of combustion = 127,900 BTU/gal
- Shell Fischer-Tropsch Diesel Fuel
 - Shell Middle Distillate Synthesis fuel from Malaysia
 - Cetane Number >74
 - <5 ppm sulfur
 - 0.3% aromatics
 - Net heat of combustion = 123,600 BTU/gal
 - Fuel sample was a raw product, so commercially available lubricity improver was added

Truck Performance Over 5-mile Drive Cycle

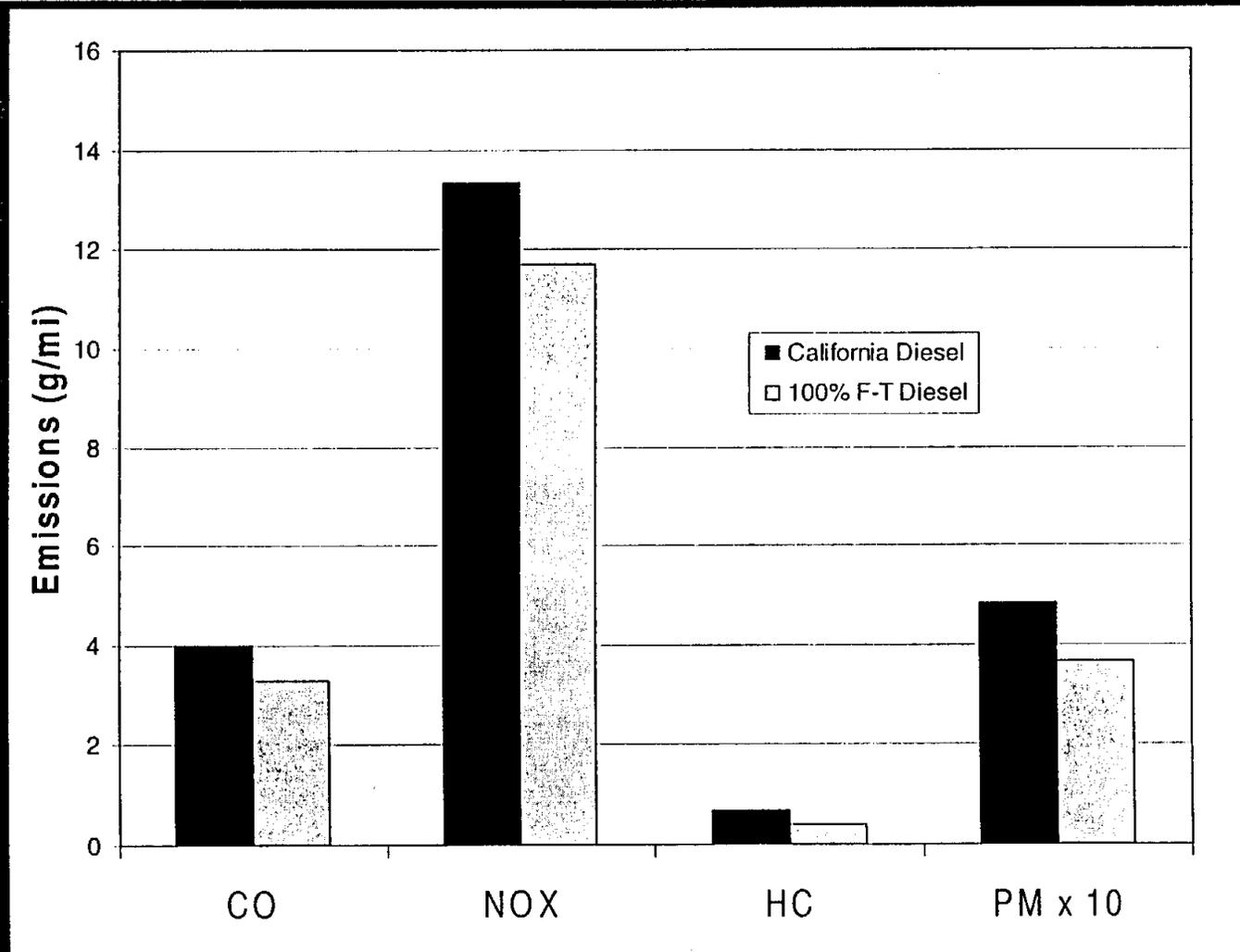
Truck performance was essentially the same for both fuels



Source: SAE Paper 982526

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Average Emissions From 4 Trucks Operating on Fischer-Tropsch and California Diesel Fuels



Source: SAE Paper 982526

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Conclusions from Fischer-Tropsch Diesel Fuel Testing in Class 8 Trucks

- Shell Fischer-Tropsch synthetic diesel fuel had properties conducive to low emissions
- Drivers could not detect a performance difference between trucks operating on F-T diesel and California diesel
- Use of Fischer-Tropsch diesel in place of California diesel in the test trucks led to
 - 12% lower NO_x
 - 24% lower PM
 - 18% lower CO
 - 40% lower HC

Source: SAE Paper 982526

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Synthetic Diesel Fuel Testing in Older-Model Transit Buses



Testing of transit buses equipped with DDC 6V92 2-stroke engines
is underway at West Virginia University

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- U.S. Department of Energy-
Office of Heavy Vehicle
Technologies
- NREL Subcontractors-
 - West Virginia University
 - Southwest Research Institute
 - University of California at Berkeley
- Industry Participants-
 - Amoco Exploration and Production
 - Cummins Engine Company
 - Power Systems Associates & Caterpillar Inc.



CENTER FOR TRANSPORTATION TECHNOLOGIES AND SYSTEMS

Catalytic Conversion by Coupling Chemical Reactions & Separations

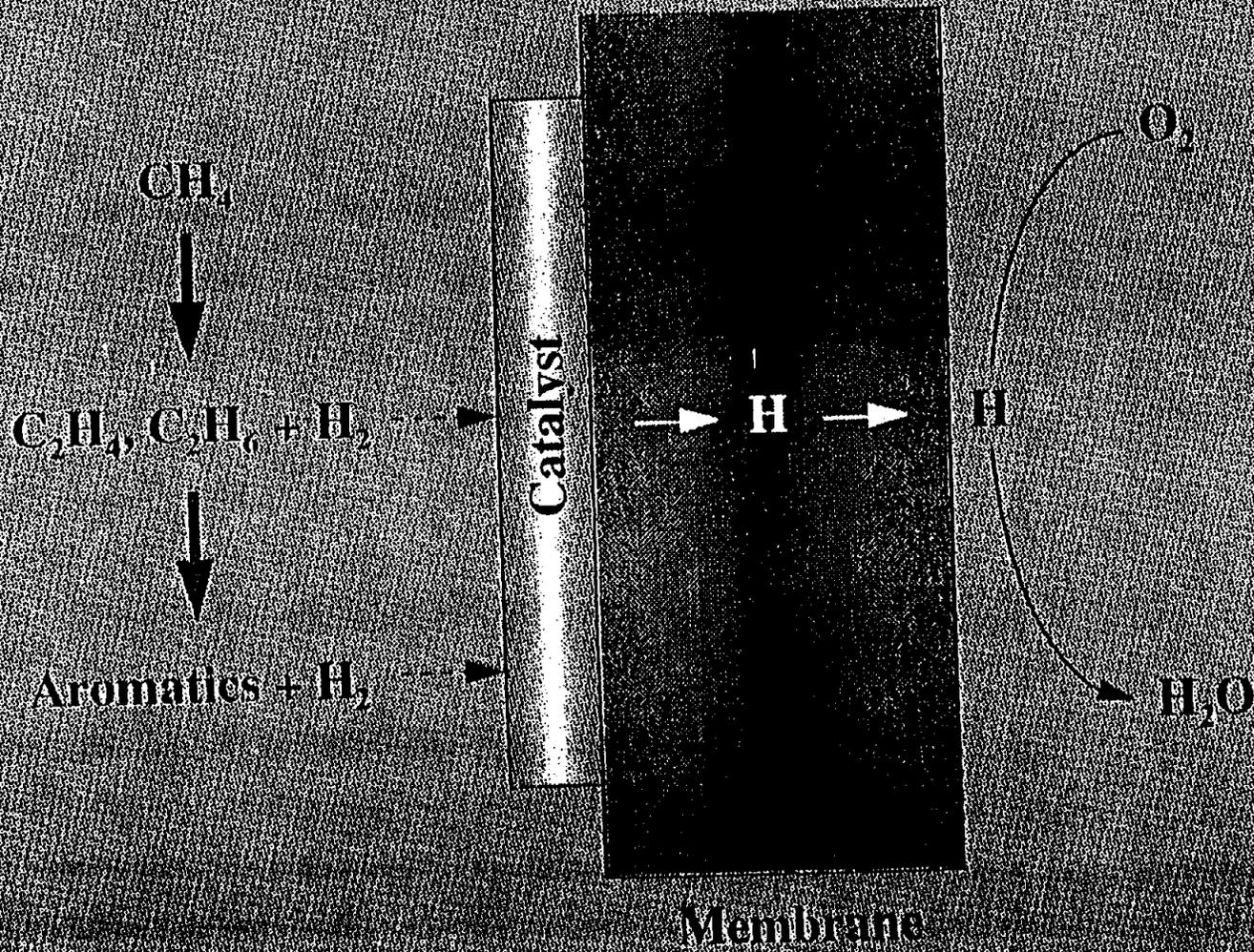
Lawrence Berkeley National Laboratory

Project Objectives

**To overcome the limitations of non-oxidative
methane pyrolysis and oxidative coupling via
hydrogen transfer across a selective inorganic
membrane**



Hydrogen Transport Membrane Reactor



Project Status

- Computer simulations indicate that $C_2 - C_{10}$ yields of ~ 60% can be achieved at 765C when hydrogen removal is in effect (vs ~23%)
- Mo/H-ZSM5 achieves thermodynamic limit of $C_2 - C_{10}$ yield at 600-700C
- Issues: H₂ transport rate
Reactivity of membrane



FETC In-House Research

Acetylene Conversion

HC • CH • Liquids

Carbon Dioxide Reforming

$\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2$

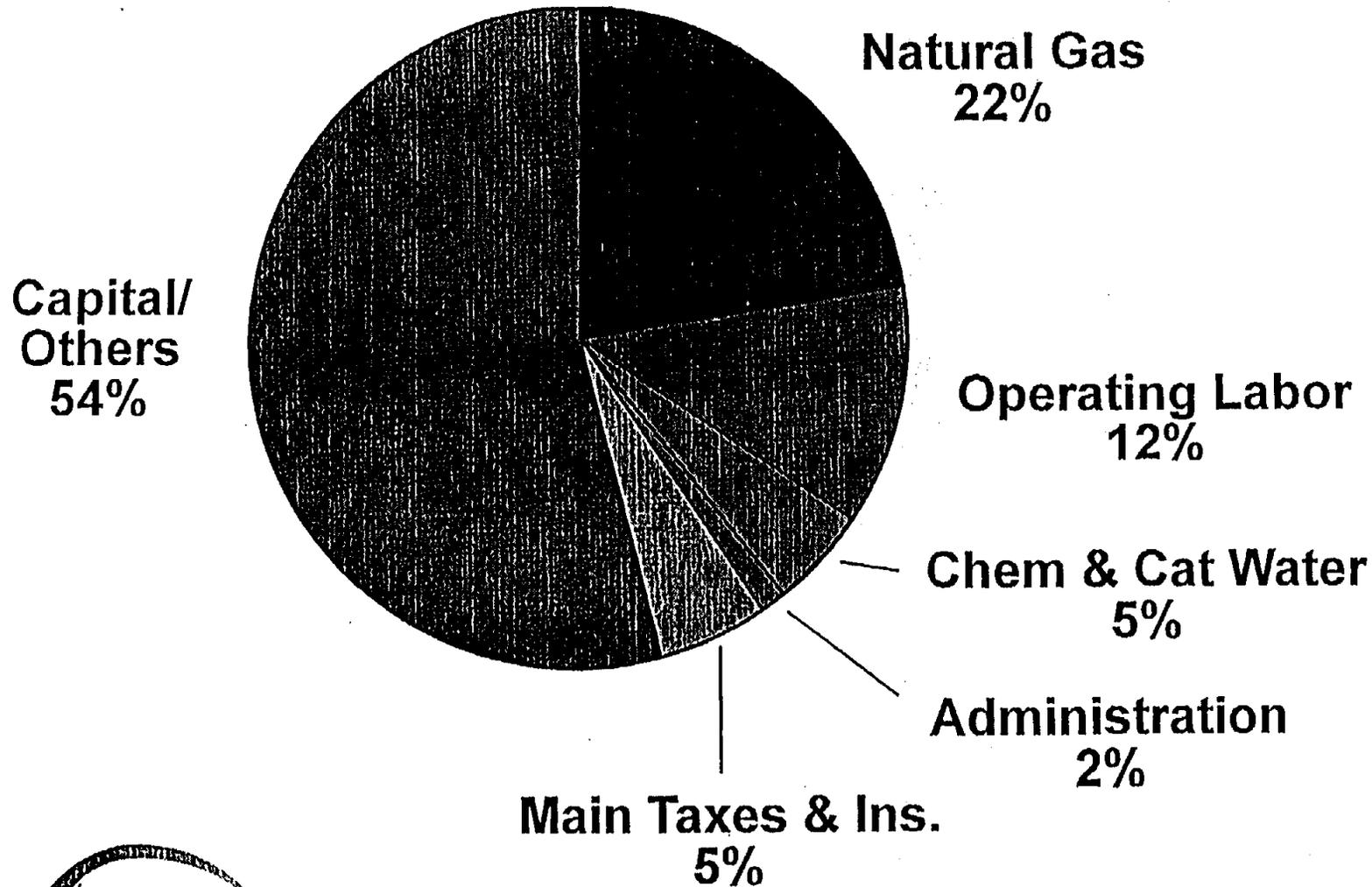
Photocatalytic Conversion of Methane

$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}_2$

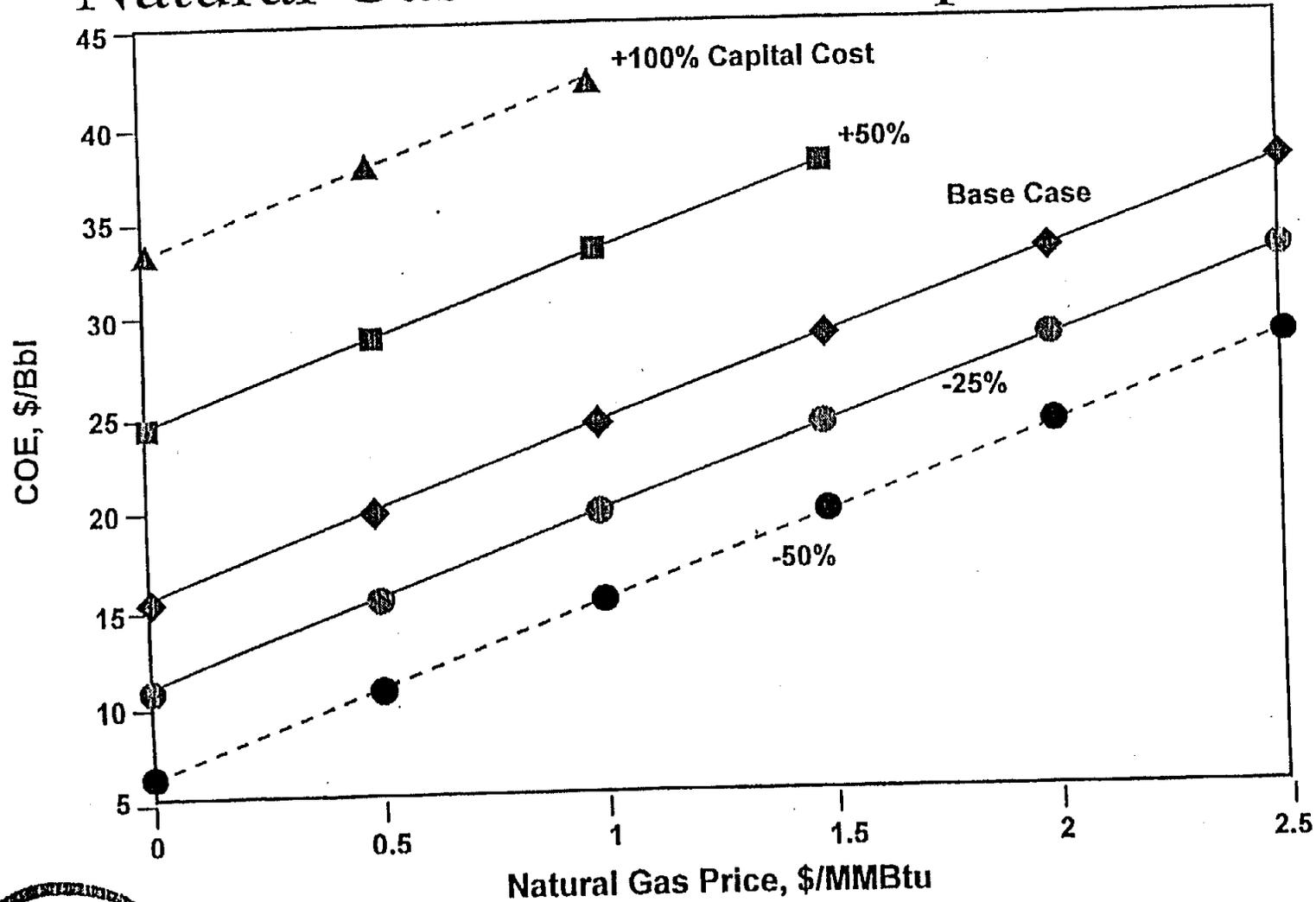


COE Cost Distribution @ 0.50 \$/MMBtu Gas

COE = 19.70 \$Bbl at Southern Illinois



COE as a Function of Natural Gas Prices and Capital Cost



Baseline Design/Economics for Natural Gas Fischer-Tropsch Case

Bechtel

Project Objectives

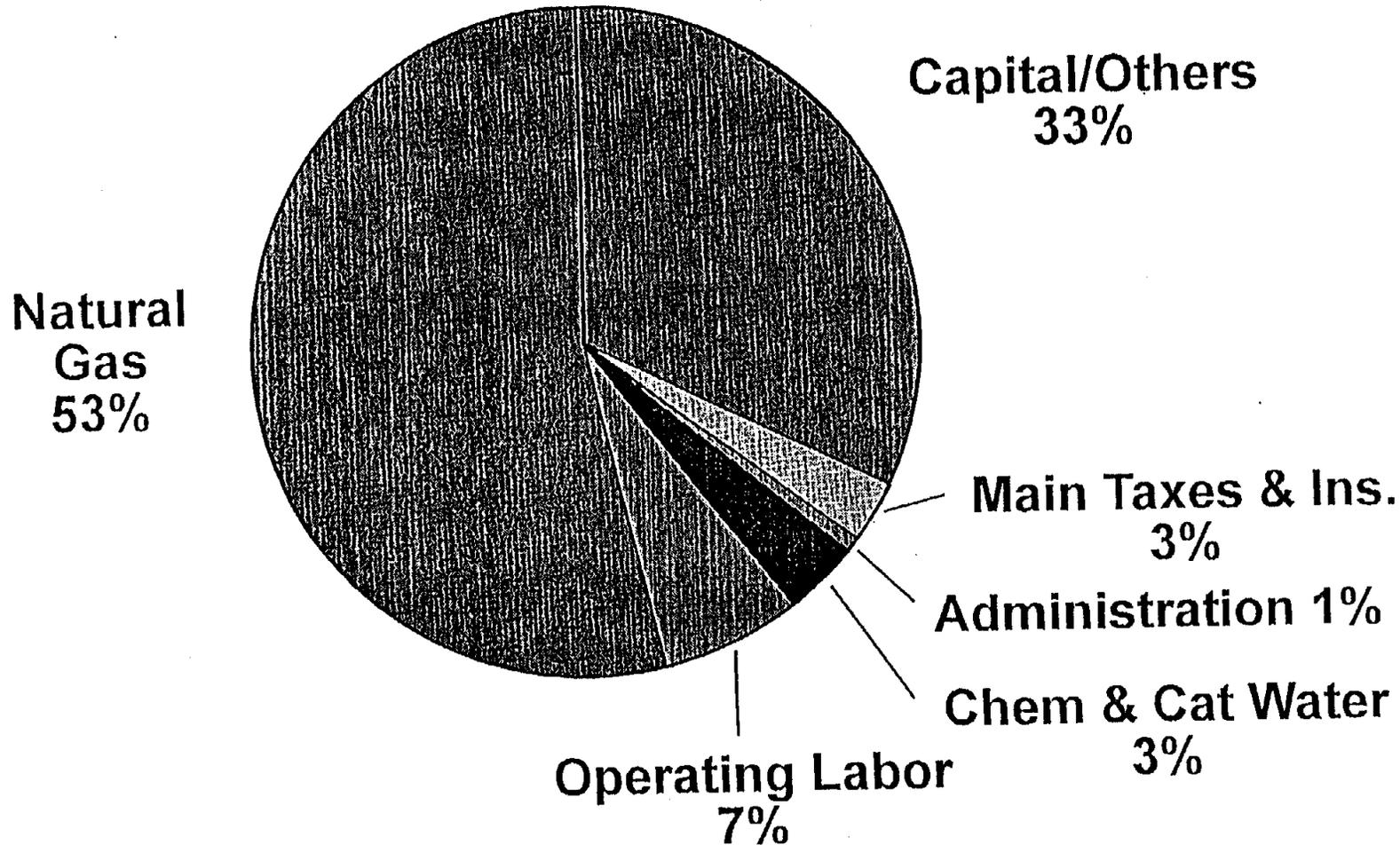
**To develop economics for a grass-root natural
gas-based Fischer-Tropsch plant for the
production of transportation fuels
and**

**Perform preliminary sensitivity studies of key
process variables and economic assumptions**



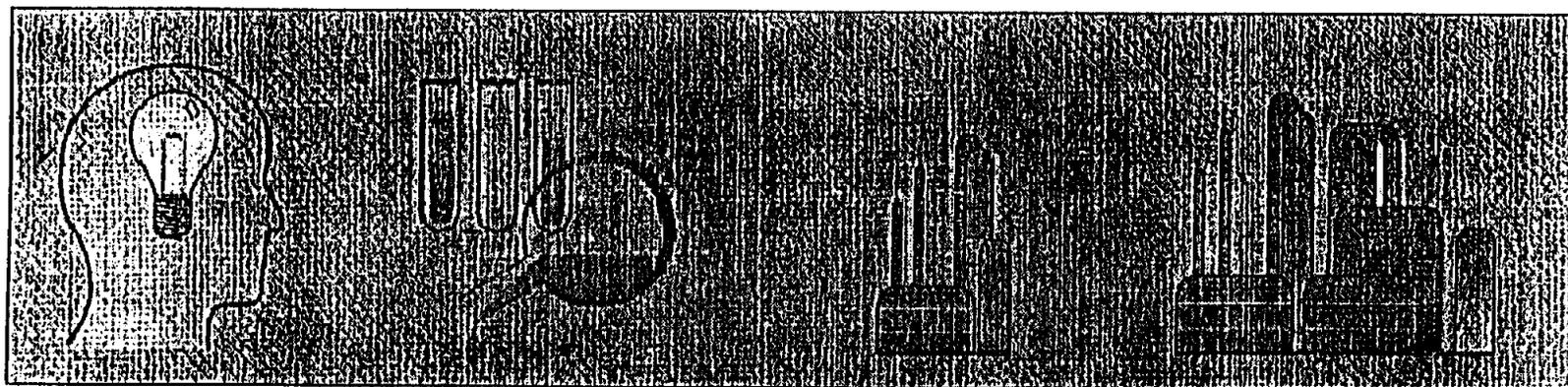
COE Cost Distribution @ 2.00 \$/MMBtu Gas

COE = 32.80 \$Bbl at Southern Illinois



Gas to Liquids

Technology Development Timeline



Explore

Bench and
Engineering
Scales

Proof-of-
Concept

Pioneer
Plants
(10,000 - 50,000 Bbl/day)

1992

1996-2000

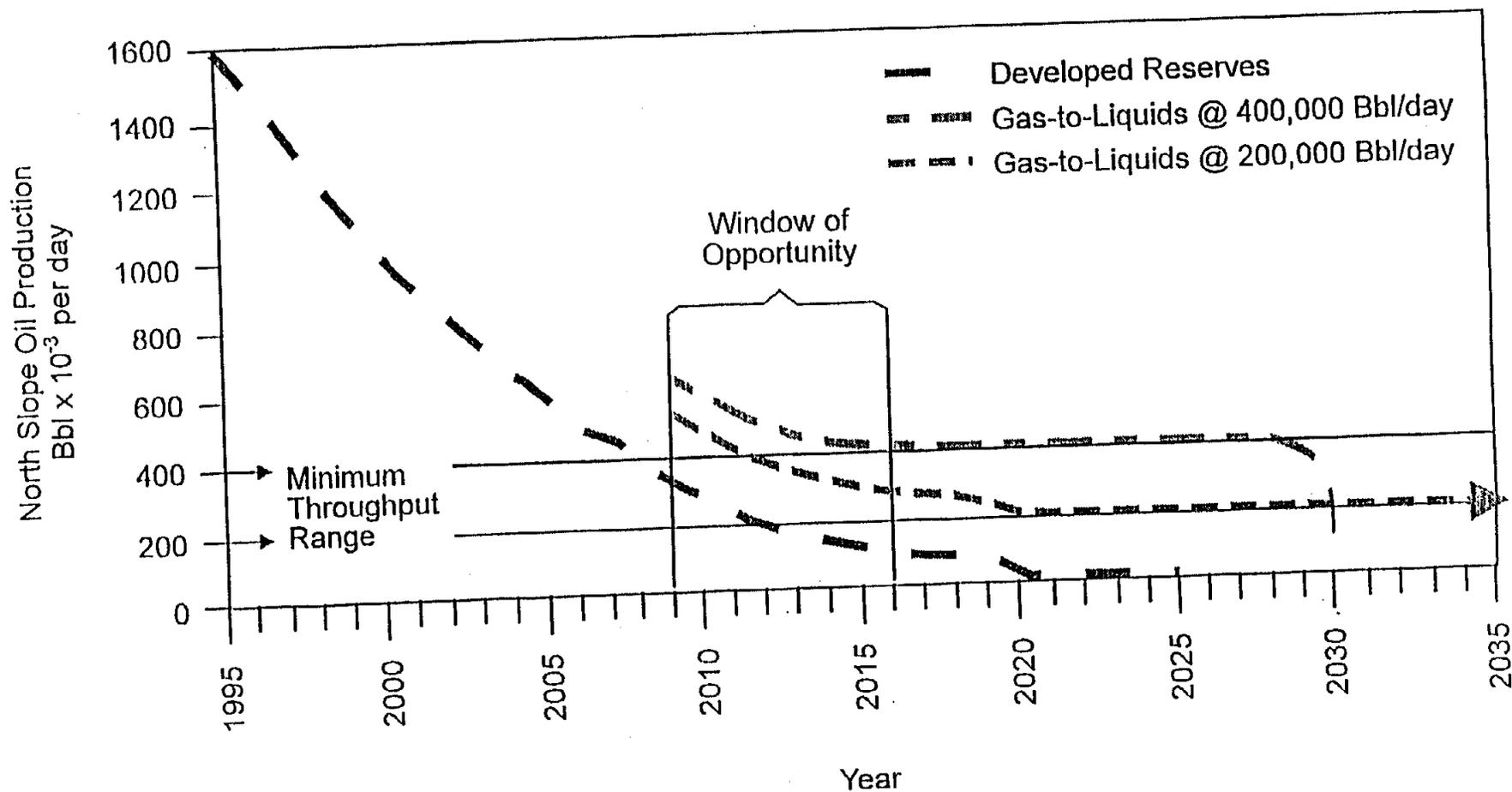
2004

2008

Alaskan North Slope
U.S. Offshore/Onshore



Window of Opportunity (2009-2016) for Deployment of Gas-to-Liquids Technology to Maintain Operation of the Trans Alaska Pipeline



M980340.PPT
M98000157.C31

Emissions Performance of Synthesis Gas-Derived Diesel Fuels Is Superior to Petroleum Diesel Fuels

Emissions Reduction Relative to Low Sulfur Petroleum Diesel

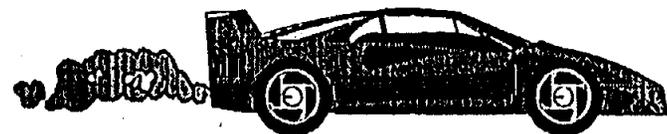
| | |
|--------------|--------|
| Hydrocarbons | 41-46% |
| CO | 45-47% |
| NOx | 9% |
| Particulates | 27-32% |

Emissions Reduction Relative to Low Sulfur/Low Aromatics Petroleum Diesel

| | |
|--------------|--------|
| Hydrocarbons | 25-31% |
| CO | 34-38% |
| NOx | 5% |
| Particulates | 23-29% |



Results are Independent of feedstock origin



Ranges based on three fuels, i.e., summer, winter, and California formulations, produced from natural gas and coal feedstocks.



Summary

Advanced gas-to-liquids conversion technology that yields ultra clean burning diesel fuels that meet the most stringent emissions requirements, at costs below those of comparable fuels made from crude oils, provides energy security

Small-scale gas-to-liquids technology for both natural gas liquefaction and chemical conversion to higher hydrocarbon liquids will enable economic and environmentally sound production of remote offshore reservoirs with associated gas, and also onshore gas reservoirs without pipeline access



Summary

FETC/DOE plays a role in developing novel, high-risk energy technology through government-industry partnerships to share initial market risk and technology transfer to target segments of industry

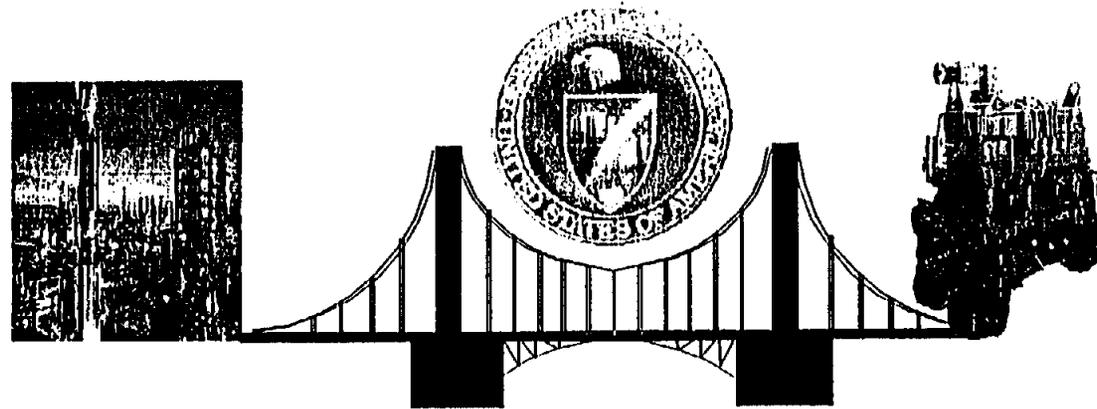


ALTERNATIVE FUELS IN HEAVY DUTY VEHICLES

**Identifying technologies
and markets for new
fuels**

**Gurpreet Singh
Programme Manager, Office of
Heavy Vehicle Technologies
US Department of Energy**

Alternative Fuels in Heavy Duty Vehicles

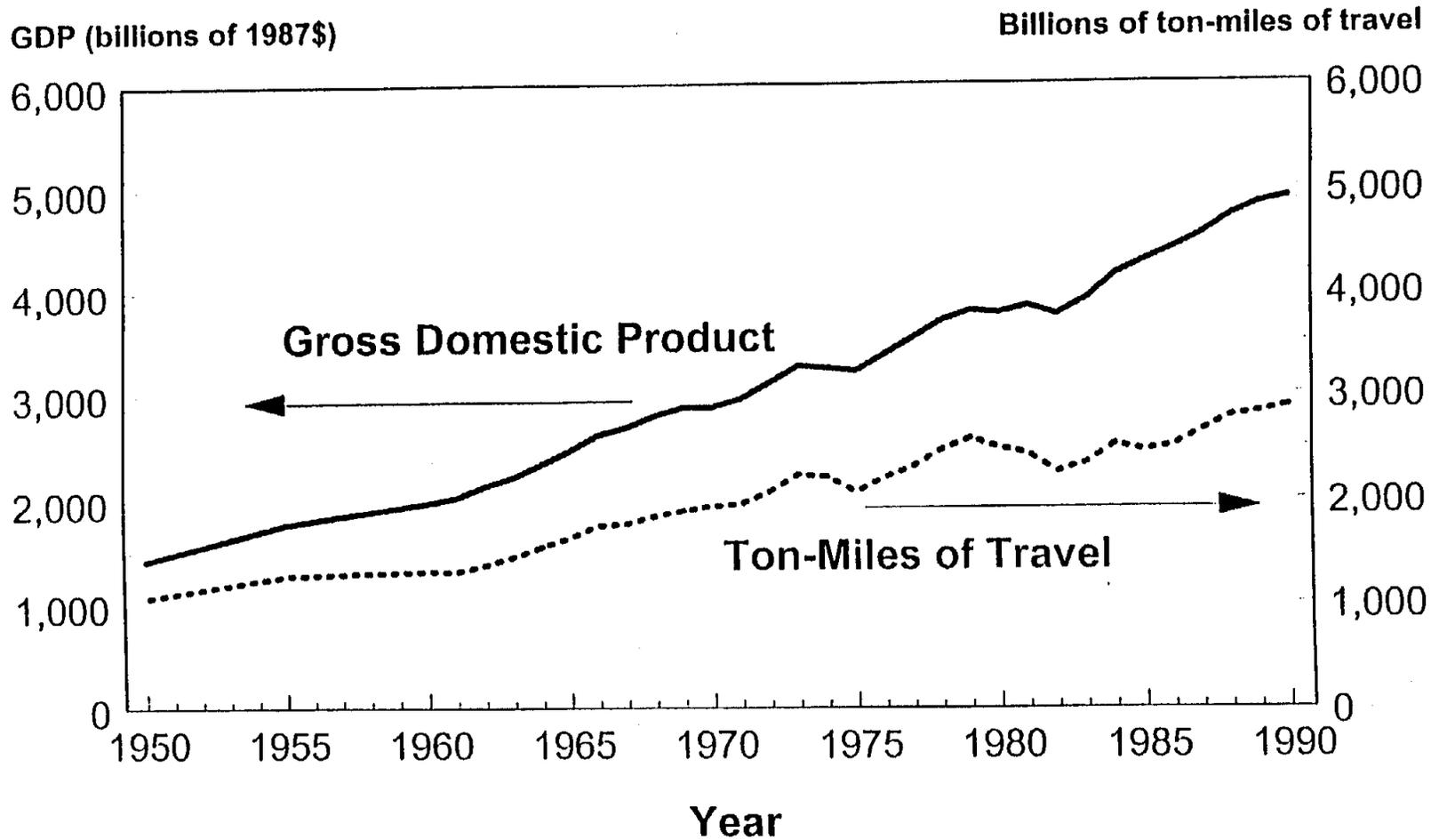
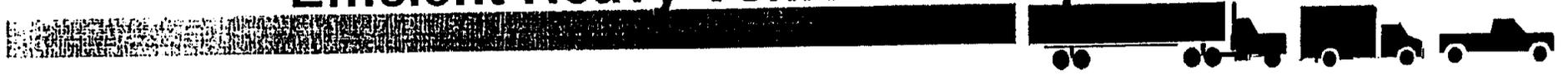


Gurpreet Singh, Programme Manager
Office of Heavy Vehicle Technologies
U.S. Department of Energy

Presented at the Meeting on
Gas-to Liquids: Clean Fuels Strategy
London, UK
November 16-17, 1998



A Healthy National Economy Depends Upon Efficient Heavy Vehicle Transportation



Challenges for Trucks in the 21st Century



Commercial Trucks (Class 3-8)

Challenge:

How to deliver more goods in a timely manner, at a lower cost, at *ever increasing fuel efficiency* and *ever decreasing emissions!*

DOE/SWRI Alternative Fuels Test Program



- **13 steady-state test modes**
 - ◆ NO_x, HC, CO, PM, PM size distribution, fuel consumption
 - ◆ Measured before catalyst

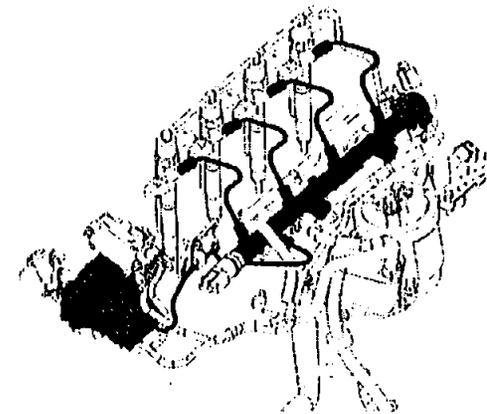
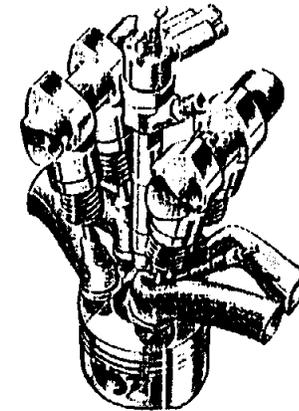
- **7 fuels, including an EPA 2-D certification fuel as the reference**
 - ◆ Pseudo-CARB
 - ◆ Low-Sulfur, Low-Aromatics diesel
 - ◆ Neat Fischer-Tropsch
 - ◆ Fischer-Tropsch Blend
 - ◆ Dimethoxy methane (DMM) Blend
 - ◆ Biodiesel Blend

No engine adjustments for variations in fuel properties

Daimler Benz OM 611 Engine



- Inline 4 -Cylinder, 4-valves per cylinder
- 88.0 mm bore x 88.4 mm stroke
- Turbocharged with air-to-air intercooling
- High pressure, common rail fuel injection
- Centrally located, 6-hole nozzle injectors
- Variable intake air swirl
- Modulated exhaust gas recirculation
- Oxidation catalyst



Office of Heavy Vehicle Technologies

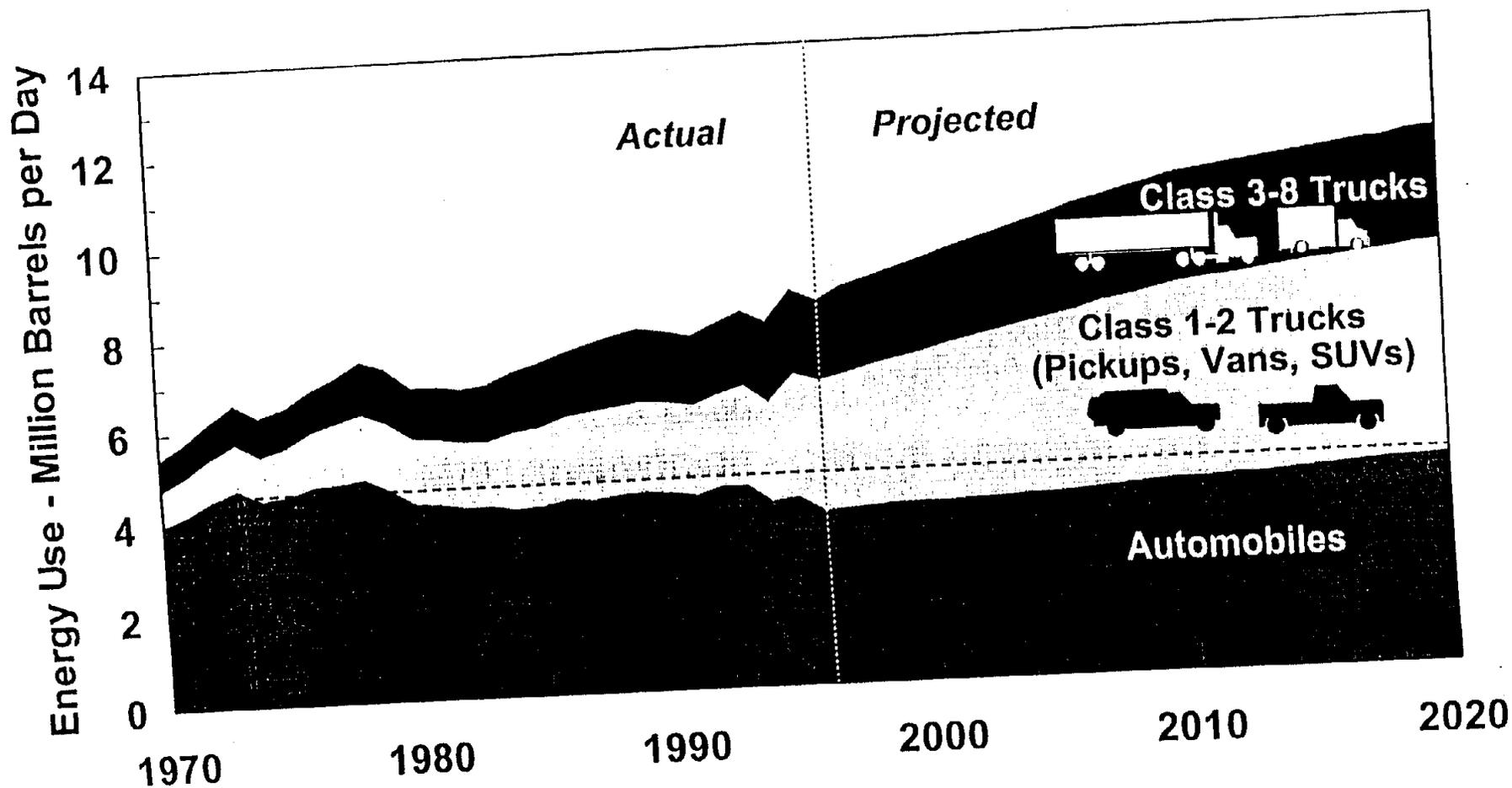


- ◆ The U.S. Department of Energy - Secretary
- ◆ Efficiency and Renewables - Deputy Assistant Secretary, Transportation Technologies
 - ◆ **Office of Heavy Vehicle Technologies**
 - ◆ Created in the DOE/Office of Transportation Technologies restructuring (March 1996)
 - ◆ Focuses research and development on critical areas identified with heavy vehicle customers



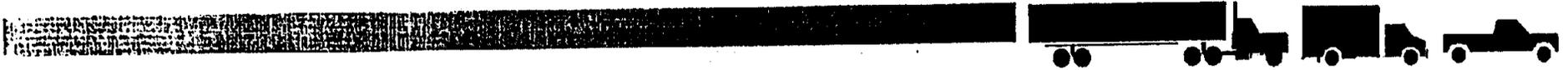
Gurpreet Singh, Programme Manager
Office of Heavy Vehicle Technologies
U.S. Department of Energy
phone: (202) 586-2333
fax: (202) 586-4166
e-mail: gurpreet.singh@ee.doe.gov

Since the 1973 Oil Embargo Essentially All of the Increase in U.S. Highway Fuel Consumption has been due to Trucks



source: EIA Annual Energy Outlook, 1998
Federal Highway Administration, Highway Statistics

DOE Truck Technologies R&D



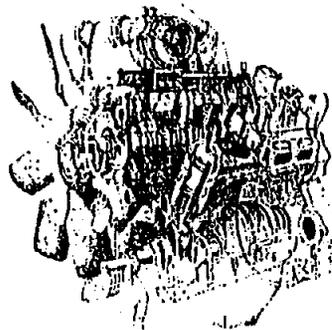
Approach

The development of a **fuel-flexible**, energy efficient, near-zero emissions, heavy-duty U.S. **Diesel cycle engine** technology devolving into all truck applications

OHVT Strategy: Focus on the Diesel Cycle Engine



**Efficiency 55%
or Higher**



**Alternative Fuels/
Flexible-Fuel**

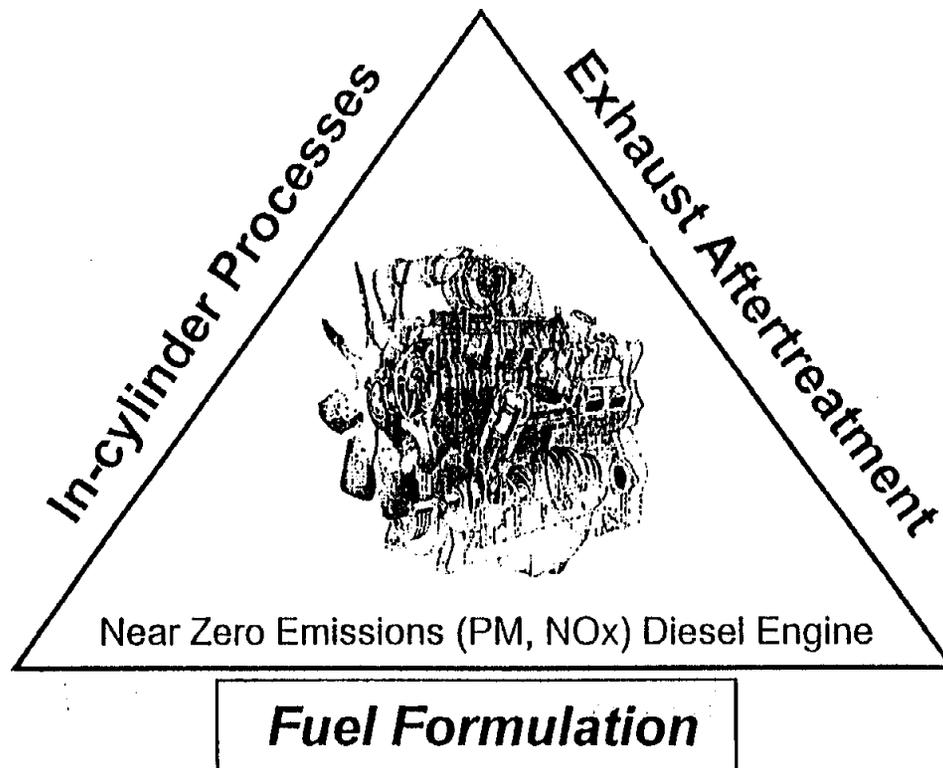
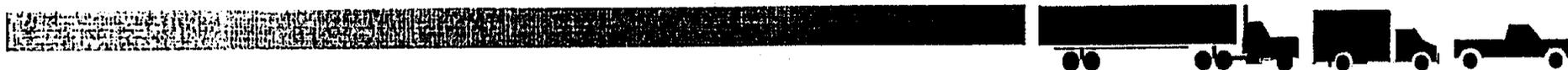
*Emissions Control
is the Key Enabling
Technology*

**Very Low
Emissions**

Benefits

- ◆ Decrease Highway Energy Use
- ◆ Reduce Greenhouse Gas Emissions
- ◆ Reduce Environmental Impact
- ◆ Enhance Energy Security

Diesel Cycle Engine Emissions Control Strategy



Three-pronged systems approach appears necessary to meet very low emissions without sacrificing engine efficiency

Alternative Fuels for Heavy Vehicles



In a systems approach, alternative fuels could:

- ◆ Shift the tradeoffs among NO_x, particulate matter, and engine efficiency;
- ◆ Shift the balance between engine technologies and aftertreatment; and
- ◆ Make advanced aftertreatment technologies technically- and cost-competitive.

Strategy



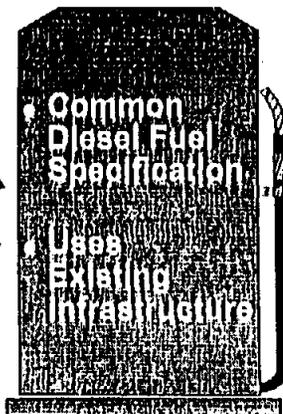
High-efficiency clean diesel-cycle engines utilizing compression ignitable fuels/blends derived from diverse feedstocks

Multiple Alternative Feedstocks

- Coal
- Biomass
- Natural Gas

- Petroleum

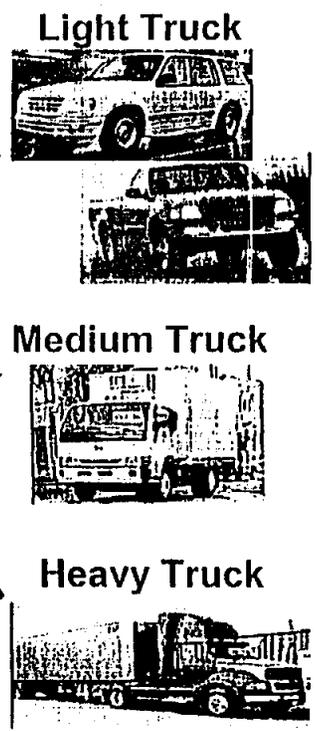
Synthesis gas route to:
Liquid Fuels
Conventional petroleum refining



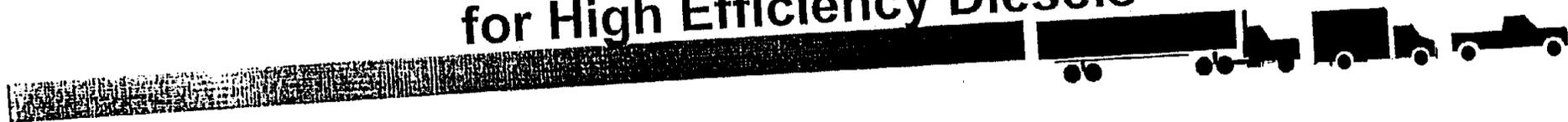
Advanced High-Efficiency Clean Diesel Engine Technologies

Fuel Quality
Exhaust Aftertreatment
Diesel Engine
In-cylinder Processes

More Efficient Trucks

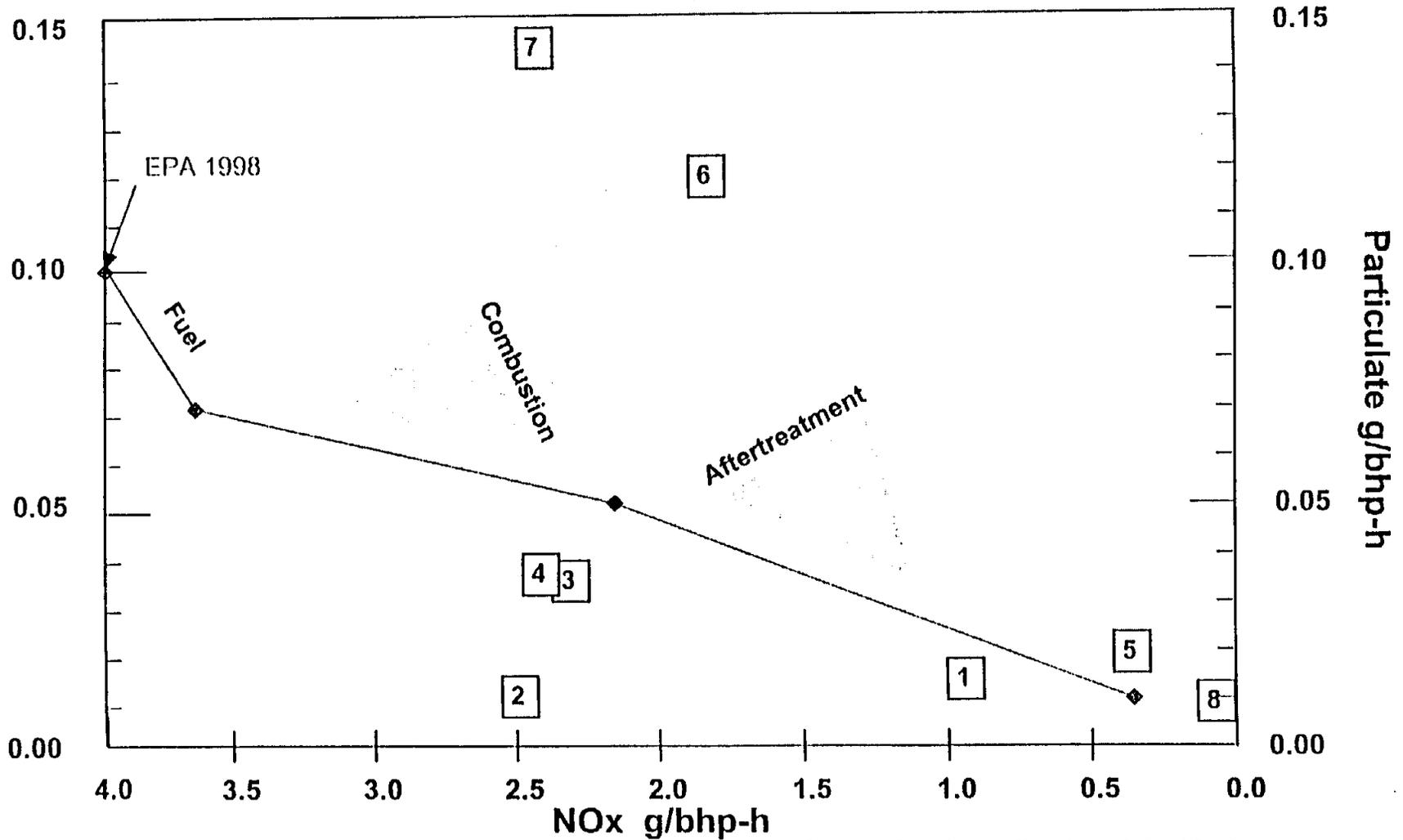


Compression Ignitable Fuels for High Efficiency Diesels



- ◆ Fischer-Tropsch diesel (cetane number 76)
- ◆ Dimethoxymethane (cetane number 49)
- ◆ Dimethyl ether (cetane number 55)
- ◆ Diethyl ether (cetane number 125)
- ◆ Biodiesel (cetane number 76)

Very Low Diesel Emissions Technically Possible



- 1. DME/SCTE, turbo + EGR
- 2. Natural gas/Cummins C8.3-250 G with catalyst
- 3. Natural gas/Cummins L10-300 G with catalyst
- 4. DME/Navistar Diesel Engine (without EGR)

- 5. Conventional gasoline (spark-ignition)
- 6. Gasoline direct injection (GDI)
- 7. VW TDI (turbocharged direct injection diesel)
- 8. Zero-sulfur diesel and advanced aftertreatment

Advanced Heavy Vehicle Technologies R&D



Strategy for Future Fuels

- ◆ **Focus on the requirements of the Diesel cycle engine**
 - ◆ high cetane number for compression ignitability
 - ◆ low sulfur and low aromatics for clean emissions
 - ◆ lubrication requirements
 - ◆ additive requirements, e.g., fuel injector detergents
 - ◆ chemical compatibility, e.g., fuel solubility characteristics
- ◆ **Use existing liquid diesel fuel infrastructure**
- ◆ **Use domestic resources**
- ◆ **Use diverse feedstocks**

Synthetic Fuel From Natural Gas Raises Auto Makers Interest In Clean Diesel Engines



New generation of diesel engines, using synthetic fuel from natural gas, would burn as cleanly as the cleanest gasoline engines

Diesel engines would allow ever-bigger sport utility vehicles and pickup trucks to comply with Federal fuel-efficiency rules

THE NEW YORK TIMES, TUESDAY, OCTOBER 20, 1998

Auto Makers Experiment With New Fuels

Cleaner-Burning Synthetic-Diesel Mix Could Go in Bigger Vehicles

By KEITH BRADSHIR

DETROIT, Oct. 19 — Struggling to comply with Federal fuel-economy and emissions regulations even as Americans buy ever-bigger family vehicles, auto makers have quietly begun experiments with oil companies to develop new and potentially cleaner fuels.

Ford and General Motors have already entered long-term partnerships with oil companies, while Chrysler plans to announce on Wednesday a program with immediate goals: testing vehicles over the next two years that would burn a promising type of synthetic fuel made from natural gas instead of crude oil.

The synthetic fuel is similar to diesel and can be burned in diesel engines. Chrysler's goal is to develop a new generation of diesel engines that, using the synthetic fuel, would burn as cleanly as the cleanest gasoline engines, said Loren K. Beard, Chrysler's manager of fuels technology. Many auto makers are planning to replace some of their gasoline engines with more fuel-efficient diesel engines. For one thing, this would allow them to build ever-bigger sport utility vehicles and pickup trucks without violating Federal fuel-efficiency rules.

But obstacles remain. The Syntro-

leum Corporation, which has a small factory that will supply synthetic fuel for the tests, estimates that mass production would push the fuel's cost down to \$1.50 or less a gallon. Still, even reducing the cost to that level would require considerable investments in new equipment at natural gas fields, as well as persuading service stations to set aside pumps and tanks for the new fuel.

A principal Chrysler experiment will involve a blend of only 20 or 30 percent synthetic fuel with the rest being regular diesel, said Mark A. Agee, the president and chief operating officer of Syntroleum, which is based in Tulsa, Okla. The blend might then be competitive in price with premium grades of gasoline.

Bernard I. Robertson, Chrysler's vice president for engineering technologies, predicted that premium grades of diesel, consisting of a blend with synthetic fuel, would become available within five years. Future diesel cars and light trucks will probably require the premium grades, much as current models require unleaded gasoline to reduce pollution, he said.

Diesel engines produce up to 30 percent better fuel economy than gasoline engines. But they emit more air pollution, although the latest models are far cleaner than the sooty diesels of the 1980's.

The domestic auto makers are all developing diesel engines now for

large sport utility vehicles and pickup trucks, which earn the highest profits per vehicle. So-called light trucks — a category including vans as well as sport utility vehicles and pickup trucks — are allowed to meet a lower average fuel economy than cars. But auto makers have had trouble meeting even this standard with the recent popularity of such models as the Dodge Ram full-size pickup and the huge Ford Expedition and Chevrolet Suburban sport utility vehicles.

Federal and California regulators are drafting new, tougher emissions regulations that could be hard for diesel engines to meet. In response, auto makers have been working on cleaner engines and cleaner fuels.

The process for making the synthetic diesel from natural gas is loosely based on a technique first developed in the 1920's. But tighter air quality standards and auto makers' difficulties with fuel-economy standards are forcing a reconsideration of the technology.

Ford has already begun experimenting with the synthetic substitutes for diesel, while G.M. plans to do so in the coming months, as part of their efforts to produce an extremely high-mileage car in cooperation with the Federal Government. Because the fuel burns so cleanly, it could have applications in cars as well as light trucks, said Sara R. Tatchio, a Ford spokeswoman.

Natural Gas to Liquid Fuels Technology Becoming Economically Feasible



THE WALL STREET JOURNAL, WFT

Exxon Project To Expand Use Of Natural Gas

By Peter Brattin
Exxon Corp. is set to build the world's first plant to produce synthetic liquid fuels from natural gas, a move it would make when the uses of natural gas.

Downstream, No Problem
Exxon Corp. is prepared to start the refining and marketing operations, which has been hard hit by a recession.

Exxon Corp. is set to build the world's first plant to produce synthetic liquid fuels from natural gas, a move it would make when the uses of natural gas.

Should Exxon go forward with its plan? "It would differentiate and create a niche in a market for says J. Robinson West of the Petroleum Institute in Washington. "It could be the computer industry, calls the killer application for gas."

Wall Street Journal, October 30, 1996

quantities in...
in distant markets has slumped the energy industry for decades. For years, the oil...
Please Turn to Page A11, Column 3

Exxon Holds Talks With Qatar to Build Innovative Gas Plant

Exxon Corp. is set to build the world's first plant to produce synthetic liquid fuels from natural gas, a move it would make when the uses of natural gas.

DOE Selects Research Partner for Project to Make Liquids from Nation's Natural Gas Supplies

"We're looking to open the door to a vast resource of natural gas that is today beyond our economic reach. This research project could pioneer a way to tap that resource and convert it into valuable liquid fuels that will be in demand for the next century."

DOE Press release
May 20, 1997
ico Pena
release

GAS TO OIL: A GUSHER FOR THE MILLENNIUM?

Chemical society could provide the world with enough oil for almost 20 years.

Striking Black Gold in Natural Gas Wells

Striking black gold in natural gas wells.



Business Week, May 19, 1997

Entrepreneurs' Formula Intrigues the Oil Industry

By Peter Brattin
With only 30 employees and no other...
Synthroleum Corp. has the...
the oil industry's...
At the center of this plan is one...
the oil industry's...
At the center of this plan is one...
the oil industry's...
At the center of this plan is one...
the oil industry's...

ENERGY

net to follow extremely closely...
Oleg Maluk, Synthroleum Corp.'s...
after working for years on their own...
Texas Inc. and Atlantic Richfield...
have decided to also license Synthroleum's...
technology. The companies have not...
their terms of their licensing agree...
ments.

Another Synthroleum plan is to build a...
pilot facility plant in Washington...
state. The company will use hydrogen to...
create a liquid fuel that it will use to...
run its own fleet of trucks. The...
company has also been awarded a...
contract to build a pilot plant in...
Alaska.

Synthroleum is ready to start the...
development of the technology. A...
team of engineers and scientists...
is working on the technology. The...
company has also been awarded a...
contract to build a pilot plant in...
Alaska.

Wall Street Journal, December 8, 1997

highly competitive...
the oil industry...
Mr. Agre...
Synthroleum's work is something new

**A Possible Scenario For
Future Liquid
Transportation Fuels**

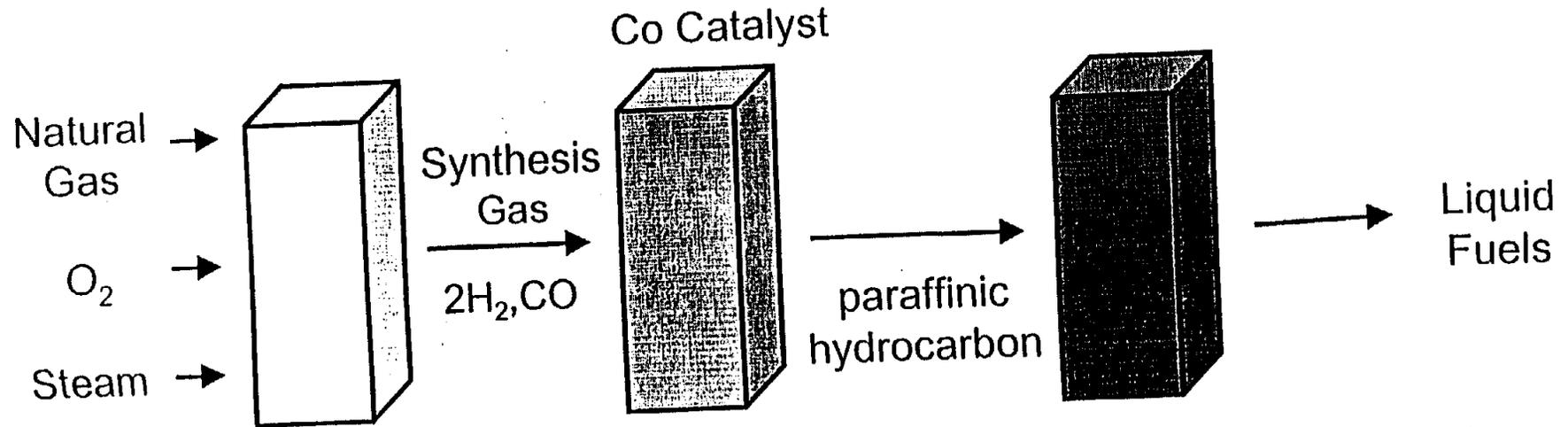
Natural Gas to Liquid Fuels Technology



Syngas
Generation

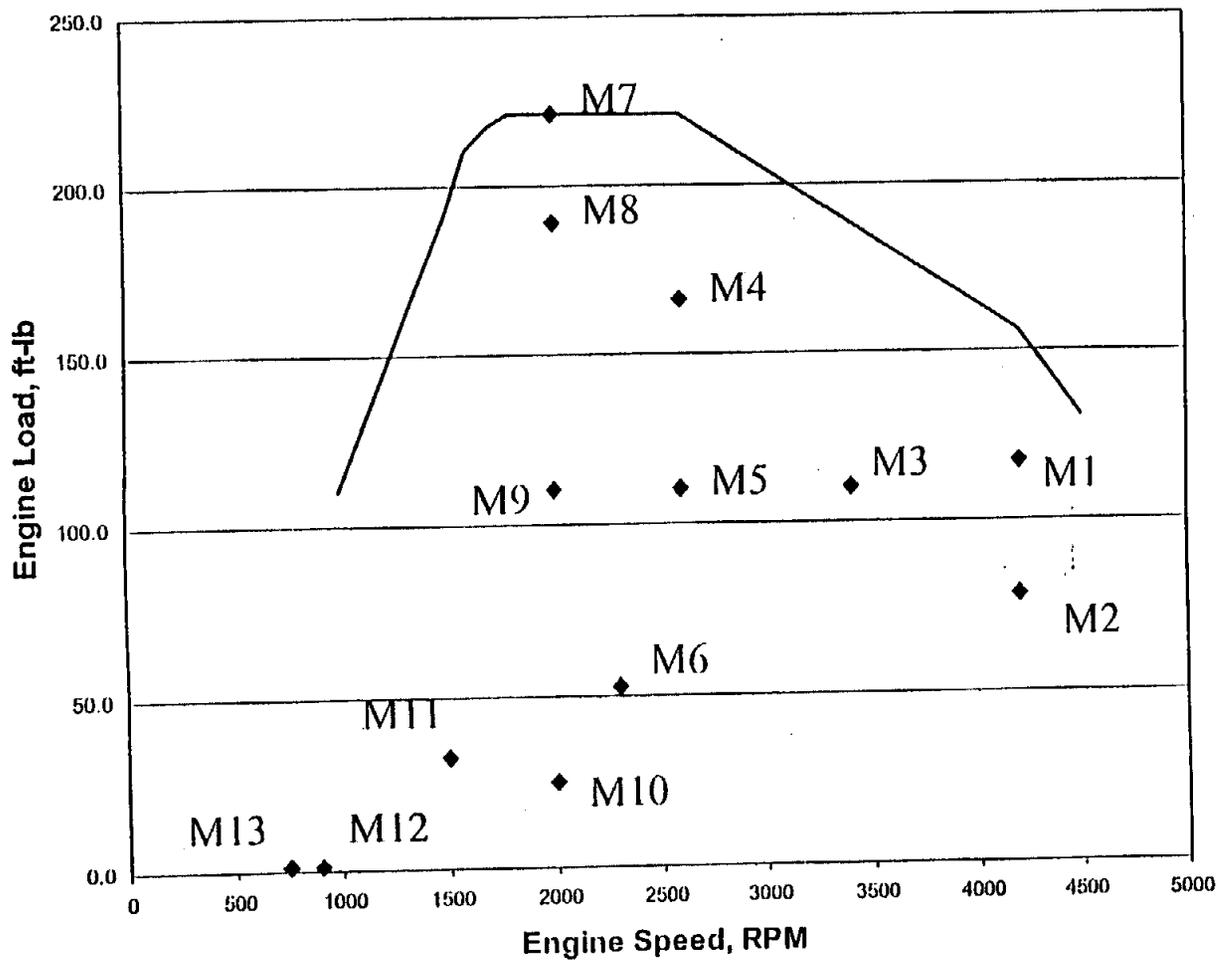
F-T
Conversion

Hydroisomerization

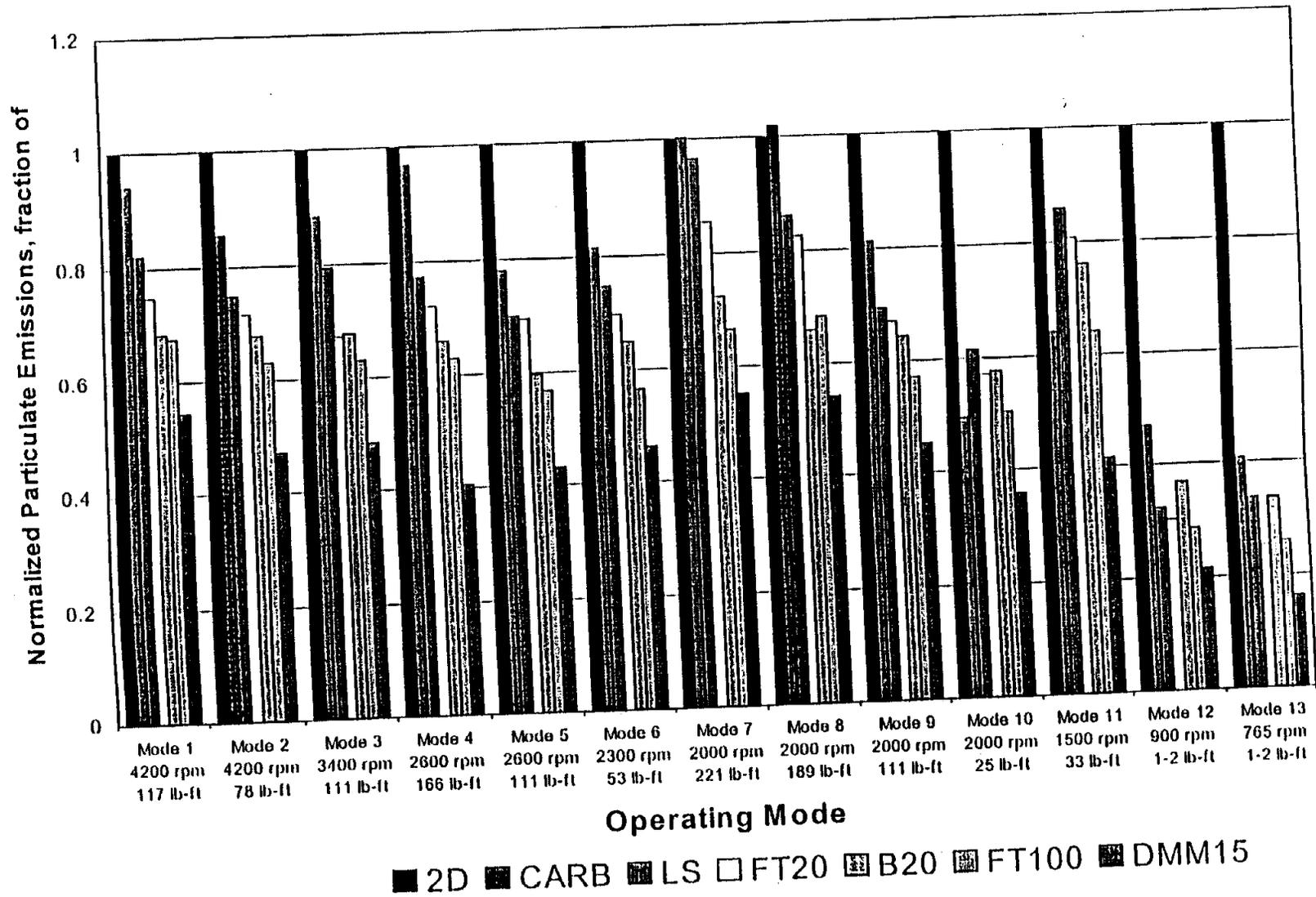
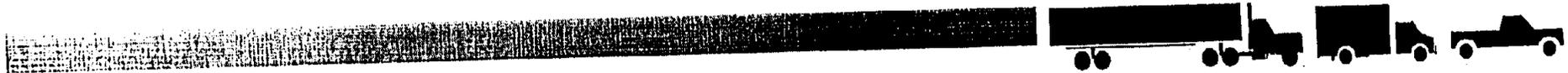


Test Sequence

13, Steady-State Speed/Load Points



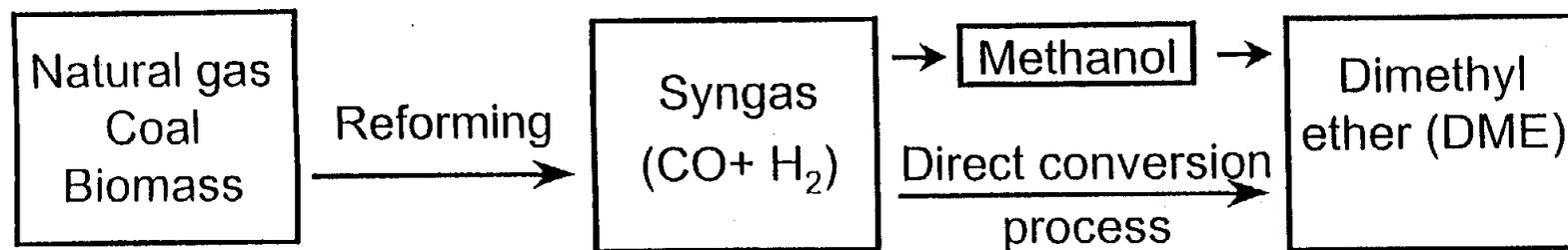
Particulate Emissions by Test Mode



Dimethyl Ether: A Clean Fuel Option



- ◆ High cetane number (55-60) makes it highly desirable for compression ignition engines
- ◆ Capable of very low emissions
- ◆ Smokeless combustion
- ◆ Low noise levels -- similar to and lower than gasoline engines
- ◆ Can be derived from natural gas, biomass, coal and methanol



U.S. Sources of Feedstocks for Fischer-Tropsch Fuels



Near term

- ◆ 37 tcf reinjected natural gas in North Slope of Alaska (would produce about 3.7 billion barrels of F-T diesel)

Mid term

- ◆ 246 tcf of sub-quality gas in lower 48 states [GRI 1993] could produce about 24 billion barrels of F-T diesel (more than twice the original Prudhoe Bay oil discovery)
- ◆ Combination of coal or biomass gasification plus use of lower 48 sub-quality gas (to furnish supplemental H₂) could lead to very large quantities of FT products.

Long term

- ◆ Virtually inexhaustible (1000's of Quads) supplies of methane tied up in methane hydrate off U.S. coastline

Preliminary Conclusions



- On average over the 13 modes, all 6 test fuels produce a reduction in particulate emissions in comparison to the baseline.
 - ◆ DMM15 ~ 50 %
 - ◆ FT100 ~ 35 %
- Particulate emissions are reduced without increases in NO_x.
- Particulate size distribution is approximately the same for all 7 fuels.
- Direct substitution of alternative fuels has potential for emissions benefits in Diesel engines such as the OM611.

What Makes Fischer-Tropsch Diesel a Good Fuel?



- ◆ High Cetane Number of 76
(compared to 48-50 for conventional diesel)
- ◆ No sulfur
- ◆ No aromatics
- ◆ Low cloud point (-10° C)
- ◆ Low emissions (compared to U.S. average Diesel fuel, based on Southwest Research Institute study)
 - ◆ 8% less NO_x
 - ◆ 30% less PM
 - ◆ 38% less HC
 - ◆ 46% less CO
 - ◆ Even lower emissions possible in engines optimized for Fischer-Tropsch

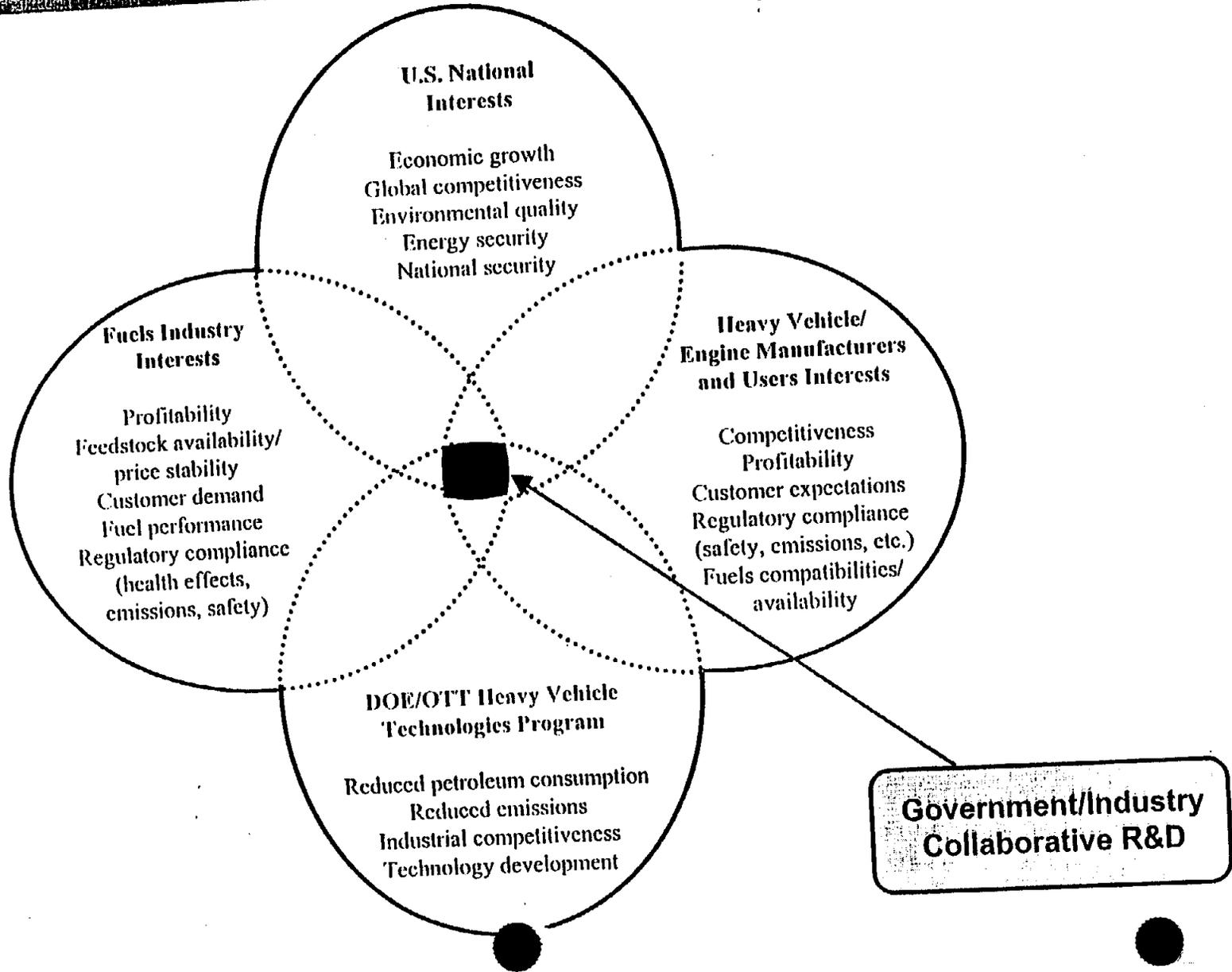
New Diesel Cycle Fuels Program



DOE's Role

**Catalyze collaboration between
engine manufacturers and fuel
companies to develop performance,
emissions and durability data on
likely future diesel fuels**

DOE/Industry Collaborative Efforts Target Common Interests



New Diesel Cycle Fuels Program



Status

- ◆ Conducted workshop (San Antonio, TX, January 15, 1998) to elicit input from engine manufacturers and fuel producers on New Diesel Cycle Fuels Program
- ◆ Program Objective:
 - ◆ To evaluate emissions, performance, and durability of advanced Diesel cycle engines running on potential future neat and blended liquid diesel fuels from alternative feedstocks (natural gas, biomass, coal, and petroleum).