**Liquid Natural Gas as a Transportation Fuel in the
Heavy Trucking Industry**
Project sponsored by US DEPARTMENT OF ENERGY
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Project 1 - Direct Diesel Replacement

Subtask 1. Atomization

1.   Effort has been made to develop a numerical code which
simulates the interactions between an isolated droplet and its
ambient gas. Since the droplet diameter considered is of a few
tens of microns to a few hundreds of microns, surface tension is
important and the droplet can be treated as a sphere. A
spherical symmetric computational domain is used for the gas flow
surrounding the droplet and for the liquid droplet itself. The
formulation takes into account the aerodynamic characteristics of
pressure gradients, viscous boundary layers, separated flows and
wakes which can appear for gas flow over the droplet. Effects of
internal liquid circulation, driven by surface shear forces, is
also included in the formulation of the problem.

2.   The numerical code is being debugged now. Test run will be
performed on Sun SPARC workstation as soon as the debugging
process is completed. Due to the extensive calculations
involved, production run will be performed on Cray Y-MP
supercomputer for best efficiency.

Subtask 2. Fundamentals of Direct Replacement

1.   An experimental facility operating at atmospheric pressure
will be designed and tested with LNG drops and sprays, and the
observations and experiences will be fed back to the task leaders
to incorporate in their work. During the second quarter the
following have been accomplished:
(i) The gas chromatograph (HP-5890) was installed in the
Combustion Research laboratory on the north campus of the
university. The GC grade gases (He, H2, Air) and the commercial
grade air cylinders and regulators were purchased and plumbed to
the GC. Three columns recommended for natural gas analysis have
been borrowed from the instrument manufacturer for the initial
set-up. These columns will have to be eventually purchased by
us. After several visits by the service technicians from the
Hewlett-Packard company, the installation of the columns, valving
arrangement to determine organic as well as inorganic components
in Natural Gas, columns were completed. The instrument has been
programmed for natural gas analysis and an operational procedure
for running the samples and shutting down the instrument have
been developed.
(ii) A student was hired to work on the atmospheric pressure test

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chamber; he has made a significant progress in the design and construction of the facility. The apparatus will be locate in the test cell no. 2 in the north campus research center. The fabrication is about 60% complete.
Plans for the next quarter:
The atmospheric test chamber construction will be completed. Plumbing of the gas flow lines and heat exchanger will be performed. We hope to begin the experiments for making LNG with the CNG for use in our tests.

Subtask 3. Distribution of Emissions

1. Autoignition - In the first phase of this work, autoignition of natural gas/air mixtures at diesel engine conditions was investigated. The chemical kinetics code, CHEMKIN, developed by the Sandia National Laboratory was used for the study. The chemical process was modeled by the chemical kinetics scheme given by Westbrook and Pitz [1987]. This scheme involving 31 species in 178 reactions has been tested previously for a variety of conditions, from turbulent flow reactor to the shock tube. There are always uncertainties associated with the use of a complex reaction mechanism, and these uncertainties must be included in any assessment made with its use. The results of this study should be considered as the trends which are unlikely to change with modifications and future improvements in the reaction mechanisms.

Figure 1 shows the computed ignition delay at different temperatures for stoichiometric mixture of natural gas and air. Plots are shown for two natural gas compositions: pure methane and 90% methane with 10% ethane. These results indicate that ignition delay is highly sensitive to the initial mixture temperature. Adding ethane to the natural gas substantially reduces the ignition delay. Results shown in Figure 1 compare well with similar results obtained by Westbrook and Pitz [1987].

2. Effects of Fluid Mixing - In diesel engines, the fuel is injected into air at high pressures and temperatures. Thus, the spatial nonuniformities in fuel/air concentrations and transport processes influence the rate of ignition. Simple studies of autoignition of natural gas/air mixtures do not accurately reflect the diesel engine conditions. In a recent study of ignition delay under diesel conditions, Naber et al. [1994] found significant differences between experimental data and calculations using only the chemical kinetics. Nabet et al. [1994] attributed these differences to the mixing-controlled combustion in diesel operation.

Incorporating fluid mixing in calculating ignition delay is the primary objective of the second phase of this work. Thus, a computational fluid dynamics code integrated with detailed chemical kinetics is used. So far, flow calculations in the absence of chemical reactions have been completed. In these calculations, the fuel (pure methane) is injected into a constant

volume cylinder occupied by air at high temperature and pressure. Calculations involve fully elliptic, time-dependent Navier-Stokes equations, and equations of mass continuity and energy conservation.

The computed flow fields at several time steps are shown in Figures 2 and 3. Figure 2 shows the velocity vectors while Figure 3 shows the streamfunction contours. These calculations were done for air pressure of 25 atmospheres and air temperature of 1,140K. 30 mg fuel was injected in 7 ms at an average velocity of 385 m/s. The radius and length of the cylinder were 40 mm each. The calculations were done in the symmetry plane using 60 grids in the radial direction, 80 grids in the axial direction and a time step of 0.24 ms. These results show the essential features of mixing (including turbulent structures) between fuel and air.

Future plans call for similar computations with detailed chemical kinetics so that the ignition delay can be predicted at realistic diesel engine conditions.

References

Naber, J.D., Siebers, D.L., Di Julio, S.S., and Westbrook, C.K., 1994, "Effects of Natural Gas Composition on Ignition Delay under Diesel Conditions," *Combustion and Flame*, vol. 99, pp. 192-200.

Westbrook, C.K., and Pitz, W.J., 1987, "High Pressure Autoignition of Natural Gas/Air Mixtures and the Problem of Knock," *GRI Topical Report PB88-108030*, GRI, Chicago.

Project 2 - Short and Long Term Storage

Subtask 1. Modified Adsorbents

Studies of fullerene modified adsorbents continues; results indicate high capacity for gases at high temperature. Current work has focussed on determining the mechanisms of storage. Additional work includes performing calculations on bulk packing densities and pore volumes per unit weight on the MCM-41 materials to increase energy storage density with simultaneous reduction in storage pressure.

Subtask 2. Vent Gas

The selection of hydrocarbon candidates for the solvation of natural gas has been accomplished. Three systems have been chosen based upon the following criteria: consumer availability, affordability, and increased storage density of the natural gas/hydrocarbon solution. The candidate solvents currently under investigation are the following: 1) commercial propane, 2) commercial butane, and 3) liquefied petroleum gas (LPG).

Bubble-point properties and critical point locations have been determined for mixtures of methane and each of the components

listed above. These calculations indicated that operational ranges providing 50-90 mole-percent methane in the liquid phase exist from 150 psia and 100°F to approximately 2400 psia and 0°F.

The selected fuel systems will be modeled using a locally generated FORTRAN program which simulates the withdrawal of vapor in the head-space of a fuel tank through a series of pressure reduction stages at constant temperature. The assumption of rapid vapor-liquid equilibrium at each stage of the draw-down allows the program to determine phase-, composition, density and energy content. The program will be further modified to simulate the withdrawal of liquid, thus allowing a comparison of property dependence on phase delivery.

Subtask 3. LNG Storage at Moderate Conditions

We have identified a strategy to store the natural gas as a part of a mixture which can be liquified by pressurization at ambient temperatures. Among the possible additives to methane - the light petroleum fractions - n-butane was selected, because of its relatively high critical point compared to methane ($T_{c\ methane}$ = 190.7 K; $T_{c\ n-butane}$ = 425.2 K), while still being in gaseous state at ambient conditions. Our calculations predict that as a liquid, an equimolar mixture of methane and n-butane will have an energy density of 0.686 lbmole/cuft that is comparable to that of LNG. If we succeed in liquefying the gaseous mixture at 100°F, its energy density will be at least 3.5 times greater than CNG at the same pressure.
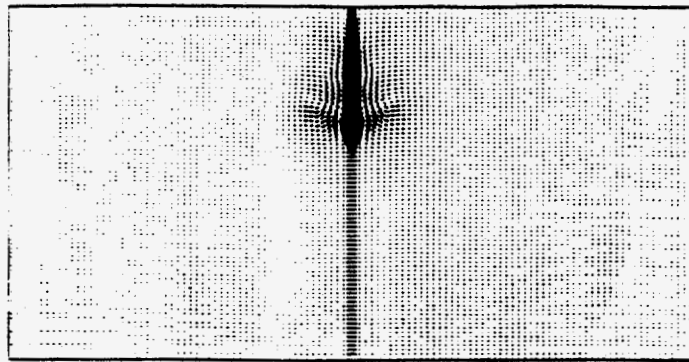
Our strategy for liquefying the gaseous mixture at ambient temperature is based on the capillary pressure effect in porous materials. By using highly porous solids with pores in the correct size range, condensation occurs in the pores at much lower pressures than those for condensation of the bulk liquid. This has to do with the surface physics of the solid material and the radius of curvature of the liquid interface in the pores.

Recently, the researchers at Mobil Oil discovered a way to synthesize solids with controlled mesoporosity by utilizing the mechanism of formation of liquid-crystal structures in surfactant systems [7-12]. By varying the surfactant chain length (10, 12, and 16 carbon atoms), we were able to synthesize and test in our laboratory materials with ordered structures of pores of size 22, 26, and 36 A respectively, with total pore volume of 2.34 cm³, and methane storage capacity in the range 5.3 - 6.8 g/100 cm³ at 1000 psi and 25°C (that is resp. 50 - 75% higher than CNG at the same conditions).
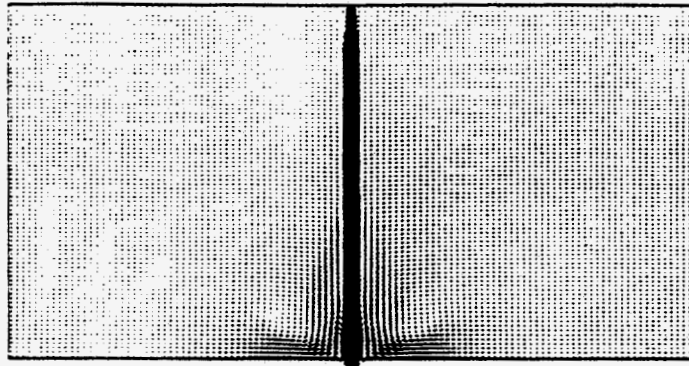
Our calculations show that at 100°F a significant reduction in the pressure from 1600 psi to 35 psi can be achieved by condensation of the equimolar mixture in porous solids with pore size of 40 A. Research is in progress of tailoring the pore size distribution and surface chemistry significantly below the vapor pressure required in a vessel.
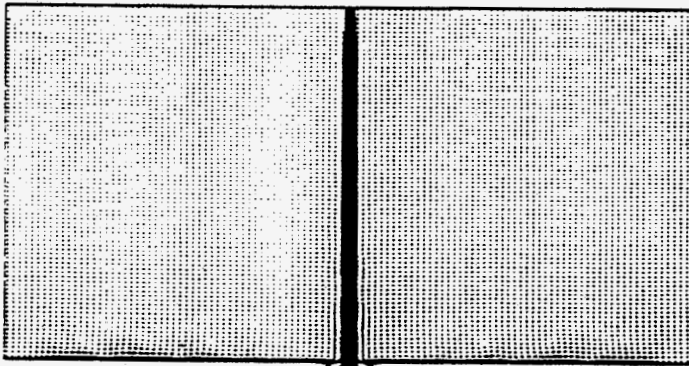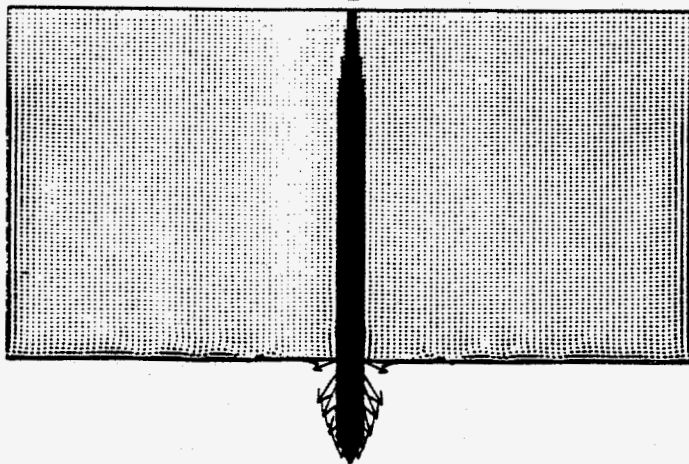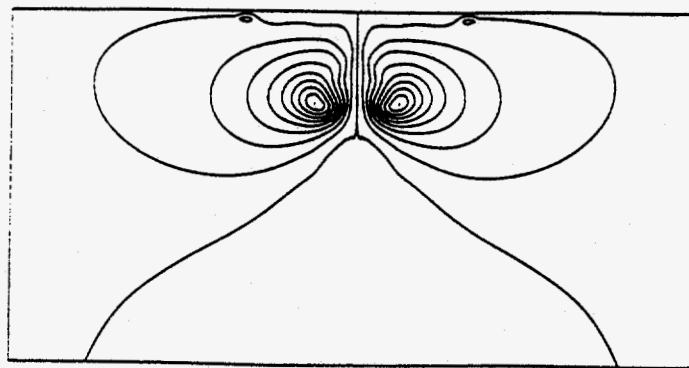
Figure 1.

Ignition delay vs. temperature

pure methane

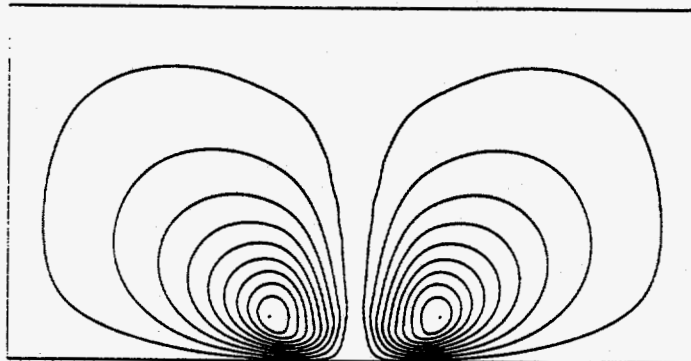10% ethane, 90 % methane

time (ms)

1000/T

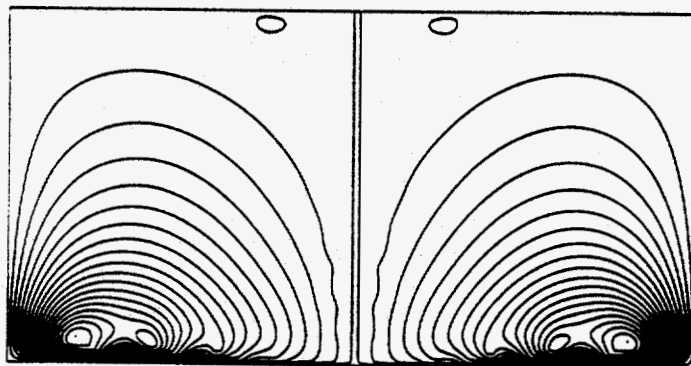**Figure 2. Velocity vectors at different time steps**
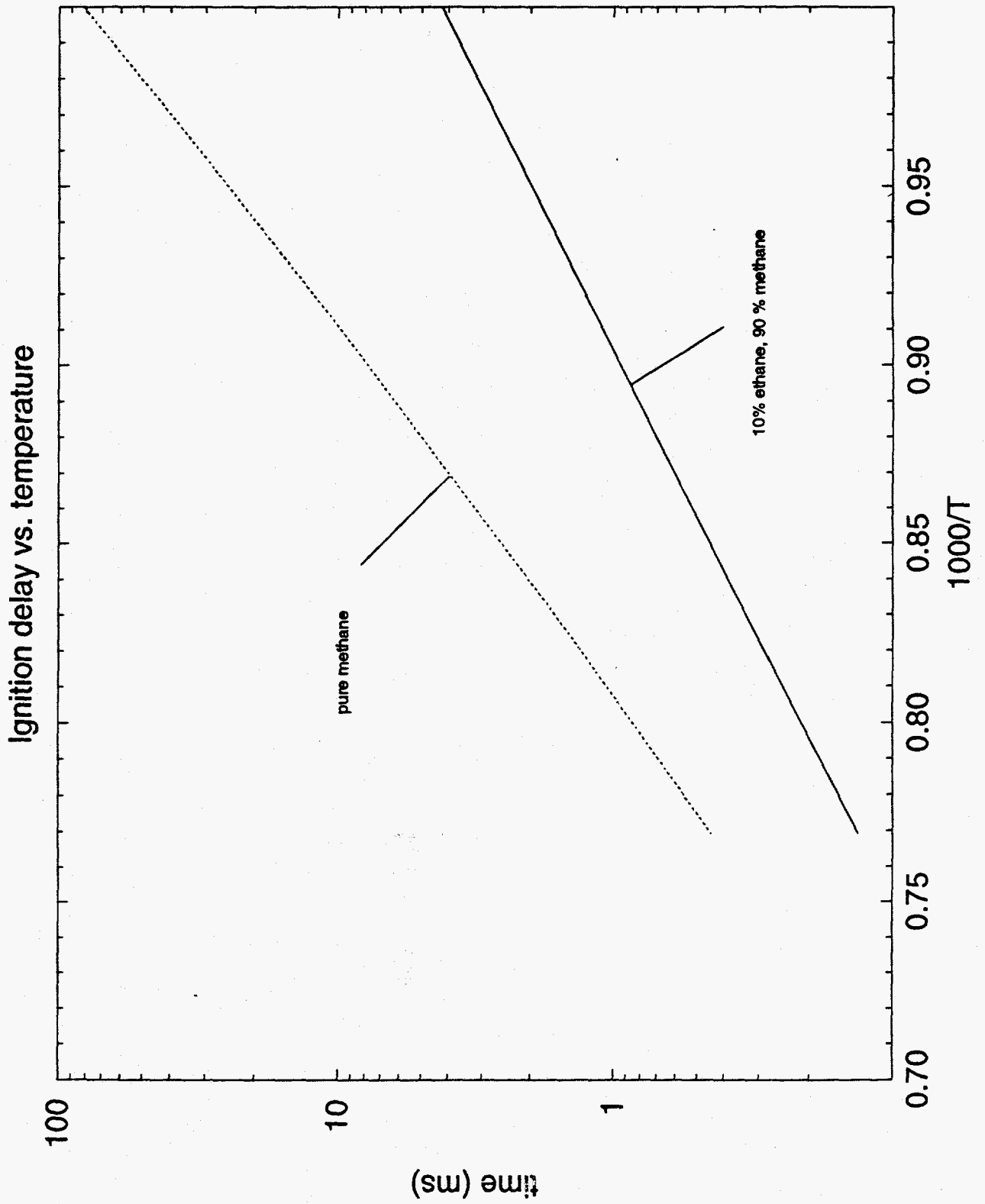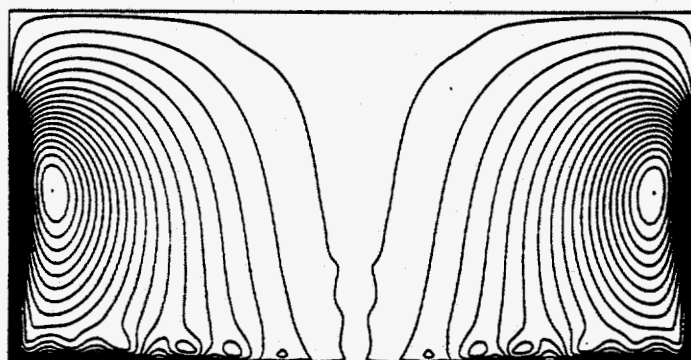
(a) 0.5 ms

(b) 1.75 ms

(c) 2.5 ms

(d) 5.0 ms

Figure 3. Streamfunction contours at different time steps