DOE/GO/10112-T1

**Liquid Natural Gas as a Transportation Fuel
in the Heavy Trucking Industry**

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Final Technical Report

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**William H. Sutton,
Principal Investigator
University of Oklahoma**

Closing Date June 30, 1997

**Prepared for United States Department of Energy
Golden Field Office
Contract DE-FG36-95GO10112**

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Liquid Natural Gas as a Transportation Fuel in the Heavy Trucking Industry

**William H. Sutton,
Principal Investigator**

*Project Sponsored by U.S. Department of Energy
Golden Field Office
Contract DE-FG36-95GO101112
Final Technical Progress Report*

This report encompasses the second year of a proposed three year project with emphasis focused on fundamental research issues in Use of Liquid Natural Gas as a Transportation Fuel in the Heavy Trucking Industry. These issues may be categorized as (i) direct diesel replacement with LNG fuel, and (ii) long term storage/utilization of LNG vent gases produced by tank storage and fueling/handling operation. Like the first year of this project, this work emphasized fundamental research in a number of related areas; many of those results have appeared (or have been submitted or accepted) in numerous technical and scientific journals and conferences. At least one masters thesis and one Ph.D. dissertation were completed in the second year directly based on the work here, while several others were partially based on this work. Follow on research on this direct work (LNG) has stopped at this time due to the lack of third year funding; however, related work continues with funding from other sources that were developed because of these two years of effort.

Copies of selected papers related to this work are reproduced in the appendix. The first set deals with the diesel replacement issues. The second set deals with the storage issues, and includes the title page and abstract of Mr. Horstkamp (Horstkamp, S. W.; "High Energy Density Storage of Methane in Light Hydrocarbon Solutions," M.S. Thesis and of Ms. Ioneva (Ioneva, M. A.; "Nanoengineered Porous Sorbents and Their Applications," Ph.D. Dissertation) on fuel storage methods.

The results of this work are expected to enhance utilization of LNG as a transportation fuel. The investigators wish to thank DoE for their support of this fundamental work.

I. Fueling Delivery to the Engine, Engine Considerations, and Emissions

1. Atomization and/or Vaporization of LNG for Direct Injection Diesel-type Natural Gas Engines

At very high pressures, compressed natural gas may achieve densities of approximately one half that of low pressure liquid natural gas. The 'direct injection natural gas' engine (DING) diesel-type 2-stroke 6V-92TA heavy duty engine by Detroit Diesel utilizes a liquid (LNG) pumping scheme and heat exchangers to inject high pressure (3000 psi) methane gas. There can be difficulties in controlling fuel delivery and in predicting the thermodynamic state of the methane under all operating conditions for this type engine; the situation must be redesigned for each application.

In 4-stroke LNG engines, low pressure gaseous methane is typically injected by using vaporized LNG provided by heat exchangers. The density of the methane is much lower than other liquid fuels, requiring extremely high volume flow rates and large diameter injectors. Use of LNG densities would greatly increase fuel delivery to the engine.

Current technology is to deliberately sacrifice volumetric flow efficiency to insure a sufficiently high temperature for the LNG vapor to support combustion and high thermal efficiency. Clearly, a tradeoff exists between flow and thermal effects.

The control problems of the injected high pressure gaseous methane relate to the relatively low volume flow rate (volumetric efficiency) compared to other liquid fuelled engines. Ideally, the original low pressure LNG density would be more suitable at the injection point for flow and pressure considerations. The fluid is super-critical (more than 673 *psi*) at the injection pressure. If the flow is high density, flow control is simplified but the temperature of the charge may be too low for practical applications. If the fluid is heated vapor, the resultant high volume flow requires large diameter, high pressure injectors which are subsequently difficult to control.

Similarly, low pressure injection of gaseous methane is even more sensitive to low density volumetric flow efficiency. Again large diameter injectors with even longer opening or pulse modulation time are required to deliver adequate fuel.

The proposed research was to determine size, distribution, pressure and temperature limits of atomized droplets of super-critical (for high pressure) and liquid (for lower pressure) natural gas that are combustible with a glow plug and hot air. Determining the limits of combustion form the second subtask of this part of the proposal. Conceptually, droplets could be made small enough, when injected with hot enough air, to overcome the thermal disadvantage of the high density super-critical or liquid natural gas; note that the injection of atmospheric pressure stoichiometric LNG with 20°C ambient air would result in a -26°C mix. Another part of the proposed work was to make a preliminary assessment of injections of high density droplets as a secondary flow control in primary natural gas injected compression combustion engines.

As noted earlier, this work has the potential of defining direct fuel replacement injection limits for compression ignition type engines primarily used for long haul trucking applications.

The LNG nozzle test set up was reconfigured from the first years work to consist of a single pass heat exchanger for converting CNG into LNG. Previously used CO₂ and water scrubbers in the CNG feed lines were eliminated. Trials to produce LNG and to determine the optimum heat exchanger inlet and outlet conditions for the liquid N₂ stream and CNG were carried out. A continuous stream of LNG was successfully produced. Two sprays, one where the atomization begins at the injector inlet itself (type A) and the other where the first few inches remains as a liquid core and then begins atomization (type B) were established. These two sprays were chosen as candidates for further study. Flow visualization experiments with schlieren and direct color photography with a helium neon laser sheet were carried out. The droplet velocity and size

distributions at various axial and radial locations of the spray were carried out using phase Doppler particle analyzer. The data were analyzed and presented as "Characteristics of Liquid Natural Gas Spray in a Quiescent Medium", S. Peters, A. Smith, R. Parthasarathy, and S.R. Gollahalli, Proceeding 5 of the 1997 Energy Week, Published by ASME and API, pp.400-407, 1997. An additional paper has been accepted related to this work as "Liquid Natural Gas Sprays injected into Air Co-Flow", R. Parthasarathy and S.R. Gollahalli, for the 1998 Energy Technology Conference and Exhibition, Houston, TX. (Jan-Feb., 1998).

2. Fundamentals of Direct Replacement of Diesel Fuel by LNG in Simulated Combustion

Liquid natural gas, as used here, refers to high density (LNG densities) super-critical high pressure methane or to low pressure cryogenic LNG. A study of the ability to atomize LNG droplets forms the basis of the previous subtask. This portion of the work was to evaluate the ability of these atomized distributions to directly or indirectly support combustion. Here, a simulated combustion cylinder will be used to assess fundamental methods of obtaining high speed distribution data on mass (concentration), velocity, pressure and temperature suitable for numerical flow, heat transfer and combustion analysis. There are numerous difficulties in simulating the dynamic internal environment of a diesel type engine in the laboratory: dynamic shock processes, high pressures (average fluid stresses) and temperatures (kinetics), nonequilibrium reacting thermodynamics, and piston dynamics.

A diesel simulator was partially constructed, by Mr. Caplinger (Dr. Sutton's student) during the second year based on design work in year one. Starting in January 1995, a project was undertaken to design, build, test, and interpret results for a large diesel-type engine to be run on liquid natural gas fuel, instead of diesel fuel. The set-up and results were to be such that they could be compared with computer simulations performed by one of Dr. Agrawal's previous students. This meant that the combustion of the natural gas was to be self-ignited, unlike some work that has been done using spark ignition. It was determined that based on the funds for this work, a single-cylinder set-up was the most feasible for building and testing purposes. The first thing done was to decide what engine to use or model the test equipment after. It was found that parts for Cummins diesel engines (used in heavy duty trucks) were easiest and cheapest to obtain. parts were obtained for the simulator: a single piston, sleeve, push rod, and dual cylinder head for an 855 Cummins diesel engine were obtained. Using these parts as a basis, plans were drawn up for how to build a single-cylinder set-up from scratch. This was thought to be better than working on an entire engine block, due to the cost and the enormous size and weight of the block itself. A used crankshaft was found, and a section was cut out of it to be used in the single-cylinder set-up. Also, the main and rod bearings, that would be needed for the crankshaft and push rod, were obtained.

After a great deal of discussions with machinists and diesel engine mechanics, it was decided that to construct the apparatus from scratch would be nearly impossible. Achieving the tolerances needed for the positioning of all the various components would be very difficult and time-consuming, and would not be within the scope of this project. Therefore, a used Cummins 855 cubic-inch-displacement diesel engine block was obtained for research purposes. The block was stripped down, except for the crankshaft, main bearings, and camshaft. A parallel effort was initiated at this time when to look at the Phoenix flow code and Chemkin chemical kinetics programs used for modeling

combustion and fluid flow. A student covered the same ground as Mr. Bi (thesis noted in year one efforts) so that modifications that needed to be made to the codes used by Mr. Bi could be compared with the experimental work that was being done.

Since the camshaft came with the engine block, we planned to use the purely mechanical camshaft to control the air intake and exhaust. To do this, cam followers, push tubes, a rocker box, and rockers were obtained for a single-cylinder. At a later point, a head gasket set was obtained, for the purpose of sealing the gap between the head and the engine block, as well as other connecting points.

It was determined that holes needed to be drilled in the cylinder head to serve as ports for taking measurements inside the combustion chamber. Measurements of temperature and pressure were to be made. An Omega pressure transducer, with a highly viscous fluid snubber, was obtained for taking the pressure readings at two points within the cylinder. Measurements would be taken for a 1/4 section and assumed to be axially symmetric. Since the cylinder head is almost 4.5 inches tall and the transducer could not be placed all the way to the bottom of the head, a method of transferring the pressure to the measurement point was needed. An open air tube could not be used due to the difficulties caused by shock waves in the closed air tube. Therefore, it was decided to fill a stainless steel tube with a viscous oil, and place a small piston at the bottom that could force the oil up and thus transfer the pressure to the diaphragm of the transducer. The temperature measurements were designed to be taken by running a thermocouple down a stainless steel tube in the cylinder head and filling the tube with epoxy, leaving the tip of the thermocouple exposed to the combustion chamber. To drill these measurement ports, the valves had to be removed from the cylinder head. This was done by the re-manufacturing shop.

Another priority of this project was to be able to view what is taking place inside the combustion chamber. We had planned to use fiber optics for these viewing purposes, but space restrictions did not allow for running the light source up through the piston. This light source is necessary for viewing through a window. It is possible to run the light source down from the top, through the cylinder head, and use a fiber optic camera to view the inside of the cylinder, but this is extremely expensive. This idea is being saved for later work, if necessary.

The next step was to begin the process of mounting the engine block. The block needed to be mounted such that access to the engine would not be difficult, but also in a manner that would give the large mass extreme stability. The best way to achieve this was to weld a 1/2 inch thick steel plate to the two I-beams that protrude from the large concrete slab in the North Campus test cell. Drilling holes in the 12 x 36 inch steel plate allowed the engine block to be bolted directly to the plate. It became evident, however, that this created a cantilever situation and that vertical support would be needed. Also, some type of damping material would be needed to keep the concrete from shattering when the engine is in use. For the vertical support, another I-beam was attached to the block and run vertically downward, being bolted to the floor. Motor mounts or other damping materials were used at every connection point to reduce the shock on the concrete slab.

The next step in the project relates to the control of the air intake and exhaust valves. The plans

were to use the mechanical camshaft to perform these duties, but the rocker box did not fit on the cylinder head with the pressure and temperature measurement devices in place. The process of welding spouts at the water openings so cooling water can be run around the cylinder sleeve was nearly completed in year two. Caps, inlets, and outlets were welded such that oil can be shot to the crankshaft and other areas that need lubrication. Also, the holes needed for measurement purposes were completed. One of the two middle cylinders of the six-cylinder engine will be used due to the balancing problems of the crankshaft

It was decided that instead of building our own set-up for making the liquid natural gas fuel, LNG will be taken from the test apparatus already being used by Dr. Gollahalli for spray visualization. However this proved to be unfeasible due to the distance between test cells. Instead the OU Alternative Fuel Research Platform was filled with CNG and parked adjacent to the test cell. A heat exchanger, similar to that developed in Dr. Gollahalli's work was designed, built and tested.

In the final months of the project considerable additional progress was made in the numerical simulations with the help of Dr. Agrawal. The fuel injector design was then undertaken by another student, Mr. Sanchez, who took a prototype controller board and modified the necessary C code to allow for flexible control of the injection. Additional work was done by Dr. Lai in this area.

A numerical code was under development, by Mr. C.P. Pan (Dr. Lai's student, who subsequently got his Ph.D.) for the study of interaction between a single isolated droplet and gas stream. 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. The numerical code developed was tested and debugged. The numerical code previously developed for the study of a single droplet was extended to include interactions between two aligned droplets. The challenge lies in the simulation of relative motion of the two droplets. The problem becomes more difficult when the size and evaporation rate of these two droplets are not the same. To be able to handle the problem at hand, an adaptive grid scheme was considered.

3. Distribution of Nitric Oxide and Emissions Formation from Natural Gas Injection

This work involved the modeling and testing of emissions from LNG. The testing required the diesel simulator which was not completed so that emphasis was made on the analysis as noted in subtask 2.

A computer code involving fluid dynamics with detailed chemical kinetics was developed and used to investigate autoignition of natural gas in diesel environments. Fluid dynamics was found to play an important role on ignition delays. The study revealed that chemical kinetics calculations alone were not adequate for accurate predictions. An interesting results was the ignition occurring in the lean regions with equivalence ratios from 0.4 to 0.7. The calculations provided location of the ignition spot which could help in determining engine modifications to accommodate different fuels. New initiatives to strengthen this computational effort are discussed below

- The existing experimental data at diesel conditions is limited to autoignition delay times

only. Thus, details of flow field and ignition location are not available. We systematically validated the fluid dynamic predictions using bench mark experimental data from the literature. This included flow distribution in steady and unsteady non-reacting axisymmetric jets.

- The numerical simulations generate a large amount of data which is difficult to visualize and present. Each simulation typically requires several hundred megabyte of disk storage. We directed our efforts to convert data into slow motion video movies. For example, one movie segment could show evolution of the temperature field in the combustion chamber while the other could reveal the fuel path. We investigated available software and hardware that could automate this digital to video transfer process.
- Numerical simulations with liquid natural gas require a model for spray formation and droplet evaporation which is part of a concurrent effort. We conducted a review of such models in the engine simulation code KIWA-3. We gained operational experience with KIWA-3 such that it could be used in conjunction with our existing codes.

Details of the numerical models, computer program and results are given in a Masters Thesis "Autoignition of Natural Gas at Diesel Environments," by Mr. H. Bi (in the first year of this work). A paper entitled "Influence of Fluid Dynamics on Ignition of Natural Gas at Diesel Environments," was presented at the Combustion Institute's Central States/Eastern States/Mexican Section Joint Technical Meeting in San Antonio, Texas, April 23-26, 1995 (in year one). Some of the results were summarized in a paper "Study of Autoignition of Natural Gas at Diesel Environments using Computational Fluid Dynamics with Detailed Chemical Kinetics," by H. Bi and Ajay K. Agrawal. This paper was subsequently submitted for publication in the journal Combustion and Flame (year two).

Efforts were initiated to develop a technique called "Computational Rainbow Schlieren Imaging" (CRSI) to visualize and compare computational results with experimental data. The schlieren technique has been used for flow visualization for many decades. A variation in the density of the medium causes a change in the refractive index. Thus, light beams passing through the test section get deflected. An image of the test section is formed by decollimating the deflected light rays and placing a filter such that as a knife edge at the focal point. The image formed is a distribution of irradiance which is proportional to the deflection of the light beam. In rainbow schlieren imaging, the knife-edge is replaced by a continuously graded, computer generated color filter. Thus, the beam deflections are transformed to color represented by the hue. This computerized system combined with video imaging could be used for quantitative analysis.

With CRSI, the computed flow field is used to generate a color coded schlieren image which could be compared with the experimentally obtained images. CRSI was developed for a simple case of mixing of laminar heated jet as an example. The analytical solution of the temperature field was used to obtain density distributions which in turn provided the variation in the refractive index. Light ray deflections through this medium were computed and related to a specified color filter to generate the color schlieren image. Gray scale image was also computed to highlight the benefits of

color imaging. A paper on this work was presented as "Computational Rainbow Schlieren Imaging," A.K. Shenoy and A.K. Agrawal, 1996, *AIAA/ASME Oklahoma Symposium XVI*.

The CRSI technique was developed earlier was generalized to non-reacting and reacting flows obtained from computational fluid dynamics (CFD) calculations. The CFD results on autoignition of natural gas were used to create color and black and white schlieren images. The color images provided greater details of the ignition process. We also analyzed how the refractive index varied with the stoichiometric fuel/air ration in a methane-air combustion system. Analytical details and results were presented in paper "Visualizing Reacting Flow Computations by Rainbow Schlieren Imaging," presented at 1996 Technical Meeting of the Central States Section of the Combustion Institute.

Next, computations were analyzed to examine the pathways leading to ignition of natural gas at diesel environments. The major radical species were HO_2 , H_2O_2 , and OH which agrees with other investigations of ignition at high pressures. CH_3 and CH_3O radicals also played an important role. Radicals such as O and H were formed in large amounts only after the ignition. The reactions produced H_2O and intermediate species of CO , CH_2O , CH_3OH , C_2H_4 and H_2 in the hot spot. The analysis indicated that the ignition originated in fuel-lean region by reactions between the fuel and oxygen producing hydrocarbon radicals and HO_2 . The HO_2 radicals react with the fuel molecules to build a pool of H_2O_2 . A pool of CH_3O and OH radicals is also formed by reactions between the methyl radical and HO_2 and by dissociation of H_2O_2 . This leads to the ignition by reactions producing the intermediate and product species.

A journal article was to revised and submitted to *Combustion and Flame*, summarizing computations of natural gas autoignition. After revisions this paper was accepted for publication in the journal and it is presently in print as a "Study of Autoignition of Natural Gas in Diesel Environments Using Computational Fluid Dynamics with Detailed Chemical Kinetics," H. Bi and A. K. Agrawal, 1997, *Combustion and Flame*.

II Short and Long Term Storage

Task 1: Modification by Partial Direct Conversion of Natural Gas Composition for Improved Storage Characteristics

There are numerous environmental, economic, and political advantages of using natural gas to provide a significant fraction of transportation fuel needs including long haul trucking. A significant barrier to such usage is the low energy density storage of natural gas. Storage density is increased greatly by use of liquefied natural gas (LNG). A disadvantage of LNG, however, is the low temperatures and/or high pressures required to maintain the natural gas in the liquid state, resulting in higher capital cost and problems associated with boil off. Tasks 2 and 3 (described in the following sections) are investigations of novel techniques by which these problems may be eliminated or alleviated. These projects involve adsorption of natural gas on high surface area supports and capillary condensation of natural gas in highly porous materials.

Methane is the lightest hydrocarbon, and as such requires very low temperature and/or very high pressure to maintain it in the liquid state. At atmospheric pressure, the boiling point of methane is -162°C . Higher hydrocarbons are liquefied under much milder conditions. For example, the boiling point of ethane is -89°C , while the boiling point of butane is 0°C . Mixtures of hydrocarbons have different thermodynamic properties than pure hydrocarbons. Addition of higher hydrocarbons to methane may result in mixtures which liquefy under less stringent (i.e., higher temperature or lower pressure) conditions than methane. We propose (Project 3) to investigate this possibility. However, higher hydrocarbons are more expensive than natural gas, of course, which decreases the desirability of this option unless they can be produced inexpensively.

The easiest and least expensive way to modify the natural gas composition to enable liquefaction at milder (higher) temperature and milder (lower) pressure is to directly convert part of the methane in natural gas to higher hydrocarbons. Presently, processes for indirect conversion of methane to higher hydrocarbons exist, but these are much too expensive. Task 1 was the investigation and development of direct conversion processes for the introduction (via conversion of methane) of higher hydrocarbons into the natural gas. This part of the work was deleted from year two.

Task 2: LNG Vent Gas Adsorption and Recovery Using Activated Carbon and Modified Adsorbents.

The use of LNG largely solves the problem of the low storage density associated with CNG in the use of natural gas as a transportation fuel. The principal problems associated with the use of LNG as a transportation fuel are related to the low storage temperature of liquid methane.

At one atmosphere pressure the boiling point of liquid methane is -162°C . When LNG is stored at ambient conditions, even the best insulation technology cannot prevent leakage of heat from the environment to the LNG. Because the LNG requires a cryogenic temperature, conventional refrigeration technology is unable to remove the heat that is transferred to the liquid. The normal method for removing heat from a stored cryogenic liquid is to allow a slow boil-off of the liquid: When the storage vessel is highly insulated only a very low rate of boil off is needed to carry away the energy being transferred to the liquid from the surroundings *via* the heat of vaporization of the cryogenic liquid.

This strategy is fine when the liquid is liquid nitrogen or liquid oxygen, but when the cryogenic liquid is liquid methane and the LNG is being used as a transportation fuel, as in interstate trucking, it is less acceptable. In an urban environment the released LNG adds to the concentration of hydrocarbons in the environment; ironically, a major reason for desiring the use of LNG as a transportation fuel in an urban environment is because it reduces the amount of uncombusted hydrocarbons released from internal combustion engines. Further, if the vehicle is parked for a long time in an enclosed or semi-enclosed environment, the possibility exists for a dangerous buildup of natural gas to occur.

An alternative means of dealing with the boil off is to use a pilot light and a flare: When the engine is not in operation and the boil off cannot be used directly in the engine, an automatic pilot light can be used to ignite a flare fueled by the boil off, converting the gaseous natural gas to CO_2 . While the

CO₂ release may be preferable to the methane release and may be less dangerous in an enclosed environment, the flare itself is an obvious safety hazard. It would be completely unacceptable, for example, from a safety standpoint, for a vehicle with such a flare to be parked near any kind of refueling station or near parked vehicles with stored liquid fuels on board.

The alternative pursued here were to use an adsorption bed to store the natural gas as it boils off, regenerating the bed while recovering the adsorbed natural gas for use in the engine using the heat generated by the engine while the vehicle is in operation. Such technology would also have potential interest in similar applications at LNG refueling stations.

There are two key elements in the design of such a recovery system, the volume of the bed required for capture of the boil off and the ease of bed regeneration during operation of the engine.

We have already built a high pressure gas adsorption apparatus using a design from the literature (K.J. Masters and H.D. Gesser, "An Apparatus for Measuring the Adsorption of Gases at High and Low Pressures," *J. Phys. E.: Sci. Instrum.*, 14, 1043, 1981. The system has been used by our research group to obtain high pressure gas adsorptions on activated carbon, surfactant activated carbon, silica gels, and modified silica gels. It is currently being used to measure methane adsorptions on high surface area aerogels, transition metal doped SiO₂-based aerogels, and zeolites based on surfactant liquid crystal templates. This research has been supported by the Oklahoma Center for Advanced Science and Technology. The system is constructed using standard "Swagelok" type high pressure fittings and Hoke valves or equivalents, all rated at or above 20MPa. Valve k, which separates the sample holder, l, from the manifold, m, from which the methane is expanded during the isotherm measurement process, is a bellows type seal valve. Rough pressure measurements are made using Bourdon dial gauges (d and g). Final pressure is measured using a pressure transducer, j, with a variety of membranes available to allow accurate measurements over a range of pressures. Degassing is done via a vacuum pump at point h. The system can be vented through the valve at b. The volume of the manifold, the dead volume in the tubing and gauges, and void volume in the sample, both with and without adsorbent present, are determined by expansion from a calibrated gas storage bulb containing helium; the pressure of the helium is measured using a calibrated 0.15 psia transducer (i). High purity methane is introduced to the system from a commercial gas cylinder at 2200 psia at point a. The system is equipped with a 3600 psia rupture disc for safety. Both the manifold and the sample holder are currently in a thermostated glycol bath equipped with a chiller and capable of temperatures as low as -20°C and as high as 200°C. We have already located a surplus cryogenic storage vessel into which the sample holder and manifold can be placed for temperatures as low as liquid nitrogen temperature (ambient pressure). The operation of the apparatus has been described by Masters and Gesser (above).

While it is generally well known that a substantial fraction of the methane storage density that can be achieved at 3000 psia can be achieved at 500 psia using activated carbon (S.S. Barton, J.R. Dacey, and D.F. Quinn, "High Pressure Adsorption of Methane on Porous Carbons," in Fundamentals of Adsorption, A.L. Meyers and G. Belford, eds, Page 65, Engineering Foundation Conference, 1983; S.S. Barton, J.A. Holland, and D.F. Quinn, "Modification of Microporous Carbon for Methane Storage," in Fundamentals of Adsorption, A.I. Liapis, ed, page 99, Engineering Foundation Conference, 1987) or advanced adsorbents, it is not as well known that the storage density increases dramatically as one approaches the critical temperature of methane. Indeed, below the critical temperature (about -80°C), capillary condensation can occur in a microporous solid that is well wet by the liquid methane, leading to LNG-like storage densities at temperatures well above the temperature of normal LNG. The temperature at which capillary condensation of the methane will occur increases with increasing partial pressure of methane, indicating that a pressurized adsorption bed is worthy of investigation.

We have looked at methane adsorption on the following adsorbents at temperatures of -100°C , -80°C , -40°C (the lowest temperature at which a regular stainless steel adsorbent bed vessel could be utilized), -20°C , 0°C , and 100°C , as a function of pressure: high surface area activated carbon, transition metal doped activated carbon, SiO-based aerogels, transition metal doped SiO-based aerogels, extra large pore zeolites, and transition metal doped zeolites.

Figure 1. Schematic of High Pressure Gas Adsorption Apparatus.

Publications during year two related to this research included:

Ioneva, M. A., R. G. Mallinson and J.H.

Harwell; "Adsorption of Light Hydrocarbons in Sorbents with Controlled Porosity," revision pending Langmuir, August 1997.

Ioneva M. A., R.G. Mallinson and J.H. Harwell; "Sorptive storage of light hydrocarbon vapors by capillary condensation in MCM-41 type mesoporous materials," Proceedings of the Materials Research Society, 454, Sept. 1997

Ioneva, M., J. H. Harwell, R. G. Mallinson and K. E. Starling "Adsorption of Gaseous Hydrocarbon Mixtures in MCM-41 Type Materials," AIChE Annual Meeting, Miami Beach, FL, Nov. 1995 (Poster).

Ioneva, M., J. H. Harwell, R. G. Mallinson and K. E. Starling "Capillary Condensation of Gaseous Hydrocarbon Mixtures in MCM-41 Type Materials," AIChE Annual Meeting, Miami Beach, FL, Nov. 1995 (Poster).

Ioneva, M. A., R. G. Mallinson and J.H. Harwell; "Adsorption of Light Hydrocarbons in Sorbents with Controlled Porosity, " AIChE Spring Meeting, New Orleans, LA, March 1996.

Ioneva, M. A., J. H. Harwell and R. G. Mallinson; "Adsorptive Storage of Methane in Sorbents with Controlled Porosity," AIChE Annual Meeting, Chicago, IL, November 10-15, 1996.(poster)

Ioneva, M. A., R. G. Mallinson and J. H. Harwell, "Organic-guest Templated Sorbents with Controlled Micro- and mesoporosity," AIChE Annual Meeting, Chicago, IL, November 10-15, 1996.(poster)

M.A. Ioneva, G.K. Newman, and J.H. Harwell, "Adsorptive Storage of Methane in MCM-41 Type Materials," AIChE Symposium Series, 309 (9), 40-48, 1995.

M.A. Ioneva and J.H. Harwell, "Introduction of Microporosity in MCM-41 Type of Mesoporous Compositions," Materials Research Society Fall Annual Meeting, Boston, Massachusetts, November 27-December 1, 1995.

Task 3: LNG Storage at Moderate Conditions

The extensive use of compressed natural gas as a vehicular transportation fuel is hindered by its limited storage capacity, thus limiting the range of CNG vehicles. The energy density of LNG can be significantly higher than CNG, but the need for storage at cryogenic temperatures complicates the storage system and reduces efficiency. Storage of natural gas at liquid densities at ambient or near-ambient conditions could greatly enhance the potential for natural gas utilization as a vehicular transportation fuel.

This project had two thrust areas devoted to LNG storage at near-ambient conditions. These areas are the use of capillary condensation of natural gas in micro-porous adsorbents and the use of additives to raise the mixture critical temperature to allow condensation of a liquid phase at much higher temperatures than possible with pure natural gas (e.g. methane). This project is synergistic with those already described. The first project would produce the additives, such as higher hydrocarbons, from the natural gas itself and the second project examines adsorption of natural gas on solids which may also have application here. The two thrusts of this project are also interrelated, as the high condensation temperature mixtures should also be able to make use of capillary condensation.

Capillary Condensation

Micro-porous solids are solids which have a preponderance of pores sufficiently small to be called micropores. micropores typically have radii from about one to perhaps several hundred nanometers.

A functional definition is that diffusion in such pores is non-fickian, proceeding predominantly by knudsen diffusion, where the radius is of the same order as the mean free path of the molecules. By controlling the distribution of pore radii one can achieve pores in the size range needed to cause capillary condensation to occur. The capillary effect takes advantage of the fact that, in a capillary (a relatively small tube such as a pore), the interface between a liquid and the vapor begins to curve in a manner that depends upon the surface tension (γ) and the contact angle between the liquid and the solid (θ). This curvature supports an increased pressure in the liquid phase. Therefore, the liquid "sees" a pressure higher than the actual pressure in the vapor. As the capillary diameter is reduced, the curvature is increased along with the pressure difference. This relationship is shown in Equation 1.

$$(2\gamma \cos \theta)/r = \Delta P \quad [1]$$

Thus by tailoring the pore size distribution and surface chemistry, one may create a solid which condenses the vapor at pressures significantly below the vapor pressure required in an open vessel. In effect then, one can have condensation and storage on the solid at lower pressures than usual. In the case of methane, its normal boiling point where condensation occurs at one atmosphere of vapor pressure (-161 °C) may be raised significantly, thus requiring less severe storage temperatures. The same is true in using elevated pressures. In order to store methane as liquid, one must at least lower the temperature below the critical temperature of -83 °C. At (or just below) this temperature, the pressure required to liquefy the gas is the critical pressure, which is 676 psia. With an appropriate micro-porous solid, this pressure could be reduced by a factor of ten or more.

The objective of this thrust then is to examine existing adsorbent materials and fabrication of new ones using techniques available in the literature to "tune" the pore size distribution to achieve high liquid loading as well as maximum capillary pressure effect. Additionally, examination of surface properties and surface modification will be made to achieve these objectives by controlling the contact angle.

Papers related to this work included:

Ioneva, M. A., R. G. Mallinson and J. H. Harwell; "Storage of Light Hydrocarbon Vapors by Capillary Condensation in MCM-41 Type Mesoporous Sorbents with Controlled Porosity," AIChE Annual Meeting, Chicago, IL, November 10-15, 1996.

Ioneva, M. A., R. G. Mallinson and J. H. Harwell; "Sorptive Storage and Separation of Light Hydrocarbon Vapors by Capillary Condensation in MCM-41 Type Mesoporous Materials," Materials Research Society Fall Meeting, Boston, MA, December 2-6, 1996.

Ioneva, M. A., R. G. Mallinson and J. H. Harwell; "Sorptive Storage and Separation of Light Hydrocarbon Vapors by Capillary Condensation in MCM-41 Type Mesoporous Materials," AIChE Spring National Meeting, Houston, TX, March 9-13, 1997.

Ioneva, M. A., R. G. Mallinson and J. H. Harwell; "Sorption Storage and Separation of Light Hydrocarbon Vapors by Capillary Condensation in MCM-41 Type Mesoporous Materials," AIChE Spring National Meeting, Houston, TX, March 9-13, 1997.

Ioneva, M. A.; "Nanoengineered Porous Sorbents and Their Applications," Ph. D. Dissertation, University of Oklahoma, Norman, Oklahoma, 1996.

Moderate Temperature LNG Storage

The second thrust is to examine the use of additives to natural gas that raise the feasible condensation temperatures of the mixture while still making use of natural gas as the primary component. A number of potential additives are possible; two types might be identified, those that remain as a liquid when the natural gas vaporizes, thus always remaining in the storage vessel, and those that would vaporize with the natural gas and be part of the fuel itself. Among the easiest potential additives to identify are those present in natural gas itself, gas liquids such as propane and butane. If a storage temperature of 0 °C is desired, a mixture of about 90 percent (Molar) methane and 10 percent butane could be condensed and stored as a liquid. The storage pressure required would be quite high, over 1000 psia. This is lower than for CNG and could be made much lower by use of the capillary pressure effect as described above. At 0 °C, The insulation requirements and heat losses are much lower than for normal LNG temperatures and evaporative cooling (using the heat of evaporation to cool the liquid as the fuel vaporizes during use) rates may be sufficient to maintain the required temperature. The use of normal refrigeration, if needed, is also feasible, resulting in much lower cost. The trade-off is of course the added cost of the fuel additives which must be considered in the overall economic outlook (the impact of which was briefly addressed in the description of Project 1).

As a preliminary study, using somewhat different premises, this concept was examined assuming a storage temperature of 57 °C. This was chosen as an ambient temperature storage condition, where with no cooling considered at all, temperatures in a vehicle storage tank as high as this might be expected during a summer day. Thus this is really a worst case scenario for liquid storage, and wouldn't be a likely prospect for development. At this temperature, a mixture of 50 percent (molar) methane and 50 percent butane may be stored with a storage pressure when filled of 1400 psia. The energy density is about 70 percent, by volume, of gasoline. As vaporization proceeds, the vapor composition is initially 100 percent methane and gradually falls as the methane is depleted. The second is determining what must be added to the tank during refill. If a standard additive such as LPG (a generally available mixture of propane and butane) is used with natural gas, then knowing tank level, pressure and temperature would be sufficient to determine how much LPG and how much NG must be added. Both of these issues are currently being considered in determining the appropriate composition of "natural gas" for transportation fuel, as some level of gas liquids may be present as a natural gas component.

The objective of this thrust is to examine mixtures of additives and natural gas to determine feasible conditions for elevating the storage temperature of LNG. Along with this will be an examination of refrigeration and cooling requirements to maintain desired tank temperatures.

Papers related to this work included:

Starling, K. E., E. R. Ding, J. H. Harwell and R. G. Mallinson; "Method for Improving Natural Gas Energy Density at Ambient Temperatures, " *Energy & Fuels*, 9, 1062 (1995).

Mallinson, R. G., "High Energy Density Storage of Natural Gas for Vehicular Use," Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, August 1995.

Mallinson, R.G., "High Energy Density Storage of Natural Gas for Vehicular Use: Problems and Solutions," AIChE Central Oklahoma Section, Norman, Oklahoma, November 11, 1995.

Horstkamp, S. W., J.H. Harwell, R.G. Mallinson and K.E. Starling "High Energy Density Storage of Methane-Light Hydrocarbon Mixtures for Transportation Use," AIChE Spring Meeting, New Orleans, LA, March 1996.

Mallinson, R.G.; Novel Technologies for Enhanced Utilization of Natural Gas, Petroleum Authority of Thailand, Bangkok, Thailand, September 4, 1996.

Mallinson, R.G., "High Energy Density Storage of Natural Gas for Vehicular Use: Problems and Solutions," International Conference on Energy and the Environment, Stillwater, Oklahoma, October 16, 1996.

Horstkamp, S. W., J.H. Harwell, R.G. Mallinson and K.E. Starling "High Energy Density Storage of Natural Gas Transportation," Second Joint China/US Chemical Engineering Conference, Beijing, China, May 19-22, 1997. (Proceedings)

Horstkamp, S. W., J. H. Harwell, K. E. Starling and R. G. Mallinson; "Calculation of Properties for Methane-Light Hydrocarbon Mixtures for use as High Energy Density, Liquid State, Transportation Fuels," *AIChE J*, 43, 1108(1997).

Horstkamp, S. W.; "High Energy Density Storage of Methane in Light Hydrocarbon Solutions," MS Thesis, Chemical Engineering, University of Oklahoma, Norman, OK, 1996.

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