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

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This project encompasses the first year of a proposed three year project with emphasis focused on LNG research issues that 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. Since this work was for fundamental research in a number of related areas to the use of LNG as a transportation fuel for long haul trucking, many of those results have appeared in numerous refereed journal and conference papers, and significant graduate training experiences (including at least one M.S. thesis and one Ph.D. dissertation) in the first year of this project. In addition, a potential new utilization of LNG fuel has been found, as a part of this work on the fundamental nature of adsorption of LNG vent gases in higher hydrocarbons; follow on research for this and other related applications and transfer of technology are proceeding at this time.

The final report for this first year portion of the project is in preparation at this time.

The results of this work are expected to enhance utilization and handling of LNG as a transportation fuel.

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

The first year research has focused efforts in the direction of static laboratory and computer simulation of direct injection of LNG into a Diesel engine environment. A low pressure droplet chamber has been constructed and LNG has been successfully injected.

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

The deliverables for the 3 year project are:
1. A range of small single orifices will be used to inject a distribution of high density droplets in 20-100°C dry air.
2. This will be observed using high speed photography to qualitatively determine size and distribution of atomized droplets.
3. Additional fundamental methods will be attempted for internal transient distribution of pressure, temperature, and other quantities of interest.
4. The LNG pressure and backpressure will be varied in two ranges to approximate the lower 4-cycle injection and high 2-cycle injection pressures.
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5. Models such as those in Lefebvre[8] will be verified, if possible. If not, new models may be proposed.

6. A suitable range of test points will then be repeated with fixed orifice gaseous methane injection supplemented with small orifice cryogenic liquid natural gas (or supercritical high density gas).

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.

Effects of thermal radiation on LNG droplet evaporation in a free gas environment have been examined. From the preliminary results, it is found that the effects of thermal radiation are not as significant as originally expected due to the low emissivity of natural gas. To enhance heat transfer, it is proposed that the cylinder wall or the injector be coated with a ceramic layer. The advantages of using a ceramic coating are two-folds: (1) the ceramic (basically, a porous medium with a very low permeability) has a better thermal properties, (2) it also has a good tribological properties against wearing for the cylinder.

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

A study of the ability to atomize LNG droplets forms the basis of the previous subtask. This portion of the work is to evaluate the ability of these atomized distributions to directly or indirectly support combustion. Here, a simulated combustion cylinder has been designed to assess fundamental medium 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. In the initial phase of this work, the ability to support combustion using spark or glow plugs in a laboratory diesel engine has been assessed relative to the literature. Preliminary numerical studies have also been done which indicate greater sensitivity to temperature than pressure. Bounding analysis indicates the need for a rapid compression machine capable of handling 25 atm and 1150K for autoignition simulation; this will be used to construct a setup for testing details of spray characteristics, local ignition characteristics, and global emissions (Subtask 3); a graduate student has just begun this work. This dynamic bounding engine data will be zone matched to a combined constant volume (15 to 30%) and constant pressure simulation the internal data will be obtained.

This program will be carried out over a period of three years in three phases, including baseline testing and/or numerical simulation of the lab diesel. The first year has encompassed static numerical simulation of chemical kinetics, and combined fluid and chemical simulation. The second year will supply more
detail of the analysis, while the high pressure constant volume/constant pressure rapid compression machine is tested and modeled. The third year will identify autoignition and characterize the effects of autoignition of the natural gas. Also, the pressure-crank angle diagrams will be obtained to study the ignition delay and knocking behavior.

This subtask will also involve preliminary analysis effort on heat transfer (delivery of LNG in liquid form, if possible, to the engine), computational combustion, and flame radiation. Research in progress in this area has involved the conjugate problem of a two fluid flows (eventually LNG injected into the hot gaseous cylinder environment) separated by a ceramic barrier.

The data has provided detailed insight to LNG in direct diesel replacement combustion. The data is not only fundamental to the application, but also to modifications involving supplemental addition of LNG for flow control purposes as noted in Subtask 1.

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

The initial plan, was to test the local distribution of exhaust gases; much of the testing has been replaced or augmented by computer simulation while the low pressure static chamber was built and tested and the high pressure rapid compression machine was being designed. Those devices were part of the first year’s budget, and will be partially available (testing for low pressure — calibration for the high pressure) for the second and third years of this work.

This program will be carried out over a period of three years in three phases, including baseline testing. NOx, CO, HC and particulate production location internal to the simulated engine will be attempted during the corresponding time period of Subtask 2 of this part of the proposal.

Preliminary data has begun to provide detailed understanding of emissions and fundamental origins of those emissions from LNG in direct diesel replacement combustion. The data is not only fundamental to the application, but also to modifications involving supplemental addition of LNG for flow control purposes as noted in Subtask 1.

II. Short and Long Term Storage

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

Partial conversion of methane to higher hydrocarbons is being pursued as one method to alter the composition of natural gas in order to enable its higher density storage. In particular, we are studying the catalytic methane oxidative coupling to ethane and ethylene. The C2 products formed in the methane coupling reaction
can be further oxidized to carbon oxides, CO2 and CO2. The formation of carbon oxides decreases the C2 selectivity resulting in considerable amounts of methane being converted to undesirable products. Models of reactor performance indicate that, even with the best of available catalysts, overall yields are disappointing due to the oxidation of the C2 products. Two routes to obviate this difficulty are being studied. The first is the development of novel techniques for simultaneous reaction and separation that might remove the C2 products from the reaction zone. This research is in the literature search stage. The second route is an examination of various process alternatives for utilization of the C2 products in subsequent reactions, followed by separation of the products. Two possible process configurations (simplified) are shown in the figure attached:

In the first configuration, available natural gas liquids are first dehydrogenated to form olefins. These olefins are the alkylating agent in the second reactor, in which the methane is alkylated to higher hydrocarbons. The dehydrogenation and alkylation reactions are active research topics nationwide. In the second configuration, methane oxidative coupling is first used to increase the fraction of C2 hydrocarbons in the feed to the condensation reactor. These two process schemes are currently being programmed using Aspen to determine the single pass conversions required in each of the reactors in order for such a process to be economically feasible.

2. LNG Vent Gas Adsorption and Recovery Using Activated Carbon and Modified Adsorbents and LNG Storage at Moderate Conditions (tasks 2 and 3)

Two common ways of achieving significant storage densities of natural gas (which consists of about 96% methane) utilize the liquefied and the compressed state. Both strategies suffer from limitations, associated with the complications of achieving and maintaining cryogenic temperatures of liquefaction (Boiling of methane is 111.7 K), in the first case, and low storage density even with multistage compression to several thousand psi in the second case. The relatively low critical temperature of methane (Tc of methane is 190.7 K) could be significantly increased if used in combination with higher hydrocarbon homologues, such as propane and n-butane. If the mixture composition is selected properly, it is possible to observe the process of liquefaction in porous materials with appropriate pore size at relatively mild conditions, i.e. ambient temperature and a pressure achievable with single stage compression. This phenomenon utilizes the well known effect of capillary condensation in porous media, which practically can be observed by the appearing knee in an adsorption isotherm, or a hysteresis loop in the adsorption/desorption isotherms when conducted up to the saturation pressure.

A recently discovered type of materials, MCM-41, offer the unique opportunity to synthesize tailored sorbents with uniform pores on the basis of a surfactant liquid-crystal templating mechanism. By varying the chain length of the surfactants used (C8-, C10-, C12-)
C14-, C16H33(CH3)3 N Br), we were able to synthesize siliceous MCM-41 type materials with controlled diameter of the pores, respectively 16-, 22-, 24-, 30-, 36 angstroms (specific surface area is about 1000 m2/g; micropore volume is about 1.0 cm3/g).

To experimentally study the process of capillary condensation of gaseous hydrocarbon mixtures in the synthesized MCM-41 type of materials, a high pressure apparatus for static volumetric measurements was constructed. Standard Swagelok fittings, 1/8 and 1/16 inch stainless steel tubing, and Autoclave Engineers valves all rated to withstand pressure in excess of 3000 psi were used. Pressure measurements are conducted using Omega pressure transducers with precision of 0.25 %, calibrated against a 0 - 5000 psi Bourdon pressure gauge of known sensitivity. Degassing was carried out by a rotary pump. Deviations from ideality above few atmospheres pressure were corrected by using the Benedict-Webb-Rubin-Starling equation of state.

High pressure adsorption of methane was conducted on the synthesized materials. Our previous studies, as well as literature studies on adsorption of methane on different porous materials, show that the surface area and the packing density of the sorbent, and the combination of both, are important parameters that affect the adsorption of methane. By increasing the surface area, the adsorption per unit mass of adsorbent increases. By increasing the packing density, the adsorption per unit volume of adsorbent increases. We performed some studies of adsorption of methane on the material with average pore diameter of 36 angstroms, when varying the packing density - 0.16, 0.34 and 0.57 g/cm3. An increase in the amount of adsorbed methane per unit volume of sorbent was observed with increasing the packing density (Fig. 1). At 1000 psi we actually doubled the adsorption per unit volume by doubling the packing density. In progress are studies for achieving an optimized packing density for optimized adsorption per unit volume.

Also in progress are studies of the process of capillary condensation of methane - higher hydrocarbon mixtures in the synthesized materials. The focus of this research has been on increasing the energy storage density of natural gas two to three times relative to compressed natural gas (CNG) at ambient temperatures with pressures substantially lower than CNG. Solutions of methane with propane, butane and LPG have been simulated to investigate the requirements of pressure, temperature and composition necessary to maintain a liquid-phase which contains a high fraction of methane. The Benedict-Webb-Rubin-Starling equation of state was used to predict the vapor-liquid equilibrium conditions for solutions in the range of 50 to 80 liquid mole percent methane over a temperature range of 30 to 100°F. The simulations indicated the following: 1) that liquid systems containing up to 50 liquid volume percent methane could be achieved at modest pressures of 1000 to 2000 psia; 2) that the energy densities of these solutions ranged from 0.50 to 0.85 the energy density of gasoline.
Natural Gas → Alkane Dehydrogenation → Methane+Olefin Alkylation → Separation → BRANCHED HYDROCARBONS IN GASOLINE RANGE Cn

Natural Gas → Methane Oxidative Coupling → C₁ → C₂ → H₂O → Separation → C₂ to Cₙ-₁ paraffins → BRANCHED HYDROCARBONS IN GASOLINE RANGE Cn
ADSORPTION OF METHANE
ON MCM-41
AT 25 deg C

Surface Area = 1000 m²/g
Packing Density:
- 0.57 g/cc
- 0.34 g/cc
- 0.16 g/cc

Pressure, psi
0 400 800 1200 1600 2000

AMOUNT ADSORBED METHANE,
g/100 cc
0.00 1.00 2.00 3.00 4.00

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