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

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Project 1 - Direct Diesel Replacement

Subtask 1. Atomization

1. A numerical code which simulates the interactions between an isolated droplet and its ambient gas has been developed. 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. This work was presented at the Joint AIAA/ASME Oklahoma Sections Symposium in February by Mr. Pan, who is being directed in his Ph.D. by Dr. Lai. A static droplet model, including radiation effects, has also been analyzed as part of Mr. Pan's graduate course work.

2. Additional extensive calculations are being run on Cray Y-MP supercomputer for best efficiency. More realistic thermophysical properties are currently being sought to tune the model.

Subtask 2. Fundamentals of Direct Replacement

1. An experimental facility operating at atmospheric pressure has been designed and tested with LNG spray by Sean Peters, who is an Honors student working with Dr. Gollahalli; the observations and experiences have been fed back to the task leaders to incorporate in their work. Dr. Gollahalli has also had another Honors student, Benny Foreman, working in this area. Both students presented papers on natural gas research at the annual Honors Day Conference held recently.

2. Mr. J.M. Zhang, a Ph.D. student working for Dr. Sutton, presented a paper at the Joint AIAA/ASME Oklahoma Sections Symposium in February - this work has also been accepted at the ASME/AIAA National Heat Transfer Conference in Portland, OR. This work focuses on fundamental mechanisms of heat transfer in porous media - an application being studied for delivery of LNG through injectors to the Diesel type engine. A more complete computer model is currently being run by Mr. Zhang.

Subtask 3. Distribution of Emissions

1. Autoignition - In the first phase of this work, autoignition

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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. Mr. Bi, a Masters student under the direction of Dr. Agrawal, presented his work at the Joint AIAA/ASME Oklahoma Sections Symposium in February, a revised version was presented at the SAE West Region Combustion Meeting at San Antonio recently, and Mr. Bi also completed his Masters work on this project - focusing on combined chemical Kinetics and Fluid dynamics. Incorporating fluid mixing in calculating ignition delay was the primary objective of the second phase of this work. Thus, a computational fluid dynamics code integrated with detailed chemical kinetics was used. Calculations involve fully elliptic, time-dependent Navier-Stokes equations, and equations of mass continuity and energy conservation. Results indicate autoignition at about 25 atm and 1150K. 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.

Project 2 - Short and Long Term Storage

Task 2, Subtask 1, Methane conversion

The C_2 products formed in the methane coupling reaction can be further oxidized to carbon oxides, CO and CO_2 . The formation of carbon oxides decreases the C_2 selectivity resulting in considerable amounts of methane being converted to undesirable products. The CO_2 formed also poisons the Li/MgO catalyst resulting in reduced activity.

Our research group has studied the oxidative coupling of methane and proposed a rate model for the production of C_2 hydrocarbons and carbon oxides formed in the reaction. A quantitative study of further oxidation of ethane and ethylene, however, needed to be performed to be incorporated into the model.

In the research reported for this quarter, experiments were performed at steady state to study the effects of operating conditions such as initial reactant partial pressures, i.e.,

partial pressures of ethane, ethylene and oxygen and effect of temperature on the partial oxidation of ethane and ethylene in the gas phase. The outline of the research is:

1. Measure quantitatively the effects of operating conditions on the rates and conversions of ethane and ethylene in the gas phase.
2. Obtain a kinetic model for the reactions.
3. Model the reactor performance incorporating gas phase conversion of ethane and ethylene.

The dependence on partial pressures and temperature of ethane and ethylene gas phase oxidation to carbon oxides was measured, and the data used to obtain an empirical power law kinetic expression. The power law expression was then used in a reactor model to determine the influence of the gas phase reactions on the C₂ yield in a tubular reactor packed with Li/MgO catalyst. The model predicts that most of the CO₂ produced is contributed by the oxidation of ethane and ethylene. Because of the gas phase oxidation, the overall selectivity of C₂ products decreases along the length of the reactor and only very low yields are obtainable. Since these yields are less than yields that have been experimentally observed, it is believed that the gas phase oxidation takes place by a radical mechanism that may be suppressed by the presence of catalyst packing the bed. This theory will be experimentally tested.

Task 2, Subtask 2, Methane storage for vehicular use

CAPILLARY CONDENSATION OF GASEOUS HYDROCARBON MIXTURES IN MCM-41 TYPE MATERIALS

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 (T_{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 (T_c 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 (C_8^- , C_{10}^- , C_{12}^- , C_{14}^- , $C_{16}H_{33}(CH_3)_3 N Br$), we were able to synthesize siliceous MCM-41 type materials with controlled pore size, respectively 16-, 22-, 24-, 30-, 36 - (Surface Area is about 1000 m^2/g ; Micropore Volume is about 1.0 cm^3/g). Some typical pore size distributions for materials synthesized with C_{10}^- , C_{12}^- , and C_{16} are shown in Fig.1. With such materials calculations indicate that an equimolar mixture of methane and n-butane condenses and achieves liquefied gas densities at ambient temperature and six times lower pressure (500 psi) than typical CNG (compressed natural gas) storage pressures. This also would be a significant improvement in storage density over adsorptive storage.

To experimentally study the process of capillary condensation of gaseous hydrocarbon mixtures in the synthesized MCM-41 type of materials, a custom built high pressure apparatus for static volumetric measurements was constructed (Fig.2). 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 BWRS-EOS.

Adsorptive studies were performed on the synthesized materials by using pure gases - methane and n-butane. In the case of methane, liquefaction can be achieved at ambient temperature if utilizing extremely high pressures of several thousand psi. In the case of n-butane, however, condensation over the synthesized materials can be observed at relatively mild conditions - ambient temperatures and pressures about 20 - 30 psi (P_{sat}), as can be seen from Fig.3. The observed knee on the adsorption isotherm above $P/P_{sat} = 1.0$ is a result of the beginning of the capillary condensation process. In progress is a research for performing adsorption/desorption studies of different methane - n-butane mixtures on the synthesized materials.

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 ($T_{c \text{ methane}} = 190.7 \text{ K}$; $T_{c \text{ n-butane}} = 425.2 \text{ K}$), 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.

We have generated two proposals to form partnerships with ONG and with Tinker Air Force base. Tinker has budgeted significant funds to directly apply this technology as a new alternative fuel.

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