

# Method for Improving Natural Gas Energy Density at Ambient Temperatures

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This paper describes a technology which provides a method for the storage of natural gas, primarily for vehicular use, as a liquid solution with other hydrocarbons at ambient temperatures which achieves an energy storage density (on a volumetric basis) up to about 80% of gasoline. The solution is stored at pressures of about 2000 psig and provides approximately 3 times the storage density of compressed natural gas. Various operating scenarios may include differing hydrocarbon "solvents", such as propane, LPG, or butanes, and different required storage temperatures, with lower temperatures allowing higher volume fractions of methane. With this technology, the low storage density of CNG and the very low storage temperatures of LNG are both overcome, thus dramatically improving the technical feasibility of large scale commercialization of natural gas powered vehicles.

## Introduction

Numerous societal benefits are expected from the increased worldwide use of natural gas (cf. refs 1 and 2). The combustion of natural gas results in the production of significantly less environmental pollutants than the combustion of coal or liquids produced from crude oil, including heating oil and gasoline. The major deterrents to the increased use of natural gas are the facts that (1) the energy density of natural gas at ambient temperatures is less than the energy density of liquid (and solid) hydrocarbons, even when the natural gas is compressed to high pressures, or (2) that it must be stored at extremely low temperatures. The low energy density, or low storage temperature requirement, of natural gas results in significant economic, safety, and technological barriers to widespread utilization of environmentally friendly natural gas vehicles.

The work presented here is part of an ongoing project seeking methods for improving the energy density of stored natural gas. This project has been sponsored by the University of Oklahoma and is now supported by the U.S. Department of Energy. In the present work, an investigation has been performed to determine the increased energy density attainable for natural gas by dissolving the natural gas in liquid hydrocarbons. The applications for the method are numerous and include use in natural gas vehicles (NGV's), storage, bulk transportation (including tanker trucks and tanker ships), and pipeline transportation. Simulation calculations are presented to evaluate use of the method for a natural gas vehicle application by comparison with the conventional use of compressed natural gas (CNG).

## Energy Densities of Pure Hydrocarbon Fluids

Table 1 presents a summary of the energy densities of a number of pure hydrocarbon liquids and gases.<sup>3</sup> Because high propane content hydrocarbon mixtures are used extensively for vehicle transportation fuels, it is interesting to compare the conditions at which the energy densities of these pure hydrocarbons equal or exceed the energy density of propane. It can be noted in Table 1 that at 100 °F the liquids isobutane through *n*-decane have volumetric heating values which exceed the liquid propane volumetric heating value. The volumetric heating value of liquid propane at 100 °F and 200 psia exceeds the volumetric heating value of ethane unless the ethane is a liquid at temperatures below -100 °F or the ethane is a highly compressed gas (e.g., pressures greater than 6700 psia at 100 °F). Similarly, the heating value of liquid propane at 100 °F and 200 psia exceeds the volumetric heating value of methane unless the methane is a liquid at temperatures below -258.7 °F or the methane is a highly compressed gas (e.g., pressures greater than 37 400 psia at 100 °F).

Because natural gas is principally methane, the gross heating value of methane at 100 °F and 3500 psia of 254 678 Btu/ft<sup>3</sup> shown in Table 1 is representative of CNG vehicle fuel at 3500 psia. A drawback to the use of CNG as a vehicle fuel is this relatively low energy density compared to gasoline, which generally has an energy densities of 850 000 to 1 000 000 Btu/ft<sup>3</sup>, depending on the gasoline composition. Thus, the energy density of CNG at 3500 psia generally is less than 30% of gasoline energy densities. On the other hand, commercial propane mixtures, which are principally propane, have been used extensively as vehicle fuels because net energy costs are lower than gasoline. The energy densities of commercial propane mixtures are generally 65–75% of the energy densities of gasolines, so that with 35% larger fuel tanks the propane fuel

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(1) *Critical Technologies: The Role of Chemistry and Chemical Engineering*; National Research Council, National Academy Press: Ottawa, 1992.

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(3) Starling, K. E. *Fluid Thermodynamic Properties for Light Petroleum Systems*; Gulf Publishing: Houston, TX, 1974.

**Table 1. Energy Densities of Pure Hydrocarbon Fluids (Ref 3)**

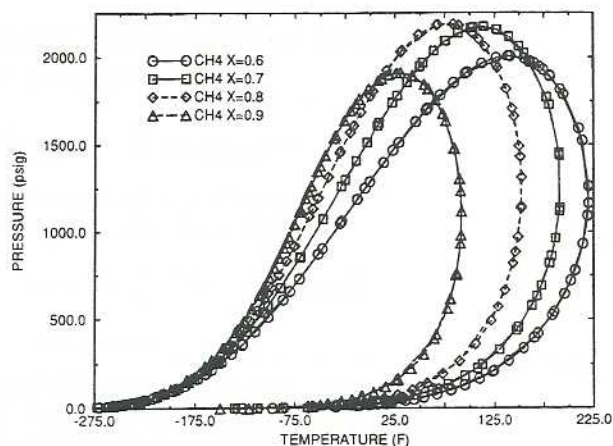
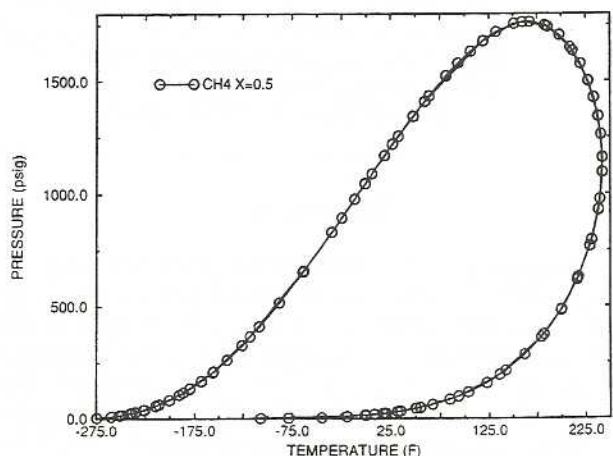
fuel	phase	temp, °F	press., psia	gross heating value, Btu/ft <sup>3</sup>
methane	liquid	-258.7	15	633 713
ethane	liquid	-100	15	633 800
propane	liquid	100	200	633 894
isobutane	liquid	100	75	707 349
<i>n</i> -butane	liquid	100	75	739 021
isopentane	liquid	100	25	785 376
<i>n</i> -pentane	liquid	100	25	789 547
<i>n</i> -hexane	liquid	100	15	838 024
<i>n</i> -heptane	liquid	100	15	861 625
<i>n</i> -octane	liquid	100	15	884 163
methane	gas	100	15	101 6
methane	gas	100	3500	254 678
methane	gas	100	37400	633 876
ethane	gas	100	15	176 9
ethane	gas	100	6700	633 879

vehicle range is the same as for gasoline fuel. The objective in the present work has been to improve the energy density of natural gas beyond the energy density of CNG at 3500 psia, with the goal of achieving energy densities comparable to propane energy densities.

### Solutions of Natural Gas in Liquid Hydrocarbons

The method which we have developed for increasing the energy density of natural gas beyond CNG at the same pressure is to dissolve the natural gas in liquid hydrocarbons. To illustrate the method, the solution of methane in *n*-butane is used. This case is chosen because methane is the principal component in natural gas, *n*-butane is a readily available hydrocarbon liquid, and methane mixed with *n*-butane in appropriate proportions meets the criteria required for this application. Other hydrocarbons, particularly propane or LPG, are also good candidates, but as the hydrocarbon size increases, the volume fraction of methane in the mixtures begins to decrease and the objective of high-density natural gas storage is compromised.

When methane is mixed with *n*-butane at temperatures above the mixture freezing point, the mixture can exist as a liquid, a gas, or a two-phase system of liquid plus gas, depending on the mixture composition, the temperature, and the pressure. The phase envelope for a given mixture composition defines the region of temperature–pressure conditions where the mixture is two-phase (liquid plus vapor). Figure 1 shows phase envelopes for four mixtures of methane with *n*-butane calculated using the ASPEN PLUS chemical process simulator using the modified Benedict–Webb–Rubin (BWRS) equation-of-state.<sup>4</sup> The mole fractions of methane for these four mixtures are 0.6, 0.7, 0.8, and 0.9. It can be noted that at 100 °F, the 0.9 mole fraction methane mixture can exist only in the single phase (gas) region. Further, although the 0.8 mole fraction mixture can be two phase over a range of pressures at 100 °F, the energy density at pressures above the phase envelope at 100 °F are lower than for the 0.7 and 0.6 mole fraction mixtures. In general, the energy density at 100 °F for pressures above the phase envelope increases as the mole fraction of methane is decreased in the methane plus *n*-butane mixture. A criterion set for the

**Figure 1.** Phase envelopes for four methane–butane binary mixtures.**Figure 2.** Phase envelope for 50/50 mole fraction methane–butane mixture.

present work, as an example of one operating scenario, was to maximize the concentration of methane in the methane plus *n*-butane mixture such that the gross heating value energy density at pressures above the phase envelope at 100 °F is at least 510 000 Btu/ft<sup>3</sup>. This energy density is twice the energy density of methane at 3500 psia at 100 °F and 80% of the energy density of liquid propane at 100 °F. This criterion can be met by a range of compositions of mixtures of methane plus *n*-butane. For purposes of illustration, the results of calculations will be presented for the 0.5 mole fraction methane mixture of methane with *n*-butane.

The phase envelope for the 0.5 mole fraction methane mixture of methane with *n*-butane is given in Figure 2. At 100 °F at pressures above the phase envelope the mixture is liquid. At 100 °F and 1700 psia (less than half of the CNG pressure) the density of the liquid mixture is 25.4 lb/ft<sup>3</sup> and the gross heating value energy density is 559 000 Btu/ft<sup>3</sup>.

### Behavior of Fuel As It Is Consumed with Vapor Removal

An illustration is presented here for the mixtures of methane with liquid hydrocarbons as fuel is continuously withdrawn as a vapor from a tank containing the mixture. It is assumed that, because the fuel is withdrawn slowly, the tank temperature does not vary appreciably during withdrawal. Therefore, because the

(4) ASPEN PLUS with Modelmanager, V. 8.5.4; Aspen Technologies, Inc., Boston, MA, 1992.

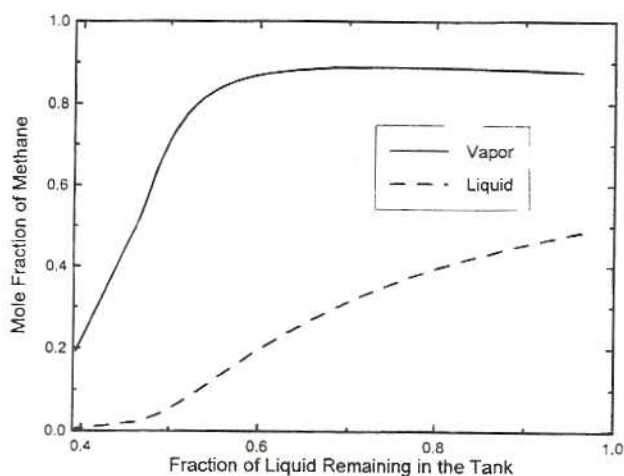


Figure 3. Vapor and liquid composition as a function of depletion of liquid from a constant volume tank.

tank is a constant volume, the process occurring in the tank corresponds to an isothermal constant volume depletion process. The constant volume depletion (CVD) process was simulated, using a BWR equation-of-state,<sup>5</sup> which is known to accurately describe the properties of mixtures of methane with *n*-butane. The results of the CVD calculations are summarized in Figure 3 and are best interpreted by moving from the right side of the graph, when the tank is completely full of liquid, to the left side as the liquid level goes down.

In such an operating scenario as this, the composition of the vapor removed is very high in methane until most of the methane has been removed from the tank. At this point, the fraction of methane in the vapor drops quite quickly with a relatively small decrease in the liquid remaining in the tank, after which the vapor is very high in butane content. Because of these characteristics, refilling to the same initial composition would require adjusting the composition of the refilling mixture, based on knowledge of the temperature, pressure, and liquid level in the tank, if it may be assumed that the mixture contains only two components. This type of scenario might be suitable for vehicular use when refilling is irregular with respect to remaining liquid volume, and higher cost butane usage may be avoided. We are also investigating this scenario in combination with the use of controlled pore size solid materials to take advantage of the capillary pressure effect to reduce the storage pressure required to achieve the same energy density as with bulk liquid storage.

The opposite scenario would be to remove the mixture as a liquid and maintain an essentially constant liquid composition. This scenario also reduces the requirement of vehicle engine sensors to adjust the engine

performance to the continuously changing fuel composition when fuel is removed as a vapor and also simplifies refueling requirements.

A large number of operating scenarios are possible and only further effort will establish the optimum. There are many parameters, other than energy density, which will influence the final result. As one example, one might look at octane number. One of the advantages of natural gas as an internal combustion fuel, in comparison with gasoline, is its high octane number (120–130 research octane number (RON) depending on CNG composition). While octane number is not an ideal concept because of its normalized basis for "performance" in a specific test,<sup>6</sup> one may qualitatively relate the octane value to the feasible compression ratio which may be used. Higher octane number implies a higher compression ratio (between 13 and 14 for natural gas) and higher compression ratios achieve higher thermodynamic efficiencies, as one benefit. As heavier hydrocarbons are added to the mixture, the octane number is reduced. Quantitative prediction of octane number for mixtures is not possible, but pure propane has an octane number of 112 RON and *n*-butane of 94.<sup>6</sup> Thus, there is an efficiency trade off (since only a lower compression ratio may be feasible) for using *n*-butane instead of *n*-propane, even though higher methane mole fractions may be achieved with *n*-butane, for the same storage operating temperature.

#### Summary

This technology provides a novel series of solutions for the most significant barrier to more widespread use of natural gas as a transportation fuel: difficult storage conditions or low storage density. The use of generally available fuel components, such as propane, LPG, or butane with natural gas provides a reasonable basis for infrastructure development and retains the primary environmental benefits of natural gas usage. Several scenarios for the application of this technology are viable candidates depending on the specific storage and operation requirements. Further development will require vehicle and fleet testing to determine procedures and facilities for convenient, safe, and environmentally sound implementation.

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