High-Energy Density Storage of Natural Gas in Light Hydrocarbon Solutions

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The storage of natural gas in other light hydrocarbons is one procedure for automotive natural gas usage that reduces the requirement of high-pressure or cryogenic storage. Model solutions of methane in n-butane, propane, and a liquefied-bottled-gas mixture were simulated using the Benedict-Webb-Rubin-Starling equation of state to determine the pressures necessary to maintain a liquid phase with perturbations in both temperature (−1°C to 38°C) and mole fraction (50 to 80 mol% methane). Methane storage in these liquid solutions is between 45 and 93% of an equal "tank" volume of compressed natural gas (CNG) at 21 MPa and 15°C. The simulation results indicate that solutions of this type contain 40 to 67% of the energy of gasoline at pressures that range from 60 to 40% that of CNG at 21 MPa and 15°C.

Introduction

Natural gas (NG) is an important competitor in the field of alternative fuels. NG is economic, and it offers a greater reduction in CO, NO_x, and nonmethane hydrocarbon (NMHC) emissions while offering higher octane numbers and, therefore, higher thermal efficiency than gasoline or diesel oil. However, the onboard storage limitations make it less appealing as an alternate fuel source (Stodolsky and Santini, 1993).

Currently, storage techniques for NG involve compression and liquefaction methods. The former is termed compressed natural gas (CNG), while the latter is known as liquefied natural gas (LNG). CNG relies on bulky, high-pressure vessels to store a quantity of NG that delivers about one-third the range of an equal volume of gasoline under normal operating conditions. LNG provides nearly two-thirds the range of a comparable volume of gasoline (Liss et al., 1992) but requires cryogenic temperatures. Both these storage techniques place somewhat extreme conditions on the tank of a vehicle.

In addition to the onboard storage problems of CNG and LNG, the logistics of the preparation and delivery of these fuel systems pose some inconvenience in themselves. CNG at 21 MPa requires a delivery system operating above the storage pressure to ensure that a full charge is provided. Therefore, a compression plant must be at or very near the vehicle refueling site. LNG is liquefied via a cryogenic procedure, and then delivered to some staging area before it is delivered to a vehicle. This method requires an insulated storage vessel to stage the fuel.

As indicated, the problems encountered in using NG as a vehicle fuel are mainly those of storage. CNG provides a fueling source, but there is a trade-off between providing NG to the engine and the vehicle's increased weight from the heavy tanks and large storage volume. This weight reduces the efficiency at which it operates, which decreases the mileage of the fuel. The LNG cooling requirement is an inconvenience to its use as a fuel. Maintenance of the cryogenic conditions involves increased insulation and a need for occasional venting of the fuel to the atmosphere, or to a vent recovery system as a means of controlling the fuel temperature.

Recent attempts to increase the storage density of NG have been made in the area of adsorption of NG onto porous solids. This technique offers greater storage of NG at lower pressures, ~ 3.5 MPa, compared to CNG (Matranga et al., 1992). However, at pressures closer to 21 MPa, adsorptive storage does not extend the comparable range of the vehicle very significantly (as compared to CNG). This adsorption technology does not currently provide a viable solution for bulk storage.

Dissolution of NG into a solvent species has been investigated as an alternative method to CNG and LNG. Remic et al. (1984) used regular solution theory to screen several potential solvents for methane storage. These solvents were perfluorocarbons, silicones, aliphatic alcohols, polymers, and aliphatic hydrocarbons. Under the conditions investigated (25°C and 3.5 MPa), Remic reported that the "best" solvent for methane storage was propane. The maximum amount of methane stored under these conditions was 15 mole %, or 0.063 gram methane per gram solvent.

Liquid solutions of methane and aliphatic hydrocarbons in the range of C_2 to C_6 have been investigated for solubilizing methane. Liquid propane (20°C and 6.9 MPa) was reported to hold up to two-thirds more methane (compared to CNG at the same pressure) per unit volume of solution (O'Brien and Turnham, 1990). Starling et al. (1995) have described an equimolar methane–butane liquid mixture (37°C and 12 MPa) that has an energy density that is more than twice that of CNG (37°C and 24 MPa) and 80% of the energy density of liquid propane. Additionally, Mansoori (1993, 1994) has been working to develop a computer technique for screening other potential hydrocarbon solvents for methane storage that is based on the refractive index of hydrocarbons. The implications of these studies are that these modest conditions offer a safer, more attractive methane storage system for the following reasons: (1) lowered storage pressure does not require high-pressure vessels (compared with CNG); and (2) the temperatures are far from cryogenic (compared with LNG).

Simulation Parameters

Determination of the vapor–liquid equilibrium (VLE), thermodynamic, and physical properties of the mixtures of interest was accomplished using the modified Benedict-Webb-Rubin-Starling equation of state (Starling and Han, 1971, 1972a,b) and the Han-Starling-Generalized-Correlation (HSGC) (Starling, 1973). This FORTRAN-based program (Starling, 1994) was run on an IBM RS/6000.

Results and Discussion

The solvents used for these predictions were *n*-butane, propane, and an arbitrary liquefied-bottled-gas (LPG) mixture that is shown in Table 1. Heavier components, C_6 and above, were investigated previously and ruled out of the solvent selection (Starling et al., 1995); while high mole fractions of methane were obtainable, the relative volume of stored methane was far less than in the lighter hydrocarbon systems. Additionally, the solvents selected seemed to be reasonable approximations of solvents that are currently available for commercial use.

The parameters for the VLE calculations were the mole fraction of methane in the individual solutions and the mixture's temperature. These parameters were selected to fix the VLE calculation to that of pressure determination alone. Considering the preliminary results, the boundaries of these parameters were as follows:

- Mole fraction of methane 0.5–0.8 incremented by 0.05
- Temperature of system −1.1–37.7°C incremented by 1.1°C.

Table 1. LPG Mixture Used in This Work

Component	Mole percent
Ethane	0.02
Propane	36.23
Isobutane	33.63
n-Butane	29.58
Isopentane	0.46
n-Pentane	0.08
Total	100.00

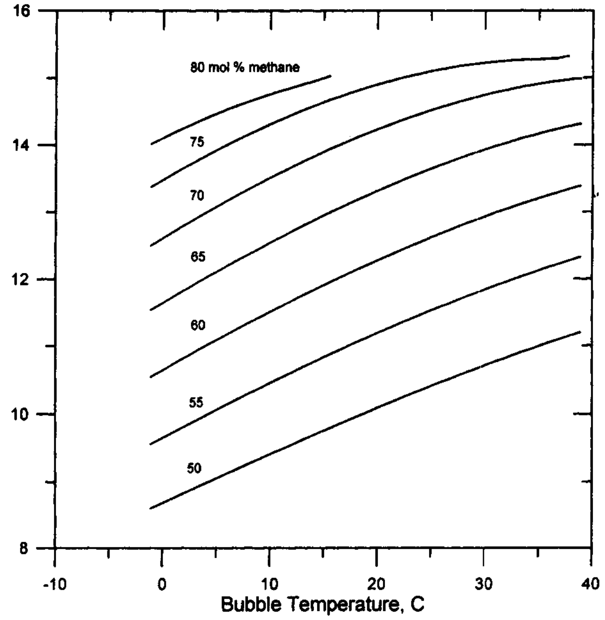

Figure 1. Bubble curves for the methane and *n*-butane solutions.

The selection of the range of methane mole fractions focused on the solutions that were greater than 50 mol % methane. This selection served as an arbitrary base line. The lower end of the scale was based on observations from previous calculations that indicated mixtures with lower methane mole fractions would exhibit properties more like the solvent.

The temperature range just listed was chosen to represent somewhat normal conditions. The upper end of the scale was thought of as the temperature that could be maintainable on a hot day. The lower temperature is indicative of a temperature that would allow more methane storage, but would not require cryogenic cooling. This range gave the problem tangible temperature boundaries.

Figure 1 shows the bubble conditions of various mole fractions of methane in butane. By inspection, the bubble pressures of all the solutions are seen to increase with a corresponding increase in the mole percentage of methane. This behavior is expected. As the mole fraction of the methane is increased, the vapor pressure of the solution increases. Therefore, a higher pressure is required to balance the higher vapor pressure of the solution.

The general shapes of the bubble curves are indicative of most hydrocarbon mixtures (Campbell, 1988). That is, at low temperatures and/or low mole fractions of the light component, the curves tend to show a constantly increasing slope. Upon inspection of the curves at higher temperatures, and/or higher molar percentages of methane, the slopes begin to decrease; some pass through a maximum and then terminate before the final temperature of 37°C is reached. These terminal temperature and pressure conditions were ascribed to the mixtures' critical points: the point, composition, and temperature at which a solution of specific composition no longer exhibits a distinct liquid phase at any pressure. This point might be regarded as the maximum temperature and pressure at which a full storage tank could operate with liquid being stored. The pressure would then correspond to the lowest pressure possible for attaining a liquid.

Figure 1 shows the bubble pressure vs. the bubble temperature (bubble curves) for the methane–butane solutions. The mole percentages of each solution are shown with their corresponding curves. The pressures vary from approximately 8.6 MPa at the lowest temperature and mole fraction of methane to about 17 MPa at the highest mole fraction. These curves show the pressures required to ensure that a liquid phase is maintained at a given temperature. For example, a 65 mol % methane, 35 mol % butane mixture would remain liquid at 5°C as long as the pressure was above 12 MPa. If the temperature were increased to 30°C, the corresponding pressure required to maintain the same methane mole percentage in the liquid would increase to 13.5 MPa. Similar trends were observed for the methane–propane, methane–LPG bubble curves.

The property required for the storage calculations was the density of the various mixtures across the operational temperature–pressure spectrum. The density of each of the solutions was calculated from the HSGC program. Figure 2 shows the methane–butane data plotted against the bubble temperature with the different mole percentages of methane as a parameter. It should be noted that the abscissa for this graph is the bubble temperature. It then follows that these mixtures are also at the bubble pressure corresponding to the individual mixture-temperature and -composition conditions.

Inspection of this density plot shows that the density decreases by two distinct routes: (1) increasing methane percentages, and (2) increasing temperature.

The tendency of higher molar percentages of methane to reduce the mixture density is due to the volume contribution of this light component to the mixture as the solution becomes enriched with methane. As more methane is added to the mixture, the volumetric contribution of methane increases and the volumes of the other components correspondingly decrease. This causes a lower mass to occupy a greater volume, which yields the lower density.

The temperature effect on the density is most likely due to the increased energy of the mixture. Like water, a liquid that absorbs heat will experience some density decrease as the internal energy increases. However, unlike water, hydrocarbon solutions have no strong intermolecular attractive forces. These solutions are nonpolar and exhibit only a weak van der Waals attraction as a result of that nonpolarity. So, as the internal energy of a hydrocarbon solution increases, the molecules in the liquid experience a greater freedom of movement in the solution.

Comparison of the predicted amounts of methane stored and the corresponding energy densities of the solutions were desired. CNG (20.7 MPa, 15°C) was chosen as the benchmark for this comparison (Starling, 1973). Comparison of the mixtures of interest to CNG was performed by normalizing the standard volume of methane, 359 ft^3 (STP) per lb-mol per liter of solution to the standard volume of methane in one liter at 20.7 MPa and 15°C. Since CNG is composed mostly of methane, this calculation was deemed reasonable.

The normalized quantities were then plotted against the bubble pressures, as shown in Figures 3–5. It should be noted that there are two parameters of interest on these graphs: the composition of the solutions and the bubble temperature at which the comparison was made. As each of the figure legends indicates, the molar composition of the solutions is incremented by 5% methane from the base value of 50% to the highest value for that particular methane–solvent mixture. The leftmost data point in each of the compositional series corresponds to a temperature of −1.1°C. Subsequent data reflect a temperature increase of 5.5°C for each data point traversed in the direction of increasing bubble pressure.

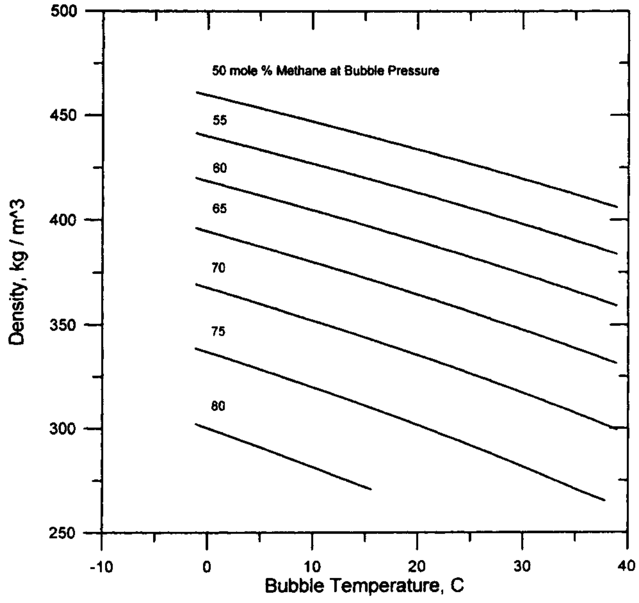

Figure 2. Density curves for the methane and *n*-butane solutions.

The pressure of the solutions is the bubble pressure.

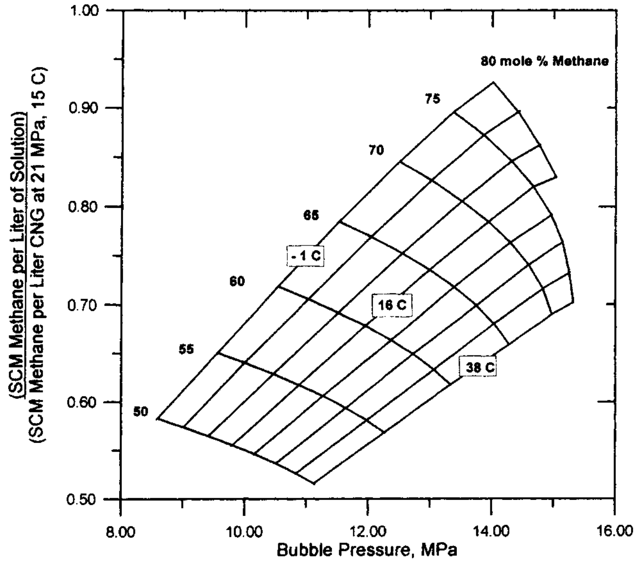

Figure 3. Amount of methane stored at 21 MPa: in *n*-butane vs. CNG.

The relative volumes are at standard temperature and pressure.

Figure 3 shows the normalized plot for the methane–butane mixture. The range of the normalized volume of methane per liter of solution is between 0.52 at about 11.2 MPa, 38°C, and 50 mole % methane, and about 0.94 at 14.5 MPa, −1.1°C and 80% methane. The compositional dependence of the volume of methane stored can be seen by examining a curve of constant temperature (e.g., the leftmost data points in each of the composition series). By inspection, each of these curves seems to exhibit a linear slope and increases over the range of bubble pressures. It is observed that the slope of each of these curves decreases with each of the incremental temperatures. This behavior of the curves seems to be consistent conceptually with the physical phenomenon. That is, the relative amount of methane stored should increase as the mole fraction of methane in the solution increases. Also, lower temperatures correspond to higher mixture densities.

The influence of temperature on the relative volume of the stored methane can also be determined from Figure 3. Inspection of the curves of constant composition show that the volume of stored methane decreases as the bubble temperature increases. Initially 50 to 60 mole % methane, this effect is linear and roughly constant for all three compositions. However, the higher mole fraction curves begin to deviate from linearity and drop faster at the higher temperature ends of the data. Thus the relative amount of methane that is stored becomes very sensitive to small perturbations in the bubble temperature. This behavior is probably due to the mixture's approach to the critical point; the shape of the curves as they drop is similar to the bubble curves depicted in Figure 1.

The severe drop in the volume of methane stored as the pressure and temperature increase could be thought of as a boundary in selecting a mixture of methane and butane that would act as a motor vehicle fuel. Since it is desirable to increase the stored methane in these liquid solutions, operational conditions might be chosen to coincide with the more predictable linear regime shown at lower temperatures for the higher compositions of methane.

Figures 4 and 5 show the normalized storage of methane for the methane–propane and methane–LPG systems, respectively. The minimum value of the normalized volume for the propane is 0.45 at 9.5 MPa and 37°C; the maximum value is about 0.77 at 11 MPa and −1.1°C. For the LPG, the maximum stored amount is 0.87 at 12.7 and −1.1°C; the minimum is 0.50 at 10.7 MPa and 37°C.

Similarities between these plots and the methane–butane plot are readily seen. In Figures 4 and 5, the curves of constant temperature and varying mole fraction are seen to increase linearly as the mole fraction of methane increases. Also, with each temperature increment the slopes of these curves decrease relative to each other. However, both the propane and LPG data show a faster drop, relative to the butane, in the relative volume of methane stored along the constant composition curves.

The utility of these charts is in their prediction of the amount of methane that can be stored in these solutions. For example, Figure 5 shows that at 15.5°C and 12 MPa, a 63–37 mol % methane–LPG mixture holds roughly 68% of the volume in CNG at 20.7 MPa and 15°C. This corresponds to a pressure reduction of 42% compared to CNG at 20.7 MPa and 15°C. If the temperature of the same composition of methane and LPG were then lowered to −1°C, the stored amount would increase to 75% that of CNG (20.7 MPa and 15°C). The pressure reduction would then be nearly 50% of the same CNG.

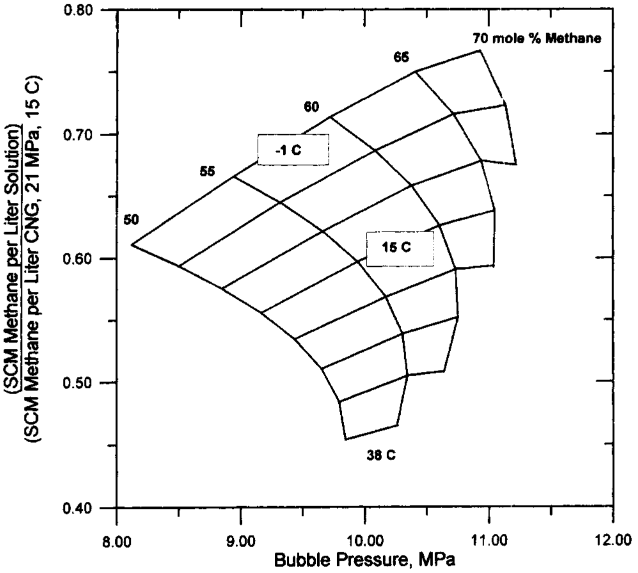

Figure 4. Amount of methane stored at 21 MPa: in propane vs. in CNG at 21 MPa.

The relative volumes are at standard temperature and pressure.

From the shapes of the curves in Figures 3 to 5, it is seen that the amount of methane stored in the liquid solutions increases as the temperatures decrease. Therefore, if a temperature-regulation system were in place for a vehicle using these types of fuels, it would be possible to achieve a greater volume of methane per stored liter than CNG. Additionally, the lowered temperature requirements would alleviate the CNG-range pressures.

The sum of a solution's components' energy contributions

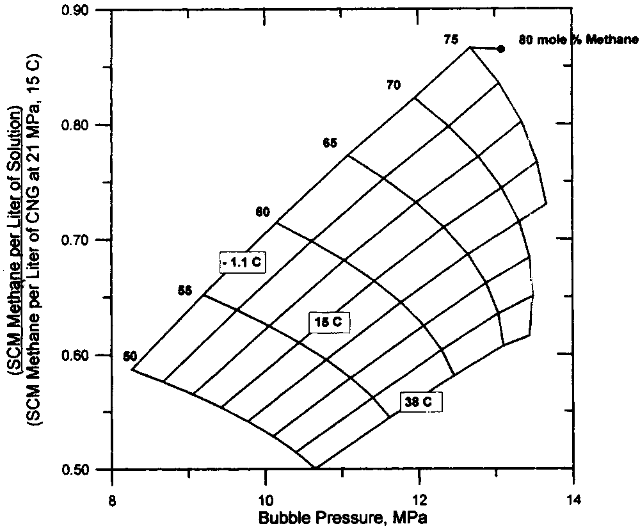

Figure 5. Amount of methane stored at 21 MPa: in LPG vs. in CNG at 21 MPa.

The relative volumes are at standard temperature and pressure.

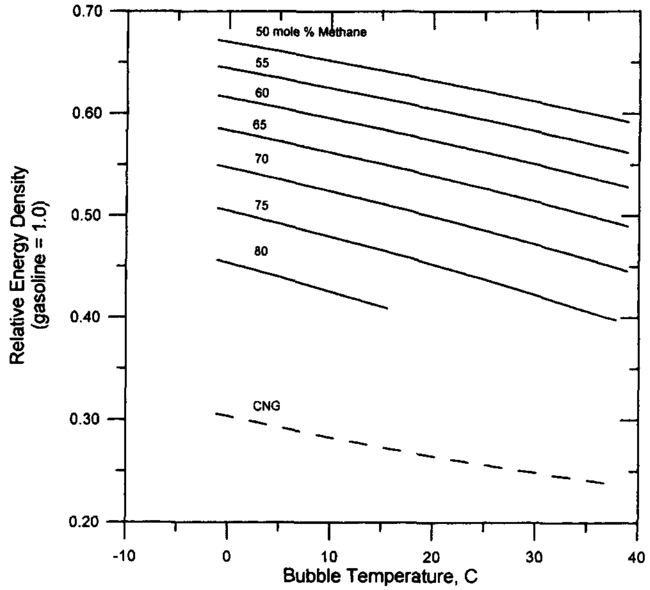

Figure 6. Energy density curves for the methane in *n*-butane solutions.

The data are displayed relative to gasoline (125,000 Btu/gal or 36.4 MJ/L).

per volume was termed the energy density of that solution. The energies of the solutions were based on the mole fractions of the components in the various systems and their gross heating values. The mole fractions were calculated from the HSGC; these are rigorous calculations based on the BWRS-EOS. The selection of the gross heating value for the energy was made to provide a readily obtainable basis (gasoline) for comparison. For this comparison an average gasoline GHV of 36.4 MJ/L was used (U.S. DOE, 1994). The energy densities of the solutions were normalized to gasoline and plotted against the bubble temperature.

Figure 6 shows the relative energy density of the methane–butane solutions and CNG at 20.7 MPa and 15°C vs. bubble temperature. The mole fractions of the different methane–butane mixtures are parameters, and the pressures of the mixtures are the bubble pressures. At −1°C, the mixture values are seen to vary from 65% to 45% at 50 and 80 mol % methane, respectively. Note that the CNG provides about one-third the energy density of gasoline.

The overall trend is for the energy of these mixtures to decrease with increasing mole percentage methane, and with increasing temperature. The energy losses attributed to the increasing mole fraction are inherent in the definition of the heating value (Campbell, 1988). Methane, and also CNG, has the lowest value (39.3 MJ per SCM; Campbell, 1988). The other components' GHVs increase as the components get heavier. Therefore, as the amount of heavier hydrocarbons is reduced, the mixture must lose energy.

As the temperatures increase, the energy of a solution of constant composition is seen to decrease. This behavior is the result of using the density of the solution in determining the energy density. Since the mole fractions do not change on a line of constant mole percentage, neither does the energy. Therefore, when the varying density is taken into account, the resultant data are observed to have the same general shapes as the density curves.

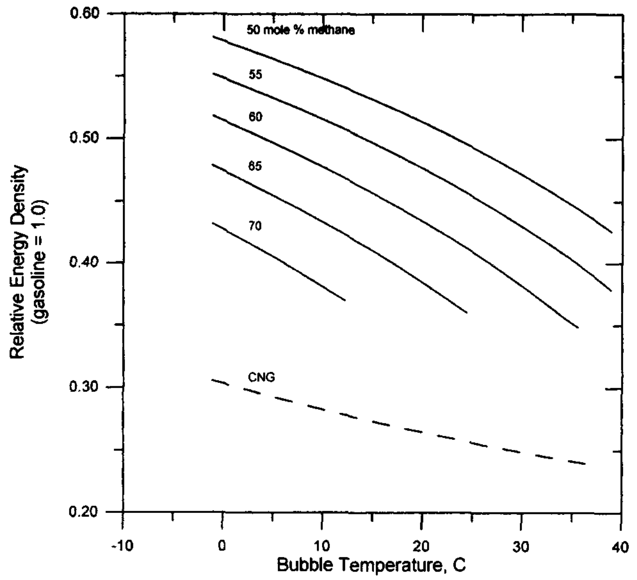

Figure 7. Energy density curves for the methane in propane solutions.

The data are displayed relative to gasoline (125,000 Btu/gal or 36.4 MJ/L).

Figures 7 and 8 are relative energy-density plots of the methane–propane solutions and the methane–LPG mixture solutions vs. the bubble temperatures. Like the butane system referred to earlier, the graphs are dependent on the mole fraction and the pressure is assumed to be the bubble pressure. Like the butane-based solutions, the propane and LPG densities decrease with an increase in the temperature, and with an increase in the mole fraction of the methane stored. At −1.1°C, the methane–propane range of data is 57 to 43% of the energy density of gasoline at 50 and 70 mol % methane, respectively. For the methane–LPG mixture, the range of

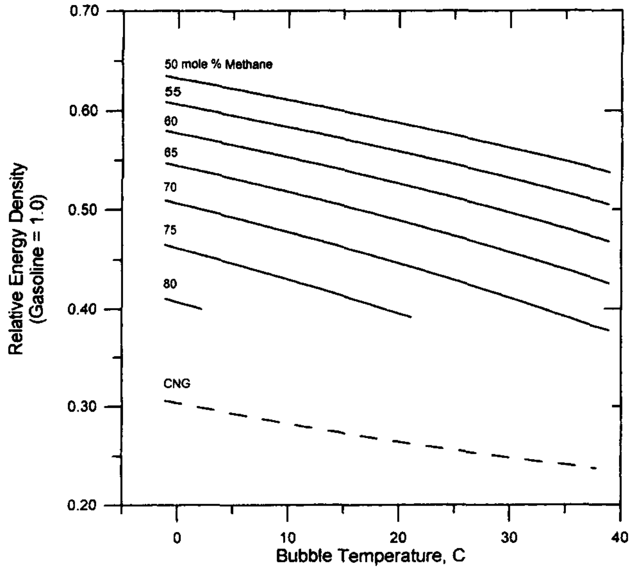

Figure 8. Energy density curves for the methane in LPG solutions.

The data are displayed relative to gasoline (125,000 Btu/gal or 36.4 MJ/L).

Table 2. Energy Contribution of Methane to the Total Energy of the Solution

	Butane	Propane	LPG Mix
Methane Mol %	Methane Energy Fraction	Methane Energy Fraction	Methane Energy Fraction
50	24	29	25
55	27	33	29
60	32	38	34
65	36	43	38
70	42	48	44
75	48	Past cp	50
80	55	Past cp	57

data is 63 to 41% that of gasoline and 50 and 80 mol % methane, respectively.

The fraction of the energy belonging to methane was determined, and a comparison of these energy fraction data for the varying solutions and mole fractions within the solutions is shown in Table 2. The data in Table 2 imply that as the mole fraction of methane increases, the fraction of the total energy attributed to methane increases. Since energy is an extensive property, the total system energy must reflect a greater contribution from the methane as the mole percentage of methane increases.

Conclusions

Storage of methane in natural-gas-type liquids offers a solution to the high-pressure storage limitations of CNG. Over the temperature range in this work, −1.1 to 37.7°C, the pressures of the mixtures were all at least 8 MPa lower than CNG at 20.7 MPa and 15°C.

Over the range of temperatures studied, the energy densities of the sample mixtures always exceed CNG. A 50-mol % methane–butane mixture at −1.1°C appears to offer the greatest energy density of all the solutions: 67% that of gasoline. This amount is more than double the energy of CNG at 20.7 MPa, but at less than half the pressure (8.5 MPa).

The trends of increasing storage density and increasing energy densities of these methane–solvent solutions occur at decreasing temperatures. Also, as the systems' bubble temperatures and pressures approach the critical points, the volume of stored methane drastically decreases. This indicates that some form of refrigeration, or other temperature-control system, might be used to maintain higher concentrations of methane in the solutions.

The use of lower temperatures would provide a threefold effect. First, the related bubble pressures would be lower than those corresponding to a higher temperature. Second, the energy of these solutions would be somewhat higher due to the increased density possible at the lower pressures. Third, maintenance of the operating conditions far from the critical regime would be ensured.

At the reduced pressures of these mixtures, the amount of *methane* stored per liter of tank volume, compared to the amount of CNG per liter of tank volume at 20.7 MPa and 15°C, ranged from a low of 45% for the methane–propane mixtures to a high of 93% in the methane–butane mixtures. However, the data indicate that lower temperatures may allow stored amounts of *methane* in these solutions to exceed CNG.

While storage of methane in NG liquids does appear to be an alternative technique relative to CNG, there are trade-offs that are introduced. The lower pressures and higher energy densities of the solutions could be outweighed by the cost of the solvents required to make the solutions and the additional energy for cooling (if desired). Therefore, the economics and logistics of this technology need to be investigated before any serious implementation can begin.

Acknowledgments

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Literature Cited

Campbell, J. M., *Gas Conditioning and Processing*, Vol. 1, 6th ed., Campbell Petroleum Ser., Norman, OK (1988).

Fleming, R. D., and R. L. Bechtold, "Natural Gas (Methane), Synthetic Natural Gas and Liquefied Petroleum Gases as Fuel for Transportation," *Proc. Soc. Automot. Eng.*, San Francisco (1982).

Liss, W. E., S. Okazaki, G. H. Acker, Jr., and D. S. Moulton, "Fuel Issues for Liquefied Natural Gas Vehicles," *Proc. Soc. Automot. Eng.*, San Francisco (1992).

Mansoori, G. A., "Miscibility, Solubility and Retrograde Predictions of Methane in Liquids: Storage of Methane in Liquids for Vehicular Fuel," GRI Contract 5090-260-2085, Annu. Report of 1991–1992 (1993).

Mansoori, G. A., "Miscibility, Solubility and Retrograde Predictions for Methane in Liquids: Liquid Storage of Natural Gas (LSNG) for Vehicular Fuel," GRI Contract 5090-260-2085, Ann. Report of 1992–1993 (1994).

Matranga, K. R., A. L. Myers, and E. D. Glandt, "Storage of Natural Gas by Adsorption on Activated Carbon," *Chem. Eng. Sci.*, **47**(7), 1569 (1992).

O'Brien, R. N., and B. D. Turnham, "Methane Solubility and Methane Storage in Suitable Liquid Hydrocarbon Mixtures," *Proc. Soc. Automot. Eng.*, Detroit (1990).

Remic, R. J., R. H. Elkins, E. H. Camara, and T. Bulicz, "Advanced Onboard Storage Concepts for Natural Gas-Fueled Automotive Vehicles," DOE/NASA Contract DEN 3-327 (1984).

Starling, K. E., "Thermo Data Refined for LPG: 1. Equation of State and Computer Prediction," *Hydrocarbon Process*, **50**(3) (1971).

Starling, K. E., and M. S. Han, "Thermo Data Refined for LPG: 14. Mixtures," *Hydrocarbon Process*, **51**(5) (1972a).

Starling, K. E., and M. S. Han, "Thermo Data Refined for LPG: 15. Industrial Applications," *Hydrocarbon Process*, **51**(6) (1972b).

Starling, K. E., *Fluid Thermodynamic Properties for Light Petroleum Systems*, Gulf, Houston, TX (1973).

Starling, K. E., *CVD Computer Program*, AIX version, Norman, OK (1994).

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).

Stodolsky, F., and D. J. Santini, "Fuel Up with Natural Gas," *Chem. Tech.*, **23**, 54 (1993).

U.S. Department of Energy, Energy Information Administration, "Energy Infocard," http://www.eia.doe.gov/ (1994).

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