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# Transportation of Natural Gas-LPG Mixtures

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## Abstract

Despite significant growth in LNG projects, relatively large investments and incremental capacity place a limit on its applicability as a means of transportation for stranded gas. The concept of compressed gas transport is currently being investigated as a lower incremental cost solution. The ability to contain large fractions of natural gas as a solution in light hydrocarbons like LPG is currently being developed as an alternate vehicle fuel, but also appears to have potential for natural gas transport as well. This paper presents initial results on storage conditions and quantities in comparison with proposed CNG carriers. Lower pressures of storage of the NG-LPG mixtures as pressurized liquids theoretically allow for lower weight pressure vessels (piping) and lower compression requirements. This results in a higher ratio of hydrocarbon cargo to pressure vessel and shows that increased natural gas capacity and energy for the same sized ship may be possible.

## Introduction

The inherent benefits of natural gas as a clean fuel are leading to substantially increased demand. This increased demand, in the US especially, is resulting in significant supply shortages that cannot be overcome in the short term, and perhaps not even in the foreseeable future. The disadvantage of natural gas is its relative un-transportability, particularly in comparison to oil. In the US, demand has very recently spurred substantial expectation of dramatic increases in marine natural gas deliveries to the US in the future. Essentially all of this is presently expected to be by the established technology of LNG, despite the fact that the delivered cost from the most convenient supply zones: Venezuela, Trinidad and possibly Colombia and Mexico in the future, have been prohibitively expensive. Despite this optimistic picture, there is substantial room for improved technologies to continue to lower the costs of LNG and room for consideration of other technologies.

Cran and Stenning (1998, 1999, 2000) have provided renewed interest in marine transport of CNG. Using long coils of pipes in structures called "coselles," they have achieved improved hydrocarbon/steel ratios and costs over earlier pressure bottle concepts. Long coils of commercially available pipe reduce fabrication costs and provide for use of industry standard inspection techniques. Additional factors suggest that the development of appropriate shipping and safety codes should be achievable. Their estimates of costs suggest a window of scenarios of moderate distances and volumes in which substantial savings over LNG may be achieved, but the cost is still higher than may be desirable for many locations as the primary limitation remains the fact that the vessel cargo load is dominated by the weight of the steel pipe. The use of higher grade steel or composite materials to further increase the hydrocarbon fraction of the cargo may increase initial cost, but reduce the lifetime cost.

Starling et al (1995, 1997, 1999, 2000) proposed a method of storing natural gas in hydrocarbon solutions. The advantage of this method is that the resultant solutions have high energy density at moderate temperature and pressure. The initial focus of that research was the development of a clean vehicular fuel, and this has achieved an energy density of twice that of compressed natural gas at half the pressure. Subsequent research has also found that at certain conditions there is a volume reduction in solutions of methane and light hydrocarbons.

The objective of this work is to explore the possibility of using these mixtures, called Supergas™, as an alternative natural gas transportation technology. In order to optimize the transport capacity, the effect of the transport pressure and the size of steel pipe to be used as the pressure vessel, the investment cost of the loading terminal and the effect of propane recovery at the receiving terminal have been studied. No consideration has been given to the actual fabrication constraints and requirements of the pressure vessel or transport ships. For comparative purposes, the published work of Cran and Stenning have been used to provide a base case scenario as a point of departure from their technology, but using their cost basis for the transport ships. Effectively, their ship size and cost are assumed, and only the steel required to carry the maximum amount of hydrocarbons or methane is optimized.

## Methane Transport Capacity and Supergas Density

Methane storage capacity and Supergas™ density are two important properties in these gas transport calculations. The former relates to the natural gas (methane) transport capacity of a ship, the latter relates to the total amount of hydrocarbons that a ship is able to carry. In this study, propane is used as a model light hydrocarbon component to create the Supergas™ solution. In practice it would of course be expected that some condensate or other available light hydrocarbon stream, such as naphtha, would be used. The ability to recycle the light hydrocarbon stream is also possible, thus reducing the required supply from areas where only dry gas is available. Methane storage capacity is measured as a standard volume. Calculations have been carried out using PROII from Simulation Sciences, Inc. using the RKS Equation of state.

Figures 1-2 show the methane storage capacity at –50 °F and 30 °F, respectively. In Figure 1, we can see the following tendencies.

- The methane storage capacity always increases with increasing pressure.
- The curve for a mixture with a higher propane concentration is flatter than a mixture with less propane.

The 50/50 (molar) mixture and the 70/30 mixture are actually in the liquid state, which is less compressible.

- In the low-pressure range, some mixtures have a higher methane storage capacity than the pure methane. For example, at 1400 psia, the methane capacity of a 90% mixture is higher than that of pure methane.

This feature is important in optimizing the natural gas transport conditions. The optimal composition changes with the pressure. When the pressure is higher than 2800 psia, pure methane has a higher methane capacity than any mixture. When the pressure is lower than 1800 psia, the 70/30 mixture has the highest methane capacity. The above tendencies are also seen at 30 °F, although the methane capacity decreases with increasing temperature. When the temperature is raised to 80 °F, however, no mixture exhibits a higher methane capacity than that of pure methane. This means that when the temperature is higher than around 80 °F, one does not enhance *methane* capacity by using a Supergas™ type mixture, although the energy capacity is not limited in this way.

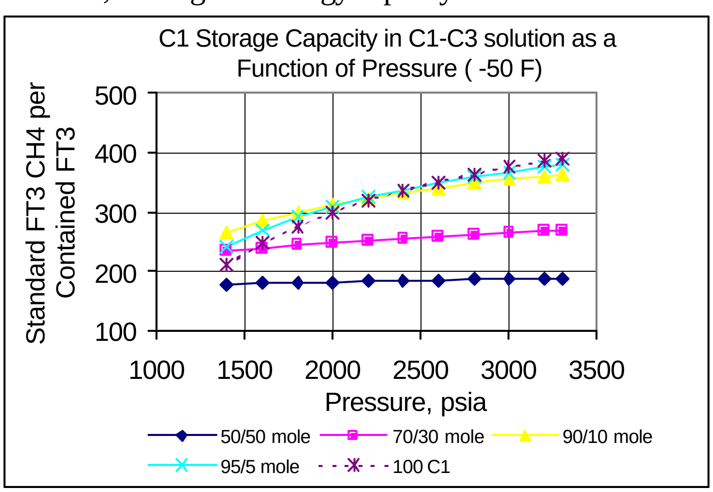


Figure 1. C1 Storage Capacity in C1-C3 solution at –50 °F

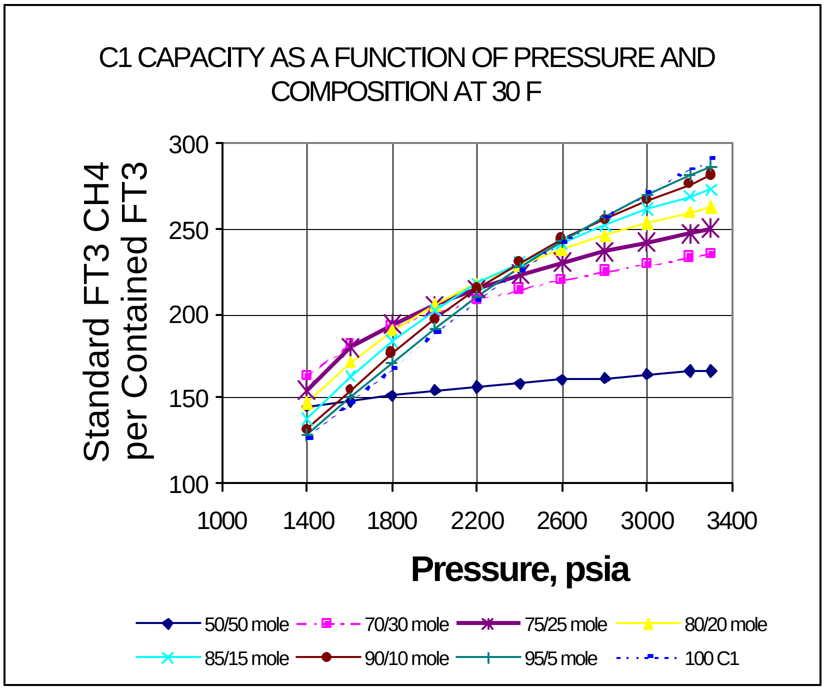


Figure 2. C1 Storage Capacity in C1-C3 solution at 30 °F

**Supergas Shipment Capacity**

The objective now is to optimize the methane shipment capacity. We assume the limiting factor is the weight of the cargo. It has been noted that in CNG marine transportation (Stenning, 1999), the weight of steel pipe accounts for a major part of the whole cargo. The essential point of this study is that to increase the amount of hydrocarbons shipped for a given size vessel (and for a given set of temperature and material constraints), the weight of piping must be reduced. The effect of the pipe size and the allowable working pressure were studied and compared to the base case scenario of Cran and Stenning, with a ship dead weight tonnage (cargo capacity) of 60,000 and a shipment temperature of 30 °F.

The effectiveness of pipe in storing the hydrocarbon solution can be measured by the contained volume per pound of steel. A large contained volume means a ship can better use its cargo capacity by carrying less steel and more hydrocarbons.

We have seen in Figure 2 that the optimal gas composition for methane storage changes with the working pressure. The optimal gas compositions are shown in Table 1. When the pressure is higher than 2800 psia, pure methane has the highest storage capacity. However, when the pressure is in the range of 2500 to 2800 psia, the 90% mixture has the highest methane storage. With the decrease of pressure, the composition of the mixture with the maximal methane capacity shifts towards more propane. When the pressure is lower than 1800 psia, the optimal composition is 70% methane.

Table 1. Optimal Gas Compositions at 30 °F

| Pressure (psia) | C1 mole % | C1 wt % |
|---|---|---|
| <=1800 | 70 | 0.459 |
| <=2000 | 75 | 0.522 |
| <=2200 | 80 | 0.593 |
| <=2500 | 85 | 0.673 |
| <=2800 | 90 | 0.766 |
| >3000 | 100 | 1.000 |

The corresponding densities are shown in Figure 3. The solid points denote the densities given by PRO II (SRK equation), and the dotted line is a 4<sup>th</sup> order polynomial correlation that is a fit of the thermodynamic prediction. The correlation is to be used to calculate the gas densities at various working pressures in the optimization.

Figure 3 can be divided into three regions according to the working pressure:

- Region I: $p \leq 1800$ psia,
- Region II: $1800 < p < 3000$,
- Region III: $p \geq 3000$ psia.

The optimal composition is constant in region I and III. In region II, however, the gas composition changes with the pressure, which accounts for some variation in the result. Note that the density curve has a peak between 1400 and 2200 psia. This feature can be utilized to maximize the total transport capacity.

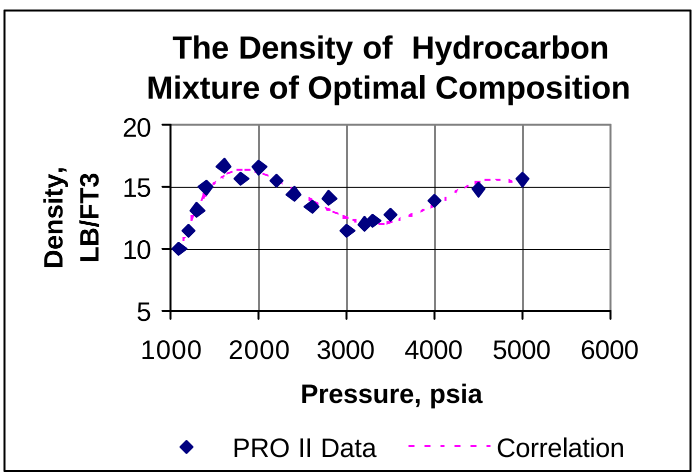


Figure 3. Density of gas mixtures of optimal composition

Table 2 below summarizes the compressed gas shipment capacity for Cran and Stennings's base case (Stenning, 1999).

Table 2. Compressed Natural Gas Shipment Capacity (Stenning, 1999)

| Item | Value |
|---|---|
| Pressure, bar | 200 |
| Temperature, F | 30 |
| Sales gas capacity per coselle, MMCF | 3.09 |
| Gas amount per coeselle, tonnes | 71 |
| No. of coselles per ship | 108 |
| Sales gas capacity per ship, MMCF | 333.72 |
| Heating value per ship*, MMbtu | 349,891 |
| Sales gas weight per ship, tonnes | 7668 |

* Natural gas heating value used is 1080 btu/scf. In this research, 1048 btu/scf is used.

The amount of methane and propane stored in a ship depends on the size and the strength of the steel pipe. The transport capacities for different sizes of steel pipe and pressures determined from the optimization are shown in Table 3. The pipe data comes from the GPSA Data book (1998) and is based on the allowable working pressure. Cran and Stenning upgrade the alloy by applying a safety factor of 2. This does not effectively change their hydrocarbon/steel ratio, but of course is taken into account in the cost. Since we are using their ship/coselle costs (even though we are using less steel), the alloy upgrade safety factor is transparent to our calculations and is accounted for. We reiterate that the ability to fabricate, certify and meet codes for these configurations, is not taken into account in considering these "best" answers.

Now we look at two scenarios:

I. Maximizing the methane (natural gas) transport capacity of a ship
II. Maximizing the Supergas™ transport capacity of a ship

The answer for the first scenario is:

- 10 inch pipe with a thickness of 0.20 in. The working pressure is 1421 psia. The methane capacity is 377 MMSCF/ship.
- 12 inch pipe with a thickness of 0.25 in. The working pressure is 1465 psia. The methane capacity is 373 MMSCF/ship.

The answer for the second scenario is:

- 8 inch pipe with a thickness of 0.16 in. The working pressure is 1349 psia. The Btu relative capacity is 1.98.
- 10 inch pipe with thickness ranging from 0.19 to 0.22 in. The working pressure ranges from 1305 to 1523 psia. The Btu relative capacity ranges from 1.96 to 1.99.
- 12 inch pipe. The thickness can be 0.22 or 0.25 in. The working pressures are 1291 and 1465 psia respectively. The Btu relative capacities are 1.98 and 1.97 respectively.

Note that the different optima are not tremendously different and so the sensitivity to composition, pressure or pipe diameter is not great. In the region of conditions in which the optimum is found, the maximization of either natural gas or energy content also does not result in large differences.

Table 3. Supergas™ Transport Capacities for Various Steel Pipe Sizes

| Pipe size In | Allow. Work pressure * lb/sq in | Wall Thickness inches | Supergas density lb/ft$^3$ | C1 wt% | C1 capacity MMSCF/ship | C3 /ship MM gal | Relative transport capacity** |
|---|---|---|---|---|---|---|---|
| 2 | 3263 | 0.15 | 12.15 | 1.0 | 206 | 0.00 | 0.52 |
| 3 | 1798 | 0.13 | 16.53 | 0.46 | 248 | 2.73 | 1.26 |
| 3 | 2248 | 0.16 | 15.50 | 0.67 | 231 | 1.26 | 0.96 |
| 6 (GR.B358.6) | 1769 | 0.16 | 16.50 | 0.46 | 355 | 3.93 | 1.82 |
| 6 (GR.B358.6) | 2118 | 0.19 | 16.04 | 0.59 | 340 | 2.47 | 1.52 |
| 6 (GR.B358.6) | 2480 | 0.22 | 14.32 | 0.67 | 335 | 1.57 | 1.20 |
| 6 *** (GR.B358.6) | 2828 | 0.25 | 12.63 | 1.00 | 328 | 0.00 | 0.95 |
| 6 (GR.B358.6) | 3162 | 0.28 | 12.00 | 1.00 | 321 | 0.00 | 0.82 |
| 6 (GR.B358.6) | 3524 | 0.31 | 13.58 | 1.00 | 304 | 0.00 | 0.82 |
| 6 (GR.B358.6) | 4235 | 0.37 | 28.21 | 1.00 | 244 | 0.00 | 1.28 |
| 6 (GR.B358.6) | 4888 | 0.43 | 30.00 | 1.00 | 197 | 0.00 | 1.16 |
| 8 (GR.B358.6) | 1349 | 0.16 | 13.89 | 0.46 | 366 | 4.27 | 1.98 |
| 8 (GR.B358.6) | 1639 | 0.19 | 16.14 | 0.46 | 366 | 4.13 | 1.91 |
| 8 (GR.B358.6) | 1769 | 0.20 | 16.50 | 0.46 | 355 | 3.93 | 1.82 |
| 8 (GR.B358.6) | 1900 | 0.22 | 16.54 | 0.52 | 348 | 3.27 | 1.71 |
| 8 (GR.B358.6) | 4337 | 0.50 | 30.00 | 1.00 | 236 | 0.00 | 1.31 |
| 10 (GR.B358.6) | 1305 | 0.19 | 13.35 | 0.46 | 356 | 4.27 | 1.98 |
| 10 (GR.B358.6) | 1421 | 0.20 | 14.66 | 0.46 | 377 | 4.30 | 1.99 |
| 10 (GR.B358.6) | 1523 | 0.22 | 15.50 | 0.46 | 372 | 4.23 | 1.96 |
| 10 (GR.B358.6) | 1740 | 0.25 | 16.45 | 0.46 | 356 | 3.97 | 1.84 |
| 12 (GR.B358.6) | 1102 | 0.19 | 10.02 | 0.46 | 332 | 3.94 | 1.82 |
| 12 (GR.B358.6) | 1189 | 0.20 | 11.62 | 0.46 | 341 | 4.13 | 1.91 |
| 12 (GR.B358.6) | 1291 | 0.22 | 13.16 | 0.46 | 358 | 4.28 | 1.98 |
| 12 (GR.B358.6) | 1465 | 0.25 | 15.06 | 0.46 | 373 | 4.26 | 1.97 |
| 12 (GR.B358.6) | 1653 | 0.28 | 16.20 | 0.46 | 367 | 4.14 | 1.92 |
| 12 (GR.B358.6) | 1827 | 0.31 | 16.55 | 0.52 | 353 | 3.41 | 1.78 |

* up to 120 °C (Type A, F=0.72, GR.B 241.4)
** relative to the capacity given by Stenning and Cran (1999), BTU basis
*** 6 in pipe used by Stenning (before alloy upgrade).

## Conclusion

An alternative natural gas transport method --- Supergas™ transportation, has been studied in a preliminary way. These hydrocarbon solutions can be utilized to increase the hydrocarbon transport capacity of a specific size ship. It is also found in

CNG transport that more than 80% of the ship's dwt is used to ship the steel pipe itself. Therefore, it is important to optimize the size and thickness of the steel pipe, though it is understood that there are constraints on fabrication and codes and standards requirements. The capacities of various size of steel pipes are studied in comparison to CNG transport (6 in, 0.25 in thick), and some pipes are found to have Btu based capacities almost twice that of the base case CNG transport, while carrying as much or more methane (natural gas).

Although the focus of this paper has been on marine transport, the application for pipelines might be noted. The dominating constraint of the weight of the pipe is not a significant factor for transmission pipelines. It appears that as higher grade steels and the codes for them are developed, higher pressure design and operation will prove advantageous. Under those conditions, probable higher ambient temperatures and operating pressures above 1500 or 2000 psia, it may not be as likely that increased methane capacity of the Supergas™ solution above that of pure methane (meaning "pure" pipeline quality natural gas), but it will be possible to increase the energy throughput significantly and might be expected to be in the same operating range as that for vehicles, where energy capacity is at least twice 3000 psia CNG at about half the pressure.

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## References

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).

Mallinson, R. G., K. E. Starling and J. H. Harwell; "High Density Storage of Methane in Light Hydrocarbons," U.S. Patent Number 5,900,515, May 4, 1999.

Mallinson, R. G., K. E. Starling and J. H. Harwell; "High Density Storage of Methane in Light Hydrocarbons," U.S. Patent Number 6,111,154, August 29, 2000.

Starling, K. E., Ding., E. R., Harwell, J. H., and Mallinson, R. G., "Method for Improved Natural Gas Energy Density at Ambient Temperatures", Energy & Fuels, **9**(6),1995.

Stenning, D. G. and Cran, J. A., "Ship Based System for Compressed Natural Gas Transport", US patent 5,803,005, 1998.

Stenning, D. G. and Cran, J. A., “The COSELLE CNG Carrier --- A new Way to Ship Natural Gas by Sea”, CERI North American Natural Gas Conference, Calgary, Alberta, March 1999.

Stenning, D. G. and Cran, J. A., The COSELLE CNG Carrier --- “The Shipment of Natural Gas by Sea in Compressed Form”, World Petroleum Conference, Calgary, Alberta, June 2000.

Engineering Data Book, Gas Processors and Suppliers Association, Tulsa, Oklahoma, 1998.