

HYDROGEN STORAGE IN INSULATED PRESSURE VESSELS

S. M. Aceves and O. Garcia-Villazana
Lawrence Livermore National Laboratory
7000 East Ave., L-641
Livermore, CA 94551, USA
saceves@llnl.gov

Abstract

Insulated pressure vessels are cryogenic-capable pressure vessels that can be fueled with liquid hydrogen (LH₂) or ambient-temperature compressed hydrogen (CH₂). Insulated pressure vessels offer the advantages of liquid hydrogen tanks (low weight and volume), with reduced disadvantages (lower energy requirement for hydrogen liquefaction and reduced evaporative losses).

This paper shows an evaluation of the applicability of the insulated pressure vessels for light-duty vehicles. The paper shows an evaluation of evaporative losses and insulation requirements and a description of the current analysis and experimental plans for testing insulated pressure vessels. The results show significant advantages to the use of insulated pressure vessels for light-duty vehicles.

Introduction

Probably the most significant hurdle for hydrogen vehicles is storing sufficient hydrogen onboard. Hydrogen storage choices can determine the refueling time, cost, and infrastructure requirements, as well as indirectly influence energy efficiency, vehicle fuel economy, performance, and utility. There are at least three viable technologies for storing hydrogen fuel on cars. These are: compressed hydrogen gas (CH₂), metal hydride adsorption, and cryogenic liquid hydrogen (LH₂), but each has significant disadvantages.

Storage of 5 kg of hydrogen (equivalent to 19 liters; 5 gallons of gasoline) is considered necessary for a general-purpose vehicle, since it provides a 320 km (200 mile) range in a 17 km/liter (40

mpg) conventional car; or a 640 km (400 mile) range in a 34 km/liter (80 mpg) hybrid vehicle or fuel cell vehicle. Storing this hydrogen as CH_2 requires a volume so big that it is difficult to package in light-duty vehicles (Pentastar Electronics 1997), and it certainly cannot be used in trucks. The external volume for a pressure vessel storing 5 kg of hydrogen at 24.8 MPa (3600 psi) is 320 liters (85 gal). Hydrides are heavy (300 kg for 5 kg of hydrogen [Michel 1996]), resulting in a substantial reduction in vehicle fuel economy and performance.

Low-pressure LH_2 storage is light and compact, and has received significant attention due to its advantages for packaging (Braess 1996). Significant recent developments have resulted in improved safety (Pehr 1996a, 1996b) and fueling infrastructure (Hettinger 1996). Disadvantages of low-pressure LH_2 storage are: the substantial amount of electricity required for liquefying the hydrogen (Peschka 1992); the evaporation losses that occur during fueling low-pressure LH_2 tanks (Wetzel 1996); and the evaporation losses that occur during long periods of inactivity, due to heat transfer from the environment.

An alternative is to store hydrogen in an insulated pressure vessel that has the capacity to operate at LH_2 temperature (20 K), and at high pressure (24.8 MPa; 3600 psi). This vessel has the flexibility of accepting LH_2 or CH_2 as a fuel. Filling the vessel with ambient-temperature CH_2 reduces the amount of hydrogen stored (and therefore the vehicle range) to about a third of its value with LH_2 .

The fueling flexibility of the insulated pressure vessels results in significant advantages. Insulated pressure vessels have similar or better packaging characteristics than a liquid hydrogen tank (low weight and volume), with reduced energy consumption for liquefaction. Energy requirements for hydrogen liquefaction are lower than for liquid hydrogen tanks because a car with an insulated pressure vessel can use, but does not require, cryogenic hydrogen fuel. A hybrid or fuel cell vehicle (34 km/l, 80 mpg) could be refueled with ambient-temperature CH_2 at 24.8 MPa (3600 psi) and still achieve a 200 km range, suitable for the majority of trips. The additional energy, costs, and technological effort for cryogenic refueling need only be undertaken (and paid for) when the additional range is required for longer trips. With an insulated pressure vessel, vehicles can refuel most of the time with ambient-temperature hydrogen, using less energy, and most likely at lower ultimate cost than LH_2 , but with the capability of having 3 times the range of room temperature storage systems.

Insulated pressure vessels also have much reduced evaporative losses compared to LH_2 tanks. These results are based on a thermodynamic analysis of the vessels, and are the subject of the next section of this paper.

From an engineering and economic perspective, insulated pressure vessels strike a versatile balance between the cost and bulk of ambient-temperature CH_2 storage, and the energy efficiency, thermal insulation and evaporative losses of LH_2 storage.

Thermodynamic Analysis

This section describes a thermodynamic model of a pressure vessel, with the purpose of calculating evaporative losses. The following assumptions are used in the analysis:

1. Kinetic and potential energy of the hydrogen flowing out of the vessel are neglected.
2. Thermal conductivity of the vessel insulation is considered to be independent of internal and external temperature.
3. Gaseous hydrogen is preferentially extracted from the vessels. LH_2 is only extracted when the amount of gaseous hydrogen is not enough to satisfy the driving requirements.
4. Temperature and pressure are uniform within the vessel. This assumption has recently been verified for small vessels of the size required for light-duty vehicles (Bunger 1996).

5. No conversion between the para and ortho phases of hydrogen is considered. This assumption is used because vessel temperature changes little during most operating conditions, so that the equilibrium concentration of each phase remains fairly constant. In addition to this, the para-ortho conversion is slow, with a transition time of the order of a few days (Mathis 1976), so that in most cases, hydrogen does not stay in the vehicle vessel long enough for any significant conversion to occur.

The first law of thermodynamics written for a pressure vessel is (VanWylen 1978):

$$M \frac{du}{dt} + M_v \frac{d(c_{p,v}T)}{dt} = Q - \left(\frac{p}{\rho} \right) \dot{m} \quad (1)$$

The two terms in the left-hand side of Equation (1) are the rates of change of the internal energies of the hydrogen and the vessel. Heat transfer into the vessel (Q in the equation) is positive and tends to increase the temperature of the vessel. However, the last term in the right hand side of Equation (1) represents a cooling effect on the vessel, when mass is extracted ($\dot{m} > 0$). Considering that the density of hydrogen is very low, this term is often significant. The last term in Equation (1) is commonly known as the flow work, since it is the work that the hydrogen stored in the vessel has to do to push out the hydrogen being extracted.

Equation (1) is solved for a low-pressure LH₂ storage and for the insulated pressure vessel. The equation is solved iteratively with a computer program which includes subroutines for calculating hydrogen properties. The required property values are obtained from McCarty (McCarty 1975). The specific heat of the vessel materials, $c_{p,v}$ is obtained as a function of temperature from correlations given in the literature (Scott 1967).

Vessel Characteristics

This paper considers three vessels, described as follows:

1. A conventional, low-pressure LH₂ tank with a multilayer vacuum superinsulation (MLVSI) and 0.5 MPa maximum operating pressure.
2. An insulated pressure vessel (24.8 MPa maximum operating pressure) with MLVSI fueled with LH₂.
3. An insulated pressure vessel with microsphere insulation (aluminized microspheres within a vacuum) fueled with LH₂.

Vessel properties are listed in Table 1. Two insulating materials (MLVSI and microspheres) are used in the analysis to study the effect of insulation level on hydrogen losses. No low-pressure LH₂ tank with microsphere insulation is studied in this paper, because low-pressure LH₂ tanks are very sensitive to heat transfer from the environment. According to Bungler and Owren (Bunger 1996), LH₂ poses requirements that are beyond the thermal performance of current vacuum powder insulation.

All vessels are designed to store 5 kg of hydrogen. The weight of the vessels, accessories, insulation, and external cover are calculated from data given by (James 1996). The vessels are assumed to have a cylindrical shape with hemispherical ends, and the length of the cylindrical segment is assumed to be equal to the diameter. Insulation properties are obtained from (Bunger 1996), which lists ranges of measured conductivity. Worst-case (highest) conductivity values are selected from these ranges.

Table I. Characteristics of the Hydrogen Vessels Being Analyzed.

	liquid Tank 1	insulated Vessel 2	pressure vessels Vessel 3
Mass of hydrogen stored, kg	5	5	5
Total weight, kg	21	30	30
Internal volume, liters	85	95	95
External volume, liters	112	144	144
Internal diameter, m	0.39	0.42	0.42
Internal surface area, m ²	0.98	1.1	1.1
Aluminum mass within insulation, kg	9	10	10
Carbon mass within insulation, kg	0	10	10
Design pressure, MPa (psi)	0.5 (70)	24.8 (3600)	24.8 (3600)
Performance factor ¹ , m (10 ⁶ in)	-	33000 (1.3)	33000 (1.3)
Safety factor	-	2.25	2.25
Insulating material	MLVSI ²	MLVSI ²	microsphere
Thermal conductivity of insulator, W/mK	0.0001	0.0001	0.0004
Insulation thickness, m	0.02	0.02	0.02
Heat transfer through accessories, W	0.5	0.5	0.5

¹ defined as burst pressure*volume/weight.

² MLVSI = multilayer vacuum superinsulation

The heat transfer rate, Q , has two components: heat transfer through the insulation, and parasitic heat transfer. Heat transfer through the insulation is assumed proportional to the temperature difference between the environment and the hydrogen inside the vessel. Parasitic heat transfer takes into account heat transfer through accessories, connecting lines, etc., and is assumed constant and equal to 0.5 W for a 2 cm insulation thickness.

This paper considers the application of hydrogen vessels to two vehicles: a hydrogen vehicle with a 17 km/liter (40 mpg) gasoline-equivalent fuel economy (Aceves 1996); and a high efficiency hybrid or fuel cell car with a 34 km/l (80 mpg) gasoline equivalent fuel economy (Smith 1995). The results can be easily scaled for application to vehicles with any other fuel economy.

Results

Figure 1 shows hydrogen losses during operation. The figure assumes that the vessels are filled to full capacity (5 kg), and then the vehicles are driven a fixed distance every day. The figure shows total cumulative evaporative hydrogen losses out of a full tank as a function of the daily driving distance. The figure includes information for 17 km/l and 34 km/l cars respectively in the lower and upper x-axes. The figure shows that a low-pressure LH₂ tank loses hydrogen even when driven 50 km per day in a 17 km/l car (100 km in a 34 km/l car). Losses from a low-pressure LH₂ tank grow rapidly as the daily driving distance drops. Insulated pressure vessels lose hydrogen only for very short daily driving distances. Even a microsphere-insulated vessel does not lose any hydrogen when driven 10 km/day or more (20 km/day in the 34 km/l car). Since most people drive considerably more than this distance, no losses are expected under normal operating conditions.

Figure 2 shows losses for a parked vehicle. The figure shows cumulative hydrogen losses as a function of the number of days that the vehicle remains idle. The most unfavorable condition is assumed: the vehicles are parked immediately after fueling. The low-pressure LH₂ tank has 2 days of dormancy (2 days without fuel loss) before any hydrogen has to be vented. After this, losses increase quickly, and practically all of the hydrogen is lost after 15 days. This may represent a significant inconvenience to a driver, who may be unable to operate the vehicle after a

long period of parking. Insulated pressure vessels have a much longer dormancy (up to 16 days). Total losses for the insulated pressure vessel with MLVSI is only 1 kg after 1 month of parking. In addition to this, insulated pressure vessels retain about a third of their total capacity even when they reach thermal equilibrium with the environment after a very long idle time, due to their high pressure capacity, therefore guaranteeing that the vehicle never runs out of fuel during a long idle period.

Figures 1 and 2 show a comparison in thermal performance for insulated pressure vessels and LH₂ tanks with equal insulation thickness (2 cm). Another important aspect of the comparison consists of determining the required insulation thickness for a LH₂ tank to have the same thermal performance as an insulated pressure vessel. This is illustrated in Figure 3. Figure 3 shows the effect of changing the insulation thickness on the thermal performance of an LH₂ tank. The figure shows the dormancy (number of days before any fuel loss occurs in a parked vehicle), and the minimum daily driving distance required for obtaining zero fuel losses, both as a function of the insulation thickness. The analysis assumes that the heat transfer through accessories is inversely proportional to the insulation thickness, so that it drops from the base-case value of 0.5 W for a thickness of 2 cm to 0.05 W at 20 cm thickness. The figure shows two diamond-shaped symbols, which indicate the corresponding dormancy (16 days, from Figure 2) and the daily driving distance for no losses (3 km/day, from Figure 1), for an insulated pressure vessel with 2 cm of MLVSI. The figure shows that, to achieve the same thermal performance as the insulated pressure vessel, an LH₂ tank requires either 13 or 20 cm of MLVSI. An insulation thickness of 13 cm is required to obtain the same period of parking without losses, and 20 cm are necessary to obtain the same minimum daily driving distance for no losses.

The big insulation requirements for LH₂ tanks with the same thermal performance as insulated pressure vessels have a major effect on external volume. Figure 4 shows internal and external volume for the insulated pressure vessel and LH₂ tank with 2 cm of MLVSI, and for LH₂ tanks with the same dormancy, and the same daily driving distance for no losses. It is clear that the vessels with equal thermal performance as the insulated pressure vessels are impractical due to their large volume. As a conclusion it can be said that insulated pressure vessels are a substantially more compact storage technology than LH₂ tanks, when vessels with equal thermal performance are compared.

Experimental Testing and Stress Analysis of Insulated Pressure Vessels

The analysis presented in this paper has assumed that insulated pressure vessels can be built to withstand the thermal stresses introduced when an initially warm vessel is filled with LH₂. It is desirable to use commercially-available aluminum-lined, fiber-wrapped pressure vessels to avoid the cost of custom-made vessels, even though commercially-available pressure vessels are not designed for low-temperature operation. While the applicability of these vessels for LH₂ storage in vehicles has not been demonstrated, an experiment has been carried out (Morris 1986) in which carbon fiber-aluminum and kevlar-aluminum vessels were cycled over a limited number of cycles (17) at LH₂ temperature. The vessels were burst-tested after cycling. The results of the experiment showed that there was no performance loss (no reduction in safety factor) due to cycling. This experiment indicates that it may be possible to use commercially-available fiber-wrapped aluminum vessels for operation at LH₂ temperature and high pressure. However, additional cyclic testing is necessary, because a vehicle requires many more than 17 fueling cycles.

To accomplish the required testing, an experimental setup has been built inside a high-pressure cell. A schematic is shown in Figure 5. The plan consists of running the vessels through 1000 high-pressure cycles and 100 low-temperature cycles. The cycles are alternated, running 10 pressure cycles followed by a temperature cycle, and repeating this sequence 100 times. Liquid nitrogen will be used for low-temperature cycling, and gaseous helium for high-pressure cycling.

This test is expected to replicate what would happen to these vessels during operation in a hydrogen-fueled car.

Cyclic testing of the pressure vessels is being complemented with a finite element analysis, which will help to determine the causes of any potential damage to the vessel during low-temperature operation. Finite element analysis is currently under progress. A mesh has been built, and a thermal analysis of the pressure vessel has been conducted. Figure 6 shows results for the early stages of the vessel filling process. The figure shows the lower part of the vessel, along with the mesh used in the simulation. Only a section of the vessel is analyzed, since it is axisymmetric. The conditions for the analysis are: the initial temperature is 300 K, the exterior of the pressure vessel is well insulated, and the interior of the vessel is being filled with liquid nitrogen. The liquid nitrogen level increases at a constant rate, and it is assumed that the vessel is full in 15 minutes. Figure 6 shows the level of liquid nitrogen with an arrow. The figure shows that the aluminum cools down very quickly due to its high thermal conductivity, while the composite material remains almost at ambient temperature. This condition is certain to introduce stresses in the vessel. These stresses will be calculated in the next stage of the analysis, when the thermal model is linked to a stress analysis model.

Validation of the finite element analysis will be done by applying strain gages and temperature sensors to the vessel. Cycled vessels will then be analyzed with non-destructive evaluation techniques, and finally they will be burst-tested, to evaluate any reduction in safety factor due to cycling.

Additional work in progress includes the design of an insulation. This is shown in Figure 7, which indicates that an outer jacket will be built around the vessel. This is necessary for keeping a vacuum space, required for obtaining a good thermal insulation with multilayer insulation (MLVSI). As a part of the insulation design, a pressure vessel outgassing experiment is currently being conducted. This is necessary, because an excessive outgassing rate from the pressure vessel material (fiber and epoxy) may result in a loss of vacuum, considerably reducing the performance of the insulation. The insulation design includes access for instrumentation for pressure, temperature, level and strain, as well as safety devices to avoid a catastrophic failure in case the hydrogen leaks into the vacuum space.

The instrumented and insulated vessel will be cycled with liquid hydrogen to test the instrumentation and insulation performance. A schematic of the experimental setup is shown in Figure 8. Testing will be conducted outdoors at a high-explosives facility to avoid the risk of an explosion that may occur as a result of hydrogen venting.

Conclusions

This paper shows that insulated pressure vessels have good packaging characteristics and thermal performance compared to LH₂ tanks, and also a potential for reduced need for liquid hydrogen. For these reasons, they are considered to be a good alternative for hydrogen storage. The most important results can be summarized as follows:

1. Insulated pressure vessels do not lose any hydrogen for daily driving distances of more than 10 km/day for a 17 km/l energy equivalent fuel economy. Since almost all cars are driven for longer distances, most cars would never lose any hydrogen.
2. Losses during long periods of parking are small. Due to their high pressure capacity, these vessels retain about a third of its full charge even after a very long period of inactivity, so that the owner would not risk running out of fuel.
3. Insulation of an LH₂ tank has to be between 6.5 and 10 times thicker than for an insulated pressure vessel to achieve equal thermal performance. Considering the large volume occupied by such a thick insulation layer, insulated pressure vessels are a more compact storage technology than LH₂ tanks, for equal thermal performance.

4. Previous testing has determined the potential of low-temperature operation of commercially-available aluminum-lined wrapped vessels for a limited number of cycles. Further testing will extend the number of cycles to the values required for a light-duty vehicle. Additional analysis and testing will help in determining the safety and applicability of insulated pressure vessels for hydrogen storage in light-duty vehicles.

Nomenclature

$c_{p,v}$	specific heat of the vessel enclosed within the insulation
\dot{m}	mass flow rate of hydrogen extracted from the vessel
M	total mass of hydrogen stored in the vessel
M_v	mass of the vessel enclosed within the insulation
p	pressure
Q	heat transfer rate from the environment into the vessel
t	time
T	temperature
u	specific internal energy of hydrogen
ρ	density of the hydrogen leaving the vessel

Acknowledgments

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

References

- Aceves, S.M., and Smith, J.R., 1996, "Lean-Burn Hydrogen Spark-Ignited Engines: The Mechanical Equivalent to the Fuel Cell," In "Alternative Fuels, Volume 3," Proceedings of the 18th Annual Fall Technical Conference of the ASME Internal Combustion Engine Division, Fairborn, OH, October 1996, pp. 23-31.
- Braess, H.H., and Strobl, W., 1996, "Hydrogen as a Fuel for Road Transport of the Future: Possibilities and Prerequisites," Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany.
- Bunger, U., and Owren, G., 1996, "Development Potentials for Small Mobile Storage Tanks with Vacuum Powder Insulations," Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1043-1052.
- Hettinger, W. Michel, F., Ott, P., and Theissen, F., 1996, "Refueling Equipment for Liquid Hydrogen Vehicles," Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1135-1143.
- James, B.D., Baum, G.N., Lomax, F.D., Thomas, C.E., Kuhn, I.F., 1996, "Comparison of Onboard Hydrogen Storage for Fuel Cell Vehicles," Directed Technologies Report DE-AC02-94CE50389, prepared for Ford Motor Company.
- Mathis, D.A., 1976, "Hydrogen Technology for Energy," Noyes Data Corporation, Park Ridge, NJ.
- McCarty, R.D., 1975, "Hydrogen: Its Technology and Implications, Hydrogen Properties, Volume III," CRC Press, Cleveland, Ohio.

Michel, F., Fieseler, H., Meyer, G., and Theissen, F., 1996, "Onboard Equipment for Liquid Hydrogen Vehicles," Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1063-1077.

Morris, E.E., Segimoto, M., and Lynn, V., 1986, "Lighter Weight Fiber/Metal Pressure Vessels Using Carbon Overwrap," AIAA-86-1504, Proceedings of the AIAA/ASME/SAE/ASEE 22nd Joint Propulsion Conference, June 16-18, Huntsville, Alabama.

Pehr, K., 1996a, "Experimental Examinations on the Worst Case Behavior of LH₂/LNG Tanks for Passenger Cars," Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany.

Pehr, K., 1996b, "Aspects of Safety and Acceptance of LH₂ Tank Systems in Passenger Cars," International Journal of Hydrogen Energy, Vol. 21, pp. 387-395.

Pentastar Electronics, 1997, "Direct-Hydrogen-Fueled Proton-Exchange-Membrane Fuel Cell System for Transportation Applications, Conceptual Design Report," Report DOE/CE/50390-9, prepared for U.S. Department of Energy, Office of Transportation Technologies, under contract DE-AC02-94CE50390.

Peschka, W., 1992, "Liquid Hydrogen, Fuel of the Future," Springer-Verlag, Vienna, Austria.

Scott, R.B., 1967, "Cryogenic Engineering," D. Van Nostrand Company, Inc. Princeton, NJ.

Smith, J.R., Aceves, S.M., and Van Blarigan, P., 1995, "Series Hybrid Vehicles and Optimized Hydrogen Engine Design," SAE Paper 951955, SAE Transactions, Journal of Fuels and Lubricants, Vol. 104, pp. 816-827.

VanWylen, G.J., and Sonntag, R.E., 1978, "Fundamentals of Classical Thermodynamics," John Wiley and Sons, New York, NY.

Wetzel, F.J., 1996, "Handling of Liquid Hydrogen at Filling Stations," Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1123-1134.

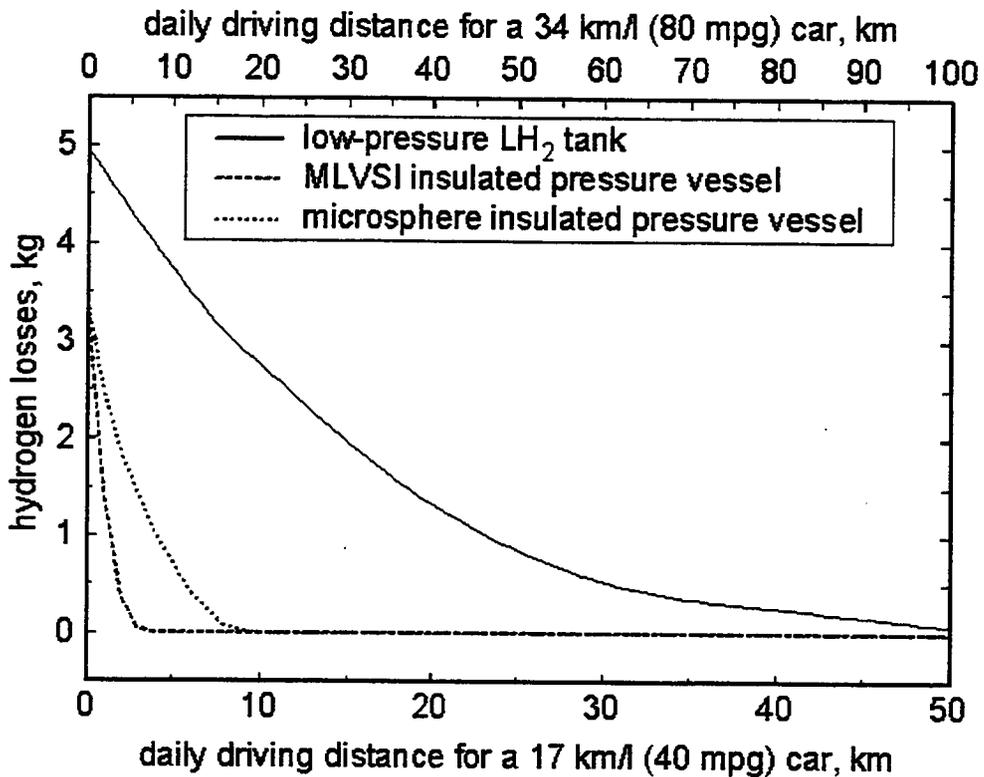


Figure 1. Cumulative hydrogen losses in kg as a function of daily driving distance, for vehicles with 17 km/liter (40 mpg); or 34 km/l (80 mpg) fuel economy, for the three vessels being analyzed in this paper.

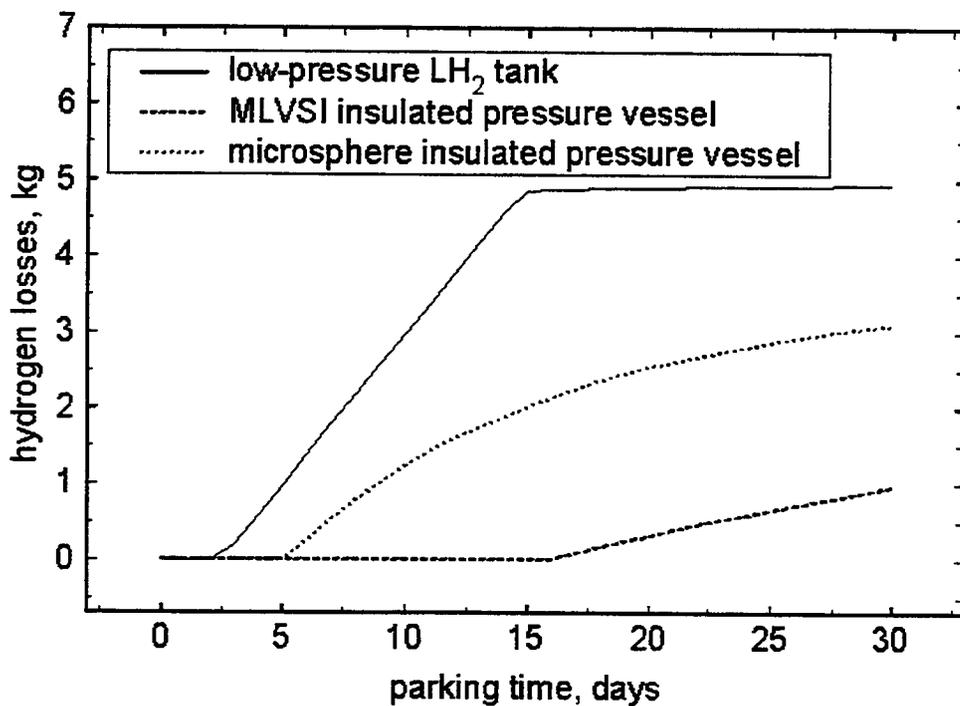


Figure 2. Cumulative hydrogen losses in kg as a function of the number of days that the vehicle remains idle, for the three vessels being analyzed in this paper, assuming that the vessels are initially full.

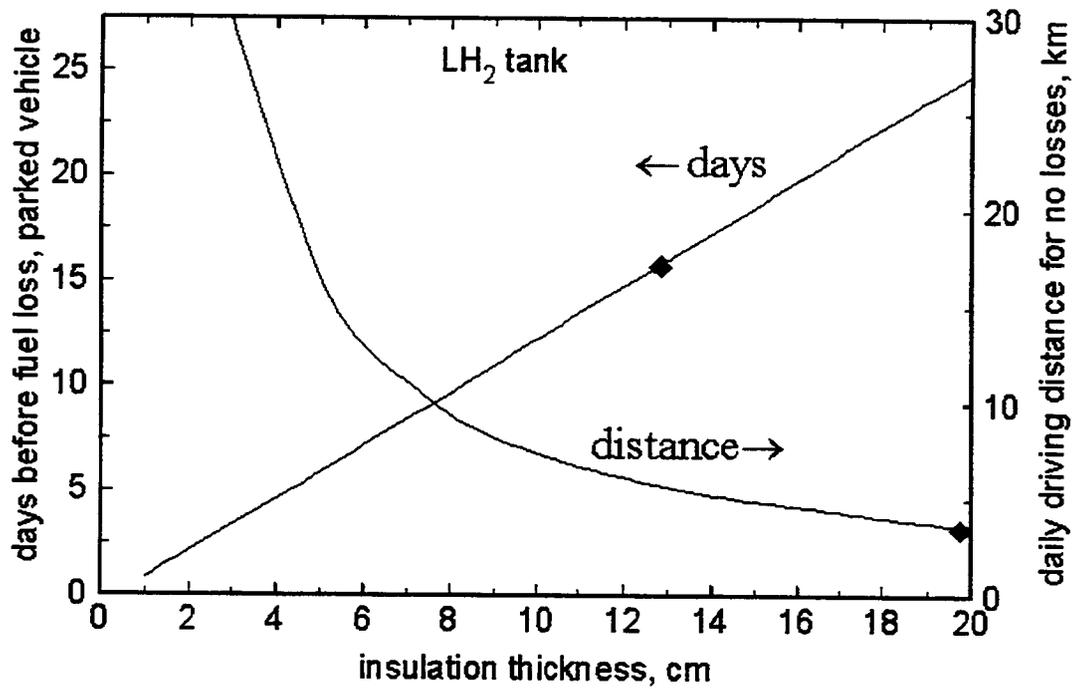


Figure 3. Dormancy and daily driving distance required for obtaining zero fuel losses, as a function of the insulation thickness, for a LH₂ tank.

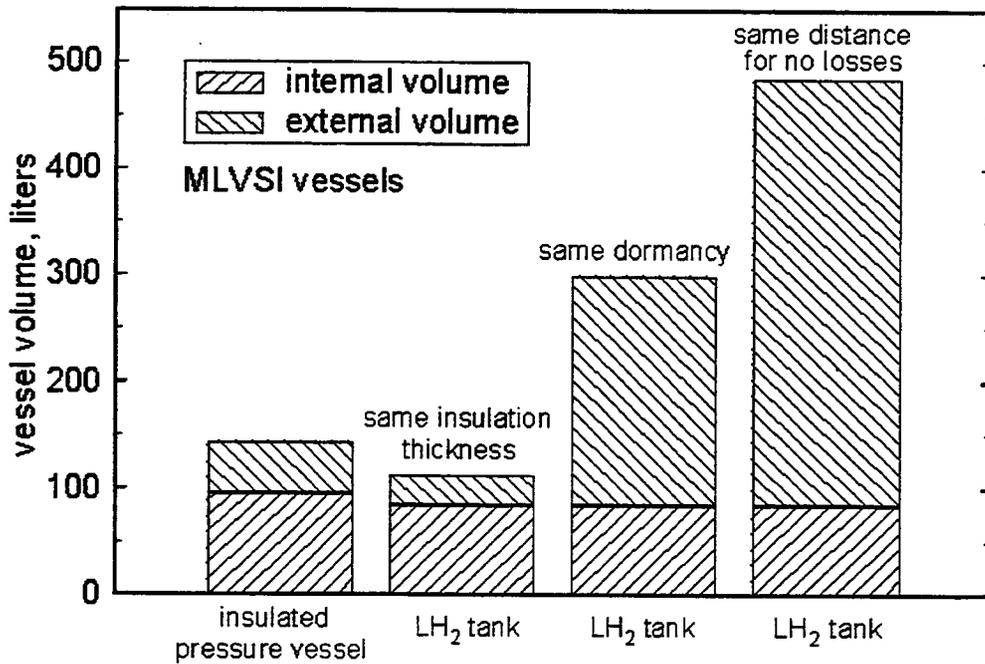


Figure 4. Internal and external volume for the base-case insulated pressure vessel and LH₂ tank, and for LH₂ tanks with same dormancy, and the same daily driving distance for no losses.

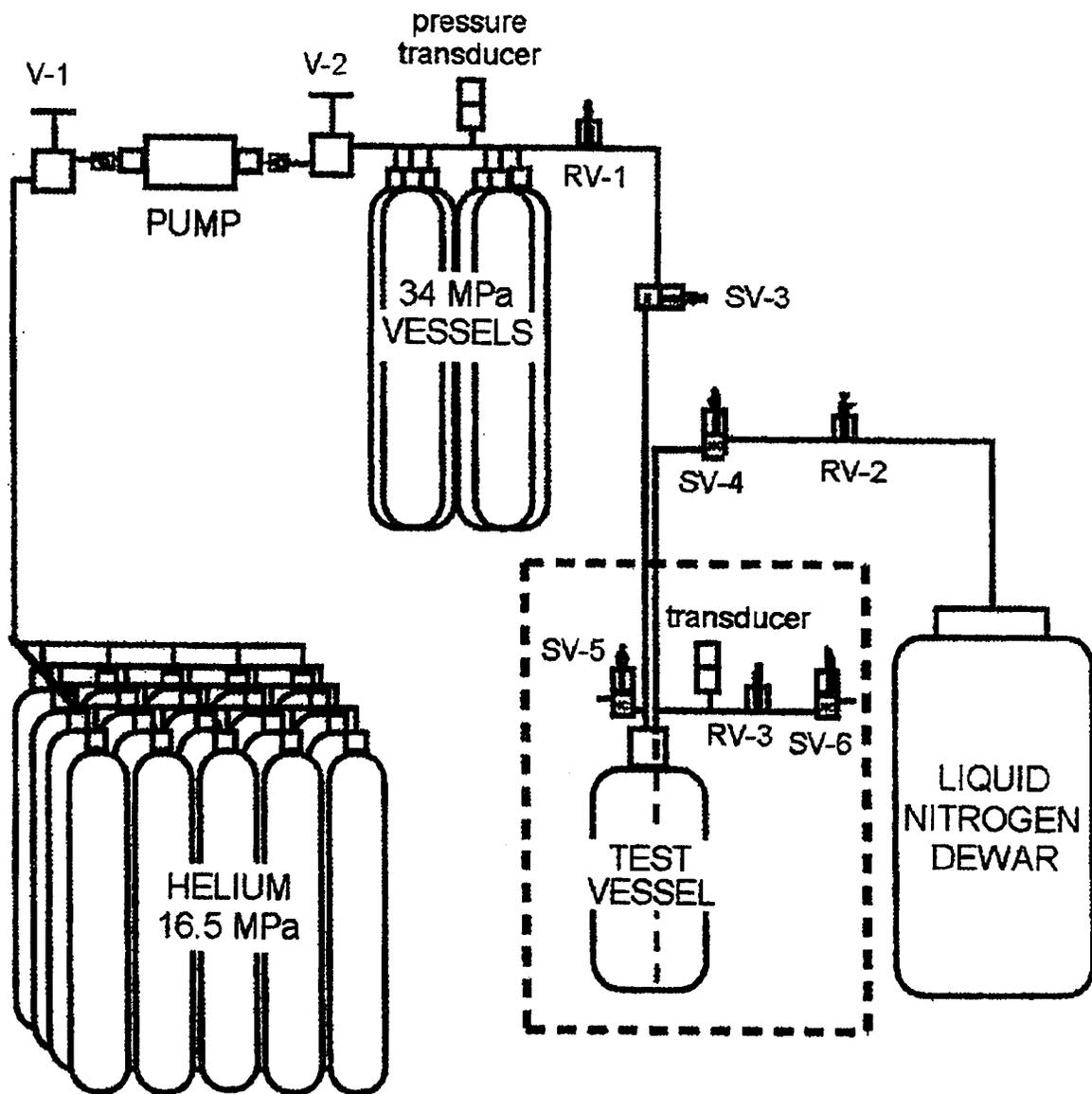


Figure 5. Schematic of the experimental setup for temperature and pressure cycling of a pressure vessel.

```

ANSYS 5.3
MAY 11 19
18:35:21
NODAL SO
STEP=1
SUB =18
TIME=9
TEMP
TEPC=96.
SMN =80
SMX =300

```

80
104
128
153
177
202
226
251
275
300

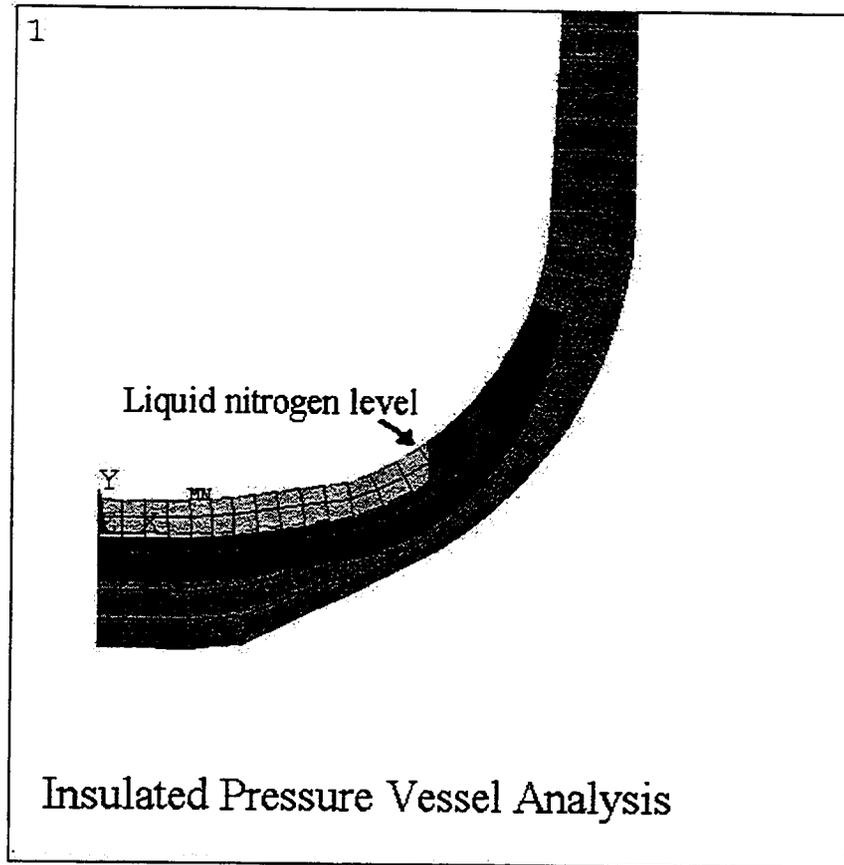


Figure 6. Finite element analysis mesh and temperature distribution during the early stage of the filling process. The figure shows the lower part of the vessel, along with the mesh used in the simulation. Only half of the vessel is analyzed, due to symmetry.

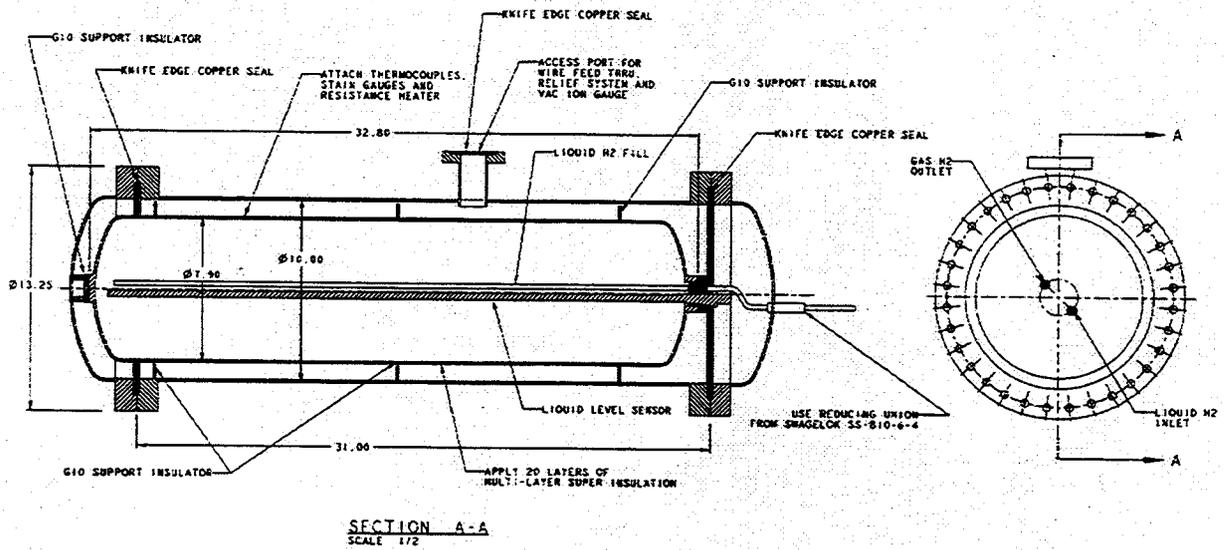


Figure 7. Insulation design for pressure vessel. The figure shows a vacuum space, for obtaining high thermal performance from the multilayer insulation, and instrumentation for pressure, temperature, level and strain.

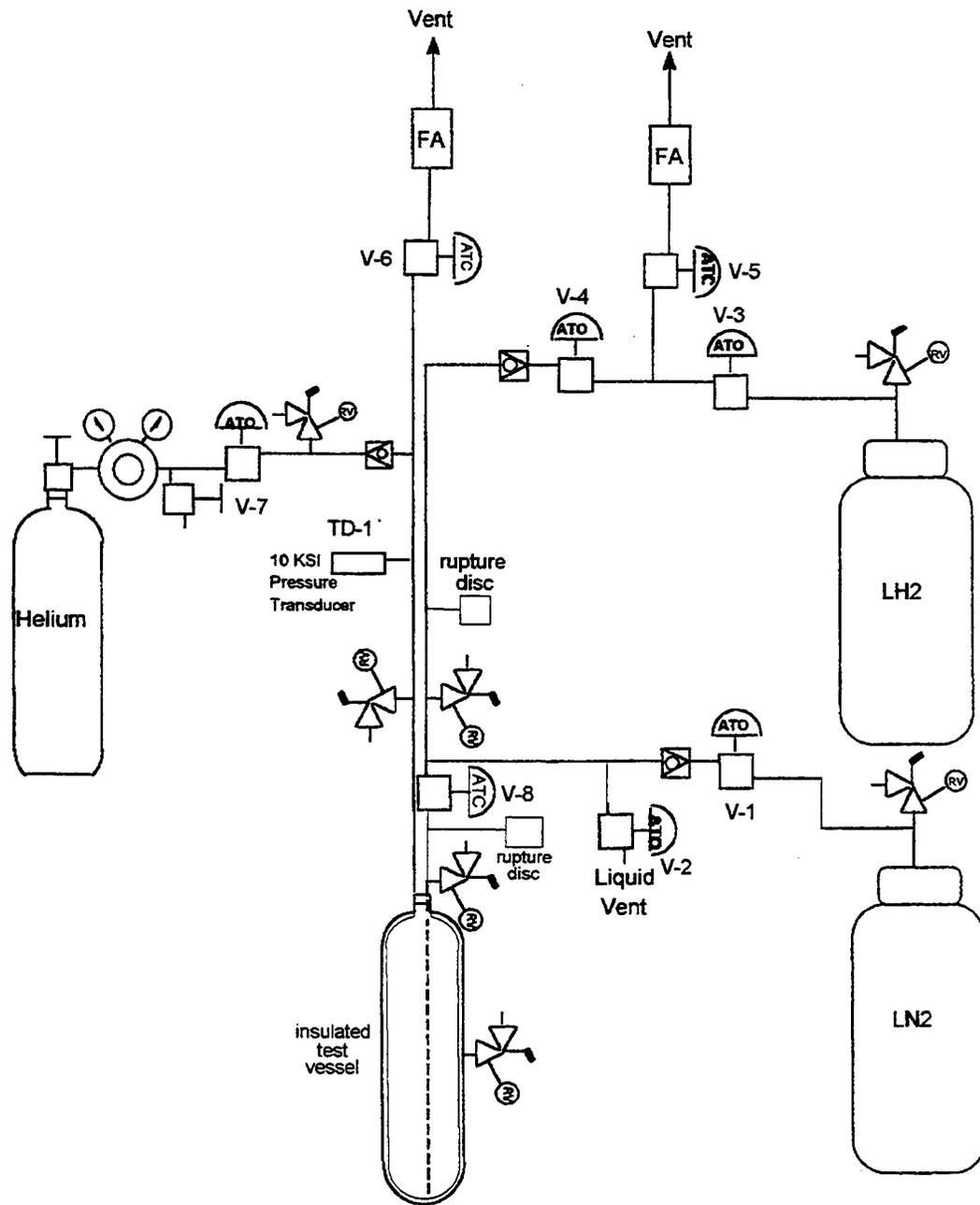


Figure 8. Schematic of the experimental setup for liquid hydrogen cycling of the instrumented and insulated pressure vessel.