VALIDATION OF CRYO-COMPRESSED HYDROGEN STORAGE (CCH_2) – A PROBABILISTIC APPROACH

Kircher, O.[1], Greim, G.[1], Burtscher, J.[1] and Brunner, T.[1]
[1] BMW Group, 80788 Munich, Germany, Oliver.Kircher@bmw.de

ABSTRACT

Due to its promising potential to overcome the challenge of thermal endurance of liquid hydrogen storage systems cryo-compressed hydrogen storage (CcH_2) is regarded as a very promising physical storage solution, in particular for use in larger passenger vehicles with high energy and long range requirements. A probabilistic approach for validation of safe operation of CcH_2 storage systems under automotive requirements and experimental results on life-cycle testing is presented. The operational regime of BMW's CcH_2 storage covers pressures of up to 35 MPa and temperatures from +65 °C down to -240 °C, applying high loads on composite and metallic materials of the cryogenic pressure vessel compared to ambient carbon fiber reinforced pressure vessels. Thus, the proof of fatigue strength under combined pressure and deep temperature cyclic loads remains a challenging exercise. Furthermore, it will be shown that the typical automotive safety and life-cycle requirements can be fulfilled by the CcH_2 vehicle storage system and, moreover, that the CcH_2 storage system can even feature safety advantages over a CGH_2 storage system, mainly due to the advantageous thermodynamic properties of cryogenic hydrogen, the lower storage pressure, and due to the intrinsic protection against intrusion through the double-shell design.

1 FUTURE AUTOMOTIVE ENERGY STORAGE – MOTIVATION AND CONSTRAINTS

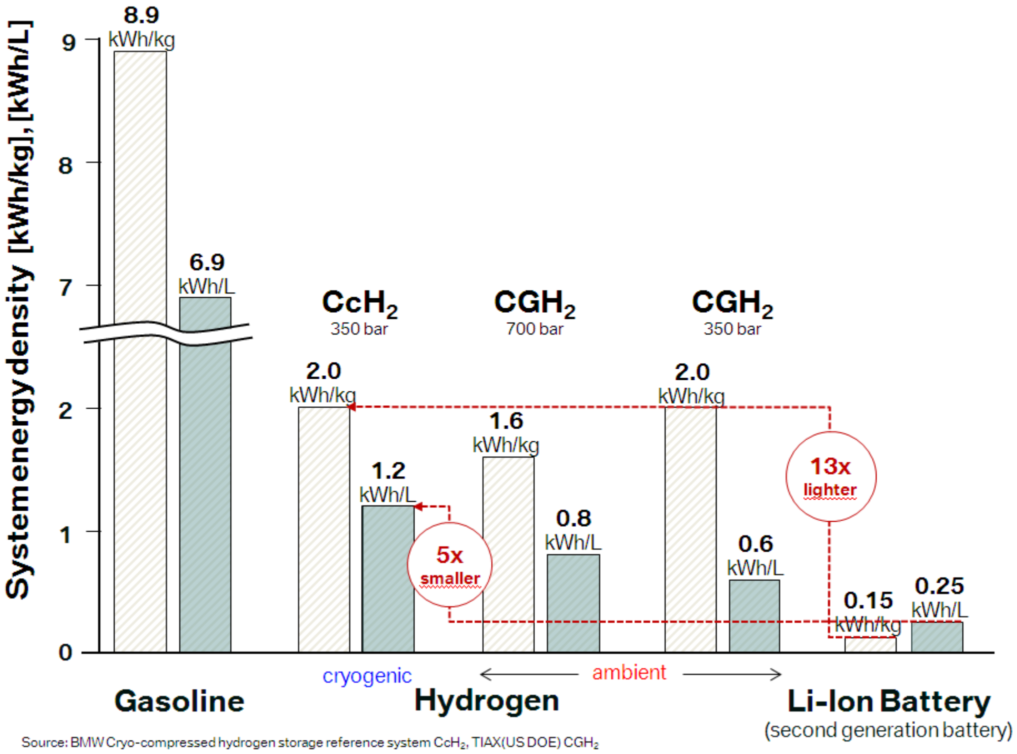
In a time of dwindling fossil resources and of climate change influenced by their use, greater efforts are being made throughout the world to make renewable energies usable and at the same time to develop alternative fuels for the mobility of the post-fossil era. In addition to the forthcoming 'peak oil' event and the resultant gradual end to cheap, readily obtainable crude oil, development activities concerned with alternative automotive drive-trains and energy storage systems are being boosted by policy requirements such as the Californian ZEV program [1], city center road-usage tolls and also CO_2-based tax legislation. A study recently published by DLR [2] demonstrates that world energy requirements in the 21st century can be economically covered by renewable energy sources and thus the dependence on fossil energy sources can be greatly reduced in the medium to long term.

Although the direct utilization of renewably generated electric power in the vehicle by means of battery storage combined with an electric drive-train is highly efficient from an energy point of view, problems of insufficient storage capacity (cf. Fig. 1) and of rapid battery charging remain as yet unsolved and limit the use of pure electric vehicles to the smaller vehicle segments and to urban or regional utilization.

In the long term there is a need to replace present-day fossil fuels with a satisfactory substitute on a chemical basis. From the present viewpoint, hydrogen is the sole chemical energy carrier which has the potential to fully replace conventional fuels. Systemic energy storage densities markedly higher than those of batteries and the considerably shorter filling times of the energy-densest hydrogen tanks already available or in development promise similar ranges and comfort functions to present-day gasoline and diesel powered vehicles.

Up to the current moment there are three different conceptual approaches to hydrogen storage in the automobile: firstly, storage in pressure tanks at ambient temperature and at pressures up to 700 bar (CGH_2 Compressed Gaseous Hydrogen); secondly, the adsorption of the hydrogen in porous solid materials or absorption in hydrides; and thirdly, cryogenic storage in the form of liquid hydrogen (LH_2) close to its boiling point.

However, faced with the challenging requirements of the automotive sector, each of these three possible methods comes up against their respective technical limits. Storage under high pressure involves relatively high installation space requirements in the vehicle; hydrogen-absorbent materials are too heavy and result into a complex energy and heat management. Liquid hydrogen storage reaches the highest gravimetric and volumetric storage densities and with regard to adequate availability of energy is the most suitable fuel storage solution for future hydrogen vehicles [3]. Despite the use of extremely high-performance super-insulation designs it has not yet been possible to find a solution for the problem of the boil-off losses occurring in liquid hydrogen storage tanks induced by heat input occurring during relatively long periods of idleness or in vehicle usage cycles with a low proportion of actual driving. In particular, the limited down-scalability of liquid hydrogen storage tanks defines the optimum field of application in the segments of large passenger cars, fleet passenger cars (multiple-driver service) as well as buses and trucks.



Source: BMW Cryo-compressed hydrogen storage reference system CcH_2, TIAX (US DOE) CGH_2

Figure 1. Energy densities of vehicle storage systems (Gasoline, CcH_2, Li-Ion battery: source BMW / CGH_2: source [4])

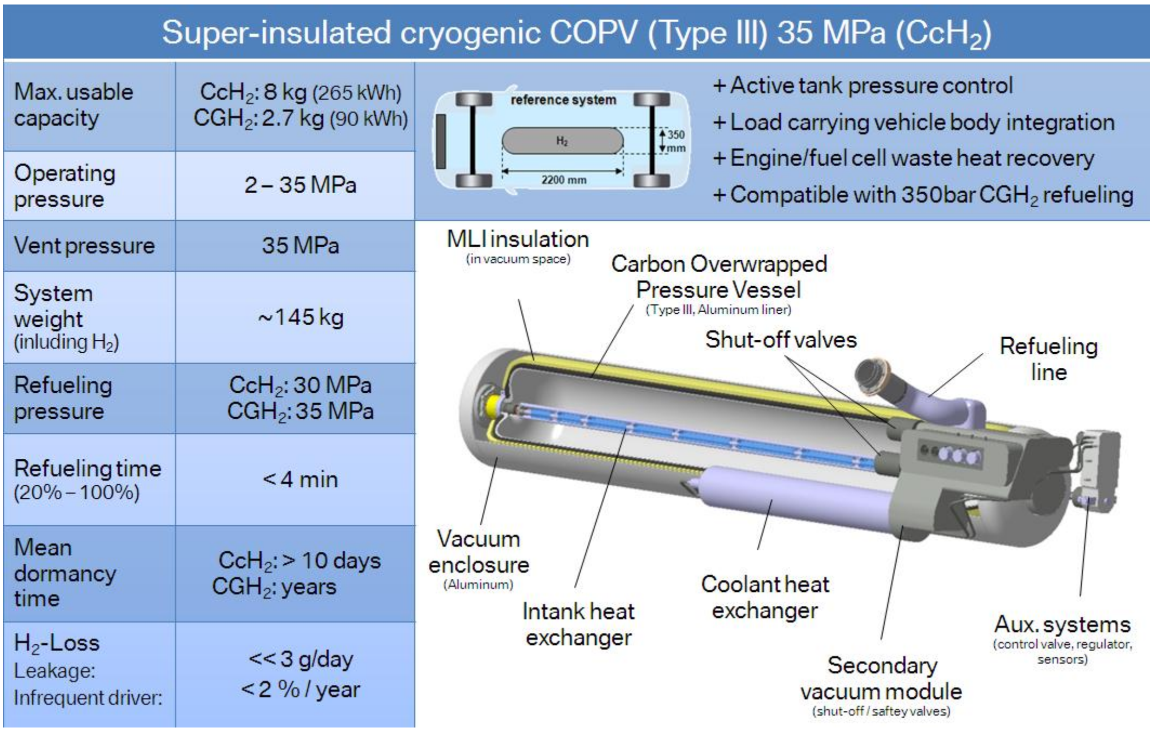
As a possible solution for the problem of boil-off losses and the high requirements regarding insulation quality, BMW has developed the concept of supercritical cryo-compressed hydrogen storage (CcH_2 Cryo-compressed Hydrogen) which promises a simpler and more cost-efficient insulation while enabling loss-free operation of the vehicle storage tank in all typical automotive customer cycles [5, 6].

Fig. 1 shows the volumetric energy density advantage offered by a cryo-compressed hydrogen storage tank in comparison with both the hydrogen storage tanks currently available (CGH_2 at 350 bar as well as 700 bar) and the Li-ion batteries used in battery electric vehicles. Compared with the hydrogen storage tanks available today, the cryo-compressed storage tank has the highest system-based volumetric and gravimetric storage density potential. Furthermore, it can also be seen from Fig. 1 that hydrogen storage tanks can have considerably higher volumetric and gravimetric system storage densities than Li-ion batteries.

Even taking into consideration the much higher total efficiency of a vehicle with a battery-based electric drive as compared to a fuel-cell drive (approx. factor of 1.5 – 2) or a hybridized hydrogen-internal combustion engine (approx. factor of 2 – 3), hydrogen storage tanks still have markedly higher storage densities available for power take-off (efficiency-corrected) which can be used for propulsion or for comfort functions. Accordingly, a fuel-cell vehicle with a cryo-compressed hydrogen storage tank stores up to 7.5 times (2.5 times) the effectively deliverable energy as a battery-powered vehicle with the same storage weight (storage volume).

2 OPPORTUNITIES, POTENTIALS AND CHALLENGES OF CRYO-COMPRESSED HYDROGEN STORAGE TANKS

Fig. 2 depicts the concept and basic performance data of the BMW cryo-compressed storage tank. It is based on the idea of compressing liquid hydrogen to a supercritical pressure level and storing it as cryo-compressed hydrogen gas (CcH_2) in an insulated pressurized vessel suitable for cryogenic temperatures. The design of the cryo-compressed storage tank is similar to that of a liquid hydrogen tank and consists of an inner vessel – taking the form of a carbon-fiber-reinforced composite pressure vessel with a metal liner – an all-enveloping layer of vacuum super-insulation with multi-layer radiation shields to minimize heat input into the inner vessel, and a lightweight outer vessel which acts as a vacuum enclosure. A decisive criterion for the feasibility of the CcH_2 tank in an automotive application is a combination of the advantageous properties of CGH_2 pressure tanks and liquid hydrogen tanks while simultaneously minimizing the demands made on the critical subsystems of both storage types – in other words, the heavy carbon fiber overwrapped pressure vessel and the complex vacuum super-insulation.



Super-insulated cryogenic COPV (Type III) 35 MPa (CcH_2)

Max. usable capacity	CcH_2: 8 kg (265 kWh) CGH_2: 2.7 kg (90 kWh)
Operating pressure	2 – 35 MPa
Vent pressure	35 MPa
System weight (inluding H_2)	~145 kg
Refueling pressure	CcH_2: 30 MPa CGH_2: 35 MPa
Refueling time (20% – 100%)	< 4 min
Mean dormancy time	CcH_2: > 10 days CGH_2: years
H_2-Loss Leakage: Infrequent driver:	<< 3 g/day < 2 % / year

+ Active tank pressure control
+ Load carrying vehicle body integration
+ Engine/fuel cell waste heat recovery
+ Compatible with 350bar CGH_2 refueling

Figure 2. Concept and performance data of the cryo-compressed storage tank

In addition to the advantages related to volumetric and gravimetric storage density which have already been discussed in the previous section, the storage of hydrogen in cryo-compressed tanks offers many more advantages, opportunities and potential as compared with pressurized hydrogen and liquid hydrogen storage technology:

- Lower requirements for expensive carbon fibers due to designing for a maximum tank pressure of 350 bar as compared with 700 bar for state-of-the-art CGH_2 storage tanks could lead to lower material and even production costs for CcH_2 in comparison with CGH_2 tanks [7].

- Long hydrogen loss-free dormancy times minimize the risk of hydrogen boil-off losses during long periods of parking or low vehicle use in comparison with LH_2 tanks.

- Energy and heat management requirements are compatible with not only internal combustion engines but also fuel cell drive systems. In particular low-temperature PEM fuel cells might benefit from the cooling power of cryogenic hydrogen that is warmed up by waste heat from the fuel cell.

- Intrinsic safety features, which will be discussed in detail in chapter 4.

The possibility filling with both, cryo-compressed hydrogen and compressed hydrogen enables a high refueling flexibility at filling stations with different hydrogen supply paths (pipeline or compressed tube trailer supply in the case of compressed hydrogen or trailer supply in the case of liquid hydrogen). From today's viewpoint, single-flow cryo-compressed refueling without pre-cooling the vehicle tank potentially is the most cost-efficient and fastest refueling method since the filling station basically only requires a cryo pump in addition to the liquid hydrogen storage tank and does not need high-pressure tank arrays, heat exchangers and gas compressors.

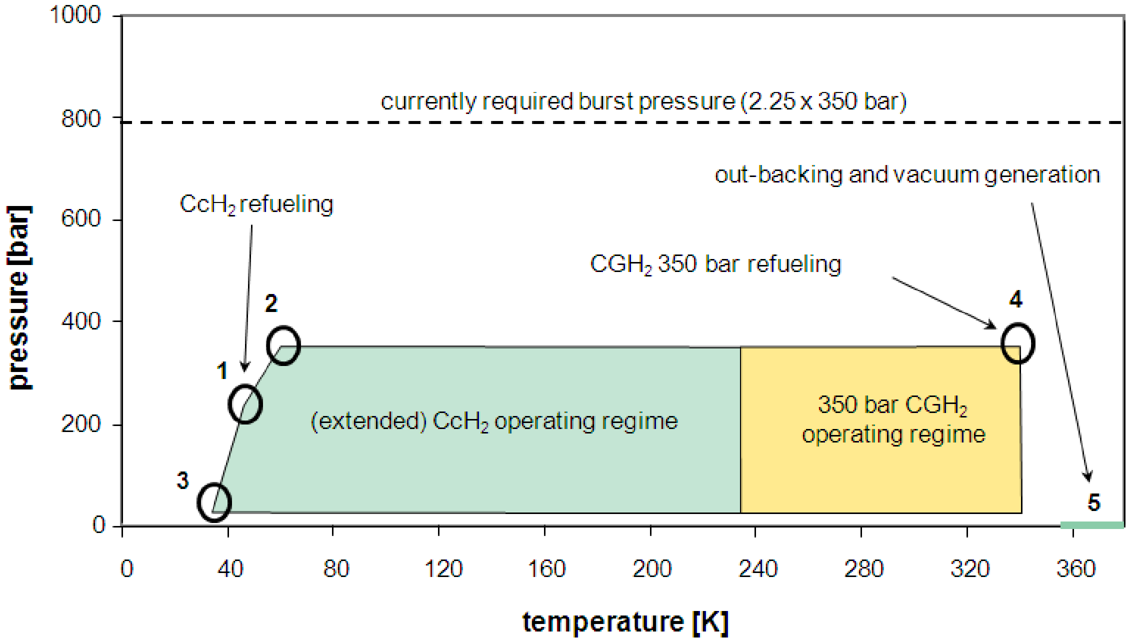


Figure 3. Operating range of a CcH_2 tank in comparison with a CGH_2 tank

However, due to the expansion of the operating range of a CGH_2 tank to temperatures down to –240 °C, new requirements arise for the metallic and composite materials used in the inner vessel as well as for all components through which cryogenic and / or hydrogen at high pressure flows (see Fig. 3). According to the latest BMW concept the CcH_2 tank is filled at 250 – 300 bar and approx. 45 – 70 K (Point 1 in Fig. 3). If refueling is immediately followed by a relatively long parking period , the pressure will build up to 350 bar (Point 2) and when hydrogen is discharged from the tank after refueling the pressure will drop as low as 20 bar at approx. 33 K (Point 3). In the case of several successive CGH_2 refuelings, the highest tank pressure of 350 bar at the highest temperature of up to 340 K can theoretically be reached (Point 4). Production-related constraints require a soaking-up phase at approx. 360 – 390 K for several days (Point 5).

3 VALIDATION OF SAFE OPERATION AND STRUCTURAL DURABILITY USING A PROBABILISTIC APPROACH

In addition to manufacturing costs and operating performance the feasibility of an adequate testing program for validation of the structural durability over a complete costumer life is also a crucial issue for a market launch of a hydrogen vehicle.

On the one hand the damage exerted on the core components of the storage system, in particular on the pressure vessel, due to costumer behavior and environmental influences is to some extent unknown or at least uncertain. On the other hand the typical failure behavior and the damage tolerance of these core components and, respectively, the distribution of these parameters when considering a huge ensemble of storage systems is also unknown to some extent in the design and development phase of a new product. Furthermore, a hydrogen storage system which is in use in a costumer vehicle in daily road traffic has to prove the highest reliability which is currently feasible.

The BMW policy requires hydrogen vehicular storage systems to be “as safe as conventional components in conventional cars”. As a consequence, the highest level of safety requirements has to be applied for the hydrogen storage system and its components. Thus, the required reliability over a cumulated costumer life is that 99.86% of the storages must not show any hydrogen leakage higher than the allowed level under normal operation for 99% of the costumers. Assuming a frequency scatter of three (ratio between the probability of 10 % and 90 %) for service loads and durability, the failure rate over the whole costumer life will be below 0.0085%. Thereby, a failure may only be hydrogen leakage, a more severe failure like burst of the pressure vessel is literally prohibited. The validation concept is illustrated in Fig. 4. The damage exerted on the storage or one of its components from the average costumer load cycle is set to one. The probability of failure in that diagram is the cutting area of costumer and component distribution curves.

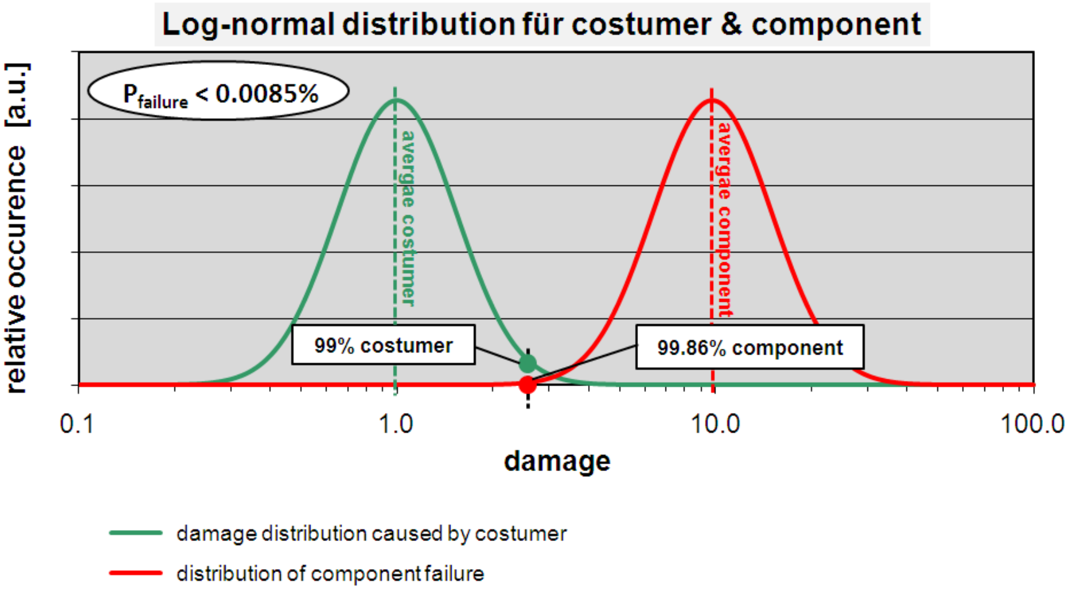


Figure 4. Validation concept of BMW CcH_2 storage system

Applying this validation concept, the storage with its core components on the one hand has to be designed to withstand at least ten times the damage exerted on storage and components by an average costumer load cycle. On the other hand, for a sufficient number of storages/components the operation of at least ten times the exerted damage by the average costumer load cycle has to be proven without failure. To design a suitable test cycle for validation BMW made a detailed analysis of the driving behavior of typical BMW costumers for different vehicle sizes. Out of these data we created a representative average costumer drive cycle and calculated pressure and temperature course on the storage and its core components using a thermal node model. With the knowledge of temperature and pressure course the damage accumulated on the storage and its components by the average costumer has been calculated using a miner calculation method[1].

Compared to compressed hydrogen storage systems cryo-compressed storage systems are not only exposed to pressure cycles but also to a significant quantity of temperature cycles as already mentioned in chapter 2. For the inner tank a suitable test cycle has been proposed for accelerated validation of its fatigue strength taking into account all relevant loads causing the most significant damage on the inner tank liner and composite. The proposed test cycle is depicted in Fig. 5. It consists of three consecutive single-flow CcH_2 refuelings starting from a near ambient temperature warm tank, a discharge phase with in tank pressure regulation making use of the inner tank heat exchanger and a CGH_2 refueling with ambient temperature hydrogen pressure gas. Both the third CcH_2 and the CGH_2 refueling are followed by a pressurization that helps to reach the highest operation pressure at cryogenic and ambient temperature conditions. As a result of applying such miner method for the calculation of the accumulated damage it turns out that about 7 test cycles represent the same damage to liner and composite than one year average costumer use[2].

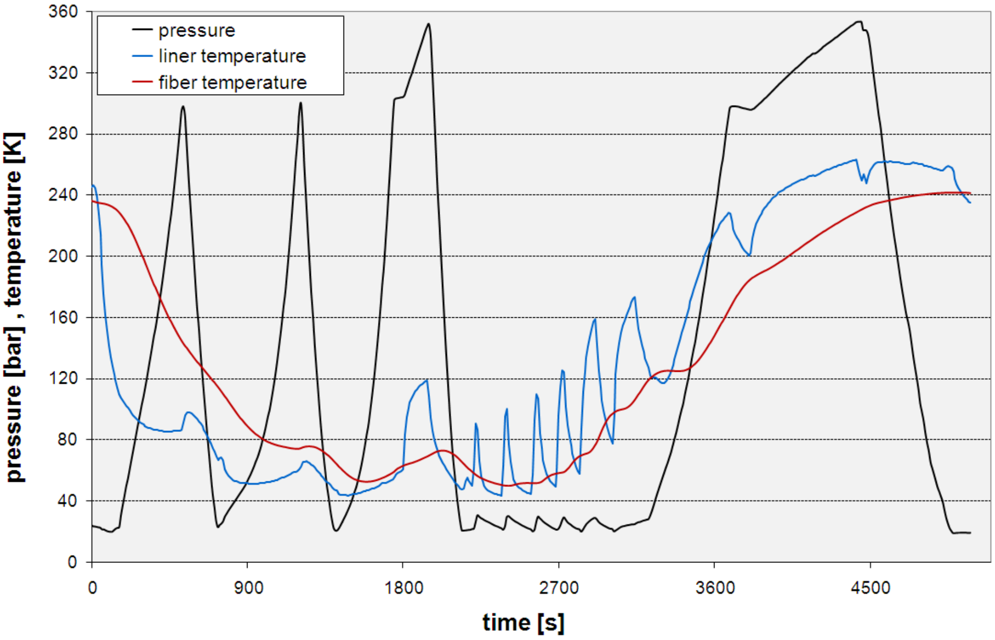


Figure 5. Test cycle for accelerated validation of a CcH_2 storage system

Like the pressure vessel in CGH_2 storage systems the inner tank of a cryo-compressed storage is designed in such way that the composite provides the necessary static strength against burst of the inner tank and the liner provides the required leak tightness. The hybrid assembly of liner and composite has to be designed in a way that the liner fails under extended cyclic pressure and temperature loads. In order to prove the fatigue strength of the inner tank for a complete costumer life

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[1] It has to be mentioned, however, that a calculation of damage accumulation with the miner method does not give any evidence in terms of absolute damage or structural durability. It is rather a comparative method between accumulated damages between different regarded load spectra.

[2] For the calculation temperature depended woehler curves with k = 5 (aluminum liner) and k = 12 (composite) have been used.

– assuming an average use of 15 years – about 1000 test cycles[3] like the one shown in Fig. 5 have to be proven without any leakage and a sufficient safety factor against burst at the end of cycling. In a first step BMW carried out a test series with one, 20 and 200 of test cycles on its CcH_2 prototype tank, each followed by burst test. The result is shown in Fig. 6. It can be seen that no tendency of degradation of static strength against burst can be detected with the applied number of test cycles.

Beyond pressure and temperature cycling also static pressure and vehicular vibration loads are considered for the validation of safe operation and structural durability. E.g., the inner tank cycled with pressure temperature cycles according to Fig. 5 was subjected to a static pressure test at 120% maximum operating pressure for 1 week after the first half of the cycles.

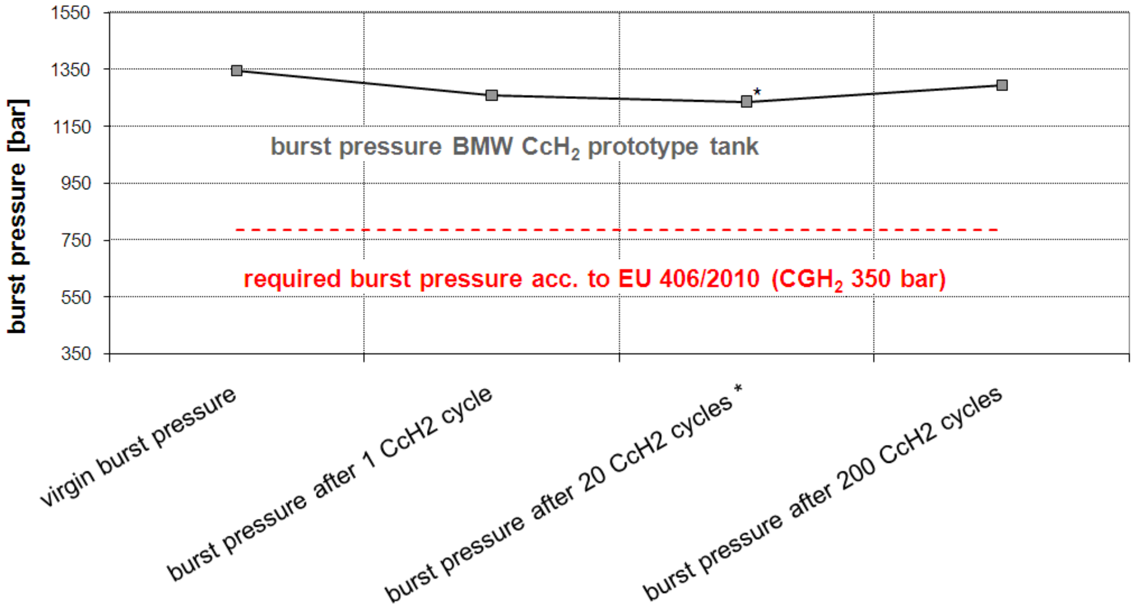

Figure 6. Evolution of CcH_2 inner tank burst pressure with increasing number of test cycles

To analyze the effect of the temperature on liner damage, a series of measurements on sub-scaled type III pressure vessels, which corresponded exactly to the original size vessel in all relevant characteristics like maximum operating pressure, composite lay-up, burst pressure, ambient temperature pressure cycles until liner fatigue and stresses in liner and composite at the corresponding operating conditions has been carried out. Altogether eight sub-scaled pressure vessels have been cycled until failure with hydraulic pressure cycles at ambient temperatures between 2 and 43.8 MPA, three of them without any pre-loads (virgin), three of them after 720 temperature cycles between 93 K and 273 K at low pressure with liquid nitrogen, one vessel after 1440 pressure temperature cycles performed with liquid nitrogen (test cycle similar to Fig. 5, two pressure changes per cycle, temperature range 93 K – 273 K) and one vessel after 1000 pressure temperature cycles performed with cryo-compressed hydrogen (test cycle nearly identical to Fig. 5, four pressure changes per cycle, temperature range 50 K – 273 K).

From Fig. 7 it can be seen that even after 1000 cryo-compressed test cycles the dynamic strength of the liner in terms of residual hydraulic cycles to failure decreased only slightly compared to a virgin sub-scaled vessel. On the other hand, pressure-temperature pre-loads (1440 cycles) and particularly temperature pre-loads (720 cycles) performed with liquid nitrogen obviously lead to a more serious

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[3] 15 years x 6 test cycles per year x factor 10 (cf. Fig. 4)

damage accumulation compared to pressure-temperature pre-loads performed with cryo-compressed hydrogen (1000 cycles).[4]

These results are not yet fully understood and further tests are necessary to verify the difference in damage through temperature and combined pressure and temperature cycling with LN_2 and CcH_2. However, it may be an indication that temperature gradients which inherently occur in the liner when cooling with a cryogenic liquid – including implications like sloshing and evaporation effects – has a more harmful impact on the fatigue strength of the liner than temperature changes caused by pressure-temperature cycles with supercritical cryo-compressed hydrogen gas. To thoroughly understand the impact of temperature cycles on the dynamic strength of the liner more data is required. Provided that the impact of temperature cycles and pressure cycles can be separated from each other, testing efforts could be reduced in a future validation program , e.g. by proving the structural durability of the inner tank in terms of combined temperature and pressure loads by isothermal pressure cycling at different temperature levels.

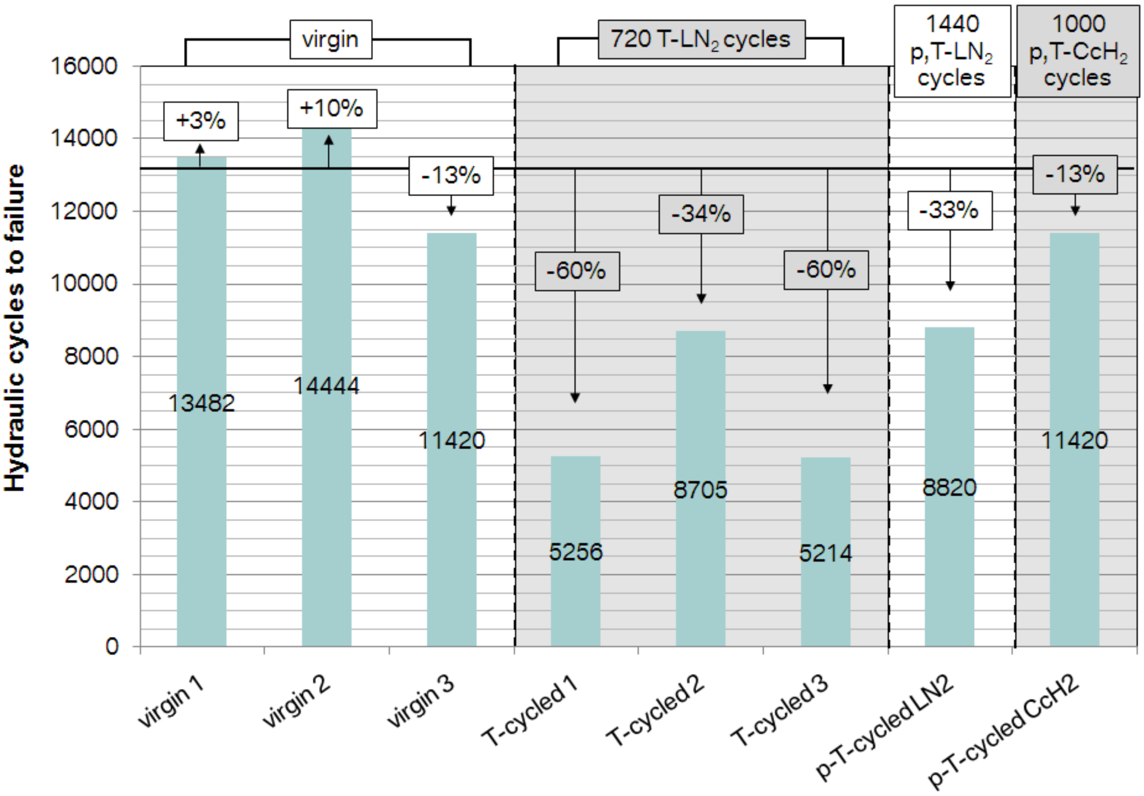

Figure 7. Number of hydraulic cycles to liner failure for virgin sub-scaled vessels and pre-loaded sub-scale vessels as marked in the diagram and described in the text

Regarding the static strength against burst of the inner tank more statistical data is necessary in terms of the influence of combined pressure and temperature cycles on the burst pressure. Currently, even a reduction of the composite wall thickness seems to be possible in future cryo-compressed storage systems because current safety factors (ratio of burst against maximum operating pressure) are well above required safety factors (see Fig.6).

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[4] On the basis of a miner calculation for the liner (temperature dependent woehler curve, k = 5) 1440 pressure temperature cycles performed with liquid nitrogen lead to an accumulated damage of only about 70%, 720 temperature cycles performed with liquid nitrogen even to a an accumulated damage of only about 1% of the accumulated damage of 1000 pressure temperature cycles performed with cryo-compressed hydrogen.

4 SAFETY ASPECTS OF CRYO-COMPRESSED HYDROGEN STORAGE

Operational safety and a sufficient safety level in case of a malfunction is an important issue for mobile energy storages, in particular for high pressure gaseous storage systems like compressed natural gas (CNG) and compressed gaseous hydrogen (CGH_2) storage systems.

The cryo-compressed storage system both exhibits intrinsic and supplemental safety features. Intrinsic safety features provided by the vacuum casing (protection against external mechanical influences, intrinsic leakage monitoring, controlled discharge of hydrogen via safety lines in the event of leakage) and, in the event of failure, the low adiabatic expansion energy of hydrogen at cryogenic temperatures provide a high level of safety.

4.1 Vacuum casing

The vacuum casing on the one hand provides protection against external mechanical and chemical intrusion as well as external thermal influence. The composite operates under vacuum conditions and does not see any humidity overv lifetime, which is known to enhance fatigue effects in the composite in particular in combination with high temperatures. On the other hand the vacuum enables a sensitive leak monitoring method of the inner pressure vessel and of all connecting pipes between the inner and outer tank. Already leakages of a few mg of hydrogen into the vacuum space would lead to a vacuum pressure increase to about 1 mbar, which then significantly increases the heat flux from the outer to the inner tank and thus, is easy to detect by monitoring the pressure in the vessel.

In case of a fire the vacuum casing protects the inner tank pressure vessel against direct flame impingement. The time until thermal pressure relief device activation is not as critical as for storage systems without additional insulation like CNG and CGH_2 storage systems.

4.2 Cryogenic temperature of the stored hydrogen

In the event of a failure of hydrogen storage, depending on the state of the stored hydrogen, a significant fraction of the stored energy can be released in a short period of time. For CNG storage, e.g., several accidents so far happened during a refueling due to misuse of the storage by the costumer.

In this context the adiabatic gas expansion energy determines the impact of a fatal storage failure. Despite intensive validation efforts and highest requirements on operational safety it will never be possible to fully exclude fatal pressure vessel failure in a serious accident or by manipulation when the number of hydrogen vehicles on the roads increases to a significant level.

In Fig. 8 adiabatic expansion energies of different hydrogen storage systems are compared. It can be seen that in particular the temperature of the stored hydrogen has a significant impact on the released energy in case of a sudden vessel failure. Thus, the low adiabatic expansion energy of hydrogen at cryogenic temperatures provides a potentially high level of safety.

4.3 Independent Safety devices against overpressure

Like liquid hydrogen storage systems cryo-compressed storage systems feature two independent pressure-triggered mechanical safety devices. These pressure relief devices protect the storage against over pressure in case of unwanted degradation or loss of vacuum or other reasons leading to an increased heat flux to the inner tank. Combined with the thermal pressure relief device(s) an overall high safety level can be achieved in a cryo-compressed storage system.

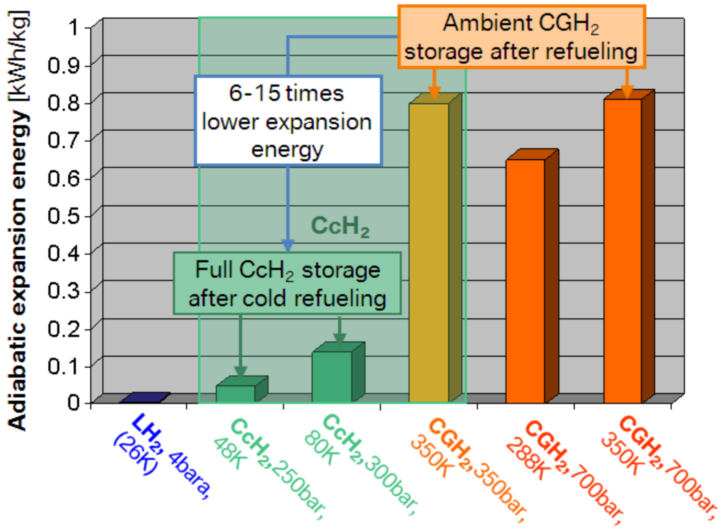

Figure 8. Comparison of adiabatic expansion energies per kg stored hydrogen for different hydrogen storage technologies

5 CONCLUSION AND OUTLOOK

Currently, BMW is validating a prototype cryo-compressed storage system under consideration of all automotive boundary constraints. Advanced functional and service-strength validation tests on the basis of a probabilistic approach have been developed and so far successfully performed on the storage vessel and all key components. Beyond that it has been shown that cryo-compressed storage features several safety advances compared to compressed hydrogen storage. Further tests to improve the statistic validity of fatigue strength and operational safety as well as a proposal for a complete test program for validation of a cryo-compressed storage system will be developed by BMW in the near future.

A fully working prototype will be available by middle of 2011. Consequently, vehicle application for demonstration of cryo-compressed storage and refueling can be started in 2011.

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