

REVIEW AND SOME RESEARCH RESULTS ON HYDROGEN LIQUEFACTION AND STORAGE

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ABSTRACT

Hydrogen is going to play a key role in the future world energy market. Production and storage of hydrogen in liquid form is an important factor in the supply chain. This paper presents a review on hydrogen liquefaction and storage techniques. In addition, some research results on magnetic refrigeration liquefaction and zero boil-off (ZBO) cryogenic liquid storage are presented. A hydrogen liquefaction cycle based on the use of magnetic refrigeration is analyzed. The magnetic refrigerator consists of two heat exchangers and two stages of periodically magnetized/demagnetized beds that produce refrigeration load on helium as heat transfer fluid. Numerical simulation is used to study the fluid flow and heat transfer in a zero boil-off cryogenic storage facility for liquid hydrogen using three-dimensional and axi-symmetric models. The system inside the storage tank includes a heat pipe for passive heat dissipation and a pump-nozzle unit that collects fluid and discharges onto the evaporator of the heat pipe in order to prevent the fluid to boil off.

Keywords: Hydrogen storage, Magnetic liquefaction, Zero boil-off cryogenic storage.

1. INTRODUCTION

Hydrogen has been recognized as a powerful and clean fuel for a few decades for space applications [1], and recently for general transportation such as automobiles [2]. Hydrogen has been identified to play a key role as an energy source in the future. It has the highest energy content per unit mass of any known fuel. When burned in an engine, hydrogen produces effectively zero emission. When powering a fuel cell, its only waste is water. Hydrogen can be produced from abundant domestic resources including natural gas, coal, biomass, and even water. However, significant technological challenges exist towards reducing its cost and storage volume and assuring its safety. The objective of this paper is to give an overview of hydrogen liquefaction and storage techniques and to talk about some recent research results on these issues. Although hydrogen has many advantages over most conventional fuels, efficient storing of hydrogen is difficult because of its very low density [3]. The technical challenge of producing and storing liquid hydrogen is that hydrogen has a very low boiling point (approximately 20 K at a pressure of 0.1 MPa or 1 bar).

Hydrogen liquefaction can be carried out by several means among which magnetic refrigeration is a promising new technique that is currently being developed. On hydrogen storage, there are generally five techniques: compressed gas, cryogenic liquid, metal hydrides, chemical hydrides, and nanostructured carbon.

Hydrogen storage as compressed gas is relatively simple and can be performed at ambient temperature. The typical storage tank pressure is in the range of 5000 - 10000 lbf/in² (345–690 bar). The storage capacity is low compared to other techniques. Cryogenic liquid storage of hydrogen requires more equipment for its liquefaction, but the storage capacity is high. One disadvantage of this technique is the boiling-off of hydrogen that creates unbearable tank pressure. Therefore, the fuel needs to be vented frequently to preserve the tank pressure limit yielding storage losses. Hydrogen can also be stored in metals and alloys in the form of metal hydrides. This technique relies on a reversible reaction of adsorption of the gas into the solid. It has low storage capacity and requires heat transfer for activating the processes. Chemical hydrides release hydrogen when they react with other substances such as water. This reaction is not reversible. This technique also has relatively low storage capacity. Hydrogen storage in nanostructured carbon is a new technique that is being developed using new carbon materials such as carbon nanotubes. This technique is expected to give high storage capacity but it is still in developing phase. Among the different storage techniques available, cryogenic liquid storage of hydrogen is preferred because of relatively lower storage volume and the ease of regeneration of the fuel with variable demand.

For production and storage of liquid hydrogen, there are two important issues: liquefaction and cryogenic

storage. Magnetic refrigeration is a new technique for hydrogen liquefaction. Magnetic refrigeration is based on the physics of the magnetocaloric effect. This effect is the physical process by which some magnetic materials experience a temperature change when subjected to a magnetic field under adiabatic conditions. Several thermodynamic cycles can be implemented using this effect typically involving magnetization and demagnetization processes coupled with heat transfer to and from magnetic materials [4]. A magnetic refrigerator is one implementation of this type of cycles.

Liquid storage of hydrogen has significant advantage over gaseous or chemical storage because of significantly smaller storage volume. However, conventional cryogenic storage tanks suffer loss of hydrogen due to boil-off of the cryogen induced by heat leak to the tank from the surrounding environment. In order to keep the inner pressure within the structural limits of the tank, the stored fluid needs to be periodically vented. The Zero Boil-Off (ZBO) concept has evolved as an innovative means of storage tank pressure control by a synergistic application of passive insulation, active heat removal, and forced mixing within the tank. The goal is that the fuel can be stored for a very long time with almost no loss.

2. LITERATURE REVIEW

There are many researches in recent decades concerning hydrogen liquefaction and storage. Domashenko et al. [5] presented a study of operating experience and development of large-scale liquid hydrogen production plant and long term storage and delivery of the fuel. Ogawa et al. [6] presented a study on the utilization of LNG latent heat for hydrogen gas production as well as the liquefied hydrogen process. They elaborated that liquefaction of hydrogen gas needs energy that cannot be recovered. Therefore, it is important to propose new methods of liquefaction that consider minimizing that loss. The power consumption depends on one hand on the basic efficiency of the chosen cycle and on the other hand on the performance of different system components. Quack [7] showed that these two factors are not independent of each other.

There has been a widespread discussion of the possibility of using hydrogen as a fuel for aircraft and automobiles as oil supplies diminish, although a novel and energy-efficient means of producing hydrogen must be developed before this becomes reality [8]. The liquefaction of hydrogen can be accomplished by employing the same principles as those used for air liquefaction; however, there are several practical limitations. The inversion temperature for the Joule-Thomson effect is at approximately 204 K; therefore isenthalpic expansion will not produce cooling unless hydrogen is first precooled below this temperature. Most of the hydrogen liquefiers employ the Joule-Thomson principle and use liquid nitrogen for precooling [9]. Large-scale hydrogen liquefaction ranges in size from 6 to 55 Mg/day. The main problems encountered in the liquefaction of hydrogen are the precooling and the liquefaction itself [10].

Magnetic refrigeration profits on the fact that the

temperature of certain materials increases when placed in a magnetic field, and likewise decreases when the magnetic field is removed. This phenomenon is known as the "magnetocaloric effect, MCE". Research on magnetocaloric effect has been associated with materials for very low temperature applications such as helium or hydrogen liquefaction as well as materials near room temperature applications such as conventional air conditioning and refrigeration [11]. Shirron et al. [12] presented test results of an adiabatic demagnetization refrigerator that produced continuous cooling at sub-Kelvin temperatures. Barclay [13] analyzed magnetic refrigeration cycles and concluded that magnetic refrigeration has a good potential for certain air conditioning applications. Hagmann and Richards [14] proposed a two stage magnetic refrigerator for astronomical applications. Barclay et al. [15] presented experimental data for a reciprocating magnetic refrigerator. Tishin et al. [16] presented an adiabatic temperature rise under a magnetic field representing the magnetocaloric effect of gadolinium. Pecharsky and Gschneider [17] presented a review on magnetic refrigeration design. They commented about the development of new magnetic refrigeration technology as an energy efficient and environmentally safe alternative to existing vapor compression refrigeration. Magnetic refrigeration has been used chiefly as a cooling method to obtain temperatures below 1 K. During the past ten years, however, the technology has been developed also for refrigeration applications at temperatures above 1 K. The former type of magnetic refrigerator utilizes an adiabatic one-shot process to approach zero Kelvin as a purely scientific goal. For applications at temperatures higher than 1 K, a continuously cycling magnetic refrigerator with reasonable refrigeration capacity is needed. This latter type of refrigerator can be utilized in actual engineering applications, such as cooling sensitive electronics and optical devices on board spacecraft. DeGregoria et al. [18] tested an experimental magnetocaloric refrigerator designed to operate within a range of about 4 to 80 K. Helium gas was used as the heat transfer fluid. A single magnet was used to charge and discharge two in-line beds of magnetic material. Zimm et al. [19] investigated magnetic refrigeration for near room temperature cooling. Water was used as the heat transfer fluid. A porous bed of magnetocaloric material was used in the experiment. It was found that using a 5T magnetic field, a refrigerator reliably produces cooling powers exceeding 500W at coefficient of performance of 6 or more. A theoretical model of the active magnetic regenerator refrigerator (AMRR) has been proposed by DeGregoria [20]. Johnson and Zimm [21] tested the AMRR model against a cryogenic experimental device. Astronautics Corporation of America (ACA [22]) presented a report regarding the construction of a subscale magnetic liquefier for hydrogen. The analysis was performed based on the study of the functioning of the magnetic materials. Iwasaki [23] presented a laboratory prototype refrigerator (liquefier) for hydrogen. His preliminary design indicates that there is a great potential for a magnetic liquefier.

In the field of hydrogen storage, most recent researches are focused on the effectiveness and portability for transportation applications, especially automobiles. Jones [24] evaluated different hydrogen storage concepts for the economic viability of hydrogen fueled vehicles based on the range of 500 kilometers. Wolf [25] presented a survey focusing on the use of liquid hydrogen as an automotive fuel in comparison with the use of compressed gaseous hydrogen. Vernersson et al. [26] presented methods for onboard storage of hydrogen for fuel cell vehicles where compressed gas and cryogenic liquid hydrogen are two most viable options. Huber [27] presented the challenge of hydrogen storage and potential solutions, focusing on hydride-based solid technique. Maeland and Hauback [28] discussed the advancement of hydrogen and fuel cell technologies in transportation and considered different storage techniques emphasizing on metal hydrides. The storage of hydrogen in activated carbon at liquid nitrogen temperature was studied by Zhou et al. [29]. Benard and Chahine [30] presented the results of a parametric and comparative study of adsorption on activated carbon and compressed gas storage of hydrogen as a function of temperature, pressure, and adsorbent properties.

Besides several new devising storage methods (carbon nanotubes, carbon fullerenes, and hydrides), conventional methods in which hydrogen is stored as a compressed gas or as a cryogenic liquid are still two primary storage techniques used in the industry. Ogden [31] discussed the storage of hydrogen for industrial applications and its safety. Chitose et al. [32] considered the transport and storage of a large quantity of hydrogen in a tank. Walter et al. [33] designed and constructed a prototype of a liquid-hydrogen storage tank for automotive application using the concept of superconducting suspension of the inner tank in an outer vessel. Wills [34] introduced an advanced hydrogen storage tank as a joint effort of General Motors and Sandia Laboratories. Mahmoud et al. [35] presented the modeling of the amount of liquid para-hydrogen vaporized during a discharging/charging process in a cryogenic storage system. Reiss [36] presented numerical simulations, using thermal networks, of shield temperature and radiative and conductive heat losses of a super-insulated cryogenic storage tank operating at 77 K. Khemis et al. [37] presented an experimental investigation of heat transfer in a cryostat without lateral insulation. Panzarella and Kassemi [38] presented a comprehensive analysis of the transport processes that control the self-pressurization of a cryogenic tank in normal gravity.

Cryogenic liquid hydrogen storage has a long history of development in space industry; most of it can be readily transferred to general transportation sectors. In recent years, a number of efforts have been done towards the development of cryogenic storage systems with the ZBO concept. Hasting et al. [39] presented an overview of the efforts in the development of the ZBO storage systems at NASA, showing that a ZBO system has mass advantage over passive storage. Kittel [40] suggested an alternative approach for the long term storage of cryogenic propellants using a re-liquefier that uses the

propellant vapor as the working fluid. Salerno and Kittel [41] presented the proposed Mars reference mission and the concomitant cryogenic fluid management technology with a combination of both active and passive technologies to satisfy a wide range of requirements. Hofmann [42] presented a theory of boil-off gas-cooled shields for cryogenic storage vessels using an analytical method to determine the effectiveness of intermediate refrigeration. Haberbusch et al. [43] developed a design tool for thermally zero boil-off densified cryogen storage system for space. The model predicted that a ZBO densified liquid hydrogen storage system reduces the overall storage system mass and volume. Wilson et al. [44] did a study with the goal of storing liquid hydrogen in space in a linerless composite tank for a period of 20 years with a 2% boil-off loss. Kamiya et al [45-46] consecutively presented the development of a large experimental apparatus to measure the thermal conductance of various insulations and used that for the testing of insulation structures. The apparatus could test specimens with dimensions up to 1.2 m diameter and 0.3 m thickness. Different insulation structures, a vacuum multilayer insulation with glass fiber reinforced plastic (GFRP) and a vacuum solid insulation were tested. Venkat and Sherif [47] studied a liquid storage system under normal and reduced-gravity conditions. Mukka and Rahman [48-49] used computational fluid dynamics (CFD) simulation to study the fluid flow and heat transfer in a cryogenic liquid hydrogen storage tank of displacement type where cool fluid enters the tank at one end, mixes with hot fluid inside, and exits at the other end. Rahman and Ho [50] studied the fluid flow and heat transfer in a closed ZBO cryogenic storage tank with a heat pipe and an array of many pump-nozzle units surrounding it as an artificial circulatory system. The numerical simulations were done using an axi-symmetric model because of the nearly axi-symmetric nature of the problem. Subsequently, Ho and Rahman [51] presented a parametric analysis for the fluid flow and heat transfer, focusing on the effect of the normal speed at the nozzle face, in a similar storage tank with only one pump-nozzle unit with a three-dimensional model.

Each of the storage technologies for hydrogen, at different levels of development and availability, has its own challenges in improving safety and reducing cost. The use of compressed gaseous hydrogen is limited by the allowable maximum pressure of the storage tank. Research on material and structure is needed to develop compressed gas tanks with higher maximum pressure. For liquid hydrogen storage, mass loss due to venting because of boiling-off is still an important challenge attracting most of the research and development efforts in the field. Combining with the search for better thermal insulation materials and structural design to reduce heat leak from the surroundings, active control techniques as used in ZBO cryogenic systems for liquid hydrogen storage are of great interest. Another concern is about techniques and equipment for handling hydrogen at cryogenic temperature especially for hydrogen liquefaction. For metal hydrides and chemical hydrides, the research efforts concentrate on increasing storage capacity and overall energy efficiency. Novel techniques

based on nanostructured carbon are very promising but still in very early stage of development. Recent research results are inconsistent and difficult to reproduce. The main storage mechanism is expected to be similar to that of metal hydrides, therefore energy efficiency would be the main issue for nanostructured carbon based techniques.

3. MAGNETIC LIQUEFACTION

3.1 Magnetic Refrigeration

The magnetic refrigeration system is schematically shown in Fig. 1. The beds are periodically magnetized and demagnetized and the fluid flows are arranged to meet the cycle requirements. Opening or closing the eight-valve set does the flow arrangement. For the first stage valves 1, 2, 3, and 4 are opened, and valves 5, 6, 7, and 8 are closed. In this case, the magnetic field is applied to the heater magnetocaloric bed while the cooler magnetocaloric bed has been demagnetized. When the magnetic field is released from the top bed and applied to the bottom bed, the cooler bed becomes the heater bed, and vice versa by exchanging roles. In this case valves 5, 6, 7, and 8 are opened and valves 1, 2, 3, and 4 are closed. The cycle then repeats itself every six seconds after the beds have switched functions (cooling or heating).

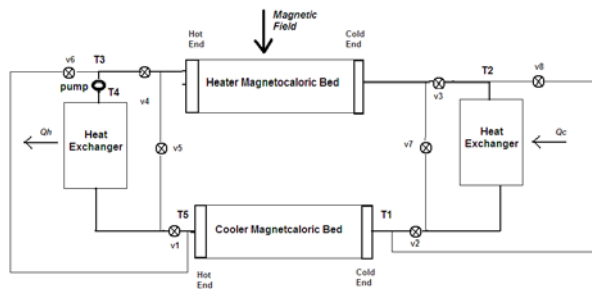


Fig 1. Configuration of eight-valve magnetic refrigerator

The thermodynamic analysis of each component was done by considering a control volume around that component. Cooling power, temperature span, and coefficient of performance were analyzed by simulations. The coefficient of performance (COP) is a dimensionless quantity that describes the performance of a refrigeration cycle, calculated from the cooling load Q_c , and the heat rejected, Q_h , by

$$\text{COP} = \frac{Q_c}{(Q_h - Q_c)} \quad (1)$$

The Carnot cycle, which is completely reversible, is a perfect model for a refrigeration cycle operating between two fixed temperatures. The Carnot limit to the COP of a refrigerator is

$$\text{COP}_{\text{Carnot}} = \frac{T_c}{(T_h - T_c)} \quad (2)$$

Figure 2 shows the cooling power as a function of the

magnetic field. The cooling power was evaluated from the magnetization data. The temperature spans of 10 K, 15 K, and 20 K were considered in this case. As can be seen, for an increase in the magnetic field, there is an increase in the cooling capacity. When the applied field is increased, the cooling load increases because of the increase in adiabatic temperature change of the magnetic material.

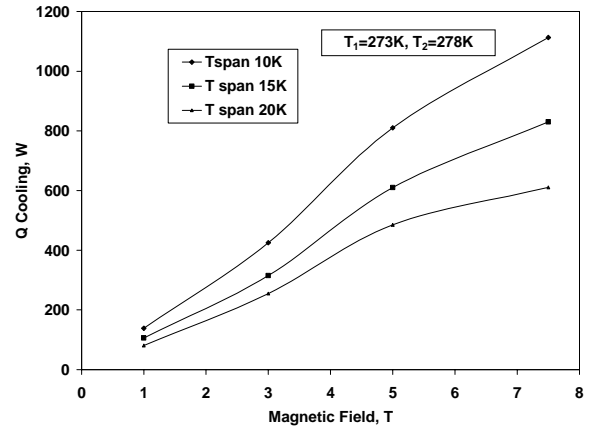


Fig 2. Cooling power vs. magnetic field for various temperature spans

Figure 3 shows the coefficient of performance (COP) dependence on temperature span for various magnetic fields. The COP ranges from about two to eleven, which compares favorably with commercial vapor cycle refrigerators.

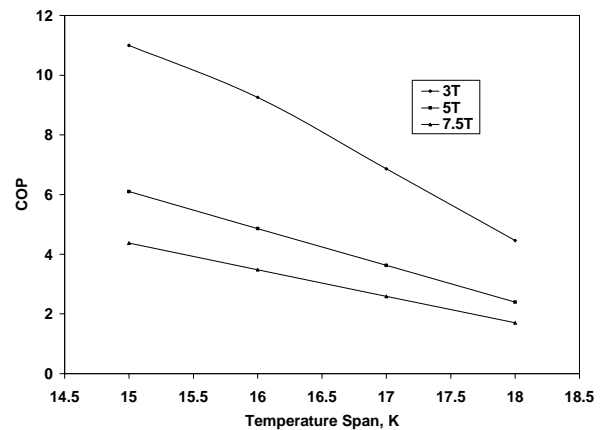


Fig 3. COP vs. temperature span for different magnetic fields

Figure 4 presents predicted and experimental ratios of $\text{COP}_{\text{actual}}/\text{COP}_{\text{Carnot}}$ vs. temperature span for 5 T magnetic field. The experimental data used is that presented by Zimm et al. [19]. As can be seen there is a reasonably good agreement between predictions by the proposed model and those from the experimental measurements.

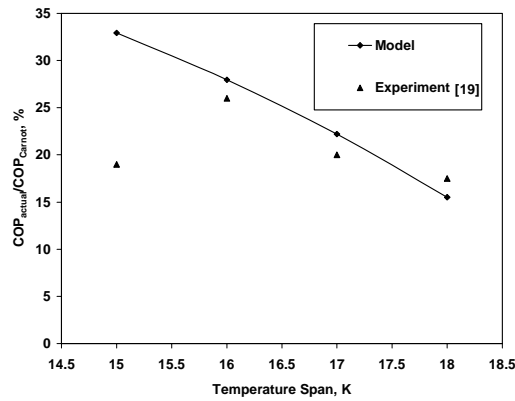


Fig 4. Predicted and experimental $COP_{actual}/COP_{Carnot}$ vs. temperature span for 5T magnetic field

Figure 5 shows the behavior of the ratio of $COP_{actual}/COP_{Carnot}$ with the temperature span for various fluids under a 5 T magnetic field. As can be seen R134a and Ammonia exhibit better performance than that showed by water as the working fluid. R134a shows ratio higher than 35% over the entire temperature span.

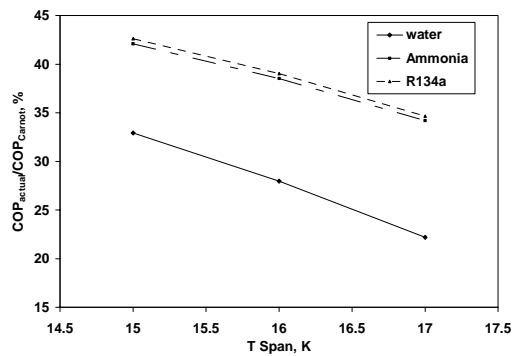


Fig 5. $COP_{actual}/COP_{Carnot}$ vs. temperature span for various fluids with a 5T magnetic field

Table 1 compares results for coefficient of performance between present model and commercial refrigerators as presented by Vineyard [52]. It can be seen that magnetic refrigerator provides significantly higher coefficient of performance compared to vapor compression refrigerator of the same capacity. Therefore, magnetic refrigeration has a great potential to reduce operating cost and maintenance cost when compared to the conventional method of compressor based refrigeration.

Table 1: COP comparison between this model and commercial refrigerators.

COP (Typical 18 ft ³ refrigerator)		
Magnetic Refrigerator	Commercial Vapor Cycle Refrigerators [52]	
N/A	Refrigerant R134a	Refrigerant R22
11	2.26	2.29

3.2 Magnetic Liquefier

Figure 6 shows a schematic of a two-stage magnetic liquefier for hydrogen with 12-valve configuration. Gaseous hydrogen at conditions defined by T_{high} and P_{high} is precooled to T_{med} by passing it through a heat exchanger having gaseous and liquid nitrogen at a temperature T_{N_2} (usually 77 K). Following precooling, the hydrogen enters a counterflow heat exchanger HE-I where it is cooled through heat exchange with a cold helium stream produced by the two-stage magnetic refrigerator to T_{low} and expanded in a thermal expansion valve to a two-phase mixture generally at 20 K. The helium recycles through the magnetic refrigerator. Because of large temperature span of about 55 K and the adiabatic temperature change of available magnetic materials is relatively small, it is necessary to use two stages. The cooling system consists of four porous media beds, two heat exchangers, and a pump. The magnetic refrigerator operates at near liquid nitrogen temperature in a magnetic field of around 7 T and uses two different magnetic materials.

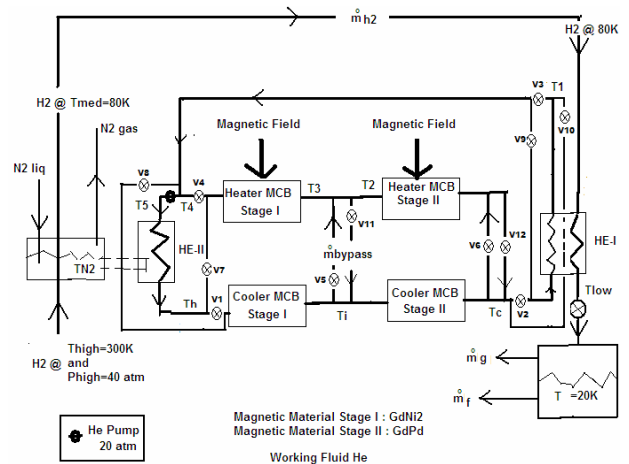


Fig 6. Configuration of 12 valve magnetic liquefier

For the upper stage, $GdNi_2$ is used as an appropriate magnetic material and, for lower stage $GdPd$ is employed. Each stage consists of two identical magnetocaloric beds. The heat transfer fluid is helium. The beds at each stage are periodically magnetized and demagnetized and the fluid flows are arranged to meet the cycle requirements. The system fluid passes through the hot heat exchanger (HE-II), which transfers heat Q_h to the nitrogen and the incoming hydrogen. The fluid then passes through the de-magnetized cooler magnetocaloric bed of the high stage and loses heat. Helium flows in this upper stage bed from the high temperature, T_h , to the intermediate temperature, T_i . The outlet flow from the upper first stage bed is split at a tee so that percentage of the outlet flow continues to the lower stage bed and the remainder is diverted to the upper second stage magnetized bed. This flow split is necessary to compensate for thermal imbalance in the beds. Flow from the lower stage demagnetized bed at T_c is diverted to the magnetized bed of the lower stage and the cold heat exchanger HE-I. This cold fluid at HE-I cools hydrogen from T_{med} to T_{low} by

exchanging heat with it. The heat transfer fluid then gets heated to T_1 by exchanging heat with hydrogen, where it continues to mix with the flow exiting of the magnetized bed of the higher stage. This total flow continues to the helium circulation pump where the flow begins again. The magnetocaloric beds in both stages are alternatively magnetized and de-magnetized, and fluid flow is channeled accordingly to continuously run the cooling operation. For the first stage valves 1, 2, 3, 4, 5, and 6 are opened, and valves 7, 8, 9, 10, 11, and 12 are closed. In this case, the magnetic field is applied to the heater magnetocaloric bed in each stage while the cooler magnetocaloric bed of each stage has been demagnetized. When the magnetic field is released from the top beds and applied to the bottom beds, the cooler beds become heater beds, and vice versa by exchanging roles. In this case valves 7, 8, 9, 10, 11, and 12 are opened and valves 1, 2, 3, 4, 5, and 6 are closed. The cycle repeats itself by switching functions at the beds (cooling and heating).

Figure 7 shows the liquefaction efficiency as a function of the temperature span at stage II. The liquefaction efficiency is defined, as the ideal work required for cooling the hydrogen divided by the real work required by the liquefier. This real work includes the net work performed by the magnetic refrigerator and the work required at the liquid nitrogen plant, which is computed assuming an efficiency of 45%. With an increase in the temperature span, there is a decrease in the liquefaction efficiency.

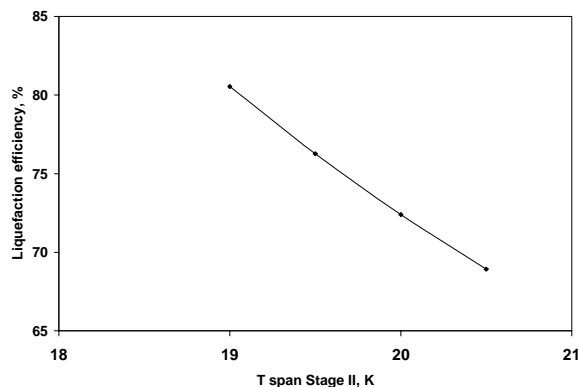


Fig 7. Liquefaction efficiency as a function of temperature span for Stage II

Figure 8 shows the liquefaction efficiency dependence on the magnetic refrigerator coefficient of performance. The liquefaction efficiency ranges from about 70% to 80%, which compares favorably with hydrogen liquefaction systems based on compression. As expected liquefaction efficiency rises with increasing COP/COP_{Carnot} . This indicates that the liquefaction efficiency can be improved by enhancing the refrigerator performance.

Figure 9 presents the behavior of liquefaction efficiency with temperatures T_c and T_h in the magnetic refrigerator. As can be seen the magnetic liquefier exhibits worse efficiency when T_c is increased, this is due to the fact that there is less cooling capacity available to cool down the hydrogen. The magnetic liquefier exhibits better efficiency when T_h is increased. In this case the

power to compress the nitrogen is decreased and therefore the efficiency of the liquefaction process increases.

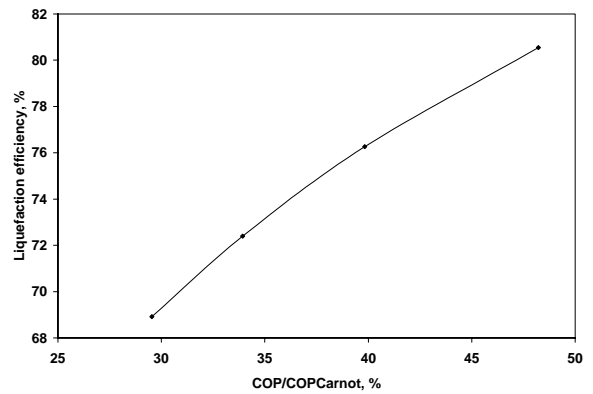


Fig 8. Liquefaction efficiency as a function of Magnetic Refrigerator COP/COP_{Carnot}

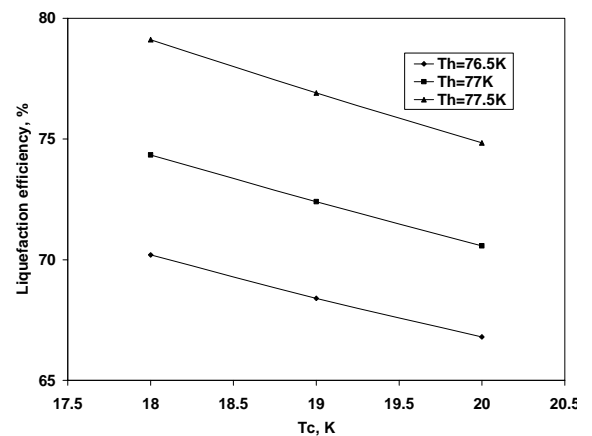


Fig 9. Liquefaction efficiency as functions of T_c and T_h

Table 2 compares results for liquefaction efficiency among present model and three other models. The laboratory liquefier model uses a prototype magnetic refrigerator for hydrogen liquefaction showing a great potential with a liquefaction efficiency of 50% [23]. The DOE model is a two-stage magnetic liquefier as presented by ACA [22]. In this case the system is modeled based on the magnetic material performance and not with the fluid flow analysis. The other model uses a small gas-cycle liquefier based on regular gas compression and a pre-cooling system for liquid-hydrogen production. It can be seen that magnetic refrigeration usually shows better performance when compared to the conventional method of hydrogen liquefaction.

Table 2: Liquefaction efficiency comparison

Present Model, %	Laboratory magnetic prototype liquefier [23], %	ACA Mode 1 [22], %	Conventional reciprocating model [53], %
72.4	50	21	33.5

Table 3 compares results for the fraction of gas flow, which is liquefied between present model and for a small gas-cycle liquefier based on regular gas compression and pre-cooled system for liquid-hydrogen production [53]. The present model shows a better hydrogen liquefaction rate than that exhibited by the other model. Therefore, magnetic refrigeration has a great prospect for hydrogen liquefaction.

Table 3: Fraction of total flow of gas liquefied comparison

Present Model	Conventional Reciprocating Model [53]
0.53	0.16

4. ZERO BOIL-OFF CRYOGENIC STORAGE

The overall schematic of the ZBO cryogenic storage system for liquid hydrogen is shown in Fig. 10. The tank wall is made of aluminum and it has a multi-layered blanket of cryogenic insulation (MLI) on its top. The tank is connected to a cryocooler via a heat pipe to dissipate the heat leak through the insulation and tank wall into the fluid within the tank. The condenser section of the heat pipe dissipates heat to the cryocooler while the evaporator section picks up the heat from the fluid within the tank. The hot fluid is directed to the evaporator section of the heat pipe by using a fluid circulatory system within the tank. This system consists of a pump, a nozzle head for discharge of fluid and a suction tube feeding to the pump. Several different discharge speeds were investigated to find an optimum operating setting for the ZBO hydrogen storage system. Equations governing the conservation of mass, momentum, and energy were solved. Steady-state distributions of velocity and temperature were computed.

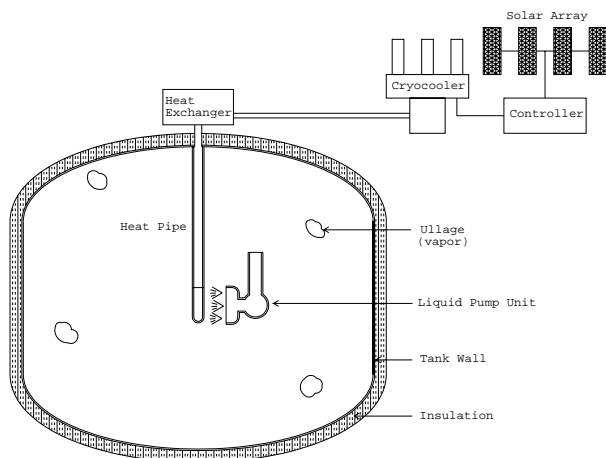


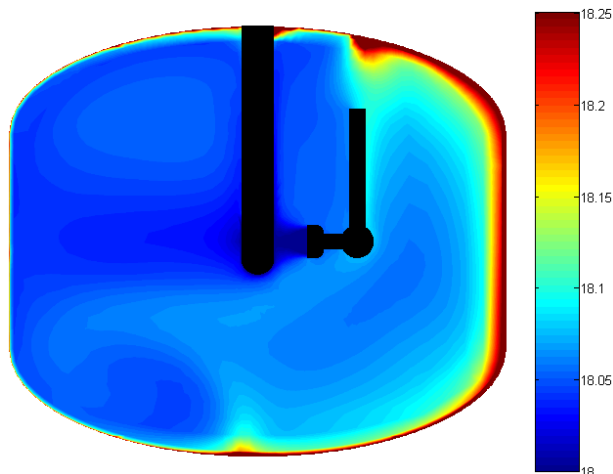
Fig 10. Schematic of cryogenic storage system for liquid hydrogen

The pump creates a pressure difference that drives the fluid in the tank towards the inlet of the suction tube. The

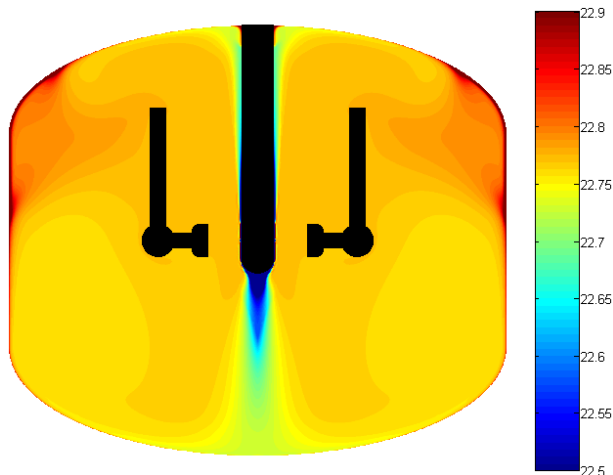
fluid enters the suction tube of the pump and moves towards the nozzle. In the nozzle, the flow expands to fill the hollow space inside, thus reducing speed, and then exiting through many tiny holes on the nozzle face. After being discharged from the nozzle, the flow spreads into many streams spraying on the cool tip (evaporator section) of the heat pipe. For three-dimensional simulation, we could roughly distinguish three groups of streams moving in three main directions. The first group sweeps along the cylindrical part of the cool tip of the heat pipe, then along the heat pipe length, until it reaches the top, sweeps along a short portion on the top before being collected again at the suction tube inlet. The second group moves down along the tip of the heat pipe, wraps around the bottom portion of the heat pipe then moves towards the bottom of the tank and creates a strong circulation in the region on the left below the heat pipe. The third group of streams is the main part which wraps around the side of the cylindrical part of the heat pipe towards the open space on the left side of the heat pipe. In the absence of any obstacle, this group of streams reaches the wall of the tank and sweeps through part of it (the streams, although seem unlikely, touch the side wall of the tank at the position of 90° from the axis of the nozzle, or the position at the middle of the half wall) before returning to the pump side and being collected at the suction tube inlet.

Figure 11 presents a comparison of the temperature distribution pattern on the symmetry plane, Fig. 11a as the typical case for three-dimensional simulations and Fig. 11b as the typical case for axi-symmetric simulations. The axi-symmetric model can be considered as the case where an array of many pump-nozzle units (instead of just one) are located axi-symmetrically around the heat pipe. Figure 11b was created by putting together a temperature distribution plot for axi-symmetric model with its mirror image. Boundary conditions and dimensions are the same for both models with the same fluid speed at the nozzle face. However, the flow rates at the nozzle face are different due to different total nozzle face area (for the axi-symmetric model, the actual nozzle face is a cylindrical surface which has the area of many times of that of the nozzle face of the three-dimensional model, a flat circle). Please note that Fig. 11a only shows temperature distribution on the symmetry plane of the three-dimensional model whereas the plot in Fig. 11b can be of any cross-section through the axis of the tank. In Fig. 11a, heat diffusion dominates in the region on the right and under the pump-nozzle unit with a clear temperature gradient from the tank wall whereas the rest has lower temperature due to convection. In Fig. 11b, the temperature distribution for the axi-symmetric model is totally different. Temperature is distributed more uniformly since the larger flow rate from the nozzle yields better mixing over the entire region. Due to the axi-symmetry of the model, the fluid flow discharged from the nozzle face after spraying on the cool tip of the heat pipe can only flow in two directions: going up along the heat pipe up to the top of the tank or going down along the axis of the tank in an axi-symmetric manner (annular flow wrapping around the heat pipe). Low temperature fluid is confined in a

small region next to the heat pipe, especially the portion right under the spherical tip. Overall temperature is higher than that for the three-dimensional model.



(a) Three-dimensional model.



(b) Axi-symmetric model.

Fig 11. Comparison of temperature distribution pattern on symmetric plane, K

Average speed, taken over the entire computational domain, can be used as a parameter for assessing the mixing effectiveness, which plays a role in leveling the temperature difference in the fluid. Figure 12 shows how the fluid speed at nozzle face affects the mixing effectiveness. As the speed at nozzle increases, the average speed also increases linearly for both three-dimensional and axi-symmetric models. The rate of increasing average speed for the axi-symmetric model is much higher than that for the three-dimensional model (about 4-5 times), meaning that the axi-symmetric model has better performance in mixing effectiveness. The value of average speed for axi-symmetric model is always higher than that for three-dimensional as expected because of higher flow rate from the nozzle as discussed above.

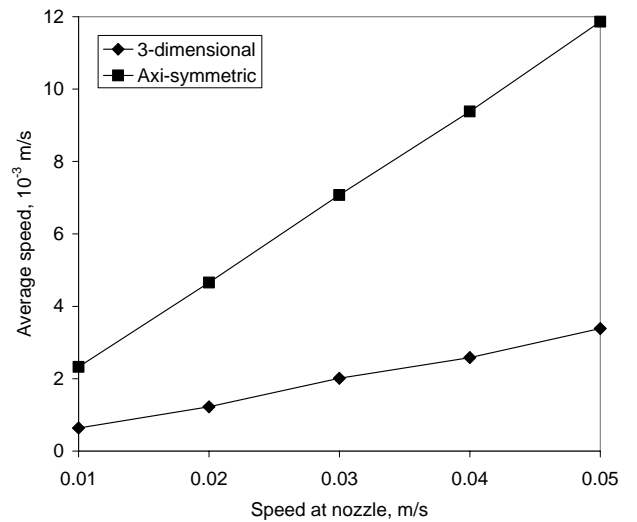


Fig 12. Effect of discharged speed on average speed

The leveling of temperature difference itself can be assessed by observing the maximum-to-average temperature difference, which is convenient for comparison between models (e.g. three-dimensional model vs. axi-symmetric model) despite different temperature ranges. Figure 13 shows the dependency of the maximum-average temperature difference on the fluid speed at the nozzle face. As the fluid speed at the nozzle increases, the temperature difference decreases for both models with much higher drop rate (about 4 to 8 times) for three-dimensional model compared to that for the axi-symmetric model. The three-dimensional model is more sensitive to the increasing of the speed at nozzle but the axi-symmetric model has better mixing effectiveness.

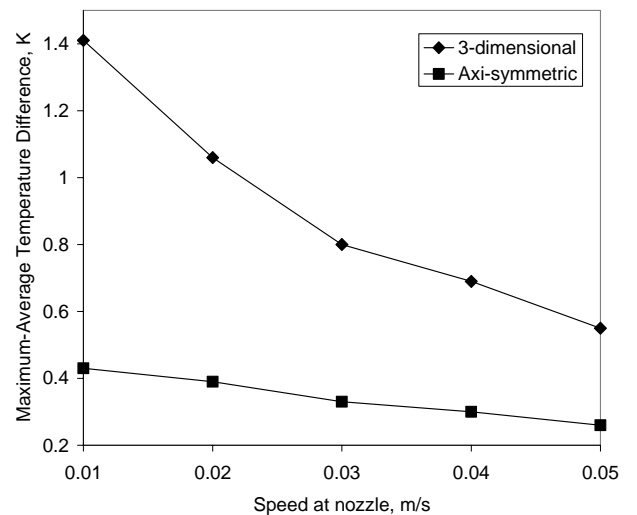


Fig 13. Effect of fluid speed at nozzle face on maximum-average temperature

The maximum temperature is the most important parameter indicating if evaporation can happen, or ZBO effectiveness. Figure 14 shows the maximum temperature as a function of fluid speed at the nozzle for both models. As the speed at nozzle increases, the

maximum temperature decreases nonlinearly but monotonously; this yields an important conclusion that increasing the fluid speed discharged at the nozzle face improves the zero-boiling-off effectiveness.

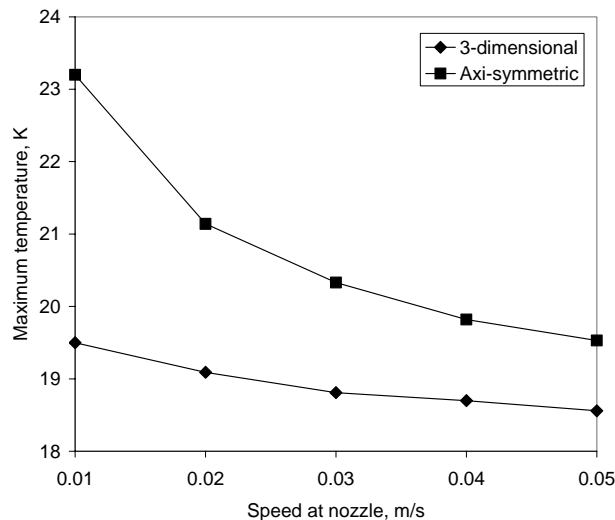


Fig.14. Effect of fluid speed at nozzle face on maximum temperature

5. CONCLUSIONS

Hydrogen is continuing to claim its role as a clean and effective fuel for the future society. There are challenges toward the goals of improving hydrogen availability and portability. Hydrogen storage is a major issue among them. Promising new storage techniques have been developed such as nanostructured carbon, and metal and chemical hydrides. Traditional techniques such as compressed gas and cryogenic liquid storage are still only method widely employed in industry. The technology developed for space applications can be readily extended to automotive applications and other industry. Two key aspects of this technology are hydrogen liquefaction and boil-off prevention. Magnetic liquefaction has been shown as a possible solution for liquefaction with less energy consumption. Zero boil-off concept has been applied for solving the mass loss due to boil-off problem. Those two aspects have been implemented by two systems presented in this paper.

A model for a magnetic refrigerator for continuous refrigeration has been developed. The thermodynamic characteristics of the magnetic refrigerator have been studied. A method has been presented for evaluating each process in the cycle and the corresponding working fluid temperatures, and the net cooling power. For this cycle, two important performance parameters were evaluated: the coefficient of performance and the refrigeration capacity. It was found that the ratio of $COP_{actual}/COP_{Carnot}$ decreases with an increase in the temperature span. The cooling capacity increases with increase in the magnetic field. The model showed good agreement with experimental data. Various working fluids were studied finding that R-134a exhibits better performance. Magnetic refrigeration exhibits a great potential by showing a very high coefficient of performance when compared to commercial vapor cycle refrigerators. A

simple thermodynamic model to represent a magnetic hydrogen liquefier has been considered. For this cycle, the performance was evaluated using the system liquefaction efficiency. It was found that the liquefaction efficiency increases with an increase in the magnetic refrigerator coefficient of performance. Magnetic liquefier exhibits a great potential by showing higher efficiency when compared to small and large scale commercial liquefiers for hydrogen.

The numerical simulations gave a more insightful understanding of the fluid flow and heat transfer phenomena needed for the design of a cryogenic storage tank for liquid hydrogen. The trend of the results from the simulations for both three-dimensional and axi-symmetric models show that the increasing of the fluid speed discharged at the nozzle face improves both mixing effectiveness (increase average speed, decrease maximum-average temperature difference) and ZBO effectiveness (decrease maximum temperature). These guidelines are very useful in designing cryogenic storage systems. Numerical modeling can be satisfactorily used in the design of these systems to obtain good predictions over a wide range of design alternatives and operating conditions.

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