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CRYO-COMPRESSED HYDROGEN STORAGE WITH COOLING RECOVERY VENTING SYSTEM FOR AUTOMOTIVE APPLICATIONS

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ABSTRACT

Cryo-compressed vessels have many advantages in storing hydrogen for automotive applications because of large storing density and thermal endurance. However, the cooling power of venting hydrogen in the processes of dormancy and discharge is not fully utilized. A throttling valve can be used to recycle the cooling power. A thermodynamic model is established to analyze the behavior of hydrogen in the insulated pressure vessel with a throttling valve. Different initial pressures and release pressures of hydrogen in the vessel are studied in the processes of dormancy, discharge and driving. The dormancy can be extended 55% with a throttling valve in the vessels of 2 MPa release pressure. The cooling capacity of the throttling valve decreases with the increase of the initial pressure. Simulations of hydrogen storage during the actual driving are performed at different initial pressures. The throttling valve in the low-initial-pressure vessel can reduce the upper pressure limit of the vessel by 50% which reduces the manufacturing costs obviously. This work introduces the great potential of the throttling valve in the vessel for automotive applications.

Keywords: cro-compressed hydrogen, throttling valve, hydrogen storage, dormancy

NONMENCLATURE

Symbols	
h	Enthalpy (J/kg)
m	Mass (kg)
$\dot{m}$	mass flow rate (kg/s)
P	pressure (Pa)
Q	heat transfer rate (W)
t	time (s)
T	temperature (K)
U	internal energy (J)
V	internal volume of vessel (m^3)
ρ	density (kg/m^3)
Subscripts/superscripts	
c	throttling cooling
e	electric
g	gas
in	inlet
l	liquid
out	outlet
r	leakage
s	structure

1. INTRODUCTION

Hydrogen vehicles have attracted extensive attentions as the next generation of clean energy vehicles. Compressed gas storage, cryogenic liquid storage and material-based hydrogen storage technologies are three main methods for on-board hydrogen storage. Different storage technologies are compared on the basis of cost, energy efficiency and performance[1]. Today's hydrogen vehicles usually use compress gas storage at 350-700 bar.[2] High-pressure storage vessels have many difficulties in manufacturing technology. Cryogenic liquid H_2 vessels are more compact since cryogenic liquid H_2 has a larger density at a low pressure (70.8 g/L for saturated liquid at 1 bar). Cryogenic storage also has advantages in safety[3]. Calculations indicate that cryogenic vessels offer the lowest total ownership cost of hydrogen storage technologies[4].

Cryogenic liquid H_2 vessels suffer from evaporative loss for a period of inactivity because of heat leakage from the ambient (~1 W in a 5 kg H_2 vessel)[5]. Pressure of the vessels will reach the upper limit because of the heat leakage, so it has to vent some hydrogen to decrease or maintain the pressure. Dynamics of cryogenic hydrogen storage in insulated pressure vessels for automotive applications presented earlier[6]. The pressure energy is not utilized fully in the periods of dormancy and discharge. Therefore, the throttling valve can be used to recover part of the pressure energy. In aerospace applications, the thermodynamic venting system (TVS) has already used to decrease the temperature and pressure of hydrogen. For hydrogen vehicles, considering the economics and the compact of the vessels, a throttling valve is efficient to recover the pressure energy. The schematic diagram of hydrogen vessels with a throttling valve is shown in Fig.1. In the process of discharge and dormancy, the released hydrogen passes through a Joule-Thomson device, resulting in a state of lower pressure and temperature, and then the lower temperature hydrogen cools the hydrogen in the heat exchanger by thermal conduction or free conversion. In the period of discharge, the pressure decreases to 8 bar which is the lower limit of discharge pressure, and the pressure decreases to 1 bar in dormancy.

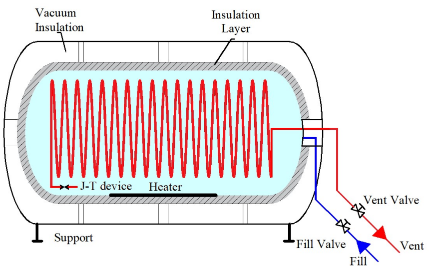

Fig. 1- The schematic diagram of hydrogen vessels with a throttling valve

The purpose of this paper is to analyze the behavior of H_2 in the vessel with a throttling valve for vehicle applications. The thermodynamic process of hydrogen in the period of discharge and dormancy with a throttling valve is compared with the one without throttling valve. Different initial conditions and venting pressures in dormancy are the variable parameters in the paper. Finally, we discuss the actual scene of the vehicles. And then the analysis of the thermodynamic benefits of the throttling valve is presented.

2. DYNAMIC MODEL

Some assumptions are used in this paper for the thermodynamic model in cryogenic vessels with a throttling valve.

(1) Temperature and pressure are uniform in the vessel.
(2) Kinetic and heat transfer of H_2 flowing out of the vessel are neglected.
(3) The cooling power at the outlet of the throttle valve is completely absorbed by the fluid in the vessel
(4) H_2 in the vessel may be as supercritical fluid, gas, liquid, or gas-liquid mixture. The hydrogen will be in phase equilibrium if it is a gas-liquid mixture.
(5) The hydrogen is normal hydrogen (75% ortho-hydrogen and 25% para-hydrogen). And the para-to-ortho hydrogen conversion is not considered

Dormancy in this paper refers to time when the vehicles park, the temperature and pressure of hydrogen in the vessel increase. If the temperature reaches 325K, there isn't heat exchange between vessels and ambient, dormancy stops. There are two periods in the dormancy, one is no venting period, the other is some hydrogen must be vented to maintain the maximum pressure when pressure reaches the upper limit. Discharge refers to time when the vehicles drive, stored hydrogen is withdrawn from the vessel.

The dynamic model for cryogenic hydrogen storage in insulated pressure vessels without throttling valve presented earlier[6]. Taking the contents of the vessel inside the vacuum insulation as a control volume, the differential forms of the mass and energy balances for vessels with a throttling valve are as follow.

$$\frac{dm_{H_2}}{dt} = \dot{m}_{H_2}^{in} - \dot{m}_{H_2}^{out} \tag{1}$$

$$\frac{d}{dt}\left[m_s U_s + m_{H_2} U_{H_2}\right] = m_{H_2}^{in} h_{in} - m_{H_2}^{out} h_{out} + \dot{Q}_{in}^{r} + \dot{Q}_{in}^{c} + \dot{Q}_{in}^{e} \tag{2}$$

where $\dot{Q}_{in}^{r}$ is the heat leakage from the ambient, $\dot{Q}_{in}^{e}$ is the electrical heat input (maintain the lowest discharge pressure), $\dot{Q}_{in}^{c}$ is the cooling capacity by throttling valve.

For a certain vessel, $dV/dt = d\left(m_{H_2}/\rho_{H_2}\right)/dt = 0$, the mass conservation can be expressed by

$$\frac{1}{m_{H_2}}\frac{dm_{H_2}}{dt} - \frac{1}{\rho_{H_2}}\frac{d\rho_{H_2}}{dt} = 0 \tag{3}$$

In the period of dormancy, both $m_{H_2}^{in}$ and $\dot{Q}_{in}^{e}$ equal to zero, while $\dot{Q}_{in}^{r}$ is constant. During the period of discharge, no hydrogen is filled, so that $m_{H_2}^{in}=0$. The ordinary differential equations of the dormancy and discharge models are developed based on the governing equations 1 to 3 which are not listed here owing to spatial confined.

2.1 Method of solution

The ordinary differential equations (ODEs) were jointly solved by MATLAB. From the solutions of governing equations, the transient variations of the thermodynamic parameters including the m_g, m_l, P and T are obtained during the dormancy and discharge processes, respectively. Special care is needed when the hydrogen is in the transition period of supercritical, subcooled, overheated and two-phase state. In the process of iterative calculation, thermophysical properties of hydrogen are calculated by using the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) Version 8.

3. RESULTS AND DISCUSSIONS

The model in this paper is based on the Lawrence Livermore National Laboratory (LLNL) second generation insulated pressure vessel that has a volume of 151 L and a mass of 49 kg with carbon fiber wrapped aluminum liner about 12 kg[7]. The full charge is 10.7 kg hydrogen at 340 bar.. The heat leakage from ambient is assumed to be 3 W. In order to achieve an effective cooling after throttling, the hydrogen temperature and pressure before and after the throttling process should meet certain requirements, e.g. the initial state should be in the cooling region. If the state is out of the cooling region, temperature increase will be observed after the throttling valve, and the throttling valve should be closed in order to avoid heating.

3.1 Model validation

The passive TVS experiment on liquid nitrogen storage[8] is employed to validate the thermodynamic model in this paper. Comparisons of experimental and simulation data are shown in Fig.2. When the pressure reaches 140 kPa, nitrogen vapor is vented, the pressure begins to decrease. At the beginning of the venting, the pressure drops quickly at a large venting rate. This is because before venting, the nitrogen is stagnated in the coil, causing a large flow rate of venting at the beginning. Therefore, there are some differences between experimental data and simulation data. However, the overall trend is consistent, which validates the thermodynamic model in this paper.

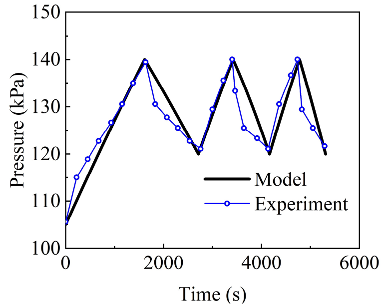

Fig. 2- Validation of the model against the TVS experiment data from the reference[8]

3.2 Hydrogen storage with a throttling valve

<u>3.2.1Dormancy dynamics</u>

The dormancy of different release pressures (2-50 MPa) between the vessel with a throttling valve and the one without throttling valve is studied in the same initial state (1 MPa, 21.4 K). Fig.3a indicates the contribution of the cooling recovery to the dormancy increase is large for vessels with a low release pressure. At a release pressure of 2 MPa, the vessel with a throttling valve have 55% (34 Wd) longer dormancy than the vessel without the throttling valve. When the release pressure exceeds 45 MPa, the throttling valve fails to crease any cooling effect because the state is outside the cooling region of the throttling valve. As shown in Fig. 3b, the initial pressure (1-35 MPa) has little effect on the dormancy increment by the cooling recovery. Similarly, the dormancy increase diminishes to zero when the release pressure is larger than 45 MPa.

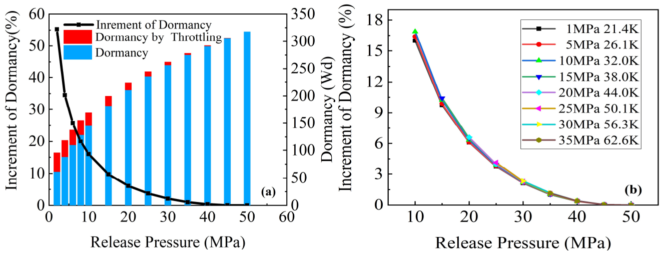

Fig. 3-Increment of dormancy with a throttling valve in the vessels at different release pressures (a), initial pressures (b).

At the same initial state (1 MPa 21.4 K), the variations of temperature, pressure, hydrogen remaining and hydrogen loss rate are discussed at low-pressure limit (10 MPa), middle-pressure limit (30 MPa) and high-pressure limit (50 MPa), respectively. As shown in Fig.4a, the temperature of 10 MPa-limit-vessels with a throttling valve is generally lower than the ones without throttling valve by 50 K to 100 K, while the temperature of 30 MPa-vessels with a throttling valve is only about 10 K lower than ones without throttling valve. The temperature of the 50 MPa-vessels with a throttling valve has no differences with the ones without throttling valve. Fig.4b compares the pressure variations between vessels with a throttling valve and vessels without throttling valve at different release pressures. The trend of pressure is similar, vessels with a throttling valve have 23 Wd, 5 Wd and 0 Wd longer dormancy at pressure limit of 10 MPa, 30 MPa, 50 MPa. Figs. 4c and 4d show the hydrogen remaining and the hydrogen loss rate in different periods of dormancy, respectively. In the same dormancy of 100 Wd, 10 MPa-vessels with a throttling valve can reduce 1.29 kg hydrogen loss, and 0.22 kg for 30 MPa venting vessels. Although high-pressure vessels have lower hydrogen loss rate, while low-pressure vessels have larger throttling effect. The reduction of hydrogen loss by recovering the cooling is more obvious for the low-pressure vessels.

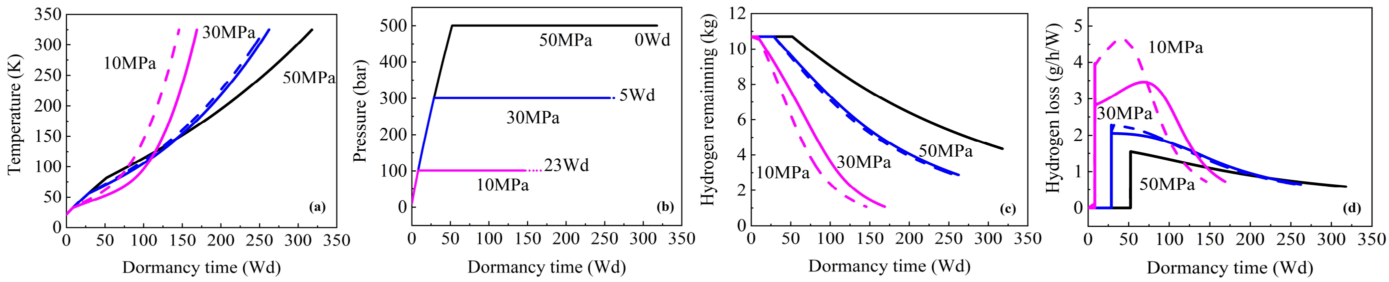

Fig. 4-Comparison of temperature (a), pressure (b), hydrogen remaining (c), hydrogen loss rate (d) between the vessel with a throttling valve and vessel without throttling valve. The solid lines denote the results for the vessel with a throttling valve, while the dashed lines denote the results for the vessel without throttling valve. Initial conditions: m_{H2}=10.7 kg, P=1 MPa, T=21.4 K.

3.2.2Discharge dynamics

Simulations are performed to at a fixed discharge rate of hydrogen (1.6 g/s). The initial states have the same hydrogen mass of 10.7 kg with different pressures at 1 MPa, 10 MPa, 35 MPa, respectively. The pressure and temperature decrease as the hydrogen is discharged. When the pressure drops to 8 bar which is the minimum limit of discharge pressure, extra heating is needed to maintain the minimum pressure. When the pressure is greater than 8 bar, the pressure of hydrogen is reduced to 8 bar through the throttle valve and the discharged hydrogen cools the hydrogen in the vessel. However, when the pressure is lower than 8 bar, the throttling valve stops working.

Fig. 5 shows the changes in the thermodynamic state of hydrogen during the process of discharge. The initial pressures are 1 MPa, 10 MPa and 35 MPa, respectively. Because of the same rate of hydrogen release, the time of discharge is the same (mass of hydrogen is reduced from 10.7 kg to 1 kg). As shown in the Figs.5 (a) and (b), the temperature and pressure in the vessels with a throttling valve are lower than the ones without throttling valve. High initial pressure vessels have larger temperature drop and pressure drop. Low initial pressure vessels (1 MPa) exhibit little throttling cooling because the state of low pressure and temperature is outside the cooling region of the Joule-Thomson throttling effect. Fig. 5 (c) shows the cooling power of throttling. The vessel with an initial pressure of 10 MPa has a very short cooling time with a maximum cooling power of 47 W. The high initial pressure (35 MPa) vessel has a longer cooling time with a maximum cooling power of 55 W. The hydrogen discharge in the vessel with a throttling valve reduces the pressure to 8 bar more quickly, causing the electric heater to be opened earlier to maintain the minimum discharge pressure.

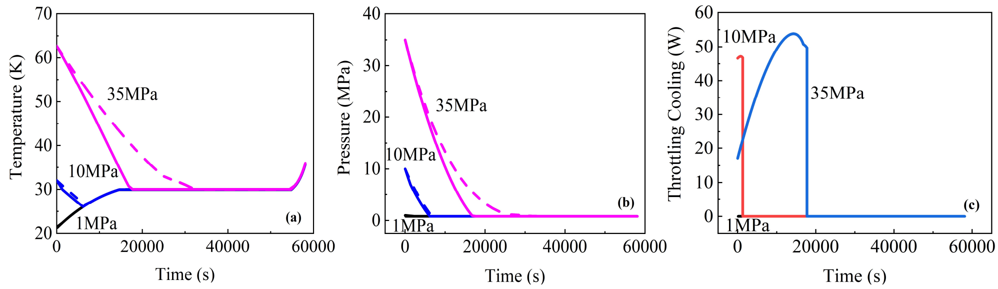

Fig. 5- Change in the thermodynamic state of hydrogen in the process of discharge. (a)temperature, (b)pressure, (c)throttling cooling capacity. The solid lines denote the results for vessels with a throttling valve, while the dashed lines denote the results for vessels without throttling valve.

3.3 Hydrogen storage during the driving process

In this section, simulations of hydrogen storage during the actual driving are performed at different initial pressures, i.e. 1 MPa, 10 MPa and 35 MPa, respectively. It was assumed that the discharge period is maintained at 30 minutes in the morning, afternoon and evening, respectively. The rest of the time is the dormancy period. The pressure and temperature rise during the dormancy process, and drop during the discharge process due to hydrogen release and the cooling energy recovery through the throttling valve. The hydrogen discharge rate of 0.0835 g/s is the average value during the driving process. The same processes are cycled in this way very day, and the car runs for 20.8 days with 1 kg of hydrogen remained in the vessel.

3.3.1 Low-initial-pressure vessels

The state of low-initial-pressure vessels is 1 MPa and 21.4 K As shown in Figs.6 (a) and (b), the throttling cooling power during the discharge process is zero in the early stage (time<20000 s), which is consistent with the observations for the low-initial-pressure vessels in section 3.2. When the initial state of hydrogen is at 3 MPa and 30 K, the throttling valve becomes effective to cool the hydrogen. The maximum pressure of the vessel with a throttling valve is 3 MPa which is the half of the one of the vessel without throttling valve. The decrease of the upper limit pressure can reduce the manufacturing costs of the vessels.

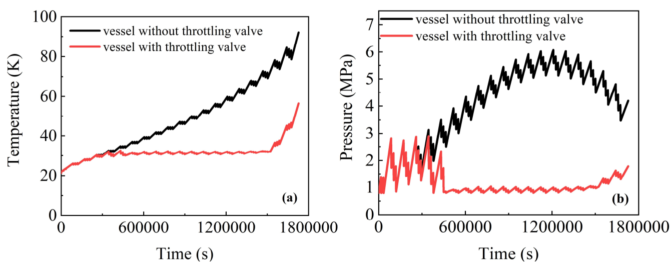

Fig. 6-Changes of temperature (a), pressure (b) for low-initial-pressure vessels.

3.3.2 Middle-initial-pressure vessels

The state of middle-initial-pressure vessels is 10 MPa and 32 K. As shown in Figs.7 (a) and (b), the temperature of hydrogen in the vessel without throttling valve rises to 93 K, and the pressure drops to 4 MPa. During the period, the state of hydrogen in the vessel changes from liquid phase to supercritical state. The temperature of hydrogen in the vessel with a throttling valve is periodically maintained at 30 K, the pressure is reduced from 10 MPa to 0.8 MPa and periodically maintained at 0.8 MPa. After entering the supercritical state (~1500000 s), the pressure and temperature start to rise.

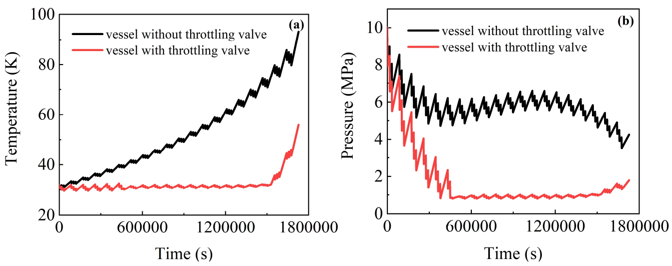

Fig. 7 Changes of temperature (a), pressure (b) for middle-initial-pressure vessels.

3.3.3High-initial-pressure vessels

The state of high-initial-pressure vessels is 35 MPa and 62.6 K. As shown in Figs.8 (a) and (b), the temperature of hydrogen in the vessel without throttling valve rises to 98 K, and the pressure drops to 4.5 MPa. The temperature of hydrogen in the vessel with a throttling valve drops to 50 K, and then rises to 78 K. The pressure is reduced from 35 MPa to 3.4 MPa. During this period, both the vessels with and without throttling valve are in a supercritical state.

During the entire process for middle or high initial pressure vessels, the temperature and pressure of hydrogen in vessels with a throttling valve are lower than vessels without throttling valve. The highest pressure is same, and equal to the initial pressure.

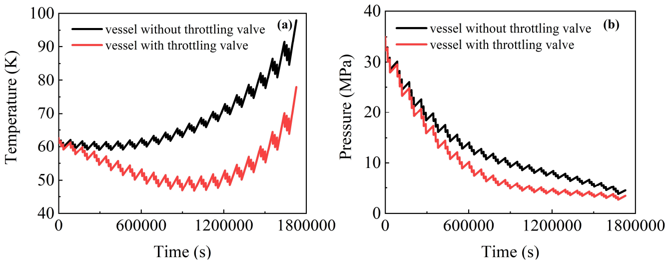

Fig. 8 Changes of temperature (a), pressure (b) for high-initial-pressure vessels

4. CONCLUSIONS

In this paper, we investigate the dynamic behavior of cryo-compressed H_2 storage in vessels with direct venting and cooling-recovery systems, respectively. The dormancy, discharge, and real-life periodic models are developed to study the effects of the cooling-recovery on the hydrogen storage for automotive applications. The conclusions are summarized as follows.

(1) The effect of cooling-recovery on the dormancy is more apparent for the vessel with a low venting pressure. 2 MPa-pressure-limit vessels can extend 55% dormancy period. The throttling valve of high-pressure-limit vessels (more than 45 MPa) fails since the state of hydrogen exceeds the throttling cooling region. The initial state has little effect on the increment of throttling cooling.

(2) In the same initial state, the hydrogen temperature of 10 MPa-pressure-limit vessels with a throttling valve is 50-100 K lower than vessels without throttling valve, and 10 K for 30 MPa. During the dormancy period of 100 Wd (initial state is 1 MPa and 21.4 K), 10 MPa-pressure-limit vessels with a throttling valve can reduce 1.29 kg H_2 loss, and 30 MPa vessels can reduce 0.22 kg H_2 loss.

(3) There is no throttling effect in the discharge process of low-initial-pressure vessels. The cooling power of the throttling valve increases with the increase of the initial pressure.

(4) In the period of driving, for low-pressure vessels, the maximum pressure of the vessels with a throttling valve can be reduced from 6 MPa to 3 MPa, and the pressure limit of vessels is reduced by 50%. The maximum pressure of the middle-pressure and high-pressure vessels is the initial pressure, so the maximum pressure of the vessels with a throttling valve and the vessels without throttling valve is the same. The temperature and pressure of hydrogen can be reduced by the throttling valve during driving.

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