Analysis of thermodynamic processes involving hydrogen[☆]

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ABSTRACT

There is a need to explore potential hazard scenarios associated with several specific thermodynamic processes involving the storage and use of hydrogen subjected to thermal exposures. A potential real-life scenario is the heating of a hydrogen storage vessel abroad a hydrogen-powered vehicle in an automobile fire or in an accident at a refueling station. The effect of thermal exposures on these thermodynamic processes has been examined using the National Institute of Standards and Technology (NIST) REFPROP, Reference Fluid Thermodynamic and Transport Properties, database. The thermodynamic processes considered are isochoric (constant density) heating, isenthalpic expansion, and isentropic expansion. In addition, isochoric heating followed by either an isenthalpic or isentropic expansion process is also discussed. The initial fill density of a hydrogen system has a significant effect on the subsequent thermodynamic processes. From a standpoint of fire safety, a hydrogen system subjected to thermal exposure or preheating before an isenthalpic expansion would potentially increase the risk of fire, especially when the exposure temperature is very close to the hydrogen autoignition temperature.

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1. Introduction

In this paper, several thermodynamic processes involving hydrogen, initially stored either in a liquid or a vapor form, are examined. The focus is on the effect of the thermal environment on these thermodynamic processes. The thermal environment could be the result of a fire or other unexpected thermal events. The thermodynamic processes considered are isochoric (constant density) heating, isenthalpic expansion, and isentropic expansion. In addition, isochoric heating followed by either an isenthalpic or isentropic expansion process is also discussed. Potential hazard scenarios are explored in terms of system pressure build-up and likelihood of autoignition due to temperature increases from some of these thermodynamic processes. Other aspects of hydrogen

safety can be found in numerous articles, to name a few, published in this journal [1–7].

The analysis is based on the calculations carried out using the NIST REFPROP database [8], which provides a current (interim) standard formulation for the properties of hydrogen. The default reference state used in the calculations is the normal boiling point convention, where the enthalpy and entropy of the saturated liquid at the normal boiling point are zero. The equation of state (EOS), as implemented in REFPROP and the NIST Chemistry WebBook [9], is based on Leachman et al [10,11] because it is currently considered to be the most accurate EOS available and is validated over wide ranges of temperature and pressure (up to 1000 K and 2000 MPa). The formulation in the database for the thermophysical properties of normal hydrogen, which is an

equilibrium mixture of 75% ortho-hydrogen and 25% para-hydrogen at room temperature, was used in the calculations. Para-hydrogen formulations are also provided in REFPROP. Ortho-hydrogen has the hydrogen molecule with nuclear spins aligned in the same direction, and para-hydrogen has the hydrogen molecule with nuclear spins in the opposite direction. Although ortho- and para-hydrogen molecules exhibit slightly different thermophysical properties, the hazards associated with the use of these two forms of hydrogen molecules are considered to be similar [12].

2. Analysis

2.1. Isochoric heating

2.1.1. Compressed gas system

This scenario pertains to the analysis of the conditions wherein compressed hydrogen gas is stored in a container subjected to heating. A vessel with different fill densities at an initial temperature of 295 K is examined. Fill density, ρ_f, is defined as the ratio of the hydrogen mass M in the vessel to the vessel volume V. Note that a different fill density will result in a different initial fill pressure at 295 K.

An example is the heating of a vessel containing hydrogen (heating at constant density). This example reflects a potential real-life situation relevant to a hydrogen storage vessel aboard a hydrogen fuel cell vehicle (HFCV) involved in an automobile fire. Current hydrogen storage cylinders are normally made of aluminum alloy wrapped with carbon-reinforced fibers and are equipped with pressure relief devices (PRDs), which are used to safely vent the hydrogen from cylinders to prevent unsafe pressure build-up. However, failure in PRD operation could result in catastrophic vessel disintegration from extreme pressure build-up. There are basically two types of PRDs depending on whether a temperature or a pressure set-point is used to activate the device. Some PRDs even have composite activation systems using both temperature and pressure set-points; the PRD will be triggered when one of the set-points, either temperature or pressure, is reached.

Fig. 1 shows the attainable internal pressure of the vessel after isochoric (constant density) heating to 445 K. This temperature exposure limit is assumed to represent a nominal set-point for a generic thermally-activated PRD used in compressed hydrogen storage aboard an HFCV. Current generic compressed hydrogen gas fuel tanks have a fill density in the range of 20 kg/m³ to 40 kg/m³ at 295 K, corresponding to a pressure range of 29 MPa to 71 MPa. Fig. 1 reveals that higher fill density results in steeper rise in pressure during heating.

A risk scenario deserves further attention. Consider if for some unexpected reasons, the thermally-activated PRD may become disabled or fail to activate at the designated temperature set-point. Assuming that the cylinder structural integrity is not compromised by the fire and no catastrophic failure of the cylinder occurs during the course of heating, the pressure inside the storage cylinder will continue to increase as a result of the cylinder being exposed to the fire. Fig. 1 also shows the prevailing pressure at different initial fill densities as the internal temperature increases beyond 445–1000 K. If the burst pressure of the cylinder is assumed to have a safety
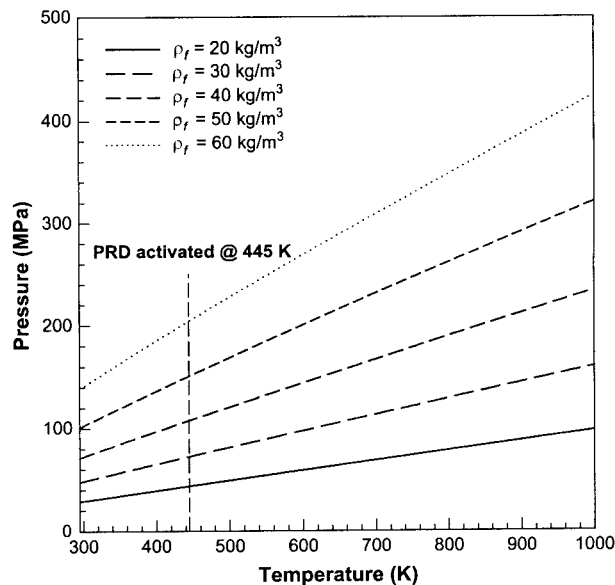

Fig. 1 – Isochoric heating from 295 K to 1000 K at different initial fill densities of compressed hydrogen gas.

factor of 2.35 of the design pressure [13], Fig. 1 demonstrates that the burst pressure can be breached when the cylinder internal temperature reaches 800 K (temperatures in excess of 800 K are typically found in fires) for the range of the initial fill densities, from 20 kg/m³ to 60 kg/m³.

Another risk scenario where Fig. 1 may find its application is the potential breach of a storage vessel in a crash event. If a vessel is suddenly compressed at a high-speed impact, the volume of the vessel will be reduced depending on the severity of the crash. Under this circumstance, the post-impact fill density of the vessel is higher than the pre-impact value because the vessel volume is reduced and the mass in the vessel remains constant (assuming the vessel does not rupture). For example, assuming the pre-impact fill density to be 20 kg/m³, the post-impact fill density will then be 40 kg/m³ if the vessel is compressed to one half of its original volume. Subsequent heating of the breached vessel from a post-crash fire will now follow the 40 kg/m³-isochore in Fig. 1, resulting in a higher vessel pressure than the value obtained using the 20 kg/m³-isochore.

Fig. 1 also reveals several important aspects to be considered for vessel design in order to extend the driving distance for an HFCV between refueling by storing more onboard hydrogen. Assuming the original vessel holds hydrogen mass of M_1 with a vessel volume of V_1, the fill density, $\rho_{f,1}$, is then M_1/V_1 with a corresponding pressure P_1 at a given storage temperature T. If the intent is to increase the amount of hydrogen storage to M_2 (>M_1), there are several ways to achieve this design goal, as listed in Table 1. In Case 1, it is assumed that the original vessel volume could accommodate an increase in hydrogen mass M_2 without compromising vessel structural integrity. Cases 2, 3, and 4 involve the use of a different vessel size V_2 (>V_1) with the assumption that the vessel with volume V_2 can handle the fill density, $\rho_{f,2}$, safely at the storage temperature before thermal exposure. However, increasing vessel volume may not be practical for

Table 1 – Potential means to increase hydrogen storage in single vessel system

Original design				Target design			Fill density	Pressure
M_1	V_1	$\rho_{f,1} = M_1/V_1$ @ P_1, T	Case 1	M_2	V_1	$\rho_{f,2} = M_2/V_1$ @ P_2, T	$\rho_{f,1} < \rho_{f,2}$	$P_1 < P_2$
			Case 2		V_2	$\rho_{f,2} = M_2/V_2$ @ P_2, T	$\rho_{f,1} < \rho_{f,2}$	$P_1 < P_2$
			Case 3				$\rho_{f,1} > \rho_{f,2}$	$P_1 > P_2$
			Case 4				$\rho_{f,1} = \rho_{f,2}$	$P_1 = P_2$

Note that $V_2 > V_1$ and $M_2 > M_1$.

a small hydrogen-powered vehicle where little available space limits the options for housing the vessel, and designing high-pressure vessels capable of handling higher fill densities faces many technical challenges [14].

From the standpoint of safety alone (pressure build-up during thermal exposure) and *without taking vessel weight, volume penalties, and tank placement location limitation into consideration*, Cases 3 and 4 are the most desirable because the resulting fill density of the target design is at most equal to or lower than the fill density of the original design; lower fill density results in a less steep rise in pressure when exposed to elevated temperatures, as clearly shown in Fig. 1.

Another option to increase hydrogen storage, if vessel weight, volume, and placement location are assumed again to be secondary in the overall design criteria, is to consider storing hydrogen in a *multiple* low-pressure vessel system with low fill density over a single high-pressure vessel system with high fill density.

2.1.2. Vapor–liquid system

Strictly speaking, the use of the normal hydrogen formulation in this case is not entirely appropriate due to *ortho–para* conversion at low temperatures. For convenience and illustration, the normal hydrogen formulation is used to examine the temperature–pressure (T–P) relationship when cryogenic liquid hydrogen is stored in a container, a condition wherein cryogenic liquid hydrogen is heated at constant fill density. In a typical cryogenic liquid hydrogen storage vessel, the system is not closed because boil-off is used to prevent pressure build-up and maintain cold temperature in the vessel. Therefore, the fill density is decreasing with time due to boil-off. However, there are possible scenarios that may approximate the condition of a constant fill density. A hydrogen-powered vehicle just finishes refilling with cryogenic liquid hydrogen, and an accident at the refueling site causes a fire and damages to the storage vessel super-insulation and its safety pressure relief valve. Another possible scenario of a vapor–liquid closed system is the trapping of cryogenic hydrogen in a section of an un-insulated pipe between two valves [12] and the pipe section is subjected to thermal exposure.

Depending on the fill density, the pressure in the container will increase either steeply or gradually as the temperature of the container rises [15]. Fig. 2 is a schematic illustrating the P–T behavior when a vapor–liquid system initially at T_A and P_A is heated along isochores (constant density lines) for the two conditions, $\rho_f (=\rho_1) > \rho_c$ and $\rho_f (=\rho_2) < \rho_c$ where ρ_c is the critical density. For $\rho_f = \rho_c$, the P–T behavior will follow the equilibrium liquid–vapor curve until the critical point is reached.

If the fill density is less than the critical density of hydrogen ($\rho_c = 31.26$ kg/m³), then the pressure will rise slowly as the

liquid hydrogen is being heated and converted into vapor. Eventually all the liquid will be completely evaporated (point D). On the other hand, if the fill density is greater than the critical density of hydrogen, then the pressure rise is very steep. As the liquid is heated, it will thermally expand. Under this condition, the liquid evaporation rate (liquid–vapor interface regression rate) cannot keep pace with the thermal expansion rate of the liquid–vapor interface. The container will subsequently become liquid-filled as temperature continues to rise. When the container is completely filled with liquid hydrogen (point B), small increase in temperature would result in a steep rise in pressure. Fig. 3 shows the actual heating behavior of hydrogen initially in vapor–liquid equilibrium at 20.37 K and 0.101 MPa. Fig. 4, which extends the temperature range of Fig. 3, shows the calculated P–T relationship from 20.37 K to 1000 K. Figs. 3 and 4 again illustrate that higher initial fill density will result in higher pressure during heating. The situation worsens if the initial fill density is greater than ρ_c of hydrogen.

2.2. Isenthalpic expansion

The adiabatic throttling of a gas, which describes the expansion of a continuous gas flow through an insulated porous plug, valve, or similar device with flow resistance, can be approximately characterized as an isenthalpic (constant enthalpy, H) process and is often referred to as Joule–Thomson expansion [15]. Fig. 5 shows some representative isenthalps (constant enthalpy lines) for hydrogen from REFPROP on a P–T diagram.
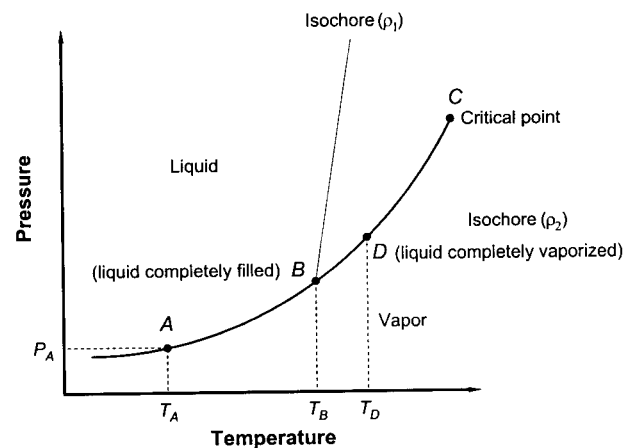

Fig. 2 – Schematic illustrating P–T behavior during heating at different fill densities with $\rho_f (=\rho_1) > \rho_c$, $\rho_f (=\rho_2) < \rho_c$, and $\rho_f = \rho_c$.
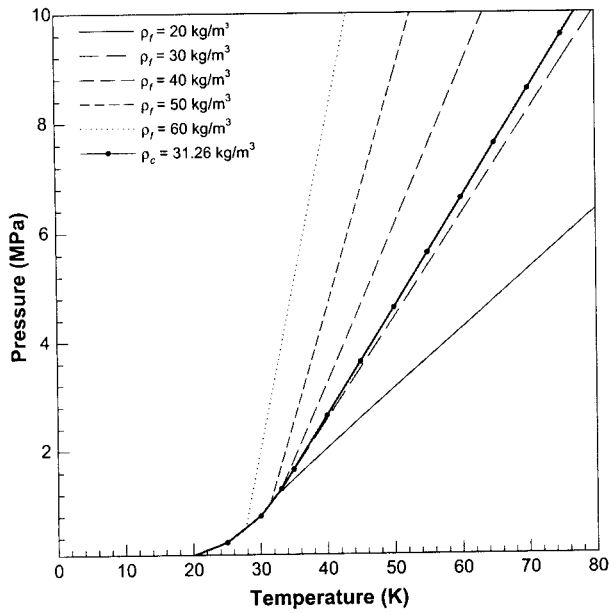
Fig. 3 – Hydrogen P–T relationship with $\rho_f < \rho_c$, $\rho_f > \rho_c$, and $\rho_f = \rho_c$.

Fig. 5 – Representative isenthalps of hydrogen.

The slope of an isenthalp, $(\partial T/\partial P)_H$, on a P–T diagram is called the Joule–Thomson coefficient. For an ideal gas, $(\partial T/\partial P)_H = 0$. For hydrogen, $(\partial T/\partial P)_H$ can be less than, equal to, or greater than zero depending on its existing thermodynamic states, as shown in Fig. 5. When $(\partial T/\partial P)_H > 0$, a reduction in pressure in an isenthalpic gas expansion results in a decrease in temperature and cooling of the gas. When $(\partial T/\partial P)_H < 0$, pressure reduction results in temperature increase and heating of the gas. This may not be desirable for hydrogen under certain conditions, especially when the initial temperature is slightly
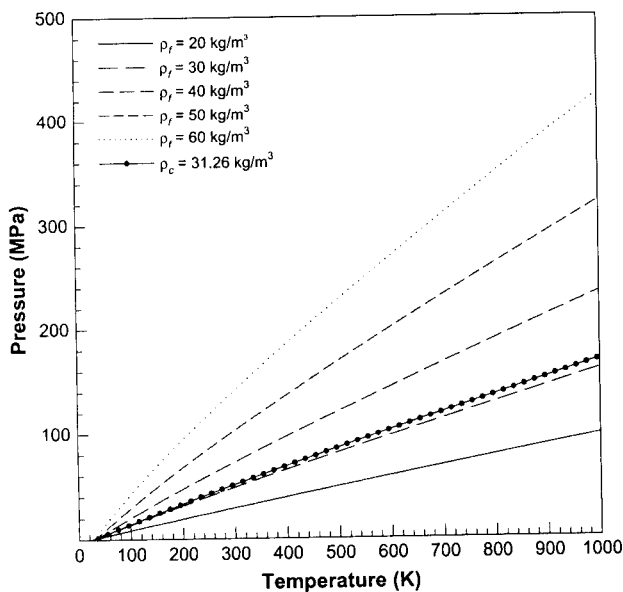
below the autoignition temperature of hydrogen (858 K from [12]) before an isenthalpic process. The locus of the isenthalp extrema, $(\partial T/\partial P)_H = 0$, is called the Joule–Thomson inversion curve, which demarcates $(\partial T/\partial P)_H > 0$ and $(\partial T/\partial P)_H < 0$ along an isenthalp.

Fig. 6 shows the Joule–Thomson coefficient of hydrogen as a function of temperature at different pressures. For the conditions encountered in high-pressure hydrogen storage at room temperature (e.g., 295 K and 30.1 MPa), the Joule–Thomson coefficient is negative, and an isenthalpic expansion will result in a temperature rise.

Fig. 7 shows several isenthalpic expansion processes from the initial conditions of 295 K and prevailing pressures at

Fig. 4 – Isochoric heating from 20.37 K to 1000 K at different initial fill densities of a hydrogen vessel initially in vapor–liquid equilibrium.
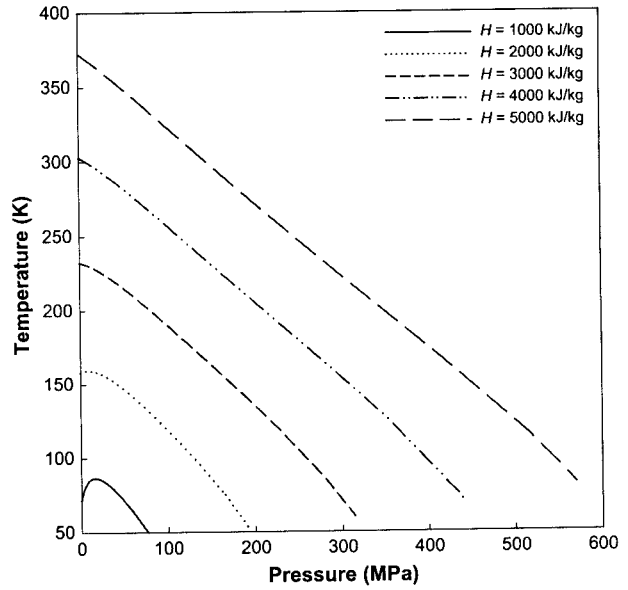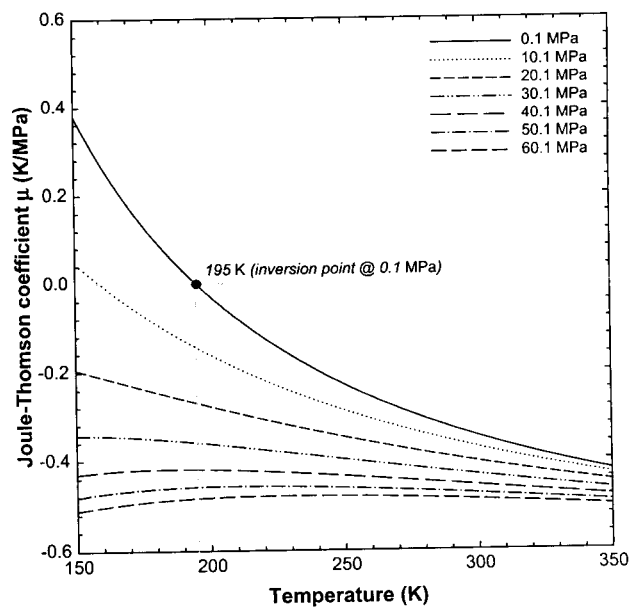

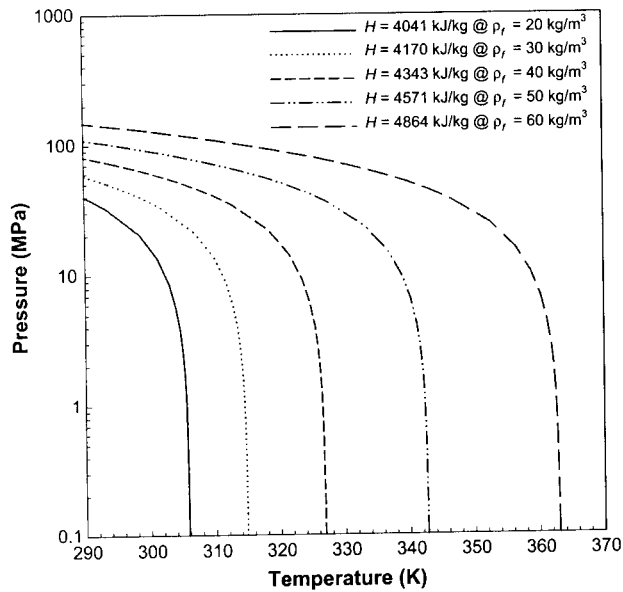Fig. 6 – Joule–Thomson coefficient as a function of temperature at different pressures.

Fig. 7 – Isenthalpic expansion from initial conditions of 295 K and prevailing pressures at different initial fill densities to 0.101 MPa.
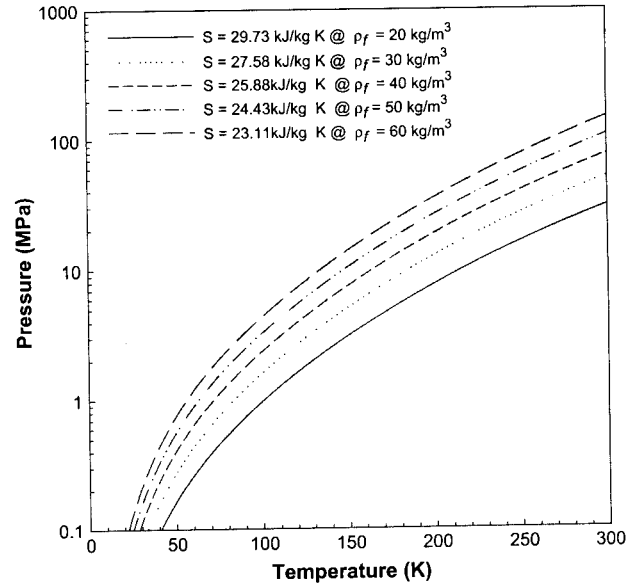

Fig. 9 – Isentropic expansion from initial conditions of 295 K and prevailing pressures at different initial fill densities to 0.101 MPa.

different initial fill densities to 0.101 MPa. Note that during the expansion process the fill density will vary. It can be seen from Fig. 7 that higher initial fill density and pressure results in higher temperature rise after the expansion.

If the storage vessel is first preheated to an elevated temperature, say the activation temperature (445 K) of a PRD, before isenthalpic expansion, the situation will be less desirable compared to room temperature condition. Fig. 8 shows the thermodynamic processes of isochoric heating from room

temperature to 445 K followed by isenthalpic expansion to 0.101 MPa at different initial fill densities of the storage vessel. Higher initial fill density results in higher initial pressure before isenthalpic expansion and higher temperature rise at the end of the expansion. When high-pressure hydrogen gas is preheated to a temperature close to its autoignition temperature, the resulting large increase in temperature due to a subsequent isenthalpic expansion may be considered as precarious from a fire safety point of view [12,16].
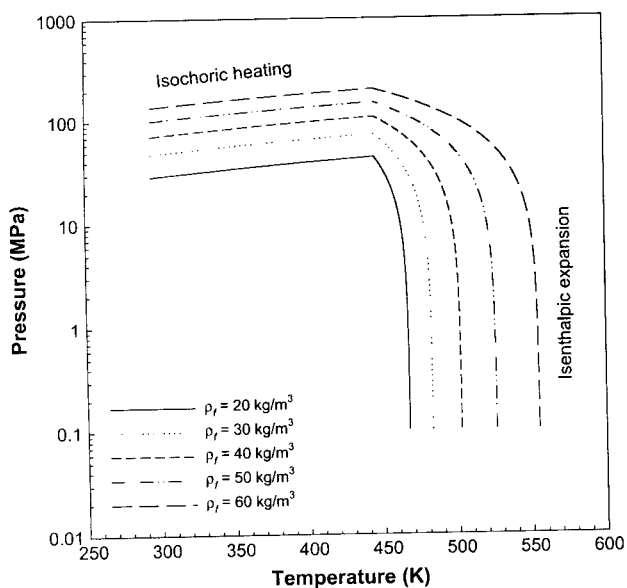

Fig. 8 – Isochoric heating from initial conditions of 295 K and prevailing pressures at different fill densities to 445 K followed by isenthalpic expansion to 0.101 MPa.
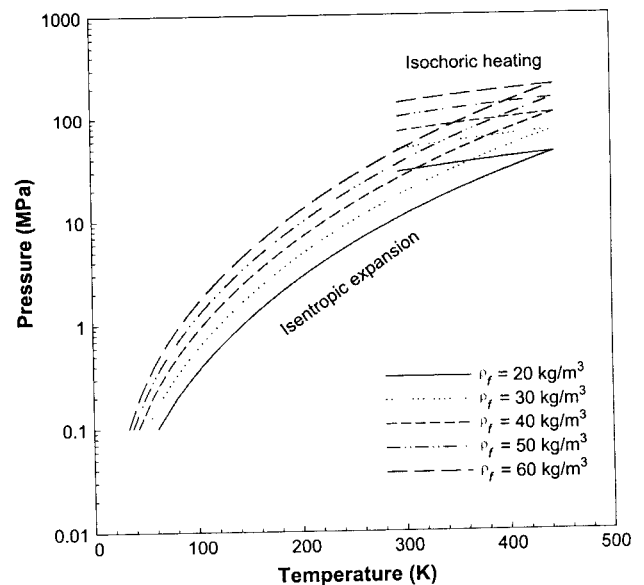

Fig. 10 – Isochoric heating from initial conditions of 295 K and prevailing pressures at different fill densities to 445 K followed by isentropic expansion to 0.101 MPa.

2.3. Isentropic expansion

A rapid release of a high-pressure gas from a vessel can be approximated as an isentropic expansion process. Fig. 9 shows the initial state and final state after an isentropic expansion at different initial compressed hydrogen fill densities in a vessel. It is clear that the isentropic expansion process *always* cools the expanded gas to a lower final temperature irrespective of the fill densities. In addition, higher initial fill density and pressure results in lower temperature after the expansion to atmospheric conditions.

Fig. 10 shows the thermodynamic process of isochoric heating (from 295 K to 445 K) followed by isentropic expansion. Again, the trends similar to Fig. 9 are observed, the higher the initial pressure before the expansion, the lower the temperature after the expansion.

3. Concluding remarks

Although it can be argued that many safety features have been built into hydrogen storage systems, this paper addresses several "what if" scenarios where these safety features malfunction or become disabled or compromised due to unexpected events. The effect of thermal exposures on several thermodynamic processes involving the storage and use of hydrogen has been examined using the NIST REFPROP database. Fill density is an important parameter for storage vessel design. Several design schemes have been proposed with some given constraints. From a standpoint of fire safety, thermal exposure before an isenthalpic expansion would increase the risk of fire, especially when the exposure temperature is very close to the hydrogen auto-ignition temperature.

Acknowledgments

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