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ABSTRACT

A thermodynamic analysis of refueling of a gaseous hydrogen fuel tank is described. This study may lend itself to the applications of refueling a hydrogen storage tank onboard a hydrogen fuel-cell vehicle. The gaseous hydrogen is treated as an ideal or a non-ideal gas. The refueling process is analyzed based on adiabatic, isothermal, or diathermal condition of the tank. A constant feed-rate is assumed in the analysis. The thermodynamic state of the feed stream also remains constant during refueling. Ideal-gas assumption results in simple closed-form expressions for tank temperature, pressure, and other parameters. The non-ideal behavior of high-pressure gaseous hydrogen is addressed using the newly developed equation of state for normal hydrogen, which is based on the reduced Helmholtz free energy formulation. Sample calculations are presented using initial tank and feed stream conditions commensurate to practical vehicular applications. Comparing to the non-ideal analysis, the ideal-gas assumption always results in under-prediction of the tank temperature and pressure irrespective of the filling condition. For a given target tank pressure, the refueling time is the shortest under adiabatic condition and is the longest under isothermal condition with the tank being maintained at the initial tank temperature. The adiabatic and isothermal conditions can be viewed, respectively, as the lower and upper bounds of the refueling time for a given final target tank pressure.

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1. Introduction

Current hydrogen fuel-cell vehicles use high-pressure hydrogen storage tanks to store gaseous hydrogen onboard. Comparable refueling times between a gasoline powered vehicle and a hydrogen fuel-cell car are expected in a future hydrogen economy for consumer acceptance. The fuel tanks of today's gasoline vehicles take less than 5 min to fill at the pump, depending on the size of the tank. The current U.S. Department of Energy (DOE) technical target set for refilling time of an onboard hydrogen tank is 3 min for 5 kg of hydrogen [1]. Detailed analysis of the refueling process is needed to identify the parameters that govern the determination of the refueling time.

Previous studies focus on very specialized hydrogen refueling systems [2–6]. The work by Reynolds and Kays [7] provides detailed formulations describing the refilling processes with heat transfer for an ideal gas. A more general treatment is considered here with the exception that a constant refueling rate and a simplified heat transfer model to describe the heat transfer between the storage vessel and the surroundings are used. The inclusion of a variable refueling rate can be easily accommodated numerically in the analysis at the expense of analytical closed-form solutions.

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This paper describes a thermodynamic analysis of the refilling process of a gaseous hydrogen tank. Hydrogen is treated as either an ideal or a non-ideal gas. The analysis using ideal-gas assumption is included here for completeness and comparison to real gas behavior. For vehicular applications, high-pressure hydrogen gas is used and warrants non-ideal gas treatment; fill tank pressure up to 70 MPa has been proposed [1]. The recently published equation of state (EOS) for normal hydrogen, which is based on the reduced Helmholtz free energy approach, is applied in the non-ideal anal-This approach facilitates the evaluation ysis. of thermodynamic variables. Three thermodynamic processes are discussed under adiabatic, isothermal, and diathermal (non-isothermal with heat interaction) conditions.

2. Analysis

Fig. 1 shows a simplified schematic of an idealized refueling process. The inlet or feed conditions do not vary with time and remain constant during refueling. The gas flow rate to the tank is assumed to be constant. The system under consideration is the hydrogen gas in the fuel tank. The following treatise follows closely to that given in Modell and Reid [8]. From the First law of thermodynamics for a simple open system,

$$dU = \delta Q - \delta W + h_e \, dn_e \tag{1}$$

where *U* is the total internal energy of the system, δQ is the heat added to the system from the surroundings, δW is the work done by the system, h_e is the molar enthalpy at the inlet and is assumed to be constant, and dn_e is the molar input to the system.

With $\delta W = 0$, Eq. (1) can be written as

$$dU = \delta Q + h_e \, dn_e \tag{2}$$

Taking the time derivative of Eq. (2) and for a single stream entering the system,



Fig. 1 - Schematic of a tank undergoing refilling.

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \frac{\delta Q}{\mathrm{d}t} + h_{\mathrm{e}} \frac{\mathrm{d}n_{\mathrm{e}}}{\mathrm{d}t} \tag{3}$$

Eq. (3) can be expressed in terms of molar internal energy, u, of the system and the total number of moles in the system, N.

$$\frac{d(Nu)}{dt} = N\frac{du}{dt} + u\frac{dN}{dt} = \frac{\delta Q}{dt} + h_e\frac{dn_e}{dt}$$
(4)

A mole balance of the system results in

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}n_{\mathrm{e}}}{\mathrm{d}t} \tag{5}$$

If a constant molar flow rate into the tank, K, is assumed, then

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}n_{\mathrm{e}}}{\mathrm{d}t} = \mathrm{K} \tag{6}$$

Integrating Eq. (6),

$$N = N_i + Kt \tag{7}$$

where N_i is the initial total number of moles in the tank at time t = 0 (before refilling).

Substituting Eqs. (6) and (7) into Eq. (4),

$$(N_i + Kt)\frac{du}{dt} + uK = \dot{Q} + h_e K$$
(8)

with $\delta Q/dt = \dot{Q}$ is the heat transfer rate to the system from the surroundings. If an equation of state, the input stream and initial tank conditions, and the thermodynamic process describing the refilling procedure are known, Eq. (8) can be used to predict the final conditions (*T*, *P*, and *N*) of the tank at any given time, where *T* and *P* are the tank temperature and pressure, respectively.

2.1. Adiabatic process (ideal)

If the refilling is rapid, then the process may be considered adiabatic. Eq. (8) becomes

$$(N_i + Kt)\frac{du}{dt} + uK = h_e K$$
 (9)

Integrating Eq. (9),

$$u = h_{\rm e} - \frac{h_{\rm e} - u_{\rm i}}{1 + (Kt/N_{\rm i})}$$
(10)

or

$$\frac{u-h_{\rm e}}{u_{\rm i}-h_{\rm e}} = \frac{1}{1+\hat{t}} \tag{11}$$

where u_i is the initial molar internal energy of the system and $\hat{t} \equiv Kt/N_i$ is a dimensionless time. If the gas is treated as ideal, Eq. (11) can be written as

$$\frac{u - (u_e + P_e v_e)}{u_i - (u_e + P_e v_e)} = \frac{1}{1 + \hat{t}}$$

or
$$\frac{u - (u_e + RT_e)}{u_i - (u_e + RT_e)} = \frac{1}{1 + \hat{t}}$$
(12)

where u_e , P_e , v_e and R (=8.314 J/mole K) are the molar internal energy, pressure, molar volume of the entering stream, and the universal gas constant respectively.

Since the molar internal energy of an ideal gas can be expressed as

$$\label{eq:u_0} \begin{split} & u = u_0 + c_v(T-T_0), \ u_e = u_0 + c_v(T_e-T_0), \ \text{and} \\ & u_i = u_0 + c_v(T_i-T_0) \end{split}$$

where u_0 is the molar internal energy at some reference temperature T_0 and c_v is the molar specific heat at constant volume and assuming c_v does not change significantly with temperature over the temperature range of interest, Eq. (12) can be simplified to

$$\frac{(T - \gamma T_e)}{(T_i - \gamma T_e)} = \frac{1}{1 + \hat{t}}$$
(13)

where $\gamma = c_p/c_v = (c_v + R)/c_v$ and c_p is the molar specific heat at constant pressure. The temperature of the tank at any time during refilling can be prescribed by the simple functional form given in Eq. (13), as shown in Fig. 2. From Eq. (13), the temperature of the tank T at any time t can be calculated during refilling for any given T_e , T_i , K, and N_i . Note that at $t \rightarrow \infty$, $T \rightarrow \gamma T_e$ and is independent of the initial conditions of the tank.

The pressure in the tank at any time t during refilling can be derived from Eq. (7) using Eq. (13) and the ideal-gas law. From Eq. (7),

$$\frac{PV}{RT} = N_i + Kt \tag{14}$$

where V is the volume of the tank. Substituting Eq. (13) into Eq. (14) and simplifying,

$$\frac{P}{P_{i}} = 1 + \left(\frac{\gamma T_{e}}{T_{i}}\right)\hat{t}$$
(15)



Fig. 2 – Dimensionless tank temperature as a function of dimensionless time for an adiabatic refilling process of an ideal gas.

Eq. (15) can be used to calculate the time it takes to refill the tank, t_f , to a given final pressure P_f for any given T_e , T_i , K, and P_i . Alternatively, Eq. (15) can be used to calculate the molar flow rate K required to fill the tank for given T_e , T_i , P_i , P_f and t_f .

2.2. Isothermal process (ideal)

Isothermal condition, which requires thermal management of the storage vessel, is not practical in actual refueling applications due to the added complexity and weight of the storage system. However, the isothermal process is included here for the completeness of the analysis. If the refueling process could be controlled using some form of thermal management method to maintain a constant tank temperature and following the same procedure as the adiabatic case above, then Eq. (8) becomes

$$(N_{i} + Kt)c_{v}\frac{dT}{dt} = \dot{Q} + c_{v}K(T_{e} - T) + KRT_{e}$$
(16)

The left-hand side of Eq. (16) is equal to zero for an isothermal process. Eq. (16) reduces to

$$\dot{Q} = -[c_v K(T_e - T) + KRT_e]$$
(17)

From Eq. (17), \dot{Q} is shown to be constant for a given T. If the temperature of the tank is maintained at T_e during refilling for a given K, then the amount of heat needed to be removed per unit time will simply be

$$\dot{Q} = -KRT_{e}$$
 (18)

A negative \dot{Q} implies heat is removed from the system to the surrounding. Alternatively, Eq. (17) can be used to calculate the tank conditions for any given K, T_e , and \dot{Q} . In this case, Eq. (17) becomes

$$T = \frac{Q}{Kc_v} + \gamma T_e \tag{19}$$

Eq. (7) can be used to calculate N at t. Knowing T and N with a given V, then the tank pressure P at t can be calculated using the ideal-gas law.

If $\dot{Q} = 0$, then Eq. (19) becomes

$$T = \gamma T_{e}$$
(20)

As a check for consistency, Eq. (13) also reduces to Eq. (20) because a steady state (dT/dt = 0) is reached as $t \to \infty$. The adiabatic tank temperature may be considered an upper bound temperature for the tank, and for practical purposes, \dot{Q} is always negative because it is expected that heat will be extracted from the tank, rather than added to the tank, during an isothermal refilling process. Fig. 3 shows the isothermal tank temperature as a function of the absolute value of \dot{Q} for two different filling rates, K_1 and K_2 , with $K_1 < K_2$. More heat removal from the tank is needed for higher filling rate to maintain a given isothermal tank temperature.

The pressure in the tank at any given time during refilling can be derived from Eq. (7) using the ideal-gas law.

$$\frac{P}{P_i} = \frac{T}{T_i} (1 + \hat{t})$$
(21)



Fig. 3 – Heat removal rates for an isothermal refilling process of an ideal gas at two different filling rates.

If the tank temperature is maintained isothermally at $T_{\rm i}$ during refilling, then

$$\frac{P}{P_i} = (1 + \hat{t}) \tag{22}$$

2.3. Diathermal process (ideal)

If there is heat transfer between the system and the surroundings, and the system is not isothermal (a special case of diathermal process), then the \dot{Q} term in Eq. (8) can be conveniently expressed in terms of an overall heat transfer coefficient, $U_{\rm HT}$, the heat transfer area of the tank, $A_{\rm t}$, and the temperature difference between the surrounding temperature, T_{∞} , and the tank temperature, T. The use of a constant overall heat transfer coefficient simplifies the detailed analysis of heat transfer from the tank interior to the interior tank surface, through the composite tank wall, and from the exterior tank surface to the surroundings.

$$(N_i + Kt)\frac{du}{dt} + uK = U_{HT}A_t(T_{\infty} - T) + (u_e + P_e\upsilon_e)K$$
(23)

Following the same procedure as the adiabatic case above, Eq. (23) becomes

$$(N_{i} + Kt)\frac{dT}{dt} = K \left[\frac{U_{HT}A_{t}}{Kc_{v}}(T_{\infty} - T) + (T_{e} - T) + \frac{R}{c_{v}}T_{e}\right]$$
(24)

Integrating Eq. (24) with the initial condition at $t\!=\!0,\,T\!=\!T_{\rm i}$ obtains

$$\left[\frac{(1+St)T - \gamma T_{e} - StT_{\infty}}{(1+St)T_{i} - \gamma T_{e} - StT_{\infty}}\right] = \left(\frac{1}{1+\widehat{t}}\right)^{(1+St)}$$
(25)

where $St \equiv U_{HT}A_t/Kc_v$, which can be considered as a form of the dimensionless heat transfer Stanton number [9]. Eq. (25),

which represents the temporal tank temperature during a diathermal refilling process, can be simply plotted in terms of two dimensionless parameters at different *St*, as shown in Fig. 4.

$$At \ t \to \infty \,, \ \left[\frac{(1+St)T - \gamma T_e - StT_\infty}{(1+St)T_i - \gamma T_e - StT_\infty} \right] \to 0 \ or \ T \to \frac{\gamma T_e + StT_\infty}{(1+St)}$$

As a check for consistency, $T = \gamma T_e$ for St = 0 (adiabatic condition), and Eq. (20) is recovered. For $St \to \infty$, $T \to T_{\infty}$, that is for infinitely fast heat transfer, the tank temperature would attain thermal equilibrium with the surroundings.

The pressure in the tank at any time during refilling can be derived from Eq. (7) using Eq. (25) and the ideal-gas law.

$$\frac{P}{P_{i}} = \left(\frac{1}{1+\hat{t}}\right)^{\text{St}} + \frac{\gamma T_{e} + \text{St}T_{\infty}}{(1+\text{St})T_{i}} \left[\left(1+\hat{t}\right) - \left(\frac{1}{1+\hat{t}}\right)^{\text{St}} \right]$$
(26)

Note that Eq. (26) reduces to Eq. (15) when St = 0 (adiabatic condition).

2.4. Adiabatic process (non-ideal)

Since very high-pressure hydrogen (35–70 MPa) is used for refilling, ideal-gas assumption may not be valid. In order to make Eq. (11), which is valid for both ideal and non-ideal conditions, useful and amenable to the analysis of storage tank refilling, u, u_i , and h_e need to be expressed in terms of practical thermodynamic variables, such as T, P, and ρ using an equation of state. This procedure has already been demonstrated using an ideal-gas law in Case 2.1 above.

For a non-ideal gas, the fundamental equation of state of normal hydrogen developed recently by Leachman et al. [10] is used here, instead of the traditional pressure-explicit or volume-explicit equations of state. The fundamental EOS is expressed in terms of the dimensionless reduced Helmholtz



Fig. 4 – Dimensionless tank temperature as a function of dimensionless filling time at various St for diathermal and ideal condition.

free energy, α , which is the Helmholtz free energy, A, normalized by RT and consists of an ideal gas contribution, α° and a residual contribution, α^{r} . The reduced Helmholtz free energy, α , can be written as

$$\alpha(\tau,\delta) = \frac{A}{RT} = \alpha^{\circ}(\tau,\delta) + \alpha^{r}(\tau,\delta)$$
(27)

where $\tau = T_c/T$ and $\delta = \rho/\rho_c$ are the reciprocal reduced temperature and reduced molar density and T_c and ρ_c are the critical temperature and critical molar density, respectively. The ideal gas and residual contributions to the reduced Helmholtz free energy are

$$\alpha^{\circ}(\tau, \delta) = \ln \delta + 1.5 \ln \tau + a_1 + a_2 \tau + \sum_{k=3}^{7} a_k \ln[1 - \exp(b_k \tau)]$$
 (28)

$$\begin{aligned} \alpha^{r}(\tau,\delta) &= \sum_{i=1}^{7} N_{i} \delta^{d_{i}} \tau^{t_{i}} + \sum_{i=8}^{9} N_{i} \delta^{d_{i}} \tau^{t_{i}} \exp(-\delta^{p_{i}}) \\ &+ \sum_{i=10}^{14} N_{i} \delta^{d_{i}} \tau^{t_{i}} \exp\left[\varphi_{i} (\delta - D_{i})^{2} + \beta_{i} (\tau - \gamma_{i})^{2}\right] \end{aligned}$$
(29)

The parameters and coefficients used in Eqs. (28) and (29) are provided in Tables 1 and 2. The molar internal energy, enthalpy, and pressure can be derived from Eqs. (28) and (29). Detailed derivations and the expressions for other thermodynamic variables are given in Leachman et al. [10,11].

$$u(\tau,\delta) = RT_{c} \left[\left(\frac{\partial \alpha^{o}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{r}}{\partial \tau} \right)_{\delta} \right]$$
(30)

$$h(\tau, \delta) = \mathrm{RT} \left\{ \tau \left[\left(\frac{\partial \alpha^{\circ}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{r}}{\partial \tau} \right)_{\delta} \right] + \delta \left(\frac{\partial \alpha^{r}}{\partial \delta} \right)_{\tau} + 1 \right\}$$
(31)

$$P(\tau, \delta) = \rho RT \left[1 + \left(\frac{\partial \alpha^{r}}{\partial \delta} \right)_{\tau} \right]$$
(32)

The partial derivatives of α° and α^{r} with respect to τ and δ are provided in the Appendix for completeness.

Substituting Eqs. (30) into Eq. (10),

$$RT_{c}\left[\left(\frac{\partial\alpha^{o}}{\partial\tau}\right)_{\delta}+\left(\frac{\partial\alpha^{r}}{\partial\tau}\right)_{\delta}\right]=h_{e}-\frac{h_{e}-u_{i}}{1+(Kt/N_{i})}$$
(33)

Since $h_{\rm e}$, $u_{\rm i}$, K, and N_i are known or can be calculated (as described below) and the left-hand side of Eq. (33) is some function of τ and δ , there are two unknowns (τ and δ) for any given t. However, δ can be obtained from ρ ,

Table 1 – Parameters and coefficients of the normal hydrogen used in α° .					
k	a _k	b_k			
1	-1.4579856475	-			
2	1.888076782	-			
3	1.616	-16.0205159149			
4	-0.4117	-22.6580178006			
5	-0.792	-60.0090511389			
6	0.758	-74.9434303817			
7	1.217	-206.9392065168			

Table 2 – Parameters and coefficients of the normal hydrogen used in α^{r} .									
i	N_i	ti	di	p_i	ϕ_i	β_i	γ_i	Di	
1	-6.93643	0.6844	1	0	-	-	-	-	
2	0.01	1	4	0	-	-	-	-	
3	2.1101	0.989	1	0	-	-	-	-	
4	4.52059	0.489	1	0	-	-	-	-	
5	0.732564	0.803	2	0	-	-	-	-	
6	-1.34086	1.1444	2	0	-	-	-	-	
7	0.130985	1.409	3	0	-	-	-	-	
8	-0.777414	1.754	1	1	-	-	-	-	
9	0.351944	1.311	3	1	-	-	-	-	
10	-0.0211716	4.187	2	-	-1.685	-0.171	0.7164	1.506	
11	0.0226312	5.646	1	-	-0.489	-0.2245	1.3444	0.156	
12	0.032187	0.791	3	-	-0.103	-0.1304	1.4517	1.736	
13	-0.0231752	7.249	1	-	-2.506	-0.2785	0.7204	0.67	
14	0.0557346	2.986	1	-	-1.607	-0.3967	1.5445	1.662	

$$\delta = \frac{\rho}{\rho_{\rm c}} = \frac{N_{\rm i} + Kt}{V \rho_{\rm c}} \tag{34}$$

Eq. (33) then reduces to one unknown, τ , which can now be solved numerically for τ or T at any given t. Knowing δ and τ , the final P at any t can be obtained using Eq. (32).

The initial molar internal energy, u_i , can be directly calculated using the initial conditions of the system, T_i , N_i , and ρ_i and Eqs. (28)–(30) evaluated at τ_i and δ_i with

$$\tau_{i} = \frac{T_{c}}{T_{i}} \rho_{i} = \frac{N_{i}}{V} \delta_{i} = \frac{\rho_{i}}{\rho_{c}}$$

The inlet molar enthalpy, $h_{\rm e}$, can be calculated using the inlet conditions, $T_{\rm e}$ and $P_{\rm e}$ (normally given) and Eq. (31), which requires $\delta_{\rm e}$ (normally not given). Eq. (32) can be used to obtain $\delta_{\rm e}$.

$$P_{e}(\tau_{e}, \delta_{e}) = \rho_{e} R T_{e} \left[1 + \left(\frac{\partial \alpha^{r}}{\partial \delta} \right)_{\tau} \right]_{\tau_{e}, \delta_{e}}$$
(35)

Eq. (35) is a nonlinear algebraic equation, which can be numerically solved for δ_e . In this analysis, the Newton–Raphson method is used [12]. With δ_e now known, h_e can be obtained directly using

$$h_{e} = RT_{e} \left\{ \tau_{e} \left[\left(\frac{\partial \alpha^{o}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{r}}{\partial \tau} \right)_{\delta} \right]_{\tau_{e}, \delta_{e}} + \delta_{e} \left[\left(\frac{\partial \alpha^{r}}{\partial \delta} \right)_{\tau} \right]_{\tau_{e}, \delta_{e}} + 1 \right\}$$
(36)

2.5. Isothermal process (non-ideal)

In this case, Eq. (8) becomes

$$(N_i + Kt)\frac{du}{dt} = \dot{Q} + (h_e - u)K$$
(37)

Then,

$$(N_{i} + Kt)RT_{c}\frac{d}{dt}\left[\left(\frac{\partial\alpha^{o}}{\partial\tau}\right)_{\delta} + \left(\frac{\partial\alpha^{r}}{\partial\tau}\right)_{\delta}\right] = \dot{Q} + (h_{e} - u)K$$
(38)

For an isothermal condition $(d\tau/dt = 0)$, it can be shown from Eq. (A-5) in Appendix that $d/dt[(\partial \alpha^o/\partial \tau)_{\delta}] = 0$. Solving for \dot{Q} , Eq. (38) becomes

$$\dot{Q} = (N_{i} + Kt)RT_{c}\frac{d}{dt}\left[\left(\frac{\partial \alpha^{r}}{\partial \tau}\right)_{\delta}\right] - (h_{e} - u)K$$
(39)

In Case 2.2, the heat removal rate, \dot{Q} , is constant for an ideal gas during an isothermal refilling process; however, Eq. (39) shows that for a non-ideal gas, the heat removal rate is not constant. This is due to the fact that the molar internal energy of a non-ideal gas is a function not only of temperature but also of density, and density is not constant during a refilling process because material is being added to the system. For an ideal gas, the molar internal energy is only a function of temperature. It can be easily shown that for an ideal gas ($\alpha^{r} = 0$), Eq. (39) reduces to Eq. (17). Eq. (39) is used to calculate \dot{Q} needed to maintain a given isothermal condition in the tank during refilling. The pressure at any given time during refilling can be obtained using Eqs. (32) and (34).

2.6. Diathermal process (non-ideal)

Following the same procedure as outlined in Case 2.3, Eq. (8) becomes

$$\frac{du}{dt} = \frac{1}{N_{\rm i} + Kt} [U_{\rm HT} A (T_{\infty} - T) + (h_{\rm e} - u) K]$$
(40)

Substituting Eq. (30) into Eq. (40),

$$\frac{\mathrm{d}}{\mathrm{d}t} \left[\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau} \right)_{\delta} \right] = \frac{1}{RT_{\mathrm{c}}(\mathrm{N}_{\mathrm{i}} + \mathrm{K}t)} \left\{ U_{\mathrm{HT}} A \left(T_{\infty} - \frac{T_{\mathrm{c}}}{\tau} \right) + h_{\mathrm{e}} \mathrm{K} - \mathrm{RT}_{\mathrm{c}} \left[\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau} \right)_{\delta} \right] \mathrm{K} \right\}$$

$$(41)$$

Eq. (41) can be non-dimensionalized using \hat{t} and $\tau_{\infty} \equiv T_c/T_{\infty}$.

$$\frac{\mathrm{d}}{\mathrm{d}\hat{t}} \left[\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau} \right)_{\delta} \right] = \frac{1}{(1+\hat{t})} \frac{U_{\mathrm{HT}}A}{KR} \left(\frac{1}{\tau_{\infty}} - \frac{1}{\tau} \right) + \frac{h_{\mathrm{e}}}{RT_{\mathrm{c}}(1+\hat{t})} - \frac{1}{(1+\hat{t})} \left[\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau} \right)_{\delta} \right]$$
(42)

For comparison to Case 2.3, Eq. (42) can be re-written in terms of St by making use of the following expression for c_v [10,11].

$$\frac{c_{\rm v}}{R} = -\tau^2 \left[\left(\frac{\partial^2 \alpha^{\rm o}}{\partial \tau^2} \right)_{\delta} + \left(\frac{\partial^2 \alpha^{\rm r}}{\partial \tau^2} \right)_{\delta} \right] \tag{43}$$

$$\frac{\mathrm{d}}{\mathrm{d}\hat{t}} \left[\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau} \right)_{\delta} \right] = \frac{\mathrm{St}}{(1+\hat{t})} \left(\frac{1}{\tau} - \frac{1}{\tau_{\infty}} \right) \tau^{2} \left[\left(\frac{\partial^{2} \alpha^{\mathrm{o}}}{\partial \tau^{2}} \right)_{\delta} + \left(\frac{\partial^{2} \alpha^{\mathrm{r}}}{\partial \tau^{2}} \right)_{\delta} \right] \\ + \frac{h_{\mathrm{e}}}{\mathrm{RT}_{\mathrm{c}}(1+\hat{t})} - \frac{1}{(1+\hat{t})} \left[\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau} \right)_{\delta} \right]$$
(44)

Note that it can be easily shown that Eq. (44) is identical to Eq. (24) for an ideal gas ($\alpha^{r} = 0$). With $\delta = N_{i} + Kt/V\rho_{c}$, Eq. (44) has the form of $d\tau/d\hat{t} = f(\tau, \hat{t})$ and can be solved for τ (or T) numerically for any given h_{e}, τ_{∞} , and St. With $\tau(\hat{t})$ known, $P(\hat{t})$ can be calculated using Eq. (32). A 4th-order Runge-Kutta scheme [12] is used here for the analysis.

Table 3 – Parameters used for the case studies.					
T _i	295 K				
Pi	$0.2 imes 10^6 \text{Pa}$				
V	0.0724 m ³				
T _e	300 K				
Pe	$35 imes 10^6 \text{Pa}$				
K	14 mole/s				
T_{∞}	295 K				

3. Case studies

To illustrate the various cases discussed above, a set of initial conditions in the tank and in the feed stream is selected, which is listed in Table 3. Some of the values in the table are representative of the conditions in the current proposed onboard applications. The tank volume, V, is assumed to be 0.0724 m³ (72.4 L) which is commensurate to the current carbon fiber-reinforced composite compressed hydrogen gas tank (Type HGV-4) volume [13]. Based on the U.S. DOE 2010 technical target for onboard hydrogen storage refilling time of 3 min for 5 kg of compressed hydrogen [1], a constant molar feed-rate of 14 mole/s is used in the analysis. The initial temperature and pressure in the tank are arbitrarily chosen to be 295 K and $0.2 \times 10^6 \, \text{Pa}$ respectively although other values can be assigned. In practice, the initial tank pressure is much higher than 0.2×10^6 Pa at refueling.

Fig. 5 shows the dimensionless tank temperature as a function of the dimensionless time during refilling under adiabatic condition for ideal and non-ideal cases. In order to check consistency and ensure that the computation is



Fig. 5 – Dimensionless tank temperature as a function of dimensionless time for an adiabatic refilling process of hydrogen treated as an ideal or a non-ideal gas.



Fig. 6 – Temporal variation of dimensionless tank temperature for an adiabatic refilling process of hydrogen treated as an ideal or a non-ideal gas.

free of programming errors, the calculated results using the ideal-gas law formulation, Eq. (15) with $\gamma = 1.4$, and those based on the fundamental EOS expressed in the form of the reduced Helmholtz free energy with the residual contribution, α^{r} , set to zero are both plotted in Fig. 6 and are shown to be essentially identical. Fig. 6, which contains the same information as given in Fig. 5 but plotted differently, clearly shows that the tank temperature increases



Fig. 7 – Temporal variation of dimensionless tank pressure for an adiabatic refilling process of hydrogen treated as an ideal or a non-ideal gas.



Fig. 8 – Temporal variation of dimensionless tank pressure for an isothermal refilling process of hydrogen treated as an ideal or a non-ideal gas.

initially and then levels off as time progresses during refilling. For the case of the ideal gas, the asymptotic value of the tank temperature T as $t \rightarrow \infty$ is $\gamma T_{\rm i}~(=\gamma T_{\rm e})$ in this case, as indicated in Eq. (13). The tank temperature at any given time is predicted to be higher if the gas is treated as non-ideal instead of ideal.

The dimensionless tank pressure as a function of the dimensionless time under adiabatic refilling condition is



Fig. 9 – Dimensionless tank temperature as a function of dimensionless time for a diathermal refilling process of hydrogen treated as an ideal or a non-ideal gas.



Fig. 10 – Temporal variation of dimensionless tank temperature for a diathermal refilling process of hydrogen treated as an ideal or a non-ideal gas.

shown in Fig. 7. Comparing to the non-ideal analysis, the ideal-gas calculations indicate lower tank pressures at any given time and longer filling time at any given target final tank pressure.

Fig. 8 shows the dimensionless tank pressure as a function of the dimensionless time under isothermal (same as initial tank temperature) condition. The ideal-gas approach again predicts lower tank pressure and longer filling time.

Figs. 9 and 10 show the dimensionless tank temperature as a function of the dimensionless time, expressed in two different



Fig. 11 – Temporal variation of dimensionless tank pressure for a diathermal refilling process of hydrogen treated as an ideal or a non-ideal gas.

ways, under diathermal refilling conditions with four different values for the heat transfer Stanton number. Since the results obtained using Eq. (25) with $\gamma = 1.4$ are essentially identical to those calculated using the fundamental EOS with $\alpha^r = 0$, they are not plotted in the two data-populated figures for sake of clarity. At St = 0, the results are identical to those obtained at adiabatic condition, irrespective of whether the gas is treated as ideal or non-ideal. At large St, in this case St = 100, the filling process is approaching an isothermal condition. Independent of the value of the Stanton number, the tank temperatures calculated using the ideal-gas assumption are always lower than those obtained using the non-ideal approach.

The temporal variation of the dimensionless tank pressure under several diathermal filling conditions is shown in Fig. 11. For all the conditions considered, the ideal-gas calculations under predict the tank pressures. For a given target tank *P*, the refilling time is the shortest under adiabatic condition (St = 0) and is the longest under isothermal condition (St = 100) with the tank being maintained at the initial tank temperature. Irrespective of ideality or non-ideality, the adiabatic and isothermal conditions can be viewed, respectively, as the lower and upper bounds of the refilling time for a given final target tank pressure.

4. Conclusions

A thermodynamic and heat transfer analysis of the refueling process of a gaseous hydrogen fuel tank for onboard vehicular applications has been performed. During the refilling process, the tank is treated as adiabatic, isothermal, or diathermal. Ideal and non-ideal behaviors of hydrogen are considered in the analysis. Non-ideality is treated using the newly developed equation of state for normal hydrogen, which is based on the reduced Helmholtz free energy formulation. With the ideal-gas assumption, simple analytical expressions were derived for the tank temperature and pressure during adiabatic, isothermal, and diathermal refueling conditions. Although a constant feed-rate is assumed in this study, the analysis can be readily expanded to include variable feedrates, which may not result in closed-form expressions for the tank temperature and pressure, even in the case of an ideal gas. Comparing to the non-ideal analysis, lower tank temperatures and pressures and longer filling times are always predicted when the ideal-gas assumption is invoked in the calculations irrespective of the refilling conditions.

Appendix

$$\left(\frac{\partial \alpha^{\circ}}{\partial \tau}\right)_{\delta} = \frac{1.5}{\tau} + a_2 - \sum_{k=3}^{7} a_k \frac{b_k \exp(b_k \tau)}{1 - \exp(b_k \tau)}$$
(A-1)

$$\begin{split} \left\langle \frac{\partial \alpha^{r}}{\partial \tau} \right\rangle_{\delta} &= \sum_{i=1}^{7} N_{i} \delta^{d_{i}} t_{i} \tau^{t_{i}-1} + \sum_{i=8}^{9} N_{i} \delta^{d_{i}} t_{i} \tau^{t_{i}-1} \exp(-\delta^{p_{i}}) \\ &+ \sum_{i=10}^{14} N_{i} \delta^{d_{i}} \tau^{t_{i}} \exp\left[\varphi_{i} (\delta - D_{i})^{2} + \beta_{i} (\tau - \gamma_{i})^{2}\right] \\ &\left[\frac{t_{i}}{\tau} + 2\beta_{i} (\tau - \gamma_{i})\right] \end{split} \tag{A-2}$$

(A-3)

$$\begin{split} \left(\frac{\partial \alpha^{r}}{\partial \delta}\right)_{\tau} &= \sum_{i=1}^{7} N_{i} d_{i} \delta^{d_{i}-1} \tau^{t_{i}} + \sum_{i=8}^{9} N_{i} \tau^{t_{i}} \exp(-\delta^{p_{i}}) \delta^{d_{i}} \left(\frac{d_{i}}{\delta} - p_{i} \delta^{p_{i}}\right) \\ &+ \sum_{i=10}^{14} N_{i} \tau^{t_{i}} \exp\left[\varphi_{i} (\delta - D_{i})^{2} + \beta_{i} (\tau - \gamma_{i})^{2}\right] \delta^{d_{i}} \\ &\left[\frac{d_{i}}{\delta} + 2\varphi_{i} (\delta - D_{i})\right] \end{split}$$

$$\left(\frac{\partial^2 \alpha^o}{\partial \tau^2}\right)_{\delta} = -\frac{1.5}{\tau^2} - \sum_{k=3}^7 a_k \left\{ \frac{b_k^2 \exp(b_k \tau)}{\left[1 - \exp(b_k \tau)\right]^2} \right\}$$
(A-4)

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau}\right)_{\delta} = -\left\{\frac{1.5}{\tau^{2}} + \sum_{k=3}^{7} a_{k} \frac{b_{k}^{2} \exp(b_{k}\tau)}{\left[1 - \exp(b_{k}\tau)\right]^{2}}\right\} \frac{\mathrm{d}\tau}{\mathrm{d}t}$$
(A-5)

$$\begin{split} \left(\frac{\partial^{2} \alpha^{r}}{\partial \tau^{2}} \right)_{\delta} &= \sum_{i=1}^{7} N_{i} \delta^{d_{i}} t_{i}(t_{i}-1) \tau^{t_{i}-2} + \sum_{i=8}^{9} N_{i} \delta^{d_{i}} t_{i}(t_{i}-1) \tau^{t_{i}-2} \exp(-\delta^{p_{i}}) \\ &+ \sum_{i=10}^{14} N_{i} \delta^{d_{i}} t_{i} \tau^{t_{i}-1} \exp\left[\varphi_{i}(\delta-D_{i})^{2} + \beta_{i}(\tau-\gamma_{i})^{2}\right] \\ &\left[\frac{t_{i}}{\tau} + 2\beta_{i}(\tau-\gamma_{i}) \right] \\ &+ \sum_{i=10}^{14} N_{i} \delta^{d_{i}} \tau^{t_{i}} \exp\left[\varphi_{i}(\delta-D_{i})^{2} + \beta_{i}(\tau-\gamma_{i})^{2}\right] \left[2\beta_{i}(\tau-\gamma_{i}) \right] \\ &\left[\frac{t_{i}}{\tau} + 2\beta_{i}(\tau-\gamma_{i}) \right] \\ &+ \sum_{i=10}^{14} N_{i} \delta^{d_{i}} \tau^{t_{i}} \exp\left[\varphi_{i}(\delta-D_{i})^{2} + \beta_{i}(\tau-\gamma_{i})^{2} \right] \\ &+ \sum_{i=10}^{14} N_{i} \delta^{d_{i}} \tau^{t_{i}} \exp\left[\varphi_{i}(\delta-D_{i})^{2} + \beta_{i}(\tau-\gamma_{i})^{2} \right] \\ &\left[-\frac{t_{i}}{\tau^{2}} + 2\beta_{i} \right] \end{split}$$
(A-6)

$$\begin{split} \left[\frac{\partial}{\partial\delta}\left(\frac{\partial\alpha^{r}}{\partial\tau}\right)_{\delta}\right]_{\tau} &= \sum_{i=1}^{7} N_{i}d_{i}\delta^{d_{i}-1}t_{i}\tau^{t_{i}-1} + \sum_{i=8}^{9} N_{i}d_{i}\delta^{d_{i}-1}t_{i}\tau^{t_{i}-1}\exp(-\delta^{p_{i}}) \\ &+ \sum_{i=8}^{9} N_{i}\delta^{d_{i}}t_{i}\tau^{t_{i}-1}\exp(-\delta^{p_{i}}) \left(-p_{i}\delta^{p_{i}-1}\right) \\ &+ \sum_{i=10}^{14} N_{i}d_{i}\delta^{d_{i}-1}\tau^{t_{i}}\exp\left[\varphi_{i}(\delta-D_{i})^{2} + \beta_{i}(\tau-\gamma_{i})^{2}\right] \\ &\left[\frac{t_{i}}{\tau} + 2\beta_{i}(\tau-\gamma_{i})\right] + \sum_{i=10}^{14} N_{i}\delta^{d_{i}}\tau^{t_{i}}\exp\left[\varphi_{i}(\delta-D_{i})^{2} + \beta_{i}(\tau-\gamma_{i})^{2}\right] \\ &\left(\tau-\gamma_{i})^{2}\right] \left[2\varphi_{i}(\delta-D_{i})\right] \left[\frac{t_{i}}{\tau} + 2\beta_{i}(\tau-\gamma_{i})\right] \end{split}$$
(A-7)

$$\begin{split} \frac{d}{dt} & \left(\frac{\partial \alpha^{r}}{\partial \tau}\right)_{\delta} = \frac{d}{dt} \sum_{i=1}^{7} N_{i} \delta^{d_{i}} t_{i} \tau^{t_{i}-1} + \frac{d}{dt} \sum_{i=8}^{9} N_{i} \delta^{d_{i}} t_{i} \tau^{t_{i}-1} \exp(-\delta^{p_{i}}) \\ & + \frac{d}{dt} \sum_{i=10}^{14} N_{i} \delta^{d_{i}} \tau^{t_{i}} \exp\left[\varphi_{i} (\delta - D_{i})^{2} + \beta_{i} (\tau - \gamma_{i})^{2}\right] \\ & \left[\frac{t_{i}}{\tau} + 2\beta_{i} (\tau - \gamma_{i})\right] \end{split}$$
(A-8)

with

$$\frac{d}{dt}\sum_{i=1}^{7}N_{i}\delta^{d_{i}}t_{i}\tau^{t_{i}-1} = \sum_{i=1}^{7}N_{i}\delta^{d_{i}}t_{i}(t_{i}-1)\tau^{t_{i}-2}\frac{d\tau}{dt} + \sum_{i=1}^{7}N_{i}d_{i}\delta^{d_{i}-1}t_{i}\tau^{t_{i}-1}\frac{d\delta}{dt}$$
(A-9)

$$\begin{split} \frac{d}{dt} \sum_{i=8}^{9} N_i \delta^{d_i} t_i \tau^{t_i - 1} \exp(-\delta^{p_i}) &= \sum_{i=8}^{9} N_i \delta^{d_i} t_i (t_i - 1) \tau^{t_i - 2} \exp(-\delta^{p_i}) \frac{d\tau}{dt} \\ &+ \sum_{i=8}^{9} N_i d_i \delta^{d_i - 1} t_i \tau^{t_i - 1} \exp(-\delta^{p_i}) \frac{d\delta}{dt} \\ &+ \sum_{i=8}^{9} N_i \delta^{d_i} t_i \tau^{t_i - 1} \exp(-\delta^{p_i}) \frac{d\delta}{dt} \\ &+ (-p_i \delta^{p_i - 1}) \frac{d\delta}{dt} \end{split}$$
(A-10)

$$\begin{split} \frac{d}{dt} \sum_{i=10}^{14} N_i \delta^{d_i} \tau^{t_i} exp \Big[\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \left[\frac{t_i}{\tau} + 2\beta_i (\tau - \gamma_i) \right] \\ &= \sum_{i=10}^{14} N_i \delta^{d_i} t_i \tau^{t_i - 1} exp \Big[\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \left[\frac{t_i}{\tau} + 2\beta_i (\tau - \gamma_i) \right] \frac{d\tau}{dt} \\ &+ \sum_{i=10}^{14} N_i \delta^{d_i} \tau^{t_i} exp \Big[\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \\ \left[\frac{t_i}{\tau} + 2\beta_i (\tau - \gamma_i) \right] 2\beta_i (\tau - \gamma_i) \frac{d\tau}{dt} \\ &+ \sum_{i=10}^{14} N_i \delta^{d_i} \tau^{t_i} exp \Big[\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \left[-\frac{t_i}{\tau^2} + 2\beta_i \Big] \frac{d\tau}{dt} \\ &+ \sum_{i=10}^{14} N_i \delta^{d_i - 1} \tau^{t_i} exp \Big[\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \left[\frac{t_i}{\tau} + 2\beta_i (\tau - \gamma_i) \Big] \frac{d\delta}{dt} \\ &+ \sum_{i=10}^{14} N_i \delta^{d_i - 1} \tau^{t_i} exp \Big[\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \left[\frac{t_i}{\tau} + 2\beta_i (\tau - \gamma_i) \Big] \frac{d\delta}{dt} \\ &+ \sum_{i=10}^{14} N_i \delta^{d_i} \tau^{t_i} exp \Big[\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \right] \\ &\left[\frac{t_i}{\tau} + 2\beta_i (\tau - \gamma_i) \right] [2\varphi_i (\delta - D_i)^2 + \beta_i (\tau - \gamma_i)^2 \Big] \end{split}$$

with

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = \frac{\mathrm{K}}{\mathrm{V}\rho_{\mathrm{c}}}$$

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