ISSN 0040-5795, Theoretical Foundations of Chemical Engineering, 2018, Vol. 52, No. 3, pp. 465–472. © Pleiades Publishing, Ltd., 2018.

Thermodynamic Analysis of Single Reservoir Filling Process of Hydrogen Vehicle[1]

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Received November 20, 2015

Abstract—The accurate modeling of the fast-fill dynamics occurring in hydrogen fueled vehicle storage cylinders is a complex process, and to date those dynamics have not been thoroughly studied. In this paper, based on the first and second laws of thermodynamics, conservation of mass and real gas assumptions, a numerical method has been developed to study the fast filling process of the hydrogen vehicle's cylinder. Thermodynamic properties' table has been employed for the case of the real gas model. The model has been applied for a single reservoir tank. The results indicate that there is a temperature rise on the order of 100 K or more during the charging process. The results also indicate that ambient temperature has a strong effect on the filling process and final hydrogen cylinder conditions.

Keywords: hydrogen, hydrogen fueling, thermodynamic modeling, filling process, entropy generation

DOI: 10.1134/S0040579518030077

INTRODUCTION

The use of hydrogen as a clean alternative to other automobile fuels such as gasoline (petrol) and diesel will have a positive impact on the environment. Other motivating factors for hydrogen include energy security for oil importing countries and ever increasing oil prices. With the development of hydrogen fuel technology in recent years, the expansion of hydrogen fueling stations has gained greater attention in the world [1, 2]. Based on previous researches, the high-pressure compression storage approach is more advantageous (more practical, dependable, durable and admissible) for the storage of hydrogen [3, 4] as compared with the liquid hydrogen storage. According to statistics, about 80–90% of hydrogen is stored using high-pressure compression in hydrogen fuelling stations and vehicle cylinders [5].

Although there are many advantages in using hydrogen, but it has not been widely accepted as an alternative fuel to gasoline by most countries. The one obvious reason is low driving range of hydrogen vehicles, which is partly associated with the hydrogen fueling station's technology.

Hydrogen vehicles commonly receive hydrogen from high-pressure reservoirs at the fuelling stations during filling. The first problem with the hydrogen fuelling stations is the refueling time of a hydrogen vehicle. The hydrogen vehicle industry has made excellent advancements in the industry to provide a system to refuel a hydrogen vehicle to be comparable to that of a gasoline dispenser. The problem with the long refueling time has been remedied, for the most part, to be comparable to the fill time (<5 min) taken to fill a gasoline powered automobile. This fill time can be referred to as a fast fill or rapid charge [6].

The on-board storage capacity of hydrogen vehicles is the other problem to the wide spread marketing of these vehicles. The on-board storage cylinders encountered a rise in the gas temperature (in the range of 70 K or more [6]) during the fast filling due to complex compression and mixing processes. This temperature rise reduces the density of the gas in the cylinder, resulting in an under-filled cylinder, relative to its rated specification. If this temperature rise is not compensated for, in the fueling station dispenser, by transiently over-pressurizing the tank, the vehicle user will experience a reduced driving range. Although the hydrogen on-board cylinder volume plays the main role in storage capacity, the fueling station reservoirs'

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pressure also has strong effects on the amount of the charged mass.

To our knowledge, there have been no previous researches on performance enhancement of hydrogen fuelling stations. However, the limited researches in the field of filling process modeling in the literature can be found. Zheng et al. [7] modeled an optimizing control method for a high utilization ratio and fast filling speed in hydrogen fuelling stations. The result of this research shows that an optimizing control method can significantly improve the utilization ratio and allow refueling in a widely acceptable time. The researchers are also underway to model the fast filling of hydrogen-based fuelling infrastructure, including the study by Liss and Richards [8]. Liss et al. [9] and Newhouse and Liss [10] have studied the fast filling of a hydrogen cylinder using a number of experiments. They reported a high temperature increase in the cylinder during the process.

A few experimental studies were also carried out to study the fast filling of an on-board cylinder, including the work of Chan Kim et al. [11] for hydrogen, Thomas and Goulding [12] and Shiply [13] for compressed natural gas (CNG). It should be noted that there is similarity between CNG hydrogen and CNG infrastructures.

For the hydrogen fast filling process, Chan Kim et al. [11] have studied thermal characteristics during the filling of a type IV cylinder. Computational fluid dynamics (CFD) analysis was also conducted to simulate the conditions of the experiments. The results predicted by the CFD analysis show reasonable agreement with the experiments, and the discrepancy between the results decreases with higher initial gas pressures.

For the CNG fast filling process, Shiply [13] concluded that ambient temperature could affect the process. He also concluded that the test cylinder was under-filled every time it was rapidly recharged.

Farzaneh-Gord et al. [14, 15] have modeled the fast filling process in CNG stations. They developed a computer program based on the Peng-Robinson state equation and methane properties table for a single reservoir. They investigated the effects of ambient temperature and initial cylinder pressure on the final on-board cylinder conditions. In another study, Farzaneh-Gord et al. [16] presented a thermodynamic analysis of the cascade reservoirs filling process of a cylinder. The results of this research indicated that ambient temperature has a strong effect on the filling process and the final natural gas vehicle (NGV) on-board cylinder conditions.

Farzaneh-Gord et al. [17] have carried out a theoretical analysis to study the effects of reservation type on the performance of CNG filling stations and the filling process. It is found that the time (filling time) required for bringing up the NGV on-board cylinder to its final pressure (20 MPa) in the buffer storage system is about 66% less than the cascade one. The charged mass for the cascade system is about 80% of the buffer system, which is an advantage for the buffer type. The biggest advantage of the cascade system over the buffer system is 50% less entropy generation for this configuration, which probably causes much lower required compressor input work as compared with the buffer system. The results show that each storage type has advantages over the other. The best configuration should be selected by balancing these advantages.

The second law has been employed in this study to calculate the amount of entropy generation theoretically. Entropy generation is associated with thermodynamic irreversibility, which is common in all types of thermal systems. Various sources are accountable for entropy generation. There have been numerous researches in the field of entropy generation. Bejan [18, 19] has concentrated upon the different mechanisms responsible for entropy generation in applied thermal engineering. The generation of entropy destroys the available work of a system. Therefore, it makes good engineering sense to focus on the irreversibility (see [18–20]) of heat transfer and fluid flow processes and try to understand the function of related entropy generation mechanisms. Since then, a lot of investigations have been carried out to compute entropy generation and irreversibility profiles for different geometric configurations, flow situations, and thermal boundary conditions. Here, entropy generation minimization has been employed as the main tool to determine the amount of work destruction during the filling process.

HYDROGEN FUELING STATION

Figure 1 shows a typical hydrogen fueling station. In these stations, hydrogen is compressed using a big multistage compressor into a storage system [21]. The storage system consists of several large cylinders, which are available in a variety of sizes, typically from 50 L internal capacity to well over 100 L. This system is maintained at a pressure higher than that in the vehicle's on-board cylinder so that gas flows to the vehicle.

MATHEMATICAL MODELING AND NUMERICAL PROCEDURE

In this study, to model the fast filling process and develop a mathematical method, the hydrogen on-board cylinder is considered to be a thermodynamic open system which goes through a quasi-steady process. Figure 2 shows a schematic diagram of the ther-

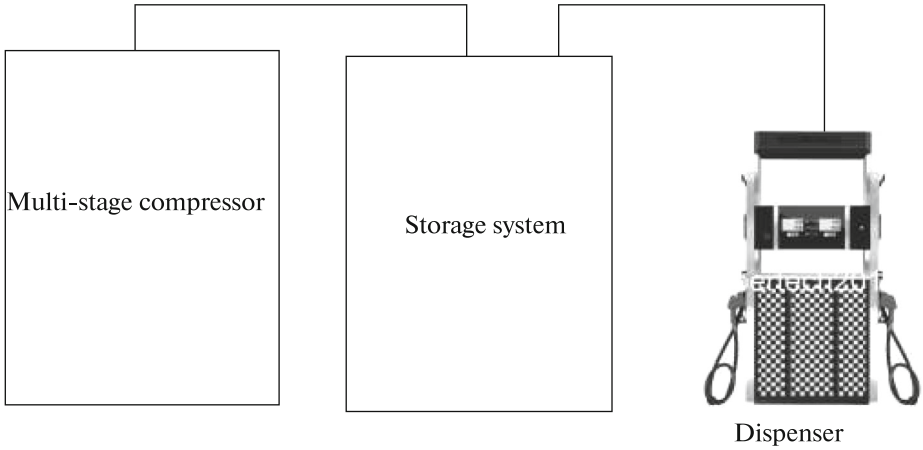

Fig. 1. Schematic diagram of a hydrogen filling station.

modynamic model which has been employed. In the actual filling process, an orifice flow meter is employed for accounting purposes. The diameter of current orifice flow meters is varied from 1 to 4 mm.

To develop a numerical method, the continuity equation and the first law of thermodynamics have been applied to the cylinder to find two thermodynamics properties. Considering the on-board hydrogen cylinder as a control volume and knowing it has only one inlet, the continuity (conservation of mass) equation may be written as follows:

$$\frac{dm_c}{dt} = \dot{m}_i. \quad (1)$$

In this equation, $\dot{m}_i$ is the inlet mass flow rate and can be calculated by considering an isentropic expansion through an orifice. Applying gas dynamics' laws:

$$\dot{m}_i = C_d \rho_r A_{\text{orifice}} \left(\frac{p_c}{p_r}\right)^{\frac{1}{\gamma}} \left\{ \left(\frac{2\gamma}{\gamma-1}\right)\left(\frac{p_r}{\rho_r}\right)\left[1-\left(\frac{p_c}{p_r}\right)^{\frac{\gamma-1}{\gamma}}\right]\right\}^{\frac{1}{2}} \quad (2)$$
$$\text{if } \frac{p_c}{p_r} \succ \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}},$$

$$\dot{m}_i = C_d \sqrt{\gamma p_r \rho_r} A_{\text{orifice}} \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{2(\gamma-1)}} \quad (3)$$
$$\text{if } \frac{p_c}{p_r} \le \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}.$$

In these equations, C_d is the discharging coefficient of the orifice and stands for irreversibility. For the reversible process, $C_d = 1$.

The first law of thermodynamics for a control volume in the general form can be written as follows:

$$\dot{Q}_{cv} + \sum \dot{m}_i (h_i + V_i^2/2 + gz_i) = \sum \dot{m}_e (h_e + V_e^2/2 + gz_e) + d/dt[m(u + V^2/2 + gz)]_{cv} + \dot{W}_{cv}. \quad (4)$$

The work term is zero in the filling process and the change in potential and kinetic energy can be neglected. For simplicity, heat transfer through the cylinder walls into the environment is not considered. By applying the above assumptions, Eq. (4) can be rewritten as follows:

$$d(mu)_{cv}/dt = \dot{m}_i (h + V^2/2)_i. \quad (5)$$

Considering stagnation enthalpy as $h_r = h_i + V_i^2/2$, which is actually equal to the enthalpy of reservoir tanks, Eq. (5) is now as follows:

$$\frac{d(mu)_{cv}}{dt} = \dot{m}_i h_r. \quad (6)$$

The second law of thermodynamics and flow processes occurring in the "single" storage system of the hydrogen filling station, adopted in this study, makes

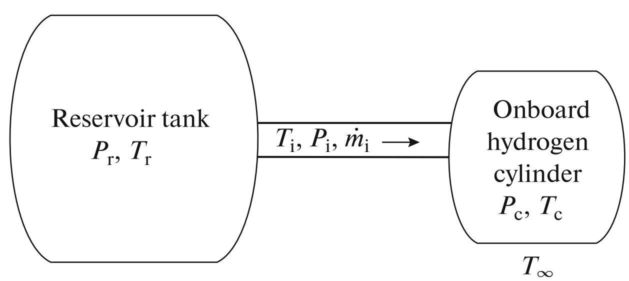

Fig. 2. Schematic diagram of the thermodynamic model.

it possible to estimate the entropy generation rates, $\dot{S}_{\text{gen}}$, for the characteristic nodes of the system.

The second law of thermodynamics for the filling process of an on-board hydrogen cylinder can be represented as

$$\dot{S}_{\text{gen}} = \frac{dS_C}{dt} - \frac{\delta \dot{Q}}{T_\infty} - \dot{m}_i s_i \geq 0. \quad (7)$$

Here, all irreversibility is assumed to occur from inlet to in-cylinder position. This makes an isentropic expansion from reservoir to inlet position, which means $s_i = s_R$. Considering this assumption and combining Eqs. (1) and (7), the following equation can be obtained:

$$\dot{S}_{\text{gen}} = \frac{d(m_C S_C)}{dt} - \frac{dm_C}{dt} s_R + \frac{U_{\text{Hc}} A_C (T_C - T_\infty)}{T_\infty}, \quad (8)$$

or in the following form:

$$\dot{S}_{\text{gen}} dt = d(m_C s_C - m_C s_R) + \frac{U_{HC} A_C (T_C - T_\infty)}{T_\infty} dt. \quad (9)$$

The above equation can be integrated from "start" of filling to "current" time as below:

$$S_{\text{gen}} = \int_s^c d(m_C s_C - m_C s_R) + \int_s^c \frac{U_{HC} A_C (T_C - T_\infty)}{T_\infty} dt. \quad (10)$$

For a fueling station with a single reservoir in which s_R remains constant throughout the filling process, the integration of the above equation resulted in the following simple equation:

$$S_{\text{gen}} = m_C(s_C - s_R) - m_{Cs}(s_{Cs} - s_R) + \frac{U_{HC} A_C (T_{av} - T_\infty)}{T_\infty}. \quad (11)$$

Equation (11) can be more simplified for an adiabatic system as

$$S_{\text{gen}} = m_C(s_C - s_R) - m_{Cs}(s_{Cs} - s_R). \quad (12)$$

If the cylinder is empty at the start of the filling process ($m_{\text{cs}} = 0$), the following relation can be obtained:

$$S_{\text{gen,max}} = m_C(s_C - s_R). \quad (13)$$

It should be noted that Eqs. (11)–(13) are only valid for a single reservoir fueling station. Calculating entropy generation for a fueling station with cascade reservoirs system demands more efforts.

NUMERICAL SOLUTIONS

In theory, it should be possible to calculate all thermodynamic properties by knowing two independent properties. The numerical procedure starts using Eqs. (2) and (3) to calculate the inlet mass flow rate.

Differential equations that should be solved simultaneously are the first law and continuity equations. With using the real gas model and discretization method, these equations can be written as follows:

$$\frac{m_{\text{cv}}^{j+1} u_{\text{cv}}^{j+1} - m_{\text{cv}}^{j} u_{\text{cv}}^{j}}{\Delta t} = \dot{m}_i^j h_i \Rightarrow u_{\text{cv}}^{j+1} = \frac{1}{m_{\text{cv}}^{j+1}} (m_{\text{cv}}^j u_{\text{cv}}^j + \Delta t \times \dot{m}_i^j h_i), \quad (14)$$

$$\frac{\Delta m_{\text{cv}}}{\Delta t} = \dot{m}_i^j \Rightarrow m_{\text{cv}}^{j+1} - m_{\text{cv}}^j = \Delta t \times \dot{m}_i^j \Rightarrow m_{\text{cv}}^{j+1} = m_{\text{cv}}^j + \Delta t \times \dot{m}_i^j, \quad (15)$$

$$\rho^{j+1} = \frac{m_{\text{cv}}^{j+1}}{V_{\text{cv}}}. \quad (16)$$

Internal energy is known from Eq. (14) and density is calculated with m_{cv} and cylinder volume from Eq. (16). Now, by knowing two independent thermodynamics properties (ρ, u), other thermodynamic properties can be calculated by using the hydrogen properties table provided by the NIST website. Solutions end when the hydrogen cylinder pressure reaches a user-input pressure (37 MPa) level.

Also, entropy generation in each time is computed as follows:

$$S_{\text{gen C}}^{(j+1)} = m_C^{(j+1)} s_C^{(j+1)} - m_C^{(j)} s_C^{(j)} - (\dot{m}_{\text{in}} s_R) \Delta t. \quad (17)$$

Finally, total entropy generation can be calculated as

$$S_{\text{gen}C(\text{total})} = S_{\text{gen}\,C}^{(1)} + S_{\text{gen}\,C}^{(2)} + \ldots + S_{\text{gen}\,C}^{(j)} + S_{\text{gen}\,C}^{(j+1)}. \quad (18)$$

Figure 3 shows a flowchart of thermodynamic simulation during the filling process.

RESULTS AND DISCUSSION

In this study, the hydrogen cylinder has been considered adiabatic; as a result, the characteristics of the orifice will not affect the end temperature state in the cylinder. The orifice diameter and the cylinder volume were considered to be 1 mm and 150 L, respectively. To study the effect of ambient temperature, the initial temperature of the hydrogen cylinder and reservoir tanks is set to the ambient temperature. The results have been presented here for a single reservoir tank at 37 MPa.

Figure 4 shows the effects of the initial cylinder pressure on the dynamic pressure of the hydrogen cylinder. It can be seen that, as the initial pressure increases, the filling time decreases. This is due to the fact that the cylinder encountered under-charged filling.

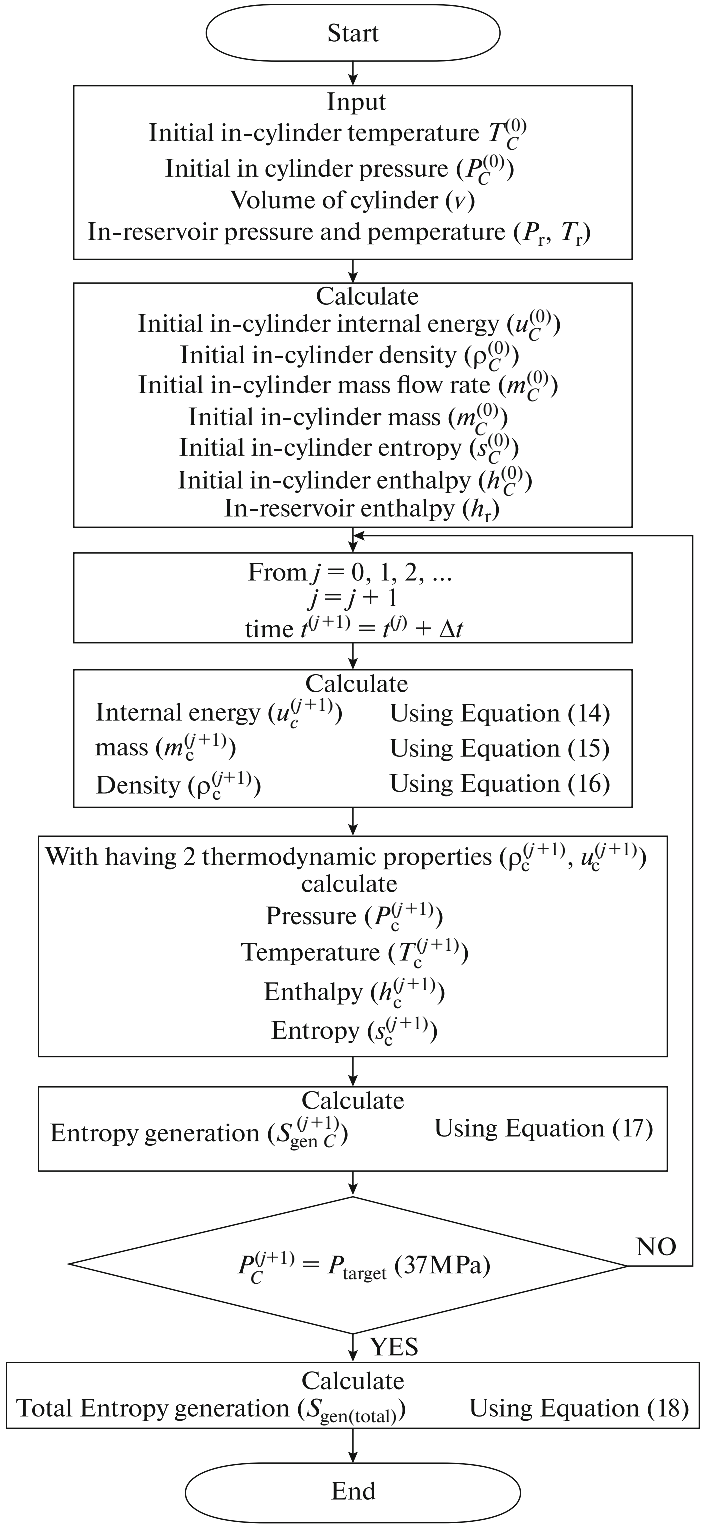

Fig. 3. Flowchart of simulation code.

In Fig. 5, the hydrogen on-board in-cylinder mass change during the filling process is shown for different initial pressures, while the initial temperature is kept constant at 300 K. It can be seen that, as the initial pressure increases, the final in-cylinder mass increases.

Figure 6 shows the effects of the initial cylinder and reservoir tank temperature on the filling time of the

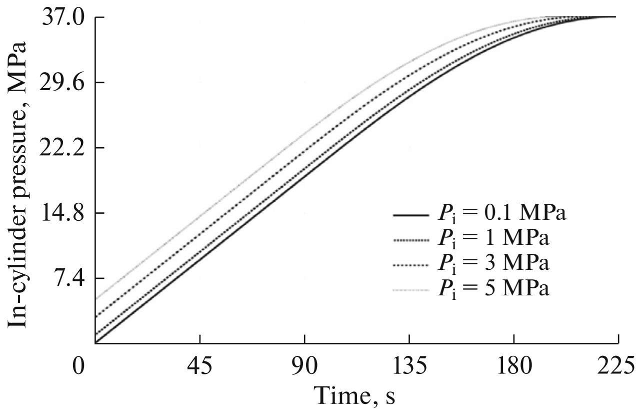

Fig. 4. Effect of the initial pressure on the dynamic pressure profile.

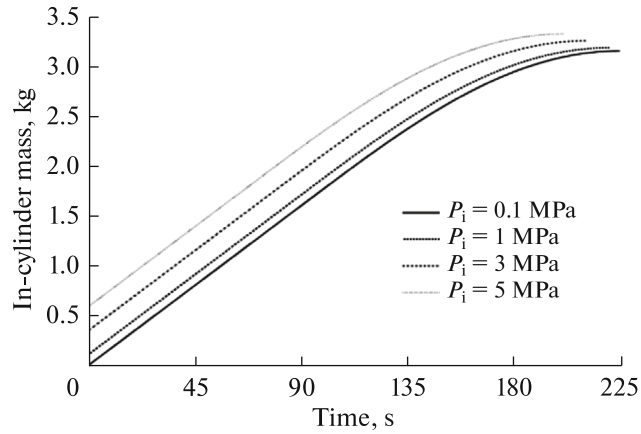

Fig. 5. Effect of the initial pressure on the mass profile during the filling process.

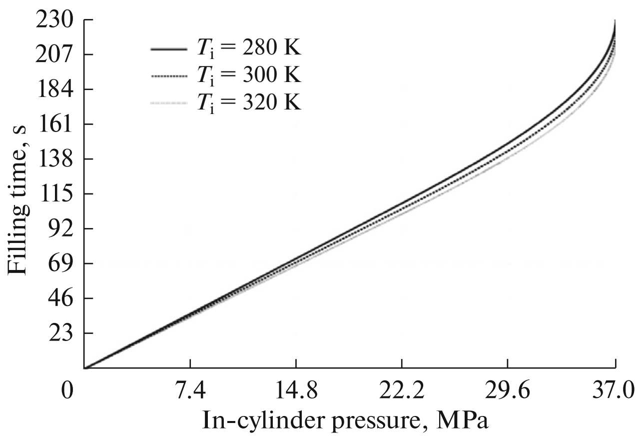

Fig. 6. Effect of the initial (ambient) temperature on the filling time.

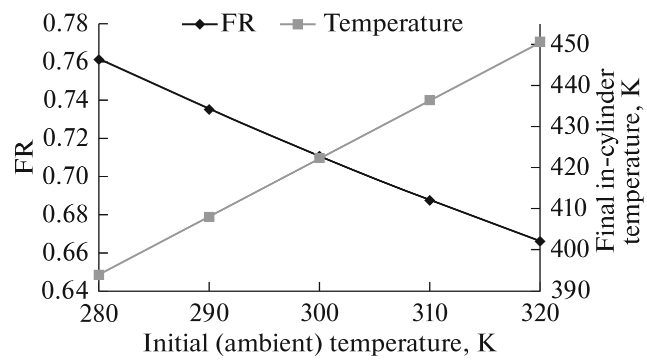

Fig. 7. Effect of the initial (ambient) temperature on the fill ratio and the final in-cylinder temperature.

hydrogen cylinder during the filling process. It can be seen that, as the initial temperature increases, the filling time decreases.

The cylinder "fill ratio" is defined as the charged cylinder mass divided by the mass which the cylinder could hold at the rating condition of 300 K ambient temperature and a pressure of 37 MPa. This parameter is directly related to the driving range of hydrogen vehicles. Figure 7 shows how the mass fill ratio varies with the initial temperature (in the hydrogen cylinder and reservoir tanks) which could describe the effect of ambient temperature. It can be seen that, as the initial temperature increases, the fill ratio decreases. This means that the driving range of a hydrogen vehicle will probably be decreased for hot weather compared to the colder conditions. The same conclusion can be made by studying the effect of ambient temperature on the final in-cylinder temperature of hydrogen within the cylinder in the same figure. It can be seen that the final in-cylinder temperature increases as ambient temperature increases.

Figure 8 shows the effects of the initial cylinder and reservoir tank temperature on entropy generation. The second law analysis has been employed to calculate the amount of entropy generation during the filling process. It is well known that the less entropy generation associates to less required work by the compressor. It can be seen from the figure that, as the initial temperature increases, entropy generation during the filling process decreases.

CONCLUSIONS

In this study, a numerical method has been developed based on the first and second laws of thermodynamics, conservation of mass and real gas assumptions to simulate the fast filling process of the hydrogen cylinder. The model has been applied for a single reservoir tank.

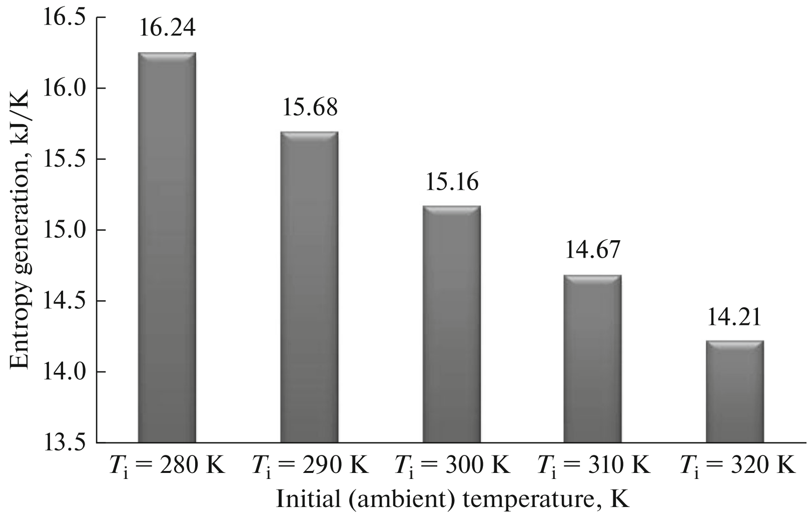

Fig. 8. Effect of the initial (ambient) temperature on total entropy generation.

The results indicate that there is a temperature rise on the order of 100 K or more during the charging process. This would lead to an under-filled hydrogen cylinder and reduce the driving range of hydrogen vehicles. The results also indicate that ambient temperature has a strong effect on the filling process and the final hydrogen cylinder conditions. As ambient temperature rises, the fill ratio and the amount of charged gas drop, which causes a low driving range as a result, filling the hydrogen during the night probably more efficient than during the day, especially during summer. In other words, as ambient temperature rises, the amount of total entropy generation drops, which causes low energy consuming for compressing hydrogen by compressors as a result.

NOTATION

A	area, m^2
C_d	orifice discharge coefficient
c_p, c_v	constant pressure and volume specific heats, kJ/(kg K)
g	gravitational acceleration, m/s^2
h	specific enthalpy, kJ/kg
M	molecular weight, kg/kmol
$\dot{m}$	mass flow rate, kg/s
P	pressure, MPa
$\dot{Q}$	heat transfer rate, kW
T	temperature, K or °C
u	internal energy, kJ/kg
V	velocity, m/s
v	specific volume, m^3/kg
W	actual work, kJ/kg
$\dot{W}$	actual work rate, kW
z	height, m
ρ	density, kg/m^3

SUBSCRIPTS AND SUPERSCRIPTS

c	NGV cylinder
i	initial or inlet condition
r	reservoir tank

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