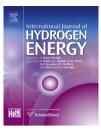


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# Gas tank fill-up in globally minimum time: Theory and application to hydrogen



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#### ABSTRACT

The process of filling-up high-pressure gas storage vessels consists of a gas source tank, an isenthalpic (Joule–Thomson or J–T) valve, a cooling system, and a gas storage vessel. These units are assumed to be thermally insulated. The fill-up process is formulated as a minimum time optimal control problem. Despite the nonlinear nature of the aforementioned optimal control problem, its global solution is obtained analytically. A novel transformation technique is employed, to decompose the problem into a process simulation problem independent of time, and a simpler minimum time control problem that only depends on the final molar density value and the maximum allowable feed mass flowrate. The feasibility of the fill-up is uniquely determined by the process simulation problem, and upon fill-up feasibility, the minimum time control problem is then globally solved. Two fillup case studies, involving two different system configurations are analyzed. In Case 1, the fill-up process has a constant molar enthalpy feed, and no cooling system. Case 2 considers a fill-up process with a constant temperature feed, delivered by an efficient cooling system. It was demonstrated that the optimal control strategy to achieve minimum fill-up time is to have the mass flowrate at its maximum allowable value during the entire duration of the fill-up. The presented problem formulation is general and can be applied to the fill-up of other gases, such as compressed natural gas.

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#### Introduction

A significant issue faced by fueling stations that serve gaseous fuels, such as hydrogen and compressed natural gas (CNG), is to provide a rapid, complete, and safe replenishment of the fuel. In the case of gaseous hydrogen fuel, all fill-up specifications are subjected to a limitation of the gas storage vessel of hydrogen fuel cell car vehicles. From Ref. [1], type IV tanks with polyamide or plastic liner and carbon fiber wrap, may exhibit mechanical failure if the temperature of the gas inside them is raised above 85 °C (358.15 K) during their repeated fillups. Consequently, it is required that during fill-up the gas temperature inside the vehicle tank be kept below the maximum temperature limit of 85 °C (358.15 K). Subject to this safety requirement, the fill-up needs to be performed in as short time as possible, so the end-user does not see the hydrogen car fill-up process as a hindrance, compared to the fill-up of gasoline cars.

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To address the aforementioned safety and time constraints, current hydrogen fueling stations slow down the hydrogen fill-up process or pre-cool the hydrogen below 0°°C so they can employ a higher hydrogen fill-up rate. For example, Ref. [1] refers to fill-ups of on-board 700.00 bar and 150 L type III and type IV tanks with warm and cold fill-up processes. The warm process of Ref. [1] filled-up to 90% of completion a type III tank in 3-4 min with hydrogen starting at ambient temperature; a fill-up to 100% completion required cooling down the hydrogen to temperatures around 0 °C (273.15 K). Both warm fill-ups avoided the hydrogen's temperature rise reaching 85 °C. The cold fill-up process reported in Ref. [1] was performed on a type IV tank, with hydrogen from the station storage tank pre-cooled to temperatures between 253.15 K and 233.15 K (-20 °C to -40 °C), and the fill-up carried out in 3-4 min. Ref. [1] also carried out a cold fill-up in less than 3 min, when hydrogen was pre-cooled to 188.15 K (-85 °C). Ref. [1] discusses hydrogen pre-cooling to liquid nitrogen temperatures, 77.00 K or -196.15 °C, for fast fill-ups. Likewise, Ref. [2] states that for fill-ups under 4 min, precooling to temperatures from 248.15 K to 233.15 K (-25 °C to -40 °C) is required for 700.00 bar tanks, but pre-cooling may not be required for 350.00 bar tanks.

The fill-up of CNG cars faces similar issues to the ones described above for hydrogen. The typical pressure rating of CNG tanks is 250.00 bar (3600 psi). Ref. [3] describes two types of CNG fill-ups: fast-fill and time fill. A fast-fill of CNG can last 5 min and lacks control on the temperature of CNG during the under which the fill-up can be performed in four to 1 min, without violating safety limits. The problem formulation is general and can be employed in commercial applications like fill-up of hydrogen vehicles, fill-up of CNG vehicles, and fill-up of high-pressure storage tanks.

#### Conceptual framework and solution approach

#### Thermodynamic modeling for real gases

Modeling the fill-up of high-pressure storage vessels with gases requires that a detailed thermodynamic model be employed for the gas phase. In this work, a gas phase that consists of only one chemical species is considered, and Gibbs' phase rule then suggests that two independent thermodynamic variables (in this work temperature (T) and molar density ( $\rho$ )) are required to fully define the system state. The Generic Cubic (GC) equation of state is then employed to describe the dependence of pressure on these independent variables as follows:

$$P: \mathbb{R}^2 \to \mathbb{R}, \quad P: (T,\rho) \to P(T,\rho) \triangleq \frac{RT\rho}{1-b\rho} - \frac{a(T)\rho^2}{(1+\varepsilon b\rho)(1+\sigma b\rho)}$$
(1)

In addition, a self-consistent thermodynamic model for the gas molar internal energy, using residual properties and an ideal gas heat capacity model is employed, as described in Ref. [4] and shown below:

$$\begin{aligned} u: \ \mathbb{R}^{2} \to \mathbb{R}, \quad u: \ (T,\rho) \to u(T,\rho) &\triangleq u^{\mathbb{R}} + \ln\left(\frac{1+\sigma b\rho}{1+\epsilon b\rho}\right) \left[ \left(T \frac{\Psi \mathbb{R}^{2} T_{c}}{\mathbb{P}_{c} b(\sigma-\epsilon)}\right) \left(-0.5 \left(\frac{T}{T_{c}}\right)^{-1.5}\right) - \frac{1}{b(\sigma-\epsilon)} \frac{\Psi \mathbb{R}^{2} T_{c}^{2}}{\mathbb{P}_{c}} \left(\frac{T}{T_{c}}\right)^{-0.5}\right] \\ &- \ln\left(\frac{1+\sigma b\rho^{\mathbb{R}}}{1+\epsilon b\rho^{\mathbb{R}}}\right) \left(T^{\mathbb{R}} \frac{\Psi \mathbb{R}^{2} T_{c}}{\mathbb{P}_{c} b(\sigma-\epsilon)} \left(-0.5 \left(\frac{T^{\mathbb{R}}}{T_{c}}\right)^{-1.5}\right) - \frac{1}{b(\sigma-\epsilon)} \frac{\Psi \mathbb{R}^{2} T_{c}^{2}}{\mathbb{P}_{c}} \left(\frac{T^{\mathbb{R}}}{T_{c}}\right)^{-0.5}\right) \\ &+ \left(C_{p_{\mathbb{A}}}^{0} - \mathbb{R}\right) \left(T - T^{\mathbb{R}}\right) + \frac{1}{2} C_{p_{\mathbb{B}}}^{0} \left(T^{2} - (T^{\mathbb{R}})^{2}\right) + \frac{1}{3} C_{p_{\mathbb{C}}}^{0} \left(T^{3} - (T^{\mathbb{R}})^{3}\right) + \frac{1}{4} C_{p_{\mathbb{D}}}^{0} \left(T^{4} - (T^{\mathbb{R}})^{4}\right) \\ &+ \frac{1}{5} C_{p_{\mathbb{E}}}^{0} \left(T^{5} - (T^{\mathbb{R}})^{5}\right) \end{aligned}$$
(2)

fill-up process. On the other hand, a time fill can last several hours, is usually performed overnight, and provides complete control over the CNG temperature.

In this work, a novel solution methodology, that tackles the issues mentioned above, is proposed for the fill-up process of any high-pressure storage vessel. Based on a self-consistent thermodynamic, and conservation law based model described in Ref. [4], the fill-up process is formulated as a minimum time optimal control problem that incorporates all safety and efficiency concerns as problem constraints. Then, a novel transformation allows the decomposition of the minimum time control problem into a simulation problem that determines problem feasibility, and a time optimal control problem that can be analytically solved. Two fill-up cases are explored: gas fed at constant molar enthalpy and gas fed at constant temperature. The first case gives rise to a set of algebraic equations, while the second case gives rise to a differential-algebraic-equation (DAE) system. Finally, the solution methodology for both cases is applied to the case of a hydrogen fuel cell car fill-up, and conditions are identified

Then, the gas molar enthalpy is readily derived as:

$$h: \mathbb{R}^2 \to \mathbb{R}, \quad h: (T,\rho) \to h(T,\rho) \triangleq u(T,\rho) + P(T,\rho)/\rho$$
 (3)

#### Gas storage vessel fill-up model

Two gas storage vessel fill-up configurations are illustrated in Fig. 1a and b. The first does not employ a cooling system, while the second one does. They both employ the following pieces of equipment: gas source tank, isenthalpic (Joule–Thomson or J–T) valve, and gas storage vessel.

The following set of assumptions is employed in creating a model for the above system configurations:

- The overall process is adiabatic, so no heat transfer is allowed between any of the system components and the environment, at any point in time.
- The pressure of the isenthalpic valve outlet is equal to the pressure inside the gas storage vessel (whether a cooling system exists or not).

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