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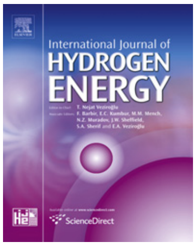

Small-scale hydrogen liquefaction with a two-stage Gifford–McMahon cycle refrigerator

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ABSTRACT

We manufactured a small-scale hydrogen liquefier with a two-stage 10 K Gifford–McMahon cycle (GM) refrigerator. It had a hydrogen tank with the volume of 30 L that was surrounded by a radiation shield. This liquefier continuously liquefied gaseous hydrogen with the volumetric flow rate of 12.1 NL/min. It corresponds to the liquefaction rate of 19.9 L/day for liquid hydrogen. We proposed a simple estimation method for the liquefaction rate and confirmed that the estimation method well explained the experimental result. To evaluate the estimation method, we applied the estimation method to other liquefiers. In case of a liquefier with the GM refrigerator, we confirmed the estimation method was available for predicting the liquefaction rate. However, in case of a liquefier with the pulse tube refrigerator, the results of the estimation indicated small values as compared with the experimental data. We discuss the details about the estimation method of the liquefaction rate for the small-scale liquefiers.

1. Introduction

We have investigated the totalized hydrogen energy utilization system for applying it to commercial buildings that consists of a unitized reversible cell, which has the fuel cell and the water electrolysis functions, and of metal hydride tanks using AB5 type metal hydride alloy [1,2]. We produce hydrogen using water electrolysis mode of the unitized reversible cell and store the hydrogen in the metal hydride tanks in nighttime, and generate electric power by means of the fuel cell mode of the unitized reversible cell in daytime. In case of emergency, we have a plan to use liquid hydrogen, which is transported from a hydrogen station. In this case, the metal hydride tanks store the boil-off gas from liquid hydrogen. To investigate the absorption/desorption characteristics of the metal hydride alloy for the boil-off gas, we designed and manufactured a small-scale hydrogen liquefier, which was the liquid hydrogen supplier, using a two-stage 10 K Gifford–McMahon cycle (GM) refrigerator.

At the present day, large-scale liquefier industrially produces liquid hydrogen. The Joule–Thomson cycle (Linde cycle) is the simplest liquefaction cycle. The hydrogen gas is compressed and then cooled below the inversion temperature of 202 K in a heat exchanger before it passes through a throttle

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valve where it undergoes an isenthalpic Joule–Thomson expansion. After the expansion, a part of gas transforms to the liquid state and the rest of the cooled gas is returned to the compressor via the heat exchanger. In the real field, the multistage compressor Claude system, which is the system with the Joule–Thomson cycle and the helium Brayton cycle, is widely used [3–5]. In these systems, hydrogen is usually pre-cooled using liquid nitrogen before the first expansion process [6].

On the other hand, there are a few reports in case of small-scale hydrogen liquefaction system. NASA manufactured and tested a zero boil-off hydrogen tank for the purpose of space application [7]. A pulse tube refrigerator was used for cooling liquid hydrogen and the cooled liquid was pumped and sprayed in the vapor phase in the tank through a spray bar. This system adopted an intricate technique in order to apply it under micro-gravity conditions. Walker et al. proposed a two-stage Stirling refrigerator for the application to hydrogen vehicle [8].

As for the production of small-scale liquefied gas using refrigerators, the helium liquefaction systems provide a lot of useful and helpful information. Yoshimura et al. reached under liquid helium temperature by using a three-stage GM refrigerator [9,10]. Around the same time, Kuriyama et al. also reached the temperature by using a two-stage GM refrigerator and successfully liquefied helium gas at room temperature [11,12]. After that, the investigation of pulse tube refrigerator became an active area of research and development. Nowadays, 4 K pulse tube refrigerators are used in the sensitive superconducting systems, such as NMR, MRI, and SQUIDs, etc. The pulse tube refrigerators have no moving parts in the cold stages that provide considerable reliability. Thummers et al. manufactured a two-stage 4 K pulse tube refrigerator for helium liquefaction [13]. Wang improved the refrigerator and applied it to the helium re-condensing system [14,15].

We manufactured a hydrogen liquefier with a two-stage GM refrigerator and carried out the liquefaction experiment. In this paper, we propose a simple estimation method for the liquefaction rate and the predicted value is compared with the experimental result. We also evaluate the validity of the estimation method by comparing the results of the method with the experimental data obtained by other researchers.

2. Hydrogen liquefaction

A hydrogen molecule possesses two protons and two electrons. The combination of the two electron spins only leads to a binding state if the electron spins are anti-parallel. The wave function of the molecule must be anti-symmetric in view of the exchange of the space coordinates of two fermions (spin = 1/2). Thereby, there are two groups of hydrogen molecules according to the total nuclear spin. One group has parallel nuclear spin that is called the ortho-hydrogen. The other group has anti-parallel nuclear spin that is called the para-hydrogen. Since these two forms differ in energy, the physical properties also differ. Hydrogen at room temperature is composed of the ortho-hydrogen and the para-hydrogen at the ratio of 3–1. We call it 'normal hydrogen' and the density is 0.081 kg/m^3 at 300 K under 0.1 MPa. Immediately after the liquefaction of the normal hydrogen, the ratio of the ortho-hydrogen and the para-hydrogen remains unchanged. The saturation temperature is 20.324 K at 0.1 MPa, and the vapor density and the liquid density are 1.317 kg/m^3 and 70.901 kg/m^3, respectively. After the liquefaction, the ortho-hydrogen contained in the liquid converts slowly to the para-hydrogen from 75% to 0.2%. The conversion reaction from ortho-hydrogen to para-hydrogen is exothermic and the heat of conversion depends on the temperature. At the temperatures lower than 77 K, the enthalpy of conversion is 523 kJ/kg, which is larger than the latent heat of 451.9 kJ/kg. The conversion rate is very slow [16], but we can accelerate the conversion rate to a few minutes by using an appropriate ortho–para catalyst. The suitable catalysts are metals such as tungsten, nickel, or any paramagnetic oxides like chromium or gadolinium oxides [6]. Iron oxide is cheap and widely used in the industrial field.

When we liquefy hydrogen by using GM, Stirling, or pulse tube refrigerators, we have to cool-down gaseous hydrogen to the saturate temperature under the isobaric condition. Here, we consider the liquefaction of the normal hydrogen from the room temperature, 300 K, to the saturation temperature, 20.3 K, at 0.1 MPa. A refrigerator has to remove the sensible heat from 300 K to 20.3 K and the latent heat for condensation from gas to liquid. The power, W, can be written as follows,

$$W = \dot{m}\int_{T_{\mathrm{sat}}}^{T_0} c_{\mathrm{P}}\{(T_0 - T)/T\}\mathrm{d}T + \dot{m}L\{(T_0 - T_{\mathrm{sat}})/T_{\mathrm{sat}}\} \tag{1}$$

where $\dot{m}$ is the mass flux, c_{P} is the specific heat at constant pressure, L is the latent heat, and T shows the temperature. The subscripts 0 and sat show the initial state and the saturated vapor pressure condition, where the initial state is a condition at the room temperature under atmospheric pressure. The $(T_0 - T)/T$ shows the reciprocal number of the theoretical Carnot efficiency for a refrigerator. The work required for the liquefaction per unit mass, E_f, can be obtained from $W/\dot{m}$, which is called the minimum work for liquefaction. In case of the normal hydrogen, we can calculate that $E_f = 12.26$ MJ/kg. This shows the specific exergy difference between the liquid state and the initial state, and it can be easily obtained from the following equation,

$$E_f = (h_f - h_0) - T_0(s_f - s_0) \tag{2}$$

where h shows the specific enthalpy and s shows the specific entropy. The subscript f indicates the liquid. Using Eq. (2), we can obtain that $E_f = 12.10$ MJ/kg, which is nearly equal to the value obtained from Eq. (1). In these calculations, the thermodynamic properties were read from the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP Ver. 8.0).

3. Description of the hydrogen liquefier

To investigate the absorption/desorption characteristics of the metal hydride alloy for the boil-off gas, we needed to prepare liquid hydrogen. The main component of the boil-off gas is para-hydrogen. Of course, we can buy liquid hydrogen, but in that case we have to construct a special storage area,