# A STUDY ON DISPERSION RESULTING FROM LIQUEFIED HYDROGEN SPILLING

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## ABSTRACT

For massive utilization of hydrogen energy, it is necessary to transport a large quantity of hydrogen by liquefied hydrogen carriers. However, the current rule on ships carrying liquefied hydrogen in bulks do not address the maritime transport of liquefied hydrogen, and the safety assessment of liquefied hydrogen carriage is thus very important. In the present study, we spilled liquefied hydrogen and LNG (Liquefied Natural Gas) on the surface of various materials, and compared the difference of their spread and dispersion. Liquefied hydrogen immediately dispersed upward compared to LNG. Furthermore, we also measured the flammability limit of low temperature hydrogen gas. Its range at low temperature was narrower than the range at normal temperature.

## 1. INTRODUCTION

It is imperative for global society to shift to become a low carbon society and the target of Japan has been set to reduce $CO_2$ emissions by 80% in 2050 from 1990 [1]. To achieve this, it is necessary to convert most of our energy from fossil fuels to renewable energy. As one solution, it is hoped that the so-called $CO_2$-free hydrogen can be introduced, which is produced by naturally-derived energy without emitting $CO_2$ or produced with $CO_2$ capture and storage. As the utilization amount of hydrogen is expected to increase in the future, it will be necessary to construct a hydrogen infrastructure that can produce hydrogen at low cost in countries which have unused resources and to transport it in large quantities by the most suitable method such as liquefaction to make it available in consuming countries. As the transportation means to enable this, maritime transport of liquefied hydrogen will be efficient. However, the IGC Code, "International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk " [2], does not currently address liquefied hydrogen because there has not been a past record of maritime transport of liquefied hydrogen in bulk. Therefore, the safety assessment and standardization of the IGC Code for liquefied hydrogen are needed as well as technological development of liquefied hydrogen carriers.

We have to consider the assumptions of and countermeasures for serious hazards in advance. The possible main serious hazards consist of the following three kinds: 1) damage of the hull during transportation, 2) leakage of liquefied hydrogen and 3) fires and explosions. It is especially important to evaluate the behaviour of liquefied hydrogen leakage in 2) above because there is a possibility of explosion and fire from an ignition source.

First of all, when the above-mentioned danger is evaluated, it is necessary to understand the diffusibility of liquefied hydrogen in the atmosphere. It is especially important to understand the difference in diffusing behaviour between LNG (Liquefied Natural Gas) which is already subject to maritime transport and liquefied hydrogen. However, there is little experimental research on the comparative diffusibility of liquefied hydrogen and LNG. Moreover, as the hydrogen atmosphere formed after evaporation of leaked liquefied hydrogen is expected to be at a low temperature, it is preferable to understand the flammability limit of hydrogen in a low temperature atmosphere. However, not much concrete information on the flammability range in the low temperature atmosphere is available. This paper describes the element tests which were conducted on the following two points: 1) qualitative understanding of the

diffusibility of liquefied hydrogen when it spills out based on comparison with LNG and 2) investigation of the upper/lower flammability limits of hydrogen in low temperatures.

## 2. Study on spilling and dispersion of liquefied hydrogen

### 2.1 Purpose of the experiment

Table 1 shows the difference of physical properties between hydrogen and methane which is the main component of LNG [3], [4]. From the viewpoint of ignitability, hydrogen has a wider flammability range and smaller minimum ignition energy compared to methane. However, from the viewpoint of diffusibility, hydrogen has the tendency to promptly evaporate after spilling, not to stay downward and to easily diffuse upward by its buoyancy due to having smaller evaporation latent heat and smaller gas density than methane. Then, an attempt was made in this test to compare the diffusibility of liquefied hydrogen and LNG based on the spread of the vapour cloud generated by their spill. Moreover, as the diffusibility may be greatly affected by the kind of contact surface touched by spilled liquefied hydrogen (hereafter contact surface), the test was conducted on various contact surfaces.

**Table 1  Comparison of physical properties between liquefied hydrogen and methane [3], [4].**

| Material | Boiling point [K] | Gas density [kg/m$^3$] | Gas density at boiling point [kg/m$^3$] | Liquid density [kg/m$^3$] | Evaporation latent heat [kJ/L] | Flammability range [vol.%] | Minimum ignition energy [10$^{-5}$J] |
|---|---|---|---|---|---|---|---|
| Hydrogen | 20.3 | 0.09 | 1.34 | 70.8 | 31.6 | 4-75 | 1.6 |
| Methane | 111.7 | 0.72 | 1.82 | 422.4 | 215.8 | 5-15 | 28 |

Remarks
1) The gas density is a value in the standard condition (273K, 1atm).
2) The liquid density and evaporation latent heat are the values in the 1atm and saturated condition.
3) The flammability range and the minimum ignition energy are the values in the normal temperature and pressure condition.

### 2.2 Experimental procedure

Fig. 1 shows the image of this test with liquefied hydrogen flowing out on the contact surface. Approximately 6 liters of liquefied hydrogen contained in a stainless open dewar vessel was spilled by inclining from a certain height onto the contact surface. To confirm the reduction of temperature in the space by the spilling of the liquefied hydrogen, the temperature distribution was measured by thermography. It flowed out completely in about 15 seconds. The test was executed by providing three kinds of contact surfaces including an austenite stainless steel plate (hereafter SUS plate), concrete and gravel to investigate the difference of evaporation and diffusion phenomenon depending on the kind of contact surface. The physical property of the contact surfaces is shown in Table 2. The SUS plate is generally used as a material for cryogenic application. Concrete was selected as a contact surface as it is a general building material and gravel was also selected as it is generally used as a material for road surfaces in flammable liquefied gas facilities such as LNG storage plants. The size of each contact surface was assumed to be 1.20m×1.20m. The distance between the container and the contact surface was assumed to be approximately 0.90m for each contact surface. Moreover, similar tests were executed for LNG as for liquefied hydrogen by using two kinds of surfaces (SUS plate and concrete) for comparison. The volume of LNG spilled was the same as liquefied hydrogen (6 liters). The weather condition in each test is shown in Table 3.

|                         |                         |
| :---------------------: | :---------------------: |
| **(a) Front view**      | **(b) Side view**       |

**Figure 1  Image of liquefied hydrogen spilling test (with liquefied hydrogen flowing out on the SUS plate).**

**Table 2 The physical property of the contact surfaces [5].**

| Contact surface | Density [kg/m³] | Thermal conductivity [W/(m·K)] | Thickness [mm] |
| :-------------: | :------------: | :----------------------------: | :------------: |
| SUS             | 7920           | 15.9                           | 8              |
| Concrete        | 1900-2300      | 0.8-1.4                        | 8              |
| Gravel          | 1800-2000      | 0.33-0.40                      | Approximately 50 |

Remarks
1) We assume that concreate and gravel have general physical properties.
2) The values of density and thermal conductivity are in the normal temperature and pressure condition.
3) The gravel used in this study is hard sand stone.

4) The grain size of gravel is 20-30mm.

**Table 3 The weather condition in each test.**

| Contact surface | Liquid | Temperature [°C] | Relative humidity [%] | Wind velocity [m/s] | Wind direction |
| :-------------: | :----: | :--------------: | :-------------------: | :-----------------: | :------------: |
| SUS             | LH2    | 4.7              | 36                    | 2.5                 | NW             |
|                 | LNG    | 9.0              | 23                    | 2.4                 | NW             |
| Concrete        | LH2    | 6.2              | 15                    | 1.6                 | NE             |
|                 | LNG    | 6.1              | 24                    | 3.1                 | WNW            |
| Gravel          | LH2    | 3.6              | 40                    | 0.9                 | NNW            |

**2.3 Result and discussion**

**2.3.1 Relationship between vapour cloud and concentration of hydrogen/methane**

Fig. 2 and Fig. 3 show an example of the test result. A vapour cloud was generated as the atmosphere was cooled and the moisture was condensed both for liquefied hydrogen and LNG. Fig. 2 and Fig. 3 show the image when the horizontal diffusion distance of the generated vapour cloud reached the maximum after spilling the liquid on each contact surface. Moreover, Fig. 4 and Fig. 5 show the comparison of temperature distribution and vapour cloud distribution when using the SUS plate as the contact surface. It can be confirmed that the range where the vapour cloud is generated roughly corresponds to the range below the dew point temperature.

It is very important for safety assessment whether the flammability range can be visually confirmed when leakage of flammable liquefied gas occurs. Therefore, in this test, we assumed that LNG equaled methane which was the principal ingredient of LNG, and estimated the concentration of the hydrogen/methane at the boundary inside and outside of the vapour cloud. In the calculation, we assumed that mixing of the atmosphere and the low temperature gas (hydrogen and methane) were adiabatically mixed under atmospheric pressure, and then determined the hydrogen or methane concentration when the atmosphere dropped to dew point [6]. The way of calculation is as follows.

(1) Setting the vapour pressure of moisture from atmospheric temperature and relative humidity

(2) Calculating the dew point temperature (calculating the temperature when the vapour pressure in (1) equaled the saturated vapour pressure)

(3) Determining hydrogen or methane concentration when the atmosphere and hydrogen/methane are adiabatically mixed and mixed gas equals the dew point temperature.

In this calculation, we assumed that the evaporation latent heat of liquefied hydrogen or LNG was all exchanged with the contact surface. The temperatures of the gases before mixing were assumed to be 20.3K for hydrogen gas (equal to boiling point), 111.7K for methane gas (equal to boiling point), and the measurement value for the atmosphere. We did not take into account condensation of moisture. Taking it into account, the concentration of the hydrogen or methane in the vapour cloud is higher because mixed gas is warmed up more by the condensation latent heat. However, in this study, because we focused on the concentration of hydrogen or methane at the boundary of inside and outside the vapour cloud, we consider that the amount of the vapour cloud at the boundary was low and the increase in temperature by condensation latent heat of moisture were ignorable. It is considered that this assumption is valid because the range where the vapour cloud is generated roughly corresponds to the range below the dew point temperature (Fig. 3, Fig.4).

Table 4 shows the results for concentration of hydrogen and methane at the boundary of inside and outside the vapour cloud obtained in each condition. Thus, it is considered that the values at the boundaries of inside and outside the vapour cloud are below the flammability limits both for hydrogen and methane and it is safe to be outside the vapour cloud. Moreover, the hydrogen concentration at the boundary of inside and outside the vapour cloud became smaller compared with that of methane. This is attributable to the fact that the smaller amount of liquefied hydrogen cools down the atmosphere to the dew point faster than LNG, as liquefied hydrogen is lower than LNG in temperature.
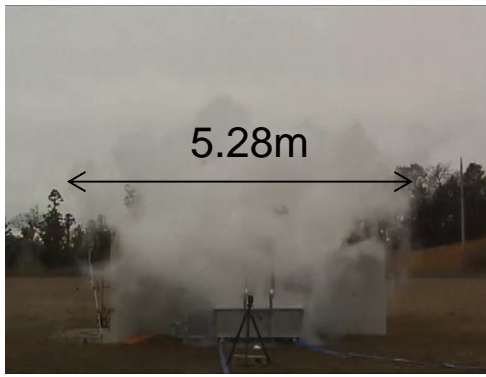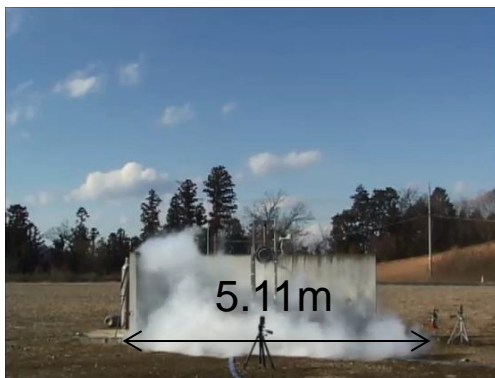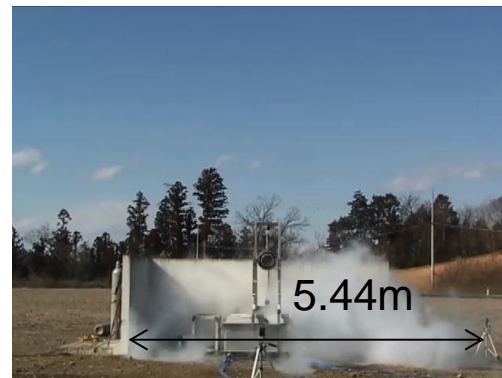
**(a) SUS plate**
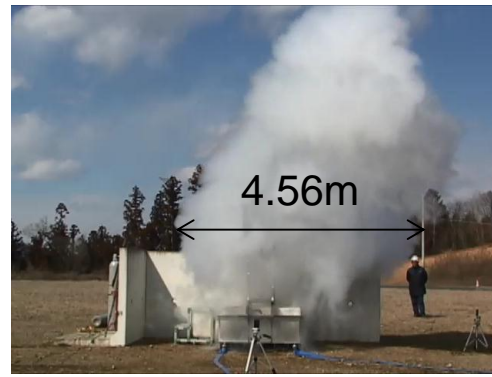
**(b) Concrete surface**
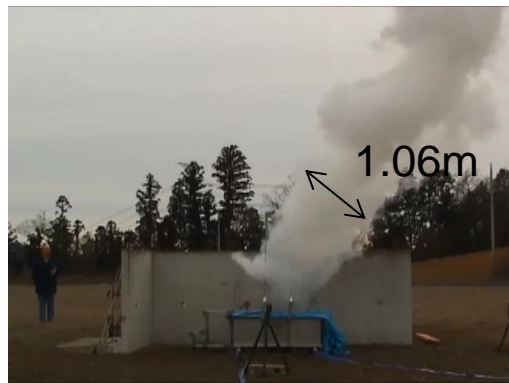


**(c) Gravel surface**

**Figure 2  Result of liquefied hydrogen spilling test (image when the horizontal diffusion distance was maximized).**



**(a) SUS plate**

**(b) Concrete surface**

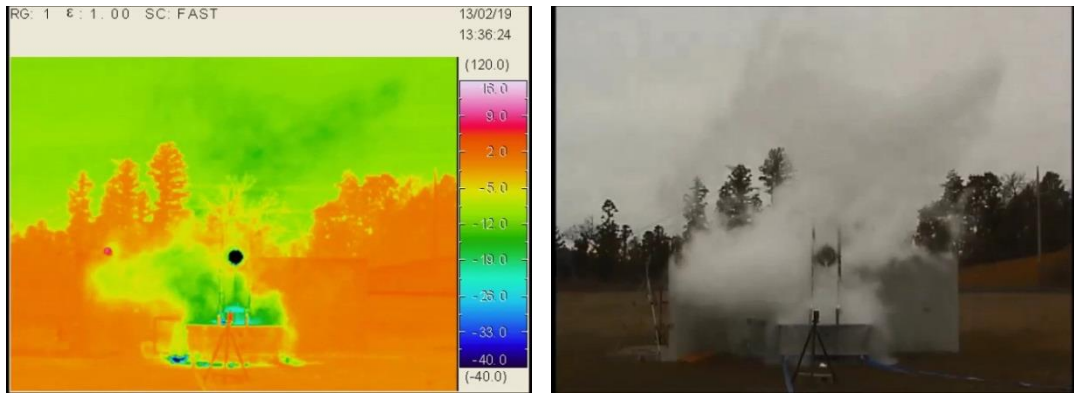**Figure 3  Result of LNG spilling test  (image when the horizontal diffusion distance was maximized).**

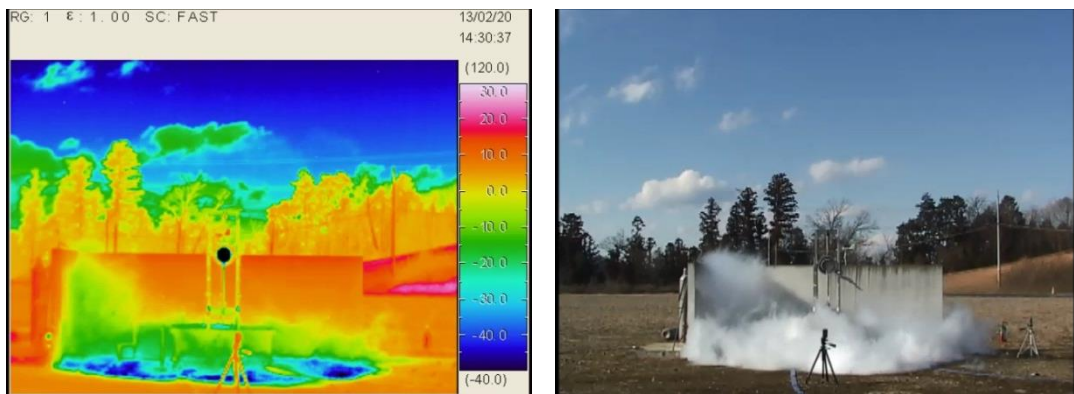**Figure 4  Temperature distribution and vapour cloud distribution (contact surface: SUS plate) when the liquefied hydrogen was spilled. The dew point temperature was -9.2°C.**



**Figure 5  Temperature distribution and vapour cloud distribution (contact surface: SUS plate) when LNG was spilled. The dew point temperature was -12.9°C.**

**Table 4 Concentration of hydrogen and methane at the boundary of inside and outside the vapour cloud under the assumption of adiabatic mixture.**

| Contact surface | Liquid | Concentration of hydrogen or methane at the boundary of inside and outside the vapour cloud [vol.%] |
|---|---|---|
| SUS | LH2 | 0.3 |
|  | LNG | 3.7 |
| Concrete | LH2 | 0.5 |
|  | LNG | 3.3 |
| Gravel | LH2 | 0.3 |

### 2.3.2 Comparison of diffusibility of liquefied hydrogen and LNG

From the spread of the vapour cloud in Fig. 2 and Fig. 3, it is found that the horizontal diffusion distance of liquefied hydrogen is shorter than that of LNG and the vertical diffusion distance is longer. In addition, considering that the concentration of hydrogen at the boundary of inside and outside the vapour cloud is smaller than that of LNG from Table 4, it is presumed that the horizontal diffusion distance of hydrogen gas is considerably shorter than that of LNG. The liquefied hydrogen does not stay on the contact surface after spill, and rapidly evaporates because the boiling point and evaporative latent heat is lower than that of LNG (Table 1). Moreover, the evaporated hydrogen gas rises promptly due to buoyancy immediately after evaporation as the specific weight at 23K is less than air at normal temperature (298K). On the other hand, although the specific weight of evaporated LNG is also less than air at the normal temperature, it is greater than air immediately after evaporation (112K) up to the vicinity of 160K. It is understood that this contributes to the diffusion behaviour of LNG floating near the surface of the ground.

### 2.3.3 Effect of contact surface on the diffusibility

In the case of liquefied hydrogen, as shown in Fig. 2, when the contact surface is gravel, the horizontal diffusion distance of the vapour cloud became the smallest. This result shows that the heat transfer rate of gravel to the liquefied hydrogen was larger than the other surface, and so it promptly evaporated and diffused upward without staying on the contact surface because the surface area of gravel was considerably greater compared to the other contact surfaces. On the other hand, the thermal conductivity of gravel is lowest in the contact surfaces (Table 2). This fact shows that the contribution of the surface area of the contact surface overtakes the effect of thermal conductivity.

### 3. Study on the flammability limit of hydrogen gas at low temperature

### 3.1 Purpose of the experiment

In general, the flammability range of hydrogen in the air is assumed to be the concentration of 4 - 75vol.% of hydrogen. This is the flammability range at normal temperature and pressure and it is known that the flammability range depends on temperature and pressure [7]. However, we could only find little concrete information on the flammability range in the low temperature atmosphere. As shown in the preceding chapter, the temperature of hydrogen ambience formed after the evaporation of liquefied hydrogen becomes low. Therefore, we investigated the flammability range of hydrogen gas at low temperature.

### 3.2 Flammability limit at low temperature

The definition of the flammability range is the concentration range for flammable gas capable of spreading flames by combustion [7]. Therefore, it is not regarded as combustion in the case that the combustion does not continue and flames are not transferred, even if it is ignited locally by discharge. According to the thermal combustion theory, in order for combustion to continue, a fast reaction rate is required as the heat generated by the oxidation reaction (combustion) needs to overcome the heat which escapes outside [4]. The chemical reaction rate changes depending on the temperature, and generally, the Arrhenius Equation is established between the rate constant and temperature. From the Arrhenius Equation, it is assumed the rate constant of combustion reaction becomes small along with the temperature drop and simultaneously the reaction rate is lowered. Therefore, the flammability range is expected to be reduced at low temperatures. In the case of saturated hydrocarbon gas, the temperature dependency of the lower flammability limit is shown by the expression (1) [8].

$$L_t = [1 - 0.000721(t - 25)]L_{25} \tag{1}$$

where $t$ is temperature [°C], $L_{25}$ is the lower flammability limit [vol.%] at 25°C (normal temperature) and $L_t$ is the lower flammability limit at temperature $t$ [vol.%]. As the lower flammability limit at 25°C is 4.0%, the lower flammability limit at -25°C and -75°C of hydrogen is calculated by using the expression (1) as 4.1% and 4.3%, respectively.

### 3.3 Experimental procedure

The investigation test of both flammability upper/lower limits of hydrogen was executed by using the test equipment shown in Fig. 6. The test equipment is made of stainless steel of 100A (Sch20), 244mm in height, and the discharge electrode made of copper is inserted from the cylinder upper flange at the position of 150mm and the clearance is set to 3mm.

Fig. 7 shows the image of the test. The test was executed in a hydrogen-air mixture system at three temperatures of normal, -25°C and -75°C. First of all, the combustion container was immersed in the low temperature liquid tank (dry ice/ethanol) for cooling to the target temperature. After reaching the target temperature, the temperature was adjusted by appropriately adding dry ice. Afterwards, the container was evacuated by vacuum drawing, and hydrogen and dry air were introduced to attain the target concentration. After leaving the introduced gas for three minutes until it was sufficiently mixed and stabilized, it was discharged by the spark discharge method and ignited. A discharge spark by a neon transformer with the secondary output of 15kV, 20mA was used as the ignition source. Discharge time was assumed to be 0.25 seconds. The experimental method in this study basically followed the standard of TIIS (Technology Institution of Industrial Safety, Japan). The TIIS standard is almost identical to a method by Yamaguma (2008) [9]. The clearance of the discharge electrode in this study (3mm) was however different from the TIIS standard (5mm), which was attributed to the low temperature atmosphere in this study. The clearance of the discharge electrode in this study was narrowed because the discharge spark did not occur under the clearance of the TIIS standard.

The presence of combustion was judged by the temperature rise of the thermo-couple in the combustion container located at the 135mm upper position from the copper electrode. First of all, the combustion test was executed at normal temperature corresponding to the flammability range which is already-known, and the judgment criteria of combustion (temperature rise and temperature drop) was determined so that the flammability range at normal temperature would become 4.0-75.0%. The flammability range at low temperature was determined according to the judgment criteria.
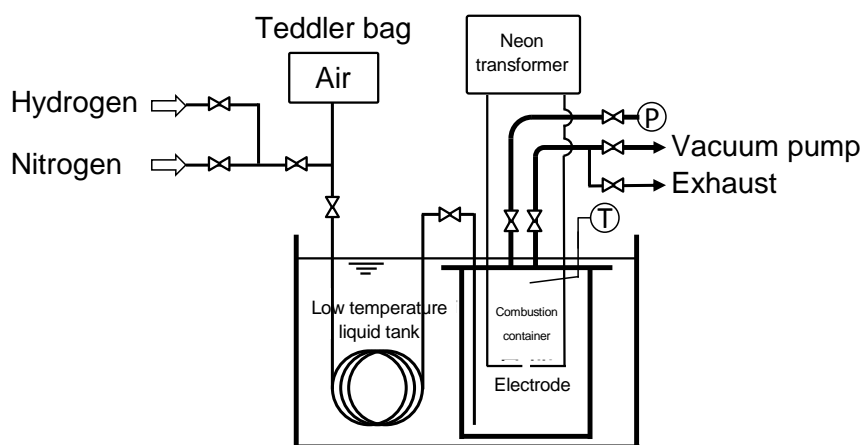


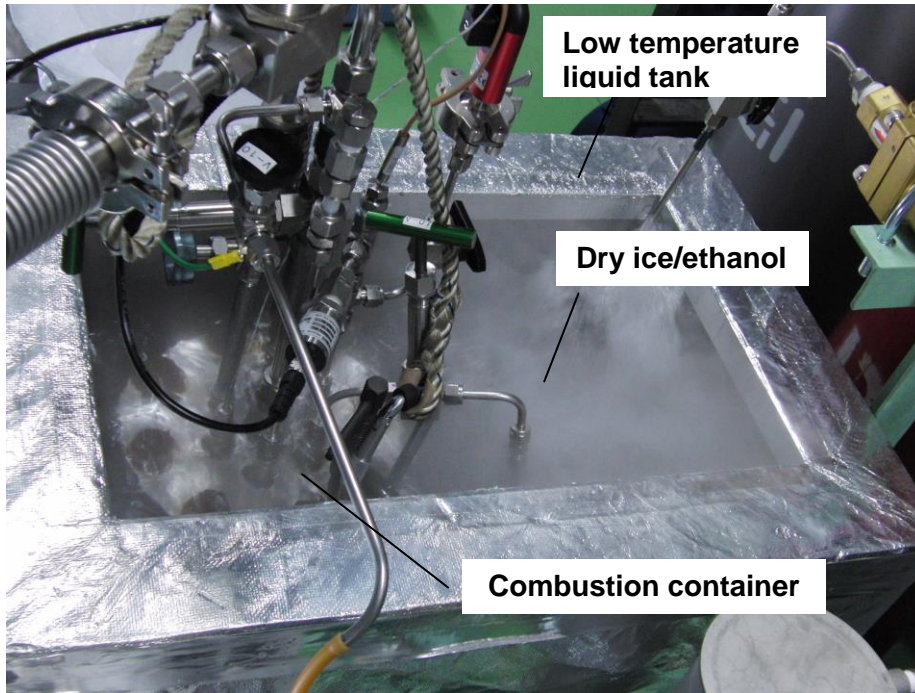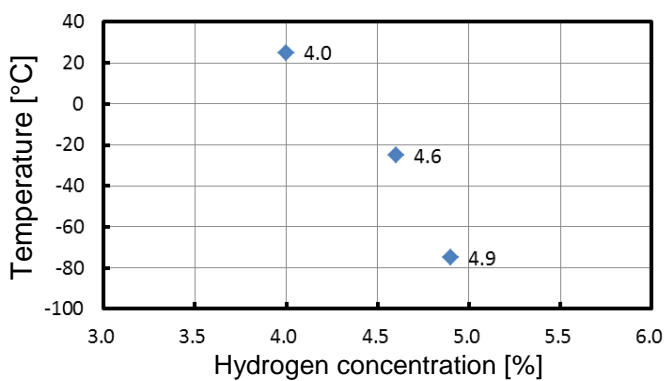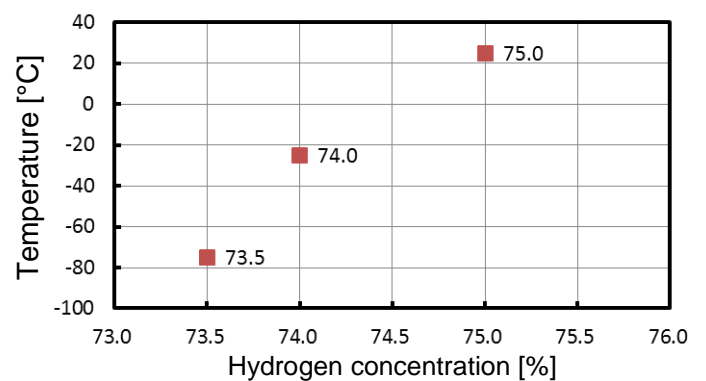**Figure 6  Test equipment of flammability range of low temperature hydrogen gas.**

**Figure 7  The image of the test about the flammability range of low temperature hydrogen gas (Temperature in liquid tank:-25°C).**

## 3.4 Results

Fig. 8 shows the test results. The flammability range of the hydrogen-air system became gradually narrower according to the reduction in temperature from the normal temperature to -75°C. It was consistent with the prediction in Section 3.2. Moreover, the experiment value increased by 0.5% at -25°C and by 0.6% at -75°C for the lower flammability limit compared to the values expected by the expression (1).



**(a) Lower flammability limit**          **(b) Upper flammability limit**

**Figure 8  Flammability range of low temperature hydrogen gas.**

## 4. Conclusions

In this study, element tests were conducted for the purpose of acquiring the basic data for risk assessment of liquefied hydrogen leakage for the safety assessment/standardization of liquefied hydrogen carriers. As a result, important findings were obtained as follows.

1) The spill and diffusion phenomenon of liquefied hydrogen

- It was suggested that the outside of the vapour cloud generated by the spill of liquefied hydrogen and LNG should be below the lower flammability limit from the relation between the spatial temperature distribution and the vapour cloud during the spill.

- From the comparative study of the diffusibility of the liquefied hydrogen and LNG, it was confirmed that, the horizontal diffusion distance of liquefied hydrogen is smaller than that of LNG and the liquefied hydrogen promptly evaporates and diffuses upward.

- The horizontal diffusion distance of liquefied hydrogen was smaller when the contact surface is gravel compared with concrete and SUS plate, which shows that gravel is effective for suppressing the horizontal diffusion distance.

2) The flammability limit of hydrogen gas in the low temperature atmosphere

- It was confirmed that both upper/lower limits of explosion at low temperature (−25°C,−75°C) were narrower than at normal temperature. The tendency was the same as that of general flammable gas such as hydrocarbon gas.

In order to understand the diffusion range of liquefied hydrogen leakage more quantitatively, it is preferable to execute the test indoors so that it is not affected by weather conditions such as winds, and to measure concentration distribution of hydrogen directly by using concentration meters. In addition, we will establish the simulation technology of diffusion behaviour of liquefied hydrogen based on those test result and the result of flammability limit at low temperature, and apply this to predict the diffusion behaviour in liquefied hydrogen carriers when leakage and spills occurs.

## 5. Acknowledgement

## 6. References

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