

New Measurement Technique for Vaporization Velocity of Spreading Cryogenic Liquid

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ABSTRACT

The study of liquid pool spreading plays an essential role in the quantitative risk assessment of accidentally released cryogenic liquids, such as LNG and liquefied hydrogen because the spreading of such liquids is the first step in the development of multi-staged accident sequences leading to a major disaster. There is a wide range of models used to describe the spreading of a cryogenic liquid pool. Many of these models require vaporization velocity, which has to be determined experimentally because the heat transfer process between the liquid pool and the surroundings is too complicated to be modeled. A constantly-released-flow onto unbounded ground was intended to generate the spreading pool because in almost all real accidents, a cryogenic liquid spills and spreads over a large or unbounded ground. According to the results, a greater release flow rate results in a greater vaporization velocity, and the vaporization velocity decreases with the spreading time. Measured vaporization velocities are compared to those obtained from a theoretical model to show good agreement in magnitude and trends. This agreement validates the semi-theoretical method to measure the vaporization velocity for the spreading pool without providing the information about the spill rate and pool mass.

KEYWORDS: Leak, hazard, vaporization velocity, spreading pool, cryogenic liquid.

NOMENCLATURE

A pool area (m²)
 E vaporization velocity (m/s)
 k thermal conductivity of the ground (W/(m·K))
 L latent heat of the liquid (J/kg)
 q'' heat flux (W/m²)
 R pool radius (m)
 r' pool radius (m)
 T temperature (K)
 t time (s)
 t' arrival time at pool radius r' (s)
 W liquid nitrogen mass (kg)
 \dot{W} spill rate (kg/s)
 z distance measured downward from the ground surface (m)

Greek

α thermal diffusivity of the ground (m²/s)
 Δ difference in measured quantity (-)
 ρ liquid density (kg/m³)

Subscripts

1 non-spreading pool
2 spreading pool
 a ambient
 B boiling point of the liquid
 e vaporization
 i thermocouple location
 p pool
 s spill

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INTRODUCTION

Cryogenic liquids, e.g., liquid hydrogen, liquefied natural gas, liquid nitrogen, etc., play important roles in a broad spectrum of industries as energy sources or coolants. However, most of these liquids are flammable and might cause cold burns and cold damage. The hazard of an accidental leakage of these liquids out of their containments needs to be considered. This is important because the liquid pool vigorously boils while it spreads on the ground in response to the significant difference between the ground temperature and boiling point of the cryogenic liquid. As a result, a vapor cloud forms quickly and disperses. The vapor cloud may cause an explosion or fire if ignition sources are available. Hence, studies on the spread and vaporization of liquid pools are necessary for risk management.

Many contributions involved in this phenomenon can be found in the literature on numerical and experimental works. Briscoe and Shaw [1] derived an unsteady one-dimensional heat conduction model to calculate a vaporization rate for a spreading and non-spreading pool of cryogenic liquid. Webber [2] developed the Gas Accumulation over Spreading Pool model, abbreviated as GASP, to predict the vaporization rate and pool size of an evaporating liquid pool. Kim et al. [3] presented high-order perturbation solutions to a liquid hydrogen spreading model with a continuous spill, in which the vaporization velocity has been assumed to be constant for simplification. Regarding experimental studies, Verfondern and Dienhart [4] investigated the spread and vaporization of liquid hydrogen on two different grounds, i.e., water and aluminum. Olewski et al. [5, 6] conducted experiments on a non-spreading pool to study the vaporization rate of liquid nitrogen. Reid and Wang [7] studied the boiling rate of liquefied natural gas on various dike floor materials. Takeno et al. [8] investigated the vaporization rates of liquid hydrogen and liquid oxygen spilled on a bounded ground. Kim et al. [9] presented an experimental study of the vaporization of spreading liquid nitrogen.

The vaporization for a non-spreading pool has been investigated in many other studies. The liquid in a non-spreading pool is bounded by a dike. In contrast, the liquid in a spreading pool can spread outward. A spreading pool with a continuous spill is more likely than a non-spreading pool from an instantaneous spill from accidents, and then the measurement of the vaporization velocity for the spreading pool is meaningful [9].

In the present study, in order to develop a new measurement method for the vaporization velocity in the spreading pool, the experimental data were compared to a semi-theoretical model based on an unsteady one-dimensional heat conduction formulation.

VAPORIZATION MODEL

It can be said that for cryogenic liquid spills on land, the dominant heat source to vaporize the spill is heat contained in the ground. Initially, the heat flux into the pool may be affected by the rate of heat transfer across a vapour blanket between the ground and the liquid, i.e., film boiling condition. However, as the surface temperature of the ground falls, the vapour blanket collapses and allows for better thermal contact and faster heat transfer in the nucleate boiling condition. Heat conduction through the ground then controls heat flux into the pool. A model was developed based on the assumption that heat transfer through the ground is always the controlling mechanism. This model has the additional assumptions that the liquid pool is thin and at a uniform temperature equal to its boiling point, that the pool is in perfect thermal contact with the ground, and that heat conduction in the ground is vertically one-dimensional.

Considering a liquid pool of constant area, the governing equations and boundary conditions are:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2}, \quad (1)$$

$$T = T_a \text{ for } 0 \leq z \leq \infty \text{ at } t = 0$$

$$T = T_b \text{ for } 0 < t \text{ at } z = 0$$

$$T = T_a \text{ for } 0 < t \text{ at } z = \infty$$

where z is distance measured downwards from the ground surface (m), T is the ground temperature (K), α is the thermal diffusivity of the ground (m^2/s), T_a is an ambient temperature (K) and T_b is boiling point (K).

Heat flux into the pool from the ground is [10]:

$$q'' = \frac{k(T_a - T_b)}{(\pi\alpha)^{0.5}} t^{-0.5}. \quad (2)$$

Since the vaporization velocity is defined as the vaporized volume per unit area of the pool and unit time, the following formula can be developed:

$$E_1 = \frac{q''}{\rho L} = \frac{k(T_a - T_b)}{\rho L (\pi\alpha)^{0.5}} t^{-0.5}, \quad (3)$$

where E_1 is the vaporization velocity for the non-spreading pool (m/s), ρ is density of the liquid (kg/m^3), and L is latent heat of the liquid (J/kg).

Based on the vaporization velocity of the non-spreading pool shown in Eq. (3), the vaporization velocity for a radially spreading pool when it spreads to a radius R is defined as [1]:

$$E_2 = \frac{1}{\pi R^2} \frac{k(T_a - T_b)}{\rho L (\pi\alpha)^{0.5}} \int_0^{R(t)} \frac{2\pi r' dr'}{(t - t')^{0.5}}, \quad (4)$$

where E_2 is the vaporization velocity for the spreading pool (m/s), t is the arrival time of the spreading pool at radius R (s), t' is the arrival time at radius r' (s), and the pool is assumed to be a circular cylinder.

The vaporization velocity of the non-spreading pool may be determined quickly because it is a function of time alone. On the other hand, it is not straightforward to obtain the vaporization velocity for the spreading pool because it depends on both the time and pool area, and annular ground elements contact the liquid for different time periods.

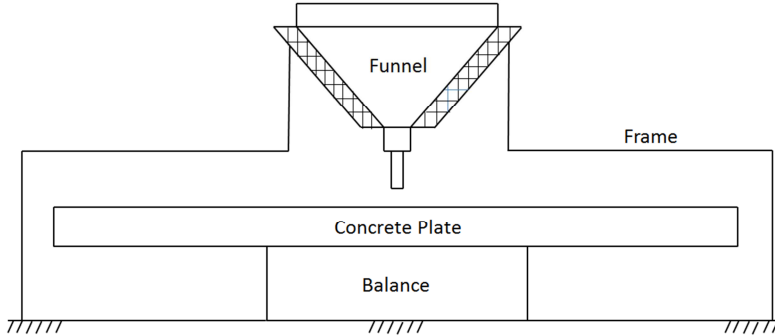
EXPERIMENTAL SET UP

In this work, liquid nitrogen was selected as the working fluid for safety reasons. Its properties are shown in Table 1. The liquid was continuously spilled onto a concrete plate to simulate an accidental discharge of a cryogenic liquid on land.

The overall experimental apparatus designed for laboratory-scale spills of liquid nitrogen on a concrete ground is shown in Fig. 1. The setup consisted of a cone-shaped funnel, a circular concrete plate, fifteen thermocouples, a digital balance and a data acquisition system.

Table 1. Properties of liquid nitrogen [11]

Density (kg/m ³)	Latent heat of vaporization (kJ/kg)	Boiling temperature (K)
808	199	77

**Fig. 1.** General schematic layout.

Liquid nitrogen was spilled onto the center of the concrete plate through a discharge nozzle from the cone-shaped funnel. The distance between the nozzle exit and the plate was about 0.01 m. The concrete plate with the diameter and thickness of 1 and 0.025 m, respectively, was thick enough to represent a semi-infinite ground in the experimental cases. The gasified nitrogen was able to freely disperse to the atmosphere. Experiments were performed for seven discharge nozzles with diameters of 6, 7, 8, 9, 10, 11 and 12 mm to analyze the effect of spill rate on the vaporization velocity. The funnel was well insulated to prevent heat transfer from the ambient environment to the liquid nitrogen through the funnel wall. The concrete plate presented a solid ground. Its thermal properties and conditions are described in Table 2. The digital balance with a resolution of 0.1 g measured the mass of the spreading liquid pool on the plate. The data acquisition system was used to record data from the thermocouples and balance.

Table 2. Thermal properties and conditions of the plate [5]

Material	Density (kg/m ³)	Thermal conductivity (W/(m·K))	Thermal diffusivity (m ² /s)	Initial temperature (K)
Concrete	2300	1.04	9.5×10^{-7}	293

Thermocouples were used to obtain the arrival time of the spreading pool. The pool was considered to have spread to a thermocouple location if the thermocouple temperature fell to the boiling point of the liquid. Fifteen thermocouples were mounted into the concrete plate, as shown in Fig. 2. Thermocouple TC-0 at the center of the plate was employed to determine the time when the experiment started. The liquid pool was assumed to be circular, but actually it was not. Two thermocouples, e.g., TC-R6 and TC-L6, were mounted at the same radius to consider the non-circularity of the pool. As can be expected, the arrival times of the liquid pool at two thermocouples located at the same radius were different. The average value of these two arrival times was considered the nominal arrival time at that radius. The maximum ratio between the difference in arrival times at two thermocouples and the nominal arrival time at that pool radius was 0.357. Two thermocouples TC-L7 and TC-R7, located at the boundary of the plate, were used to determine the time when the liquid pool spread out of the plate. The distance from the centre to the first two thermocouples is 0.2 m, and the rest of the thermocouples have an equal spacing of 0.05 m.

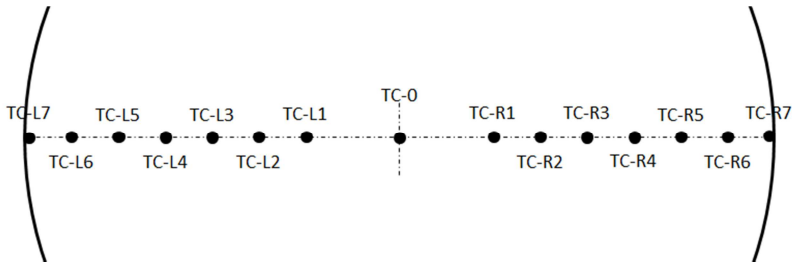


Fig. 2. Thermocouple distribution in the concrete plate.

The measurement method for the spill rate of liquid nitrogen using a funnel is described by Kim et al. [9]. The spill rates were not constant during the discharge time; instead, they varied slightly, i.e., less than 15.8 %. The results for the seven discharge nozzles are shown in Fig. 3. Four repeat experiments were conducted for each case of the spill rate, for a total of 28 experiments.

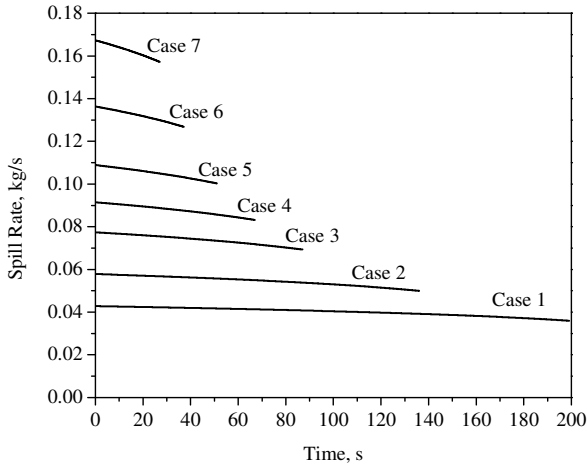


Fig. 3. Spill rates with time.

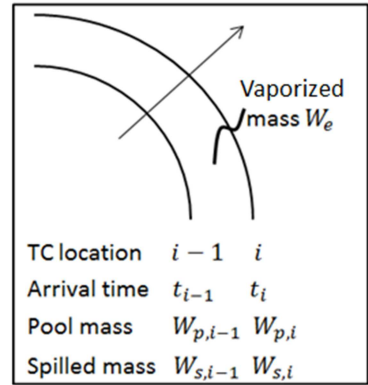


Fig. 4. The illustration of some notations.

When the pool spread to thermocouple i , the spilled liquid nitrogen mass $W_{s,i}$ was estimated by integrating the spill rate as follows

$$W_{s,i} = \int_0^{t_i} \dot{W} dt, \quad (5)$$

where t_i denotes arrival time of the pool at thermocouple i .

It was found that $W_{p,i} < W_{p,i-1} + (W_{s,i} - W_{s,i-1})$, where $W_{p,i-1}$ and $W_{p,i}$ denote the pool mass when the pool just arrived at thermocouples $i-1$ and i , respectively. The difference between both sides of the inequality accounts for the vaporized mass W_e . The illustration of the mentioned notations can be found in Fig. 4.

$$W_e = (W_{s,i} - W_{s,i-1}) - (W_{p,i} - W_{p,i-1}). \quad (6)$$

Then, when the pool spread from thermocouple $i-1$ to thermocouple i , the vaporization velocity was defined as

$$E_{i-1 \rightarrow i} = \frac{W_e}{\rho A_{i-1 \rightarrow i} (t_i - t_{i-1})}, \quad (7)$$

where $A_{i-1 \rightarrow i} = \frac{1}{2}(A_i + A_{i-1})$ is the average pool area.

RESULTS AND DISCUSSION

The average vaporization velocity shown in Fig. 5 illustrates that the greater the spill rate is, the higher the vaporization velocity is. In addition, the vaporization velocity decreases with the pool radius.

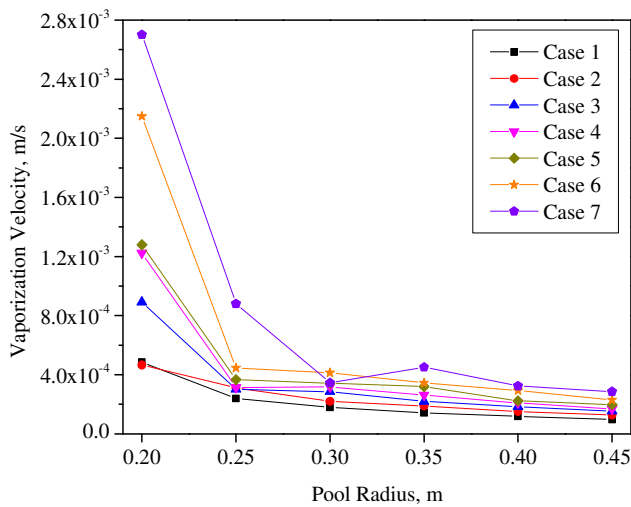


Fig. 5. Vaporization velocity versus pool radius.

Table 3. The difference in arrival time, s

$\Delta t_{i-1 \rightarrow i}$	Case						
	1	2	3	4	5	6	7
$\Delta t_{0 \rightarrow 1}$	29.04	13.67	8.68	5.81	4.89	3.64	3.00
$\Delta t_{1 \rightarrow 2}$	21.40	11.74	6.58	6.77	4.15	2.84	2.21
$\Delta t_{2 \rightarrow 3}$	28.57	17.15	10.24	8.72	6.35	5.72	2.89
$\Delta t_{3 \rightarrow 4}$	38.45	31.03	16.64	12.90	8.57	6.54	5.57
$\Delta t_{4 \rightarrow 5}$	35.29	28.78	19.53	14.29	10.39	7.08	5.00
$\Delta t_{5 \rightarrow 6}$	45.28	32.66	25.28	18.35	16.38	11.31	8.31

The main difficulty for theoretically determining the vaporization velocity for the spreading pool with the unsteady one-dimensional heat conduction model is that annular liquid elements are successively in contact with the ground. In Eq. (4), the term $(t-t')$ on the right-hand side is the period that the corresponding annular liquid element is in contact with the ground. It is the same as the difference in arrival times between two values of the pool radius, R and r' . Experimental data

for the difference in arrival times based on the average value are shown in Table 3. Experimental data for the difference in arrival times show that the time difference for a fast-spreading pool is shorter than that for a slow-spreading pool. As a result, at a specified pool radius, the vaporization velocity in the fast-spreading pool is greater than that in the slow-spreading pool. The vaporization velocity expressed in Eq. (4) was obtained with experimental data for the pool radius with time. To calculate the integral, the pool radius was assumed to be a linear function with time over each interval between two neighboring thermocouples.

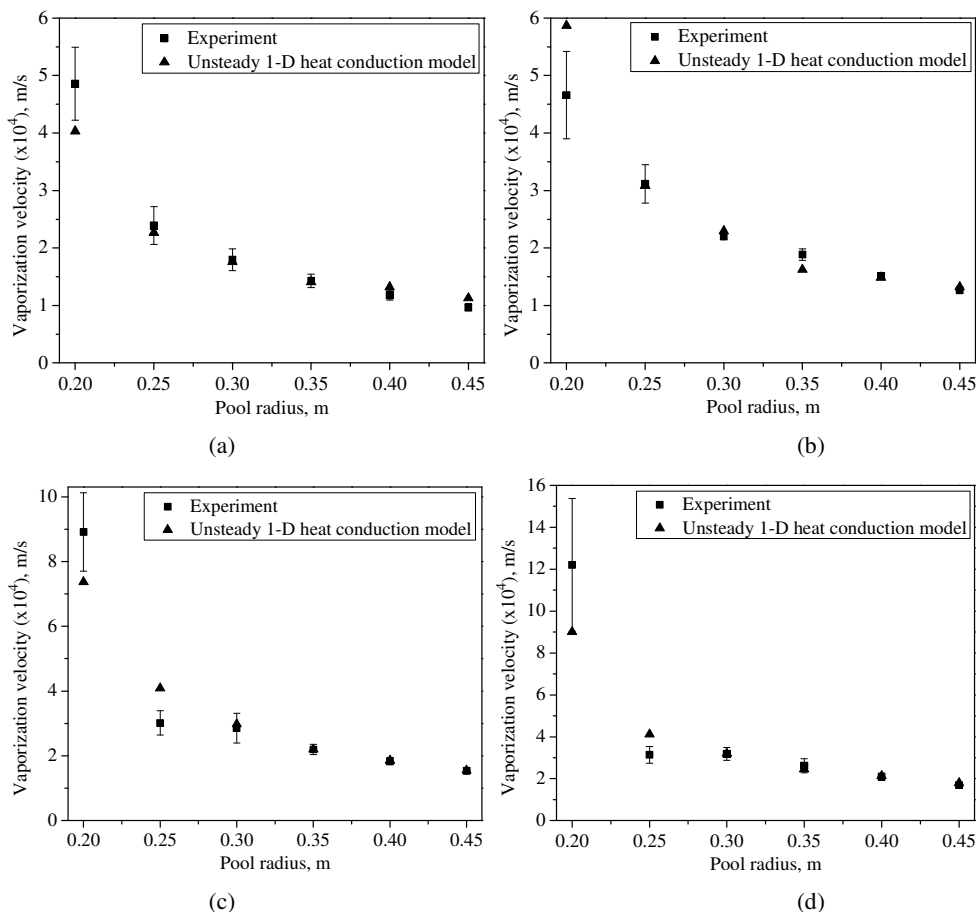


Fig. 6. Vaporization velocity versus pool radius. (a) Case 1; (b) Case 2; (c) Case 3; (d) Case 4.

The theoretical and experimental results for the vaporization velocity with the pool radius are shown in Fig. 6 for comparison. Error bars are included to represent the variation in the experimental results. It can be seen that the theoretical results are in good agreement with those obtained from the experiments, except for the first values, where the highest discrepancies between experimental results are also observed. The significant differences between the model and experimental results at pool radius $R = 0.2$ m exist because of the characteristics of the pool spreading. It was observed that liquid droplets were separated from the main pool and spread faster than the pool front at the initial stage of the spill ($R < 0.3$ m) due to high momentum of the liquid. These droplets might attached to the thermocouple, which made the thermocouple temperature drop to the boiling point of the liquid despite the main pool has not arrived yet. This is the reason why the uncertainty is high at the start

of the spread and increases with the spill rate. The high level of agreement supports the reliability of the experimental results obtained in this work. Consequently, the unsteady one-dimensional heat conduction model can be used to evaluate the vaporization velocity for the spreading pool if the data for changes in the pool radius with time are available.

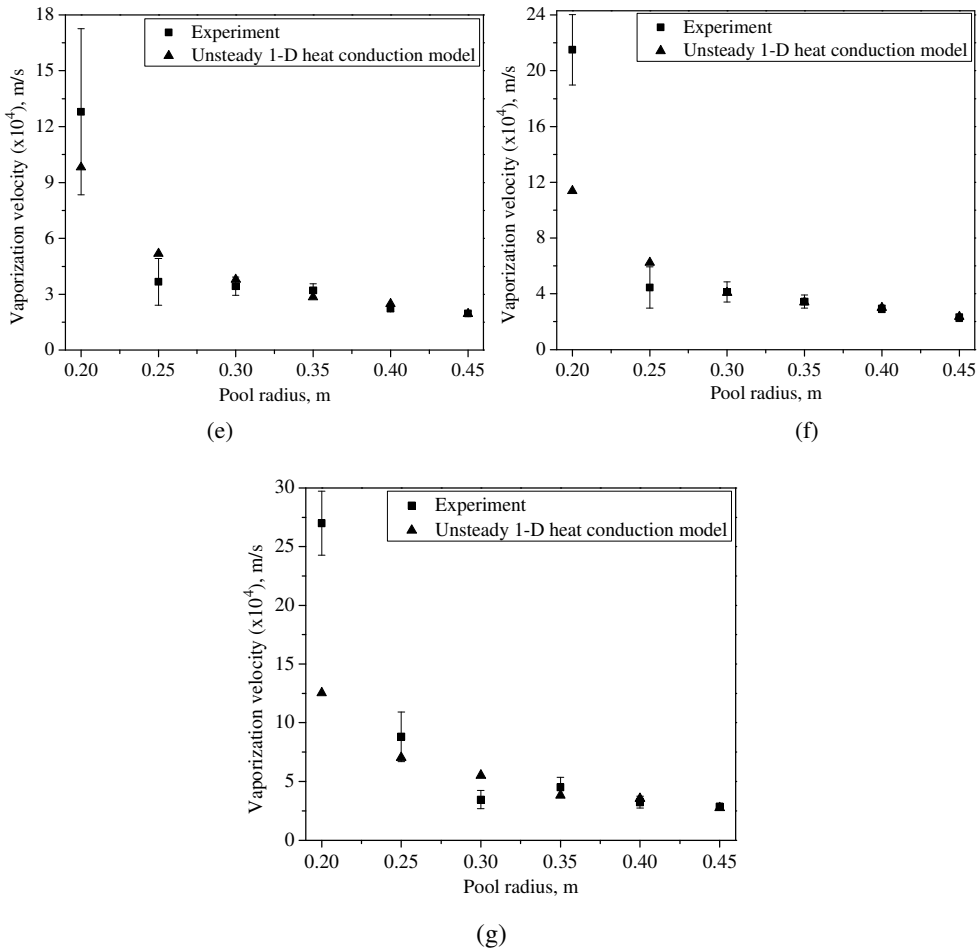


Fig. 6 (cont.). Vaporization velocity versus pool radius. (e) Case 5; (f) Case 6; (g) Case 7.

CONCLUSIONS

The measured vaporization velocities were compared to those obtained from the theoretical model, i.e., the unsteady one-dimensional heat conduction model. The theoretical results showed good agreement with the experimental data in terms of magnitude and trends. This agreement provides a semi-theoretical method for measuring the vaporization velocity of the spreading pool without the information about the spill rate and pool mass. The spill rate, pool mass, and the spread rate are necessary for measurement of the vaporization velocity in the existing method while only the spread rate is needed in the new method. In summary, the vaporization velocity can be reliably decided based on both the unsteady one-dimensional heat conduction model and experimental data of the pool radius with time.

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REFERENCES

- [1] F. Briscoe, P. Shaw, Spread and evaporation of liquid, *Prog. Energy Comb. Sci.* 6 (1980) 127-140.
- [2] D.M. Webber, A model for pool spreading and vaporization and its implementation in the computer code GASP, SRD/ HSE/ R521 (1990).
- [3] M. Kim, K. Do, B. Choi, Y. Han, High-order perturbation solutions to a LH2 spreading model with continuous spill, *Int. J. Hydrogen Energy* 37 (2012) 17409-17414.
- [4] K. Verfondern, B. Dienhart, Pool spreading and vaporization of liquid hydrogen, *Int. J. Hydrogen Energy* 32 (2007) 256-267.
- [5] T. Olewski, S. Mannan, L. Vechot, Validation of liquid nitrogen vaporization rate by small scale experiments and analysis of the conductive heat flux from the concrete, *J. Loss Prevent. Process Ind.* 35 (2015) 277-282.
- [6] T. Olewski, L. Vechot, S. Mannan, Study of the Vaporization Rate of Liquid Nitrogen by Small and Medium-Scale Experiments, *Chem. Eng. Trans.* 31 (2013) 133-138.
- [7] R.C. Reid, R. Wang, The boiling rate of LNG on typical dike floor materials, *Cryogenics* 18 (1978) 401-404.
- [8] K. Takeno, T. Ichinose, Y. Hyodo, H. Nakamura, Evaporation rates of liquid hydrogen and liquid oxygen spilled onto the ground, *J. Loss Prevent. Process Ind.* 7 (1994) 425- 431.
- [9] M. Kim, D. Nguyen, B. Choi, Experimental study of the evaporation of spreading liquid nitrogen, *J. Loss Prevent. Process Industries* 39 (2015) 68-73.
- [10] H.S. Carslaw, J.C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, Oxford, 1959.
- [11] G.J. Van Wylen, R.E. Sonntag, *Fundamentals of Classical Thermodynamics*, John Wiley and Sons, 1976.