THE SPREADING AND EVAPORATION OF LNG- AND BURNING LNG-SPILLS ON WATER

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Summary

This paper contains the results of a theoretical investigation into the evaporation and spilling of LNG and the burning of LNG on open water and on a confined water surface.

The spreading and evaporation of LNG spilled on open water are calculated and compared with experimental results. As little is known about the evaporation of LNG on a confined water surface a model has been derived which describes the evaporation including the forming of an ice layer. The models derived for the spreading and evaporation of LNG on open water and on a confined water surface are also used to calculate the spreading and evaporation of burning LNG-spills. The heat radiation from the flames into the pool has been calculated from experimental data from LNG-fires on land.

It is concluded that the results of this investigation concerning the evaporation of LNG on water agree well with the available experimental data, but that the calculated results for burning LNG can only be considered as a rough estimate.

Introduction

Of late a rapid increase has been observed in the transport and storage of LNG. This growth particularly manifests itself in a considerable scaling up. With this growth there is a rising need to gain more insight into the risks involved in the transport and storage of LNG.

In view of this development the Netherlands Government has commissioned TNO* to further study the risks involved in the storage and transport of large quantities of LNG. In this paper part of this study is dealt with, consisting in an investigation into the spreading and evaporation of LNG and burning LNG-spills on water. It is shown that in the evaporation of LNG on water a distinction has to be made between the evaporation process on open water and that on a confined water surface.

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Evaporation rate of LNG spilled on open water

The evaporation of LNG spilled on open water differs from the evaporation of LNG on a confined water surface in that upon the spreading on open water practically no ice is formed. The inherent consequences for the evaporation of LNG are considered below.

Immediately after the onset of spilling on open water, film boiling occurs because of the large difference in temperature between LNG and water. As a result of the evaporation of methane from the LNG, the boiling temperature of the non-evaporated liquid rises. Upon the subsequent spreading of LNG, however, the non-evaporated LNG will mix with "fresh" LNG as a result of which the concentration of the higher hydrocarbons and the temperature of the mixture will not change appreciably. In other words: during the spillage on open water the temperature difference between LNG and water will remain practically constant, and the Leidenfrost-point will therefore never be passed. For the above reasons it will be clear that some ice is formed only at the edge of the LNG-pool.

The evaporation rate of LNG on open water will now be calculated with the aid of the theory for heat penetration in a semi-infinite medium. The result of this calculation is that the evaporation rate is inversely proportional to the square root of the evaporation time. As the decrease of the evaporation rate for long periods of time cannot be completely explained physically, the transfer of heat from water to LNG will be calculated with reference to convective heat transport in the water.

It has been stated already that during the spillage of LNG on water practically no ice is formed. This means that the heat to the LNG—water interface is supplied by convection flow in the water. If the temperature difference between the water—vapour interface and the water is equal to ΔT, then according to [1] the following formula is valid for the convective heat flux through the interface:

$$Q_w = 0.085 \, k_w \left(\frac{g \alpha \Delta T^4}{a \nu} \right)^{1/3} \tag{1}$$

If, in accordance with [2], we assume that ΔT is equal to 47.4 K, then after elaboration of the convective heat flux, which in this case is assumed to be equal to the heat flux for the evaporation of LNG, it appears that:

$$Q_w = 2.3 \times 10^4 \ W/m^2$$

corresponding to an evaporation rate of:

$$m'' = 0.045 \ kg/m^2 s \tag{2}$$

This calculated value agrees very well with the experimental values according to [3]. Fig. 1 shows that this calculated value does not agree with the experimental values according to [4] and [5]. However, these results are
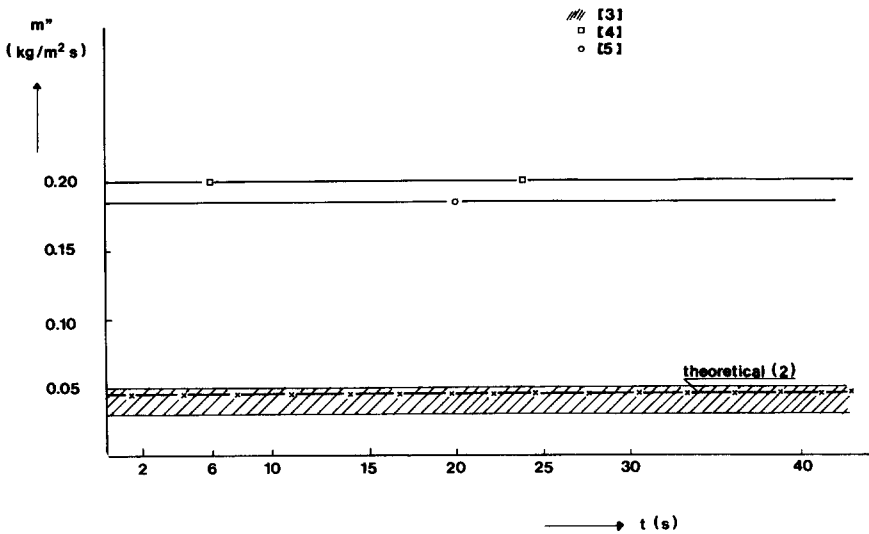
Fig. 1. Evaporation rate of LNG spilled on open water.

derived and not direcly measured ones; therefore in what follows, for the evaporation rate of LNG on open water use will be made of the constant value in accordance with [3]:

$$m'' = 0.05 \text{ kg/m}^2\text{s} \tag{3}$$

The difference in heat flux that follows from eqns. (3) and (2) is caused by the forming of small pieces of ice.

After determination of the evaporation rate, the total evaporation and spreading of an LNG-pool on open water can be calculated.

Spreading and evaporation of an LNG-pool on open water

In the evaporation process of LNG spilled on open water a number of phases can be distinguished. If we assume that spillage is momentary, the LNG will spread on the water, continuous evaporation taking place. As during spreading hardly any ice is formed, the heat transfer between LNG and water will take place through film boiling. LNG will continue to spread on the water until the minimum layer thickness corresponding to the maximum pool diameter is reached. After the maximum pool diameter has been reached, the pool area decreases, as with constant evaporation the layer thickness remains constant. At a certain moment, the surface tension is no longer capable of keeping the layer continuous so that the LNG-layer breaks up.

Opinions differ on the minimum layer thickness of LNG on water. According to [3], this value is equal to the constant value of 0.17 cm, irrespective of the quantity of LNG spilled. By contrast, it is said in [4] that the minimum

layer thickness of LNG on water satisfies the following empirical equation:

$$h_m = 0.001 \, D^{0.56} \tag{4}$$

For the sake of completeness it must be stated that eqn. (4) is based on two facts of observation, while the statement in [3] is supported by five experiments.

As minimum layer thickness highly depends upon surface tension, it can also be expected on physical grounds that this layer thickness does not depend on the amount spilled. Consequently, 0.17 cm will be used further in this paper for the minimum layer thickness.

To set up the equation governing the spreading of a fluid we make use of the concept of the equilibrium of the spreading and resisting forces and the global continuity equation.

For radial spreading the following holds true:

$$F_g = \pi \Delta \rho \, \rho_l g h^2 R / \rho_w \tag{5}$$

The spreading fluid experiences an inertial resistance; the inertial force appears to be equal to:

$$F_t = -\pi \rho_l h C R^2 \, \frac{d^2 R}{dt^2} \tag{6}$$

The geometric relation is approximately equal to:

$$V = \pi h R^2 \tag{7}$$

while for the mass conservation equation the following can be written:

$$V\rho_l = V_i \rho_l - \int_0^t \pi m'' R^2 dt \tag{8}$$

Equating eqn. (5) to eqn. (6), and substituting the result and eqn. (7) in eqn. (8) gives a relation which can be solved analytically by first making it dimensionless and then differentiating it once and integrating it three times [6] The result is:

$$R = \left[\frac{0.44 \, m'' g \Delta \rho t^3}{\rho_w \rho_l} + \frac{1.3 \, g^{1/2} \Delta \rho^{1/2} V_i^{1/2} t}{\rho_w^{1/2}} \right]^{1/2} \tag{9}$$

for LNG: $R = [3 \times 10^{-4} t^3 + 3.1 \, V_i^{1/2} t]^{1/2}$

In Fig. 2 the calculated radius of a spreading LNG-pool on water is plotted as a function of time. For comparison, in the same Fig. 2 some experimental results are given concerning the extension of an LNG-pool on water. From the figure it can be concluded that the theoretical curve agrees well with the experimental data according to [3]. However, in particular when the periods of
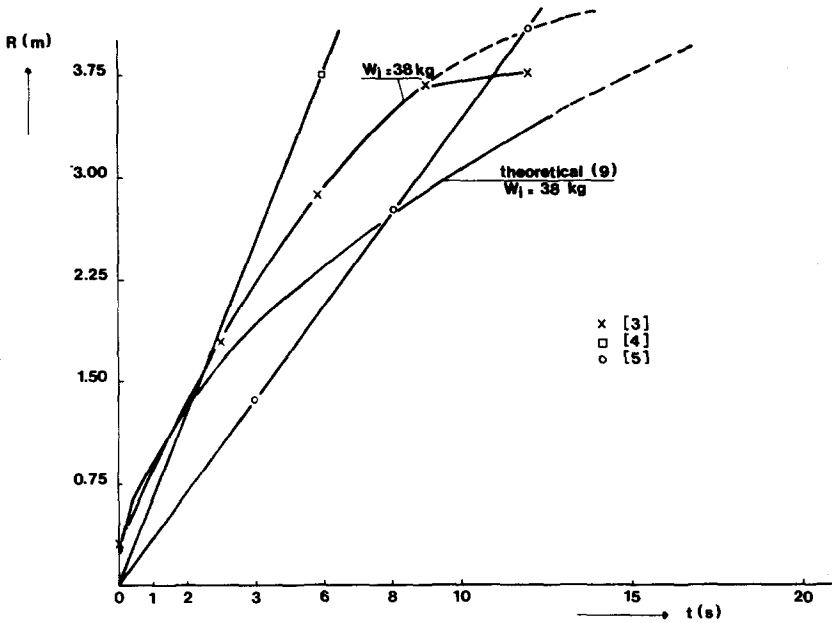
Fig. 2. Pool radius of an LNG-spill on open water.

time are long, the experimental results according to [4] and [5] show considerable deviations in respect of the theoretical curve.

It has already been pointed out that LNG spreads on water until the minimum layer thickness (0.17 cm) is reached; after this the layer thickness remains constant, while the LNG-area becomes smaller. Calculating the maximum evaporation time and maximum pool radius of an LNG-spill on water assuming a minimum layer thickness appeared to be a difficult matter [7]. Therefore, the maximum evaporation time and maximum pool radius of an LNG-spill on open water will be calculated neglecting the minimum layer thickness. In this case the maximum pool radius is reached at the moment that all LNG has evaporated. This moment can be calculated by putting $V = 0$ in relation (8). The result is:

$$t_e = 0.67 \left[\frac{\rho_l^2 \rho_w V_i}{\Delta \rho g m''^2} \right]^{1/4} \tag{10}$$

for LNG:

$$t_e = 40 \ V_i^{1/4}$$

Substitution of the time t_e in eqn. (9) gives for the maximum pool diameter:

$$R_e = 1.02 \left[\frac{\Delta \rho \rho_l^2 g V_i^3}{\rho_w m''^2} \right]^{1/8} \tag{11}$$

for LNG:

$$R_e = 12.2 \, V_i^{3/8}$$

In [7] it is shown that for a spill of 10^4 m^3 LNG on water the difference between the calculated results using eqns. (10) and (11) and those taking into account the minimum layer thickness is less than 5%. This implies that eqns. (10) and (11) can be used for LNG-spills on open water.

In setting up the above-discussed calculations the loss due to evaporation of LNG that is under water during spillage has not been taken into account.

Evaporation rate of LNG on a confined water surface

Spillage of LNG on a confined water surface can be subdivided into two phases. During the first phase, LNG will spread out on the water surface until the moment has been reached that the water is fully covered with LNG. Because of the great difference in temperature, film boiling will occur during the first phase and practically no ice will be formed. The heat transfer during film boiling is not great, but this changes when the water is fully covered with LNG and the second phase starts.

As LNG mainly consists of a mixture of hydrocarbons, evaporation will mainly remove methane from the LNG. This manifests itself in an increase of the temperature of the non-evaporated liquid mixture. This means that the temperature difference between LNG and water decreases. This process can continue until the temperature difference becomes so small that the Leidenfrost-point is passed. At that moment the vapour layer cannot keep LNG and water separated any longer, and direct contact takes place between LNG and water. After the Leidenfrost-point has been passed the heat transfer between LNG and water increases considerably as the transition area of the boiling curve has been entered and the formation of ice is highly stimulated, which may result in the forming of a solid ice layer. Heat being continuously transferred, the ice layer will cool down, so that after a certain time nucleate boiling occurs.

The model for calculation of the evaporation rate of LNG spilling on ice is based on the assumption that the heat released by the freezing of water and subsequent cooling of ice is dissipated by the evaporation of LNG. For this heat flux the following relation can be written:

$$Q_i = \frac{k_e \Delta T_e}{\delta} = \left(\rho_w h_1 + \frac{\rho_e C_{p,e} \Delta T_e}{2} \right) \frac{d\delta}{dt} \tag{12}$$

boundary condition: $\delta = 0$ for $t = 0$.

After solving the differential equation and equalizing the heat flux according to eqn. (12) to the evaporation heat flow to LNG, the evaporation rate is

found to be equal to:

$$m_i'' = \left[\frac{(2\rho_w h_1 + \rho_e C_{p,e} \Delta T_e) k_e \Delta T_e}{4 h_v^2 t} \right]^{1/2}$$ (13)

In the case where LNG is spilled on ice, ΔT_e is taken to be equal to 162K; upon substitution of ΔT_e in eqn. (13) the following holds for the evaporation rate of LNG spilled on ice:

$$m_i'' = 0.517 \, t^{-1/2}$$ (14)

In deriving eqn. (13) the assumption has been made that upon spilling of LNG an ice layer is already present. In practice, however, a layer of ice will be formed only after a certain time. In order to arrive at a method for calculating the rate of evaporation that describes the entire process of evaporation, some experimental data referring to the evaporation rate of LNG spilling on a confined water surface will first be considered.

The experimental data are presented in Fig. 3. The result mentioned in [5] is based on only one experiment; admittedly, this value is in fair agreement with the other experimental results. It is not correct, however, to assume that this value is independent of time. The same can be remarked about the experimental data as stated in [4]. Moreover, Fig. 3 clearly shows that the value of [4] for $t = 6$ s deviates considerably from the rest of the results. Besides, some data have been derived from [3]. Parameter h in these curves represents the initial layer thickness of LNG on water.
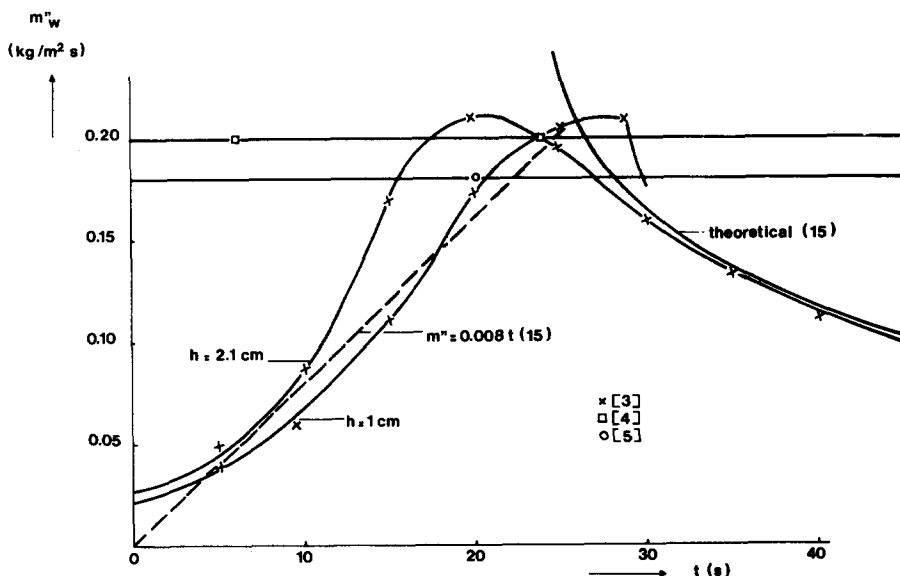

Fig. 3. Evaporation rate of LNG spilled on a confined water surface.

Now it appears that the derived formula (13) agrees well with the experimental results stated in [3] from the point of time $t = 25$ s. Thus it can be assumed that for quantities of LNG spilling on a confined water surface, and corresponding to an initial layer thickness of at least 2 cm, an ice layer will have formed about 20 s after spillage has started. Before this point of time, therefore, film boiling and metastable boiling takes place. In Fig. 3 it is shown that the evaporation rate during this period can be approximated by a simple mathematical relationship.

On the grounds of the above discussion the evaporation rate for every point of time after the spilling of LNG on a confined water surface may be approximated by:

$$m_w'' = 0.008\, t \qquad\qquad \text{for } 0 \leqslant t \leqslant 25$$

$$m_w'' = \frac{0.517}{(t-20)^{1/2}} \qquad \text{for } t > 25 \tag{15}$$

It has been stated above that in deriving the formulas in eqn. (15), in particular the experimental results in [3] have served as a guidance. These results are related to a specific composition of LNG (95% CH_4) and to a water temperature of 288K. If these parameters change, deviations from the derived formulas can be expected. Moreover, for every case of LNG-spillage on water, the extent of agitation of the water has a strong influence on the formation of ice, and consequently also on the evaporation rate.

Spreading and evaporation of LNG spilled on a confined water surface

Suppose a given amount of LNG is spilled on a confined water surface. During spilling a certain quantity mostly evaporates as a result of the fact that a given fraction of LNG is under water. In the calculations presented below, this quantity has not been taken into account.

Immediately after spilling, the LNG will spread on the confined water surface. The moment t_0 at which the water is completely covered with LNG, can approximately be calculated with eqn. (9). Neglecting the first term in eqn. (9) the calculation yields [8]:

$$t_0 = 0.24 \left[\frac{\rho_w A_0^2}{\Delta \rho g V_i} \right]^{1/2} \tag{16}$$

for LNG:

$$t_0 = 0.1\, A_0 V_i^{-1/2}$$

The total amount of LNG evaporated during spreading can be found with

the following relationship:

$$m_0 = \int_0^{t_0} m'' \pi R^2 \, dt \qquad (17)$$

For R eqn. (9) can be substituted.

At the point of time t_0 the non-spreading period starts. The assumptions made for calculation of the evaporation of LNG in this period are that the heat to the LNG is delivered by heat transfer from the water or ice and that the heat transfer from the vertical wall can be neglected.

The point of time at which all LNG has been evaporated can be calculated with the aid of the mass conservation equation:

$$W_i - m_0 = \int_0^{t_e} A_0 m_w'' \, dt$$

For the evaporation rate, eqn. (15) must be taken. Upon elaboration of this integral, the following relationship appears to hold for the evaporation time:

$$t_e = \left(\frac{W_i - 0.05 \, A_0^2 \, W_i^{-1/2}}{0.004 \, A_0} \right)^{1/2} + t_0 \qquad \text{for } t_0 \leqslant t_e \leqslant 25 + t_0$$

$$\qquad (18)$$

$$t_e = \left(\frac{W_i - 0.05 \, A_0^2 \, W_i^{-1/2} - 0.2 \, A_0}{1.03 \, A_0} \right)^2 + t_0 + 20 \quad \text{for } t_e > 25 + t_0$$

The derived formulas hold true for a confined surface. In practice it is possible, however, that the surface is only partly confined. An estimate must then suffice.

Evaporation heat flux to a burning LNG-spill on open water

Consider a certain amount of LNG that is spilled on open water and causes a fire. The heat flux to the evaporating LNG can be divided into a flux from the water to the LNG and a heat flux produced by radiation from the LNG-fire.

The heat flux from the water has already been dealt with. The radiation from a fire is a complex function of the temperature distribution in the flame, the attenuation coefficient and the shape, dimensions and inclination of the flame. The universal equation describing the radiation heat flux to the surface of a burning liquid is:

$$Q_r = \epsilon_s \epsilon_l \epsilon_f \sigma T_f^4 - \epsilon_s \sigma T_i^4 \approx \epsilon_s \epsilon_l \epsilon_f \sigma T_f^4 \qquad (19)$$

corresponding to:

$$m_r'' = \epsilon_s \epsilon_l \epsilon_f \sigma T_f^4 / h_v$$

In the above equation $T_f \gg T_i$, so the second term in eqn. (19) can be neglected.

In relation (19) T_f denotes the mean flame temperature. Strictly speaking, it is not possible to speak of "the" temperature of a flame, because it does not represent an equilibrium state. For the mean flame temperature of an LNG-fire on land the following value was chosen [9]:

$$T_f = 1400K$$

As no appreciable difference exists between the mean flame temperature of an LNG-fire on land and on water, the chosen value will also be used for the mean flame temperature of an LNG-fire on water.

For the mean effective emissivity of a flame the following relation is mostly used:

$$\epsilon_f = 1 - \exp\left(-\beta D_h\right) \tag{20}$$

The value of the absorption coefficient β cannot be determined theoretically. The coefficient depends on the type of fluid, but is strongly dependent on the concentration of soot particles in the flame. So the value of the absorption coefficient can only be estimated on a basis of extensive measurements. In [9] the value $\beta = 0.5/m$ was utilised, which agrees well with experimental results of LNG-fires on land. Because no fundamental difference exists between an LNG-fire on land and on water with regard to the absorption coefficients, the mentioned value will also be used for the absorption coefficient of an LNG-fire on water.

The mean beam length D_h depends on the shape and size of the flame and may be obtained by means of numerical integration. This procedure is rather complicated and in many cases it will do to use an approximate value, defined as:

$$D_h = 4 \; \frac{\text{flame volume}}{\text{total flame surface}} = 4 \text{ hydraulic radius .}$$

For a cylindrical flame with pool diameter D and flame length L, D_h equals:

$$D_h = \frac{D}{D/2L + 1} \tag{21}$$

To obtain the relationship between D_h and D, the factor D/L should be eliminated in eqn. (21), which can be done with the help of [10]:

$$\frac{L}{D} = 42 \left(\frac{m''}{\rho_a\sqrt{gD}}\right)^{0.61} \tag{22}$$

So substitution of eqn. (22) in eqn. (21) and of the resulting equation in

eqn. (20) yields:

$$\epsilon_f = 1 - \exp\left[\frac{-\beta D}{\dfrac{1}{84}\left(\dfrac{\rho_a\sqrt{gD}}{m''}\right)^{0.61} + 1}\right] \tag{23}$$

The total evaporation heat flux to burning LNG on open water can now be written as:

$$Q_v = Q_w + Q_r = 0.085\,k_w\left(\frac{g\alpha}{a\nu}\right)^{1/3}\Delta T^{4/3} +$$

$$\epsilon_1\epsilon_s\sigma T_f^4\left[1 - \exp\left\{\frac{-\beta D}{\dfrac{1}{84}\left(\dfrac{\rho_a\sqrt{gD}}{m''}\right)^{0.61} + 1}\right\}\right] \tag{24}$$

for LNG:

$$Q_v = 2.5 \times 10^4 + 3.1 \times 10^4\,\epsilon_f$$

corresponding to:

$$m'' = 0.05 + 0.06\,\epsilon_f$$

or

$$m'' = 0.11\ \text{kg/m}^2\text{s} \qquad \text{for } D > 20\ \text{m.}$$

Eqn. (24) is plotted in Fig. 4 as a function of pool diameter D. For the elaboration of eqn. (24) the following constants are used: $\Delta T = 47.4$K [2]; $T_f = 1400$K; $\beta = 0.5$/m; $\epsilon_1 = 0.5$ and $\epsilon_s = 0.28$ [9].

The values for ϵ_s and ϵ_1 were chosen in [9] from experimental results of LNG-fires on land, and in this paper these values will also be used for LNG-fires on water.

Comparing the calculated evaporation heat flux to a burning LNG-spill on water with the experimental one for LNG-fires on land [9] shows that there is hardly any difference between these two values.

Spreading and evaporation of a burning LNG-spill on open water

For derivation of the model describing the simultaneous spreading and evaporation of burning LNG on open water, the LNG is supposed to catch fire at the moment of spillage. Further it will be assumed that the heat of evaporation of LNG comes primarily from the water and the flames, and that the spill occurs instantaneously.

To calculate the spreading of a burning LNG-pool on open water use is made again of the idea of equilibrium between the spreading and resisting forces and the global continuity equation. This means that relationship (9) can
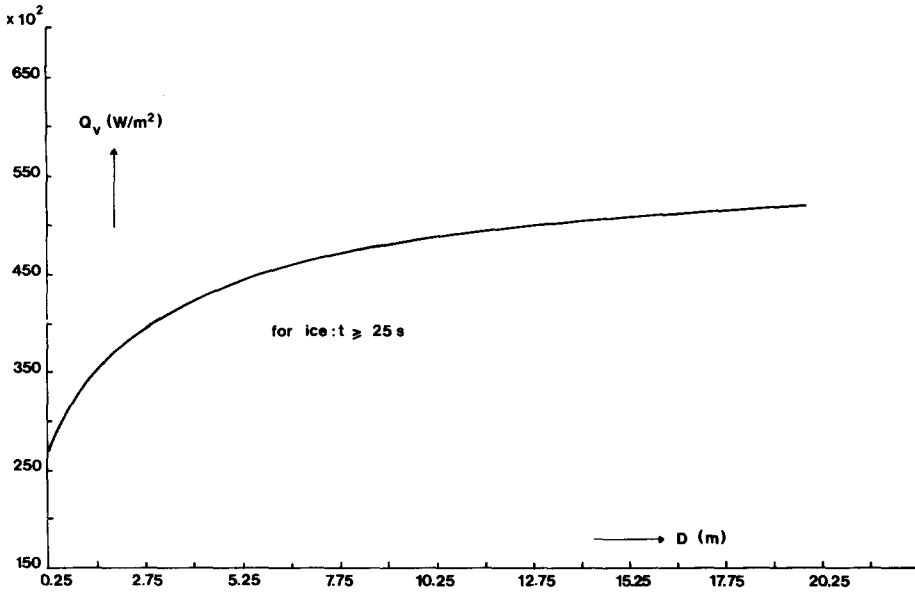
Fig. 4. Calculated evaporation heat flux to LNG during a fire on ice and on water.

be used; however, for the evaporation rate m'' calculated in eqn. (24) should be taken. So the radius of a burning LNG-pool on open water equals:

$$R = (6.4 \times 10^{-4} \, t^3 + 3.1 \, V_i^{1/2} t)^{1/2} \quad \text{for } D > 20 \text{ m} \tag{25}$$

The time t_e at which all LNG is evaporated can be calculated by substitution of m'' (of eqn. (24)) in eqn. (10). The result is:

$$t_e = 27.1 \, V_i^{1/4} \tag{26}$$

Substitution of t_e in eqn. (25) delivers the maximum pool radius of a burning LNG-pool on open water; it appears that:

$$R_e = 10 \, V_i^{3/8} \tag{27}$$

This result can also be found by putting $m'' = 0.11$ kg/m^{2}s (eqn. (24)) in eqn. (11).

In the calculated results of eqns. (26) and (27) the formation of a minimum layer thickness is not taken into account. However in [7] it is shown that the differences in the calculated evaporation time and maximum pool radius are less than 5%.

Evaporation heat flux to burning LNG on a confined water surface

When LNG is spilled on a confined water surface two periods of time can be distinguished. During the first period, LNG spreads on the water surface until

the moment has been reached that the water surface is fully covered with LNG (spreading period). Then the second period starts in which ice is formed (non-spreading period).

For the evaporation heat flux to burning LNG, which spreads on the water surface during the first period, the same relations can be taken as calculated for burning LNG on open water.

On the contrary, the heat flux to burning LNG on a confined water surface after the surface is completely covered with LNG (second period) differs from the above-mentioned heat flux.

It was stated earlier in this paper that during the first phase of the second period ice is formed. For the evaporation rate of LNG during this phase it was found:

$$m_w'' = 0.008\,t \quad \text{for } t < 25 \text{ s} \tag{28}$$

Taking into account the heat flux from the flames to the evaporating LNG (eqn. (19)) the total evaporation rate of LNG can be written as:

$$m_w'' = 0.008\,t + \epsilon_f \epsilon_l \epsilon_s \sigma T_f^4 / h_v \quad \text{for } t < 25 \text{ s} \tag{29}$$

and after elaboration:

$$m_w'' = 0.008\,t + 0.06\,\epsilon_f \quad \text{for } t < 25 \text{ s}$$

The first phase in the second period is finished when an ice layer has formed. Then the second phase starts, lasting until the moment that all LNG has evaporated. At this last moment the second period is also finished. During the second phase in the second period LNG poured out on a confined water surface burns on a growing ice layer. This implies that this fire can be compared with an LNG-fire on land.

The experimental results of burning LNG-pools on land have proved that the total evaporation heat flux to LNG is independent of time. It is now assumed that the total evaporation heat flux to burning LNG on ice is also independent of time. As the heat radiation from the flames to the LNG-pool is also constant in time, the heat flux from the ice layer to LNG must also be time-independent. However, calculations based on the model of heat released by the freezing of water show that the conductive heat flux from the ice layer to the LNG diminishes with the square root of time. This contradiction can be explained by the fact that part of the radiated heat from the flames is not absorbed by the LNG, but transmitted through the LNG and is absorbed by the ice layer. The result of heat absorption by the ice layer is that the surface of the ice layer is heated to a given temperature and that the heat transfer from the ice layer to the evaporating LNG becomes independent of time.

The matters discussed above are illustrated in Fig. 5, in which the heat fluxes to burning LNG on ice are given. Starting from the total experimental heat flux to burning LNG on land [9] and taking into account the differences in thermal properties between ground and ice, the total heat flux to burning
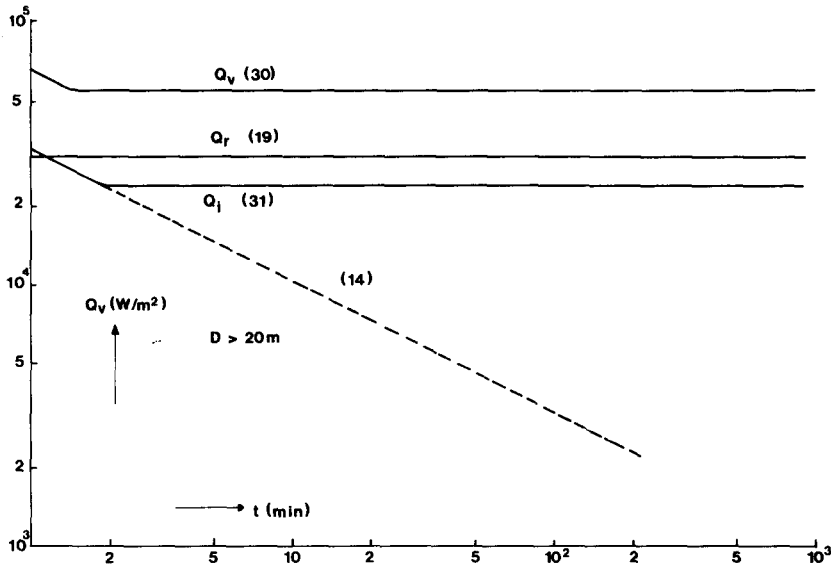
Fig. 5. Estimated instantaneous evaporation heat fluxes for large burning LNG-pools on ice.

LNG on ice is estimated to be:

$$Q_v = 5.5 \times 10^4 \ W/m^2 \tag{30}$$

Because the radiative heat flux to a burning LNG-pool on land is equal to the radiative heat flux to burning LNG on ice, its value is also given by eqn. (19). This value is presented in Fig. 5 as Q_r.

In Fig. 5 the conductive heat flux from ice to LNG calculated from the heat released by the freezing of water is also given as a function of time (eqn. (14)). Because the total heat flux and the radiative heat flux are constant after a given run-in period of time, the influence of radiative heat absorption by the ice must become important at $t = 2$ min. Therefore the heat flux from ice to LNG must be equal to:

$$Q_i = 26 \times 10^4 \ t^{-1/2} \qquad W/m^2 \qquad \text{for } 25 \leqslant t < 120 \text{ s} \tag{31}$$

$$Q_i = 2.4 \times 10^4 \qquad W/m^2 \qquad \text{for } t \geqslant 120 \text{ s}$$

Then the total evaporation heat flux to burning LNG on ice can be written as:

$$Q_v = Q_i + Q_r \tag{32}$$

for LNG:

$$Q_v = 26 \times 10^4 \ t^{-1/2} + 3.1 \times 10^4 \ \epsilon_f \qquad \text{for } 25 \leqslant t < 120 \text{ s}$$

$$Q_v = 2.4 \times 10^4 + 3.1 \times 10^4 \ \epsilon_f \qquad \text{for } t \geqslant 120 \text{ s}$$

corresponding to:

$$m_w'' = 0.51\, t^{-1/2} + 0.06\, \epsilon_f \qquad \text{for } 25 \leqslant t < 120 \text{ s}$$

or:

$$\overline{m}_w'' = 0.06 + 0.06\, \epsilon_f \qquad \text{for } 25 \leqslant t < 120 \text{ s}$$

and:

$$m_w'' = 0.05 + 0.06\, \epsilon_f \qquad \text{for } t \geqslant 120 \text{ s}$$

To simplify calculations performed later in this paper it is of advantage to work with a mean evaporation rate during the time interval $25 \leqslant t < 120$ s instead of the time-dependent value.

It is striking that the estimated total evaporation rate to burning LNG on ice for $t \geqslant 25$ s and $D > 20$ m practically equals the total evaporation rate to burning LNG on open water. Thus the curve presented in Fig. 4 is also valid for burning LNG on ice for $t \geqslant 25$ s.

Spreading and evaporation of burning LNG spilled on a confined water surface

The evaporation process of burning LNG on a confined water surface can be considered to take place in two well-distinguished periods of time. The first period starts at the moment of pouring out until the point of time when the water surface is completely covered with LNG (spreading period). The second period lasts till the moment that all LNG has evaporated (non-spreading period).

For calculating the evaporation of burning LNG during the spreading period, it is supposed that LNG pours out instantaneously and that LNG catches fire at the moment of pouring out. The time t_0 at which the confined water surface is completely covered with LNG can also be found with eqn. (16), thus

$$t_0 = 0.1\, A_0\, V_i^{-1/2} \tag{33}$$

The total amount of LNG evaporated during spreading can be found from eqn. (17); however, for m'' the value given in eqn. (24) should be substituted. The result is:

$$m_0 = 5.5 \times 10^{-5}\, t_0^4 + 0.53\, V_i^{1/2}\, t_0^2 \tag{34}$$

At the point of time t_0 the non-spreading period starts. Assuming the heat to LNG to be delivered by heat transport from water or ice and by heat radiation from the flame, the mass conservation equation for the first phase in the

second period ($t < 25$ s) becomes:

$$W_i - m_0 = \int_0^{t_e} A_0\, m_w{}''\mathrm{d}t \tag{35}$$

In the above relationship the heat transfer from a vertical wall has been neglected, as it is justified in most practical cases. However, in [7] the heat transfer from the vertical wall is taken into account. Putting $m_w{}''$ (eqn. (29)) in eqn. (35), t_e is found to be:

$$t_e = -7.5\,\epsilon_f + \left\{ 56.3\,\epsilon_f^2 + 250 \left(\frac{W_i - m_0}{A_0} \right) \right\}^{1/2} + t_0 \tag{36}$$

$$\text{for } t_0 \leqslant t_e \leqslant 25 + t_0$$

When ice has been formed ($t > 25$ s) the second phase in the second period starts. During this time interval the mass conservation equation equals:

$$W_i - m_0 = \int_0^{25} A_0\, 0.06\, \epsilon_f \mathrm{d}t + \int_0^{25} 0.008\, A_0\, t\, \mathrm{d}t + \int_{25}^{t_e} A_0\, m_w{}''\mathrm{d}t \tag{37}$$

After substitution of $m_w{}''$ (eqn. (32)) in eqn. (37) for the time at which all LNG is evaporated, the following results:

$$t_e = \frac{W_i - m_0 - 1.25\, A_0}{A_0\,(0.06\,\epsilon_f + 0.06)} + t_0 \qquad \text{for } t_e > 25 + t_0 \tag{38}$$

In eqn. (37) the heat transfer from the vertical wall has been neglected. The influence of this heat component has been calculated in [7].

Conclusions

The results of this investigation have shown that in the evaporation of LNG on water one should distinguish between the evaporation on open water and on a confined water surface.

Studying the spreading and evaporation of LNG on open water we found that the heat for evaporation is for the greater part delivered by convective heat transport in the water, while during the spreading of the evaporating LNG practically no ice is formed.

The result of the investigation into the evaporating of LNG on a confined surface is that during the evaporation process an ice layer is formed. The model developed during this study for the calculation of the evaporation of LNG on a confined surface appears to agree well with experimental results.

To estimate the evaporation and spreading of burning LNG-spills both on open water and on a confined water surface, use has been made of the models derived for non-burning LNG. The heat radiation from the flames to the LNG-

pool has been estimated from experimental results on LNG-fires on land. The models derived could not be verified with experimental results because of the lack of data in the literature.

Summarizing it can be concluded that the results of this investigation for calculating the evaporation of LNG on water agree well with the available experimental data, and that the results obtained for burning LNG-spills on water can only give a rough estimate, as they have been calculated from exper-imental data for LNG-fires on land.

Notation

A_0	area of confined water surface	(m^2)
a	thermal diffusivity of water	(m^2/s)
C	correction factor for inertial force (0.75)	$(-)$
$C_{p,e}$	specific heat of ice	$(J/kg\ K)$
D	pool diameter	(m)
D_h	mean beam length of flame	(m)
F_g	gravitational force	(N)
F_t	inertial force	(N)
g	gravitational acceleration	(m/s^2)
h	mean thickness of LNG-spill on water	(m)
h_l	heat of fusion of water	(J/kg)
h_m	minimum layer thickness of LNG on water	(m)
h_v	heat of vaporisation of methane	(J/kg)
k_e	thermal conductivity of ice	$(W/m\ K)$
k_w	thermal conductivity of water	$(W/m\ K)$
L	flame length	(m)
m_0	evaporated quantity of LNG until moment t_0	(kg)
m''	evaporation rate of LNG on open water	$(kg/m^2\ s)$
m_i''	evaporation rate of LNG on ice	$(kg/m^2\ s)$
m_r''	evaporation rate of LNG due to heat radiation to an LNG-pool	$(kg/m^2\ s)$
$\overline{m_w}''$	mean evaporation rate of burning LNG on a confined water surface	$(kg/m^2\ s)$
m_w''	evaporation rate of burning LNG on a confined water surface	$(kg/m^2\ s)$
Q_i	heat flux from ice to LNG	(W/m^2)
Q_r	radiative heat flux through LNG-pool surface	(W/m^2)
Q_v	evaporation heat flux to burning LNG	(W/m^2)
Q_w	convective heat flux from water to LNG	(W/m^2)
R	radius of LNG-spill on water	(m)
R_e	maximum radius of LNG-spill on water	(m)
T_f	mean flame temperature	(K)
T_i	surface temperature of burning LNG-pool	(K)
ΔT	temperature difference between water and water-vapour interface	(K)

ΔT_e	temperature difference between ice and LNG-ice interface	(K)
t	time	(s)
t_e	time at which all LNG is evaporated	(s)
t_0	time at which the confined water surface is completely covered with LNG	(s)
V	volume of spilled LNG	(m^3)
V_i	initial volume of spilled LNG	(m^3)
W_i	initial quantity of spilled LNG	(kg)
α	coefficient of expansion of water	(1/K)
β	absorption coefficient	(1/m)
δ	thickness of ice layer	(m)
ϵ_f	emissivity of flame (opacity term)	(—)
ϵ_1	emissivity of LNG-flame	(—)
ϵ_s	emissivity of LNG-pool surface	(—)
ν	kinematic viscosity of water	(m^2/s)
ρ_a	density of air	(kg/m^3)
ρ_e	specific mass of ice	(kg/m^3)
ρ_1	density of methane	(kg/m^3)
ρ_w	density of water	(kg/m^3)
$\Delta\rho$	difference in densities between water and methane	(kg/m^3)
σ	constant of Stefan—Boltzmann	$(W/m^2\ K^4)$

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