Modeling a Boiling-Liquid, Expanding-Vapor Explosion Phenomenon with Application to Relief Device Design for Liquefied Ammonia Storage

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This paper addresses a fictitious accident scenario involving an ammonia storage tank in a refinery. Ammonia is used in a deNO*x* system. In a selective catalytic reduction environment, a refinery stack gas containing nitric oxide and nitrogen dioxide is decomposed into nitrogen and water vapor. In this study, a cylindrical ammonia tank is "bleved" (boiling-liquid, expanding-vapor explosion (BLEVE)) with an external fire. We developed a computer model in order to determine the thermal response of a horizontal ammonia tank involved in fire engulfment accidents. The assessment of the separation distance between tanks and protection measures such as water spray cooling were also discussed. Further, we examined the relief device design and studied the open-system thermal response as well as pressure response effects in the event of a BLEVE for the ammonia tank.

Introduction

Compressed liquefied gases such as ammonia, chlorine, and propane are stored or transported in a large variety of pressure vessels and containers. Historically, these gases were involved in accidents called boiling-liquid, expanding-vapor explosions (BLEVE)s. BLEVE differs from other explosions and has unexpectedly severe consequences. It is a physical phenomenon that results from the sudden release from confinement of a liquid at a temperature above its atmospheric-pressure boiling point. The sudden decrease in pressure results in the explosive vaporization of a fraction of the liquid and a cloud of vapor and mist with the accompanying blast effects. For flammable liquids, most BLEVE releases are ignited by a surrounding fire and result in a fireball. For nonflammable liquids, the cause-and-effect discussions of BLEVEs are important for process safety analyses, particularly for toxic chemicals.

Ammonia is mainly consumed in the fertilizer industry such as the manufacture of ammonium sulfate and urea. Other major uses include the manufacture of nitric acid by oxidation of ammonia, the manufacture of hydrazine which is used as a rocket fuel, the production of a variety of resins and fibers, and its use as a refrigerant in low-temperature applications. Some of the minor uses of ammonia include the manufacture of rubber, water purification, and food and beverage treatment, the production of pulp and paper, the preparation of cleaners and detergents, and leather and the treatment of textiles.[1]

The term "BLEVE" was first coined following the rupture of a chemical plant reactor resulting from overpressure to explain the damage done by the explosion.[2] BLEVE was defined as a major container failure when the contained liquid is at a temperature well above its boiling point at atmospheric pressure. Many types of vessel failure fall within this category. The accompanying debris, or missiles, can travel up to several hundred meters doing extensive damage to surrounding property in the event of BLEVEs. Notable BLEVE incidents from 1926 to 1986 were reported.[3] And the most recent notable disaster occurred at large LPG storage facilities in Mexico City, Mexico in 1984. More than 500 people were killed and over 7000 were injured. Pietersen[4] presented a detailed report on this accident. Birk and Cunningham[5] conducted a series of tests to study the BLEVE phenomena for LPG. Tank-scale effects with fire impingement were also examined.[6] Some methods for the prevention of BLEVE are known, such as the prevention of fire, cooling of the tank walls in a fire by dispersed water, thermal isolation of tank walls, and use of appropriate venting devices.[7] Several researchers have proposed mathematical models describing the thermal response of an LPG tank,[8,9] yet the simulation concepts were not alike. While Ramskill[8] left out the most vital differential equations in his lumped-parameter model because of a trade secret, Beynon[9] used a distributed-parameter approach. This paper addresses a fictitious accident scenario involving an ammonia storage tank in a refinery. In a selective catalytic reduction (SCR) deNO$_x$ system, refinery stack gas containing nitric oxide and nitrogen dioxide is converted into nitrogen and water vapor by the addition of ammonia via

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O(g)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O(g)$$

In this study, a cylindrical ammonia tank is "bleved" with an external fire. We developed the worst-case thermal response models for a horizontal ammonia tank involved in fire engulfment accidents. The assessment of the separation distance between tanks and protection measures such as water spray cooling were discussed. Additionally, we examined the relief device design and investigated the open-system thermal response as well as pressure response effects for the ammonia tank. Since the thermal response of a BLEVE is essentially the same at all points in the process, we will lump the model

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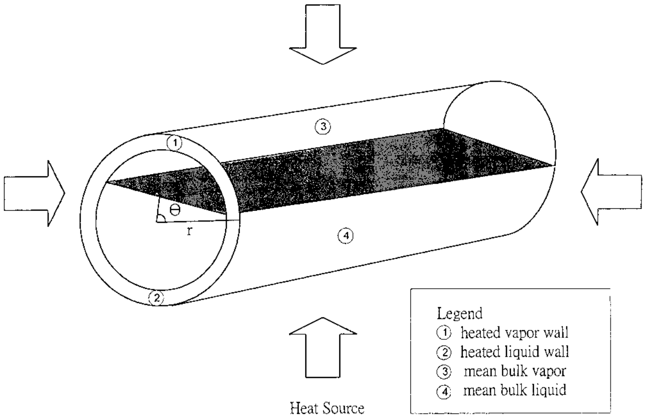

Figure 1. Four temperature nodes of a completely fire-engulfed horizontal tank.

as a single unit with four temperature nodes in the study. This research may provide a useful reference for those who are concerned with the safety of pressure-liquefied gases (PLGs) storage.

Closed-System Thermal Response Model

Figure 1 schematically illustrates a horizontal tank containing liquid ammonia. This figure shows a partially full but completely fire-engulfed situation. The arrow mark symbolizes the heat source which can be thermal radiation resulting from an adjacent fire, in situ jet flame, or pool fire. It is tantamount to a worse-case scenario. Note that when the tank is only subjected to partial fire engulfment, it will delay somewhat the induction of a BLEVE. This seems more likely to be the case; however, to gain insight into the most devastating outcome, we will only focus on building thermal response models with complete fire impingement in the study. As such, there are four temperature nodes to be calculated (i.e., the heated vapor wall, the heated liquid wall, the mean bulk vapor, and the mean bulk liquid). The system can then be described by a set of coupled differential equations. The following assumptions are made: (1) homogeneous node temperatures, (2) uniform thermal energy received by the tank, (3) negligible volumes of two horizontal tank heads, and (4) negligible solar radiation as compared with fire radiation on the tank. Applying energy balance equations between nodes and the fluids, we obtain

$$\rho_w V_1 C_{Pw} \frac{dT_1}{d\tau} = h_{1a}A_1(T_a - T_1) - h_{13}A_1(T_1 - T_3) - h_{12}A_{12}(T_1 - T_2) + Q_E A_1 \quad (1)$$

$$\rho_w V_2 C_{Pw} \frac{dT_2}{d\tau} = h_{2a}A_2(T_a - T_2) - h_{24}A_2(T_2 - T_4) - h_{12}A_{12}(T_2 - T_1) + Q_E A_2 \quad (2)$$

$$\rho_g V_g C_{Pg} \frac{dT_3}{d\tau} = h_{13}A_1(T_1 - T_3) - h_{34}A_{34}(T_3 - T_4) \quad (3)$$

$$\rho_l V_l C_{Pl} \frac{dT_4}{d\tau} = h_{24}A_2(T_2 - T_4) - h_{34}A_{34}(T_4 - T_3) \quad (4)$$

The liquid level angle, as shown in Figure 1, is used to calculate the heated-vapor transfer area and the heated-liquid transfer area. It can be shown that

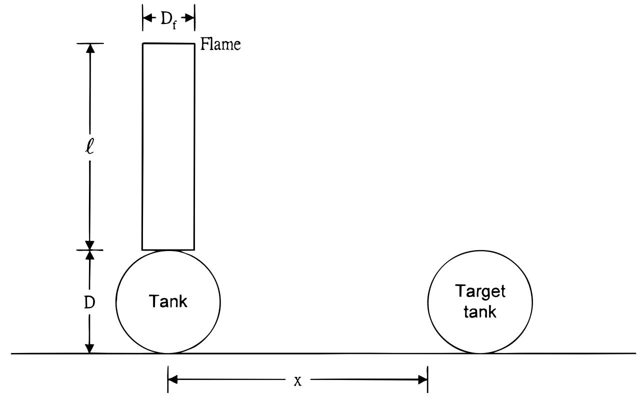

Figure 2. Solid flame model of a tank jet fire.

$$A_1 = 2r\theta L + 2r^2\left(\theta - \frac{1}{2}\sin 2\theta\right) \quad (5)$$

and

$$A_2 = 2r(\pi - \theta)L + 2r^2\left(\pi - \theta + \frac{1}{2}\sin 2\theta\right) \quad (6)$$

Note that $A_1 + A_2 = 2\pi rL + 2\pi r^2$. The interfacial wall area between the bulk vapor and liquid, A_{12}, is written as

$$A_{12} = 2Lt + 4t(r \sin\theta - t) \quad (7)$$

and the boiling heat-transfer area, A_{34}, is written as

$$A_{34} = 2(r\sin\theta - t)(L - 2t) \quad (8)$$

It can also be shown that the relationship between the liquid volume and liquid level angle is as follows:

$$V_l = Lr^2\left[\pi - \left(\theta - \frac{1}{2}\sin 2\theta\right)\right] \quad (9)$$

Note that once V_l is known, θ can be calculated. The convective heat-transfer coefficients, h_{1a} and h_{2a}, are calculated using[10]

$$h = 1.31(T_w - T_a)^{1/3} \quad (10)$$

Thus, we have $h_{1a} = 1.31(T_1 - T_a)^{1/3}$ and $h_{2a} = 1.31(T_2 - T_a)^{1/3}$.

The heat-transfer coefficients between the vessel wall and the fluids, h_{13} and h_{24}, are calculated using[11]

$$Nu = \frac{hH}{k} = C(Ra)^n \quad (11)$$

where $Ra = (g\beta\Delta TH^3)/(\alpha\nu)$.

The effective heat-transfer coefficient within the vessel wall, h_{12}, is calculated using[8]

$$h = \frac{k_w}{\Delta x} \quad (12)$$

where $\Delta x = (k_w t)^{1/2}[(1/(h_{1a} + h_{13})^{1/2}) + (1/(h_{2a} + h_{24})^{1/2})]$.

Finally, the boiling heat-transfer coefficient, h_{34}, is calculated using[12]

$$Nu = \frac{Ja^2}{C_{nb}^3 Pr_l^m} \quad (13)$$

where $Ja = [C_{Pl}(T_w - T_{sat})]/h_{fg}$, the Jakob number.

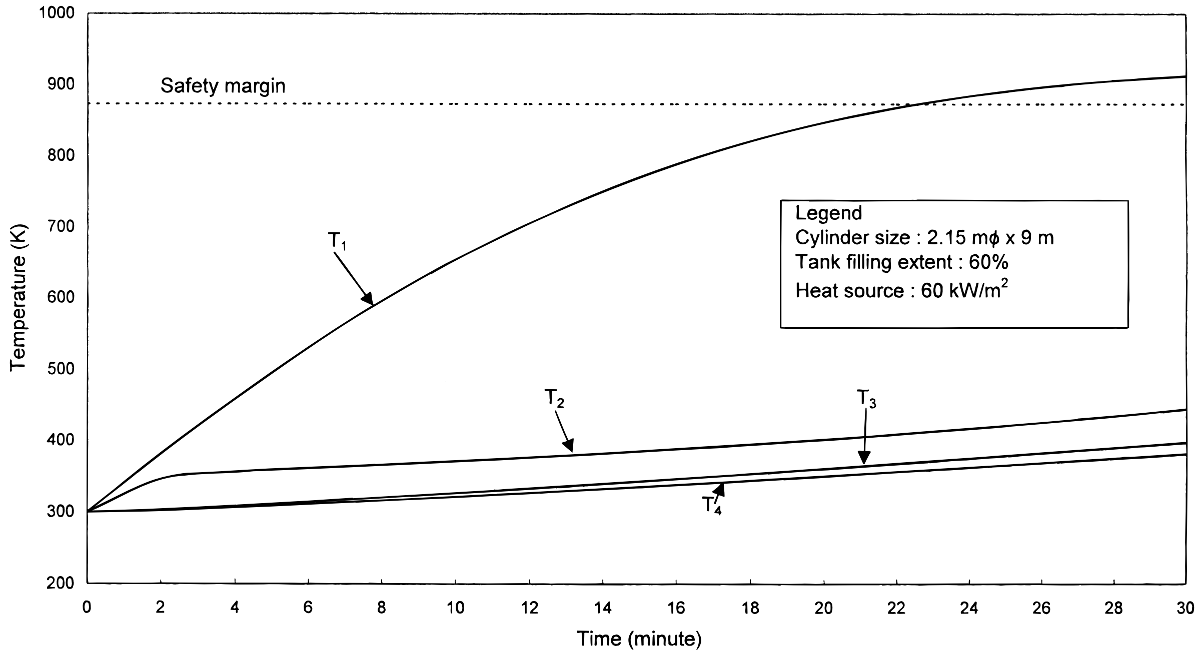

Figure 3. Profiles for four node temperatures at constant external heat.

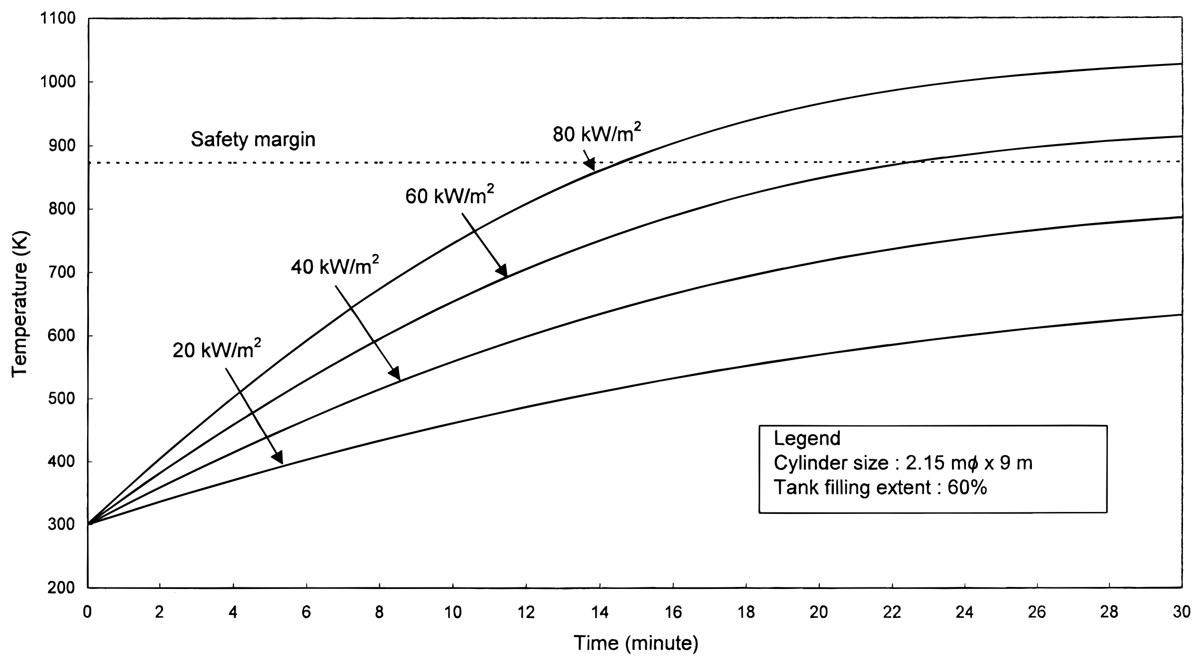

Figure 4. Variation in heated-vapor-wall temperature with varying external heat.

Robertson[13] suggested that it may be hazardous for a tank adjacent to a fire to receive an amount of 37.8 kW/m^2 thermal radiation. It is, therefore, advantageous to study the tank-to-tank separation distances by using the proposed thermal response model. Figure 2 depicts a model in which the flame is represented as a solid cylinder (solid flame model) with a uniformly radiating curved surface. Then the Stefan–Boltzmann equation may be applied, if an average flame temperature and uniform emissivity are assumed.

$$Q_E = F\phi\epsilon\sigma(T_f^4 - T_a^4) \tag{14}$$

where the view factor, F (i.e., the fraction of radiation leaving the flame that is incident upon the target), is given by[14]

$$F = \frac{1}{\pi S}\tan^{-1}\left(\frac{L_r}{\sqrt{S^2-1}}\right) + \frac{L_r}{\pi}\left[\frac{(A-2S)}{S\sqrt{AB}}\tan^{-1}\sqrt{\frac{A(S-1)}{B(S+1)}} - \frac{1}{S}\tan^{-1}\sqrt{\frac{S-1}{S+1}}\right] \tag{15}$$

in which $R_f = D_f/2$, $S = x/R_f$, $L_r = l/R_f$, $A = (S+1)^2 + L_r^2$, and $B = (S-1)^2 + L_r^2$. Note that the flame length, l, has been correlated as[15]

$$l = 42D_f\left(\frac{m''}{\rho_o\sqrt{gD_f}}\right)^{0.61} \tag{16}$$

where the mass burning rate, m'', can be written as

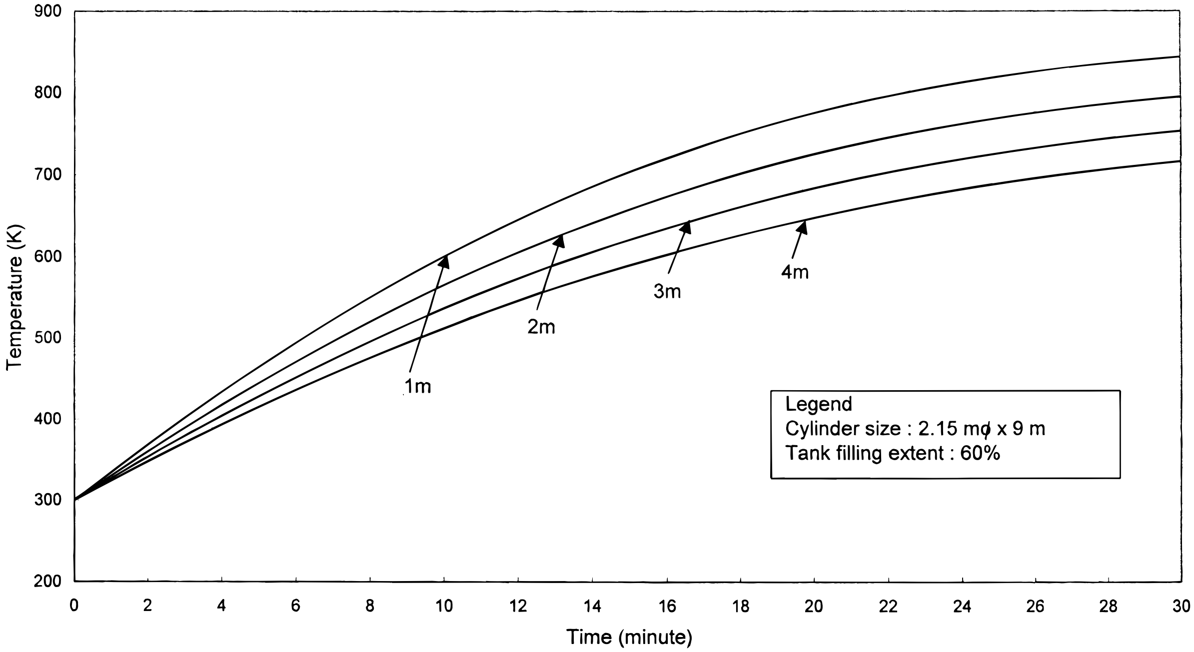

Figure 5. Effect of tank-to-tank spacing in case of a tank fire.

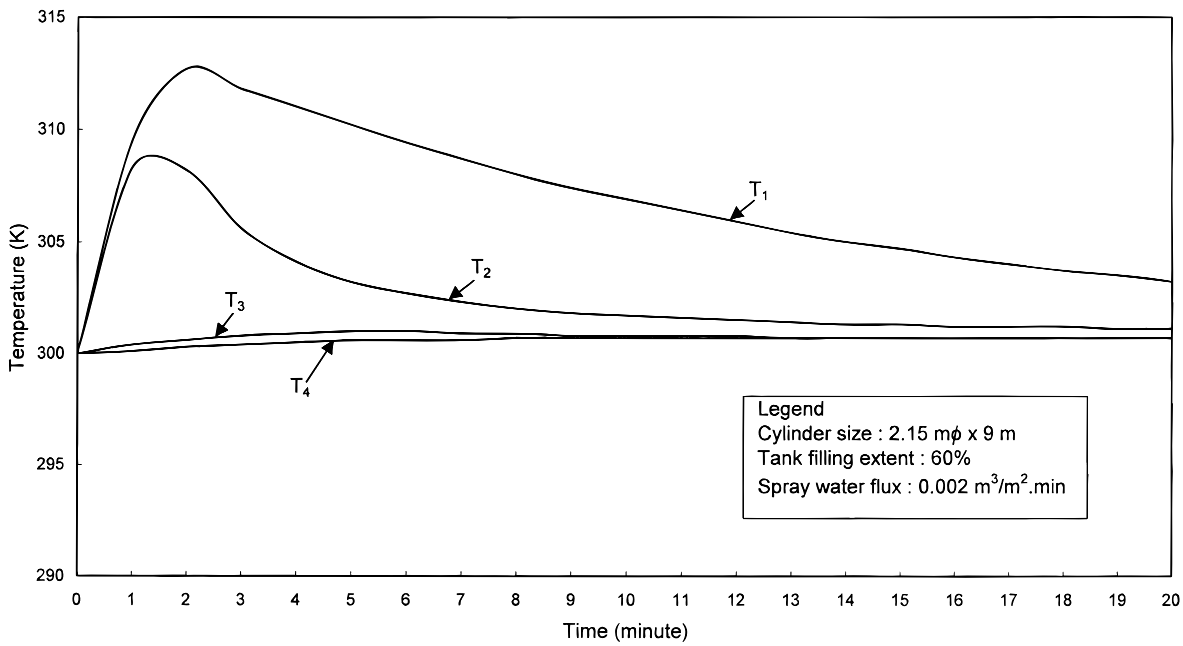

Figure 6. Variation in four node temperatures showing the effect of water spray.

$$m'' = m_\infty[1 - \exp(-\kappa\lambda D_f)]$$

in which

$$m_\infty = 10^{-3}\frac{\Delta H_c}{\Delta H_v^*}$$

and

$$\Delta H_v^* = \Delta H_v + \int_{T_a}^{T_b} C_P(T)\, dt$$

Effect of Water Spray

Water spray cooling is an effective way of protecting a vessel from being in BLEVE circumstances. If water sprays are used, we should add one more differential equation accounting for the temperature of water film:

$$\rho_{wat}V_{wat}C_{Pwat}\frac{dT_{wat}}{d\tau} = MA_sC_{Pwat}(T_{wati} - T_{wat}) + h_aA_s(T_a - T_{wat}) + h_{wat}A_1(T_1 - T_{wat}) + h_{wat}A_2(T_2 - T_{wat}) + Q_EA_s - Q_{wat}\lambda_{wat} \quad (17)$$

Note that the right-hand-side terms in eq 17 represent sensible heat, atmospheric convective heat, convection due to node-1 temperature, convection due to node-2 temperature, heat input due to surrounding fire, and evaporative heat, respectively. Additionally, we should modify eqs 1 and 2 as follows:

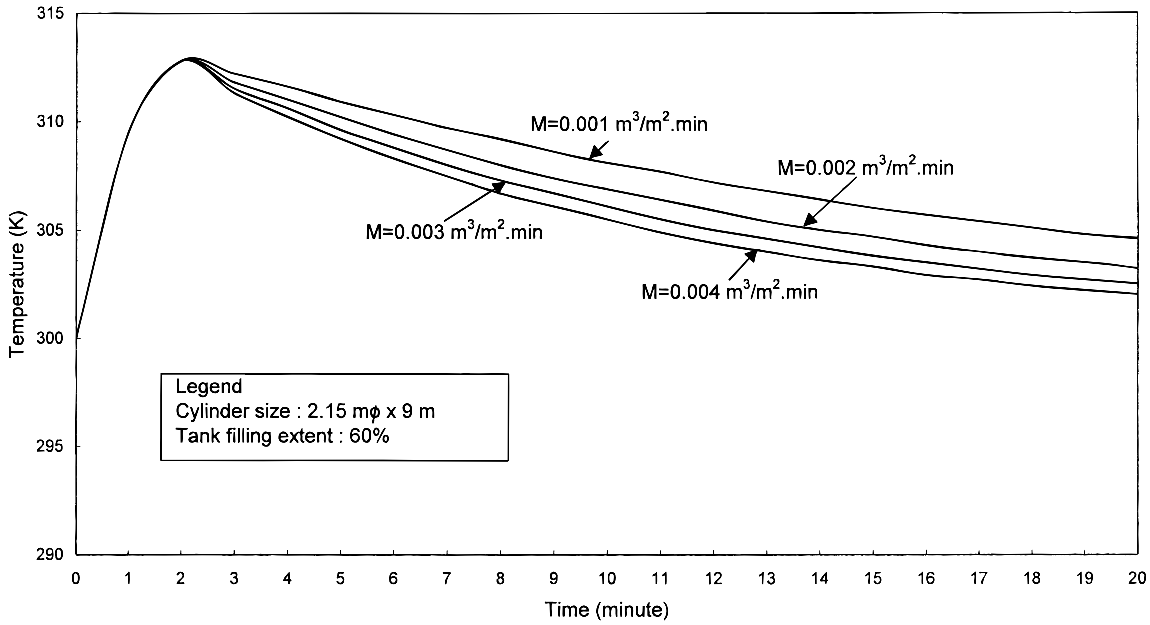

Figure 7. Variation in heated-vapor-wall temperature showing the effect of increasing amounts of water spray.

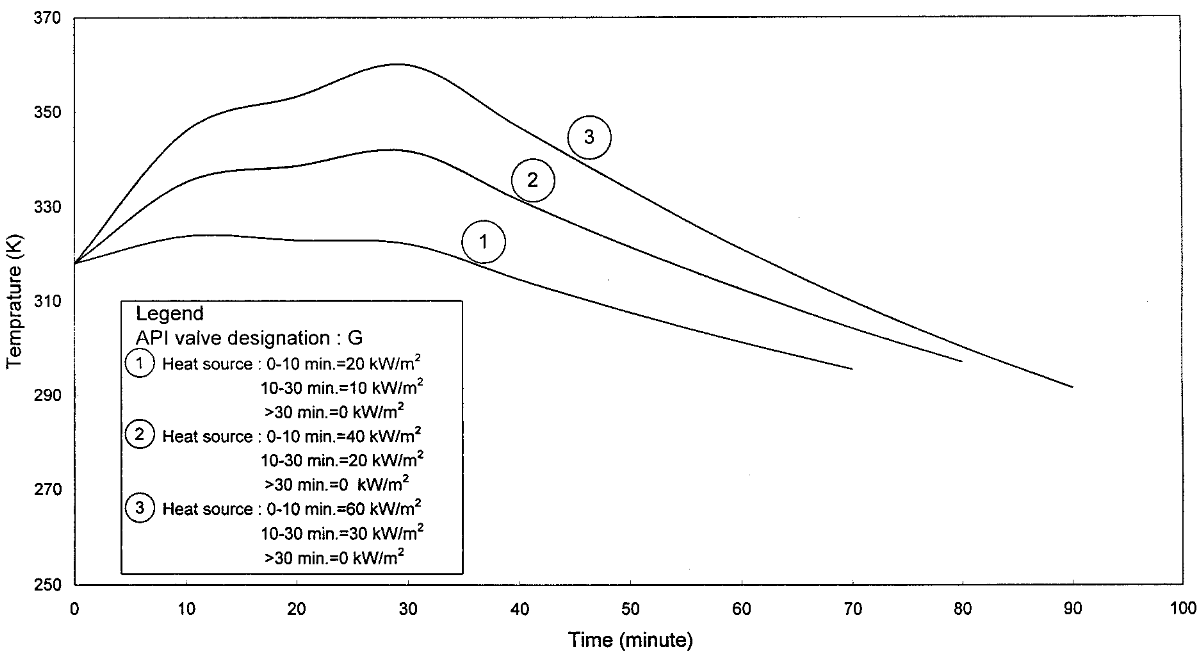

Figure 8. Temperature profiles versus time.

$$\rho_w V_1 C_{Pw} \frac{dT_1}{d\tau} = h_{wat} A_1 (T_{wat} - T_1) - h_{13} A_1 (T_1 - T_3) - h_{12} A_{12} (T_1 - T_2) \quad (18)$$

$$\rho_w V_2 C_{Pw} \frac{dT_2}{d\tau} = h_{wat} A_2 (T_{wat} - T_2) - h_{24} A_2 (T_2 - T_4) - h_{12} A_{12} (T_2 - T_1) \quad (19)$$

Note also that the empirical heat-transfer coefficient, h_{wat}, used for this cooling term is[16]

$$h_{wat} = 8500(Mr)^{1/3} \quad (20)$$

where r is the tank radius. The evaporation rate for spray water, Q_{wat}, is calculated from[17]

$$Q_{wat} = \frac{M_{wat} K A_s P^{sat}}{R_g T_{wat}} \quad (21)$$

It should be pointed out that in eq 17, V_{wat} is the water volume clinging to the vessel surface. To calculate this amount, it is necessary to know the water film thickness, b_{wat}, and that is taken from Chen:[18]

$$b_{wat} = 0.304 \left[\frac{(MH)^{1.75} \mu^{0.25}}{g \rho_{wat}^2} \right] \quad (22)$$

Relief System Sizing

Depressuring systems are used extensively in process plants for protecting vessels from overpressure. Overpressure has many causes, such as external fire, exothermic reactions, loss of power, inadequate cooling,

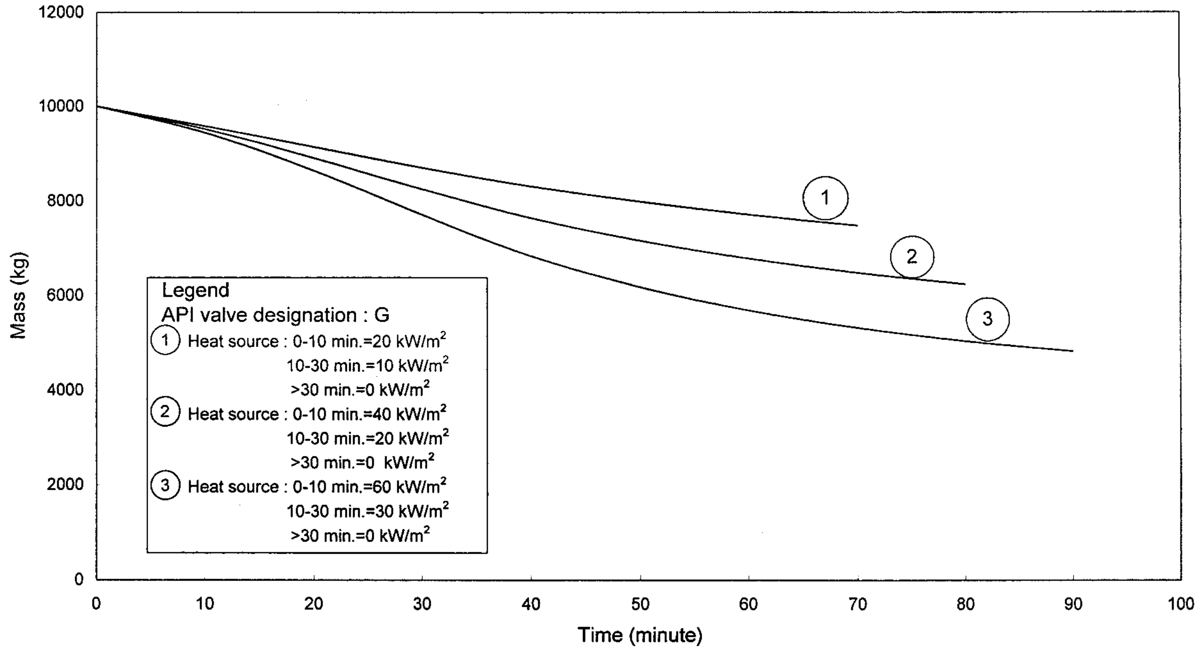

Figure 9. Profiles of tank liquid mass versus time.

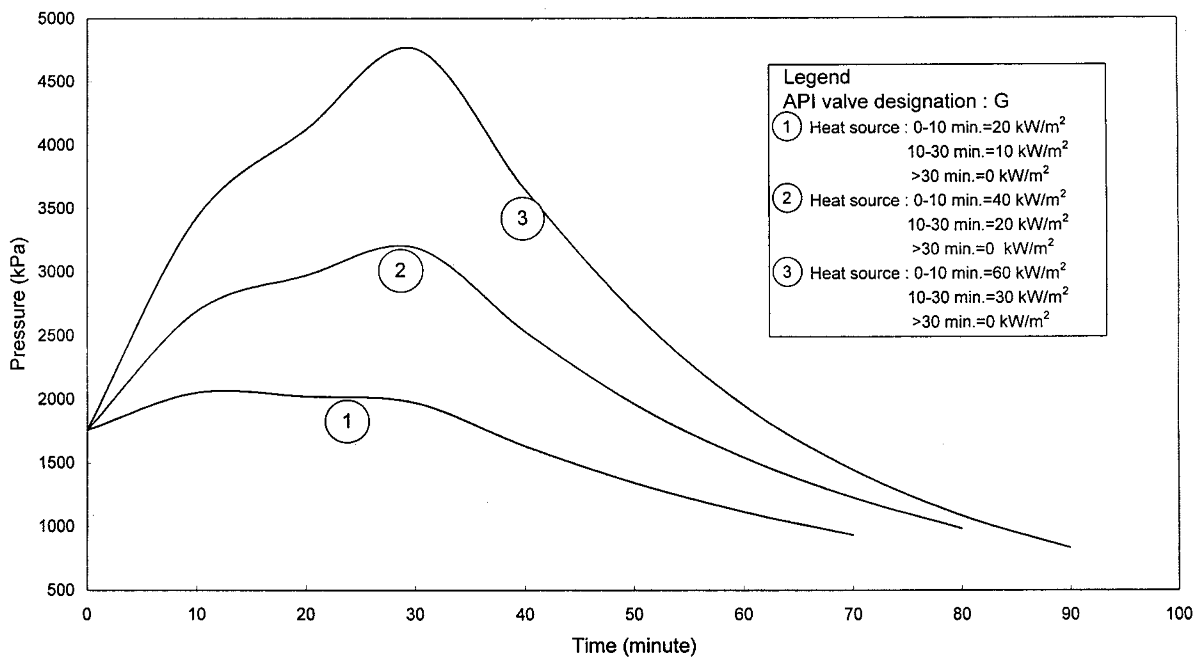

Figure 10. Pressure profiles versus time.

blocked lines, equipment failure, or human error. Proper sizing of a relief system is therefore essential. This requires the determination of proper relieving conditions (for example, flows, pressures, and temperatures) such that relief valves and their associated pipework can be properly sized for the worst scenario.[19] API RP-520[20] recommends that the vessel pressure should be reduced to 100 psia or 50% of the design pressure, whichever is lower, in 15 min. We used CHEMCAD III[21] to size the relief device for the ammonia storage tank and obtained the following results: the selected valve type is 1.5G2.5 with an actual nozzle area of 0.00032452 m^2.

Open-System Thermal Response Model

A simple model for the temperature dynamics of the ammonia tank during discharge can be described by the following equation:

$$\frac{dT}{d\tau} = \frac{1}{C_{Pl} m_l}(Q_E A_t - Q_m \Delta H_v) \tag{23}$$

where Q_E is the effective thermal energy to the contents stored in the tank and A_t the tank surface area. The time dependence of the liquid mass is described by the equation

$$\frac{dm_l}{d\tau} = -Q_m \tag{24}$$

The value of the mass flow rate Q_m is given by the following well-known expressions: (1) for subsonic flow, $P/P_a < \gamma_c$, where $\gamma_c = [(\gamma + 1)/2]^{\gamma/(\gamma-1)}$ is the critical heat-

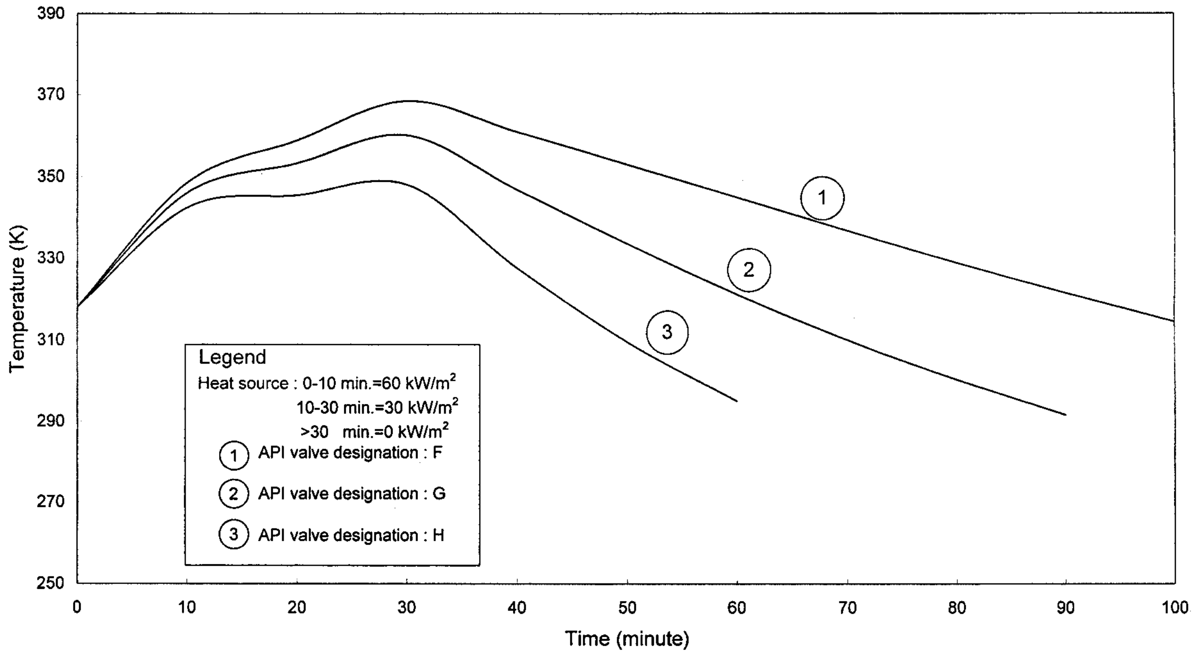

Figure 11. Effect of valve orifice on temperature versus time.

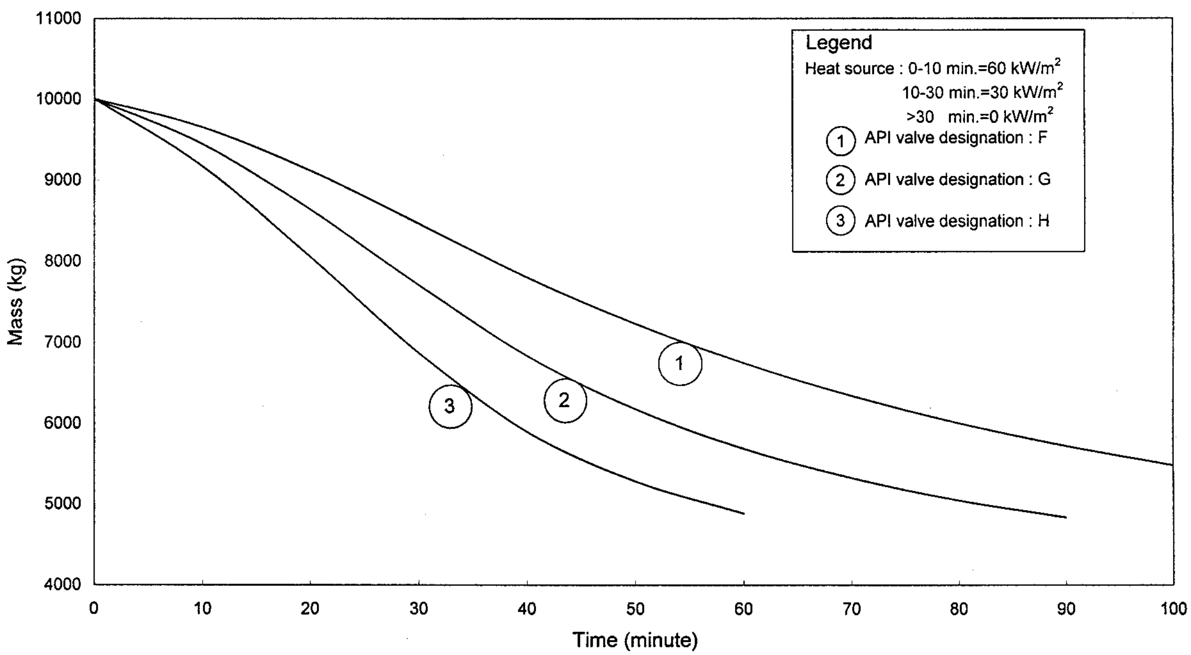

Figure 12. Effect of valve orifice on tank liquid mass versus time.

capacity ratio:

$$Q_m = C_0 A_0 \sqrt{\frac{2\gamma}{\gamma - 1} P \rho_g \left[\left(\frac{P_a}{P}\right)^{2/\gamma} - \left(\frac{P_a}{P}\right)^{(\gamma+1)/\gamma}\right]} \quad (25)$$

where C_0 is the discharge coefficient, A_0 the discharge area, and γ the heat-capacity ratio; (2) for sonic flow, $P/P_a > \gamma_c$, and

$$Q_m = C_0 A_0 \sqrt{\gamma \left(\frac{2}{\gamma + 1}\right)^{(\gamma+1)/(\gamma-1)} P \rho_g} \quad (26)$$

Finally, the time-dependent tank pressure is simply the time derivative of the following Antoine-type equation:

$$\log P = a + b/T + c \log T + dT + eT^2 \quad (27)$$

where a, b, c, d, and e are constants.

Results and Discussion

Equations 1−13 were programmed in FORTRAN and solved numerically using the algorithm of adaptive Runge−Kutta−Fehlberg.[22] To simulate BLEVE phenomena, several varied process variables were programmed in. The process variables include external heat input, tank fill level, and tank size. Figure 3 shows the four node temperatures at a constant external heat of 60 kW/m^2. The safety margin for the ammonia tank is set at 873 K (600 °C). Beyond this line the tank metal is likely to fail because of tensile stress. Figure 4 shows the variation in temperature (node 1) for Q_E corre-

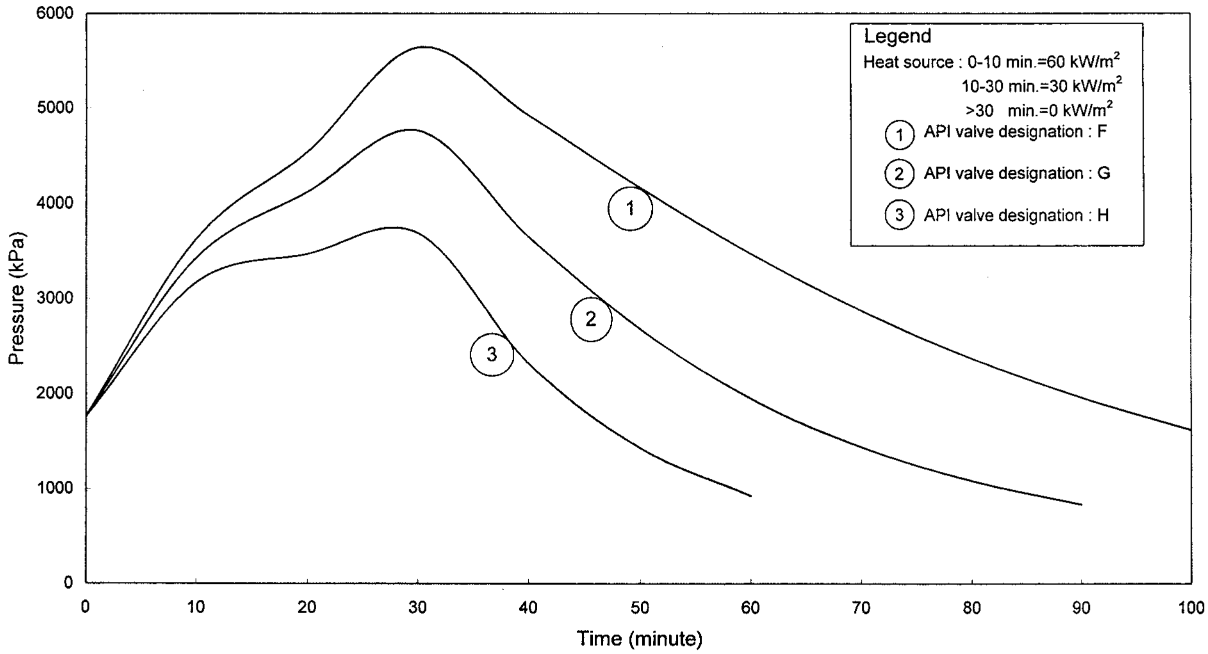

Figure 13. Effect of valve orifice on pressure versus time.

sponding to 20, 40, 60, and 80 kW/m^2, respectively. Clearly, the higher the external heat, the sooner the tank fails. To study the effect of tank-to-tank separation distances in case of a fire, eqs 14−16 were linked with eqs 1−13. The simulation result of node 1 temperature is shown in Figure 5. As can be seen from the figure, the greater the spacing, the safer the tank is. It is a common practice to spray cooling water on the ammonia tanks when ambient temperature reaches about 313 K (40 °C). To simulate this situation, eqs 17−22 were united with eqs 3−13. The variation in temperatures is shown in Figure 6. The effect of increasing the amount of water spray (from 0.001 to 0.004 m^3/m^2·min in steps of 0.001 m^3/m^2·min) is clear, as can be seen from Figure 7.

To simulate the effects of appropriate vent device, an open-system thermal response model is employed by using eqs 23−27. Figure 8 shows the temperature profiles for a G-type orifice of an API relief valve. The simulation incorporates three time increments: (1) heat input at 0−10 min; (2) half the heat input at 10−30 min; (3) no heat input after 30 min. Figure 9 shows the ammonia liquid mass in the tank versus time. And the pressure profiles corresponding to Figure 8 are shown in Figure 10. It is important to readily put out the external heat source as can be seen from Figures 8 and 10. To investigate the effects of varied valve orifice size, types F, G, and H are utilized and compared. This will ensure one not to underestimate or overdesign. The results are shown in Figures 11−13. Note that the orifce areas for F, G, and H are 0.00019807, 0.00032452, and 0.00050646 m^2, respectively. The results from Figures 8−13 will help us set up the criteria which allow the determination of appropriate protection measures.

According to API,[23] fires impinging on the outside surface of an unfireproofed pressure storage vessel above liquid level can be very dangerous. After approximately 10−30 min of direct flame exposure, the vessel usually ruptures violently. The time lapse depends on the heat intensity and the thickness of the exposed area of the vessel shell. The results of this thermal response model show good agreement.

Conclusions

This paper has presented thermal response models for worse-case scenarios of a horizontal ammonia tank with complete fire engulfment. The study also investigated the effects of pressure response when an appropriate relief valve does open in case of a BLEVE situation. The result of this research might help those who are concerned with the safety of ammonia storage. In addition, the technique presented in this paper may be useful in assessing the safety of other kinds of pressure-liquefied gases (PLGs), such as ethylene, vinyl chloride, and so forth. Further research is warranted to study the thermal/pressure response for a partial fire-impingement scenario.

Nomenclature

A_0 = discharge area (m^2)
A_1 = heated-vapor transfer area (m^2)
A_2 = heated-liquid transfer area (m^2)
A_{12} = interfacial-wall transfer area between bulk vapor and liquid (m^2)
A_{34} = boiling heat-transfer area (m^2)
A_s = water-film area on tank surface (m^2)
A_t = tank surface area (m^2)
b_{wat} = water-film thickness (m)
C = constant in eq 11 (=0.1)
C_0 = discharge coefficient
C_{nb} = constant in eq 13 (=0.015)
C_{Pg} = specific heat of vapor (kJ/kg·K)
C_{Pl} = specific heat of liquid (kJ/kg·K)
C_{Pw} = specific heat of tank wall (kJ/kg·K)
C_{Pwat} = specific heat of water (kJ/kg·K)
D = tank diameter (m)
D_f = flame source diameter (m)
F = view factor used in eq 14
g = acceleration due to gravity (9.81 m/s^2)
H = tank height (m)
h = convective heat-transfer coefficient (kW/m^2·K)
h_a = heat-transfer coefficient of ambient air (kW/m^2·K)
h_{1a} = heat-transfer coefficient from ambient to heated vapor surface (kW/m^2·K)

h_{2a} = heat-transfer coefficient from ambient to heated liquid surface (kW/m^2·K)
h_{12} = heat-transfer coefficient from heated vapor wall to heated liquid wall (kW/m^2·K)
h_{13} = heat-transfer coefficient from heated vapor wall to bulk vapor (kW/m^2·K)
h_{24} = heat-transfer coefficient from heated liquid wall to bulk liquid (kW/m^2·K)
h_{34} = heat-transfer coefficient from bulk vapor to bulk liquid (kW/m^2·K)
h_{fg} = enthalpy of vaporization (kJ/kg)
h_{wat} = heat-transfer coefficient of spray water (kW/m^2·K)
Ja = Jakob number
K = mass-transfer coefficient of water (=0.0083 m/s)
k = thermal conductivity (W/m·K)
k_l = liquid thermal conductivity (W/m·K)
k_w = tank wall thermal conductivity (W/m·K)
L = tank length (m)
L_r = mean flame length/flame source radius
l = mean flame length (m)
M = water spray rate (m^3/m^2·min)
M_{wat} = molecular weight of water (kg/kmol)
m = constant in eq 13 (=4.1)
m'' = mass-burning rate per unit area (kg/m^2·s)
m_l = liquid mass in tank (kg)
n = constant in eq 11 (=$^1/_3$)
Nu = Nusselt number
P = tank pressure (kPa)
P_a = ambient pressure (kPa)
P^{sat} = saturation pressure of water (Pa)
Pr_l = Prandtl number
Q_E = thermal energy (kW/m^2)
Q_m = mass flow rate (kg/s)
Q_{wat} = evaporation rate of spray water (kJ/kg)
Ra = Rayleigh number
R_f = flame source radius (m)
R_g = gas constant (=8.314 kPa·m^3/kmol·K)
S = distance from flame source center/flame source radius
r = tank radius (m)
T = bulk liquid temperature (K)
T_1 = heated-vapor-wall temperature (K)
T_2 = heated-liquid-wall temperature (K)
T_3 = bulk-vapor temperature (K)
T_4 = bulk-liquid temperature (K)
T_a = ambient temperature (K)
T_b = normal boiling point (K)
T_f = average flame temperature (K)
T_{sat} = saturation temperature (K)
T_w = tank wall temperature (K)
T_{wat} = spray-water-on-tank temperature (K)
T_{wati} = inlet temperature of spray water (K)
t = wall thickness (m)
V_1 = volume of heated vapor wall (m^3)
V_2 = volume of heated liquid wall (m^3)
V_g = vapor volume (m^3)
V_l = liquid volume (m^3)
V_{wat} = water volume on tank surface (m^3)
x = tank-to-tank separation distance (m)

Greek Symbols

α = thermal diffusivity (m^2/s)
β = volumetric expansion coefficient of vapor (1/K)
γ = heat-capacity ratio
γ_c = critical heat-capacity ratio
ΔH_c = heat of combustion (kJ/kg)
ΔH_v = heat of vaporization at the boiling point (kJ/kg)
ΔH_v^* = modified heat of vaporization (kJ/kg)
ΔT = temperature difference (K)
ϵ = flame emissivity
θ = liquid angle (rad)
κ = extinction coefficient
λ = mean flame length corrector
λ_{wat} = evaporation heat of water (kJ/kg)
μ = water viscosity (N·s/m^2)
ν = kinematic viscosity (m^2/s)
ρ_w = tank wall density (kg/m^3)
ρ_g = vapor density (kg/m^3)
ρ_l = liquid density (kg/m^3)
ρ_{wat} = water density (kg/m^3)
ρ_0 = ambient air density (kg/m^3)
σ = Stefan−Boltzmann constant (5.67 × 10^{-11} kW/m^2·K^4)
σ_l = surface tension (N/m)
τ = lapse time (min)
ϕ = atmospheric transmissivity

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