

## Modelling of LNG Pool Spreading on Land with Included Vapour-Liquid Equilibrium and Different Boiling Regimes

Omar Basha<sup>a</sup>, Yi Liu<sup>a</sup>, Marcelo Castier<sup>a</sup>, Tomasz Olewski<sup>a</sup>, Luc Vechot<sup>\*a</sup>, Sam Mannan<sup>b</sup>

<sup>a</sup>Texas A&M University at Qatar, PO Box 23874, Doha, Qatar

<sup>b</sup>Mary Kay O'Connor Process Safety Center, Texas A&M University, College Station, TX 77843, USA  
[luc.vechot@qatar.tamu.edu](mailto:luc.vechot@qatar.tamu.edu)

This paper presents a source term model for estimating the rate of unconfined LNG pool spreading on land. The model takes into account the composition changes of a boiling mixture, the variation of thermodynamic properties due to preferential boiling in the liquid mixture and the effect of boiling regime on conductive heat transfer. The heat, mass and momentum balance equations were solved for continuous and instantaneous spills. A sensitivity analysis was conducted to determine the relative effect of each of these phenomena on pool spreading. The model was compared to a commonly used gravity-inertia integral pool-spreading model with one-dimensional conductive heat transfer.

### 1. Introduction

Although some pool spreading models have been developed as outlined by Webber et al. (2010), most of them are integral models and based on work carried out in the early 1970's on non-volatile liquid spills. These early models tend to overlook the complexity associated with cryogenic pool spreading. Cryogenics (e.g. LNG: boiling point = -162 °C) exhibit vigorous boiling upon being released on land or water at ambient temperature. In the case of an LNG release, some of the LNG will flash while rest will spread very quickly. The conditions of heat transfer from the surroundings and the composition of the LNG mixture may affect the spread rate and the vaporization rate. Most of the current modelling work on LNG spillage estimates the LNG properties either using fixed thermo-physical properties of a mixture or using those of pure methane as an analogue. This is questionable since the vaporization behaviour of a mixture is different from that of a pure fluid due to preferential boil-off of the lighter hydrocarbons, which in turn results to time varying properties of the spilled mixture.

The complex phenomena governing the spread and vaporization of a LNG pool have to be accounted for and their relative importance must be understood to develop a comprehensive model that is both adaptable and applicable to a variety of scenarios. In this paper, a pool-spreading model that takes into account the composition changes of a boiling LNG mixture, the effect of different boiling modes on conductive heat transfer as well as the varying mixture thermodynamics and vapour liquid equilibrium effects is proposed. A sensitivity analysis is conducted to identify the relative importance of each of the governing parameters on the pool spreading process. The model incorporates the multicomponent nature of LNG and its effect on the behaviour of the spill with the aim of developing the most accurate and comprehensive representation of the pool spreading process.

### 2. Pool spread modelling – base case

The pool spreading models developed and discussed in this paper were chosen and used to identify the relative importance of the phenomena involved in the pool spreading process of a cryogenic liquid mixture like LNG on land. This was achieved by defining a base case model and comparing it with pool spreading models which differ from the base case by the addition of one of the following phenomena: heat transfer boiling regimes and vapor liquid equilibrium (VLE).

The models developed are based on assumption of circular pool of the liquid with radius ( $r$ ) and radial liquid flow velocity and spreading on flat, horizontal, solid surface. The equations for a momentum balance and a vaporization rate of the pool were adopted from the literature. For the momentum balance, the model from Webber et al. (2010), called "improved integral model" has been taken for spill on the smooth surface. This assumes gravity-inertia regime with the addition of a resistance term corresponding to the friction at the base of the pool. Other regimes like the gravity-viscous or surface tension-viscous are assumed to be negligible for the duration of the pool spreading as the LNG tends to vaporize quickly (references summarized in Woodward and Pitblado (2012)). Thus, the equation describing the spreading rate of the pool is given by:

$$\frac{\partial^2 r}{\partial t^2} = 4g' \frac{h}{r} - C_T \frac{1}{h} \left( \frac{dr}{dt} \right)^2 \quad (1)$$

The first term of the forces on the right side of the equation represents the gravity-inertia regime and the second represents friction at the pool base for turbulent flow. The  $g'$  represents gravity for spreading if spill is on land, the  $h$  represents an area-average pool height (depth), and  $C_T$  is a dimensionless skin friction coefficient of the order of  $10^{-3}$  ( $1 \cdot 10^{-3}$  was chosen in this paper), and which depends in principle on ground roughness (Webber et al., 2010). The value 4 in the gravity-inertia term was derived by Webber et al. (in their previous publications summarized in (Webber et al., 2010)) from an examination of the shallow water equations.

It is assumed in this paper, the liquid pool temperature does not change (which is valid at least for an early stage or not very big spills) and thus the vaporization rate is directly proportional to the total heat ( $Q=q \cdot A$ ) provided to the pool:

$$\frac{dm}{dt} = \frac{q \times A}{\Delta H_{vap}} \quad (2)$$

It is also assumed that liquid vaporization rate is due to the conduction from the solid only and no convection from ambient air or radiation is included. Moreover, a perfect thermal contact between liquid and solid is assumed and thus the temperature of the solid surface equals to the liquid's temperature. With these assumptions, the liquid vaporization rate ( $dm/dt$ ) was adopted from Briscoe and Shaw (1980), which is the modified solution of an one-dimensional (1-D), vertical conductive heat transfer from semi-infinite solid (Carslaw and Jaeger, 1986) to the circular liquid pool:

$$\frac{dm}{dt} = \frac{\chi k (T_\infty - T_B)}{\Delta H_{vap} (\pi \alpha)^{0.5}} \int_0^{r(t)} \frac{2\pi r' dr'}{(t-t')^{0.5}} \quad (3)$$

$\Delta H_{vap}$  is a latent heat of vaporization, and  $t'$  is the time at which spreading pool front reaches the radius  $r'$ . The liquid temperature is uniform and equal to its boiling point ( $T_B$ ). The temperature at the infinite depth ( $T_\infty$ ) is constant and the properties of the solid, thermal diffusivity ( $\alpha$ ) and conductivity ( $k$ ), do not change with time ( $t$ ) and solid's depth. However, it has to be noted that Briscoe and Shaw (1980) modified the ideal 1-D conductive heat transfer equation by introducing an empirical correction factor ( $\chi$ ), which, they explained, represents the solid's surface roughness (giving greater pool contact area), the uncertainties in solid thermodynamic properties (e.g.  $\alpha$ ,  $k$ ), and possibly other effects. They estimated  $\chi$ -factor equal to 3 to match the experimental data given by Burgess and Zabetakis (1962) and American Gas Association (1974).

Table 1: LNG properties used in this work

Parameter	Value
LNG density, $\rho$	59 kg m <sup>-3</sup>
LNG molecular weight	16.043 kg kmol <sup>-1</sup>
LNG latent heat, $\Delta H_{vap}$	510 kJ kg <sup>-1</sup>
LNG composition	CH <sub>4</sub> : 89.9 %, C <sub>2</sub> H <sub>6</sub> : 6 %, C <sub>3</sub> H <sub>8</sub> : 2.2 %, C <sub>4</sub> H <sub>10</sub> : 1.5 %, N <sub>2</sub> : 0.4 %
Concrete thermal conductivity, $k$	0.92 W m <sup>-1</sup> K <sup>-1</sup>
Concrete thermal diffusivity, $\alpha$	4.16 $\cdot 10^{-7}$ m <sup>2</sup> s

Equations (1) and (3) define the "base case" model of pool spread and vaporization in this paper and subsequent modifications are referred to this base case. All models were compared for two spill scenarios taken from Briscoe and Shaw (1980): (1) instantaneous spill of 1000 m<sup>3</sup> of liquid, and (2) continuous spill

at the rate of  $10 \text{ m}^3\text{s}^{-1}$ . Both were performed for spill of liquefied natural gas (LNG) on concrete. The properties of the LNG mixture and concrete are shown in Table 1. For the base case, the properties of LNG were calculated as average values using mixing rules. They were obtained for the boiling point of mixture and were independent of the temperature.

### 3. Heat transfer to the pool and boiling regimes

As described in section 2, for spills on land, the heat transfer from the ground surface to the cryogenic liquid pool may be modeled using 1-D heat conduction and assuming the pool is in perfect thermal contact with the ground. This approach is commonly used with correction factors, however some of the assumptions, like perfect contact between solid and liquid, are still questionable.

It is more realistic that a film or bubbles will be created between the ground and the spilled cryogen, which will limit the direct contact between the liquid and the solid surface and create thermal resistance. This would be an effect of large temperature difference between the liquid and the ground. Thus, a boiling model should be incorporated into the heat transfer and pool spreading models. Three boiling regimes can occur during pool boiling in such a model depending on the temperature difference between the liquid and the ground: film, transition and nucleate (Figure 1a). It is a challenge to correlate the heat flux for each of these regimes. Little work has been done on LNG, however some data can be found for pure components, like liquid nitrogen (Barron, 1999), methane (Woodward and Pitblado, 2012), pentane and carbon tetrachloride (Berenson, 1962). Although most of them are obtained for the smooth (mostly metallic) surfaces, it is worth to note that Berenson (1962) has done measurement for different surfaces and he concluded that the Leidenfrost point (Min on Figure 1a) and the maximum value of critical heat flux point (CHF in Figure 1a) do not change with the surface roughness. A valuable summary of the developed heat flux correlations for each boiling regimes has recently been done by Woodward and Pitblado (2012). Liu et al. (2011) developed a methodology using Computational Fluid Dynamics (CFD) to simulate the boiling process of liquid nitrogen. This approach is promising and may be extrapolated to calculate the boiling curve for cryogenic liquid mixtures like LNG.

In this paper, the correlations summarized in Woodward and Pitblado (2012) have been used to calculate heat flux during film and nucleate boiling as well as to calculate the CHF and Leidenfrost points. The film boiling correlation was taken from Klimenko (1981), nucleate boiling correlation from Opschoor (1980). The transition boiling correlation is an interpolation between CHF and Leidenfrost points based on Kalinin et al. (1976) and Opschoor (1980). All the above mentioned correlations were coupled together and the heat flux curve for methane, ethane, propane and butane were calculated. The result is shown in Figure 1b. This heat flux goes directly into Eq. (2).

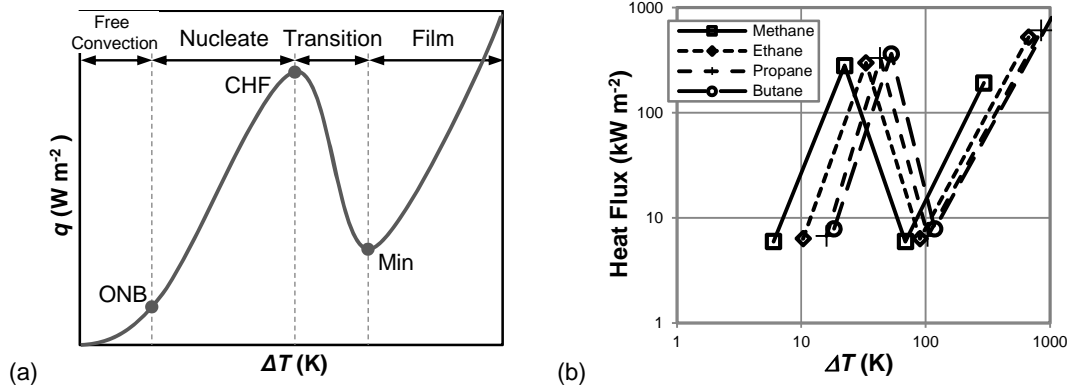


Figure 1: General concept of heat flux curve for a boiling cryogen (a); and the heat flux curve for LNG components: methane, ethane, propane and butane (b)

Unlike 1-D conduction, the ground's surface temperature is not constant when boiling is considered, as the thermal resistance between the ground surface and the liquid pool should be accounted for. Thus the surface temperature needs to be calculated, using a Neumann type boundary condition. The details of this approach are given in Liu et al. (2012). The above described boiling model was coupled together with the pool spreading from Eq. (1) neglecting the friction term. The latest was neglected with the assumption that the liquid slides on the vapor film at the edge of the pool. The modified model was compared to the base case model calculated for several values of the correction factors  $\chi$ . The result is shown in Figure 2.

#### 4. Mixture Thermodynamics

The use of pure fluids or constant property analogues to represent LNG may not provide an accurate representation of its mixture thermodynamics (Conrado and Vesovic, 2000). Varying thermo physical properties and composition throughout the pool spread period have to be accounted for. LNG will behave differently than pure methane, or in fact a pure cryogen, as transient changes in the composition may affect the physical properties of the mixture. Vapor-liquid equilibrium (VLE) relations can be used to predict such properties and were incorporated in the pool spreading model as follows.

Since the system will always be at low pressure, Raoult's law was used to calculate the partial pressure of each component in the vapor phase. The saturation properties for each of the pure components were calculated using the Antoine Equation. The enthalpy of vaporization was determined as the difference between the vapor and liquid enthalpies, whereas, the enthalpy of each of the phases is calculated as the sum of the ideal gas and residual enthalpies: The reference state was taken to be at 298 K and 1 atm (101.325 kPa). The ideal gas heat capacity of each of the components was determined using the Shomate equation, while the residual enthalpy of the vapor phase was ignored because the system will be at the low pressure. When determining the enthalpy of the liquid phase, an ideal solution mixing rule was used and the mixing energy was neglected. The pure component residual enthalpy was taken to be equal to the negation of the vaporization energy, because the saturated vapor is assumed to behave as an ideal gas at the temperature of interest. The heat of vaporization of the pure components was determined using the Pitzer correlation.

The base case was compared to the model incorporating VLE effects. VLE and mixture thermodynamics were implemented to calculate the pool temperature, latent heat and vapor and liquid compositions of throughout the pool lifetime. The initial composition of the LNG mixture was same as this for base case and is shown in Table 1.

As shown in Figure 2a, incorporating mixture and thermodynamic effects will not result in a significant enhancement to the pool spread model for continuous spills. This can be explained by the continuous supply of LNG to the pool, which maintains high methane content. For instantaneous spill (Figure 2b), the VLE effect on radius change rate becomes significant during the later stages of the spill as the pool is decaying. This is justified by the immediate effect of preferential boil-off on the pool's thermo-physical properties. As the content of heavier hydrocarbons increases, the latent heat of vaporization of the pool will increase and its molar vaporization rate will decrease.

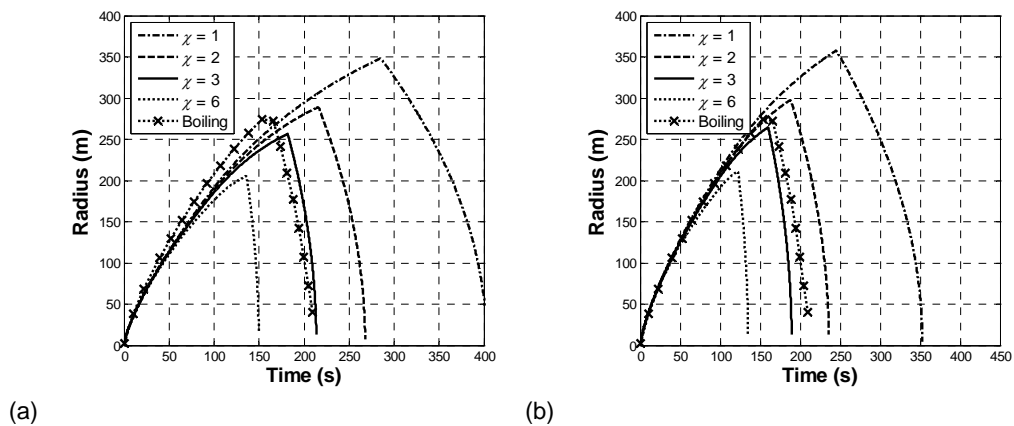


Figure 2: The VLE effect on pool radius for continuous (a) and instantaneous (b) spill

#### 5. Summary and Conclusions

A pool spread model was developed by incorporating momentum, boiling heat transfer and thermodynamic effects with the aim of developing a predictive model that does not incorporate any empirical values or corrections to account for the unique nature of LNG. A sensitivity analysis was conducted to determine the relative importance of boiling heat transfer and VLE effects on the rate of pool spreading and decay.

The boiling model incorporated into the pool spreading, governed by gravity-inertia regime only, is in good agreement to 1-D conduction model with the correction parameter  $\chi$  equals to 3, without any empirical

correction factors. It has to be noted that the 1-D conduction model was found to be very sensitive to the correction parameter  $\chi$ , which brings into question the versatility of applying 1-D conduction to represent heat transfer under different scenarios.

Vapor-liquid equilibrium and mixture effects seem to have a negligible effect on the pool spreading process, however they provide an insight to the thermo-physical properties as the function of temperature and the pool's lifetime.

Future work includes further analysis of the boiling regimes governing the heat transfer within the pool and investigating possible conditions for film breakup and stability. The CFD modeling of the pool boiling process based on the work of Liu et al. (2011) to incorporate the effects of mixture thermodynamics and surface roughness will also be developed to further improve of the proposed pool spread and vaporization model. At last but not least, the medium and large scale experimental work needs to be done to provide good quality data that can be used to validate the developed models and to provide a better understanding of the phenomena governing the pool spreading process.

### Acknowledgement

The authors would like to acknowledge the long term, not only financial, support provided by BP Global Gas SPU for the LNG safety research being conducted at Texas A&M University at Qatar (TAMU at Qatar). They also acknowledge the support of Qatar Petroleum in the form of the facilities used for experiments at RLESC and the provision of staff to work with the TAMU's at Qatar LNG research team.

### Nomenclature

$r$	= radius (m)	$\Delta H_{vap}$	= latent heat of vaporization ( $\text{J kg}^{-1}$ )
$t$	= time (s)	$T$	= temperature (K)
$h$	= pool height (m)	$m$	= mass (kg)
$g'$	= acceleration due to gravity ( $\text{m/s}^2$ )	$q$	= heat flux ( $\text{W m}^{-2}$ )
$C_T$	= skin friction coefficient for turbulent flow (-)	$Q$	= total heat (W)
$\chi$	= correction factor (-)	$k$	= thermal conductivity ( $\text{W m}^{-1}\text{K}^{-1}$ )
$\alpha$	= thermal diffusivity ( $\text{m}^2\text{s}^{-1}$ )	$A$	= pool area ( $\text{m}^2$ )

### References

- American Gas Association, 1974. LNG Safety Program: Interim Report on Phase II Work ( No. Project IS-3-1). American Gas Association, Columbus, Ohio, USA.
- Barron, R.F., 1999. Cryogenic heat transfer. Taylor and Francis, Philadelphia, PA, USA; London, UK.
- Berenson, P.J., 1962. Experiments on pool-boiling heat transfer. International Journal of Heat and Mass Transfer 5, 985–999.
- Briscoe, F., Shaw, P., 1980. Spread and Evaporation of Liquid. Progress in Energy and Combustion Science 6, 127–140.
- Burgess, D., Zabetakis, M.G., 1962. Fire and explosion hazards associated with liquefied natural gas. U.S. Dept. of the Interior, Bureau of Mines, Report 6099, Washington, DC., USA.
- Carlsaw, H.S., Jaeger, J.C., 1986. Conduction of Heat in Solids, 2nd ed. Oxford University Press, USA.
- Conrado, C., Vesovic, V., 2000. The influence of chemical composition on vaporisation of LNG and LPG on unconfined water surfaces. Chemical Engineering Science 55, 4549–4562.
- Kalinin, E.K., Berlin, I.I., Kostyuk, V. V, Nosova, E.M., 1976. Heat transfer in transition boiling of cryogenic liquids. Advances in Cryogenic Engineering 21, 273–277.
- Klimenko, V.V., 1981. Film boiling on a horizontal plate - new correlation. International Journal of Heat and Mass Transfer 24, 69–79.
- Liu, Y., Gao, X., Olewski, T., Vechot, L., Mannan, M.S., 2012. Modelling the vaporization of cryogenic liquid spilled on the ground considering different boiling phenomena, in: Symposium Series No. 157, Hazards XXIII. North West, UK.
- Liu, Y., Olewski, T., Vechot, L., Gao, X., Mannan, S., 2011. Modelling of a cryogenic liquid pool boiling using CFD code, in: 14th Annual Symposium, Mary Kay O'Connor Process Safety Center "Beyond Regulatory Compliance: Making Safety Second Nature". College Station, TX, USA, pp. 512–524.
- Opschoor, G., 1980. Spreading and evaporatoin of LNG spills and burning LNG spills on water. Journal of Hazardous Materials 3, 249–266.
- Webber, D.M., Gant, S.E., Ivings, M.J., Jagger, S.F., 2010. LNG source term models for hazard analysis: A review of the state-of-the-art and an approach to model assessment ( No. Research Report: RR789), HSE Books. Buxton, Derbyshire, UK.

Woodward, J.L., Pitblado, R., 2012. LNG Risk Based Safety - Modeling and Consequence Analysis. AIChE, John Wiley & Sons, Inc., Hoboken, NJ, USA; Published simultaneously in Canada.