



A review of data on spreading and vaporisation of cryogenic liquid spills

A.M. Thyer*

Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire SK17 9JN, UK

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Abstract

This review summarises the availability and utility of experimental data on the rates of spread and vaporisation of spillages of pressure liquefied and cryogenic liquids on a variety of surfaces including: soil; sand; concrete; and water. It is intended that the paper acts as a review of those sources of information that can be used to allow the validation of current and future computer software which is to be used to predict the likely effects of such spillages, and also to extend the range of materials to which it may be applied.

The majority of investigations found cover LNG or LPG, due to their widespread bulk usage, with others studying liquid nitrogen, oxygen, hydrogen, or ammonia.

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1. Introduction

Large quantities of so-called cryogenic liquids which may give off toxic/asphyxiating and/or flammable vapours are commonly stored, transported and used in industry. The Health and Safety Executive (HSE) must assess the resultant hazards as part of its assessment of COMAH safety reports and land use planning responsibilities. This it does by the application of predictive mathematical models. These models can range in complexity from simple experimentally derived correlations of vaporisation rate against the controlling parameters such as temperature and wind speed, to more physically based formulations of the important processes. Calculations based on numerical solution of the shallow layer equations or using computational fluid dynamics (CFD) also have potential applications to the calculation of spreading and vaporisation rates.

* Tel.: +44-114-2892060; fax +44-114-2892045.

E-mail address: aubrey.thyer@hsl.gov.uk (A.M. Thyer).

In the event of a spillage of a cryogenic liquid, the fluid spreads over the ground at a rate determined by a number of parameters, namely:

- the size and nature of the release, i.e. is it a fixed volume or a continuous release;
- the boiling point of the material and the degree of sub-cooling to which it is subjected;
- the thermal properties of the surface it is spilled upon;
- the roughness and porosity of the surface; and
- the presence of any retaining walls or dykes.

Detailed mathematical models are required to take account of these processes to model the effects reliably. However, the use of models is often limited since they have been validated only against a narrow range of materials or storage/release conditions. Good experimental data can extend the range of materials to which these models apply, and is also vital for the development of new, and the assessment of existing materials. It is the purpose of this review to critically comment on the ability of currently available information on the spread and vaporisation of cryogenic liquids to provide quality data for model development and validation.

2. Predictive models

2.1. Classes of theoretical model

The simplest models rely on the work of Sutton [1] and comprise simple formulae for mean vaporisation rate with power law dependencies on wind speed and pool size; typical of this type is that contained in the early computer code SPILL. Often these models contain correlations that are expressed in dimensional term, often raised to non-integer powers. Such correlations can only be regarded as valid over their range of derivation. Typically they disagree about the dependence of turbulent mass transfer on the molecular diffusivity of the vapour.

Secondly, there are methods involving numerical solutions of turbulent mass transfer equations using various theoretical models. These are potentially the most flexible methods but are expensive to apply. The model of Reijnhart et al. [2] would probably fall into this category. However, the utility of such models is not certain as spill progression will be influenced by both turbulent mass transfer and heat transfer from the ground, thus model validation would be required before use.

Of intermediate complexity are solutions, often analytically obtained, of the diffusion advection equation, by use of various approximations for turbulent diffusion and an approximate representation of the wind profile. The degree of complexity varies as the degree of approximation made about the turbulent diffusivity and other approximations involved to obtain a tractable solution. An example is Brighton [3].

In addition, more complex models simulating the combined effects of spreading, vaporisation, and the interaction with retaining walls or dykes are now becoming available. Currently, HSE is participating in the development of the computer programme Liquid Spill Modelling System (LSMS), developed by Cambridge Environmental Research Consultants in collaboration with British Gas, Gaz de France, the US Gas Research Institute, and HSE.

A further model, CONCRY, similar in concept to LSMS has been developed at Imperial College. This may have some of the abilities of LSMS. Like LSMS, it uses shallow layer equations and includes modifications to allow treatment of boiling liquids. Early reports suggest it was not entirely successful due to uncertainties in the rate of heat transfer from the ground, the volume of vapour produced, and the size and behaviour of bubbles of evaporated liquid. These issues were investigated in the work of Rochmadi [4] and Michels [5a], and have now reportedly been solved [5b].

2.2. The data requirement

The data required to validate these different classes of models can vary considerably. Thus, for the simplest models only a vaporisation rate, a single wind speed at a given reference height, the temperature, again at a reference height, and a pool size might suffice. This is because the influence of the other parameters or the effect of items such as the pool containment are not included.

However, for the more complex models such as LSMS, it might be required to provide both temperature and wind speed gradients, ground porosity, the dimensions of any retaining bunds and for cryogen spills, and the thermal characteristics of the ground, to fully specify the initial conditions required for a model to run. The pool temperature might also be a start parameter and could be used as a check on model accuracy alongside vapour concentration above the pool.

3. Summary of data on the spillage and vaporisation of cryogenic materials

A list of publications reporting data on the spillage or vaporisation of cryogenic materials is given in Table 1. This is broadly categorised by material type, spill location and scale. An indication is also given on the type of model for which the data may provide suitable input. For the sake of completeness, reference is also made to work by Advantica on large scale water spills. Whilst water behaves in a different manner to cryogens, the work serves as an additional source of data for non-boiling liquids [6].

One paper by Prince [7] was itself a review of cryogen spill experiments, citing 28 references. Whilst this is a useful review, some information therein is of limited use as items such as starting temperatures and wind speeds are sometimes omitted. These omissions may, however, be due to factors not being quoted in the original sources.

Inspection of Table 1 shows that whilst many experiments provide data suitable for validating simple models, few seem suitable for validating more complex models.

The available data is divided into broad categories and briefly discussed in the following sub-sections.

3.1. Vaporisation studies on typical dyke floor materials

A number of studies have been performed to investigate heat transfer from the ground to an overlying pool. The data reported varies in detail depending on whether the primary aim was the development and use of models, or the collection of experimental data.

Table 1
Summary of the applicability of data to model types, and type of chemical studied

Usable for simple models	Usable for complex models	Too lacking in detail for use	Chemical studied	Surface spill released upon	References
✓	✓		Review of cryogen spills	Variety of substrates	[7]
✓ (S)			LNG	Concrete, soil, etc.	[10]
✓ (S)			LNG	Soil	[11]
✓ (S–M)			Hydrogen and oxygen	Concrete and sand	[12]
✓ (S)			Methane, ethane and propane	Water	[13]
✓ (VL)	✓		LNG	Concrete, soil, steel	[15]
✓ (VL)	✓		LNG	Water	[16]
✓ (VL)	✓		LNG	On land of unspecified soil type	[17]
✓ (VL)	✓		Ammonia	Damp clay-like soil	[18]
✓			Propane and butane	Ice/water in calorimeter	[19]
		✓ (S)	LNG	Concrete	[20]
	✓ (S)		LNG	Soil, sand, concretes	[21]
✓ (S–M)			LNG	Insulating concrete	Koppers (Work quoted in Reid 1980, above)
✓ (VL)			LNG	Insulating concrete	Texas A&M University (Work quoted in Reid 1980, above)
	✓ (S, VL)		LNG and nitrogen	Water, ice, salt water	[22,23]
✓ (M)			Chlorine	Water	[24]
✓ (L)			LNG and nitrogen	Water	[25]
		✓ (S–M)	LNG	Water	[26]
		✓ (M)	Butane	Insulated concrete	[27]
✓ (M)			Oxygen and nitrogen	Laboratory study in Dewar	[28]
✓ (S)			Nitrogen, methane and ethane	Water	[29]
✓ (S)			Methane and LNG	Water	[30]
✓ (S–M)			LPG	Water	[31,33]
✓ (S–M)			Methane and nitrogen	Water	[32]
✓ (S–M)			Chlorine	Asphalt, concrete, gravel	[34]
(S)		✓	Methane	Corrugated Al sheet on soil	[35]
		✓	LNG	Soil?	[36]
✓ (VL)			LNG	Water	[37]
✓ (L–VL)			LNG	Water	[38]

✓	✓ (VL)	LNG	Sea water	[39]
✓ (S)		Nitrogen, methane and ethane	Water	[40]
	✓ (VL)	LPG	Sea water	[41]
✓ (VL)		LNG	Moist clay	[42]
✓? (VL)		LNG	Sand, soil	[43]
✓ (VL)		LNG	Bricks	[44]
(VL)		Water	Concrete	[6]

Key: S, small scale; M, medium scale; L, large scale; VL, very large scale.

Two studies falling into the former category are those of Dilwadi and Mudan [8] and Raj [9].

The most detailed experimental investigation is that of Reid [10], performed for the US Gas Research Institute. This extends earlier work of Drake and Reid [11]. The latter gives detailed information on both thermal properties of floor materials and vaporisation rates of LNG over a variety of substrates. The examples of floor materials investigated were:

- soil;
- sand;
- two types of insulating concrete;
- crushed rock;
- polyurethane; and
- corrugated aluminium sheet over soil.

It was found that results for soil and concrete could be correlated using a simple 1D heat-transfer conduction model with a boiling rate proportional to $t^{-1/2}$, and the effect of different substrates modelled by changing the proportionality constant.

It was noted that the rate of boil-off was about an order of magnitude less for insulated concretes than for sand or soil, and the rate for polyurethane about half that of an insulated concrete. In terms of decreasing vapour evolution, the results for corrugated aluminium sheet laid over soil were the most promising. The vapour evolution could be well predicted using a 1D modelling approach as the rate of vapour evolution was approximately linear for about an hour after the spill, once the initial rapid boiling stage was complete and the metal cooled.

Several tests performed by others were also discussed by Reid. The most significant were those of Koopers, and the Fire Fighting School at Texas A and M University (no references to this work are quoted in Reid's paper). The Koopers tests used a boil-off tray of Dycon concrete, thought to be similar to the K-35 composition containing 2–3 mm polystyrene beads.

3.2. Effects of ground porosity

Detailed reports on the effects of ground porosity appear limited despite its significance. The majority of investigations of spills on porous substrates appear to examine only heat conduction, with only a limited number measuring penetration rates. Drake and Reid [11] have measured the vaporisation rate of LNG on a variety of soil types and found that the rate was proportional to $t^{-1/2}$ regardless of ground conditions, and that changes in ground conditions could again be modelled by using a different proportionality constant. However, Takeno et al. [12] noted that the nature of vaporisation mechanisms would change with the cryogen, since liquid penetration and freezing of ground water depend on a large number of parameters including: density; viscosity; surface tension; and latent heat of vaporisation. In studies using liquid hydrogen, which boils at 20 K, both the water and air in interstices in the soil solidify, creating an effective barrier which the spilled fluid cannot penetrate. Where no ice barrier forms, for example with a dry medium and a higher boiling point cryogen such as liquid oxygen, they reported that the penetration velocity (V_L), and the heat flux

(q), may be expressed as the following:

$$q = \rho_s C_p \Delta T (1 - \varepsilon) V_L$$

where ρ_s , C_p , ΔT and ε_p represent the density and specific heat of sand, the difference between the initial temperature of the sand and the boiling point of the cryogen, and the void space ratio in the sand layer, respectively.

The relationship for wet media was found more complex due to the need to take account of the physical properties of water such as its freezing point, density, and latent heat, and also the position of the dynamic boundary between the frozen surface layer and the liquid sub-surface layer.

Using dry sand with a mean particle size of 0.4 mm and a void space ratio of 0.29–0.30 the penetration rate for liquid oxygen was found to be 1.35–1.41 mm s⁻¹. No penetration into the sand was observed for hydrogen, whether the sand was wet or dry.

3.3. Spills on water

Most spill tests on water have investigated the behaviour of LNG, LPG, methane or propane. Other gases studied include, ethane, pentane, nitrogen and chlorine.

Of the reports available, 10 were medium or large scale spills investigating both the rate of spread and evaporation, and 8 were laboratory studies investigating evaporation alone, using a water-filled Dewar or a spill channel.

A full listing of chemicals studied and workers is included in [Table 1](#), with further details being given in [Section 3.4](#), where the cryogen studied contained a mixture of components.

3.4. Spillage of multi-component cryogenic mixtures

The boiling rates of chemical spillages can be strongly influenced by the nature of the material involved, for example, whether it is a mixture or a pure substance. One of the most widely studied cryogenic mixtures is LNG, comprising primarily methane with up to 10% ethane and smaller quantities of nitrogen, propane, or other light hydrocarbons. The initial boiling point varies depending on composition, but is approximately 111 K at 1 bar. As the liquid gains heat progressive fractionation is observed, with the lower boiling fractions, such as nitrogen or methane evolving first, followed by those with higher boiling points. This leads to a dynamic situation with the composition and properties of the mixture varying with time.

The composition of vapour evolved from LNG spills on water has been measured by Valencia-Chevez and Reid [13]. Their data showed that the pool temperature remained relatively constant until the majority of the lowest boiling fraction in the LNG had volatilised, at which point the temperature rose sharply until the next highest boiling point was reached. It was also found that the boil-off rate and time to peak vaporisation rate for pure methane differed substantially from the values for a ternary mixture of methane, ethane, and propane (i.e. LNG). With increased contaminant concentration, the peak boil-off rate shifted to lower temperatures, and the rate of vapour evolution increased. Similar effects were also observed by Reid [10], when monitoring the rate of mass loss of a rich LNG spill containing 66.9%

methane, 22% ethane and 11.1% propane, on a 945 cm² section of an insulating concrete. He reported that vapour plumes from the spillages consisted of essentially pure methane, ethane or propane depending on the degree of weathering of the spill.

4. Conclusions

It is evident that there are only a limited number of experiments summarised here which are applicable for use in validating more complex codes. Of the 34 papers reviewed, 24 may be of use for validating simple codes, as these papers only provided a limited range of experimental detail and often lacked key features such as initial temperature. Further, as a number of experiments were performed at small scale under laboratory conditions, their relevance to real-life large spills is uncertain. It has been stated by Jones and McGugan [14], for example, that the minimum area required to enable a spill to be scaled up reliably to the dimensions of a realistic spill of tens of metres across is 1 m².

The major sources of quality data applicable for use in assessing the accuracy of model predictions on pool regression and vaporisation rates of cryogenics, are experiments by Moorhouse and Carpenter [15], Koopman et al. [16,17], Goldwire [18], Reid [19,20] and Burgess and co-workers [22–25] among others. Of these, four cover LNG spills, one ammonia [18], and one nitrogen [21]; only three were concerned with spills on solid surfaces, viz. damp soil; sand; and concrete. The most detailed work on spills on land was that performed for the US Gas Research Institute by Reid in 1980. This gives wide ranging information on both thermal properties of floor materials and boil-off rates of LNG on a variety of substrates.

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