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Pool boiling of hydrocarbon mixtures on water

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Abstract—Transient experiments with liquefied binary mixtures of methane–ethane and methane–propane boiling on water, show great differences in the boiling characteristics compared to pure methane. The high initial boil-off rates observed in some of the experiments, are believed to occur due to breakdown of film boiling while the water surface has a higher temperature than the superheat limit of the cryogenic liquid. The high initial boil-off rates were most profound in the methane-rich mixtures, comparable to commercial liquefied natural gas (LNG). These findings may have significance to the way heat transfer is implemented in the models describing rapid phase transitions (RPT) in the LNG–water system. © 1997 Elsevier Science Ltd.

INTRODUCTION

The boiling experiments described in this article, were part of a collaborative research programme between the companies Statoil, Gaz de France and British Gas, with the overall goal to address the potential hazards induced by rapid phase transitions (RPT) in the case of accidental spills of LNG into the sea.

An RPT, which can be interpreted as an "explosive evaporation", may occur in situations where two liquids come into contact, the one having a higher temperature than the boiling point of the other. Given the right circumstances, significant amounts of energy can be liberated by RPTs when LNG is spilled on water.

The earliest hypothesis to explain this phenomenon for the LNG–water system, related the occurrence of RPTs to the composition change during LNG boiling. Preferential evaporation of methane would bring the process from stable film boiling into the regime of transitional boiling, as the boiling point temperature increased. If direct contact between the aged LNG and the liquid water was established upon breakdown of film boiling, it was believed that a portion of the colder liquid would be heated to its superheat limit due to the lack of nucleation sites on the water surface, and explosively turn into vapour [1].

Porteous and Reid [2] established a criterion which said that the temperature of the water had to lie between 1.0 and 1.1 times the superheat limit of the cryogenic liquid if RPTs should occur simply by bringing the two liquids together. They also observed that RPTs were more violent in mixtures than in pure liquids.

The superheat limit temperature of hydrocarbon mixtures has been found to approximate the mole fraction average of the superheat limit temperatures of the pure components [3], and since LNG consists mainly of methane, RPTs should not occur in contact with water unless most of the methane content was already evaporated [4].

Another hypothesis formulated for fuel–coolant interactions, which is the term for RPT in a water–molten metal system, suggested that the reaction could be modelled analogous to a chemical detonation [5]. This model assumes that the two liquids exist in a premixed configuration, where one of the liquids is dispersed within the other as drops surrounded by vapour pockets. When a pressure pulse is applied to such a system, the relative motion between the species will induce fragmentation and increased heat transfer rate. The energy liberated by evaporation of the volatile liquid sustains the pressure pulse, and allows the phenomenon to propagate through the premixed areas.

The energetic RPTs which have been observed in the LNG–water system, were always localized to the areas where the two liquids were mixed, either by the action of breaking waves or in the discharge zone from liquid jets into the water [4]. There were also no indication that the LNG was particularly aged in these events, and thus these observations favour the last mentioned hypothesis.

The results presented in this study show that there are great differences in the boiling characteristics depending upon the cryogenic liquid composition, and that the heat transfer mechanism between water and LNG should be taken into account when developing the RPT models further.

FILM BOILING ON REAL SURFACES

The traditional correlations describing the film boiling regime are established for systems of pure, saturated liquids boiling in contact with metal objects. Implicitly these models assume the absence of tem-

NOMENCLATURE

$\overline{\Delta C}$	dimensionless concentration difference
$\tilde{c}_p$	specific heat
$\tilde{h}$	enthalpy
$\tilde{h}_{lg}$	enthalpy of evaporation
N	molar amount of liquid
$\dot{N}$	molar boil-off rate
p	pressure
$\dot{Q}$	heat
T	temperature
ΔT	temperature difference
t	time
$\tilde{x}$	molar concentration in liquid
$\tilde{y}$	molar concentration in vapour.

Greek symbols

τ_{cf}	time constant
ζ	damping ratio
ω_0	natural frequency.

Subscripts

i, j	component number
f	freezing
l	liquid
v	vapour
sat	saturation
surf	surface.

perature gradients, both within the liquid phase and along the heated surface. These correlations are thus not necessarily applicable to cryogenic hydrocarbon mixtures boiling on a water surface.

Two generally different hypothesis exist to predict the point for breakdown of stable film boiling on a horizontal surface. The widest one used is attributed to Berenson [6], and predicts the lowest temperature difference which produces a vapour flux sufficient to maintain a continuous film. The vapour production is dependent on the heat flux, and so this hypothesis is said to be heat flux controlled [7], and it defines a lower temperature limit required to suspend the liquid, and prevent it from touching the hot surface.

The other hypothesis, attributed to Spiegler *et al.* [8], simply states that the surface temperature upon breakdown of film boiling corresponds to the superheat limit temperature of the boiling liquid. This hypothesis is said to be temperature controlled, and it defines an upper temperature limit for which physical contact between the liquid and the hot surface is possible.

In their basic form these hypothesis consider the hot surface as being isothermal, implicitly assuming a surface material with infinite thermal diffusivity. For a real surface material, temperature gradients along the surface may be set up by the oscillating vapour–liquid interface, leading to local spots where wetting of the surface occurs. This transient wetting, followed by evaporation, will lead to increased heat transfer in the film boiling regime, especially in the vicinity of the minimum point of film boiling. The minimum point itself will be shifted towards a higher temperature difference.

Henry [9] and Baumeister *et al.* [10] proposed correlations for the minimum temperature of film boiling based upon the heat-flux controlled and the temperature controlled hypothesis, respectively, taking account for the physical properties of the hot surface. For surface materials having the same physical properties as ice, both correlations predict a significant increase in the minimum temperature of film boiling compared to an ideal surface (see Table 1).

FILM BOILING IN BINARY MIXTURES

For stable film boiling in binary mixtures, Yue and Weber [11] have predicted an increased heat transfer coefficient, compared to a pure liquid of similar physical properties, by the solution of the set of free convection boundary layer equations for a vertical geometry.

The explanation for this increased heat transfer coefficient is that mass transfer by diffusion creates an extra resistance towards the mass flux, and leads to a lower evaporation rate at the vapour–liquid interface. The lower evaporation rate gives a thinner vapour film, and at the same time the higher local temperature at the vapour–liquid interface allows the heat not consumed by the evaporation to be convected into the liquid as sensible heat.

Experimental studies by the same authors [12] show that the minimum temperature difference in film boiling is shifted towards a higher value for binary mixtures, compared to a similar pure liquid. They also correlate the minimum temperature with the dimensionless concentration difference, $\overline{\Delta C}$, which is the ratio of the equilibrium concentration difference between liquid and vapour at a particular bulk concentration to the maximum concentration difference for that system. The basis for this correlation is the heat flux controlled hypothesis of Berenson.

The Leidenfrost temperature for binary liquid mixtures, which is the minimum surface temperature for film boiling of discrete drops, has been shown by Godleski and Bell to approximate the mole fraction average between the Leidenfrost temperatures of the pure components [13]. This is in accordance with the temperature controlled hypothesis, as the superheat limit temperature of mixtures also has been shown to approximate the mole fraction average between the pure component values [3].

Table 1. Minimum surface temperature for film boiling as predicted from correlations in the literature

System	Heat-flux controlled hypothesis	Temperature controlled hypothesis
Methane—ideal surface	(Berenson) -102°C	(Spiegler *et al.*) -113°C
Methane—surface with physical properties of ice	(Henry) -63°C	(Baumeister *et al.*) -48°C
Methane–ethane mixture—ideal surface	(Yue and Weber)	(Godleski and Bell)
$\tilde{x} = 0.016$	-25°C	-16°C
$\tilde{x} = 0.49$	-53°C	-56°C
$\tilde{x} = 0.94$	-90°C	-96°C
Methane–propane mixture—ideal surface		
$\tilde{x} = 0.36$	-10°C	-19°C
$\tilde{x} = 0.73$	-59°C	-67°C
$\tilde{x} = 0.97$	-86°C	-97°C

For methane–ethane and methane–propane mixtures the two correlations correspond reasonably well, although the temperature controlled hypothesis predicts the lowest surface temperature in most cases (see Table 1).

PREVIOUS WORK

Previous experimental work, studying cryogenic liquids boiling on water has concluded that pure liquids, like methane and nitrogen, are in the film boiling regime at the temperature differences present (180–220 K), with corresponding low heat fluxes. When spilling mixtures and cryogens with higher boiling points, like ethane and propane, the water surface freezes rapidly, with nucleate boiling as the result [14].

Assuming the presence of an ice layer at all times, Valencia-Chávez *et al.* [15] predicted the transient boil-off rates for binary and ternary hydrocarbon mixtures on water by a heat transfer model which coupled the conduction through a growing ice shield (Stefan problem) with an ageing calculation for the boiling liquid mixture.

The authors attribute the rapid formation of an ice layer on the water surface to mixture effects in film boiling. It is supposed that film boiling occurs initially, but due to the large differences in volatility between methane and the heavier components present, the vapour flowing into a bubble will consist essentially of pure methane. Thus, the liquid from which the vapour is emanating will be enriched in heavier components. As the mass diffusivity of the various components in a liquid mixture is much smaller than the thermal diffusivity, it is suggested that there will be no significant temperature gradient in the liquid, and that the methane depleted liquid will be brought into a subcooled state, which lowers the vapour pressure and shuts off the evaporation. The result will be vapour film collapse in the area beneath the departing bubbles. This will again lead to rapid solidification of the water, and onset of transitional boiling.

Aziz *et al.* [16] identified a boiling regime very different from film boiling during quenching experiments with nickel plated copper spheres in water. For water subcoolings below approximately 20 K, film boiling was absent for high surface temperatures. Instead an apparently small amount of vapour was emitted in the form of very small bubbles. The rate of heat transfer in this "microbubble regime" exceeded the stable film boiling heat flux by an order of magnitude. The surface temperature during this regime is given to be between 430 and 540°C, and that is significantly higher than the superheat limit temperature for water at 1 atmosphere (320°C).

EXPERIMENTAL

Observation of the boiling phenomena was carried out in a boiling cell shown in Fig. 1. The inner walls were made from 25 μm mylar sheets to minimize the thermal bridge between the water and the cryogen, and thus minimize the edge effects. Partly filled with water, the surface area for heat transfer was 200 cm^2. The boiling cell was placed on an electronic balance to measure the boil-off.

The construction was open to the atmosphere, and the material of the outer wall and bottom (acryl plastic) was transparent, which allowed some degree of visual observation of the boiling process.

The boiling cell was equipped with 3 thermcouples, one positioned to measure the temperature of the boiling liquid, one in the vapour, and one in the water just below the surface.

A spreading device, which consisted of a cone inside a tube, served the purpose of directing the cryogenic liquids so it would pour down along the inner wall of the cell. As the spreading device was supported independently of the cell, it damped the fall of the cryogenic liquid, so that the time it took for the liquid to settle on the water surface became of the same order of magnitude as the transient part of the balance's step response (see the Appendix). The spreading device also served as support for the thermocouples in the cryogenic liquid and vapour.

An experiment was performed by first filling the cell with approximately 3 l of water of the desired

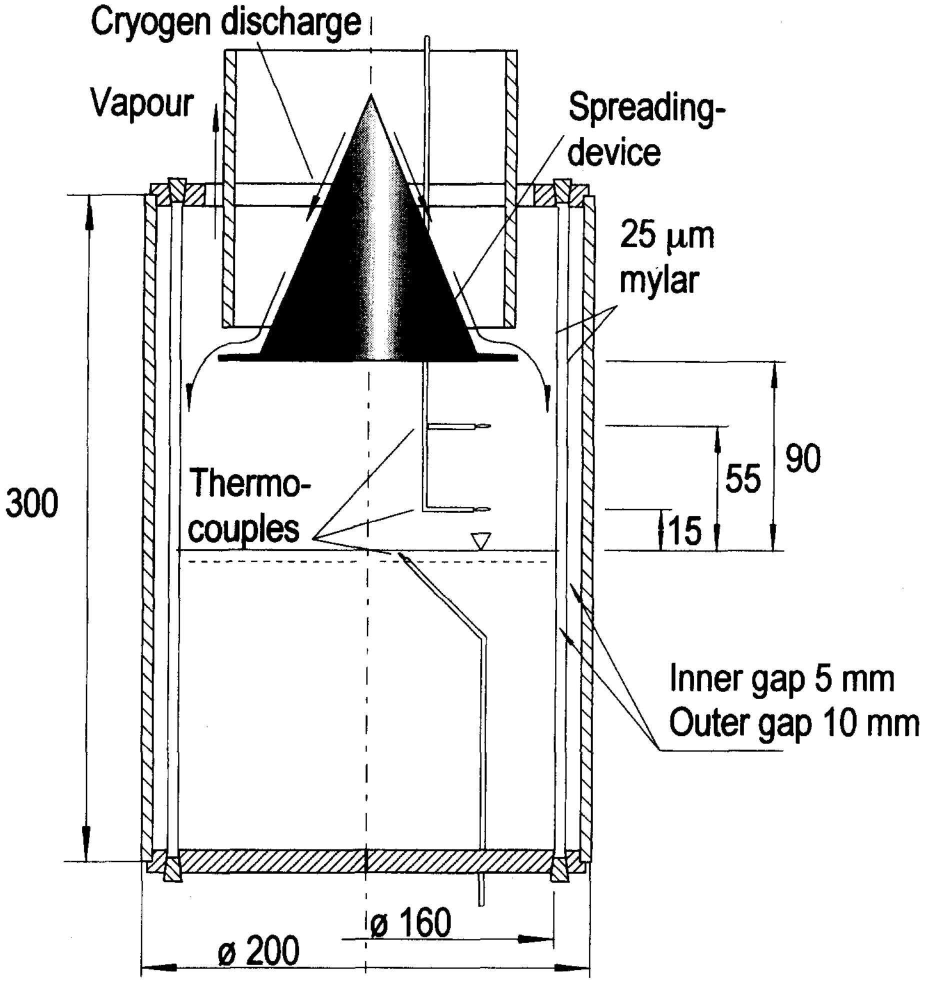

Fig. 1. Boiling cell.

temperature. For the experiments covered in this study, the water temperature was varied at the two levels 25 and 40°C. A sample containing approximately 600 cm^3 of liquefied hydrocarbon of predetermined composition was then poured onto the water surface, via the spreading device. Mass and thermocouple signals were recorded simultaneously at intervals of 0.096 s.

The liquid samples consisted of pure methane and binary mixtures of methane–ethane and methane–propane. The mixtures were prepared by weighing the pure components into an evacuated container in the gas phase. The gas was then condensed to liquid with a Philips cryogenerator.

To calculate the boil-off rate (in g/s), points in the mass signal were first interpolated by a third degree polynomial. These points were chosen at different time intervals, or stages, of each run. Then the average boil-off rate within the time interval was derived by differentiating the interpolating function.

By applying a control volume analysis for the boiling liquid layer, the heat flow was derived by coupling the first law of thermodynamics to an ageing calculation for the liquid:

$$\dot{Q} = \dot{N}\left[\tilde{h}_v - \sum_{i=1}^{nc} \tilde{y}_i \left(\frac{\partial(N\cdot\tilde{h}_l)}{\partial N_i}\right)_{p,T,\tilde{x}_{j\neq 1}}\right] + N\cdot\tilde{c}_{pl}\cdot\frac{\mathrm{d}T_l}{\mathrm{d}t} \tag{1}$$

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} = \frac{\mathrm{d}(N\cdot\tilde{x}_i)}{\mathrm{d}t} = -\dot{N}\tilde{y}_i \tag{2}$$

$\dot{N}$ is the measured boil-off rate in mole/s. The thermodynamic calculations were implemented by a program library package using the SRK equation of state, implying the assumption that the vapour and liquid always were in phase equilibrium. This assumption has previously been found valid by experiments by Valencia-Chávez *et al.* [15].

For the pure liquid methane experiments, the equations are reduced to:

$$\dot{Q} = \dot{N}(\tilde{h}_v - \tilde{h}_l) = \dot{N}\tilde{h}_{lg}. \tag{3}$$

Immediately before an experiment was run, a small amount of the liquid mixture was withdrawn by a cannula and allowed to evaporate into an evacuated cylinder. These samples were later analyzed by gas chromatography, and together with the total mass spilled, derived from the balance signal, the analysis result provided the necessary initial values of N and $\bar{x}_i$ to carry out a numerical solution of eqns (1) and (2). Further details are given in ref. [17].

It is natural to compare the current results with those reported by Valencia-Chávez [15, 18]. These experiments were quite similar to the current experiments, but two differences in the experimental procedures must be taken into account.

First, the spreading device used by Valencia-Chávez was constructed to deposit the cryogen as gentle as possible at the centre of the cell, while in the current experiments the cryogen was poured down along the cell wall.

Second, the water temperatures for otherwise comparable runs were lower, ranging between 11 and 24°C, while in the current experiments the water temperature was either 25 or 40°C.

RESULTS

Figure 2 shows the boil-off curves for one of the runs with virtually pure liquid methane (LCH18) and one of the runs with a liquid mixture, initially containing 97% (by mole) methane, 1.7% propane, 0.4% O_2 and 0.9% N_2 (LNG13). The liquid density and normal boiling point temperature of this mixture is practically identical to pure liquid methane (425 kg/m^3 and −162°C), and the amount spilled and the initial water temperature were also virtually the same for these two runs (320 g and 40°C).

All the boil-off curves from the pure liquid methane runs had a similar shape as LCH18, a few of them are shown in Fig. 3. The curves from the mixture runs had certain qualitative features in common, shown in Fig. 4 for methane–ethane runs, and in Fig. 5 for methane–propane runs. These features may also be described by the example given in Fig. 6, which shows the boil-off curve together with the liquid temperature for one of the runs. The liquid used in this run (LNG16) consisted of 83.5% methane, 15.4% ethane and about 0.4% O_2 and 0.7% N_2 initially.

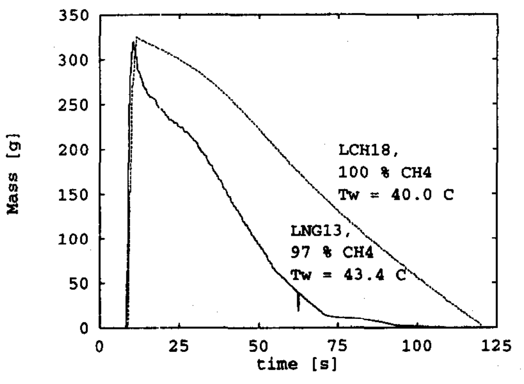

Fig. 2. Boil-off curves for a methane–propane mixture compared to pure methane.

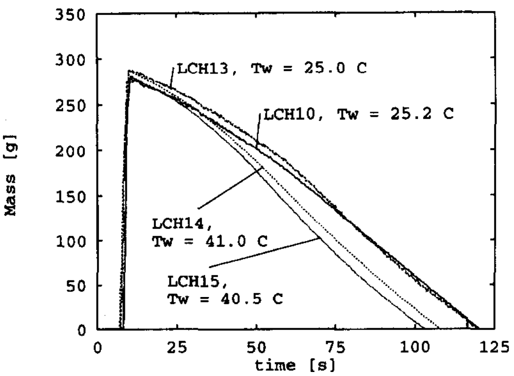

Fig. 3. Boil-off curves for pure methane.

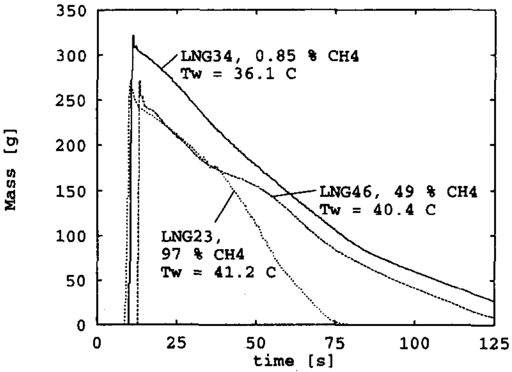

Fig. 4. Boil-off curves for methane–ethane mixtures of various composition.

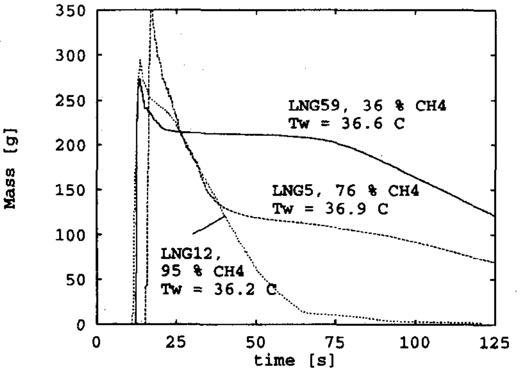

Fig. 5. Boil-off curves for methane–propane mixtures of various composition.

The curves can be divided into three stages, or time intervals:

(1) Initial stage, lasting in this case for about 3 s after completion of the spill (the completion of a spill is defined where the balance reads the highest value). The curve is very steep here, and the boil-off rate often shows values about 10 times higher than for pure methane.
(2) Intermediate stage, lasting for about 40 s in this case, which begins with a marked decrease in the boil-off rate. Then follows an acceleration

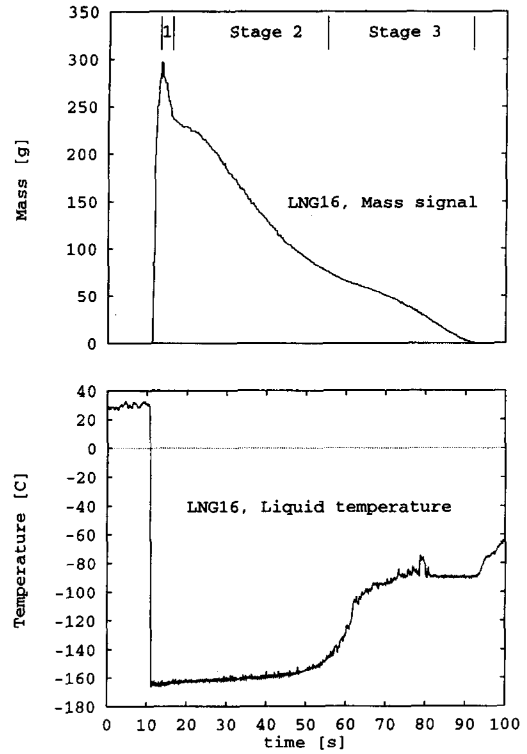

Fig. 6. Boil-off curve and liquid temperature for a methane–ethane mixture. Initial methane content was 83.5%, initial water temperature 39.9°C.

towards a relatively large and almost linear boil-off.

(3) The transition between stage 2 and 3 is characterized by a jump in the liquid temperature to the normal boiling point of the second component, as the methane becomes exhausted. The boil-off rate decreases when this happens, as some of the transferred heat is required to raise the temperature.

For the methane–ethane mixtures, Fig. 4, the initial composition was varied over the entire range from pure methane to virtually pure ethane, and for runs with low methane content, the first and second stages became of shorter duration, and were virtually degraded to zero duration for pure ethane.

For the methane–propane mixtures, Fig. 5, the composition was varied from pure methane down to 36% methane. For all these runs, there was always an initial period where the boil-off rate was high. The third stage was prolonged and exhibited very low boil-off rates for the mixtures with the lowest methane content.

Figure 7 shows the heat fluxes [kW/m^2] derived from the initial stage of the mixture runs. The corresponding values from the pure methane runs are also shown, gathered at $\bar{x} = 1$. The theoretical values for the critical heat flux (244 kW/m^2) [19], and the film boiling heat flux for $\Delta T = 200$ K for methane (44 kW/m^2) [20], are indicated in the figure.

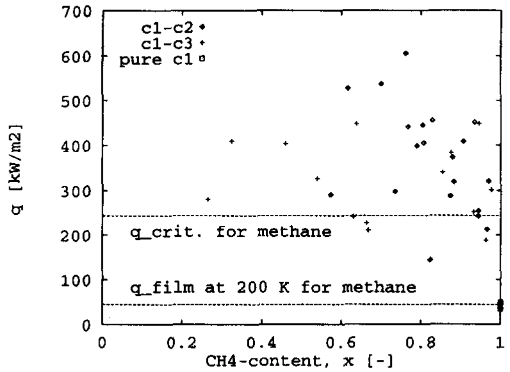

Fig. 7. Heat fluxes derived from the early stage of the runs.

As can be seen, the majority of the values derived from the mixture runs are significantly in excess of the theoretical value for the critical heat flux for methane. For the pure methane runs, the values agree with the correlation for film boiling.

The heat transfer model for the water–ice surface with a boiling cryogenic mixture on top described by Valencia-Chávez *et al.* [15], was tested for the present experiments. In the current implementation, the model calculates the boil-off from the heat flow by a scheme similar to eqns (1) and (2). The heat flow is derived from assuming conduction heat transfer through both the water and ice shield, which grows in thickness with time. The surface temperature of the ice is determined as a function of the equilibrium temperature of the cryogen, T_{sat}:

$$T_{surf} = \begin{cases} \frac{t}{\tau_{cf}}(T_{sat} - T_f) & t < \tau_{cf} \\ (T_{sat} - T_f) & t > \tau_{cf} \end{cases} \qquad (4)$$

τ_{cf} is a time constant tuned for each simulated case.

When testing the model for the current measurements, it predicted the boil-off curves fairly well when the simulations were started at the beginning of stage 2. Two of the runs are shown in Fig. 8, compared with the simulated results.

The model increasingly underpredicted the amount boiled off at later times of a run, and this is believed to arise from additional heat transfer from the surroundings through the side walls of the cell, due to poor steady-state thermal insulation.

DISCUSSION

Pure methane

The numerical values of the derived heat flux from early times of the pure methane runs correspond with Sciance's correlation for stable film boiling [20]. Stable film boiling is thus believed to be the situation for pure methane on water, and also to be sufficiently far from the point of breakdown of film boiling, that the thermal properties of the hot surface plays an insignificant role for the heat transfer.

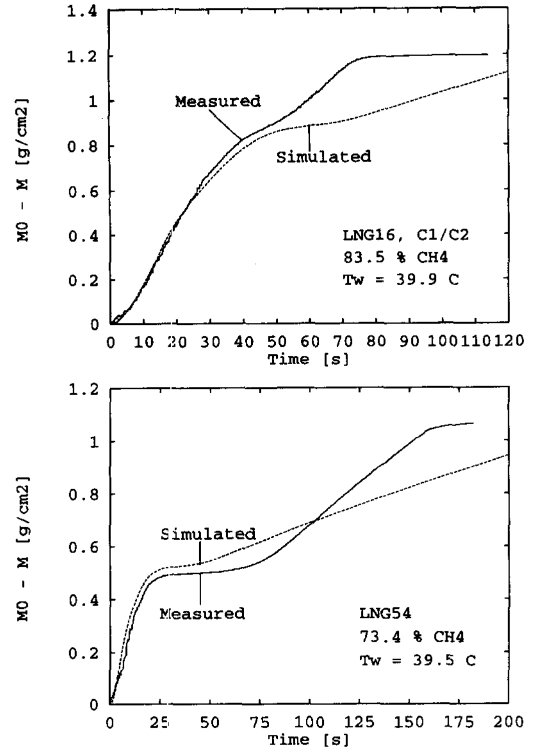

Fig. 8. Comparison between measured and simulated boil-off for one methane–ethane run (upper graph) and one methane–propane run (lower graph).

Mixtures

As the heat transfer model of Valencia-Chávez *et al.* [15] assumes the presence of an ice shield at all times, it is deduced that the transition between stage 1 and 2, where this can be distinguished, marks the time where the water surface is frozen. The high initial boil-off rates observed in many of the runs are, therefore, believed to be connected to the presence of liquid water.

The traces of O_2 and N_2 revealed by the gas chromatography analysis, are believed to originate from the atmosphere, as the cryogenic liquids were directly exposed to air. It seems likely that these contaminants also are present in the pure liquid methane samples, although no analysis were carried out for these liquids to confirm this. Thus, the main difference between the two runs shown in Fig. 2 is the relatively small amount of propane, leading to the intuition that the high initial boil-off rates also are connected to the presence of heavier components.

The mixture effect suggested by Yue and Weber's simulations [11], that the depletion of the volatile component at the vapour–liquid interface leads to a higher temperature, should increase with the mixture's relative volatility. They consider a relative volatility of around 80 as high, and so this effect should be pronounced for the current mixtures. The relative volatility for the methane–ethane system ranges in the order from 50 to 600, and for the methane–propane system in the order from 50,000–90,000 when calculated from the SRK equation of state. Furthermore, this effect should be largest for the mixtures with high bulk concentration of the volatile component, as the maximum difference in concentration between the interface and the bulk may be larger for these mixtures.

The convection of heat into the liquid due to the temperature difference between the vapour–liquid interface and the bulk liquid will be an effect which is also present for film boiling in a subcooled liquid. In a mixture this temperature difference occurs as a result of the altered liquid properties close to the vapour–liquid interface through the changes in local concentration. In a subcooled liquid the temperature difference is set up because the liquid must be heated to its boiling point temperature before evaporation takes place. It thus seems relevant to view the high initial boil-off rates observed in the current results in light of the observations by Aziz *et al.* [16] for subcooled water. No physical explanation for the observed microbubble regime was explicitly given, but it may be deduced from the photographs shown, that the vapour production rate around the sphere is low, probably too low to support a continuous vapour film. Thus a significant amount of heat must be convected into the liquid instead of being removed by the departing vapour. The surface temperature is probably below the lower temperature limit for a supporting vapour film given by the heat-flux controlled hypothesis, at the same time as the upper temperature limit for physical contact, i.e. the superheat limit temperature of water, is exceeded.

The following explanation is suggested for the high initial boil-off rates observed in the current experiments. The initially high temperature difference causes film boiling to be the intrinsic mode of heat transfer. The preferential evaporation of methane at the vapour–liquid interface causes the liquid in the close vicinity of the interface to attain a higher saturation temperature than the bulk liquid. Whether this causes the actual temperature to increase at the interface as suggested by Yue and Weber for a vertical surface, or the liquid to become subcooled at the interface as suggested by Valencia-Chávez for a horizontal surface, the result will be a decreased vapour production. The film will break down according to the heat-flux controlled hypothesis, which defines a lower temperature limit to maintain a supporting vapour film. Should this lower temperature limit exceed the superheat limit temperature of the liquid falling in on the water surface, physical contact is prohibited, and either the water surface must freeze, initiating nucleate boiling on the ice crust, or vapour must be formed from the liquid close to the vapour–liquid interface. The action of discharging the cryogenic liquids onto the water surface, which made the liquids pour down the inner wall of the boiling cell, will create a certain mixing of the fluids at the wall early in the runs. It is believed that this mixing stirs up convection currents in the water, which prevents the water from freezing the first few seconds, and thus maintains a high surface temperature.

For the methane rich mixtures, the ability to form a concentration boundary layer close to the vapour–liquid interface will be large, according to Yue and Weber [11]. For these mixtures also the bulk superheat limit temperature is low, according to Porteous and Blander [3], making the probability larger for these mixtures that the surface temperature is below the lower limit for vapour support while the upper limit for contact is exceeded.

It might be speculated that the effect of pouring the liquid down along the walls of the cell could contribute to the high initial boil-off rates, but since these high rates are absent in all the runs with pure liquid methane, this may not be the sole reason. It is however likely that the convection initiated by pouring is a necessary condition to create the situation with high boil-off rates, as the results from Valencia-Chávez [15, 18] showed no such characteristics. In those runs, the deposition of the cryogen was more gentle, and the water temperatures lower, leading to rapid freezing of the water surface.

In relation to RPT in the LNG–water system, the results indicate significant differences in the heat transfer mechanism between hydrocarbon mixtures and pure methane when boiling on water. Furthermore, these differences are most pronounced for methane rich mixtures, which are more comparable to commercial LNG than those *a priori* known to undergo spontaneous RPTs in contact with water. The more intimate contact mode suggested between a cryogenic mixture and water, compared to a pure cryogenic liquid, might have significance to the way heat transfer is implemented in the RPT models.

CONCLUSIONS

The most significant conclusions from this study are:

- Pure methane poured onto water is in the stable film boiling regime.
- Methane rich binary mixtures exhibit large initial boil-off rates when poured onto water, which translated into heat flux give values in excess of the critical heat flux for methane. These large boil-off rates are present as long as the water surface is liquid, and at later times the boil-off can be predicted by a heat transfer model assuming a growing ice shield.
- Pure ethane and ethane rich mixtures are in the transitional boiling regime when poured onto water, with an almost instantly solidification of the water surface as the consequence.
- The high initial boil-off rates observed for the methane rich mixtures, occur due to the higher heat flux. This is caused by the more intimate contact mode created by the unstable situation as the surface temperature is below the lower temperature limit to maintain a continuous vapour film, while the upper limit to allow physical contact is exceeded. Convection in the water, stirred up during pouring, maintains a high temperature difference for a few seconds. For gentle spills the high heat flux will lead to rapid freezing of the water instead of a high boil-off rate.

This suggests that the breakdown of film boiling for mixtures on water occurs at temperature differences comparable to those present initially in the experiments (180–200 K). The default assumption that LNG spilled on water will be in film boiling is hereby questioned.

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APPENDIX

To test the dynamic response of the electronic balance, some tests were carried out in which an object (weight approximately 325 g) was placed on the balance, and the transient output recorded. A typical output is shown in Fig. A1. The shape of the curve shows that the response is of second-order, and underdamped. The natural frequency, ω_0, and the damping ratio, ζ, were estimated to

$$\omega_0 = 7.0\ \text{Hz}$$

$$\zeta = 0.5$$

by "eye-fitting" the second-order response equation.

As can be seen from Fig. A1, the output signal is stable after 1.5 s, which is about the time it took to spill a sample of cryogen onto the water.

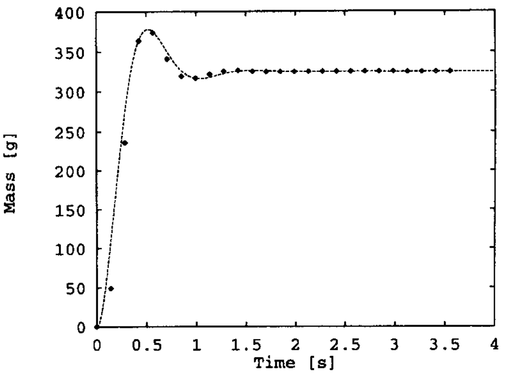

Fig. A1. Step response of electronic balance together with fit of second-order response equation (dotted line).