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Predicting triggering and consequence of delayed LNG RPT

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ABSTRACT

We develop a model for delayed rapid phase transition (RPT) in LNG spills based on thermodynamics and nucleation theory which includes predictions of both triggering and vapor explosion consequence. We discover that the model predictions can be accurately characterized by two independent parameters alone: The initial fraction of methane and the molar mass of the remaining non-methane part. Based on this we develop correlations for risk assessment which may be used without access to the underlying advanced algorithms, and we give practical advice for risk mitigation. The model is consistent with an often reported empirical triggering criterion for cryogen RPT. We show that spilled LNG must typically boil down to about 10–20% of the original amount before RPT may occur, and after triggering one may expect energy yields of 10–20 g TNT per kg of triggered LNG. Explosive pressures in the range 20–60 bar can be expected.

1. Introduction

Natural gas is a common fossil fuel mainly consisting of methane (CH_4) and with progressively smaller amounts of the heavier alkanes ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), etc. Some nitrogen may also be present. For the purposes of ship transport it is commonly cooled to form liquefied natural gas (LNG), a cryogen at about − 162°C. This is the hazardous material considered in this work.

In the LNG safety literature of the last couple of decades, the phenomenon called rapid phase transition (RPT) (Reid, 1983) is typically listed among the main concerns. This can range from giving it significant attention (Luketa-Hanlin, 2006; Shaw et al., 2005; Pitblado and Woodward, 2011; Cleaver et al., 2007), to little more than noting it as a concern (Alderman, 2005; Hightower et al., 2005; Havens and Spicer, 2007; Raj and Bowdoin, 2010; Forte and Ruf, 2017). The present work concerns the risk of RPT when LNG is spilled onto water, which is a possibility in maritime LNG operations, either during production, transportation, or usage. In such a spill, LNG will spread in a pool on the water surface while gradually boiling off, often without incident. However, in some cases it is observed to suddenly, and seemingly at random, explosively vaporize in large quantities at once. This is an RPT event, whose peak pressures and released mechanical energy can be large enough to displace and damage heavy equipment (Luketa-Hanlin, 2006; Pitblado and Woodward, 2011; Forte and Ruf, 2017) and could theoretically cause secondary structural damage and cascading containment failure (Havens and Spicer, 2007). Note that this is not an explosion in the common sense of the word, i.e. it does not involve combustion or other chemical reactions. It is what is sometimes called a vapor explosion or a physical explosion.

LNG has been transported in carriers at sea for roughly 50 years and is commonly stated to have an excellent safety record (Alderman, 2005; Forte and Ruf, 2017). However, there are still good reasons to address the issue of RPT risk: First, there is a record of actual unintended (though small scale) RPT-related incidents in the industry (Nédelka et al., 2003). Second, small accidents or near-accidents are not necessarily in the public record, so the risks may be higher than they appear to be. Third, the offshore activities of the LNG industry are growing more diverse. The use of LNG as a marine fuel is projected to increase significantly, which will lead to more small-scale bunkering operations. The industry is also moving towards increased use of floating facilities for production, storage, offloading and regasification (FPSO/FSRU) in order to make remote gas fields economically feasible (see emerging FLNG vessels). These developments introduce additional scenarios for LNG leakage, as well as potentially more severe consequences due to the addition of passengers, workers and more sensitive equipment. Such operations may not necessarily inherit the good safety record of the established LNG carrier operations. Overall, in the interest of preserving the excellent safety record of the industry, no significant theoretical risk should remain poorly understood.

Several research programs have been dedicated partly or fully to the subject of LNG RPT in the last few decades. The results and lessons from these projects have been thoroughly reviewed in the past (Cleaver et al., 1998; Nédelka et al., 2003; Luketa-Hanlin, 2006; Koopman and Ermak, 2007; Melhem et al., 2006). In parallel to this research, the RPT

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phenomenon has also received considerable attention in the context of fuel–coolant interactions in the nuclear power industry (Fletcher and Theofanous, 1994; Berthoud, 2000), which shares many of the same features. Overall, due to the small spatial scales (film boiling), small temporal scales (rapid nucleation) and poor reproducibility, exact quantification of LNG RPT risk and consequence has so far been elusive.

Models for RPT usually fall into one of two categories: Triggering prediction or consequence prediction. The former is concerned with then “if, when and where“ of RPT, while the latter is concerned with the resulting energy yield and pressure peaks given that RPT does occur. LNG RPT triggering prediction have mostly been in the form of empirically based relationships between water temperature and thermodynamic properties of the LNG such as the superheat limit (Reid, 1983). Some more sophisticated methods have appeared in recent years (Melhem et al., 2006), based on gradual compositional change, but the details of the triggering criteria are not always clear. RPT consequence prediction is somewhat more mature. Thermodynamic methods to estimate the explosive yield of vapor explosions first appeared in the 1960s, in the context of nuclear fuel–coolant interactions. This is commonly referred to as the Hicks and Menzies (1965) method (Cleaver et al., 1998; Berthoud, 2000), and uses an idealized thermodynamic path of equilibration and isentropic expansion. While these methods may be applied directly to immediate RPT, that is not the case for delayed RPT due to the unknown LNG composition at the time of triggering.

Overall, the practical assessment of risk and consequence from a given LNG spill seems to still be unsettled, mostly due to the lack of reliable triggering prediction. A report made for the US Federal Energy Regulatory Commission in 2004 concluded that there was no satisfactory theoretical method for practical risk assessment of RPT in the case of LNG carriers (ABS Consulting, 2004). Still, a quite clear qualitative consensus has emerged in the literature regarding the mechanisms behind the RPT process:

1. Initially, after LNG spills on water, film boiling occurs. Since the heat transfer rate is limited, all the heat is spent on evaporation and the LNG stays in its quasi-equilibrium state while boiling (at the bubble point).
2. For some reason, film boiling collapse occurs, which suddenly increases the heat transfer rate by orders of magnitude. We call this the *triggering event*.
3. The sudden and large increase in heat transfer rate causes the liquid to superheat and then rapidly evaporate.
4. Since the vapor takes over 200 times as much space as the liquid, and the evaporation is so rapid, the event seems explosive in nature.

There is an established distinction in the literature between *early RPT* and *delayed RPT* in large scale LNG spills (Hightower et al., 2004; Luketa-Hanlin, 2006; Koopman and Ermak, 2007; Bubbico and Salzano, 2009). Early RPT triggers at the chaotic spill point at any time during the spill, while delayed RPT occurs in the outer parts of the spreading pool after considerable time has passed.

In the present work we concern ourselves with delayed RPT, whose probability appears to depend strongly on the composition of the LNG. While it has been shown that RPT will not occur with pure methane (Enger et al., 1973; Porteous and Reid, 1976), they may occur with low-methane mixtures or with high-methane LNG mixtures who have had time to lose significant methane through boil-off (Luketa-Hanlin, 2006; Koopman and Ermak, 2007; Cleaver et al., 2007, 1998). In fact, it has been shown that usually a methane molar fraction below about 40% is necessary to make LNG-like mixtures experience RPT (Enger et al., 1973). This is much lower than the typical initial fraction of 90%, thus explaining the boil-off time necessary for delayed RPT. As we will show, the composition is important because it changes important parameters such as the Leidenfrost point (minimum temperature of film boiling) and the liquid superheat limit.

The focus of this work is to predict the risk and consequence of delayed RPT when spilling LNG on water. Underpinning this model are the following common hypotheses or assumptions regarding its mechanisms:

- The RPT event occurs if and only if the LNG is superheated to its superheat limit.
- Considerable superheating is only possible after film boiling collapse because it enables direct LNG–water contact.
- Film boiling collapse occurs due to the LNG's Leidenfrost temperature reaching the water temperature.
- The Leidenfrost temperature for saturated liquid-liquid film boiling depends only on the composition of the boiling fluid.

While it may be worth questioning these assumptions, that is outside the scope of this work. In this work, we take them at face value and follow them to their conclusions through the use of thermodynamic modelling and nucleation theory. Specifically, the assumptions lead to the following RPT triggering criterion,

$$T_{\mathrm{SHL}} < T_{\mathrm{w}} < T_{\mathrm{leid}}, \tag{1}$$

where T_{w} is the water temperature, T_{SHL} is the LNG superheat limit, and T_{leid} is the LNG Leidenfrost temperature. Here, we consider T_{w} to be constant and equal to the freezing temperature of water, since the water is cooled by the LNG but rarely forms ice (Luketa-Hanlin, 2006). The variables are T_{SHL} and T_{leid}, which both increase as methane is removed from the mixture during boil-off. The right hand side inequality in Eq. (1) expresses that film boiling collapse is necessary to superheat the LNG. The left hand side in equality in Eq. (1) expresses that the water must be hot enough to heat the LNG to the superheat limit.

Note that the distinction between delayed and early RPT lies in the last two assumptions listed above. In the present work *delayed* RPTs are defined as RPTs that are triggered due to purely thermodynamic changes leading to Eq. (1) being satisfied. Given this, delayed RPTs may occur in a completely undisturbed LNG pool on top of water. Any RPT events that occur before Eq. (1) is satisfied, such as due to external flow disturbances, are by the present definition *early* RPTs.

The theorized delayed RPT triggering event is illustrated in Fig. 1, which shows how we effectively move to the left along the boiling curve as methane boils off from the LNG mixture, eventually passing from

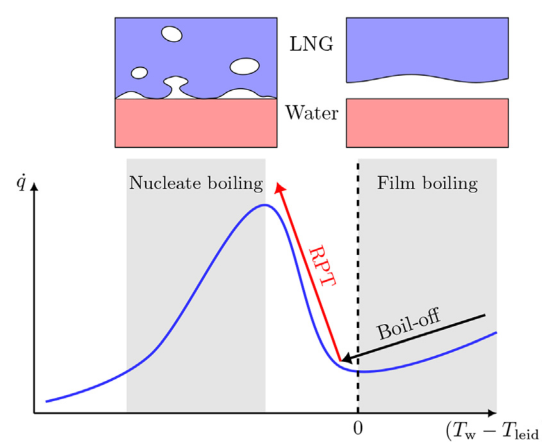

Fig. 1. An illustration of the boiling curve, here as a plot of boiling heat flux ($\dot{q}$) against the difference between water temperature T_{w} and LNG Leidenfrost temperature T_{leid}. When T_{w} approaches T_{leid}, heat flux drops as we transition into the film boiling regime. When methane-rich LNG spills onto water, we initially have that $T_{\mathrm{w}} \gg T_{\mathrm{leid}}$. However, as the arrows show, when methane is removed from the mixture through boil-off T_{leid} is increased, which effectively moves us towards the left along the curve. Eventually the Leidenfrost point is crossed, film boiling breaks down, and RPT is triggered due to a sudden large increase in heat flux.