

Theories and Mechanism of Rapid Phase Transition

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Light hydrocarbons and hydrogen can replace high-alkane fuels with the benefit of reduced CO₂ emissions. Their liquefaction to a cryogenic state is one of the most suitable solutions for storage and transport. An unexpected release of these fuels might lead to a rapid phase transition (RPT). RPT is a physical explosion well-known for liquefied natural gas (LNG), and may occur when this substance is spilled onto water. The heat provided by the water to the cryogenic fuel might lead to a sudden evaporation of the liquid, resulting in an explosion. The generated blast wave has the potential to damage equipment and personnel. The RPT phenomenon can also occur in different types of industrial applications when molten metals accidentally come in contact with water. In these cases, the water is the cold fluid which expands violently.

In this study, the RPT phenomenon is investigated for cryogenic fluids (liquefied hydrocarbons, nitrogen and hydrogen) as well as for smelts (molten inorganic salts) and molten metals (aluminum). The contribution has a twofold purpose as it addresses relevant past accidents and lay the foundation for future modelling activities to simulate the cryogenic-pool formation on water, triggering of an RPT event and the RPT explosion consequences. Furthermore, the RPT theories and mechanisms comprehension is critical to qualitatively evaluate the probability for a liquid hydrogen (LH₂) RPT. In particular, a comparison between liquid nitrogen (LN₂) and LH₂ is conducted to understand under which conditions an LH₂ RPT might occur. The results of this study are to be validated through the Safe Hydrogen Fuel Handling and Use for Efficient Implementation (SH₂IFT) project, in which a series of LH₂ spill tests onto water will be conducted.

1. Introduction

Hydrogen is considered a clean and renewable fuel that can replace hydrocarbon fuels, thus reducing the environmental pollution. The liquefaction of hydrogen increases its density so that it can be transported in larger amounts. The gaseous hydrogen is cooled down below its boiling point (-253°C (NIST, 2019)) obtaining a cryogen fluid. This is an energy intensive process, but can be advantageous for large-scale transport and applications where a high energy density is required (DOE, 2009). Although hydrogen is employed in several industrial processes, its application in new technologies might unveil unexpected risks. For this reason, hydrogen can be considered an emerging technology and emerging risks could arise from different accident scenarios (Jovanović & Baloš, 2013). For instance, it is still unclear how liquid hydrogen (LH₂) behaves when accidentally spilled onto water. In the case of liquefied natural gas (LNG), stored at -161°C (NIST, 2019), this type of accident scenario may lead to a physical explosion known as rapid phase transition (RPT), which is the sudden evaporation of a cryogenic fluid after contact with a heat source (Woodward & Pitbaldo, 2010). RPT can be found in the literature under different names which are water explosion, vapor explosion, steam explosion, explosive boiling, thermal explosion, thermal interaction, thermal detonation and molten fuel coolant interaction (MFCI). Verfondern & Dienhart (1997) spilled LH₂ onto a pool of water without observing any RPT, and there are no records in the literature for such a phenomenon. However, the stochastic nature of the RPT phenomenon calls for additional experiments and a thorough analysis of the underlying mechanisms before a conclusion is drawn. RPT might occur for different fluid pairs (one cold and one hot liquid) in various industrial applications such as in the paper (water – smelts) or metallurgic industries (water – molten metals) and nuclear plants (water – molten fuel). In these cases, water is the colder liquid which explosively vaporizes.

Similar phenomenon has also been observed with mineral oils or other hydrocarbons instead of water (Burgess et al., 1970). The aim of this study is to comprehend from a theoretical point of view if an RPT can occur when LH₂ is spilled onto water. Hence, theories developed for the fluid pairs listed above were collected to provide a qualitative overview on the RPT mechanisms for different substances. After the methodology description, the different system configurations for which an RPT has occurred are analyzed. Finally, the common aspects of the different theories are summarized in the discussion and used to discuss the LH₂-water system.

2. Methodology

Different RPT events with different underlying mechanisms depending on the fluids involved and the setup, were reviewed and qualitatively compared. In particular, the considered systems can be divided in two categories. In the first one, water is the subcooled liquid which transfers heat to the colder fluid, while in the second category water acts as the coolant. The following substances were considered for the first and second category, respectively:

1. Liquefied Natural Gas (LNG), liquefied hydrocarbons (e.g. propane, ethane), liquid nitrogen (LN₂) and liquid refrigerants (e.g. R22 -CHClF₂).
2. Smelt (molten inorganic salts) and molten metals (e.g. aluminum, tin).

Moreover, an RPT can happen in three geometrical arrangements: spilling of the hot liquid into the cold one, injection of the cold liquid into the hot one or, stratified layers of the hot and cold liquids (Bang & Corradini, 1991). All three geometries were considered in this study, and an overview of the theories and mechanisms developed for each system is provided. The purpose is to pinpoint the common aspects of the theories even though the conditions to achieve an RPT vary for each configuration due to the different properties of the involved substances. The approach of Archakositt et al. (2004), where the fuel-coolant interaction of a nuclear plant was simulated by a water-liquid nitrogen interaction, is an example of how the common aspects can be used. In this paper, the knowledge gained on molten metals RPT is exploited to understand this explosion for cryogenic fluids. The common steps leading to an RPT event are the liquid-liquid interaction (with eventual mixing), film boiling formation and consequent collapse, and nucleation (heterogenous or homogenous). Finally, these steps are evaluated in case of an LH₂-water interaction.

3. RPT theories and underlying mechanisms for different liquid-liquid systems

In this section, the theoretical models for describing the RPT event for the different liquid-liquid systems previously mentioned are presented. In this study, "early" indicates the RPT that occurs immediately after the release of one liquid onto or inside the other, while a "delayed" explosion manifests several seconds after the spill, usually when the liquid-liquid system has a stratified geometry. Furthermore, an RPT event can be spontaneous due to film-boiling collapse or externally triggered (e.g., by an artificial pressure pulse or waves).

3.1 LNG – water

The first well documented LNG RPT accident occurred in 1968 during the Bureau of Mines test series (Burgess et al., 1970). Several small- and large-scale tests followed to investigate this phenomenon. Porteous & Reid (1976) conducted small-scale experiments where they spilled LNG onto water to understand under which conditions an early spontaneous RPT may be achieved. They observed that (i) a liquid-liquid interface must be present to obtain an RPT (e.g. RPT will not occur when LNG is spilled on ice), (ii) the hot liquid temperature must exceed a lower limit, i.e. the homogeneous nucleation temperature (called also superheat-limit temperature, T_{sl}) of the cold fluid, (iii) the time scale of the event is very short (< 5 ms), (iv) the probability of an RPT event depends on the LNG (or hydrocarbon) composition, (v) a high momentum of the cryogenic fluid on top of the hot one can trigger the explosion, (vi) the RPT are rare if ice is formed, and (vii) the RPT probability decreases if the hot liquid temperature is much higher than the T_{sl} of the cold liquid. Moreover, the authors noted that spontaneous film boiling collapse occurs only if the LNG has a low methane content (< 19%mol) and no other perturbation are present. From these observations, the superheat theory was developed by Reid (1976). According to this theory, the following steps lead to a small-scale early spontaneous LNG RPT:

- Film boiling due to the high temperature difference between the two fluids: The LNG and water are separated by a thin vapor film which prevent large heat transfer. This happens when the water has a temperature higher than the LNG Leidenfrost temperature (T_L).
- Film-boiling collapse due to a triggering process leading to transition boiling. The vapor film is less stable if the water temperature is close to T_L .

- Rapid increase of heat transfer due to the direct liquid-liquid contact with consequent metastable temperature rise of the LNG toward its T_{sl} temperature. In this phase, the liquid has a temperature higher than its boiling point at atmospheric pressure, hence it is thermodynamically metastable.
- Violent expansion of the cold liquid caused by a perturbation when the liquid is vaporizing by heterogeneous nucleation. If the T_{sl} is reached, the homogeneous nucleation leads to an extremely rapid vaporization even without any perturbation.

The LNG RPT chain of events is depicted in Figure 1.

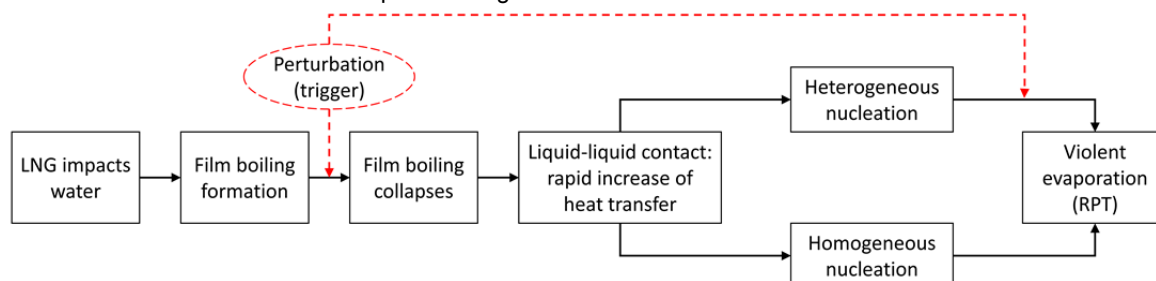


Figure 1: chain of the events for an LNG RPT.

During some of the large-scale tests (Goldwire et al., 1983), early and delayed spontaneous RPTs occurred close to the spill origin, or on the evaporating pool formed on top of water after the LNG release respectively. The triggering conditions to generate an early RPT can be attributed to the LNG impact with water or the high degree of mixing of the two fluids. For delayed RPT, evaporation of methane causes a shift in the Leidenfrost temperature, eventually leading to film-boiling collapse. For this reason, even LNG with an initially high methane content could undergo either an early or a delayed spontaneous RPT. Furthermore, Reid (1983) proposed that the following criteria must be satisfied to reach an early spontaneous RPT from large spills of LNG with a high methane content: (i) significant LNG and water mixing, (ii) the water-LNG interface temperature must be higher than the T_{sl} of LNG, and (iii) a triggering event that produces a significant pressure pulse to collapse the vapor film. For this early-RPT event, LNG-water-temperature ratios are not in the range defined by the superheat theory. Therefore, this theory should be slightly modified to explain this RPT type.

3.2 Liquefied hydrocarbons and refrigerants – water

Porteous & Reid (1976) poured onto water both pure and mixtures of hydrocarbons during the tests described in Sec. 3.1. Spontaneous RPTs were achieved under certain conditions for ethane, propane, isobutane, propylene and isobutylene during these tests. Recently, the combustion-induced RPT phenomenon which may occur after the ignition of methane, CO_2 and air mixtures was investigated by Salzano et al. (2013). In the 1970s, numerous tests of liquid refrigerants spill on water were conducted. In most of these experiments, R-22 (CHClF_2) was investigated and spontaneous RPTs for this substance were obtained when injected into water with temperature higher than 350 K (Anderson & Armstrong, 1977). The results attained in these analysis for both liquefied hydrocarbons and refrigerants are in agreement with the superheat theory since the RPTs occurred only when the estimated interface temperature was closed to the T_{sl} of the cold fluid (Reid, 1983).

3.3 Liquid nitrogen – water

Bang & Corradini (1991) analyzed the formation and consequences of the LN_2 RPTs starting from a stratified geometry (LN_2 over water). These authors demonstrated that a delayed spontaneous RPT cannot occur for this configuration, because the interfacial temperature between water at 0°C and saturated LN_2 is -30°C (~ 243 K) while the LN_2 T_L is around -150°C (~ 123 K). Therefore, the water surface solidifies before film boiling becomes unstable. As follow-up of these investigations, different LN_2 RPTs were achieved by forcing the film-boiling collapse with external pressure pulse by means of an electromagnet or a detonator. The necessary pressure can also be achieved by injecting the LN_2 onto water with a high velocity (Anderson & Armstrong, 1972). In later studies, RPTs occurred when LN_2 was injected directly into water. For instance, Archakositt et al. (2004) measured the overpressure generated by the LN_2 vaporization and the heat transfer from the cryogenic liquid to water by varying the LN_2 jet velocities and pressures. The LN_2 RPTs achieved by Bang & Corradini (1991) and Archakositt et al. (2004) have the same chain of events shown in Figure 1. Moreover, Zhang et al. (2017) observed a similar boiling process for LNG and LN_2 when injected into water, confirming

that this chain of events is suitable for different cryogenic substances. However, the superheat theory cannot be directly applied since the water temperature is much higher than the LN₂ T_{sl}, as previously mentioned.

3.4 Water – smelt

Soda and kraft smelts are mixtures of molten inorganic salts employed in the paper industry. The soda smelt is mainly composed by sodium carbonate (Na₂CO₃) (Shiang et al., 1989) while the kraft smelt contains in addition a large amount of sodium sulfide (Na₂S) (Nelson & Kennedy, 1956). If water enters the boiler in which the smelt is contained due to operational errors or equipment failures, an RPT might be generated by the rapid evaporation of water (Reid, 1983). Sallack (1955) discovered that NaCl and NaOH were responsible for the explosion of the soda smelt. These results were confirmed by Nelson & Kennedy (1956) who demonstrated that Na₂S enhances the explosion of the kraft smelt. These authors claimed that three different RPT types might occur during the water-smelt interaction: instantaneous, short-delayed and delayed.

The superheat theory developed and considered valid for LNG and the other cryogenic fluids cannot be applied here since the smelt temperature (1100 – 1200 K) is much higher than the T_{sl} of pure water (577 K) (Reid, 1983). Shick (1980) proposed a modified superheat theory by supposing that the salt and water concentrations vary at the interface of the two liquids. The mass flow of salt in the water increases the solution concentration and thus its T_{sl}. The water flux into the smelt is responsible to delay its solidification due to change in its melting point. The solubility in water depends on the salt type and the water temperature. This theory explains the impossibility to achieve an RPT of molten Na₂CO₃ and water, since the solubility of this salt decreases with increasing water temperature.

3.5 Water – molten metals

Early and delayed spontaneous RPT might occur under certain circumstances when a molten metal interacts with cold water. In different studies and accidents, RPTs were obtained for molten tin, zinc, lead, aluminum and steel. An extremely large interface area is required to superheat water, i.e. reach its homogeneous nucleation temperature, and then generate an RPT. This is very arduous to achieve with molten metals because their densities are usually much larger than water, hence the interface area between the two fluids is limited. Fragmentation of the molten metal becomes a critical phase in the path toward an RPT for water-molten-metal interaction. A positive feedback between pressure pulse and film-boiling collapse is initiated by a localized overpressure induced by a local film-boiling collapse. Thus, film-boiling collapse is the triggering event of the fragmentation process which propagates through the coarse metal globules. A correlation between the fragmentation degree and the liquid aluminum-water explosion intensity was found by Shen et al. (2020). For the water and molten-metal systems an alternative mechanism to the superheat theory was proposed by Buchanan & Dullforce (1973). Their model starts from the triggering mechanism, which puts the two liquid in contact by collapsing the vapor film with a consequent formation of a vapor bubble (step 1). The bubble then collapses due to condensation in the subcooled liquid generating a jet of coolant toward the hot liquid (step 2). The high-speed coolant jet penetrates the molten metal increasing the interface area and initiating the fragmentation of the hot liquid (step 3). The total heating rate grows as an effect of the increased interface area (step 4). The liquid jet suddenly vaporizes forming a high-pressure bubble due to the temperature increase (step 5). These last four steps are repeated cyclically leading to an RPT under favorable conditions. Obviously, these conditions vary for each of the considered liquid pairs (water-metal). A simplified path, displayed in Figure 2 which derives from the Buchanan and Dullforce model was recognized by different authors when an RPT from molten metals and water is described (Fletcher & Anderson, 1990).



Figure 2: four steps for the water-molten metal RPT adapted from (Shen et al., 2018).

An RPT can be initiated with an external trigger for the water-molten metal systems. However, if the interfacial temperature is lower than the metal-melting point, an RPT cannot be achieved even when the vapor film is collapsed by an external pressure pulse (Abe et al., 2002).

3.5.1 Water – molten aluminum

The first molten aluminum water tests were the Alcoa experimental program described by Long (1957). In these experiments 23 kg of molten aluminum was dropped into water, and RPTs were obtained under certain circumstances. A recent study conducted by (Shen et al., 2020) confirmed that the following conditions are

required to achieve an RPT from a water-molten aluminum interaction: (i) the aluminum mass should be heavier than a critical mass, (ii) a long drop path through the air must be avoided to not cool down the metal, (iii) the aluminum temperature must be higher than its solidification point ($> 730^{\circ}\text{C}$) and (iv) the water temperature must be lower than 33°C . It has also been observed by Shen et al. (2020) that a low melt/water mass ratio (~ 2) provokes more energetic explosions compared with a higher ratio. The main mechanism for a spontaneous aluminum-water RPT is the impact with the bottom of the water reservoir. Shen et al. (2020) demonstrated that such RPT occurs spontaneously if the inside of the water vessel bottom is composed by a water-wettable surface. For instance, this type of RPT cannot occur if the aluminum impact glass, solid aluminum or organic paint coated surfaces which are non-wettable surfaces. The superheat theory cannot be applied since the temperature of molten aluminum is much higher than the T_{sl} of water. Still, an RPT can be achieved for this pair if an external trigger is applied, such as a strong hammer blow on the external side of the water vessel (Reid, 1983).

4. Discussion

In this section, the common aspects of these theories and mechanisms are collected. Firstly, the conditions required to achieve this type of explosion depends mainly on the properties of the two liquids. The geometry arrangement affects the interface area between the fluids, and thus the total heat transfer. For this reason, the multiphase flow together with film boiling are the most important and complex phenomena to simulate in order to estimate the triggering of RPT. Furthermore, the interface area is also influenced by the degree of mixing after the release and the potential fragmentation of one of the fluids after the film boiling collapse. Another fundamental aspect is the determination and quantification of the triggering conditions to understand if and which RPT type (early or delayed, and spontaneous or externally) might occur.

Hydrogen has a very low boiling point (-253°C) and density (70.8 kg m^{-3}) at atmospheric pressure (NIST, 2019). Since the boiling points of LH_2 and LN_2 are both very low, an LH_2 RPT could have some similarities compared with an LN_2 RPT. Therefore, experimental results on LN_2 RPT tests available in the literature can give relevant insights for LH_2 RPTs. As for LN_2 , the LH_2 vapor film formed when poured onto water in an initial stratified geometry is not expected to collapse spontaneously due to the large temperature difference between the cryogen and water. The difference in densities of LH_2 and LN_2 (806 kg/m^3 at atmospheric pressure (NIST, 2019)) means that the fluid-flow behaviors are quite different, and this influences the steps preceding an RPT. For instance, only 7% of an LH_2 evaporating pool height is submerged in water, while 80% of an LN_2 pool is below the water level. It is expected that the mechanisms that trigger an RPT are similar for the two fluids once appropriate conditions are met. Therefore, delayed spontaneous RPT seems very unlikely for LH_2 on water. Spreading of cryogenic liquids on a surface after release is generally slower for lighter fluids (Verfondern & Dienhart, 1997), hence the degree of water-cryogen mixing is lower for LH_2 than LN_2 . This indicates that early spontaneous RPT with LH_2 is more difficult to achieve than with LN_2 . Sufficient water-cryogen mixing can be forced by high-momentum injection of LH_2 either onto or into water. It should be noted that LH_2 T_{sl} (29.5 K), estimated with the method proposed by Reid (1983), is lower than for LN_2 (112.3 K). This means that LH_2 undergoes homogeneous nucleation for a lower increase in temperature compared with LN_2 . The LH_2 and LN_2 properties are collected in Table 1 for a direct comparison. Furthermore, the trigger type and the intensity to collapse the vapor film and initiate the fragmentation process must be properly determined. Finally, flash vaporization is expected to be significant for LH_2 ($< 30\%$ of the volume in the work by Verfondern & Dienhart (1997)), and must be considered when estimating the released volume.

Table 1: comparison between LH_2 and LN_2 properties

Substance	Boiling point ($^{\circ}\text{C}$)	Density (kg m^{-3})	T_{sl} ($^{\circ}\text{C}$)	Pool penetration in water
LH_2	-252.9 (20.3 K)	70.9	-243.7 (29.5 K)	7%
LN_2	-195.8 (77.4 K)	806.1	-160.9 (112.3 K)	80%

5. Conclusions

An overview of the RPT theories and mechanisms for different configuration and fluid pairs was provided. The main phenomena and processes which lead to an RPT, and thus form the basis for future modelling activities, were highlighted. The mixing of the fluids, film boiling, triggering and fragmentation are the most critical phenomena and mechanisms involved in the RPT chain of events. Some considerations about LH_2 -water RPT were given based on the analyzed theories. The formation of a delayed spontaneous RPT seems to be very unlikely while the possibility to provoke an early or delayed RPT by external triggering or an early spontaneous RPT by injecting LH_2 into water cannot be excluded. The results of this study will be confirmed by the

experimental tests during the Safe Hydrogen Fuel Handling and Use for Efficient Implementation (SH₂IFT) project.

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