

Modeling and Simulation of Rollover in LNG Storage Tanks

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Abstract

Liquefied Natural Gas (LNG) is generally stored in refrigerated tanks at temperatures of about -160°C and pressures slightly above atmosphere in liquefaction plants and LNG regasification terminals. Heat leaks, even in well-insulated tanks, cause a slow boil-off of the LNG, and this requires removal of some vapor. During this weathering process the composition of the LNG changes because the small amount of nitrogen present is much more volatile than the methane and the heavier hydrocarbons are effectively non-volatile at storage conditions. Natural convection causes circulation of the LNG within the storage tank, maintaining a uniform liquid composition. The addition of new liquid, however, can result in the formation of strata of slightly different temperature and density within the LNG storage tank. "Rollover" refers to the rapid release of LNG vapors from a storage tank caused by stratification. The potential for rollover arise when two separated layers of different densities (due to different LNG compositions) exist in a storage tank. This paper gives a more adequate theoretical framework for rollover analysis and presents quantitative computer results for the simulation of the La Spezia Rollover incident. Therewith some recommendations have been proposed in order to minimize risk of rollover incident in refrigerated LNG storage tank.

Keywords: LNG, Storage, Rollover, Safety, Protection, Simulation, Modeling

Introduction

The first production and storage facility for Liquefied Natural Gas (LNG) was established more than 35 years ago [3]. Since that time, the demand for this cryogenically stored product has increased significantly. To accommodate the worldwide demand for the clean-burning and environment-friendly fuel, more than 470 facilities have been constructed and are on stream in approximately 25 countries, and plans are in place for at least 20 more facilities [4]:

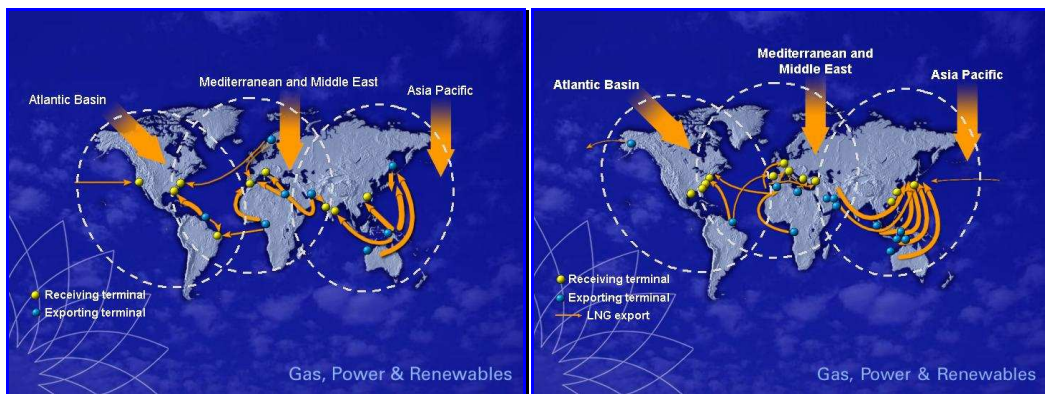


Figure1: LNG Market in 2002 (Left) and 2020 (Right)

LNG usage around the world continues to grow rapidly, and emerging countries are particularly attracted to LNG for power generation. Some industry analysts have predicted that demand for LNG will double by the end of the next decade.

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For refiners, LNG may become a profit center, as gas that was perhaps flared in the past can be processed into a valuable product. LNG is not a homogeneous material. There are appreciable differences in composition between LNGs from different sources. Chatterjee and Geist [1] give composition of typical LNGs as follows:

Table1: Typical Composition of Different LNGs

Source	Composition (Mole Percent)					
	Nitrogen	Methane	Ethane	Propane	Butane	Pentane+
US	0.40	95.90	2.70	0.4	0.30	0.30
Algeria	1.70	87.00	7.90	2.30	0.80	0.30
Iran (Estimated)	5.5 max	82 max	12.0 max	4.0 max	1.0 max	0.4 max
Libya	0.40	68.00	24.20	4.40	2.00	0.40

LNG Refrigerated Storage

Refrigerated storage of LNG has undergone an evolution as the properties of this fuel became better understood. The basic preparation for storage includes the cryogenic cooling of methane-rich natural gas to a temperature in the range of -155°C to -160°C . LNG refrigerated storage tanks have multi-wall construction and heavily insulated internally, with no external cooling:



Figure 2: LNG Refrigerated Storage Tank

During the LNG formation process, carbon dioxide, water and heavy hydrocarbons are systematically removed through adsorption, absorption and/or separation techniques. The physical nature of the product and its sensitivity to temperature fluctuations can make LNG potentially unstable in storage. The most common sources of these instabilities in LNG storage tanks are related to:

- Extended storage time of LNG, which may occur in secondary tanks that are used for peak shaving adjustments or seasonal needs
- Fluctuations in the quality of the product
- Pumping in or out of the tank
- High nitrogen content suspected of adding instability to LNG storage

From these items nitrogen-induced or auto-stratification occurs if a sufficient quantity of nitrogen, greater than 1 %, is present in LNG (Nitrogen Induced stratification can be prevented by ensuring low nitrogen content). According to relative magnitude of k-value (Figure3) Nitrogen is the most volatile component of LNG.

It boils off preferentially leading to an increase in the bubble point of the mixture and a reduction in liquid bulk density. In nitrogen-free LNG, loss of the more volatile component methane leads to a slight increase in saturation temperature without a significant change in the liquid density. The density variations resulting due to loss of nitrogen lead to stratification and can cause rollover which is explained in next paragraph [5].

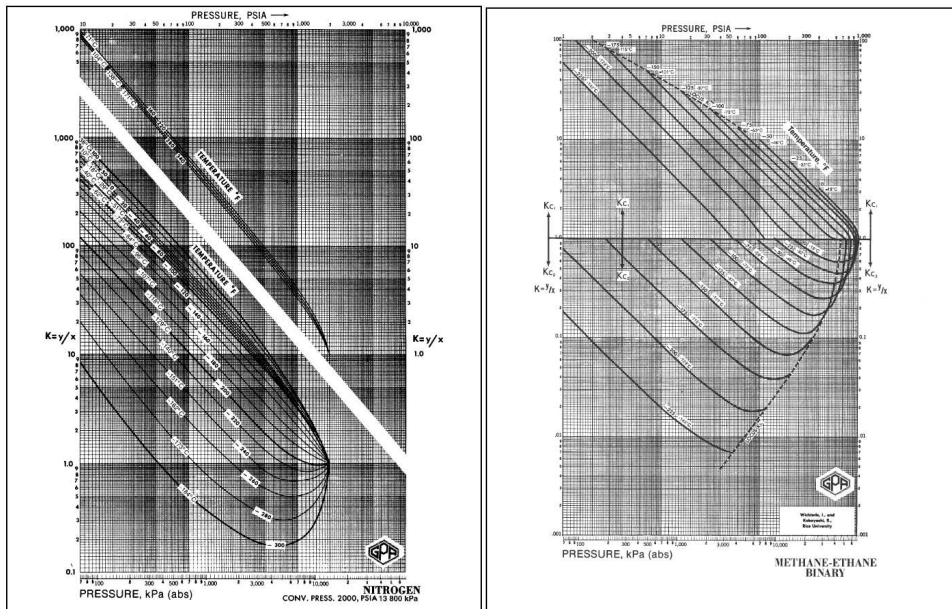


Figure3: Equilibrium Ratio (k-value) for Methane, Ethane and Nitrogen

In any of aforementioned instances, the temperature creep will ultimately cause a slightly warmer layer of product to "boil off". This layer will then rise to the top in the tank's vapor space, and it will evaporate and become denser. This phenomenon is called "Weathering". Subsequent heating then can cause the product to stratify in the tank, with the lighter layer on top. If the bottom layer continues to heat, its density can begin to resemble that of the upper layer, and this will cause rapid mixing and instability in the tank.

As the densities of two layers approach each other, the two layers mix rapidly, and the lower layer which has been superheated gives off large amounts of vapor as it rises to the surface of the tank. This phenomenon is known as rollover. The large amounts of vapor generated by this phenomenon can cause a dramatic vapor expansion and increase in internal tank pressure.

LNG rollover phenomena received considerable attention following a major unexpected venting incident at an LNG receiving terminal at La Spezia, Italy in 1971 [2]. The main hazard arising out of a rollover accident is the rapid release of large amounts of vapor leading to potential over-pressurization of the tank. It is also possible that the tank relief system may not be able to handle the rapid boil-off rates, and as a result the storage tank will fail leading to the rapid release of large amounts of LNG.

In order to model rollover phenomena, heat and mass balances, including tracking of compositional variations and densities, allow both the prediction of the approximate time until rollover occurs and the total amount of vapor that will be released in the rollover.

Mathematical Modeling of Rollover

Usual methods for prediction of boil off rate in LNG storage tanks can cause poor designs and excessive investment and operating costs. Use of these methods tends to oversize the tank pressure control system which in turn causes excessive vaporization and creates undue need for reliquifaction. Better, more precise designs can be made using a new mathematical model which more closely predicts actual boil off rates. With these better predictions the sizing of pressure control

LNG or other cryogenics in static storage are in state of dynamic and thermodynamic equilibrium. The heat being absorbed by the tank is dissipated by evaporative cooling at the surface. When the system is disturbed by pressure changes in the vapor space above the liquid, the system reacts to reestablish equilibrium. Evaporation of LNG in a large insulated storage tank occurs essentially on the liquid surface with no visible bubble formation.

Experiments with water and other liquids indicate that the temperature of the evaporating liquid at the surface is extremely close to the equilibrium saturation temperature of the vapor phase. However, about two millimeters below the surface the liquid temperature should be higher than the surface temperature in order to effect any appreciable surface evaporation. For any temperature difference between the surface and the liquid below the surface there is a constant steady state evaporation rate and a condition of supersaturation of the subsurface liquid [7].

Previous models for rollover in LNG storage tanks have been developed by Chatterjee and Geist [1] and by Germeles [2]. In these models the liquid in the tank is assumed to be stratified into a number of "cells" with heat in-leak from the sides and from the bottom of the tank as shown in Figure 3. The model consists essentially of the unsteady-state heat and mass balance equations for these cells and of supporting correlations. Both of these models used the thermohaline experiments of Turner [6] as a basis for treating the heat and mass transfer between cells. Both of the models simplify the problem to consideration of methane and a non-volatile heavy component. Unfortunately these adjustments have the effect of shortening the time to rollover in both models [10]. Another relation used in the Germeles model is the boil-off model by Hashemi and Wesson [7] as follow:

$$b = 0.328 \frac{\rho_0 C_p (g \alpha k^2)^{1/3}}{H_v \rho \mu C_p^2} (T_n - T_s)^{4/3}$$

Where b is the boil-off mass flux, Cp is the specific heat of the liquid, g is the acceleration due to gravity, Hv is the latent heat of vaporization of methane, k is the thermal conductivity of the liquid, Tn is the absolute temperature of the top or nth cell, Ts is the absolute saturation temperature of methane in LNG, μ is the viscosity of the liquid, ρ is the density of the liquid and ρ0 is the average reference density of the liquid.

In the Germeles model, equilibration of the liquid densities is taken as the necessary and sufficient criterion for mixing. In this aspect his model differs from that of Chatterjee and Geist, which requires equilibration of both temperature and composition. Some results from a simulation of the La Spezia rollover obtained by Germeles using his model are given in Figure5. As Figure5 shows, there is at rollover equilibration of density, but not necessarily of temperature or composition. Figure5 shows the rapid increase in boil-off. The computed time to rollover is 34 hours, which compares with a time of 31 hours in the actual incident. Clearly the previous models while containing the general features required are inadequate for prediction and development of rollover prevention strategies.

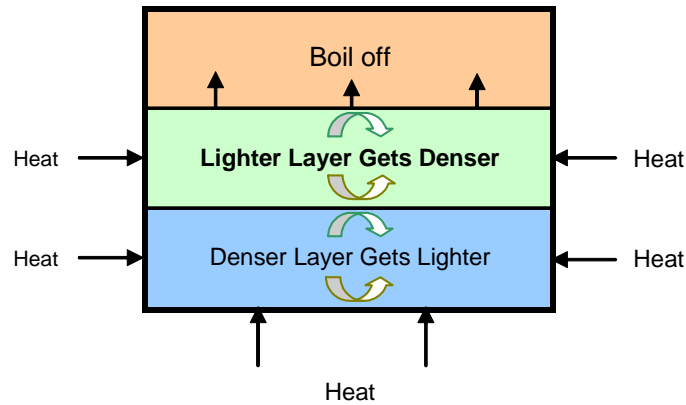


Figure4: An LNG Storage Tank with the Liquid Stratified into n Cells [2]

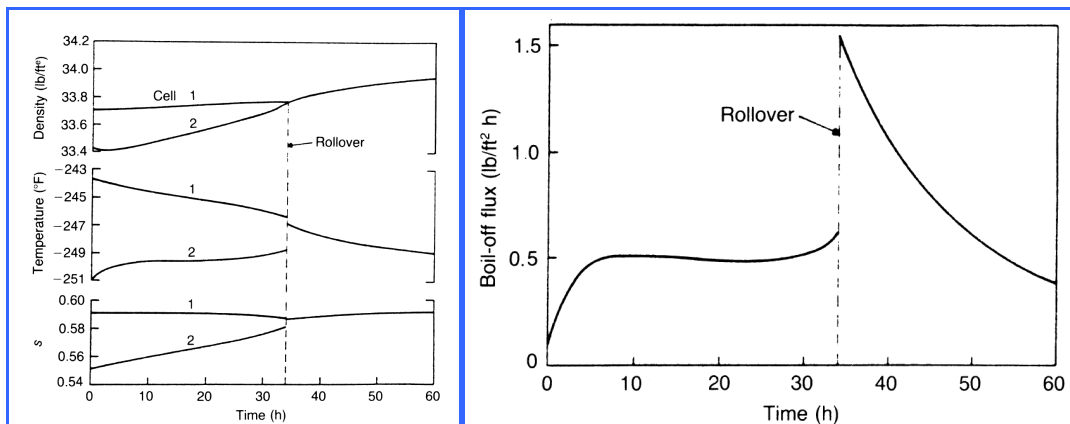


Figure5: Simulation of the Rollover in the LNG tank at La Spezia Incident: Density, Temperature and Impurity Concentration (Left), Boil off flux (Right)

Basis of Proposed Analysis

This work presents an integrated thermo-physical model for the stored LNG, which is capable of predicting boil off gas rates as well as the ageing properties for the bulk LNG over time, from initial conditions within an LNG tank. From the numerical prediction, we analyze how the boil off gas rates depend on the degree of super saturation of the stored LNG, in terms of the tank pressure and the initial temperature of bulk LNG. In addition, the reliability of the predictive model is tested using the real data of tank operation. In a typical LNG storage tank, the heat from outside gradually leaks into LNG, warming the liquid near the bottom relatively buoyant and causes upward liquid flow in a boundary layer along the walls. When slightly superheated liquid arrives at the free surface, it flashes in part at the top of LNG surface under a thermodynamic condition of the vapor space.

Here, due to a decrease in hydrostatic pressure, super-saturation may become greater under the same thermodynamic condition [1]. Then, the flash-cooled liquid (denser liquid) flows across the surface to sink back toward the bottom, and mixing with the bulk core of LNG and thus maintaining most of the bulk at an essentially uniform composition and temperature. In order to predict vapor evolution rate as well as compositional change of the LNG, it is assumed that a state of thermodynamic equilibrium is imposed on an arbitrarily film where a convective circulation flow enters and evaporation takes place [2]. Table 2 represents general features of the proposed model for rollover prediction.

The net rate of escape of a liquid into the vapor phase depends on the degree of supersaturation of the liquid phase on the vapor-liquid interface. The experimental data obtained by many investigators of fluids of vastly different properties demonstrate that for a horizontal fluid layer heated from below:

$$Nu = C.Ra^{1/3}$$

Where Nu is Nusselt Number (Dimensionless), Ra is Rayleigh Number (Dimensionless) and C is a dimensionless constant. The computed vaporization rate with proposed model is compared with that reported by Sarsten in Figure 6. At this time only one rollover incident has been reported in the open literature with sufficient detail for testing a computer model. Sarsten carefully documented a rollover event at La Spezia, Italy [9]. These data represent the experiment against which any model must be tested. The successful model will match the experimentally observed rates of vapor evolution and the time from loading to the observed rollover event with the initial conditions given by Sarsten.

Table 2: General Features of Proposed Model for Rollover Simulation

Model Feature	Present Work
Chemical Species Considered	Methane, Ethane, Propane, Butane and Nitrogen
Rollover Criterion	Equalization of Density between cells
Mass Transfer between Liquid Cells	Equimolar Counter Diffusion
Saturation Conditions of the Top Layer Temperature	Film Liquid and Vapor at Equilibrium in Film Temperature
Vapor Liquid Equilibria Model	Peng Robinson Equation of State
Boil off Rate Expression	Hashemi Wesson Correlation with minor Modification

Rollover Prevention Methods in LNG Storage Tanks

There are several methods available to reduce the probability of rollover. One method is to practice proper transfer procedures to assist in deterring fill-induced stratification. When transferring product into an LNG tank of a different product density, it is prudent to bottom-fill the lighter LNG while top-filling heavier product. This procedure will promote a natural mixing of the two product densities.

Flashing the vapors prior to transfer will reduce significant amounts of heat present during transit and transfer. Another possible deterrent to rollover is to constantly run the recirculation pumps to maintain a homogeneous density and temperature profile. These pumps are resident in each tank, but running them continuously is expensive, especially with today's high energy costs, and the pumps do not last forever.

Typically when loading a new batch of LNG into a tank that already has product, especially if the load has been aging for an extended period, stratification will occur. Tank operators will usually start recirculation pumps specifically for that situation. Still another method, although costly, is to re-liquify the vapor. This method entails passing the vapors and liquid product through an external liquefaction process at the LNG storage facility. After the process, the product is more homogeneous and can be re-introduced into the tank. Although product rollover is potentially of great concern to the storage facility operator, it is also predictable. By utilizing a software-driven system, along with precise instruments, the liquid temperature and density can be monitored at multiple points throughout the depth of the tank. The modeling software provides the operator with a very accurate, real-time sense of what is going on inside the tank. A detailed study on rollovers performed by a study group of International LNG Importers Group (GIIGNL) concluded that the boil-off rates resulting from rollovers are manageable.

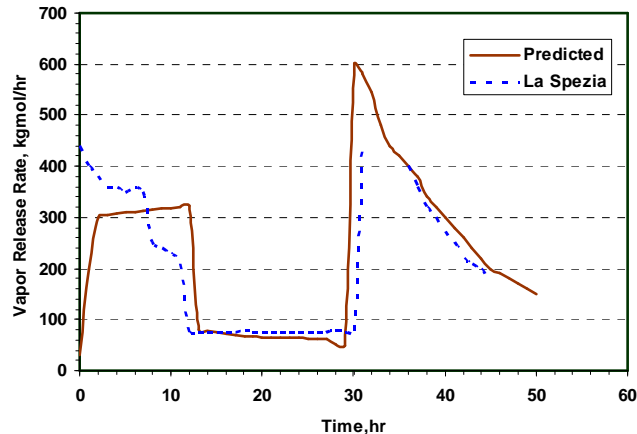


Figure6: Predicted Boil off rate for the La Spezia Rollover vs. to Sarsten's Reported Data

This study of 41 LNG rollover incidents revealed that only in a few cases the peak vapor evolution rate exceeded 20 times the normal boil-off rate. NFPA 59A requires consideration of rollover during relief sizing. EN 1473 requires sizing of relief valves for rollover based on 100 times the boil-off rate. Density differences of the order of 5–10 kg/m³ have been reported without any rollovers (<http://www.iomosaic.com>) [11].

LNG rollover is more likely to occur in peak-shaving facilities when the contents of the tank will weather during periods of low or no demand. LNG operators avoid stratification by mixing different density liquids using jet nozzles, recirculation, distributed fill systems, and alternate top and bottom filling. A layer of protection analysis (LOPA) is recommended for choosing appropriate mitigation and prevention measures [11]. Tanks receiving LNG from a single source on a regular basis have little risk of experiencing a rollover. However, as LNG trade becomes more globalized and multiple sources are delivered to land storage tanks, vigilance against potential rollover conditions will become a major part of facility risk management.

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