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Modeling the blanketing and warming effect of high expansion foam used for LNG vapor risk mitigation

Pratik Krishnan, Bin Zhang, Anas Al-Rabbat, Zhengdong Cheng and M. Sam Mannan

Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122, United States

Corresponding author: Pratik Krishnan, Tel.: +1 979 9850839; E-mail: pratik@tamu.edu

Abstract

Natural Gas is a cleaner energy when compared to other sources like oil or coal. Its consumption has been drastically increasing over the past few years and is projected to increase further. Liquefying natural gas is an effective way of easily storing and transporting it because of the high ratio of liquid to vapor densities. However, a leak of liquefied natural gas (LNG) can result in the formation of a huge vapor cloud, which poses a potential risk. This cryogenic vapor cloud has the potential to ignite and can migrate downwind near ground level because of a density greater than air. NFPA recommends the use of high expansion foam to mitigate the vapor hazard due to LNG. The primary objective of this paper is to study the effects of heat transfer mechanisms like convection and radiation on foam breakage to be able to accurately quantify the amount of foam required to mitigate the vapor risk of LNG spills.

Keywords: Liquefied Natural Gas (LNG); vapor cloud; high expansion foam; foam stability; mitigation

Introduction

The consumption of natural gas is expected to increase by nearly 70 percent over the next few decades as it is a cleaner source of energy compared to oil or coal and because technological innovations like hydraulic fracking have helped obtain shale gas from sources previously considered economically infeasible. (US EIA, 2016) Natural gas produces lesser amount of carbon dioxide, sulfur oxide and nitrogen oxide per unit of energy produced (Figure 1) Liquefaction of natural gas can be an effective way of storing and transporting it because its volume is around 600 times lower in its liquid form. (Table 1) Therefore, it is likely that the transportation of natural gas as LNG will increase. (Figure 2) However, a leak of liquefied natural gas (LNG) can potentially result in a catastrophic scenario. It can result in the formation of a vapor cloud, which can migrate downwind near ground level, exhibiting dense gas behavior, and has the potential to ignite. There are several documented instances of LNG related incidents and they can be expected to increase due to the increased use of LNG. (Table 2) There are several methods to mitigate the vapor risk of an LNG spill, such as the use of high expansion foam as suggested by the NFPA. (National Fire Protection Association, 2016) Therefore, it is crucial to understand the fundamentals of foam behavior and effectively model it in order to estimate how much foam needs to be applied.

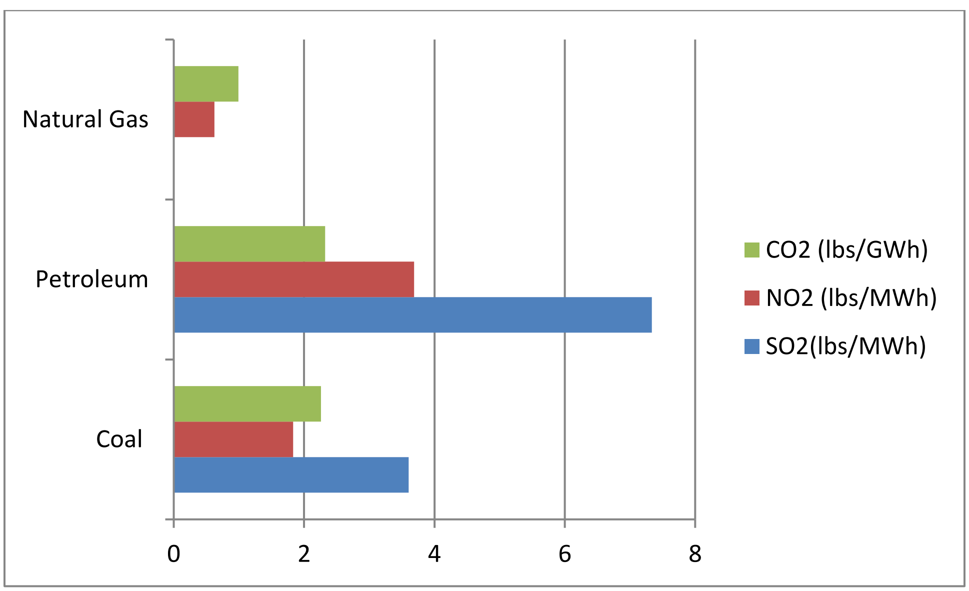


Figure 1- Comparison of carbon dioxide, sulfur dioxide and nitrogen oxide emissions due to electric power generation from natural gas, coal and petroleum (US EIA, 2015a)

Property	LNG (Methane)
Boiling Point	112 K
Liquid density*	423 kg/m^3
Vapor density*	1.78 kg/m^3
LFL-UFL	5-15 %

*At the boiling point

Table 1 - Salient properties of LNG

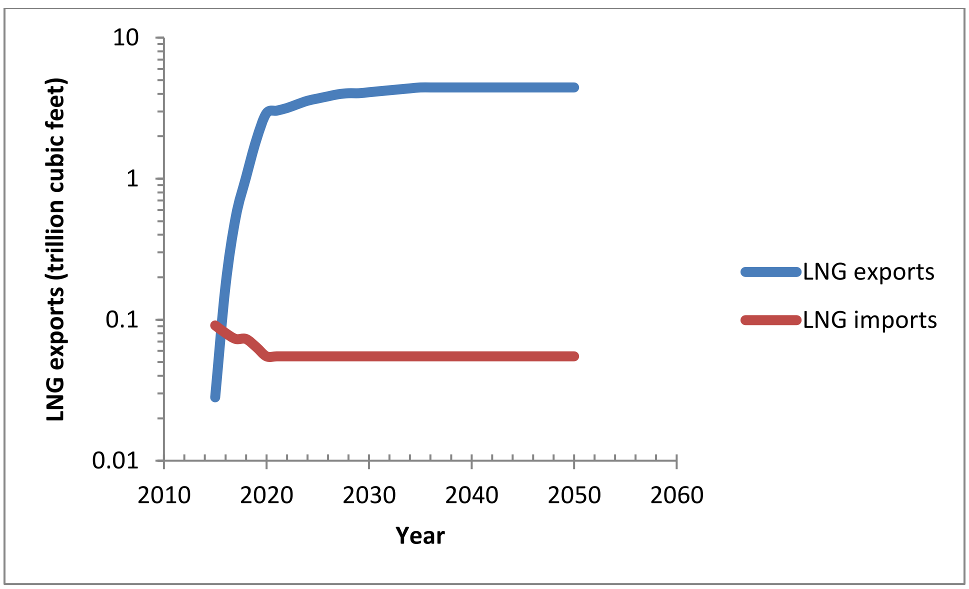


Figure 2 - Projected increase in the import and export of LNG from the US (US EIA, 2015b)

Ship / Facility Name	Location	Year	Affect on human life
East Ohio Gas LNG Tank	Cleveland, OH	1944	128-133 deaths
LNG Import Facility	Canvey Island, UK	1965	1 person burned
LNG export facility	Arzew, Algeria	1977	1 worker frozen to death
Columbia Gas LNG import	Cove Point, MD	1979	1 killed, 1 injured
LNG export facility	Bontang, Indonesia	1983	3 workers died
Skikda I	Algeria	2004	27 killed, 72-74 injured
Atlantic LNG (Train 2)	Port Fortin, Trinidad	2006	1 person injured
LNG Facility	Plymouth, WA	2014	5 workers injured

Table 2 - A few major incidents related to LNG (Department of Transportation, 2007; Hamutuk, 2008; Powell, 2016; Weinberg, 1975)

Foam is a colloidal dispersion in which the dispersed phase is gas and the dispersion medium is liquid. (Walstra, 1989) Foam is thermodynamically unstable because the bubbles have high interfacial energy. Thus, over time, the bubbles coarsen and eventually are destroyed. It is important to note that the rates of decay of different types of foam will vary and some foam may be so unstable that they last only for a few seconds while there are others that can last for several days or months. The liquid fraction of foam is used classify foam as low, medium or high expansion. When the liquid fraction is low, foam tends to have a high expansion ratio (Ratio of foam volume to liquid volume) and is termed as high expansion foam. High expansion foam typically has an expansion ratio higher than 200. (Chemguard, 2017)

High expansion foam used for LNG application forms a vapor barrier containing the hazardous cryogen. In case there is a fire, the bubbles will help suffocate the flames and will help prevent re-ignition. (Chemguard, 2017) They are also gaining more attention as they tend to be biodegradable, making them environmentally friendly. (Conroy, Taylor, Farley, Fleming, & Ananth, 2013)

Several heat transfer mechanisms can affect the vaporization rate of LNG in the presence of foam. (Zhang, Liu, Olewski, Vechot, & Mannan, 2014) The foam blocks the effect of both convection and radiation on LNG vaporization; conduction remains the dominant mechanism for transfer of heat to the foam. This is called as the “blocking effect” of foam. Liquid from foam can drain over time and can increase the rate of vaporization of LNG. This is termed as the "boil-off" effect of foam. Over time, an ice layer forms since the temperature of the cryogenic is far lower than the freezing point of water. This acts as a physical barrier preventing the direct contact of foam with LNG. However, as this ice is porous, it allows vapors to pass through it. The two effects ("blocking effect" and "boil-off effect") are clubbed together and termed as the "blanketing effect" of foam. This highlights the net effect of foam addition and determines the vaporization rate of LNG. There is a third, unintuitive effect of foam application on LNG. The vapors that pass through the foam layers' exchange heat with the foam layers, increasing their temperature. This allows the vapors leaving the foam to have a higher temperature, making their dispersion easier. (Figure 3) This is termed as the "warming effect" of foam.

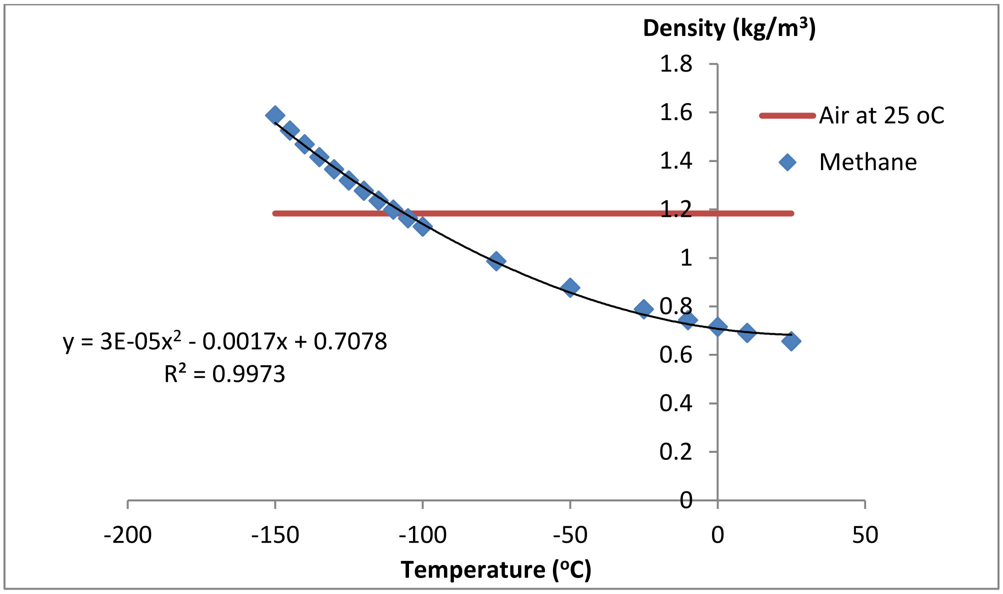
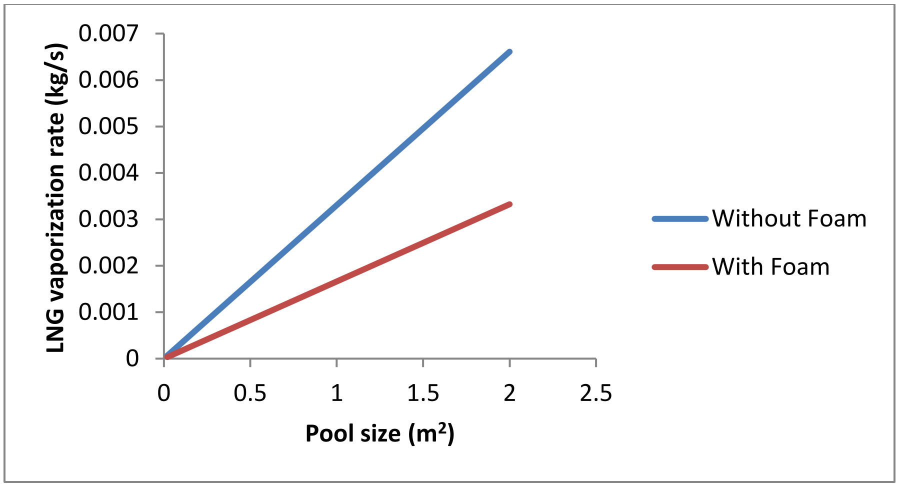


Figure 3 – Density of methane as a function of temperature, methane density is equal to air density at 100.7 °C. (Easy-Unit, 2013)

Some of the effects of foam on LNG vaporization based on previous work have been shown in Figure 4. By extrapolating results obtained by Zhang et al., (Zhang et al., 2014) it can be seen that both LNG vaporization rate and Hazard Distance may be considerably reduced with foam application. In order to estimate how much foam needs to applied, it is extremely important to understand how the "blanketing effect" and "warming effect" work. If too little foam is applied, the vapor dispersion may not be sufficient and a dense vapor cloud may form. If too much foam is applied, it is possible that the water drainage from the foam will be so significant that it increases the vaporization rate of LNG. Therefore, understanding the heat and mass transfer phenomena affecting foam stability and LNG vaporization may be crucial in estimating the amount of foam that needs to be applied.



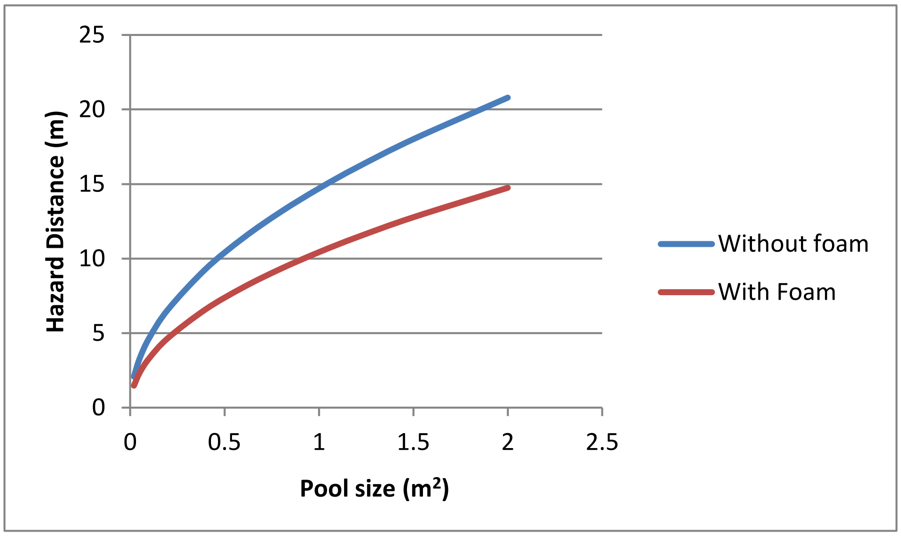


Figure 4 – Estimated effects of foam based on cumulative heat fluxes for different heat transfer mechanisms obtained by (Zhang et al., 2014) The values have been extrapolated for different pool sizes. The Hazard Distance has been calculated based on DOW's CEI.

Pugh has listed out the phenomena destabilizing the foam. (Pugh, 2016) These may include liquid drainage, external disturbances, Ostwald ripening, evaporation and coalescence. All these mechanisms can contribute to making foam less stable and ultimately causing its breakage.

Liquid drainage is the liquid that is drained out of the foam due to gravity. The loss of liquid from foam can significantly affect its effectiveness. (Conroy et al., 2013) If more liquid drains out of the foam, it can significantly increase the rate of vaporization of LNG, especially before an ice layer is formed.

External disturbances include natural convection, forced convection or radiation. Zhang et al. found that foam application could significantly reduce the heat flux due to natural convection, forced convection and radiation, which contribute to vaporizing cryogenic liquids. (Zhang et al., 2014) However, it is important to understand the affect of these external disturbances on foam breakage itself to ensure that the foam forms a blanket that remains stable for a longer period.

Ostwald ripening is the coarsening of bubbles due to the diffusion of air from one bubble to another over time to attain thermodynamic equilibrium. Smaller bubbles tend to lose gas and become smaller and eventually disappear while larger bubbles grow over time. This eventually increases the average size of bubbles. (Stevenson, 2012)

Evaporation due to convection and radiation can decrease the critical liquid fraction of bubbles in the upper layers of the foam. Carrier and Colin found that when the liquid fraction drops below a critical value, bubbles tend to break. (Carrier & Colin, 2003) Li et al. also performed experiments verifying the influence of environmental humidity on foam stability and found that change in humidity can significantly alter foam stability. (Li, Karakashev, Evans, & Stevenson, 2012) Thus, it is possible for evaporation to affect the stability of foam.

Coalescence can also influence the rate of foam breakage. Coalescence occurs due when the film separating two bubbles breaks. This can be a cooperative process resulting in a series of rupture of many bubbles. (Carrier & Colin, 2003; Stevenson, 2012) Coalescence observed in foam may be different from that observed in isolated thin films and its mechanism is not very well understood.

While all these phenomena can destabilize foam, it is important to estimate their effect on foam breakage to identify factors that may be controlled in order to minimize foam breakage. It is important to note that several factors may be dependent on each other and may exhibit synergistic effects. Such an analysis may also offer insight on how to mitigate the vapor risk due to an LNG spill, making such operations safer.

Materials and Methods

Materials

The foam concentrate used in this work was C2 high expansion foam by Chemguard. The foam solution was prepared as prescribed by the foam manufacturer. (2%) The expansion ratio of high expansion foam is usually over 200. This was measured by measuring the weight of the foam and knowing the volume of the container.

Experimental work

A foam generator apparatus was designed at the Mary Kay O’Connor Process Safety Center by Harding et al. (Harding, Zhang, Chen, & Mannan, 2015) This device was an improvement on the original design suggested by the NFPA (National Fire Protection Association, 2016) These improvements offer several advantages over the conventional design including higher foam outlet, enhanced safety without depending on pressurized air, easier shutdown procedure, smaller pressurized volume negating the requirement of a solenoid valve and a deflector plate for directing the foam to the required location.

Using this in-house foam generator device, foam was generated and its stability over time was studied. The foam height with time was studied under two different conditions. Initially, the foam was left to break on its own. In the second test, the foam generator fan was left ‘ON’ to study the effect of external forces like convection on foam breakage. To automate the data collection process, images were obtained every 15 minutes. The images for some experiments were then analyzed using free image processing software developed by the NIH known as ImageJ. This information was then collected and evaluated and was found to be similar to eye measurements, more so for experiments without convection. (Supplementary information Figure 1)

Theoretical modeling

Several mechanisms of foam instability need to be considered for the model including evaporation, coarsening, coalescence, external disturbances and liquid drainage. Models for each cause of instability need to be assessed individually and consolidated to get a holistic model that could be used to develop a model that can quantify foam stability. The preliminary model for foam stability includes evaporation and liquid drainage. Efforts are under way to create a comprehensive model including all other effects. All the models were programed using MATLAB.

Results

Experimental Results

The first set of experiments involved obtaining foam height as a function of time for foam generated using the generator and stored in the foam container, exposed to air. (Primarily natural convection will affect the foam breakage) These experiments were performed over three different days.

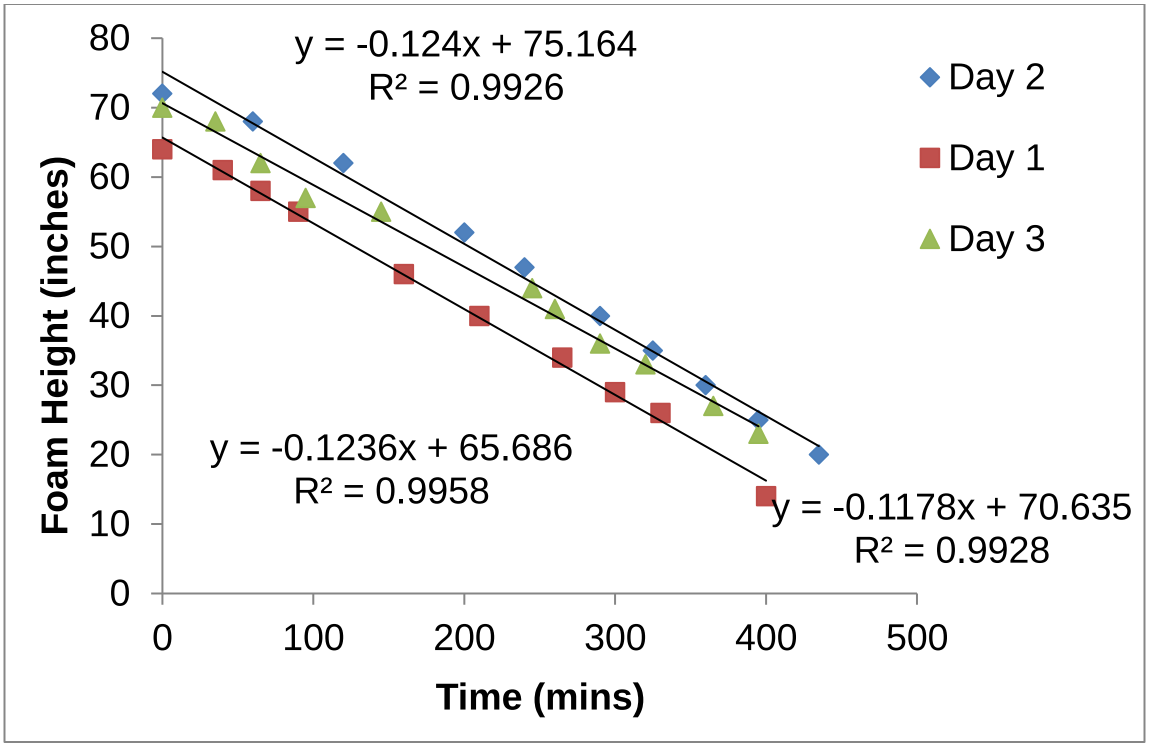


Figure 5- Foam height vs time under without forced convection

The second set of experiments involved obtaining foam height as a function of time for foam generated and leaving the foam generator 'ON' to simulate the effect of forced convection on foam breakage. These experiments were performed over two different days.

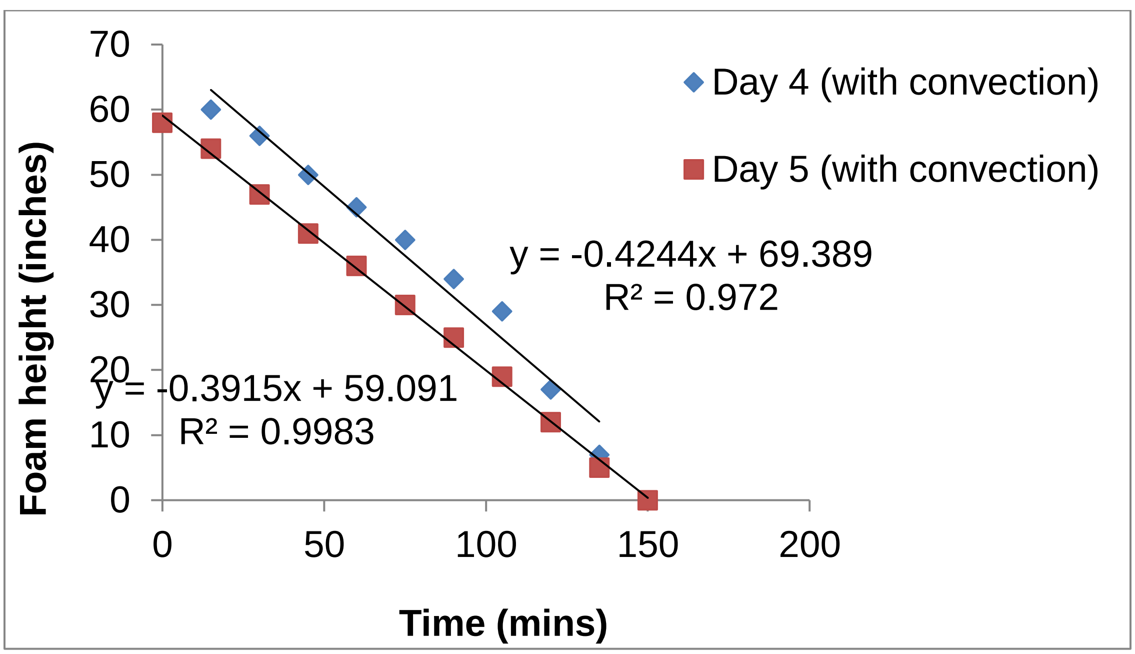


Figure 6 – Foam height vs time under forced convection

The expansion ratios and other experimental parameters were also recorded and have been tabulated below.

Expansion ratios

Day1	268
Day2	295
Day3	330
Day 4	297
Day 5	344

Experimental parameters

Damper opening	100%	To control fan speed
Volumetric flowrate of foam solution	5.49	L/min

Table 3 – Expansion ratios and experimental parameters for the experiments performed

Theoretical model

Modeling liquid drainage

Conroy et al. have solved volume averaged ordinary differential equations to obtain analytical solutions for the height of the liquid drained and the induction time in the case of free drainage from foam. (Conroy et al., 2013) The expressions they obtained are as follows:

$$h_w = \alpha_w H - [H/\frac{1}{\alpha(\infty)} + \left[\frac{1}{\alpha_f} - \frac{1}{\alpha(\infty)}\right] \exp\left[\frac{(-B\sqrt{\alpha_w}\,[t-t_{ind}])}{H^2}\right]] \quad \text{- Equation 1}$$

Where h_w is the height of the drained liquid, α_w is Liquid volume fraction at the foam-liquid interface, H is the height of the container filled with foam (initial height of foam)

$$\alpha(\infty) = \frac{B\sqrt{\alpha_w}}{AH} \quad \text{- Equation 2}$$

$$t_{ind} = \frac{B\left[\sqrt{0.26} - \sqrt{\alpha_f}\right]^2}{A^2 \alpha_f^2 \sqrt{0.26}} \quad \text{- Equation 3}$$

$$B = 0.458\,\frac{\zeta L \gamma}{\mu} \quad \text{- Equation 4}$$

$$A = \frac{\zeta L^2 \rho g}{\mu} \quad \text{- Equation 5}$$

$$\zeta = \text{Permeability coefficient} = \frac{k}{\alpha^2 L^2} \quad \text{- Equation 6}$$

Where k is the permeability

$$L = 0.41\ D_b \quad \text{- Equation 7}$$

Where D_b=Bubble diameter

Conroy et al also compared these solutions with PDE solutions and numerical solutions to the ODE. We have considered the analytical solution to the ODE for simplicity. Therefore, we can obtain the liquid drainage from the foam under static conditions from this model.

Modeling the effect of evaporation

Effect of natural convection on evaporation rate

The Hertz-Knudsen-Schrage equation was used to estimate the evaporation rate due to natural convection from foam. The presence of surfactant was accounted for based on coefficients obtained from experiments. (Marek & Straub, 2001)

$$\Gamma=\frac{2}{2-H_c}\left(\frac{M}{2\pi R}\right)^{\frac{1}{2}}\left(\frac{H_c P_v}{T_v^{\frac{1}{2}}}-\frac{H_E P_l}{T_l^{\frac{1}{2}}}\right) \quad \text{- Equation 8}$$

Where Γ is the evaporation rate, M is the molar mass, R is the gas constant, T_V and T_L are temperatures of the vapor and liquid, P_V and P_L are the saturated pressures of vapor and liquid, H_C and H_E are the condensation and evaporation coefficients determined experimentally.

Effect of forced convection on evaporation rate

The Smith-Lof-Jones model has been used to obtain the relationship between wind velocity and evaporation rate. This helps determine the evaporation rate due to forced convection. (Smith, Löf, & Jones, 1994)

$$E=\frac{(30.6+32.1\times U)\,(P_W-P_A)}{\Delta H} \quad \text{- Equation 9}$$

Where E is the evaporation rate in $kg/m^2/hr$, U is the wind speed propagating over the water surface in m/s, P_W and P_A are the saturation vapor pressures at the specific water temperature and at the air dew point temperature in mm Hg and ΔH is the latent heat of water at the specified water temperature in the tank in kJ/ kg.

Since this relation is obtained for pure water, an effect similar to that observed experimentally for natural convection was assumed for the presence of surfactant.

Effect of radiation on evaporation rate

The effect of radiation is modeled based on the energy method of evapotranspiration, assuming all radiative heat is used in evaporating water.

$$Er = \frac{Rn}{Lv*\rho} \qquad \text{- Equation 10}$$

Where Er is the evaporation rate due to radiation, Rn is the radiation intensity, Lv is the latent heat of vaporization and ρ is the density of the liquid (water)

All these effects are combined once again to give the effect of evaporation on foam breakage.

It is assumed that foam breaks due to evaporation once it reaches a critical liquid fraction. This assumption will be discussed more in detail later.

From Figure 7, it is very clear that liquid drainage seems to increase in the presence of these effects. Forced convection seems to have the most impact on increase in drainage followed by radiation. Evaporation due to natural convection seems to have little effect on the liquid drainage.

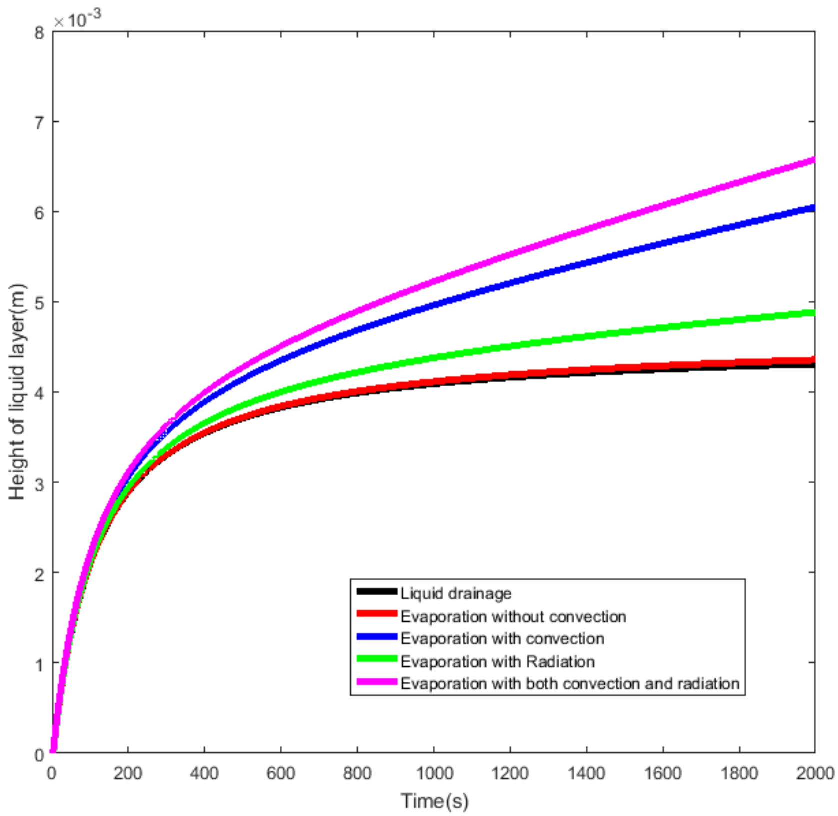


Figure 7 – Effect of evaporation on liquid drainage

Discussion

Experimental observations

A comparison of the results with and without forced convection has been shown in Figure 8.

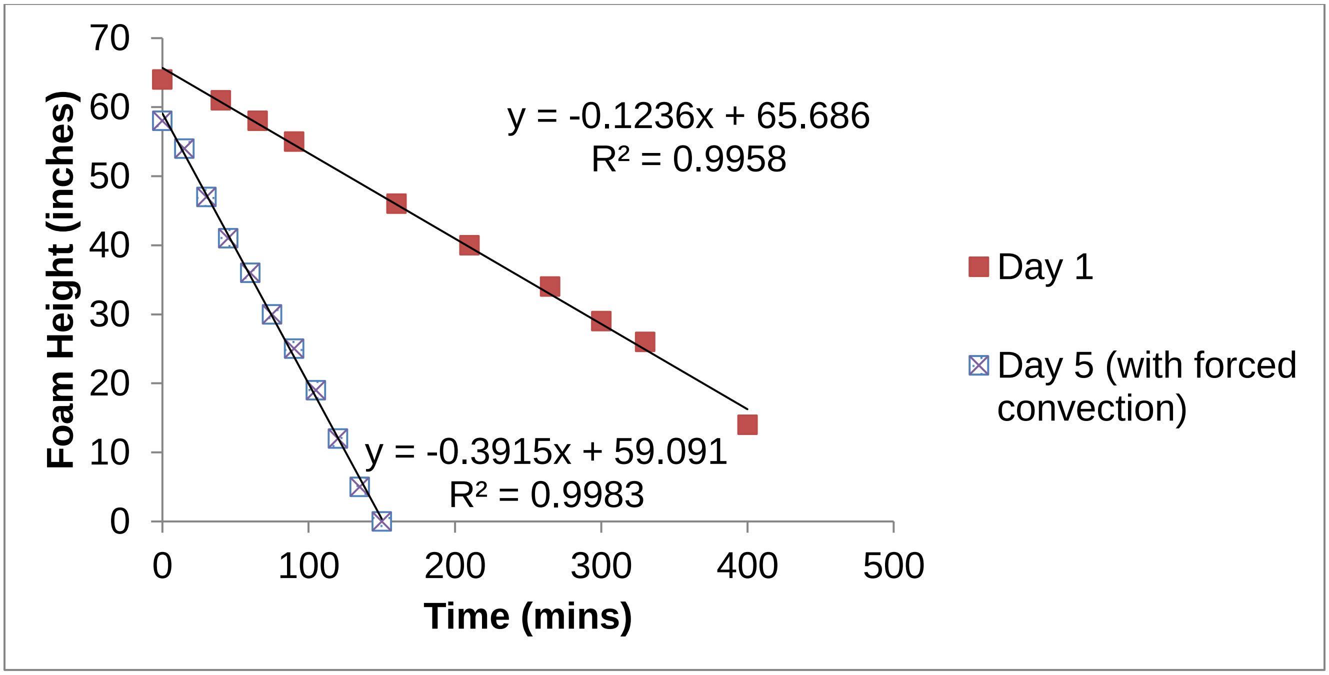


Figure 8: Comparing the results with and without forced convection over two days.

It is evident from the observations based on the slope of the graph (foam breaking rate) that convection can have a significant impact on the foam breakage rate. The foam stability can be quantified in terms of time to half height. (Table 4) Clearly, the time to half height is around 300 mins for foam under natural convection and reduces to around 80 mins under forced convection. This change is drastic as the time to half height is reduced around 4 times. This implies that forced convection could radically alter the effectiveness of foam as a mitigation agent. Therefore, it is crucial to account for such factors during foam application.

Day	Time to half height (mins)	Initial Height (inches)	Foam breaking rate (inches/min)
Day 1	272.5	64	0.1236
Day 2	315.8	72	0.124
Day 3	302.5	70	0.1178
Day 4	86.9	65	0.4244
Day 5	76.9	58	0.3915

Table 4 – Time to half height and foam-breaking rate

Theoretical model

Several mechanisms to destabilize foam have been mentioned including: Ostwald ripening (coarsening), evaporation, external disturbances and coalescence. It is important to understand the magnitude to which each factor contributes to foam destabilization, especially under the influence of external factors like convection and radiation.

Some of the fundamental properties crucial to foam stability can be identified as surface tension, surface elasticity, surface viscosity, electrical repulsion. Surface tension depression allows the formation of stable foam and can be ensured by the addition of surfactant. Surface elasticity is dependent on the rates of diffusion of surfactant through the liquid as this determines how fast any weak spots in the foam bubble can be repaired. Surface viscosity affects the drainage of the liquid, affecting foam stability. Charged surfactants may help reduce the rates of foam thinning because the surfactant molecules on opposite sides of bubble walls can repel each other, resulting in electrical repulsion.

Our model shows that evaporation can affect the liquid drainage from foam and influence foam stability. However, other mechanisms including external disturbances, Ostwald ripening and coalescence need to be studied and modeled to conclusively identify the dominant mechanism resulting in the foam breakage observed experimentally.

Conclusion and Future Work

It is evident from the experimental results and the theoretical model that convection and radiation can affect the rate of foam breakage and therefore vary the LNG vaporization rate. This can affect the ability of high expansion foam to serve as a mitigation agent and therefore, it is crucial that such factors be considered before estimating foam application rates. To get more conclusive data and observations, a modification to the existing foam container needs to be done to get important information about liquid drainage from foam under forced convection and radiation. Tests can be performed with and without the cryogenic liquid and the results can be compared. Such an apparatus will allow the quantification of liquid drainage from foam and simultaneous efforts in modeling this behavior will enable a better understanding of foam as a mitigation agent for LNG spills.

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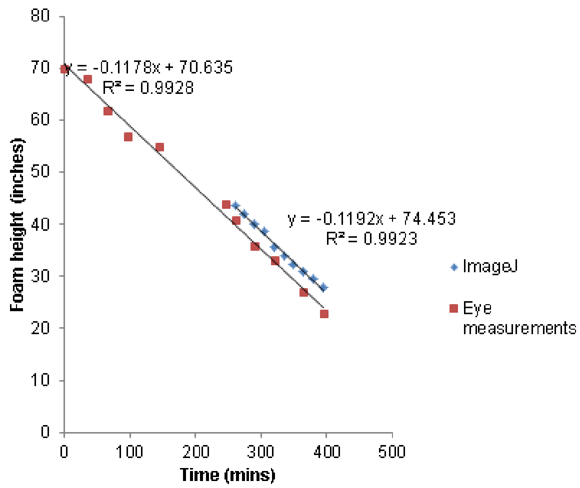
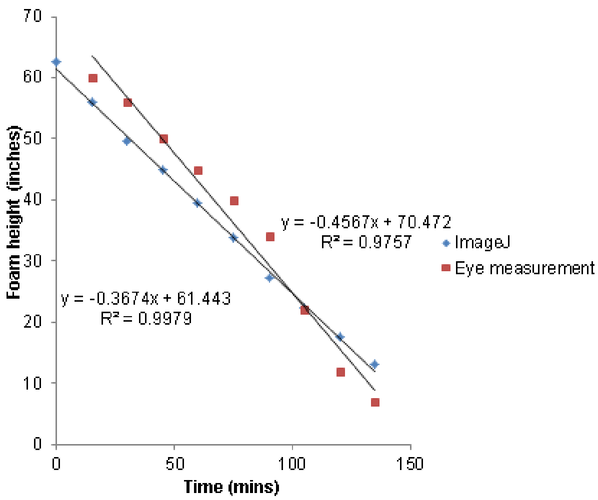
Supplementary Information

Images for some experiments were then analyzed using free image processing software developed by the NIH known as ImageJ. This information was then collected and evaluated and was found to be similar to eye measurements, more so for experiments without convection.

(A) (B)





Supplementary Information Figure 1: Comparison of measurements made by eye and Image J. (A) without convection (B) with convection