LNG Hazards
and
Their Assessment

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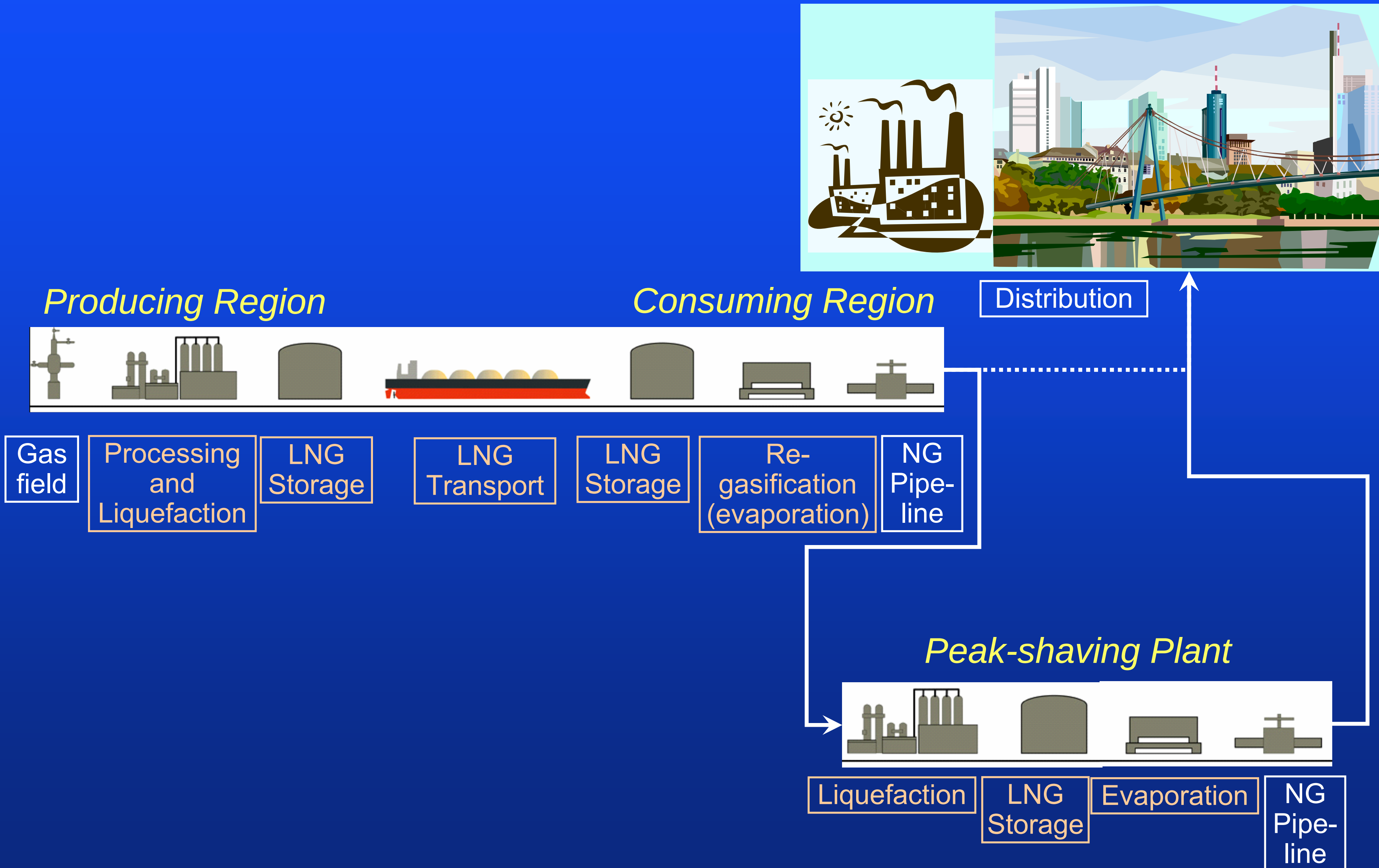
Background – Why LNG?

- Liquefied Natural Gas (LNG) is poised to play a larger role in the North American energy picture.
- Declining oil reserves has been putting pressure on oil-fired electricity generation and space heating, thus providing incentives to switch to natural gas (NG) fired power plants and space heating.
- The relatively clean burning characteristics of NG provide an additional incentive to switch to this fuel in an era of increasing awareness of environmental issues.
- With this increased interest, LNG has become a hot topic, with many LNG re-gasification terminal projects appearing on the books in North America.

Background – Why LNG? (cont. 2)

- NG is flammable.
- LNG can therefore pose fire and explosion risks if released from containment and is ignited.
- LNG vapour is heavier than air, and can travel large distances before dispersing to safe levels.
  - Hence, significant public safety concerns exist regarding large volumes of LNG near populated areas, be it in a storage vessel on land or a marine tanker in a waterway or harbour.

NG Supply Chain Based on LNG



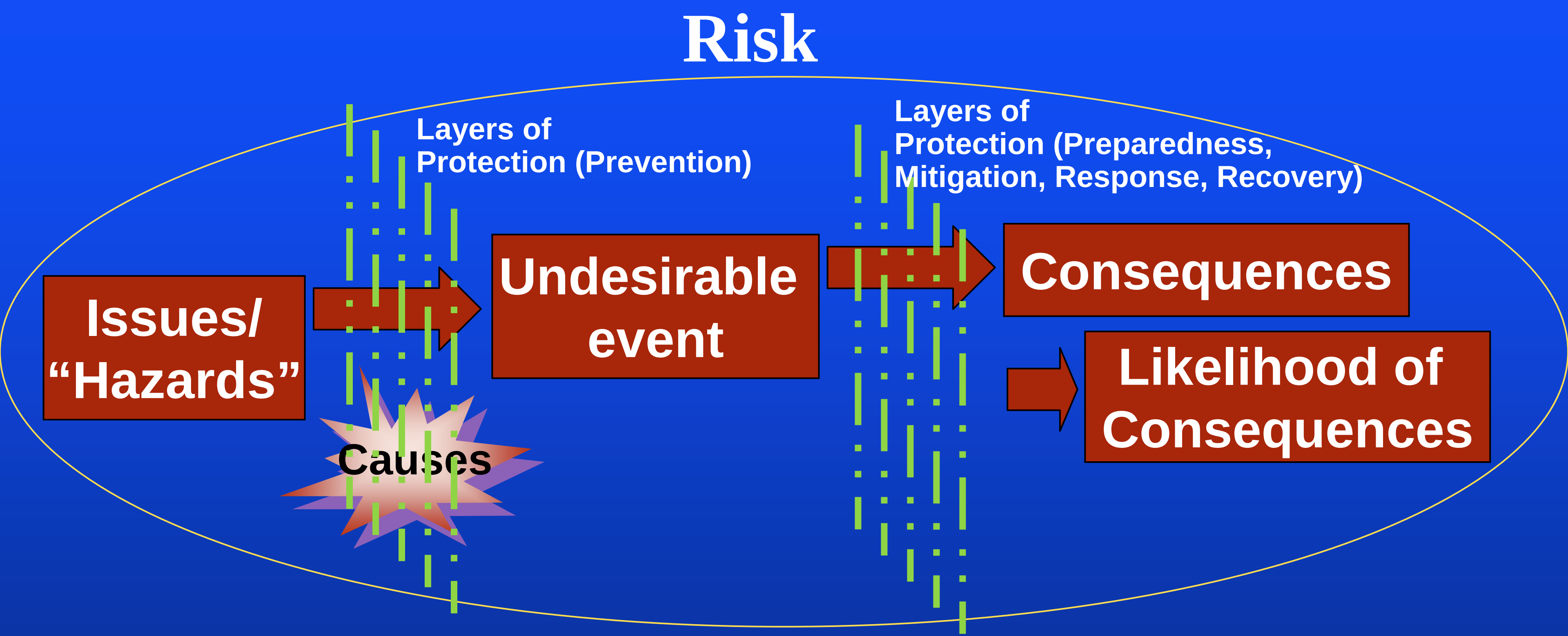
NG Supply Chain Based on LNG (2)

- On land, NG is transported to points of consumption as a pressurized gas by pipeline.
- Many large sources of NG are overseas, requiring transoceanic transportation before they can reach North American markets.
- Although some under-sea pipelines exist in the world for transporting NG (e.g., Russia-Turkey pipeline under the Black Sea), the transoceanic distances involved for transporting NG to North America require shipping by marine tanker.
- In order to take advantage of gas-to-liquid volume reduction, marine tanker shipping of NG is in liquefied form, or LNG.
- Once this LNG reaches land, it needs to be stored in liquid form, and then evaporated to gas for further distribution by pipeline.
- As pipeline capacity is limited and NG consumption can fluctuate from season to season, some of this gas may be liquefied in peak-shaving plants and stored as LNG near major consumption centres, ready for re-evaporation and distribution for pipeline when needed.

This Paper

- The objective of this paper is to
  - Describe the major processes in the NG supply chain based on LNG;
  - Discuss the safety hazards of LNG;
  - Describe some of the tools available to us for assessing these hazards; and
  - Describe some of the challenges in assessing these hazards.
- The material in this presentation is not original scientific research
  - It is a collection of facts from available technical and scientific literature, with occasional interpretation by the author, especially regarding current challenges in hazard assessment.
  - Some of the modelling presented here were undertaken by the author.

Hazard, Risk, Hazard Assessment and Risk Assessment



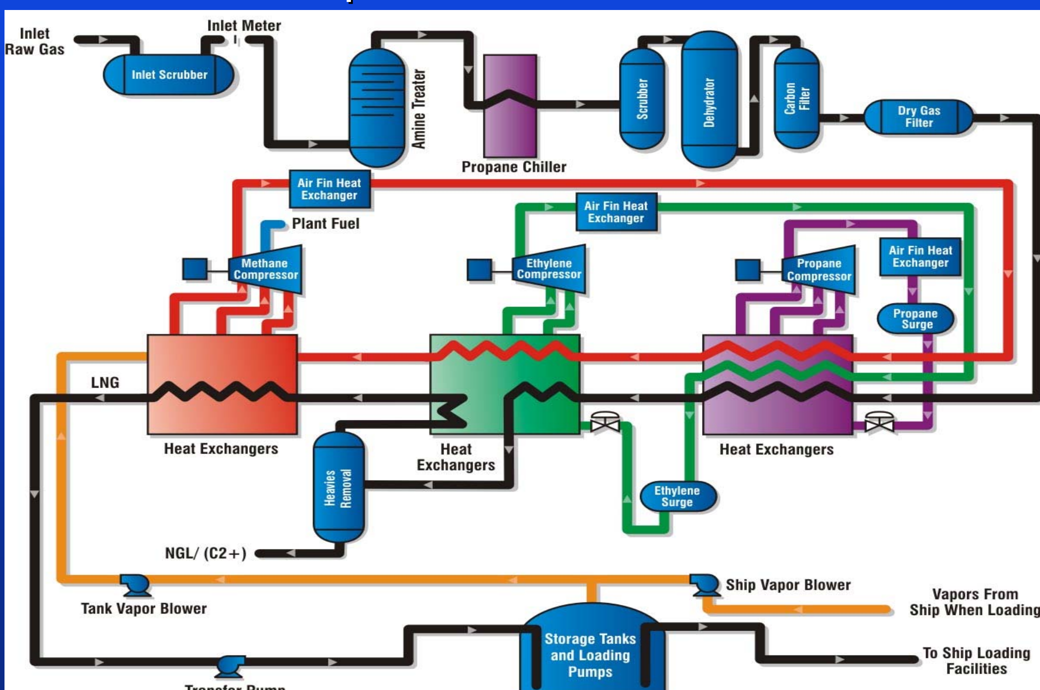
- Risk Assessment: Identification of potential undesirable events, and developing an understanding of their importance to us considering their potential consequences and likelihood, for the purpose of deciding whether we should reduce their risk or continue living with that potential
- Hazard Assessment: Concerns itself with only the consequence aspects of risk

Major Processes in the Supply Chain (1)

- Field gas processing, to produce clean gas and remove most LPGs (propane, butane, pentane, etc.)

Major Processes in the Supply Chain (2)

- Liquefaction of NG from field processing (LNG "cascade" process)
  - Refrigeration to -162 °C is required
  - Typical refrigerants include ethylene, propane and butane
  - Refrigerant quantities stored are on the order of 5-30 tonnes
  - Ethylene is stored near its boiling point (-73 °C)
  - The others are stored under pressure-liquefied conditions at ambient temperature



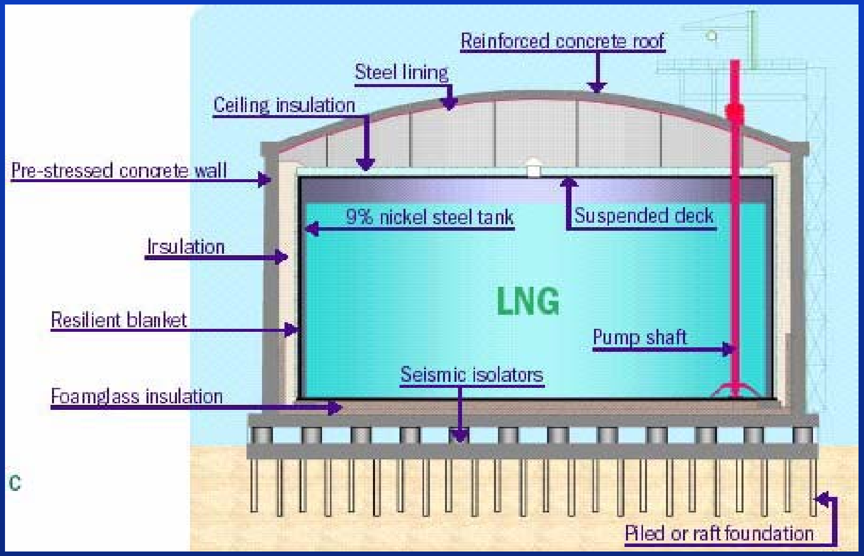
CoP LNG Process[SM]

Picture reference: Meher-Homji, et al., AIChE/CSChE LNG Conferenece, 2005; Eaton, et al., AIChE Spring Mtg, 2004

Picture reference: CEE, Introduction to LNG, 2003

Major Processes in the Supply Chain (3)

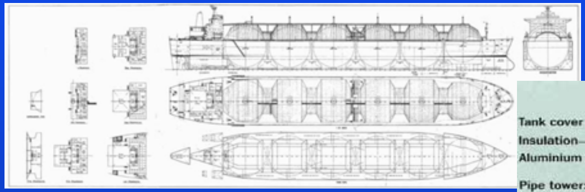
- LNG Storage
  - Quantities stored in above-ground or in-ground double-walled cylindrical tanks with capacity ranging from 7,000 m^3 to 200,000 m^3
  - Stored at pressures slightly above atmospheric at boiling point (-162 °C)
  - Inner wall requires to be for “cryogenic service”: 9% nickel steel, aluminum or pre-stressed concrete
  - Outer wall: carbon steel or pre-stressed concrete
  - Heavily insulated between the two walls
  - The outer wall is sometimes built only to support the insulation and the roof
    - The trend is to construct the outer wall such that it can also withstand the LNG temperatures and contain it in case the inner wall fails.

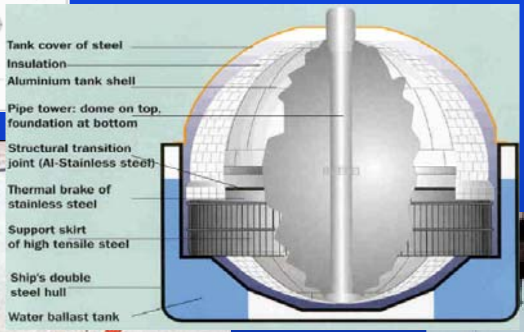


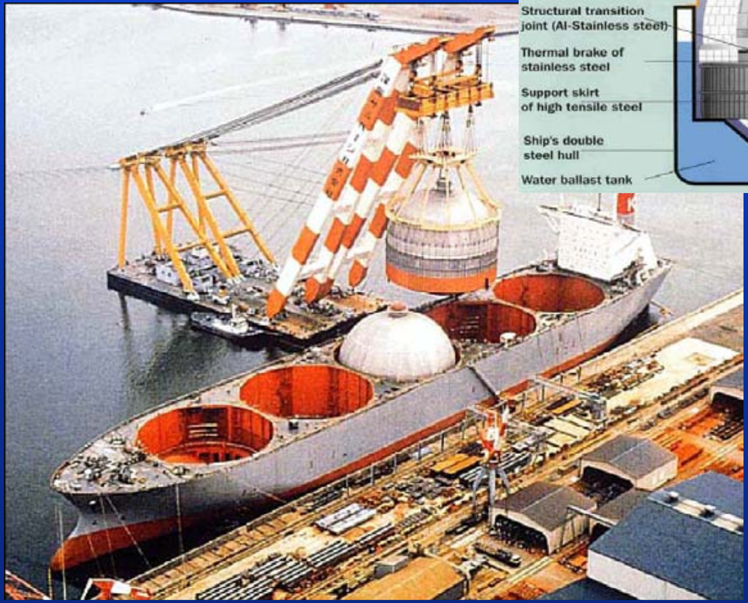
Picture reference: CEE, LNG Safety & Security, 2003

Major Processes in the Supply Chain (4)

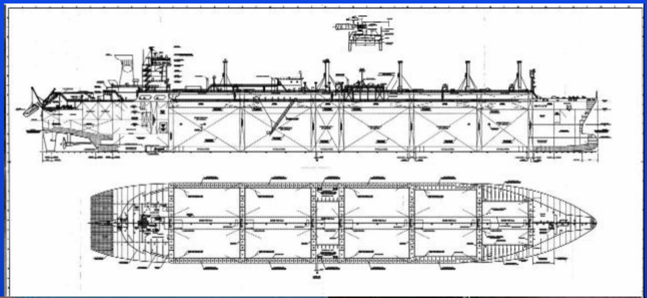
- Marine transportation
  - LNG is loaded onto specially designed marine tankers using loading arms
  - A marine tanker can hold 120,000 to 200,000 m^3 of LNG, typically in four or more tanks of 20,000 to 30,000 m^3







Moss-Spherical LNG Tanker Ship

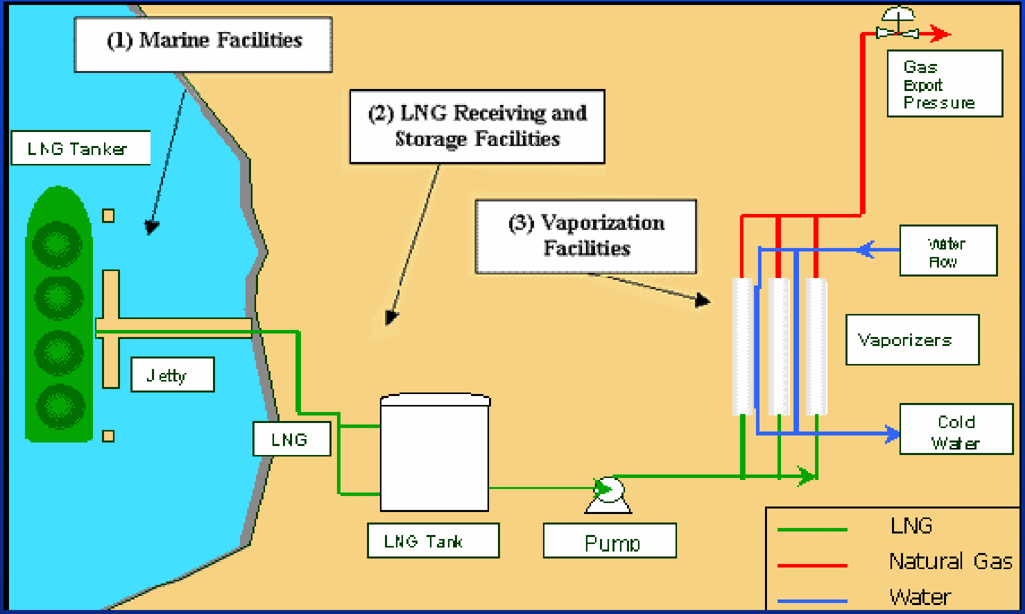


Prismatic Tanker Ship

Picture references: Sandia Report SAND2004-6258, 2004; QatarGas Intertanko, 2004; Pitblado, et al., 2004

Major Processes in the Supply Chain (5)

- Re-gasification (evaporation)
  - At re-gasification terminals, LNG is
    - unloaded,
    - stored as LNG,
    - evaporated in heat exchangers using fired heaters, seawater or warm water, and
    - fed into pipelines under pressure, for transmission and distribution.
  - Re-gasification terminals are generally near population centres where NG is consumed.



Picture reference: CEE, LNG Safety & Security, 2003

Major Processes in the Supply Chain (6)

- Peak-shaving plants
  - They receive NG through transmission pipelines, liquefy the NG, and store it as LNG.
  - LNG is re-gasified and fed into the distribution system during periods of high demand

- Small satellite storage facilities also exist
  - They serve a similar function as peak-shaving plants
  - They only have storage and re-gasification facilities (no liquefaction)
  - Delivery is typically by LNG truck

Picture reference: CEE, LNG Safety & Security, 2003

LNG Properties and Associated Hazards

- Example Composition of Natural Gas

Component in Natural Gas	Higher Limit (mole %)	Lower Limit (mole %)
methane	95.3	93.9
ethane	3.5	2.25
propane	0.48	0.077
iso-butane	0.057	0.003
n-butane	0.07	0.002
iso-pentane	0.017	0.0000
n-pentane	0.013	0.0000
C6+	0.0120	0.0000
nitrogen	1.8	1.7
carbon dioxide	0.76	0.66

- Boiling Point = -162 °C at 1.7 kPag (typical LNG storage temperature and pressure)
  - Cryogenic
    - Freeze burns
    - Brittle fracture of metals if not specifically prepared for LNG service
- Its main component methane is considered to be a simple asphyxiant
- Flammable range in air : ~5% (LFL) to ~15% (UFL)
  - Jet fires
  - Flash fires
  - Pool fires
  - Building explosions
  - Vapour cloud explosions

LNG Properties and Associated Hazards (2)

- Methane (CH_4) molecular weight: 16 (air: 29)
  - NG is lighter than air at equal temperatures
    - specific gravity (air = 1): 0.55 at 21 °C and atmospheric pressure
  - When LNG at -162 °C is spilled, the vapour is heavier than air until it warms up to approximately -110 °C
    - *This results in a heavier-than-air flammable gas cloud, that can travel relatively large distances before it disperses to below LFL*
    - *The flammable range of the cloud is generally visible due to condensation of humidity in the air*
- Liquid density (1.013 bar at boiling point) : 422.62 kg/m^3
  - Floats on water
- Liquid/gas expansion : ~600 times
- Critical temperature : -82.7 °C; Critical pressure : 45.96 bar
  - Unlike, for example, propane and butane, NG cannot be kept as a liquid at normal ambient temperatures
- Auto-ignition temperature : 595 °C (for LPG: 450 to 500 °C)

Hazard Modelling (Focus: large spills)

- Spills may occur
  - on land or on water,
  - from piping, loading/unloading arms, breach of storage tanks, and breach of marine vessels

Picture reference: Kytomaa, et al.; 2005, Vancouver)

- Source term
  - Calculating the mass release rate from containment is based on the classical hole discharge equation

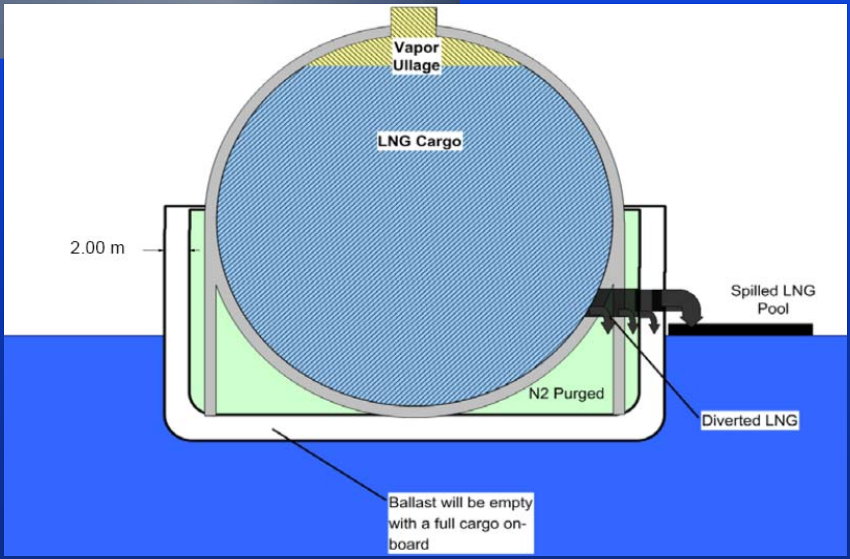
$$\dot{m}_l = \rho_l \, v \, A_0$$

$$v = C_d \sqrt{g h_l}$$

  - The height h_l of the liquid inside the vessel above the hole can be calculated using the time-dependent differential equation for conservation of mass

$$\frac{dm_l}{dt} = -\rho_l \, v \, A_0$$

$$m_l = \rho_l A_{\text{tank}} h_l$$



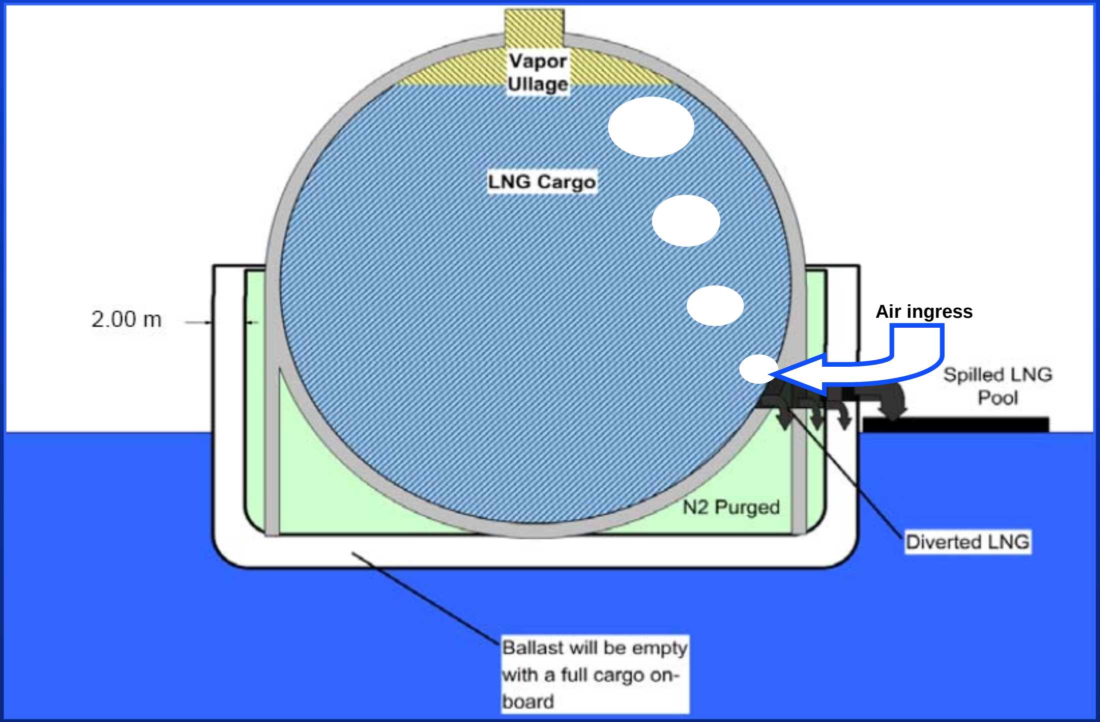
Picture reference: Sandia Report SAND2004-6258, 2004

Source Term Modelling

- Establishing the hole size remains a challenge.
- For land-based facilities, US EPA RMP type guidance can be used for establishing worst-case and alternative-case scenarios.
- For marine tankers, models to estimate hole sizes on tankers given collisions with other ships at different speeds are available (see Sandia, 2004).
  - The author has developed and used such models starting in 1980s.

Source Term Modelling

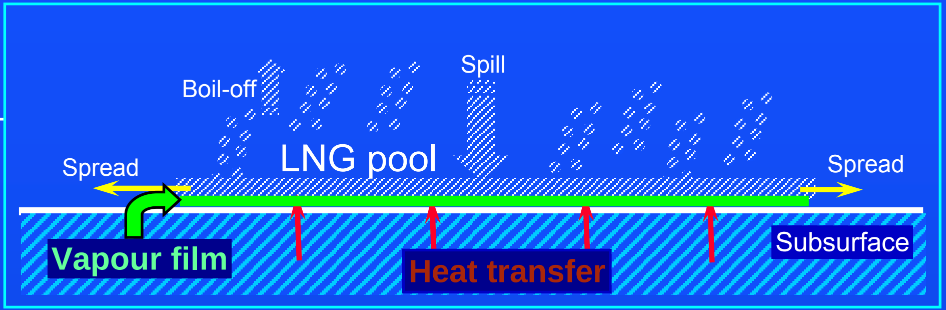
- *Possible complication:* the “glug-glug” phenomenon
  - When a liquid is spilling from an otherwise sealed container, the flow is not continuous, but comes out in “blobs”, with breaks in between for air to enter the container
  - This will slow down the spill rate, unless vacuum breaks and vents on an LNG tank are large enough to pass sufficient air into the tank
  - This phenomenon is not accounted for in any models
  - Some research is being undertaken by Kytomaa, et al. (2005, Exponent)
  - Neglecting this effect will lead to overestimates of spill rate, possibly more than a factor of 2



Modelling of Liquid Pool Spread

- Spread of liquid takes place under the influence of gravity.
  - The size of the pool as a function of time can be calculated using
    - the mass conservation differential equation, balancing the incoming spill rate with the outgoing boil-off, and
    - Newton's equation of motion, balancing the gravity head of the liquid pool height and its acceleration in the direction of spread.
  - In a spread and boil-off model, it is usually assumed that the pool will spread until a minimal layer thickness is reached, if unconfined.
  - The spread is very fast, as a layer of vapour builds between the spreading liquid and the subsurface.
    - It is usually assumed that the pool spreads to this minimum thickness very quickly
  - *Complication: For spills on large bodies of water, the effect of wave action could significantly reduce pool size (Quest, see Sandia Report, 2004)*
    - *However, this approach has been later criticized (Havens, LNG Summit, 2004)*
  - *Complication: For spills on land, the effect of topography and surface roughness on spread can significantly change pool shape and limit pool size*
    - *These effects are generally not taken into account in hazard studies*

Modelling Boil-off (1)



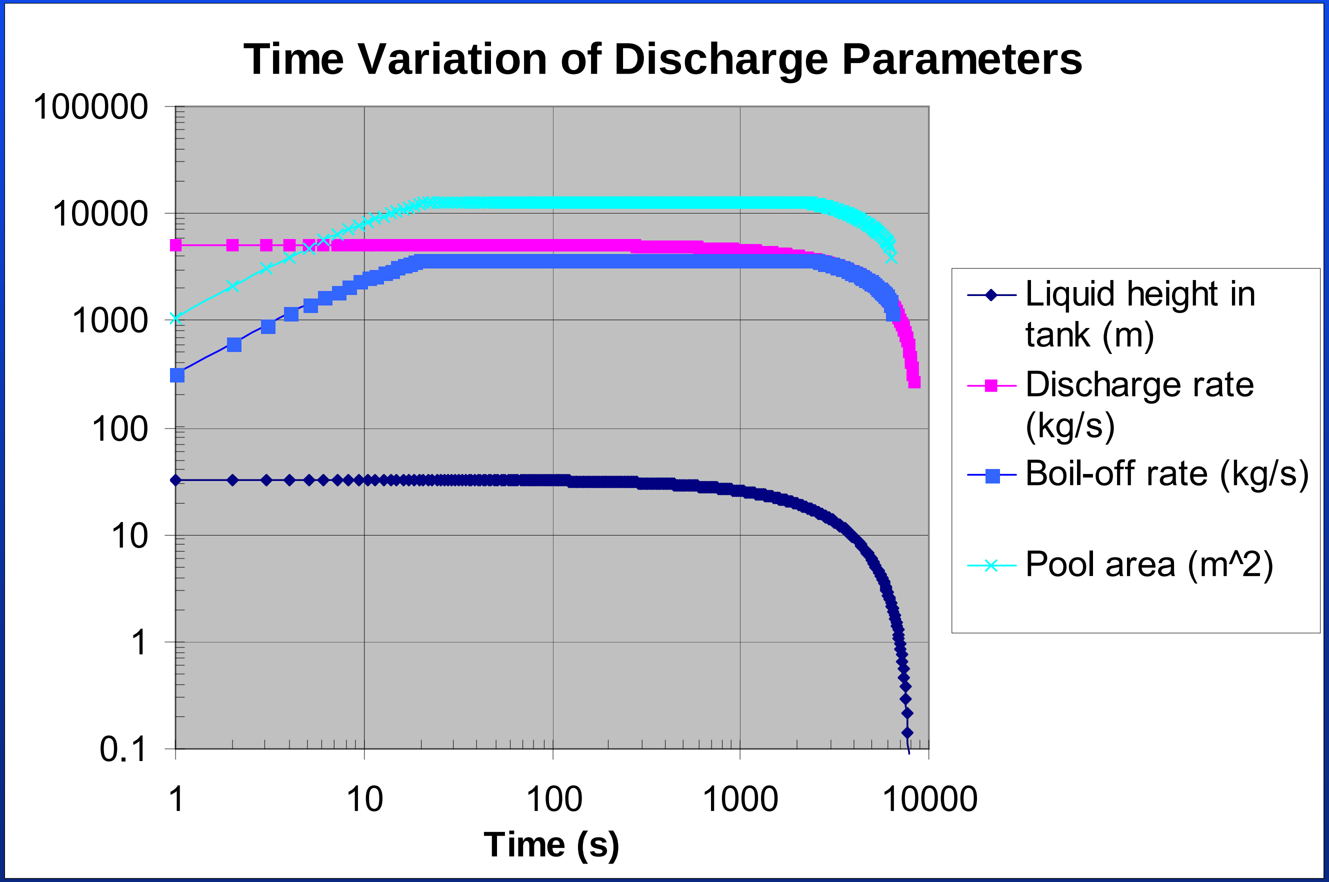
- Boil-off takes place primarily as a result of the heat flow from the subsurface (land or water) and any solar radiation.
  - Solar radiation is generally negligible compared with the heat from the subsurface.
- For spills on land, this holds true until boiling stops due to cooling of the ground to the boiling point of the liquid. Evaporation and evaporative cooling may then take over.
- For spills on unconfined water, there is sufficient water circulation in the vertical that the heat flux to the LNG can be assumed constant over time.
- For spills on confined water, the water surface freezes over, decreasing the heat transfer into the LNG with time.
- The rate of boil-off also depends on the kind of subsurface (e.g., concrete, soil types).

Modelling Boil-off (2)

- Because of the vapour layer between the subsurface and the liquid pool, the heat transfer is limited.
  - It has been shown that the boil-off rate for LNG on water could be up to twice as much as that for pure methane, possibly due to patchy breakdown of this film for LNG (Sandia, 2004).
- If the LNG vapour above the liquid pool is burning, the additional heat from the flames need to be taken into account in modelling boil-off.
- Boil-off flux estimates vary (Sandia, 2004)
  - 0.02 to 0.2 kg/m^2-s for un-ignited pools (experimental),
  - 0.1 to 0.5 kg/m^2-s if the pool is also burning

Modelling results – spill from a 50,000 m^3 LNG tank

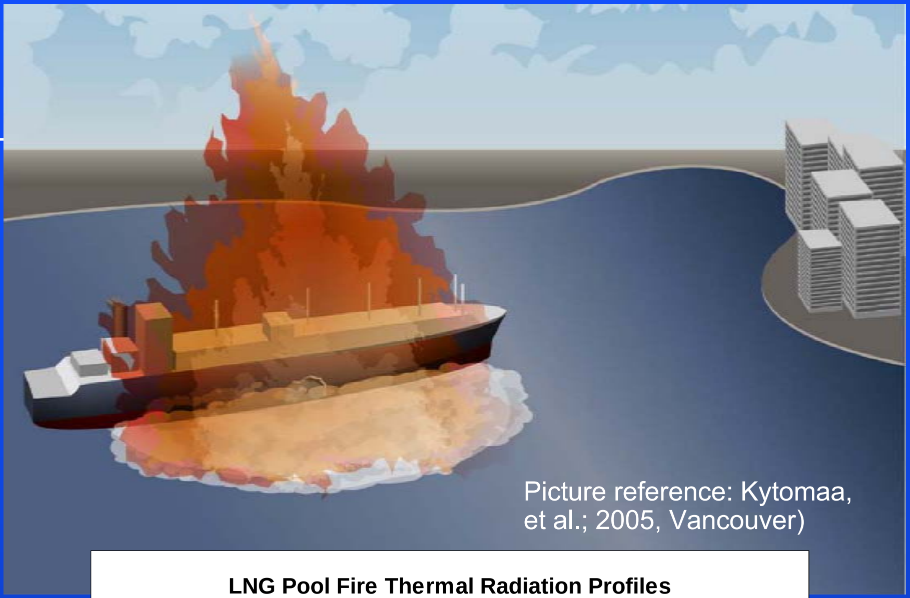
- Hole size: 0.5 m^2
- Critical assumption: boil-off flux 0.3 kg/m^2-s (a burning flux)
- Critical assumption: minimum pool thickness = 1 cm



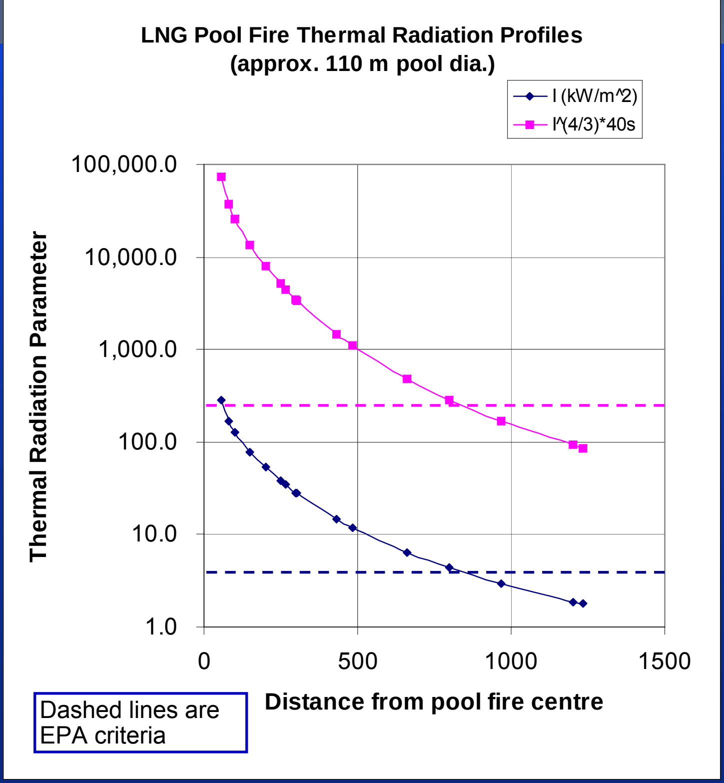
Model: Alp & Associates

Pool Fire Modelling

- If vapour above the liquid pool ignites, it forms a pool fire.
- The thermal radiation exposure zone should be based on 5 kW/m^2 for 40 s exposure equivalent (US EPA criterion).
  - 342 $(kW/m^2)^{(4/3)} \cdot s$
- Typically, point source or solid flame models are used for calculating radiation exposure.
- Estimation of a flame temperature or the radiative energy fraction remain practical challenges.



Picture reference: Kytomaa, et al.; 2005, Vancouver)



Model: Alp & Associates based on CCPS, 1994

Pool Fire Modelling (2)

- A significant component of these models is estimation of the flame height.
  - *Complication*: For very large diameter pools, it is likely that not enough air will penetrate to the centre, resulting in broken up fires.
  - This effect could result in overestimates of hazard zones up to 2 times. (Sandia, 2004)
  - This effect is not accounted for in the hazard models.

Picture reference: Havens, LNG Summit, 2004

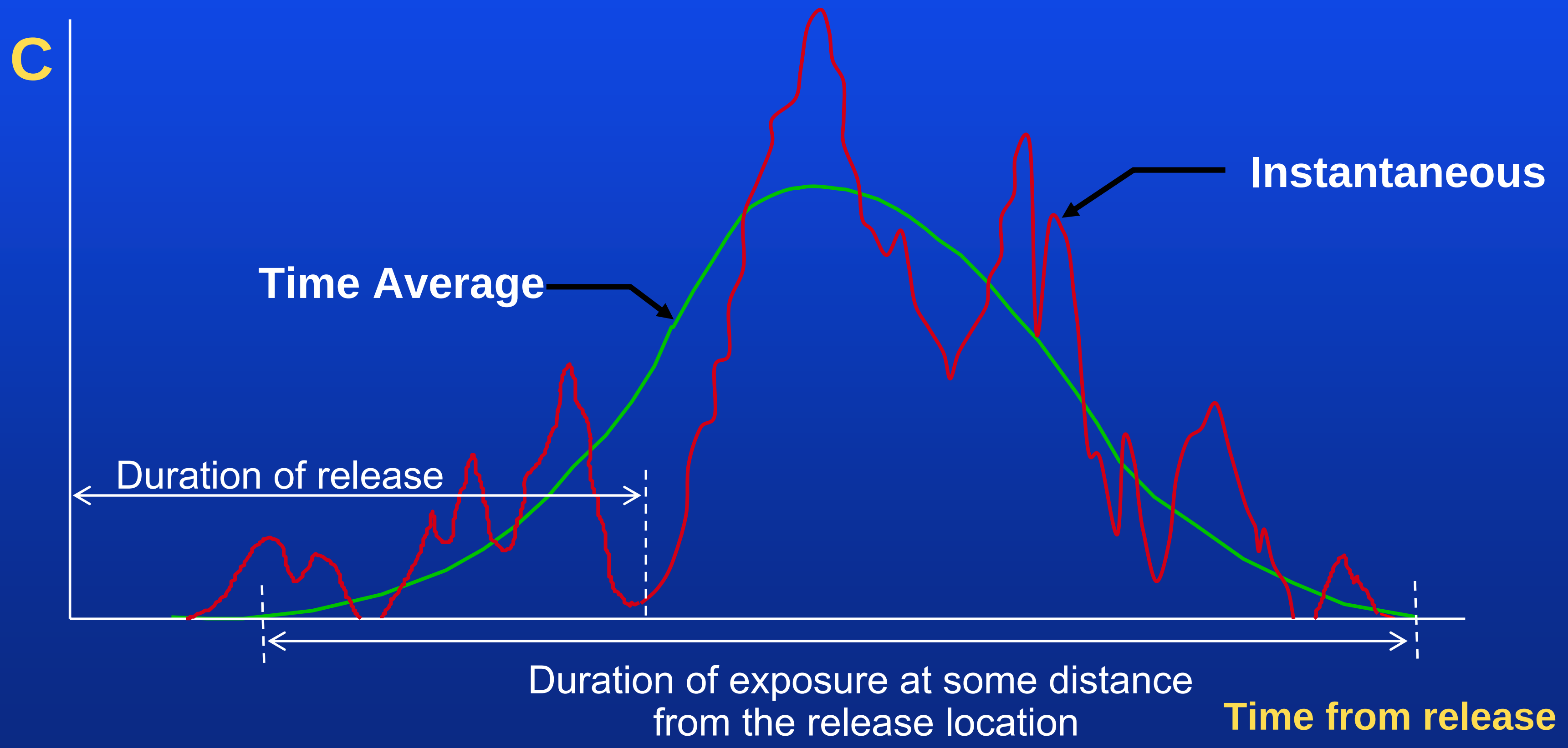
Vapour Cloud Dispersion and Flash fire

- Spills of LNG forms heavier-than-air plumes.
- The three most commonly used models are SLAB, HEGADAS/ DEGADIS, and FEM3
- The author has developed a heavy gas model for Environment Canada in the 1980s based on published HEGADAS formulations for dispersion (and others for spill, spread, and boil-off) (Alp, et al., 1994, J Loss Prev.)


Picture reference: Havens, LNG Summit, 2004

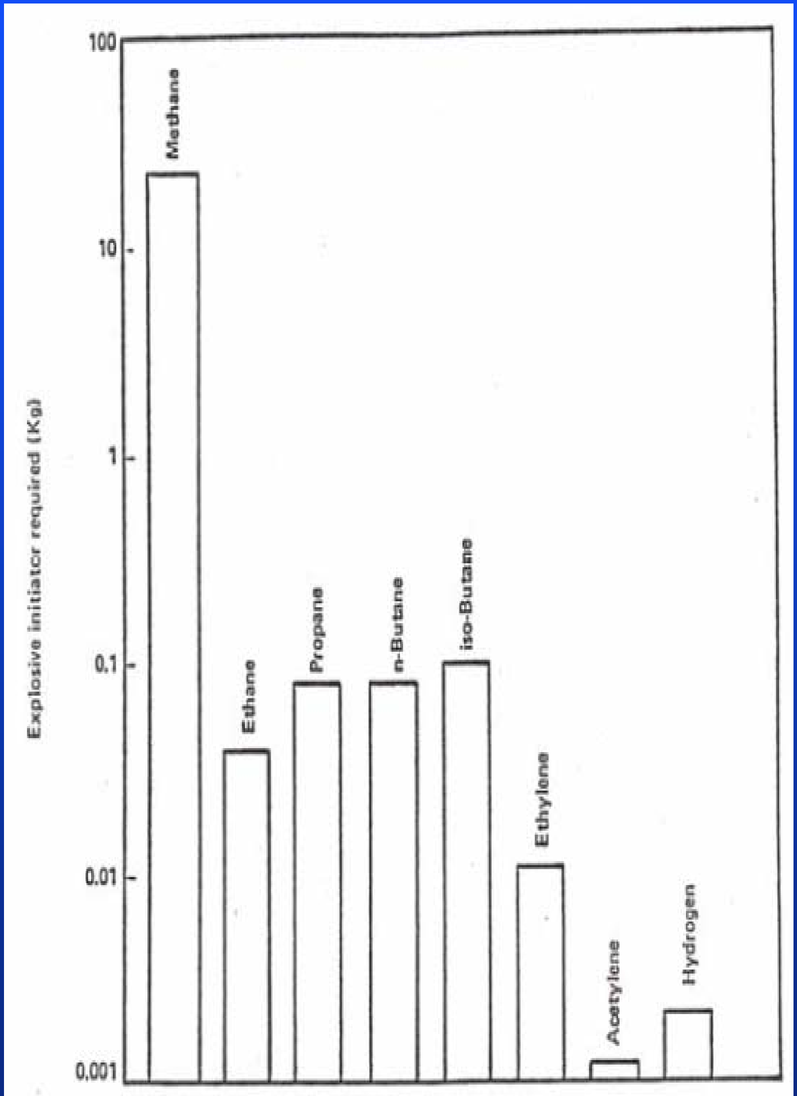
Vapour Cloud Dispersion and Flash fire (2)

- Flash fire exclusion zones are based on 50% of LFL, to take into account potential high concentration pockets in the plume resulting from concentration fluctuations due to turbulence in the atmosphere



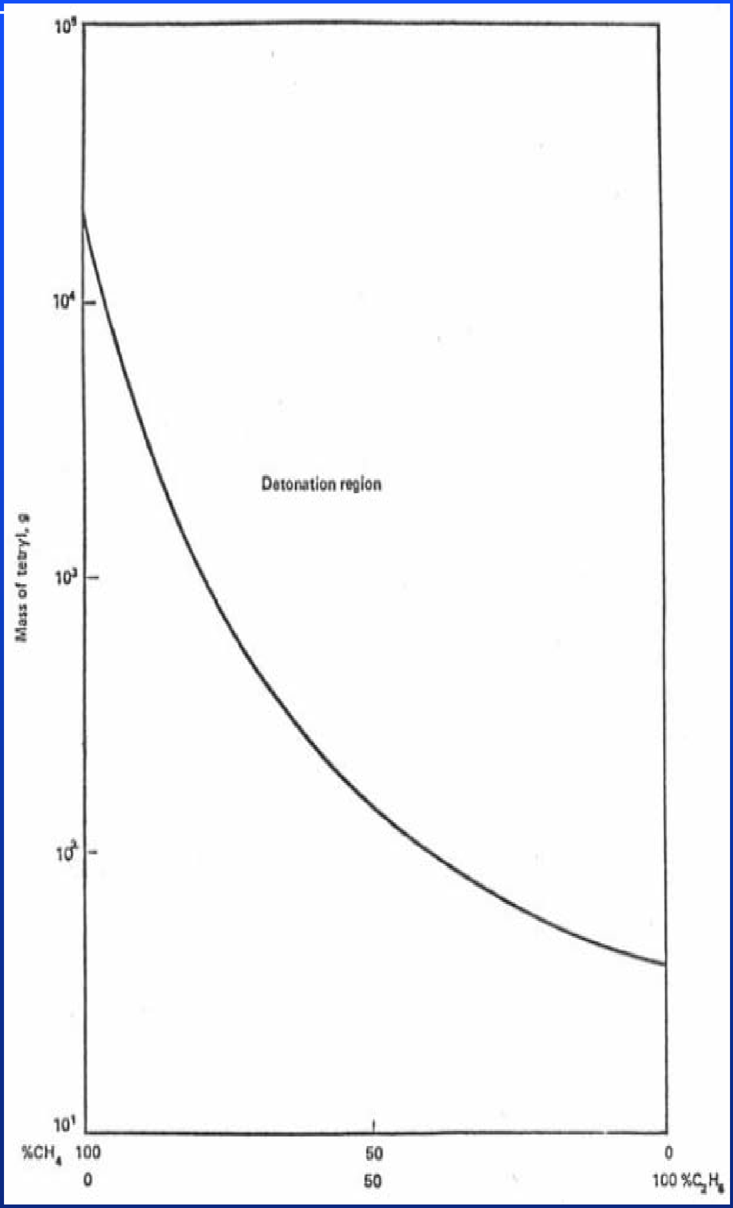
Vapour Cloud Dispersion and Explosion

- Fuel-air mixtures, when ignited, can result in local overpressures.
  - Deflagration or detonation, depending on the speed of flame front and the local overpressures generated.
- Methane-air mixtures are much more difficult to explode than other hydrocarbons such as propane or ethylene.
  - The amount of “initiator” needed to explode a methane-air mixture is several hundred times more than propane and several thousand times more than ethylene (Sandia, 2004)



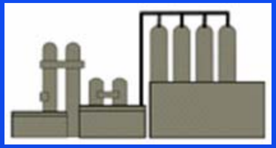
Vapour Cloud Dispersion and Explosion (2)

- The amount of ethane in the LNG is a critical factor in ease of explosion of LNG vapour-air mixtures, an explosion becoming easier with increasing ethane content (Sandia, 2004)
- For an ethane content of approximately 3%, the energy requirement is estimated to be 100 MJ (Bull and Elsworth, 1979)
  - At an LNG facility, an explosion of a building infiltrated by an LNG cloud can provide this energy to the LNG cloud that is around the building.
  - *This is a controversial area regarding the safety of LNG facilities.*

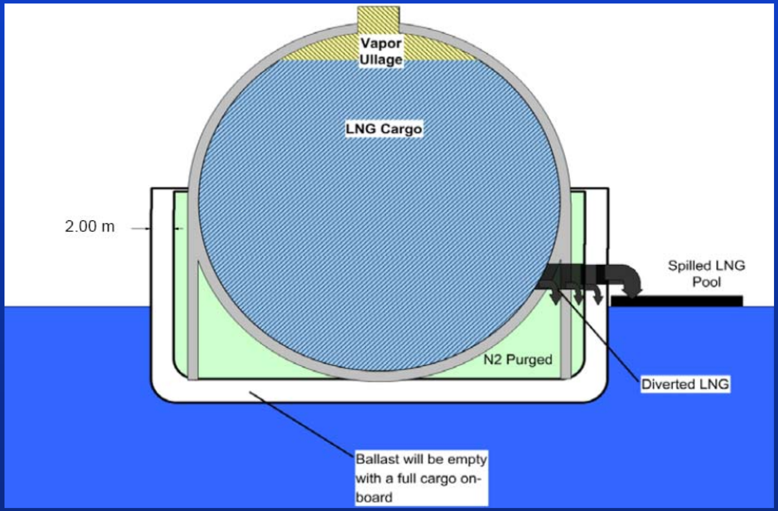


Other Hazards (1)

- In an LNG liquefaction facility hazard assessment, the relatively large amounts of hydrocarbon refrigerants should be taken into account.



- In case of a large spill of LNG from a marine tanker, *could the cryogenic temperatures of the LNG lapping the hull of the tanker result in loss of structural integrity of the hull?*

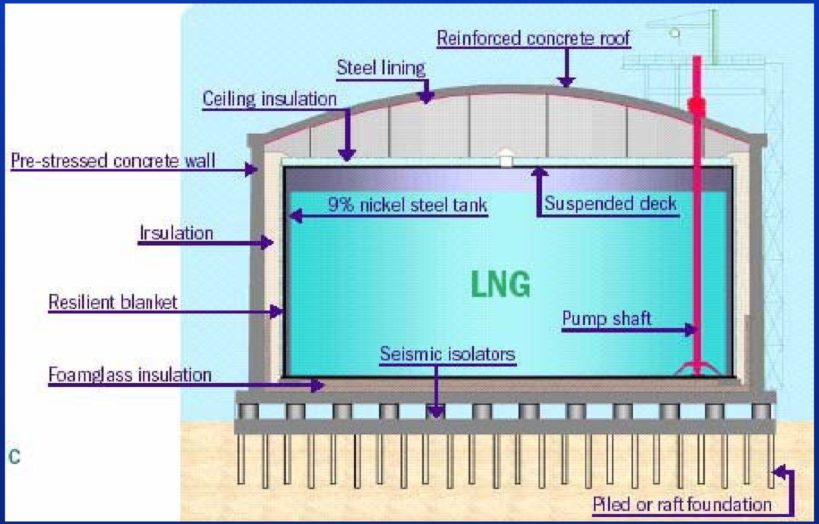


Other Hazards (2)

- Rapid Phase Transition
  - If large volumes of LNG are released on water, it may vaporize too quickly causing a rapid phase transition (RPT).
  - Water temperature and the presence of substances other than methane also affect the likelihood of an RPT. An RPT can only occur if there is mixing between the LNG and water.
  - RPT explosions range from small pops to blasts large enough to potentially damage lightweight structures.
  - *Could RPT explosions be large enough to cause loss of integrity of marine tanker hulls?*

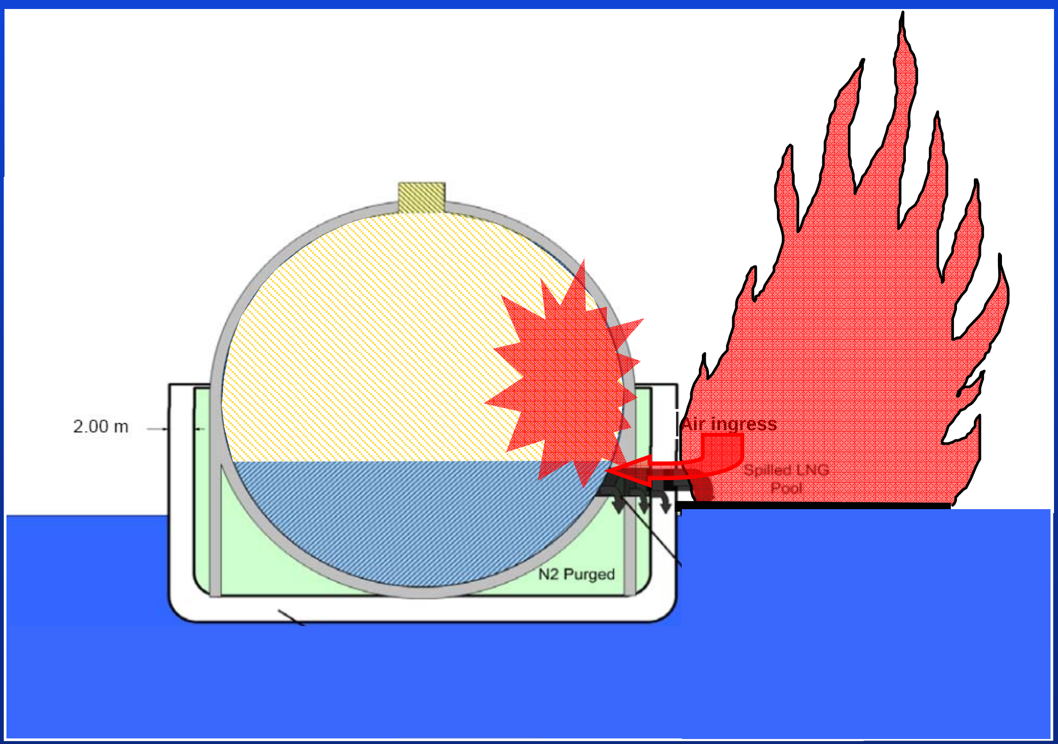
Other Hazards (3)

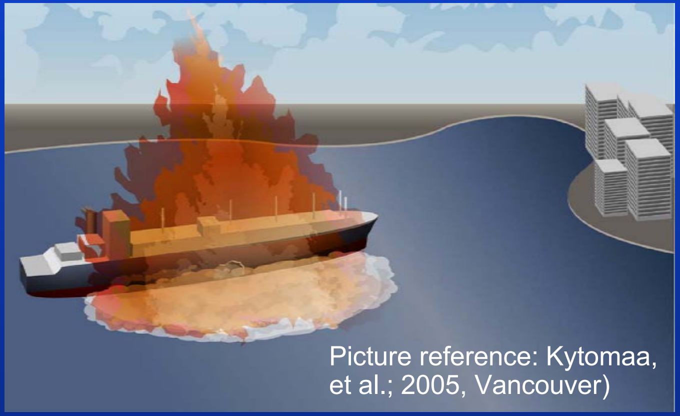
- Rollover
  - When LNG supplies of multiple densities are loaded into a tank one at a time, they do not mix at first; they layer themselves.
  - As the lower LNG layer is heated by normal heat leak, it changes density until it finally becomes lighter than the upper layer.
  - At that point, a liquid rollover would occur with a sudden vaporization of LNG that may be too large to be released through the normal tank pressure release valves.
  - At some point, the excess pressure can result in cracks or other structural failures in the tank.
  - To prevent stratification, operators unloading an LNG ship measure the density of the cargo and, if necessary, adjust their unloading procedures accordingly.
  - LNG tanks have rollover protection systems, which include distributed temperature sensors and pump-around mixing systems.



Other Hazards (4)

- Considering that there will be air ingress into a tank during a spill from a hole on its size, if there is a large fire going on outside, *could pockets of ignited gas also get into the tank, especially after the liquid level has dropped to or near the hole?*
  - *Could there be a flammable atmosphere in the vapour space to cause a confined explosion inside the tank? Could that damage the surrounding structure, resulting in a larger release?*





Picture reference: Kytomaa, et al.; 2005, Vancouver)

Conclusions

- A large amount of information is available about LNG hazards
- Some practical challenges exist in modelling these hazards
- Large scale field experiments are needed to reduce the uncertainty around
  - "glug-glug" effect on spill rates,
  - breakup of large pool fires,
  - rapid phase transition explosions,
  - cryogenic impact on tanker hulls, and
  - vapour cloud explosions.

THANK YOU!