Problem of Boil - off in LNG Supply Chain

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This paper examines the problem of evaporation of Liquefied Natural Gas (LNG) occurring at different places in the LNG supply chain. Evaporation losses in the LNG supply chain are one of the key factors for LNG safety, technical and economic assessment. LNG is stored and transported in tanks as a cryogenic liquid, i.e. as a liquid at a temperature below its boiling point at near atmospheric pressure. Due to heat entering the cryogenic tank during storage and transportation, a part of the LNG in the tank continuously evaporates creating a gas called Boil-Off Gas (BOG), which changes the quality of LNG over time. The general methods of handling and utilization of the Boil-Off Gas at different points in the LNG supply chain are presented. Attention is given to the issue of LNG energy content transferred during loading and unloading of LNG tankers, as well as to the Boil-Off Gas generated by evaporation of the cargo during maritime transport. The results presented in the paper have been derived from the scientific research project 250 - 2502209 - 2366 „Management of Ship Power Systems under Fault Conditions and Failure" supported by the Ministry of Science, Education and Sports of the Republic of Croatia.

KEY WORDS:
~ Liquefied
~ Natural gas
~ Supply chain
~ Boil-off gas
~ Gas utilization and use
~ LNG energy content

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1. INTRODUCTION

Owing to the ever increasing share of the natural gas in the world consumption of power sources, international maritime traffic with liquefied natural gas is continuously growing, with even greater expectations for the future.

A large portion of natural gas is located far from large customers. Most of the international trade in natural gas, depending on the distance, takes place by pipelines and LNG ships in liquid form, and rarely in special heat insulated tanks by rail or road transportation. Due to lower investment costs, the transportation of gas by pipelines is preferred up to distances of about 2000 km. After that, the costs grow significantly faster than the costs of transportation of gas in liquid form, with a tendency for change if advances in technology are made. The LNG market has greater flexibility because, in general, the capacity of one exported unit may cover the capacity needed for two or three imported units.

Furthermore, it is clear from the current worldwide liquefied natural gas market that LNG tends to be exported to regions where gas prices are higher (Asia, USA and Europe), and this flexibility does not exist or exists to a lesser extent in transportation by pipelines.

LNG has been steadily increasing its market share in the global gas trade. According to data from the IEA (International Energy Agency) statistical review for 2010, the global LNG market now accounts for about 9% of demand for natural gas or 299 billion m^3.

Liquefied natural gas is stored and transported in tanks as a cryogenic liquid, i.e. as a liquid at a temperature below its boiling point. Just like any liquid, LNG evaporates at temperatures above its boiling point and generates BOG. Boil-off is caused by the heat ingress into the LNG during storage, shipping and loading/unloading operations. The amount of BOG depends on the design and operating conditions of LNG tanks and ships.

The increase in BOG increases the pressure in the LNG tank. In order to maintain the tank pressure within the safe range, BOG should be continuously eliminated. In the LNG supply chain, BOG can be used as fuel, re-liquefied or burned in a gasification unit. Furthermore, the more volatile components (nitrogen and methane) boil-off first, changing LNG composition and quality over time. This phenomenon, known as ageing, is especially important in LNG trade since LNG is sold depending on its energy content, i.e. specification at the port of unloading determined depending on the volume of the LNG transferred, its density and heat value.

This paper deals with the problem of boil-off in the LNG supply chain and its main causes. The general methods of handling and utilization of BOG at different points in the LNG supply chain are presented. Furthermore, the paper presents a calculation method used in the LNG industry to determine LNG energy content transferred during loading and unloading of LNG tankers.

2. FEATURES OF LNG AND ITS SUPPLY CHAIN

Liquefied natural gas is a liquid substance, a mixture of light hydrocarbons primarily composed of methane (CH_4, 85-98% by volume), with smaller quantities of ethane (C_2H_6), propane (C_3H_8), higher hydrocarbons (C4+) and nitrogen as an inert component. The composition of LNG depends on the traits of the natural gas source and the treatment of gas at the liquefaction facility, i.e. the liquefaction pre-treatment and the liquefaction process. It can also vary with storage conditions and customer requirements (Benito, 2009; British Petrol and International Gas Union, 2011).

Namely, LNG producers determine the quality of their LNG based on the composition of field gas and more importantly, market demand.

Liquefied natural gas is a colourless, odourless, non-corrosive and non-toxic liquid, lighter than water. Typical thermo-physical properties of LNG are presented in Table 1.

Table 1.
Thermo-physical properties of LNG.

Parameter	Value
Boiling point	-160°C do -162°C
Molecular weight	16 – 19 g/mol
Density	425 - 485 kg/m^3
Specific heat capacity	2,2 – 3,7 kJ/kg/°C
Viscosity	0,11 – 0,18 mPa•s
Higher heat value	38 - 44 MJ/m^3

LNG may be classified in accordance with several criteria: Density, Heat Value, Wobbe Index, Methane or Nitrogen amount, etc. The parameter most commonly used for its classification is density. Accordingly, we differentiate between heavy, medium or light LNG's. The typical composition and density of three typical LNG qualities are depicted in Table 2.

Table 2.
Classification of LNG by density (Sedlaczek, 2008).

Composition (%)	LNG Light	LNG Medium	LNG Heavy
Methane	98.00	92.00	87.00
Propane	1.40	6.00	9.50
Propane	0.40	1.00	2.50
Butane	0.1	0.00	0.50
Nitrogen	0.10	1.00	0.50
Density (kg/m^3)	427.74	445.69	464.83

The LNG supply chain consists of extraction and production of natural gas, liquefaction, marine transportation of LNG, and LNG storage, re-gasification and delivery of natural gas to consumers.

The extraction of natural gas from the earth's surface is the first step in the supply chain and includes drilling and gas extraction. The gas produced can come from a gas field (non-associated gas) or be produced along with oil (associated gas). The distinction between associated and non-associated gas is important because associated gas must have liquefied petroleum gas (LPG) components (i.e., propane and butane) extracted to meet the heat value specifications of the LNG product. Natural gas derived directly from the gas field is called "raw" gas. Such gas is associated with a number of other compounds and gases that may have an adverse effect on liquefaction and combustion.

The produced natural gas is transported by pipelines from gas fields to a liquefaction facility, located in large areas along the coast. One of the primary purposes of liquefaction plants is to ensure the consistent composition and combustion characteristics by cooling and condensing natural gas to allow its loading onto tankers as LNG and delivery to the end user. Therefore, their design must include several parallel processing modules (trains) for the preparation and liquefaction of natural gas, LNG storage tanks, facilities for loading LNG tankers, general purpose facilities, i.e. sea water pumping stations, electricity generation plants, nitrogen production plants, compressor stations, workshops and system security.

The technical processes of purification of gas from harmful components to obtain gas acceptable for use and liquefaction are performed in the preparation trains. Therefore the following need to be removed prior to liquefaction: components that would freeze at cryogenic process temperatures during liquefaction (carbon dioxide-CO_2, water and heavy hydrocarbons), components that must be removed to meet the LNG product specifications (hydrogen Sulfide-H_2S), corrosive and erosive components (mercury), inert components (helium and nitrogen) and oil. Typical specifications of gas for liquefaction are less than 1 ppm of water, less than 100 ppm CO_2 and less than 4 ppm H_2S.

Following the removal of most contaminants and heavy hydrocarbons from the feed gas, the natural gas is subjected to the liquefaction process. Natural gas is converted to its liquefied form by the application of refrigeration technology making it possible to cool the gas down to approximately -162°C when it becomes a liquid.

The produced LNG is stored in cryogenic tanks below the boiling point at the pressure of 0.05-0.2 bar until an LNG tanker arrives to transport the product. Upon the arrival of the tanker, LNG from the storage tank is loaded from the loading plant into the LNG tanker, which will transport the gas to the receiving terminal. For safety reasons, storage tanks at loading and receiving terminals in which liquefied gas is stored usually consist of two tanks designed to be fully loaded. The inside of the container in which liquefied gas is stored is usually made of stainless steel resistant to low temperatures. The outer tank is made of pre-stressed concrete and designed to fully contain LNG in case of spillage and be fully loaded in the event of damage to the inner tank. Apart from safety aspects, LNG tanks are also designed to minimise the ingress of heat into the tanks to prevent the boiling (evaporation) of a fraction of the LNG. The usual tank volumes range from 80.000 to 160.000 m^3.

Step three in the LNG supply chain is the transportation of liquefied natural gas to the receiving terminal. Liquefied natural gas is carried by specially designed ships, LNG tankers, in specially insulated tanks inside the hull at near atmospheric pressure, at the temperature of -163°C. In these tanks, the cargo is kept fully refrigerated using insulation and the effect of a small amount of evaporated cargo generated during the voyage. LNG tankers are a combination of classic ship design, special materials and advanced containment systems for handling cryogenic cargo. Today there are four containment systems in use on these vessels. Two of the designs are of the self supporting type, namely Moss spherical tanks and SPB tanks (Self supporting Prismatic type B tank). The other two are of the membrane type and today their patents are owned by Gaz Transport & Technigaz (GTT). Operating pressure in containment tanks ranges between 0.05 and 0.12 bar, at which LNG cargo reaches the equilibrium temperature corresponding to the operating pressure. All LNG tankers have double hulled design, which greatly increases the reliability of cargo containment in the event of grounding and collision.

The majority of existing LNG tankers have the cargo capacity ranging between 120,000 m^3 and 150,000 m^3, with some ships having the storage capacity of up to 264,000 m^3. Due to the required high-capacity, re-liquefaction plants for evaporated cargo are generally not installed into these vessels. Since evaporated cargo provides a source of clean fuel, most LNG tankers have a steam-turbine propulsion system. The reason is high reliability and safe use of evaporated cargo that burned in the boilers. Q-flex type tankers having the capacity of 210,000-216,000 m^3 and Q-max tankers having the capacity of 260,000-270,000 m^3 constructed with re-liquefaction plants are exceptions. These vessels are intended for long distance transportation of liquefied natural gas, for example from Qatar to the United Kingdom or the United States. Loading and unloading rates vary between 12,000 and 14,000 m^3 per hour depending on the size of the LNG tanker. During loading, according to IMO (International Maritime Organization) requirements each tank is filled to 98% of its total volume. The remaining 2% of storage volume is required to prevent any entry of the liquid into ventilation pipeline and from spilling into the surrounding hull structure. Between 98.5 and 99% of the cargo is unloaded. The remaining quantity of LNG remaining on board after unloading, called a "heel", is used during the ship's ballast voyage to keep the tanks cold, as well as fuel for the propulsion system and the ship's energy system.

The receiving terminal (sometimes called a re-gasification facility) is the fourth and last component of the LNG supply chain. Its basic task is to receive and unload liquefied natural gas from LNG tankers, store, vaporise LNG and distribute the gas into the distribution network (Dundović et al., 2009). The receiving terminal is designed to deliver the specified quantity of gas into the distribution pipeline and maintain a reserve quantity of LNG. Therefore, its design must include the following elements: a system for receiving and discharging LNG tankers, storage tanks, a re-gasification plant, a control system to control the LNG boil-off gas, supplying their own consumption (utilities), equipment and facilities support. Since natural gas is odourless, the odourisation of the re-gasified natural gas is required in many regions and countries before its distribution to consumers. An atypical odorant is mercaptan or tetrahydrothiophene (British Petrol and International Gas Union, 2011).

3. BOIL-OFF IN THE LNG SUPPLY CHAIN

Liquefied natural gas is stored and transported in tanks as a cryogenic liquid, i.e. liquid at a temperature below its boiling point. Due to heat leakage into LNG and its cryogenic nature, during storage, shipping and loading/unloading modes LNG continuously evaporates. Inside the tanks, LNG exists in an equilibrium between a thermodynamic liquid and vapour, depending on the given pressure and temperature. Since pressure in the tank is low, the multi-component mixture system acts in keeping with Raoult's law (Figure 1). In Figure 1, p is the total vapour pressure of the vapour phase, p_i^{sat} the saturation pressure of a pure component i in the liquid phase at temperature T, y_i and x_i the fraction of component i in the vapour phase and the liquid phase and K_i the dimensionless equilibrium ratio. Therefore, any heat ingress causes evaporation of the liquid on its surface without any visible bubbles. Namely, to keep the temperature constant and appropriate for tank pressure, LNG will cool itself (auto-refrigeration) by evaporating a small portion of the LNG and generated BOG (Dimopoulos and Frangopoulos, 2008; British Petrol and International Gas Union, 2011).

Vapor

at T, p, y_i

$$y_i \cdot p = p_i^{sat}(T) \cdot x_i$$

$$K_i = \frac{p_i^{sat}(T)}{p} = \frac{y_i}{x_i}$$

LNG

at T, p^{sat}, x_i

Figure 1.
General criteria for the vapour-liquid equilibrium for LNG as multi-component mixture.

The quantity of BOG depends on the design and operating conditions of storage tanks and a ship's cargo tanks. The LNG supply chain with boil-off source is shown in Figure 2.

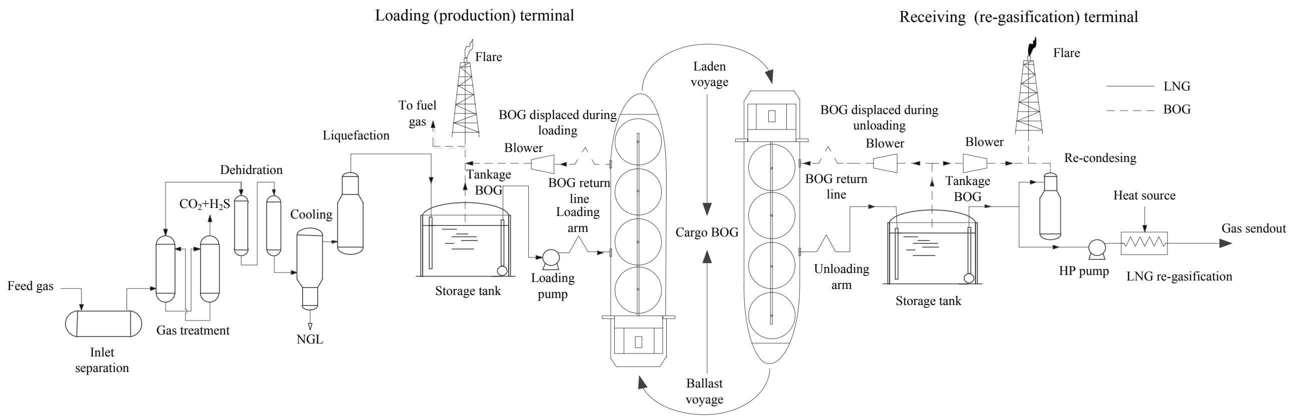

Figure 2.
LNG supply chain and boil-off source.

The increase of BOG in storage and ship's tanks increases the LNG operating tank pressure. In order to maintain the operating tank pressure within the safe range, BOG should be continuously removed. At the loading terminal, BOG is usually used as fuel in the liquefaction plant production process. At receiving terminals, it is either burned or sent to the re-gasification plant using BOG compressors.

During the journey of an LNG tanker, depending on the type of the propulsion system, BOG can be utilized as fuel, re-liquefied or burned in a gasification unit. Since the boiling points of different components of LNG widely vary, from -196ºC to +36ºC, the rates of evaporation of more volatile components, such as Nitrogen and Methane, are higher than those of heavier components, i.e. ethane, propane and other higher hydrocarbons (Sedlaczek, 2008). Therefore, the quality and properties of LNG steadily change over time. This slow but continuous process is called ageing or weathering of LNG (Faruque, Zheng Minghan and Karimi, 2009; Głomski and Michalski, 2011; Benito, 2009; British Petrol and International Gas Union, 2011).

In the LNG supply chain, LNG is sold at the receiving terminal, depending on its energy content typically measured in GJ, GWh or MMBTU. Ship charterers, mostly oil & gas or energy companies, buy LNG cargo at the loading terminal at a certain production cost, i.e. Free On Board (FOB) price and sell LNG at the receiving terminal at a higher Cost-Insurance-Freight (CIF) price which includes the cost of fuel, insurance, port charges and charter rate. Since BOG reduces the quantity of cargo delivered by LNG tankers and increases the heat value of LNG in storage and ship's tanks, the quantity of BOG is a key factor for the technical and economic evaluation of the LNG supply chain.

3.1. Boil-off of LNG in storage tanks during holding mode

The holding mode is referred to as the period between loading/unloading of LNG tankers (Sedlaczek, 2008). At loading and receiving terminals, LNG is stored in cryogenic storage tanks at standard operating pressure ranging from 0 to 0.15 bar above atmospheric pressure. There are two main sources of boil-off gas during storage of LNG in holding mode, namely heat ingress into storage and pipes from the surroundings and changes in the ambient (barometric) pressure.

Heat ingress from the surroundings means that BOG is generated continuously in the tanks. In order to reduce boil-off, storage tanks have multi-layered insulation that minimizes heat leakage. The driving force for heat ingress into an LNG tank is the difference between the outside temperature and tank temperature. Due to the large temperature differences between the medium and the environment, the heat ingress into the LNG through floor, walls and roof of storage tanks (Figure 3) may occur in three ways: by conduction, by convection and by radiation. Storage tanks are typically designed to reduce the ingress of heat from the surroundings and solar heating so that vaporisation is less than 0.05 % of the total tank content per day, although this can vary from 0.02 to 0.1% (British Petrol and International Gas Union, 2011).

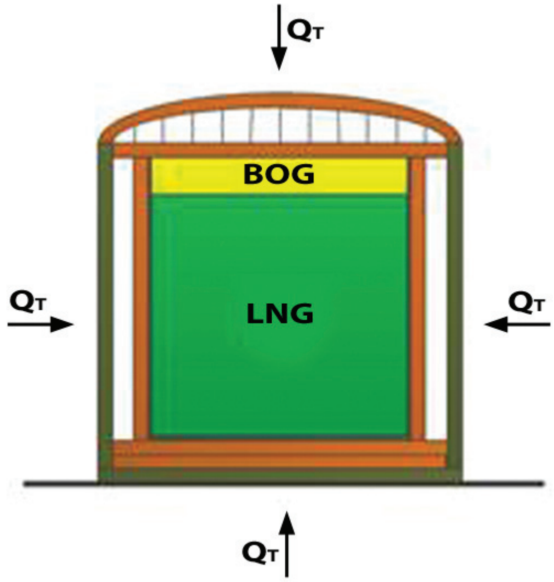

Figure 3.
Heat ingress into storage tank.

At loading and receiving terminals, a typical loading/unloading system consists of loading/unloading arms, circulation pipelines transferring LNG from ships to storage tanks and vice versa, pumps, etc. During the holding mode, a small portion of LNG circulates through the pipelines to maintain their cryogenic temperature. Circulating through the pipeline, LNG absorbs the heat from the surroundings and the heat generated from pumping, turbulent flow, and line friction. The absorbed heat generates additional BOG in storage tanks. This quantity of BOG depends on the length of the pipeline and the power of the pumps (Faruque et al., 2009; Sedlaczek, 2008; British Petrol and International Gas Union, 2011).

In storage tanks, a significant increase in the boil-off rate can cause a drop in atmospheric pressure. As atmospheric pressure drops, tank pressure and bubble point temperature of LNG decrease. To equilibrate with this lower pressure, the temperature of the LNG in the tank has to decrease by approximately 0.1°C for every 0.01 bar drop (Sedlaczek, 2008). This favours greater boil-off because the only way to decrease the temperature in the tank is to release some of the liquid into gas. A drop in atmospheric pressure only has effect if it is rapid, because it is only then that it can cause a significant increase in the boil-off rate from the storage tank.

BOG produced during holding mode in storage tanks is usually called tankage BOG (Faruque et al., 2009). When heat is added into LNG, the vapour pressure inside the tank increases. In order to maintain the tank pressure within the safe range, tankage BOG should be removed by compressors.

At loading terminals, BOG is usually compressed and exported to the plant fuel system. At receiving terminals, BOG is compressed in a re-gasification plant where it can be compressed and exported as gas or liquefied and exported as gas. In case of condensation problems, the vapour is burnt.

3.2. Boil-off during loading/unloading mode

The loading/unloading mode is the period when an LNG tanker is moored to the jetty at loading and receiving terminals and connected to onshore storage tanks with loading/unloading arms and insulated pipelines.

Modern LNG terminals are designed to accept LNG-tankers having the capacity from 87,000 m^3 to 270,000 m^3. Loading or unloading facility is of a size compatible with the standard loading rate of 10,000-12,000 m^3 per hour, allowing LNG tankers to load or unload 125,000-270,000 m^3 within 12-18 hours, depending on the size of the ship (Dundović et al., 2009; Faruque et al., 2009).

BOG generated during loading and unloading of an LNG tanker is typically 8-10 times greater than tankage BOG (Benito, 2009). The reason is mainly the return of vapour from the ship's or storage tanks. The main sources of BOG released during the ship loading/unloading process are presented in Table 3.

LNG tanker is loaded by the terminal's pumps and unloaded by the ship's pumps. During the loading/unloading operations, large quantities of LNG are pumped from the ship in a short time. This causes rapid change of pressure. During the loading process, the loaded LNG displaces an equivalent quantity of vapour in the ship's empty cargo tanks. In order to maintain the cargo tanks at their operating pressure, the displaced vapour from the ship's cargo tanks is returned to the storage tank via the vapour return line. During the cargo unloading process, the vapour pressure of the boil-off gas generated during loading and unloading is of short duration at the high flow rate usually taking 12-18 hours, depending on the terminal's loading/unloading capacity. This flow rate depends on the pressure and temperature differences between the ship's tanks and storage tanks.

LNG tanker cargo tanks are maintained by returning vapour from the storage tanks (displaced by the terminal's blowers) to fill the ullage space in tanks. With this balanced system, under normal circumstances no BOG will be released to the atmosphere from ship or shore.

The energy used by the terminal's and ship's pumps greatly influences the boil-off rate. A typical LNG tanker having the capacity of 130,000 m^3 requires over 3,000 kW of pumping energy. During pumping, due to friction and turbulence, almost all of this energy is converted into heat adsorbed by the LNG. This large amount of heat is sufficient to heat the LNG by as many as 0.5°C. To provide for the new tank conditions, LNG cools itself down by evaporating a small portion of LNG. This process is called auto - refrigeration and can generate approximately 20,000 kg per hour of BOG (Sedlaczek, 2008). Although the circulation pipelines are well insulated, some heat from the surroundings always leaks into LNG. The extent of the heat leak depends on pipeline length. If the pipeline is relatively short (under 1 km), the heat components from LNG pumping and heat leaks into pipelines are relatively small and generate typically around 5% of total BOG. In case of greater lengths, there is a significant increase in the quantity of BOG. For example, if the pipeline is 7 km long, the quantity of BOG generated by these heat components is estimated at 45% of total BOG (British Petrol and International Gas Union, 2011).

Table 3.
Main factors affecting the quantity of BOG released during the ship loading/unloading process.
Source: British Petrol and International Gas Union, (2011).

BOG generated during loading process	BOG generated during unloading process
• Vapour return from ship's tanks. • Heat transferred to LNG by loading pumps. • Heat leak into LNG from pipes and equipment. • Cooling down of the ship's manifold and loading arms. • Cooling down of jetty lines prior to loading if not continuous. • Mixing of loaded LNG with the initial amount of LNG (heel). • Cooling down of ship's tanks if necessary.	• Vapour return to ship's tanks. • Heat transferred to the LNG by the ship's pumps. • Heat leak into the LNG through the pipes and equipment. • Higher ship's operating pressure than the LNG storage tank . • Cooling down the ship's manifold and unloading arms prior to unloading. • Cooling down of jetty lines prior to unloading if not continuous. • Mixing of unloaded LNG with existing stock of different quality.

If a ship's tanks are warm, they need to be cooled down prior to loading. The cooling down of a ship's tanks may be required prior to loading if an LNG tanker is returned with insufficient heel, after dry-docking, off-hire or during initial commissioning. The cool down is carried out by initial quantities of LNG, which is evaporated when it comes into contact with the warm sides of the tanks. In this case, the loading process takes longer.

During the unloading of an LNG tanker, differences in operating pressures between the ship's and the terminal's storage tanks can also influence the quantity of BOG. The LNG cargo attains an equilibrium temperature dependent on the cargo tank pressure. If operating pressure in the ship's tanks is by 0.01 bar higher than in the storage tank, the temperature of LNG in cargo tanks will be higher by approximately 0.1°C than in the storage tank. To establish a new equilibrium, a small portion of the LNG in the storage tank will be evaporated to cool itself down. For example, if the absolute pressure of an operating cargo tank is 1.060 bar and the absolute pressure of an operating storage tank is 1.050 bar, than at the typical unloading rate of 12,000 m^3 per hour, the difference of 0.01 bar will result in a 3,600 kg per hour boil-off (Sedlaczek, 2008). The mixing of unloaded LNG with existing stock of a different quality at LNG receiving terminals can cause stratifications and rollover processes in storage tanks. Stratification refers to the formation of LNG layers of different densities within LNG storage tanks. Rollover refers to the spontaneous rapid mixing of layers and release of LNG vapours from a storage tank caused by stratification.

During the ageing (weathering) process, the density of LNG gradually increases in the storage tanks. When LNG of different composition (density) is injected into the tank, LNG may stratify. The stratification in the tank is characterized by two homogenous layers of different density and temperature, separated by a buffer zone, called the thick interface layer. The upper layer is composed of the liquid less dense than the bottom layer. In the tank, these two layers may form a steady interface layer, i.e. stable stratification. However, due to the ingress of heat into LNG in the tank, the lower layer can eventually reach a temperature at which its density is reduced to such an extent that the interface becomes unstable. This process is intensified by the movement of heavier components from the lower layer to the top layer and the result is a sudden release of heat in the lower layer and an increase in vaporization. This leads to a spontaneous rapid mixing or rollover. In case of rollover, if LNG in the bottom layer is superheated due to the conditions in the tank's vapour space, the rollover can be accompanied by a transient high rate of vapour production that can be 10 to 30 times greater than the tank's normal gas boil-off rate and over-pressurisation of the tank.

The knowledge of LNG quality at any time before unloading helps the operators of the receiving terminals to take, in advance, actions which will prevent stratification and consequently, the rollover.

3.3. Boil-off during ship's voyage

Most of BOG is generated during transportation of LNG by ships. BOG released during the voyage of an LNG tanker may occur due to the following reasons (Faruque et al., 2009; Głomski and Michalski, 2011; Sedlaczek, 2008; British Petrol and International Gas Union, 2011):

- the ingress of heat into cargo tanks due to the difference between the temperature in the cargo tanks and temperature of the environment,
- due to the cooling of a ship's tanks during ballast voyages, achieved by occasional spraying of LNG in the upper part of the tank,
- due to the sloshing of cargo in partially filled tanks due to the action of waves, causing friction on the inner wall of the tank creating an additional thermal effect.

Therefore, the quantity of BOG during a ship's voyage changes depending on the changes in ambient temperature, sea temperature, sea roughness and cargo tank's contents.

Heat ingress is the main reason for the generation of BOG on ships. In maritime transportation of LNG, the quantity of evaporated cargo is normally presented as loss expressed as a percentage of total volume of liquid cargo during a single day, i.e. as Boil-Off Rate (BOR). This value can be calculated by the expression:

$$BOR = \frac{V_{BOG} \cdot 24}{V_{LNG} \cdot \rho} = \frac{Q \cdot 3600 \cdot 24}{\Delta H \cdot V_{LNG} \cdot \rho} \cdot 100 \quad (1)$$

where BOR is in %/day, V_{BOG} volume of BOG in m^3/s, V_{LNG} volume of LNG in cargo tanks in m^3, ρ density of LNG in kg/m^3, Q heat exchange in W, and ΔH latent heat of vaporisation in J/kg.

Typical BOR caused by heat ingress for newer LNG tankers ranges from 0.10 to 0.15% for laden (loaded) voyage and from 0.06 to 0.10 % for ballast voyage (Głomski and Michalski, 2011; Sedlaczek, 2008; International Group of Liquefied Natural Gas Importers, 2011).

Cooling of a ship's tanks during ballast voyages is used to reduce the growing temperatures in cargo tanks. The cooling is achieved by sporadic spraying of LNG into the top part of the tank by pumping LNG from the bottom of the tank. LNG in contact with the warm sides of the tank evaporates and generates BOG.

In rough seas, hull movement causes the sloshing of LNG in the partially filled cargo tanks. Sloshing transfers kinetic energy from the waves into cargo tanks, causing friction and heating effect. This additional heating effect produces BOG.

During a ship's voyage BOG can be utilized as fuel, re-liquefied or burned in a gasification unit. Since BOG mostly consist of methane, it is lighter than air in ambient temperature. This allows the safe handling and utilization of BOG. Therefore, LNG is only liquid gas cargo allowed by IMO to be used as a fuel for ship's propulsion and energy systems (McGuire and White, 2000). Due to the simplicity of burning BOG in boilers and high reliability of steam turbine propulsion systems, a majority of LNG tankers are powered by steam turbines.

The continuous growth of LNG marine transportation caused a rapid increase of the capacity of newly ordered LNG tankers (Dimopoulos and Frangopoulos, 2008). However, since BOG is a part of the valuable LNG product and bunker oil is more efficient, the LNG industry recently crossed over to other propulsion systems, namely dual fuel diesel or diesel-electric propulsion systems together with BOG re-liquefaction plant (Dimopoulos and Frangopoulos, 2008; MAN Diesel A/S-LNG Carriers with ME-GI Engine and High Pressure Gas Supply System, 2009). The reason is the superior efficiency of diesel engines. These systems are installed in LNG tankers intended for long distance transportation of liquefied natural gas. Since fuel oil prices are currently high, operators are considering burning boil-off gas instead of utilising 100 % HFO, DO or gas oil.

On the basis of observations of typical BOR on LNG tankers in exploitation, it is estimated that boil-off gas equals about 80-90 % of the energy needed for the LNG tanker at full power output (MAN Diesel A/S- LNG Carriers with ME-GI Engine and High Pressure Gas Supply System) in laden voyage, and 40-50% in ballast voyage. Therefore, additional fuel oil is required or alternative forced boil-off gas must be generated. Most modern LNG tankers have forcing vaporisers which vaporise additional BOG to allow the ship to run on BOG alone. The use of forcing vaporisers depends on relative fuel economics and charterer preference (MAN Diesel A/S- LNG Carriers with ME-GI Engine and High Pressure Gas Supply System, 2009). It should be noted that during the course of the ship's voyage, the ageing process increases the heat value of BOG. With the passage of time, this fact reduces the need for additional quantity of forced BOG (Sedlaczek, 2008).

For safety reasons, BOG can be released into the atmosphere or burnt in a gas combustion unit (also called thermal oxidizer). The decision on the choice of an appropriate method depends on many primarily safety, economic and legal factors.

4. LNG ENERGY CONTENT

LNG is sold depending on its energy content which is typically measured in GJ, GWh or MMBTU (British Petrol and International Gas Union, 2011; International Group of Liquefied Natural Gas Importers, 2011).

LNG is purchased by the charterer (mostly oil & gas or energy companies) at FOB price at the loading terminal and sold at a higher CIF price at the receiving terminal.

Used LNG cargo and LNG cargo lost due to boil-off reduce the amount of cargo delivered by an LNG tanker to the receiving terminal. Furthermore, ageing decreases the percentage content of the lighter boiling point components (Methane, Nitrogen) and increases the percentage content of the higher boiling point components (heavy components) in the LNG remaining in ship's tanks (Głomski and Michalski, 2011). Therefore, the unloaded LNG has a lower percentage content of nitrogen and methane and higher content of ethane, propane and butane than the loaded LNG.

Since the composition of LNG cargo constantly changes during a ship's voyage, its quality and properties also constantly change.

The establishment and calculation of the quantity of energy of LNG transferred between LNG ships and LNG terminals is performed on both terminals. This procedure is called *"Custody transfer"* and involves the activities and measurements taken both on the LNG tanker and on the terminal jetty. Custody transfer is contractually agreed between the LNG buyer and seller.

The determination of the transferred energy is executed together with the measurement and calculation of some parameters, i.e. liquid volume, liquid density and heat value (British Petrol and International Gas Union, 2011; International Group of Liquefied Natural Gas Importers, 2011).

The transferred energy can be calculated with the following formula:

$$E = (V_{LNG} \cdot \rho_{LNG} \cdot GCV_{LNG}) - E_{GD} \pm E_{GE} \qquad (2)$$

where E is total net energy transferred from loading terminal to the LNG tanker or from the LNG tanker to the receiving terminal in kJ, V_{LNG} the volume of LNG loaded or unloaded in m^3, ρ_{LNG} the density of LNG loaded or unloaded in kg/m^3, GCV_{LNG} gross caloric value of the LNG loaded or unloaded in J/kg, E_{GD} net energy of the displaced gas from LNG tank in J, E_{GE} energy of the gas used by LNG tanker as fuel (consumed in the engine room) at the port in J.

The volume of LNG loaded V_{LNG} can be calculated using the following expression:

$$V_{LNG} = C - V_{RH} \qquad (3)$$

where C is the loading capacity of the LNG tanker in m^3 and V_{RH} the remaining LNG for cargo tank cooling (heel) during ballast voyage in m^3.

The volume of LNG unloaded V_{LNG} can be obtained using the following expression:

$$V_{LNG} = L_{LNG} - TL_{BOG} - V_H \qquad (4)$$

where L_{LNG} is the volume of LNG loaded into the ship in m^3, TL_{BOG} total used or lost LNG (BOG) during laden voyage in m^3 and V_H is minimum of LNG for cargo tank cooling (heel) during laden voyage in m^3.

The calculation used to determine LNG volume is based on the level, temperature and pressure measurements obtained from the ship's instruments, taking into account the calibration and correction tables to compile a report meeting the CTS (Custody Transfer Survey). Lately, the taking of volume measurements has become automated through the LNG tanker's custody transfer measurement system (Benito, 2009; British Petrol and International Gas Union, 2011; International Group of Liquefied Natural Gas Importers, 2011).

LNG density can also be determined by measuring its average value directly in the LNG tanker's tank by means of densitometers or by calculation from the measured composition of LNG transferred and the temperature of LNG measured in the LNG tanker's tanks.

The calculation is made by means of mathematical model equations of state connecting pressure, temperature and volume, widely used in the LNG industry. The most widely used method is the revised KLOSEK-McKINLEY method according to standard ASTM D 4784-93 and ISO 6976. This method is based on empirical evaluation of molar volume of the mixture in the thermodynamic state of the LNG considered. The density of LNG is calculated as follows:

$$\rho = \frac{M_{mix}}{V_{mix}} = \frac{\sum_{i=1}^{n} x_i \cdot M_i}{\sum_{i=1}^{n} x_i \cdot V_i - \left[k_1 + (k_2 - k_1) \cdot (x_{N2}/0.0425) \right] \cdot x_{CH_4}} \tag{5}$$

where M_{mix} is molecular weight of the mixture in g/mol, V_{mix} molar volume of the mixture in m^3/mol, x_i the molar fraction of component i in mol/mol, M_i molecular weight of component i in g/mol, V_i molar volume of the component i at the temperature of the LNG in m^3/mol, k_1 and k_2 correction factors, x_{N2} molar fraction of nitrogen in mol/mol and x_{CH_4} molar fraction of methane in mol/mol.

The calculation of volume correction factors k_1 and k_2 at a given temperature is derived by interpolation of their two known values and with respect to temperature and molecular weight.

Upper Heat value (UHV) or Gross Caloric Value (GCV) is the thermal energy produced by the complete combustion of a unit of volume or mass of the gas (vaporised LNG) in the air, at the constant absolute pressure of 1.01325 bar and at temperature T_h at which the water formed during the combustion condenses. In the case of volumetric GCV, the unit of volume of gas is considered at the gas volume metering conditions of temperature T_v and pressure p_v. The GCV can be determined by calorimeter measurements or by computation based on the composition of the gas (vaporised LNG) in the reference condition.

There are several standards that can be used to calculate GCV, such as ISO6976, ASTM 3588 GPA2145 etc. Custody transfer should state the standards and reference conditions used, namely the combustion temperature and pressure.

According to the ISO697 standard, GCV_{LNG} is calculated with the following formula (International Group of Liquefied Natural Gas Importers, 2011):

$$GCV_{LNG} = \frac{\sum_{1}^{n} x_i \cdot GCV_i}{\sum_{1}^{n} x_i \cdot M_i} \tag{6}$$

where GCV_{LNG} is mass gross calorific value in J/kg, x_i molar fraction of component i in mol/mol, GCV_i molar gross calorific value of component i in J/mol, M_i molecular mass of component i in g/mol. The physical constants GCV_i and Mi being specified in coherent standards.

The energy of the displaced gas returned from the ship during the loading operation or transferred to the LNG tanker during the unloading operation from storage tank can be determined by the following expression at the reference conditions of 15 °C and 1.01325 bar (British Petrol and International Gas Union, 2011; International Group of Liquefied Natural Gas Importers, 2011):

$$E_{GD} = V_{LNG} \cdot \frac{273.15}{273.15 - T} \cdot \frac{p}{1.01325} GCV_{GAS} \tag{7}$$

where E_{GD} is energy of the gas displaced from the LNG tank in J, V_{LNG} volume of the LNG loaded or unloaded in m^3, p absolute pressure in the tanks in bar, T mean value of the temperatures of the probes not immersed in LNG in °C, GCV_{GAS} gross caloric value of the gas in gaseous state contained in the ship's tanks in J/m^3.

Since the composition of the vapour returned is not the same as that of the LNG delivered from the ship, it is common practice to assume the return gas to be 100% methane in the calculation of the energy of the gas displaced.

The quantity of gas possibly used by the LNG tanker as fuel during loading or unloading operations can be determined by:

$$E_{GE} = V_G \cdot GCV_{GAS} \tag{8}$$

where E_{GE} is the energy of the gas used by the LNG tanker (engine room) in J, V_G the total volume of gas determined by a gas flow meter on board the LNG tanker in m^3.

During loading operations, E_{GE} has positive sign while for unloading operation has negative sign.

According to the IS06976 standard, GCV_{GAS} is calculated with the following formula (International Group of Liquefied Natural Gas Importers, 2011):

$$GCV_{GAS} = \frac{\sum_{1}^{n} y_i \cdot GCV_i}{\sum_{1}^{n} y_i \cdot MV_i} \quad (9)$$

where GCV_{GAS} is the volumetric gross calorific value of the displaced gas in J/m^3, y_i molar fraction of component *i* in the displaced gas mol/mol, GCV_i molar gross calorific value of component *i* in J/mol and MV_i molar volume of component *i* in m^3.

The molar composition of the displaced gas differs from the composition of LNG and is determined either by the analysis of gas, or by calculation.

The molar composition calculation is possible with a general formula for Vapour-Liquid-Equilibria (VLE) calculation based on equilibrium ratio (Riazi, 2005; International Group of Liquefied Natural Gas Importers, 2011):

$$K_i = \frac{x_i}{y_i} \quad (10)$$

where K_i is the dimensionless equilibrium ratio, x_i molar fraction of component *i* in liquid in mol/mol, y_i molar fraction of component *i* in the displaced gas in mol/mol.

The dimensionless equilibrium ratio K_i generally varies with *T, p* and composition of both liquid and vapour phases. Assuming the ideal solution for hydrocarbons, K_i value at various temperatures and pressures has been calculated for n-paraffins from C1 to C10 and is presented graphically for quick estimation. For hydrocarbon systems and reservoir fluids, there are also some empirical correlations for the calculation of K_i values, such as the correlation proposed by Hoffman which is widely used in the industry (Riazi, 2005). For practical calculation of the displaced gas, K_i values are usually limited to the more volatile components, i.e. nitrogen, methane and sometimes ethane.

The energy of the gas consumed as fuel in the engine room during the loading or unloading operations of an LNG tanker with cargo capacity of 145 000 m^3 and a steam turbine propulsion system, typically equals 0.05 -0.06% of the total energy of the transferred LNG (International Group of Liquefied Natural Gas Importers, 2011).

5. CONCLUSION

One of the problems in LNG transportation and storage is the generation of BOG. These vapours are created due to the heat added into the LNG during storage, transportation and loading/unloading operations.

This paper shows the causes of generation and general methods of handling and utilization of BOG at different places of the LNG supply chain.

In the LNG supply chain most BOG is generated by the LNG ships themselves. The used LNG cargo or losses of LNG cargo due to boil-off reduce the amount of cargo delivered by LNG tankers to the receiving terminal while the ageing process steadily changes the composition, quality and properties of LNG cargo during a ship's voyage. Therefore, the quantity and quality of unloaded LNG are the key factors for the economic assessment of the LNG supply chain. Consequently, this paper also describes the mathematical method for the determination and calculation of the LNG energy quantity unloaded from the ship's tanks to storage tanks in the receiving terminal. Future research will focus on simulating and computing boil-off in all parts of the LNG supply chain.

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