

Journal of Polish CIMAC Gdansk University of Technology The Faculty of Ocean Engineering and Ship Technology



PROBLEMS WITH DETEMINATION OF EVAPORATION RATE AND PROPERTIES OF BOIL-OFF GAS ON BOARD LNG CARRIERS

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Abstract

The paper discusses selected issues related to the problems of determining boil-off (evaporation) rate (BOR) of liquefied natural gas (LNG) on board LNG carriers. Review of available literature describing theoretical models of LNG boiling-off phenomenon during maritime transport is presented. Given are examples of simulation results of LNG evaporation process based on theoretical analysis. Also presented are methods of determining boil-off rate based on the results of observations of the concerned phenomenon on board selected ships. The paper draws attention to theoretical differences in a daily boil-off gas (BOG) quantity resulting from the adopted method of determining BOR. Namely, in some publications BOR values refer to the loaded quantity of LNG (or even to the ship's cargo carrying capacity), and in the rest to the current quantity on board. The paper outlines resulting theoretical differences in quantity of cargo remaining on board. Addressed are also issues related with variable, in the course of the voyage, BOG (and thus LNG) composition determining its heating value, which is of particular importance in the case of its use as a fuel for ship's engines.

Keywords: boil-off rate, evaporation rate, boil-off gas, LNG vapour properties, LNG carrier

1. Introduction

Accurate determination of the boil-off rate (BOR) of liquefied natural gas (LNG) shipped by the sea is important for a number of reasons. The most important one is safety of transport. It should be noted that, as a result of unavoidable heat transfer from the surroundings into the cargo and as a consequence its evaporation, vapour pressure in the cargo tanks increases. In order to maintain the pressure within acceptable limits, part of the boil-off gas (BOG) has to be regularly removed from the tanks. Equally important are issues of economical and technical nature. Substantial losses of LNG make the quantity discharged to the receiving terminal smaller than the quantity loaded. To remedy this situation, in some cases it is advantageous to re-liquefy BOG during the voyage. However, additional investment and operating costs of re-liquefaction plant make it often more favourable to burn evaporating cargo (BOG) in the ship's boilers, reciprocating engines or gas turbines. In such cases important issue, in addition to determining available BOG quantity, is knowledge of its heating value, which is changing in the course of the voyage due to changing BOG composition.

2. Boil-off rate determined on the basis of theoretical LNG boiling-off models

Despite high level of insulation of cargo tanks, it is not possible to completely stop the heat ingress from the surroundings into the cargo and thus to prevent its evaporation. The resulting vapours are called "boil-off" gas (BOG). Transferring from the outside into the cargo tanks heat generates convection currents in the cargo volume causing rising of a warmer layer to the surface, where is then evaporates. As long as vapours are removed in order to maintain constant tank pressure, temperature of LNG remains unchanged. If the vapour pressure in the ullage space rises, evaporation rate decreases and vice versa – if the pressure drops as a result of removal of greater quantity of vapours than evaporated since the last measurement, evaporation rate increases and consequently the LNG temperature drops. It is a result of inherent equilibrium between gas phase pressure and the corresponding temperature of the liquid phase.

The boil-off rate varies throughout the voyage along with variations of ambient sea and air temperatures, sea state and atmospheric pressure (if there is no absolute tank pressure control applied). For this reason constant control of pressure in the cargo tanks, inter-barrier spaces¹ (IBS, also called primary insulation space – PIS) and isolation spaces² (IS, also called secondary insulation space – SIS) should be maintained. Under no circumstances the tank pressure should be allowed to drop below atmospheric pressure although there is a certain design safety margin [7]. In addition, receiving terminals require tank pressure to be below predefined level for arrival. During normal operation, vapour pressure in the tanks is maintained approximately at a constant level, slightly above atmospheric. This is done in order to prevent inflow of ambient air into the tank, which could create an explosive atmosphere after dilution with cargo vapours.

In general, evaporation rate of a given substance depends on the following factors:

- value of inter-molecular forces keeping the molecules together in the liquid phase (specific enthalpy of vaporization of the substance);
- temperature of evaporating substance (if temperature is higher, more molecules have sufficient kinetic energy to transit into the gas phase);
- pressure of the gas phase (if the pressure is lower, evaporation rate is greater because there is less exertion on the surface keeping the molecules from launching themselves);
- surface area of the liquid-gas phase interface (if larger, evaporation rate is increased because more molecules with sufficient kinetic energy are at the interface);
- concentration of the evaporating substance in the atmosphere above the surface (if the concentration of the evaporating substance in the atmosphere is already high, evaporation rate is reduced; this depends largely on the flow rate of the gas phase above the surface);
- concentration of other substances in the atmosphere above the surface (if the atmosphere is already saturated with other substance, evaporation rate of the substance concerned is decreased).

In order to calculate daily quantity of evaporated LNG during the voyage, it is necessary to precisely know LNG composition, its physical properties (especially specific enthalpy of vaporization and specific heat capacity at different temperatures), vapour pressure in the ullage space, hydrometeorological conditions (especially water and air temperatures, sea state and atmospheric pressure) and technical parameters of the cargo tanks, especially heat transfer coefficients of their insulation layers.

Tab. 1 presents a list of selected insulation materials used in the construction of cargo containment systems on LNG carriers together with their approximate (coefficients of) thermal conductivity in 10 $^{\circ}$ C.

¹ i.e. in spaces between primary and secondary safety barrier of the cargo containment system.

² i.e. in spaces between secondary safety barrier and the outer wall of the cargo containment system.

Material	Thermal conductivity in 10 °C [W/(mK)]			
1	2			
balsa wood	0.05			
mineral wool	0.03			
perlite	0.04			
polystyrene	0.036			
polyurethane	0.025 (in tight cover)			

 Tab. 1. (Coefficients of) thermal conductivity of typical insulation materials used in the construction of tanks for LNG storage [7]

For comparison, thermal conductivity of aluminium equals 200 W/mK, stainless steal -12.11-45.0 W/mK, water -0.6 W/mK, and air -0.025 W/mK.

The amount of heat that is transferring can be determined on the basis of detailed thermodynamic analyses of the involved processes. However, an accurate determination of BOR is very complex. So far there is no detailed model of the evaporation process which comprises all of the mentioned factors. More accurate BOR value can be calculated on the basis of a general evaporation model created for example by Hashemi and Wesson [1] (1971) and adapted to LNG boil-off study.

Complex models have been developed to more accurately determine BOR in the course of the voyage which are based on empirical values of heat transfer rate calculated on the basis of observed boil-off rates [3, 4, 6, 8]. The results of one such simulation for gas carrier with cargo capacity of 150,000 m³ and for the heat flux inflowing into the whole cargo containment system of 600 kW are shown by [3] in Fig. 1 and 7.



Fig. 1. Variation of BOR during a voyage of LNGC with cargo capacity of 150000 m³ [3]

3. Estimation method of determining boil-off gas quantity during voyage

For rough and preliminary determination of BOR, it can be assumed that physical properties of LNG correspond to those of pure methane. Knowing heat transfer rate in given conditions and enthalpy of vaporization in the boiling temperature for methane (511 kJ/kg [2]), it is possible to estimate quantity of boiled-off LNG in a given time period.

Boil-off rate can be estimated on the basis of observations of a typical boil-off rate on previously built vessels. In the case of spherical tanks with a diameter of 36 m and the ambient air temperature of 32 °C, intensity of the heat flux penetrating the insulation is estimated at about 20 W/m² [4]. This results in daily loss of about 0.12 % of total quantity of loaded cargo during the laden voyage. Typical BOR values for various types of cargo containment system are given in Tab. 2.

Cargo containment system	TG Mark III	GT No. 85, No. 82, No. 88	GT No. 96	Kværner Moss Rosenberg	IHI SPB	TGE type C
1	2	3	4	5	6	7
Boil-off rate [%]	0.13 - 0.15 (0.26 - 1995)	0.25	0.15 - 0.16	0.10 - 0.15	0.13	0.35 - 0.45 (0.21 - 0.23)
Introduction year	<1993 (Mark I - 1971)	1969 1971 1981	<1994	1973	1965	2004
Material	stainless steel AISI 304L		36% Ni steel (Invar [®])	aluminium alloy or 9% Ni steel	aluminium alloy	9% Ni steel or stainless steel AISI 304L
Isolation layer thickness [mm]	250		250-530	220-300	abt. 300	300

Tab. 2. Typical BOR values for various designs of cargo containment system [4, 8, 9]

Fig. 2 shows a comparison of LNG evaporation rate on gas carriers built before and after 1980, according to data provided by operators/owners and for different types of tanks.



LNG evaporation rate

Fig. 2. LNG boil-off rate on carriers built before and after 1980 and for different cargo containment systems according to data provided by operators/owners [5]

Quantities of LNG evaporating during single day for various cargo capacities of LNG carriers and for typical BOR values during laden and ballast voyage are shown in Fig. 3 and 4.



Fig. 3. Daily loss of LNG due to boiling-off for various ships' cargo carrying capacities and BOR values during laden voyage



Fig. 4. Daily loss of LNG due to boiling-off for various ships' cargo carrying capacities and BOR values during ballast voyage

The BOR in maritime transport of LNG is commonly given as a loss expressed in percentage of total volume of liquid cargo arose during a single day. Typical BOR for newer LNG carriers ranges from 0.10 to 0.15% for laden voyage and from 0.06 to 0.10% for ballast voyage [4, 8, 9]. It is worth to note that in the literature of the subject there is some inconsistency as to the choice of cargo quantity value to which it refers. In the majority of publications BOR refers to the loaded quantity of LNG (or even to a ship's cargo capacity), however in some publications BOR is referred to the current volume of LNG on board. In order to illustrate the resulting differences, it is worth noting that in case of a ship which has been loaded with e.g. 125000.0 m³ of LNG and assuming BOR equalling 0.15%, after 25 days of the voyage with constant daily loss of 187.5 m³

of LNG there will be 120313.5 m³ of LNG remaining on board, whereas with changing quantity of BOG as a function of current volume of LNG (initially from 187.5 to eventually 180.87 m³/day) there will be 120395.9 m³ of LNG remaining. The difference is thus 83.41 m³ of LNG, which after vaporization gives about 50047.6 m³ of gas. The difference increases with increasing duration of the voyage caused by e.g. laying at anchor. Adoption of the first method of determining daily BOG quantity in the example above means that LNG would evaporate completely after about 667 days, while according to second method after this time there would be still 45961.9 m³ of LNG remaining in the tanks. It is also worth to note that BOR during the ballast voyage refers generally to the cargo volume loaded on board at the beginning of the laden voyage.

4. Change of boil-off gas composition and heating value during voyage

Components of LNG significantly differ from each other with boiling temperatures (from -196 to +36 °C). This means that the LNG composition gradually changes in the course of the voyage, unless re-liquefaction is put in place, because more volatile components with lower boiling temperatures evaporate with greater intensity. Therefore, unloaded LNG has lower percentage content of nitrogen and methane (i.e. two LNG components with the lowest boiling temperatures) than LNG loaded, and thus higher content of ethane, propane and butane (Fig. 5).



Fig. 5. Change of methane and nitrogen concentration in BOG during voyage [3]

The consequence of this phenomenon is the gradual increase of the boiling temperature and density of LNG during the voyage. It also affects the heating value, which is lowest in the beginning and gradually increases with the course of the voyage (Fig. 6). Variations of the thermodynamic properties and quantity of BOG in the range of 6-10% during the voyage have been observed [3]. Fluctuations of this order have a significant impact on the operation of the systems utilizing BOG, especially as a fuel supplying boilers and engines.

Over the years, it was observed that the BOR can vary considerably from voyage to voyage, which may result in an unexpected necessity of venting the excess of BOG through vent risers.



Fig. 6. Heating value change of natural, forced and total BOG during voyage [3]

Furthermore, the BOR decreases at the beginning of the voyage reaching minimum after a few days and then increases. This results from the above-described progressive change of the LNG composition.

If the quantity of the natural BOG is insufficient in relation to the requirements (i.e. to achieve the desired propulsion system power output), a special vaporizer (LNG forcing vaporizer) vaporizes required quantity of LNG supplied from a cargo tank. The resultant vapours are called forced boil-of gas [F(-)BOG] and their composition corresponds to the composition of the supplied LNG. Due to the fact that heating value of natural BOG increases along with the course of the voyage, less and less quantities of forced BOG are required to supplement for natural BOG. Heating value of forced BOG remains practically the same (Fig. 7). It should be emphasized that forced BOG has significant effect both on the quantity and the heating value of the total BOG.



Fig. 7. Total volume of boil-off gas during voyage of LNG carrier with a cargo capacity of 150000 m^3 [3]

5. Conclusion

Proper determination of BOR of LNG shipped by the sea is important not only because of the safety aspects but also due to desirability and possibility of its utilization through burning for ship propulsion.

In operational practice, BOR is determined on the basis of data obtained from the measurements taken on board. In such a case it is essential to accurately measure quantity of loaded and unloaded liquid cargo constituting the basis for further calculations.

Throughout the voyage BOR as well as vapour composition and thus its heating value change. This fact should be taken into account in the designing process of a propulsion system which utilizes BOG as a fuel.

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The paper was published by financial supporting of West Pomeranian Province

Województwo Zachodniopomorskie