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To cite this article: T Wodek 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **214** 012105

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Analysis of boil-off rate problem in Liquefied Natural Gas (LNG) receiving terminals.

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Abstract. Liquefied natural gas (LNG) has an increasingly important role in the global natural gas market. Global demand for natural gas will grow over the coming years. LNG is transported by ships to unloading points at the storage terminals. During the LNG storage processes some part of LNG evaporates into gas phase. Evaporated LNG is called Boil-off gas (BOG). LNG is stored at cryogenic temperatures. Heat flow has an impact on evaporation process. It indicates there is continuous boil-off of small fraction or portion of LNG due to warming during storage process. This boil-off gas is generated primarily due to heat flow from the ambient air through tank insulation, unloading and recirculation-line insulation. Vaporization process causes changes in the composition of stored Liquefied Natural Gas. Increased vaporization process may negatively affect the stability and safety of the LNG storage process. Rate of vaporization (boil off rate) should be precisely determined. For these reasons different calculation models to determine the LNG boil-off rate are shown in this paper, also there are presented some boil off rate calculation results for different Liquefied Natural Gas compositions. Obtained results show that Boil-off rate is higher for LNG composition which contains nitrogen. Due to lower bubble temperature nitrogen evaporates first from the LNG, it causes significant LNG density drop in surface layer in storage tank. Difference of densities in surface and bottom layer of stored LNG may cause the stratification process and consequently affect the stability of storage process (possibility of roll-over phenomenon).

1. Introduction

Liquefied natural gas (LNG) has an increasingly important role in the global natural gas market. Liquefied natural gas is transported by ships and stored in storage tanks. During the process of LNG unloading and storage some part of LNG evaporates into gas phase, which is usually called boil-off gas (BOG). BOG can be utilized as fuel, reliquefied, compressed and put into gas transportation network or burned in a flare. The boil-off gas management during the LNG storage process and the assessment of its thermodynamic properties are key issues in the technical assessment of the LNG storage terminals energy systems [1,2]. In this paper the analysis of several boil-off gas models has been performed. Models accounts for the variation of BOG mass flow, composition and thermodynamic properties during storage process. Heat flow from ambient air into storage tank and changes in the composition of stored Liquefied Natural Gas have an impact on evaporation process. Increased vaporization process may negatively affect the stability and safety of the LNG storage process. For these reasons the rate of vaporization (boil-off rate) should be precisely determined [2,3].



2. Basic assumptions

Analysis of boil-off rate will be provided for three typical LNG compositions in function of ambient temperature. Also the analysis for composition changes of bi-component mixtures methane with ethane and methane and nitrogen. Ethane besides methane is one of main components of LNG. On the other hand the higher nitrogen molar fraction in investigated compositions of LNG is a key factor for stability and safety of storage process in LNG receiving terminals. The compositions of typical liquefied natural gases used for calculations are presented in Table 1. In general there are three types of LNG, Light LNG with dominant fraction of methane (above 95%), heavy LNG with summary molar fraction of ethane, propane and butanes about 10%, and LNG with higher content of nitrogen (about 2–3%) [4,5]. Bubble point curve (p-T) for a given range of temperatures 100 to 150 K for assumed compositions are presented in figure 1. Also changes of bubble point curves for assumed bi-component mixtures simulating LNG are presented in figures 2 and 3.

Table 1. Typical compositions of liquefied natural gases from various sources with basic parameters.

Component	Short symbol	Light LNG	Heavy LNG	LNG with high nitrogen content
		(%mol)	(%mol)	(%mol)
methane	C ₁	96.15	89.52	93.95
ethane	C ₂	2.46	6.89	2.65
propane	C ₃	0.91	2.42	0.78
iso-butane	i-C ₄	0.24	0.62	0.16
n-butane	n-C ₄	0.22	0.47	0.19
nitrogen	N ₂	0.02	0.08	2.27
Latent heat of vaporization	(kJ/kg)	508.82	505.58	502.04
Boiling temperature at normal pressure	(K)	112.0	112.5	104.9

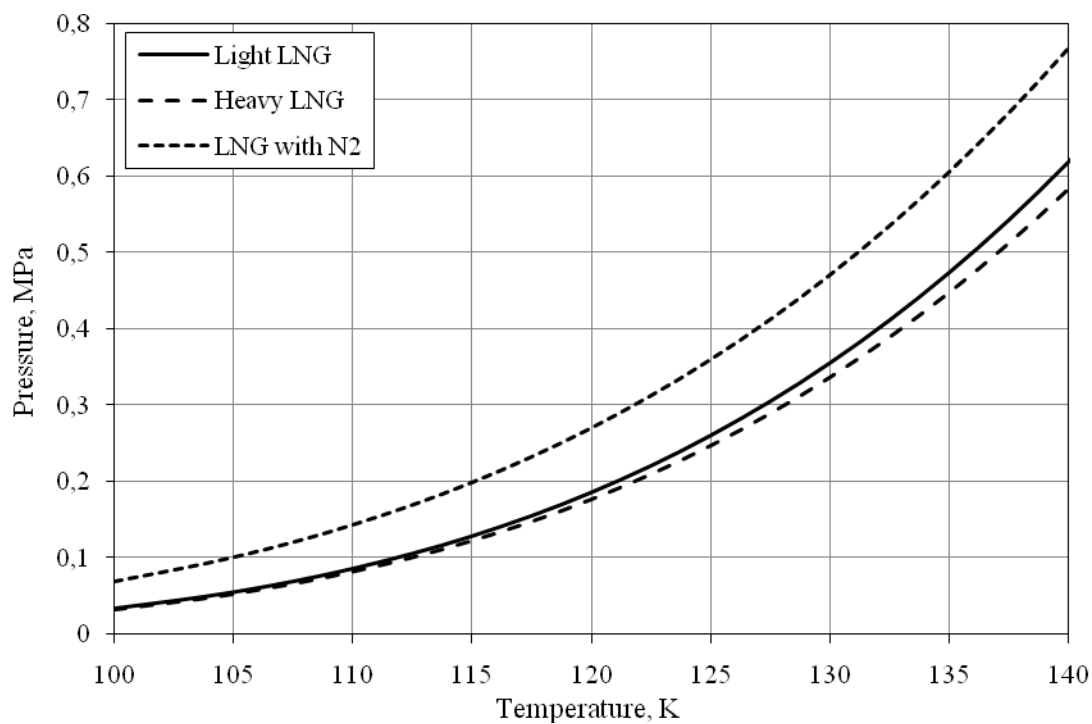


Figure 1. Bubble point curves for assumed LNG compositions (own calculations).

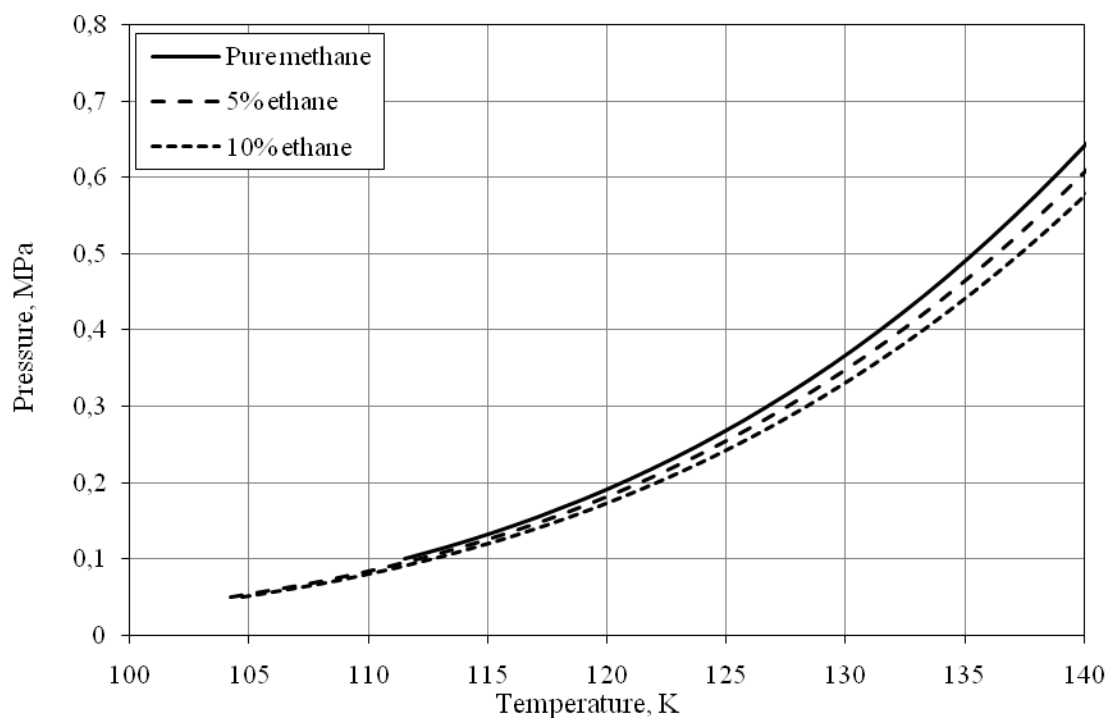


Figure 2. Bubble point curves for bi-component mixtures CH₄ - C₂H₆(own calculations).

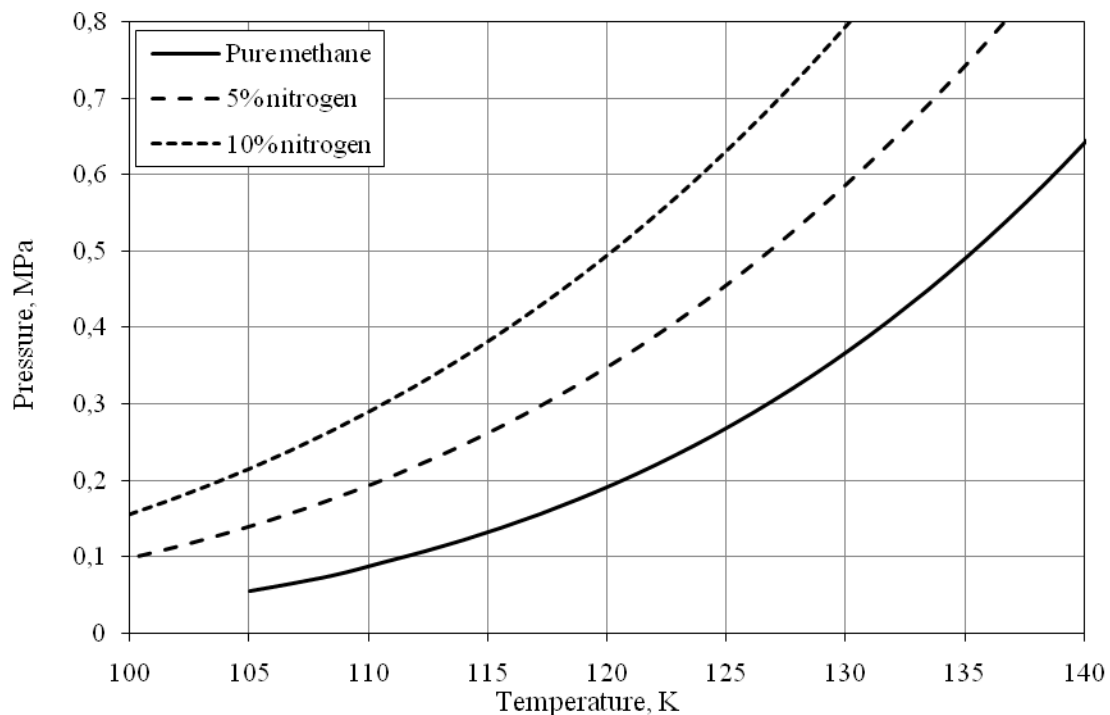


Figure 3. Bubble point curves for bi-component mixtures $\text{CH}_4 - \text{N}_2$ (own calculations).

The typical "full containment" LNG storage tank is considered for presented analysis. It consists of inner tank made of nickel steel (resistant to extremely low temperatures), original insulation (perlite), outer tank made of carbon steel, secondary insulation (polyurethane foam) and wall made of strengthened concrete. Construction of bottom part and roof of the tank also were considered in presented case (with small simplifications for roof construction). Geometry of the tank and values of important parameters for thermal analysis of storage tank are presented in Table 2. Process of Liquefied Natural Gas storage is sensitive to changes of ambient conditions. In analyzed case the wide range of ambient temperatures is considered (from 265 K (−8 deg C) in winter season to 305 K (32 deg C) in summer season).

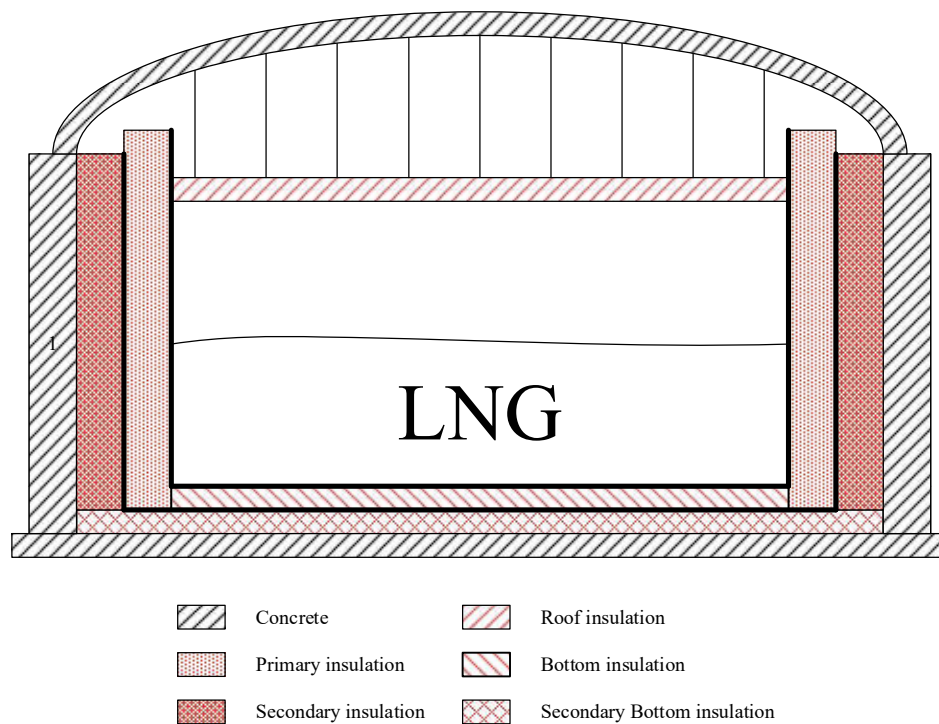


Figure 4. Scheme of LNG full containment storage tank.

Table 2. Geometrical and thermal parameters of the full-containment storage tank.

Total storage capacity of the tank		160000 m ³
Overall tank height		40 m
Tank inner diameter		74 m
Thickness	Inner tank wall (9%Ni steel)	0.2 m
	Outer tank wall (carbon steel)	0.15 m
	Primary insulation (perlite)	0.6 m
	Secondary insulation (polyurethane)	0.6 m
Thermal conductivity	9%Ni steel	90.9 W/(m·K)
	carbon steel	42.6 W/(m·K)
	perlite	0.038 W/(m·K)
	polyurethane foam	0.029 W/(m·K)
Convective heat transfer coefficient	concrete	1.8 W/(m·K)
	inner surface	35 W/(m ² ·K)
	outer surface	10 W/(m ² ·K)
Ambient temperature for composition case		293.15 K
Ambient temperature range for thermal case		265–310 K

3. Model Analysis

3.1. Heat transfer analysis

One of the most important factors for estimation of boil-off rate is correct determination of heat transfer. Heat transfer calculations are based on Fourier law, which can be written in one-dimensional formula [6]:

$$q = -k \cdot A \cdot \frac{dT}{dx} \quad (1)$$

Cylindrical coordinates should be used for storage tank walls [6]:

$$q_r = -k \cdot A \cdot \frac{dT}{dr} \quad (2)$$

where: q – heat transferred [W], k – thermal conductivity [W/(m·K)], T – temperature [K], A – area [m²], r – radius [m], x x -dimensional length [m].

The storage tank is a complex construction with multilayer structure. Each layer has different thermal properties. Also heat transfer has to be considered not only for walls of the tank. Energy as heat is transferred to cryogenic fluid (LNG) through roof and bottom of the tank. LNG tanks have a spherical dome roof, in presented case heat transfer through roof is simplified. Heat transfer through tank wall is defined with formula [6]:

$$Q_w = \frac{-2\pi \cdot H \cdot (T_{in} - T_{out})}{\frac{1}{r_{in} \cdot \alpha_{in}} + \frac{1}{k_1} \cdot \ln\left(\frac{r_1}{r_{in}}\right) + \frac{1}{k_2} \cdot \ln\left(\frac{r_2}{r_1}\right) + \frac{1}{k_3} \cdot \ln\left(\frac{r_3}{r_2}\right) + \frac{1}{k_4} \cdot \ln\left(\frac{r_4}{r_3}\right) + \frac{1}{k_5} \cdot \ln\left(\frac{r_5}{r_4}\right) + \frac{1}{r_5 \cdot \alpha_{out}}} \quad (3)$$

where: H – tank height [m], T_{in} – temperature of LNG [K], T_{out} – ambient temperature [K], k_i – thermal conductivity of layer [W/(m·K)], r_{in} – inner tank radius [m], r_1 – r_5 – radiuses of subsequent tank layers [m], α_{in} – inner convective heat transfer coefficient [W/(m²·K)], α_{out} – outer convective heat transfer coefficient [W/(m²·K)].

Heat transfer for tank roof is written as:

$$Q_t = \frac{-\pi \cdot r^2 \cdot (T_{in} - T_{out})}{\frac{1}{\alpha_{in}} + \frac{s_1}{k_1} + \frac{s_2}{k_2} + \frac{s_3}{k_3} + \frac{1}{\alpha_{out}}} \quad (4)$$

where: r –outer radius of the tank [m], s_i – thickness of each layer related to roof construction [m].

Roof of the tank is considered as a plate partition, normally it should be considered as a spherical dome of concrete with flat plate (inner tank suspended roof and insulation). Bottom of the tank is also considered as plate partition which consist of concrete foundation, inner and outer tanks walls and insulation (generally fiberglass). Heat transfer through the bottom of the tank can be expressed in formula:

$$Q_b = \frac{-\pi \cdot r^2 \cdot (T_{in} - T_s)}{\frac{1}{\alpha_{in}} + \frac{s_1}{k_1} + \frac{s_2}{k_2} + \frac{s_3}{k_3} + \frac{s_4}{k_4} + \frac{1}{\alpha_s}} \quad (5)$$

where: T_s – ground temperature [K], s_i – thickness of each layer related to bottom slab construction [m], α_s – outer convective heat transfer coefficient (from soil) [W/(m²·K)].

Liquefied natural gas in storage tank is in permanent natural circulation flow. Therefore, the convection effect should be considered in all the heat transfer calculations.

Total heat transfer from ambient air to cryogenic tank is given in formula:

$$Q = Q_w + Q_t + Q_b \quad (6)$$

3.2. Boil-off rate analysis

The boil-off gas (BOG) is a key issue for technical and economic reasons. Evaporation of LNG causes increase of pressure in LNG storage tank. It has an impact on storage process safety. Evaporation process changes conditions in storage tank, it has influence on compositions of liquefied natural gas and boil-off gas, also due to evaporation process thermodynamic properties of LNG and BOG can change. For these reasons boil off problem in whole LNG supply chain is one of key important factors. The BOG quantity changes also depending on the changes in ambient temperature and pressure in the tank. In operational conditions the BOG quantity is calculated as a percentage of total volume of liquid in the storage tank during a single day (24 hours). This value is called boil-off rate (BOR) and can be written as [7,8]:

$$BOR = \frac{Q \cdot 24 \cdot 3600}{\Delta h \cdot V_{LNG} \cdot \rho} \cdot 100\% \quad (7)$$

where: Q – total heat transfer [W], Δh – latent heat of vaporization [kJ/kg], V_{LNG} – volume of LNG in storage tank [m³], ρ – density of LNG [kg/m³].

3.3. Heat of vaporization

The latent heat of vaporization, also known as the enthalpy of vaporization or heat of evaporation, is the amount of energy that has to be added to the liquid, to transform it into a gas phase. The enthalpy of vaporization is a function of the pressure at which that transformation takes place. The value of latent heat of vaporization is specific for each substance. It is tabulated in many publications. Value of this heat may also be calculated from formula presented below [9]. Coefficients A_x , α and β also are tabulated in reference sources.

$$\Delta h = A_x \cdot \exp\left(-\alpha \cdot \frac{T}{T_c}\right) \left(1 - \frac{T}{T_c}\right)^\beta \quad (8)$$

where: Δh – enthalpy of vaporization (at saturation pressure) [kJ/mol], T_c – critical temperature [K].

Mean heat of vaporization for analyzed liquefied natural gases is determined with simple Kay's rule. Heat of vaporization for most common LNG components are presented in Table 3.

Table 3. Latent heat of vaporization for main components of LNG [10].

Component	Short symbol	Latent heat of vaporization (kJ/kg)
methane	C ₁	510.83
ethane	C ₂	489.33
propane	C ₃	425.59
iso-butane	i-C ₄	365.10
n-butane	n-C ₄	385.71
nitrogen	N ₂	199.18

4. Calculation results

The developed analysis was performed for assumed LNG compositions and variable ambient temperature changes. In analyzed case storage tank is filled in 75% and operational pressure in the tank is 0.2 barg. Basic parameters of analyzed mixtures were calculated using Peng-Robinson cubic equation of state [11,12]:

$$p = \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m) + b_m(v - b_m)} \quad (9)$$

where: R – gas constant [J/(molK)], v – molar volume [m^3/mol], a_m , b_m – equation of state coefficients

Firstly, the boiling temperature and density of assumed LNG compositions were calculated for operational pressure conditions. Nitrogen content has a significant impact on boiling temperature, which is clearly lower for LNG with nitrogen in its composition. Density of LNG depends on its composition. Light LNG has the lowest density. Density of LNG with boiling temperature has an high influence on boil-off rate determination. LNG with nitrogen content has the highest and heavy LNG has the lowest boil-off rate. In temperature of 17 deg C (290 K) the boil off rate for Light LNG is 0.02792%vol/day, for Heavy LNG – 0.02669%vol/day and for LNG with nitrogen – 0.02882%vol/day. High boil-off rate for LNG with nitrogen results from the lower boiling temperature and higher heat transfer into storage tank. The evaporation rate can also be expressed as the amount of mass evaporated at one time unit. In this situation the lowest boil off rate has the Light LNG due to lowest molar mass and density of this LNG. Boil-off rates for assumed compositions are presented in Figures 5 and 6.

Table 4. Boiling temperatures and densities of LNG for assumed LNG compositions.

	Bubble temperature (K)	Density (kg/m ³)
Light LNG	112.4	428.38
Heavy LNG	114.6	451.13
LNG with nitrogen	107.6	443.23

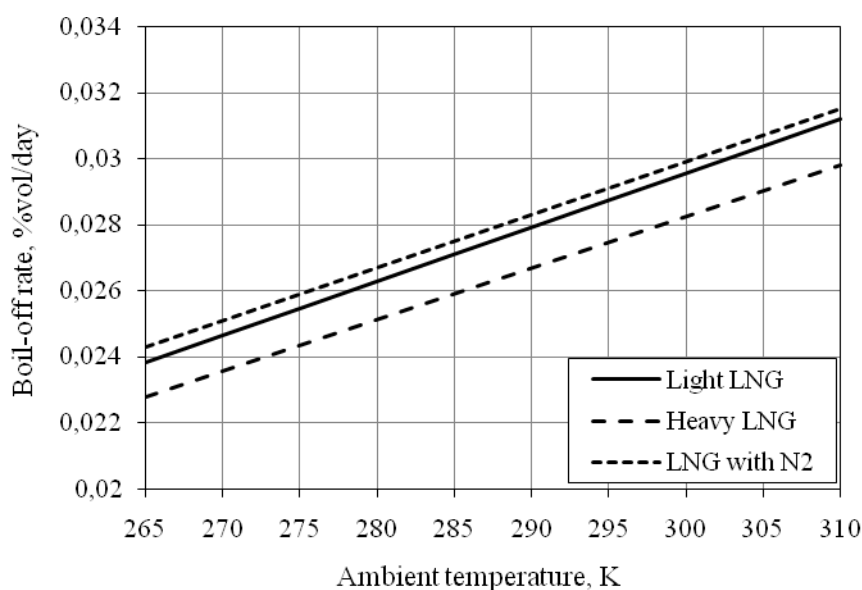


Figure 5. Boil-off rate for presented LNG compositions expressed in percent of volume per day.

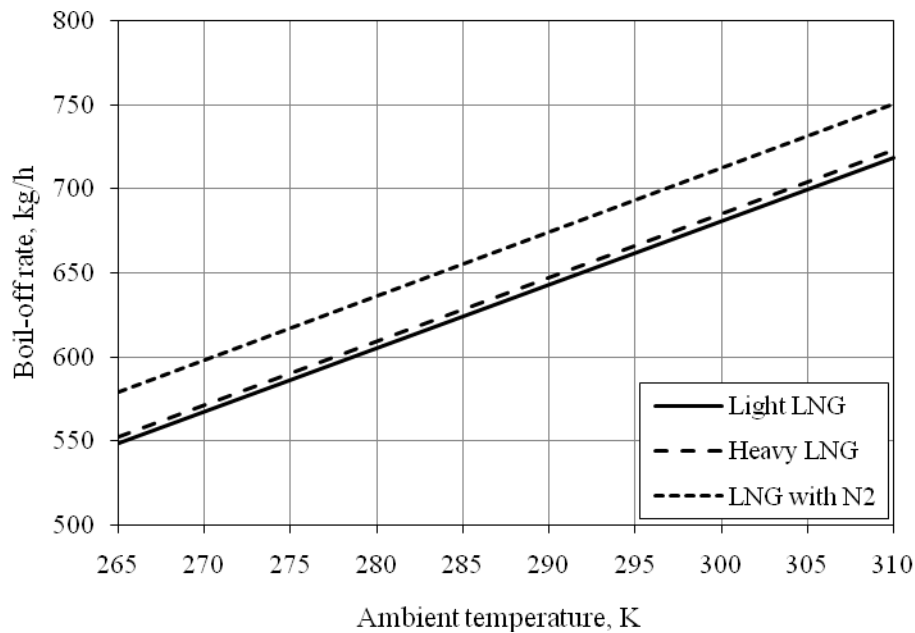


Figure 6. Boil-off rate for presented LNG compositions expressed in amount of mass per time unit.

Second analysis was performed for bi-component mixtures methane-ethane and methane-nitrogen. Ethane besides methane is second important component of LNG. Nitrogen content in LNG is usually very low, but presence of nitrogen in LNG is essential for safety reasons and to ensure the stability of storage process. For ethane content analysis was performed for constant temperature of LNG. In case of nitrogen content the temperature was changing. Higher nitrogen molar fraction causes lowering the boiling temperature of mixture. Results for ethane are presented in figure 7 and for nitrogen in figure 8.

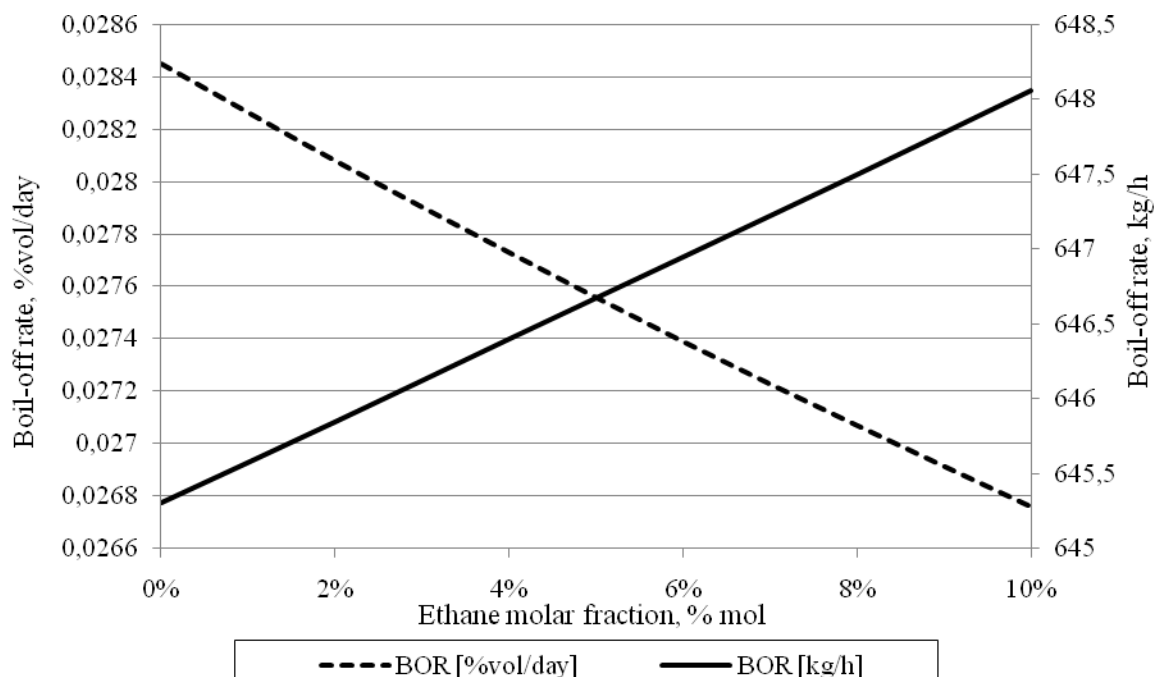


Figure7. Boil-off rate for bi-component mixture methane-ethane.

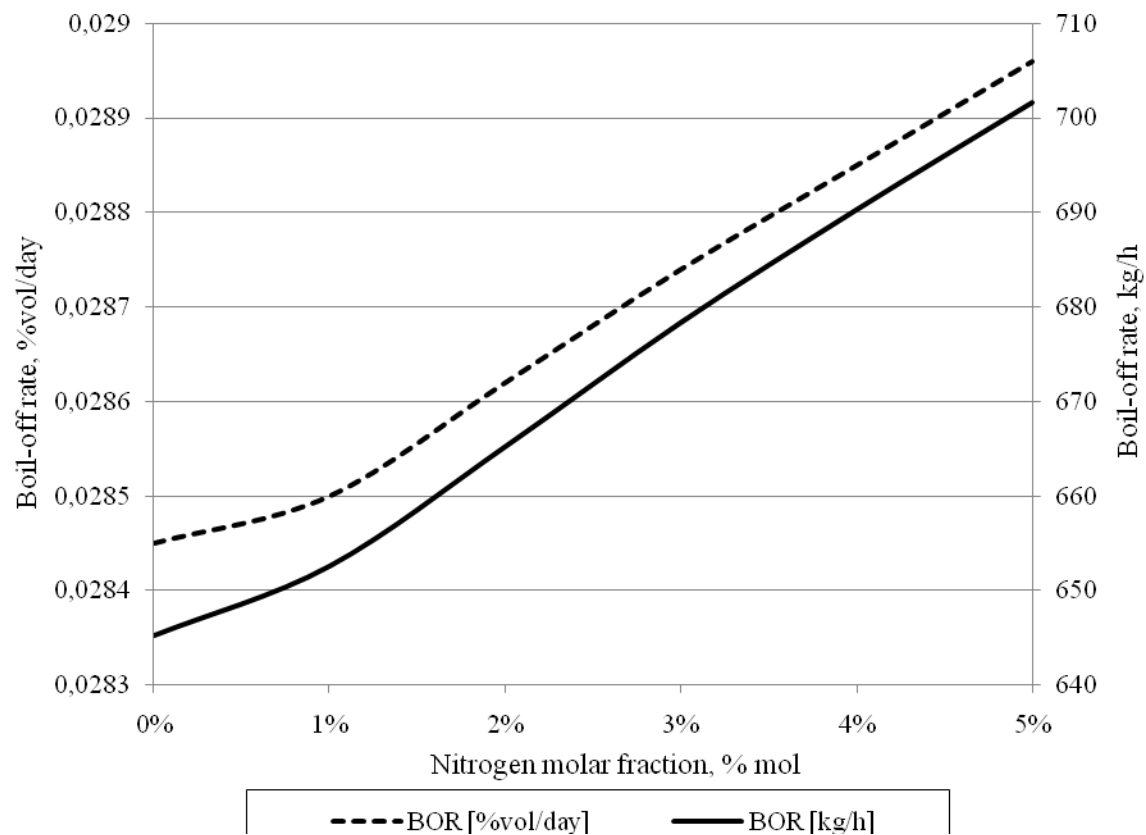


Figure 8. Boil-off rate for bi-component mixture methane-nitrogen.

The evaporation rate as a percentage of LNG volume in the tank decreases with the increase ethane molar fraction in the mixture. In mass terms, there is an slow increase of boil-off rate as a function of ethane molar fraction (from 645.3 kg/h for pure methane to 648.1 kg/h for 10% content of ethane). In the case of the nitrogen content in the mixture, there is an increase in the evaporation rate as a percentage of the volume of LNG in the tank, in mass terms the increase in the Boil Off Rate is significant and rapid as the nitrogen molar fraction in the mixture increases (from 645.3 kg/h for pure methane to 701.6 kg/h for 5% nitrogen content).

5. Conclusions

Boil-off rate problem in LNG supply chain is one of the most important factors for stability and safety of all processes. Key significance of this issue mainly refers to LNG transport by ships and LNG storage processes. Generation of boil-off gas in storage tank depends on heat transfer to tank. Boil-off gas is used during unloading process in which is transported from storage tank to tanks on the ship to prevent the negative pressure in tanks on the ship. During storage process BOG is reliquefied in recondensers and mixed with LNG from storage tank before regasification. The short analysis of boil-off rate problem at receiving terminals was presented in this paper. Boil-off gas generation depends on the composition of LNG. Evaporation rate (BOR) is considered in two ways: as percentage of LNG volume in the tank or as mass of LNG evaporated per time unit. Boil off rate is higher for LNG with nitrogen content than for Light LNG and heavy LNG has a lower BOR than light LNG (as percentage of LNG volume in the tank). Boil-off rate increase with increases of ambient temperature. It results from higher heat transfer from ambient air to LNG in the tank. Performed analysis for bi-component mixtures methane-ethane and methane-nitrogen shows that boil-off rate as percentage of LNG volume in the tank decreases with increase of ethane molar fraction, in case of nitrogen there is opposite

situation - BOR increases with increase of nitrogen content. This is caused by different changes in the boiling temperature due to the participation of ethane and nitrogen.

Acknowledgments

This work has been prepared within the Young Researchers Program; Drilling, Oil & Gas Faculty; AGH UST; grant number: 15.11.190.689.

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