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LIQUEFIED NATURAL GAS STORAGE OF VARIABLE COMPOSITION

MAGAZYNOWANIE SKROPLONEGO GAZU ZIEMNEGO O ZMIENNYM SKŁADZIE

Thanks to the increasing diversification of LNG supply sources, being a result of the growing number of LNG liquefaction installations over the World, increase of short-term trade contracts and general trend to globally liberalize gas markets, reception terminals have to cope with the broad range of qualitatively diversified LNG deliveries from various sources. Different LNG deliveries potentially have different density caused by different gas composition. Although the LNG composition depends on LNG source, it mainly consists of methane, ethane, propane, butane and trace nitrogen. When a new supply of LNG is transported to the tank, the LNG composition and temperature in the tank can be different from LNG as delivered. This may lead to the liquid stratification in the tank, and consequently the rollover. As a result, LNG rapidly evaporates and the pressure in the tank increases. More and more restrictive safety regulations require fuller understanding of the formation and evolution of layers. The paper is focused on the analysis of liquid stratification in the tank which may take place when storing LNG, and which process leads to the rapid evaporation of considerable quantities of LNG. The aim was to attempt modeling of the process of liquid stratification in an LNG tank. The paper is closed with the results of modelling.

Keywords: LNG, liquefied natural gas, regasification, energy efficiency, liquefied gas storing, LNG stratification, double diffusion

Dzięki rosnącej dywersyfikacji źródeł dostaw LNG, spowodowanej zwiększającą się liczbą instalacji skraplania gazu na całym świecie, wzrostem ilości kontraktów krótkoterminowych w handlu i ogólnej tendencji do globalnej liberalizacja rynków gazu, terminale do odbioru muszą radzić sobie z coraz większą gamą różnych jakościowo dostaw LNG z różnych źródeł. Różne dostawy LNG mają potencjalnie inną gęstość dzięki różnym składom gazu. Chociaż kompozycja LNG zależy od źródła, to przede wszystkim składa się z metanu, etanu, propanu, butanu i w śladowych ilościach z azotu. Gdy nowa dostawa LNG jest doprowadzana do zbiornika, skład i temperatura LNG już w zbiorniku może być inny niż dostarczanego. Może to prowadzić do rozwarstwienia cieczy w zbiorniku, a w konsekwencji wystąpienia zjawiska znanego jako „rollover". W wyniku tego zjawiska następuje gwałtowne odparowanie LNG i nagły wzrost ciśnienia w zbiorniku. Coraz bardziej restrykcyjne przepisy dotyczące bezpieczeństwa wymagają pełniejszego zrozumienia zjawiska tworzenia i ewolucji warstw.

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W artykule przeprowadzono analizę procesu rozwarstwienia cieczy w zbiorniku, mogącego wystąpić podczas magazynowania skroplonego gazu ziemnego, a prowadzącego do gwałtownego odparowania znacznych ilości LNG. Celem była próba modelowania procesu powstawania rozwarstwienia się cieczy w zbiorniku LNG. Przedstawione zostały wyniki modelowania tego zjawiska._

Słowa kluczowe:

Nomenclature:

A – cross-section of tank, m^2
C_l – molar concentration of LNG in lower layer, kmol/m^3
C_u – molar concentration of LNG in upper layer, kmol/m^3
$C_{L,l}$ – molar heat capacity of LNG in lower layer, kJ/(kmol·K)
$C_{L,u}$ – molar heat capacity of LNG in upper layer, kJ/(kmol·K)
C_p – specific heat, kJ/(kmol·K)
D – diameter of tank, m
f_Q – part of total heat sent out to vapour space, then returning to LNG (ca. 95%),
g – gravitational acceleration, m/s^2
G – mass content,
h – heat transfer coefficient, W/(m^2·K)
h_s – specific enthalpy, kJ/kg
H – enthalpy, kJ
$\bar{H}_B$ – liquid mass enthalpy, kJ /kmol
$\bar{H}_V$ – enthalpy of vapors formed on top of upper surface, kJ/kmol
$\bar{H}_S$ – enthalpy of liquid on top of upper surface, kJ/kmol
λ – coefficient of thermal conductivity of LNG, W/(m·K)
L – height of tank, m
M – total mass of layer,
m – mass, kg
MW_l – average molecular mass of LNG in lower layer, kg/kmol
MW_u – average molecular mass of LNG in upper layer, kg/kmol
$\dot{M}_{in}$ – total molar flow rate to tank, kmol/s
$\dot{M}_{out}$ – total molar flow rate from tank, kmol/s
$\dot{M}_l$ – molar flow from load to lower layer, kmol/s
$\dot{M}_R$ – molar flow of recirculation between two layers, kmol/(m^2·s)
$\dot{M}_u$ – molar flow from load to upper layer, kmol/s
$\dot{M}_V$ – molar boil-off rate at upper layer, kmol/(m^2·s)
P – total pressure in tank, bar
P_i^{sat} – saturated pressure in area i, bar
q_b – heat flux from tank bottom, W/m^2
q_t – heat flux from tank top, W/m^2
q_{lL} – heat flux from tank side (wall) to lower layer, W/m^2
q_{uL} – heat flux from tank side (wall) to upper layer, W/m^2
q_V – heat flux from tank side (wall) to vapour space, W/m^2

$\bar{q}$ – heat flux, W/m^2
Q – total heat flow from environment to space, W
ρ_l – average density of LNG in lower layer, kg/m^3
ρ_u – average density of LNG in upper layer, kg/m^3
$\bar{\rho}$ – average density of lower and upper layer, kg/m^3
$\Delta\rho$ – difference of lower and upper layer density, kg/m^3
t – time, s
T_l – temperature in lower layer of LNG, K
T_u – temperature in upper layer of LNG, K
T_v – temperature of vapour (LNG),
V – volume of tank, m^3
V_i – molar volume of component i, m^3/kmol
V_m – molar volume of methane, m^3/kmol
$x_l(i)$ – molar concentration of component i in liquid phase in lower layer,
$x_f(i)$ – molar concentration of component i in surface zone,
$x_u(i)$ – molar concentration of component i in liquid phase in upper layer,
$y(i)$ – molar concentration of component i in gaseous phase,
α – heat diffusivity, m^2/s
β – coefficient of thermal expansion,
κ – turbulent coefficient of mass flow, kmol/(m$^2 \cdot$ s)
ν – kinematic viscosity, m^2/s
δ_{VS} – thickness of gaseous space, m
δ_l – thickness of lower layer, m
δ_u – thickness of upper layer, m

Subscripts:

b – bottom of tank,
l – lower later of liquid in tank,
j – expansion coefficient,
R – Rayleigh recirculation,
u – upper layer of liquid in tank,
V, v – gaseous (LNG vapours).

1. Introduction

Thanks to the increasing diversification of LNG supply sources, caused by the growing number of gas liquefaction plants all over the World, increase of short-term trade contracts and general trend to liberalize gas markets, reception terminals have to cope with the broad range of qualitatively diversified LNG deliveries from various sources. Different LNG deliveries potentially have different density caused by different gas composition. Although the LNG composition depends on LNG source, it mainly consists of methane, ethane, propane, butane and trace nitrogen. When a new supply of LNG is transported to the tank, the LNG composition and temperature in the tank can be different from LNG as delivered. This may lead to the liquid stratification in the tank, and consequently the rollover. During liquefaction of natural gas, carbon dioxide, steam and heavy hydrocarbons are mostly removed. Thus obtained product, i.e. LNG is very unstable due to its physical properties, especially high sensitivity to temperature changes. Among factors affecting this instability during liquefied gas storing are:

- Long-term LNG storing, which may take place where LNG is used for covering seasonal extra gas demands,
- Oscillating quality of stored LNG,
- Cyclic processes of LNG pumping-in and pumping-out,
- High nitrogen content in stored LNG.

Each of these factors may to some extent contribute to the rollover effect, i.e. very rapid evaporation of stored LNG in the tank, caused by stratification of liquid inside the tank. The risk of cryogenic liquid stratification appears when two separate layers of different density (density differences result from different LNG compositions) are disposed in one tank.

The maximum evaporation value caused by this effect may be even 20 (or more) times bigger than the standard methane evaporation in LNG tanks, Łaciak and Nagy (2010).

Evaporation of such large amounts of methane may lead to the overpressure in the tank. Moreover, the system removing the methane vapours is not technically adjusted to cope with such a rapid and intense evaporation.

The discussed effect stems from liquid stratification in the tank. Separation of liquid into two layers of different density may be a result of refilling of the tank or too high nitrogen content. It should be also observed that liquid stratification in the tank does not have to be limited only to two layers. Stratification may have an effect in the form of a few layers, each of different density.

In literature there are a few theoretical models of LNG storing in such tanks, e.g. Chaterjee and Geist (1972 and 1976), Germeles (1975), Heestand et al. (1983) or Bates and Morrison (1997). Chaterjee and Geist (1976) analyzed only a two-component gas: methane and nonvolatile heavy hydrocarbons. The assumed input criterion of the stratification process was temperature and composition of layers. Germeles (1975) stated that instead of equal temperatures and composition, the main rollover criterion should be equal liquid densities. Heestand et al. (1983) analyzed five most frequent LNG components, i.e. methane, ethane, propane, *n*-butane and nitrogen. Heestand et al. (1983) who assumed fully turbulent conditions in LNG tank used the correlation of Glob and Dropkin (1959) for determining the amount of heat flowing between two horizontal layers of liquid heated from the bottom.

Chaterjee and Geist (1976) as well as Morrison and Bates (1997) assume the state of thermodynamic equilibrium in the upper layer of LNG resulting from the formed vapours. Hence the temperature of the upper layer is assumed to be constant. Consequently, they assumed that in normal work conditions all the heat flowing to the tank is transformed directly into boil-off heat. Heestand et al. (1983) assume the existence of a thin layer on the upper layer of LNG, which is in thermodynamic equilibrium with the developing vapours.

2. Basic equations

Changes in temperature and LNG composition in every layer may be determined with the use of mass and energy balance for each of them. It is assumed that there is no mass accumulation in the surface layer and that LNG in that area is in thermodynamic equilibrium with the changing LNG vapours.

The equations of mass and energy balance for the lower and upper layers are discussed in the next section.

2.1. Mass balance

Lower layer:

$$\frac{d}{dt}\left[C_l\delta_l x_l(i)\right]=\frac{\dot{M}_l}{A}x_l(i)-\kappa\left(x_l(i)-x_u(i)\right) \tag{1}$$

Upper layer:

$$\frac{d}{dt}\left[C_u\delta_u x_u(i)\right]=\frac{\dot{M}_u}{A}x_u(i)-\dot{M}_v\, y(i)-\kappa\left(x_u(i)-x_l(i)\right) \tag{2}$$

In eq. (1), in the lower layer the rate of composition changes in areas *i* is defined by the evaluation of molar flow rate from the load in the lower part in the tank (in the case of bottom filling of the tank) as well as transport and mass exchange between lower and upper layers. Mass balance for the upper layer is written in a similar way as for the lower layer (eq. (2)), except that evaporation molar flow rate from the upper layer to the boil-off vapour space is taken into account.

The molar evaporation rate from the upper surface layer of the liquid can be calculated from the below equation:

$$\dot{M}_v=\frac{\dot{M}_R\left(\bar{H}_B-\bar{H}_S\right)+f_Q\left(Q/A\right)}{\bar{H}_v-\bar{H}_B} \tag{3}$$

Both areas appearing in the surface layer (liquid and vapours) are in thermodynamic equilibrium. The temperature of the layer corresponds to the tank pressure and vapour pressure in the layer. The zone of equilibrium between vapours and liquid can be characterized with the use of the Peng-Robinson equation of state.

The Rayleigh recirculation flow rate between the upper and surface layer can be calculated with the Hashemi and Wesson method (1971).

Rayleigh recirculation flow rate between the upper and surface layer, $\dot{M}_R$:

$$\dot{M}_R=0{,}3276\frac{\lambda}{C_{L,u}}\left(\frac{g\Delta\rho}{\nu\alpha\,\bar{\rho}}\right)^{1/3} \tag{4}$$

The LNG concentration can be calculated from the average LNG density and average molar mass for the respective layers. The LNG density can be calculated from the Klosek & McKinley correlation (1968), which accounts for the dependence on temperature and composition of LNG.

$$\rho=\frac{\Sigma x_i MW_i}{\Sigma x_i V_i-V_m} \tag{5}$$

when:

$$V_i=f(T)$$

$$V_m=[k_1+(k_2-k_1)(x_{\mathrm{N_2}}/0.0425)]x_{\mathrm{CH_4}} \tag{6}$$

Molar volume V_i depends on temperature and this dependence is read out from molar volume tables worked out for various LNG compositions. V_m is the molar volume of methane. Correction coefficients k_1 and k_2 for various mixtures are also tabelarized (Klosek & McKinley, 1968).

The LNG composition in the evaporating surface can be evaluated with the Raoult law, which can be written as:

$$y(i) = \frac{P_i^{sat}}{P} x_u(i) \tag{7}$$

Apart from the lower and upper layer, the material balance can be also used for the surface area for determining its composition, provided that equilibrium between various LNG vapours exists there.

$$x_f(i) = \frac{(\dot{M}_R + \dot{M}_V) x_u(i) - \dot{M}_V \, y(i)}{\dot{M}_R} \tag{8}$$

The knowledge of LNG composition in the surface area can be then used for determining average molecular mass and LNG enthalpy in that zone.

2.2. Energy balance

Lower layer:

$$\frac{d}{dt}\left[C_l \delta_l C_{L,l}(T_l - T_0)\right] = \frac{\dot{M}_l}{A} C_{L,l}(T_l - T_0) + q_b + \frac{q_{LL} \pi D \delta_l}{A} - h(T_l - T_u) \tag{9}$$

Upper layer:

$$\frac{d}{dt}\left[C_u \delta_u C_{L,u}(T_u - T_0)\right] = \frac{\dot{M}_u}{A} C_{L,u}(T_u - T_0) + f_Q \frac{Q}{A} + \frac{q_{UL} \pi D \delta_u}{A} - h(T_u - T_l) \tag{10}$$

The rate with which heat values change in the lower layer is calculated by taking into account the heat transfer rate from the load to the lower layer (when the tank is filled from the bottom), heat transfer rate from the bottom, from the sides (walls) to the tank and heat transfer rate between upper and lower layers. Similarly, the rate with which enthalpy is changing in the upper layer can be calculated by accounting for the coefficient of heat transfer from the load to the upper layer (tank filled from the top), part of total heat returned from the space of vapours to the upper layer, rate of heat transfer from the sides and rate of heat exchange between the upper and lower layers.

The magnitude of heat and mass flow between layers can be defined from empirical correlations. The Globe and Dropkin (1959) correlation seems to be the appropriate correlation for assessing the heat transfer coefficient between two horizontal layers heated from the bottom:

$$\frac{h}{\lambda} = 0.0597 \left(\frac{\Delta \rho g}{\nu^2 \bar{\rho}} \right)^{1/3} \tag{11}$$

Assuming turbulences inside the tank, the mass flow coefficient can be defined by:

$$\kappa = \frac{h}{C_L} \tag{12}$$

The temperature in the surface zone in the LNG tank is evaluated on the basis saturation pressure, depending on how the vapour pressure values are adjusted to the tank pressure.

In the model proposed by Lukaszewski et al. (2013), the general equations of mass balance as well as material and energy balance equations can be used when evaluating the thickness of each layer. The development of each layer mainly depends on the initial and production conditions in the tank.

$$\frac{d\delta_l}{dt} = \frac{[\dot{M}_l / A - \kappa \Sigma_{i=1}^{N} (x_l(i) - x_u(i))] MW_l}{\rho_l} \tag{13}$$

$$\frac{d\delta_u}{dt} = \frac{[\kappa \Sigma_{i=1}^{N} (x_l(i) - x_u(i)) - \dot{M}_V] MW_u}{\rho_u} \tag{14}$$

The development of transformation of the lower layer is assessed on the basis of molar flow from the load to the lower layer (tank filled from the bottom) and mass transfer rate between two layers; however as far as the upper layer goes, the mass lost due to evaporation should be taken into account. The thickness of the boil-off space of vapours is defined on the basis of the total height of the tank and thickness of the upper and lower layers of LNG.

3. Conditions of formation and development of LNG stratification in tank

3.1. Stratification caused by tank refilling

Stratification caused by tank refilling takes place when:

- Density of added liquefied gas is lower than that of LNG in the tank, and the tank was refilled from the top,
- Density of added liquefied gas is higher than that of LNG in the tank, and the tank was refilled from the bottom,

LNG has various composition and various densities, and so the tendency to form layers on various levels. LNG stored in the tank is divided into two layers: lower and upper layers. On the surface of the top layer there exists a thin film, an interface in a thermodynamic equilibrium with LNG vapours.

Liquid making up the upper and lighter layer is heated from outside, goes up to the surface and is evaporated. Light hydrocarbons evaporate first, evoking changes in the entire composition of that layer. This is ‘weathering’, during which light hydrocarbons evaporate from LNG causing changes in the composition and consequently, in the density of the mixture. The upper layer becomes heavier and heavier. The liquid in the lower layer is also heated, and due to thermal expansion goes up towards the ‘division line’. It is not evaporated owing to the hydrostatic pressure exerted by the upper layer. Ultimately the lower layer becomes warmer and lighter.

When the densities of both layers assume similar values, the layers rapidly mix. When the lower superheated layer gets up to the surface, very intense and violent evaporation of huge quantities of methane takes place.

It is not certain whether the mixing of layers is a result of turbulent turnover, i.e. flip flop effect at the interface, or accidental mixing or in the process of pseudo steady symmetrical mixing.

We may be also faced with a situation that at the initial stage of lighter LNG going up it starts to boil before it reaches the surface. This may happen when the layers ‘flip flop’ unevenly. This may accelerate the rollover effect as the changes in fluid density cause the increase of convective current up, through the upper layer.

In the next case the lower layer starts to boil before the density of the lower liquid becomes lighter than the upper one. The lower layer reaches its bubble point and consequently liquid from the lower layer starts to penetrate the upper layer.

3.2. Influence of nitrogen on LNG stratification in tank

Nitrogen is the most volatile component of LNG. When its content in the stored LNG exceeds 1% of total composition, it may disturb the liquid balance in the tank. The evaporating nitrogen significantly affects the lowering of average density of the remaining liquid in the tank. Methane evaporating from the nitrogen-free mixture does not result in any serious changes in its density, causing only slight increase of bubbling point temperature. The density differences due to nitrogen evaporation may lead to liquid stratification in the tank.

This stratification stems from nitrogen boiling and evaporation from LNG. In such a case LNG becomes lighter, especially when this process takes place in the liquid surface layer in the tank. The causes are twofold. Firstly, nitrogen is usually heavier than the density of mixture making up LNG, therefore its gasification lowers the LNG density. Secondly, with the process of nitrogen boiling the LNG saturation temperature increases; a higher temperature results in lowered LNG density.

An example of LNG stratification was based on a concept model of LNG behaviour in the tank, where the LNG density ρ = 448,792 kg/m^3, 94% methane content, 5% ethane content and 1% nitrogen content.

The outset of spontaneous stratification is presented in Fig. 1.

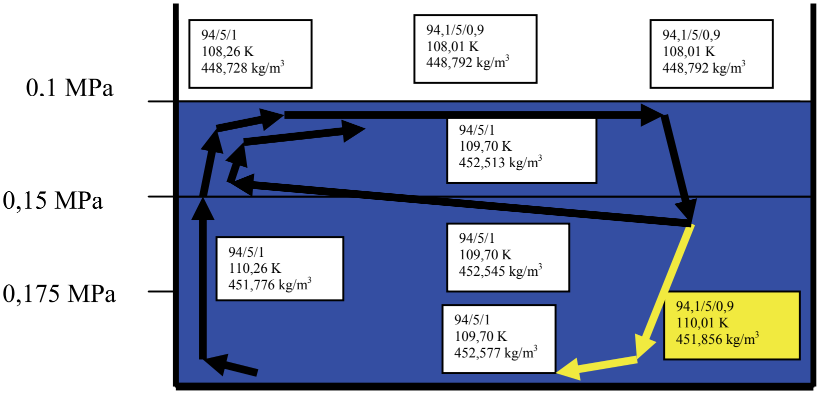

Fig. 1. LNG tank. Modelling of initiation of LNG with nitrogen stratification

The densities in the upper layer are more diversified, and so distributed in the layer itself, that they evoke a stronger recirculation flux, thus accelerating the stratification process.

When the upper layer is fully formed, the lower layer cannot lower its temperature by evaporation. The liquid starts to circulate within the layer and its temperature grows up.

The algorithm proposed method for calculation is shown in Fig. 2. This model is based on a direct search of the physicochemical parameters of LNG. To fit the kinetic parameters are used composition, levels of pressure, temperature and density of the liquid layer. The model can

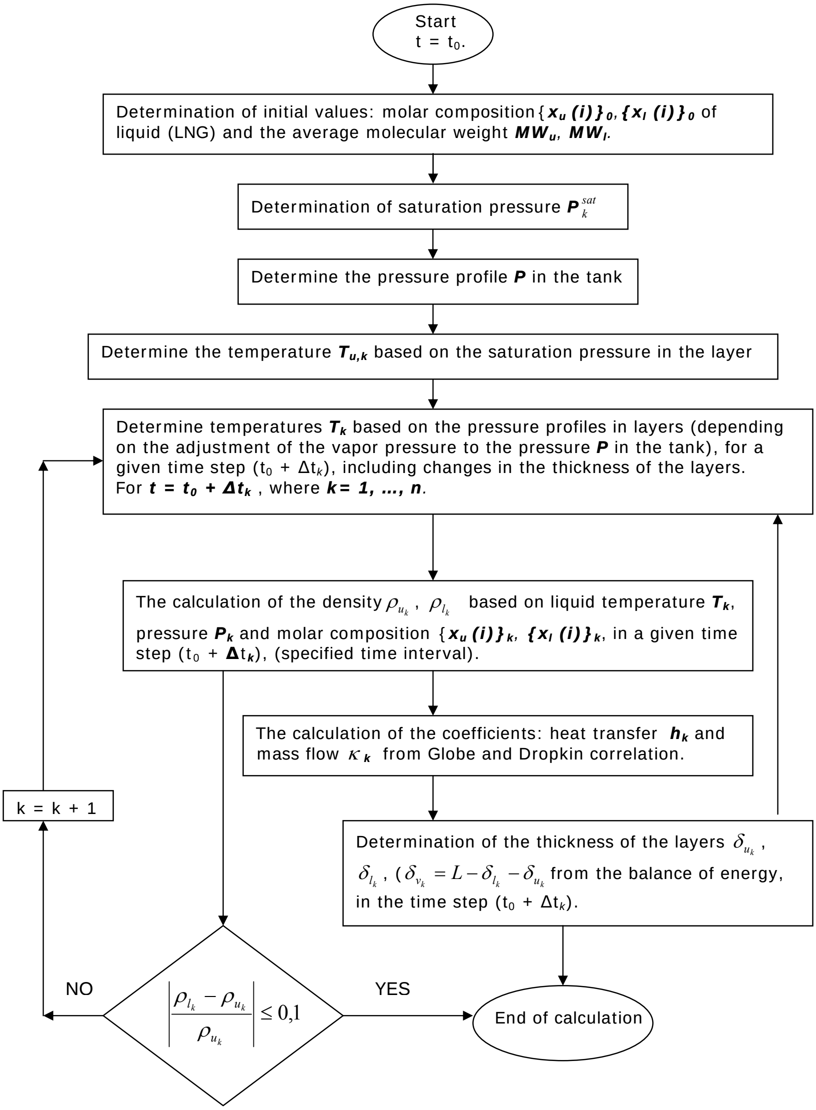

Fig. 2. The calculation of changes in density of the liquid in the tank, in order to determine the time of occurrence rollover

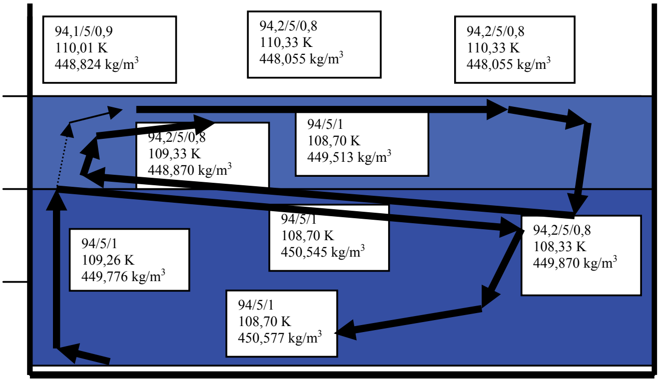

Fig. 3. LNG tank. Modelling of nitrogen induced stratification when upper layer recirculates within itself

be solved iteratively at each iteration by varying the composition and size of thermodynamics, until it comes to fit and align the anticipated changes in the density of the upper and lower layer in the tank with the specified accuracy.

This method also allows the analysis of changes in thermodynamic parameters for forming layers in the LNG tank.

Such a circulation and heating process may trigger out the stratification.

1) In the lower layer the liquid density decreases and spontaneously mixing begins to equalize the density inside (shown in figure 4, after heating up the lower layer).
2) The lower layer may reach the saturation temperature (its bubble point) and start boiling as a consequence of the commenced process of mixing.

If stratified LNG still contains sufficient amounts of nitrogen, the stratification process may take place again.

Changes in temperature and density in the lower and upper layers of the tank are sown in figures 5 and 6, respectively.

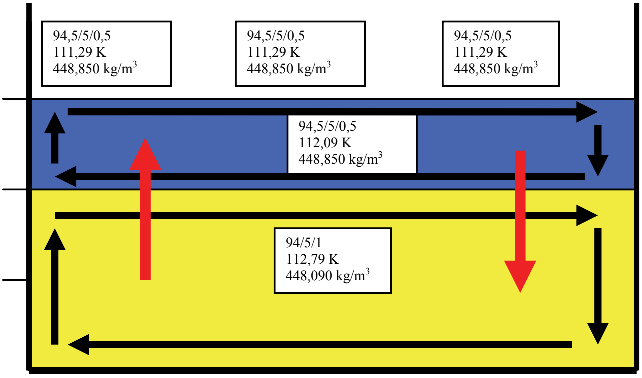

Fig. 4. LNG tank. Modeling of stratification. There is a rise in temperature in lower layer and consequently stratification of liquid in tank (*rollover*)

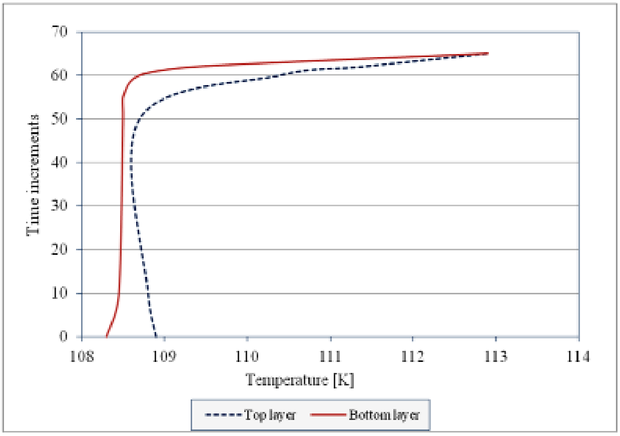

Fig. 5. Changes of temperature of liquefied natural gas containing nitrogen in a tank

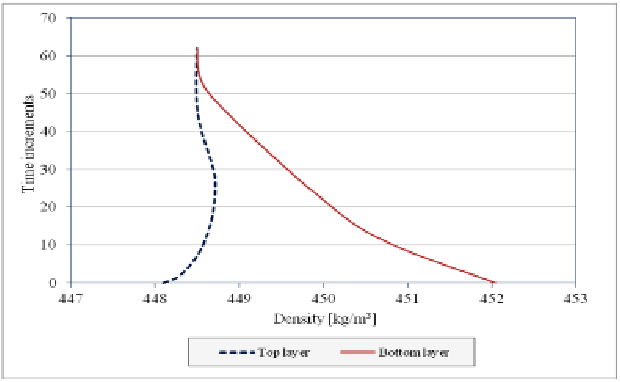

Fig. 6. Changes of the density of liquefied natural gas containing nitrogen, in a tank

Summing up, among nitrogen-related factors which may have influence on the rollover effect are:

- in an LNG tank with relatively high nitrogen content (over 1%), nitrogen is selectively evaporated on the liquid surface.
- lower nitrogen content on the liquid surface results in the increased saturation temperature of LNG. This and the fact that the specific weight of nitrogen is bigger than that of LNG causes that the density of the upper layer of condensed gas in the tank are lowered.
- lowered density in the upper layer of LNG causes spontaneous process of constant liquid mixing to stop the ongoing separation.

The density changes of natural gas having two compositions are presented in figure 7:

1. 91% methane, 8% ethane, 1% nitrogen;
2. 91% methane, 9% ethane.

In the first case, the change of LNG composition related with the presence of nitrogen was accounted for in each time-step. In each iteration, the respective composition changes in LNG tank were changed from the previous one.

The proposed modelling is based on a concept in which analyzed liquids are mixing due to induced convection. Though this is a concept modeling, it pictures the real behaviour of LNG in the storing tank.

The influence of nitrogen content on LNG boiling point is presented in figure 8.

The calculations for a liquid being a mixture of methane, ethane and nitrogen were followed by the analysis of influence of nitrogen on boiling point of the mixture. Interestingly, the mixture with 1.9% nitrogen content at a pressure of 0.155 MPa has approximately the same boiling points as the nitrogen-free mixture at a pressure of 0.105 MPa. Hence the conclusion that the boiling process may develop in the lower layer, despite the fact that it remains under pressure exerted by the upper LNG layer.

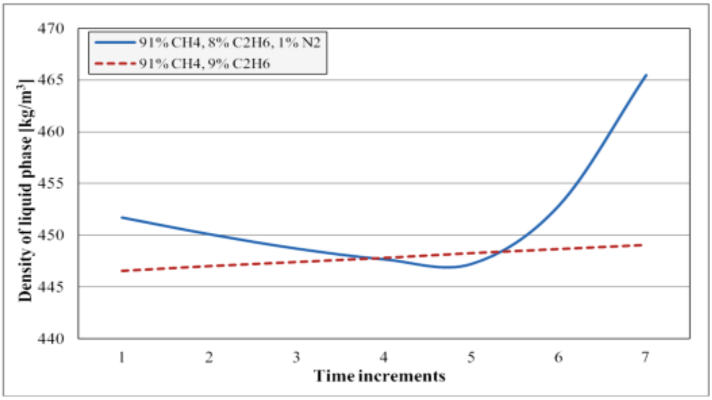

Fig. 7. Density changes of the continuously mixing liquid phase of LNG, in two different configurations (91% methane, 8% ethane, 1% nitrogen, 91% methane, 9% ethane), and in successive time steps corresponding to those temperatures

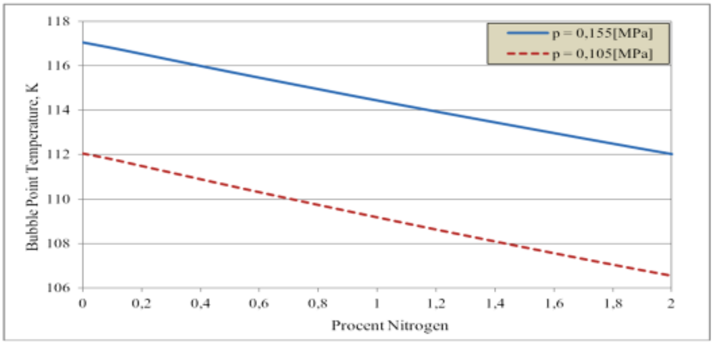

Fig. 8. Influence of nitrogen content on LNG bubble point

4. Summary

Despite numerous improvements in the LNG tank design, stratification, which may consequently lead to the rollover effect, still remains a serious hazard.

This is related with:

- Necessity to diversify the LNG import, when maintaining optimum costs and providing uninterrupted deliveries.
- Movement of LNG between tanks within one terminal (e.g. to cool down the content of one tank with the use of LNG from another one).
- Aging of LNG (in storing conditions LNG at a temperature of about -161°C and pressure over atmospheric pressure, only the boiling points of methane and nitrogen are exceeded, causing their evaporation and consequently, change of liquid composition in the surface layer).
- Operators, who in the case of a bottom inlet, fill up the tank with heavier liquid instead of using natural mixing of liquids. This can be explained by the wish to avoid a rapid transition from the liquid phase to vapours; nonetheless stratification occurs.

It seems of key importance to predict the heat and mass transfer at the liquid/liquid interface (depending on the model used and LNG properties this can be a liquid/gas interface). Both these processes are strongly influenced by heat and mass transfer coefficients, therefore should be specified as accurately as possible.

Nitrogen content has a significant impact on the rollover effect.

- In LNG tank with relatively high (over 1%) nitrogen content, nitrogen is selectively evaporated on the liquid surface.
- Decreased nitrogen content on the liquid surface results in higher LNG saturation temperature. This and the fact that the specific weight of nitrogen is bigger that of LNG cause that the density of the upper layer of condensed gas in the tank are lowered.
- Lowered density in the upper LNG layer triggers out a spontaneous process of constant mixing of liquid to overcome the ongoing stratification.

When analyzing the causes of stratification one may observe that the presence of nitrogen in LNG may result in the following problems:

- N_2 lowers the saturation temperature of LNG, e.g. saturation temperature of nitrogen-free LNG is 112.0 K, and up to 109.2 K for LNG with 1% N_2 content.
- N_2 hinders or reverses densification of LNG in time.
- N_2 increases LNG density.
- N_2 lowers calorific value of LNG.
- N_2 may be the cause of problems related with the required end composition of gas from regasification.

The paper analyzes the process of liquid stratification in a tank which may take place during liquefied natural gas storing, leading to rapid evaporation of considerable quantities of LNG. The results of modeling of this effect are presented. The modelling is focused on determining hazards related with the formation of layers and the planned solutions. The proposed model, based on a concept that the analyzed liquids are mixing due to induced convection, pictures a real course of density changes in LNG with nitrogen content.

References

Baker N., Creed M., 1996. *Stratification and rollover in liquefied natural gas storage tanks*. Trans. Chem., 74 (Part B).

Bates S., Morrison D.S., 1997. *Modelling the behaviour of stratified liquid natural gas in storage tanks: a study of rollover phenomenon.* Int. J. Heat Mass Transfer, 40 (8).

Chaterjee N., Geist J.M., 1972. *The effects of stratification on boil-off rates in LNG tanks*. Pipeline Gas J., 199 (40).

Chaterjee N., Geist J.M., *Spontaneous stratification in LNG tanks containing nitrogen*. Paper 76-WA/PID-6, ASME Winter Annual Meeting, New York, December 5.

Deshpande K.B., Zimmerman W.B., Tennant M.T., Webster M.B., Lukaszewski M.W., 2011. *Optimization methods for the real-time inverse problem posed by modelling of liquefied natural gas storage*. Chemical Engineering Journal, 170 (1).

Germeles A., 1975. *A model for LNG tank rollover*. Advances in Cryogenic Engineering. 21 Plenum Press.

Globe S., Dropkin D., *Natural convection heat transfer in liquids confined by two horizontal plates and heated from below*. J. Heat Trans, C81 (24).

Hashemi H.T., Wesson H.R., 1971. *Cut LNG storage costs.* Hydrocarbon Processing.

Heestand J., Shipman C.W., Meader J.W., 1983. *A predictive model for rollover in stratified LNG tanks.* A.I.Ch.E. Journal, 29.

Hisazumi Y., Yamasaki Y., Sugiyama S., 1998. *Proposal for a high efficiency LNG power-generation system utilizing waste heat from the combined cycle.* Applied Energy, 60.

Klosek J., McKinley C., 1968. *Densities of liquefied natural gas and of low molecular weight hydrocarbons.* First International Conference on LNG. Chicago.

Lukaszewski M.W., Zimmerman W.B., Tennant M.T., Webster M.B., 2013. *Application of inverse methods based algorithms to Liquefied Natural Gas (LNG) storage management*. Chem. Eng. Res. Des.

Łaciak M., 2011. *Problemy techniczne i technologiczne eksploatacji terminali rozładunkowych LNG.* Wiertnictwo, Nafta, Gaz, Tom 28 (4).

Łaciak M., 2012. *Properties of artificial gaseous mixtures for their safe use and support the natural gas supply networks*. Arch. Min. Sci., Vol. 57, No 2.

Łaciak M., 2013. *Thermodynamic processes involving Liquefied Natural Gas at the LNG receiving terminals*. Arch. Min. Sci., Vol. 58, No 2. p. 349-359.

Łaciak M., Nagy S., 2010. *Problemy bezpieczeństwa technicznego i charakterystyka zagrożeń związanych z terminalem rozładunkowym LNG*. Wiertnictwo, Nafta, Gaz, Tom 27 (4).

Morrison D.S., Richardson A., 1990. *An experimental study on the stability of stratified layers and rollover in LNG storage tanks.* Proceedings of the Low Temperature Engineering and Cryogenics Conference. Southampton, U.K.

Sarsten J.A., 1972. *LNG stratification and rollover*. Pipeline Gas J., 199.

Siemek J., Nagy S., 2012. *Energy Carriers Use in the World: Natural Gas – Conventional and Unconventional Gas Resources*. Arch. Min. Sci., Vol. 57, No 2.

Vitale S.A., 2012. *LNG and Gas Thermodynamics*. Vol. II. GTI.

Zimmerman W.B., 1998. *The effect of chemical equilibrium on the formation of stable stratification*. Appl. Sci. Res., 59.

Zimmerman W.B., Rees J.M., 2007. *Rollover instability due to double diffusion in a stably stratified cylindrical tank.* AIP, Physics of fluids, 19.

Gaz de France, Shell Research Ltd., Osaka Gas, Tokyo Gas, CFP-Total: *Experimental study of stratified LNG performed at Nantes Cryogenic Testing Station*, 1987 to 1990.

REFPROP, NIST SRD, Version 9.0.

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