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**SELECTED THERMODYNAMIC ASPECTS
OF LIQUEFIED NATURAL GAS (LNG) PIPELINE FLOW
DURING UNLOADING PROCESS****

1. NOMENCLATURE

- a, b – Peng–Robinson EOS parameters,
 C_p – isobaric heat capacity [J/(kg·K)];
 D_{in} – pipeline inner diameter [m],
 D_{ins} – pipeline outer diameter with insulation [m],
 D_{out} – pipeline outer diameter [m],
 g – gravity constant [m/s²],
 k – thermal conductivity of fluid [W/(m·K)],
 k_{ins} – thermal conductivity of insulation [W/(m·K)],
 k_{pipe} – thermal conductivity of pipeline steel [W/(m·K)],
 L – pipeline length [m],
 Ms – mass flow rate [kg/s],
 p – pressure [Pa],
 Q – flow rate [m³/s],
 R – ideal gas constant [J/(mol·K)],
 Re – Reynolds number [–],
 T – temperature of fluid [K],
 T_c – critical temperature [K],

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- T_{out} – ambient temperature [K],
- U – overall heat transfer coefficient [$\text{W}/(\text{m}^2 \cdot \text{K})$],
- v – molar specific volume [m^3/mol],
- w – flow velocity [m/s],
- x – pipeline segment length [m],
- δ – absolute roughness [m],
- Δp – pressure drop [Pa],
- α_{in} – inner convective heat transfer coefficient [$\text{W}/(\text{m}^2 \cdot \text{K})$],
- α_{out} – outer convective heat transfer coefficient [$\text{W}/(\text{m}^2 \cdot \text{K})$],
- ε – relative roughness [-],
- θ – angle of inclination of the pipeline [$^\circ$],
- λ – linear friction coefficient [-],
- μ – fluid dynamic viscosity [$\text{Pa} \cdot \text{s}$],
- μ_{JT} – Joule-Thomson coefficient [K/Pa],
- ρ – fluid density [kg/m^3],
- σ – pipe wall thickness [m],
- ω – acentric factor [-],

2. INTRODUCTION

Storage tanks for liquefied natural gas are localized a few hundred meters to a few kilometers from the point of unloading. The unloading of LNG which has a very low temperature (about -162°C) from the unloading pipe connecting the methane ship with the storage tank is performed through technological lines. Depending on the designed system this can be a single line 32 to 48 inches (about 800 to 1200 mm) of diameter or two identical pipelines 24 to 26 inches (about 600 to 700 mm) of diameter. While unloading, the vapor phase may appear in the line due to the heat transport from outside to the liquefied natural gas (-162°C). This is the so-called Boil Off Gas (BOG), the appearance of which considerably deteriorates the flow conditions in the line and also has an influence on the composition and properties of LNG. Boil Off Gas from the unloading pipeline and from the storage tank is returned to the ship through a technical pipeline (Vapor Return Line). This operation helps prevent excessive pressure build up in the storage tank and also prevents underpressure formation in the methane ship tanks when emptying the tank. The excessive quantities of Boil Off Gas are directed to the atmosphere which is both environmentally and economically disadvantageous [8, 9, 14]. A simplified analytical model describing the flow of liquefied natural gas (LNG) in underground unloading pipeline is presented in the paper. The proposed model can be used for determining basic parameters of transmitted LNG (pressure, temperature, density, viscosity) for a given composition in a function of pipeline length and a simplified description of heat exchange between the environment and transmitted LNG.

3. THERMODYNAMIC MODEL ASSUMPTIONS

The thermodynamic model of LNG flow was based on a selected pipeline, the parameters of which are presented in Table 1. For increasing the accuracy of calculations of the model, an exemplary pipeline of constant diameter was divided into equal sections 100 meters long, methodic scheme of pipeline is presented in Figure 1. The pipeline will be thermally insulated with polyurethane foam. The cross section of the pipeline and the thermal insulation are presented in Figure 2. The basic assumption of the presented model is a single-phase flow of a cryogenic fluid (LNG), presenting the variability of basic thermodynamic parameters in the unloading pipeline in static conditions in a function of its length.

Table 1
Basic parameters of LNG unloading pipeline

Inner diameter	D_{in}	800 mm
Pipeline Length	L	2000 m
Thermal conductivity of pipeline steel	k_{pipe}	67 W/(m·K)
Thermal conductivity of pipeline insulation	k_{ins}	0,05 W/(m·K)
Relative pipeline roughness	ε	0,000125
Heat convective transfer coefficient from ambient air	α_{out}	12 W/(m ² ·K)

The composition of liquefied natural gas used for calculations is presented in Table 2, whereas the bubble point curve (p - T) for a given range of temperatures 110 to 150 K, density of liquid phase and participation of vapor phase in a function of pressure and temperature in Figure 3.

Table 2
Example composition of LNG

Component	Short symbol	Molar fraction [%]
Methane	C ₁	89,87
Ethane	C ₂	6,65
Propane	C ₃	2,30
n-Butane	nC ₄	0,57
iso-Butane	iC ₄	0,41
n-Pentane	nC ₅	0,00
iso-Pentane	iC ₅	0,01
Nitrogen	N ₂	0,19

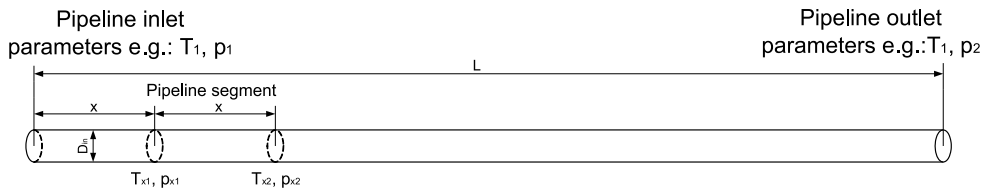


Fig. 1. Modeled LNG pipeline scheme

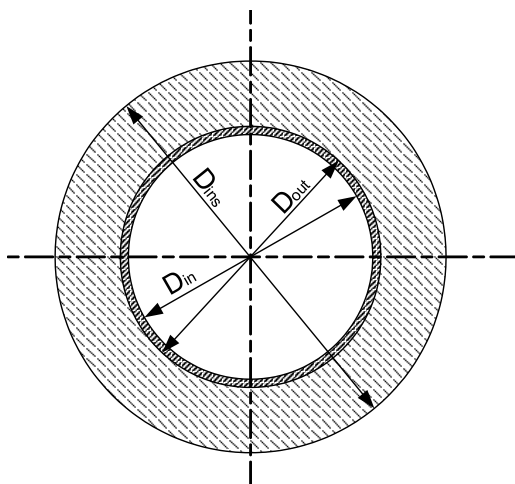


Fig. 2. Cross-section of modeled LNG pipeline

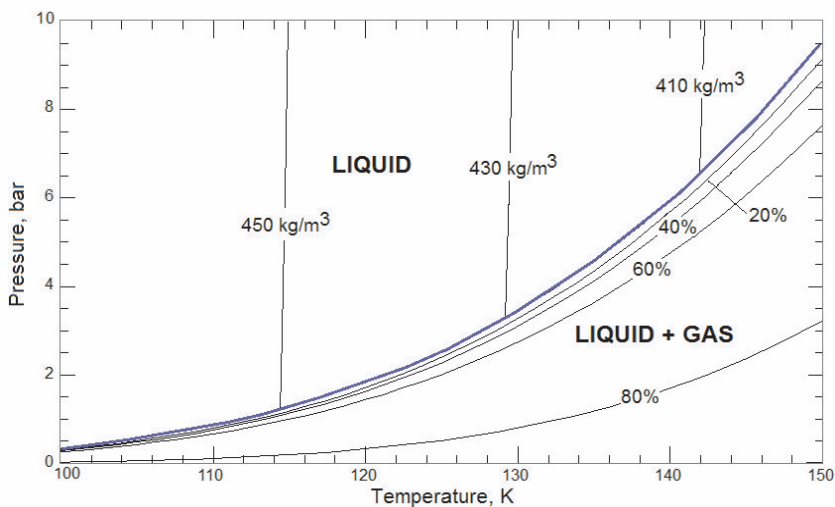


Fig. 3. P - T plot of gas mixture from Table 2 in the range of temperatures between 100 and 150 K. Also density of the liquid phase and molar fraction of vapor phase in the function of pressure and temperature

4. THERMODYNAMIC STATIC MODEL OF PIPELINE CRYOGENIC FLUID FLOW

The proposed static hydraulic model of cryogenic fluid flow in a pipeline describes changes of basic thermodynamic parameters of liquefied natural gas in a function of pipeline length. The pressure drop in a given segment of the pipeline is described with the Darcy–Weisbach equation:

$$\Delta p_i = \frac{\lambda \cdot x \cdot \rho \cdot w^2}{2D} \quad (1)$$

After introducing a dependence for the flow rate the equation:

$$w = \frac{4 \cdot Ms}{\pi \cdot D^2 \cdot \rho} \quad (2)$$

has the form:

$$\Delta p_i = \frac{8\lambda \cdot x \cdot Ms^2}{\pi^2 \cdot \rho D^5} \quad (3)$$

After introducing a dependence for the flow rate the equation:

$$P_{i+1} = P_i - \Delta p_i \quad (4)$$

The linear friction coefficient was determined on the basis of Coolebrok–White equation [2, 10]:

$$\frac{1}{\sqrt{\lambda}} = -2 \log \left(\frac{2.51}{\text{Re} \cdot \sqrt{\lambda}} + \frac{\varepsilon}{3.71} \right) \quad (5)$$

The temperature changes model in a function of line length is described with the equation [3, 4]:

$$\begin{aligned} T_{i+1} = & T_{out} + (T_i - T_{out}) \cdot \exp \left(\frac{-x \cdot U \cdot \pi \cdot D_{in}}{Ms \cdot C_p} \right) + \\ & + \frac{Ms}{\pi \cdot U \cdot D_{in}} \left(\mu_{JT} \cdot C_p \cdot \frac{dp}{dx} - g \cdot \sin(\theta) \right) \left(1 - \exp \left(\frac{-x \cdot U \cdot \pi \cdot D_{in}}{Ms \cdot C_p} \right) \right) \end{aligned} \quad (6)$$

The Joule–Thompson coefficient and the angle of inclination of the pipeline equal to $\theta = 0^\circ$ were assumed in equation (6). The following relation was obtained:

$$\begin{aligned} T_{i+1} = & T_{out} + (T_i - T_{out}) \cdot \exp \left(\frac{-x \cdot U \cdot \pi \cdot D_{in}}{Ms \cdot C_p} \right) + \\ & + \frac{Ms}{\pi \cdot U \cdot D_{in}} \left(\mu_{JT} \cdot C_p \cdot \frac{dp}{dx} \right) \left(1 - \exp \left(\frac{-x \cdot U \cdot \pi \cdot D_{in}}{Ms \cdot C_p} \right) \right) \end{aligned} \quad (7)$$

The remaining thermodynamic parameters of the transmitted LNG were calculated with the Peng–Robinson equation of state commonly used for determining phase equilibria of liquid/vapors of hydrocarbon mixtures [11]:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (8)$$

where:

$$a(T) = a \cdot \alpha(T, \omega) \quad (9)$$

$$a = 0.45724 \frac{R^2 \cdot T_c^2}{P_c} \quad (10)$$

$$b = 0.07780 \frac{R^2 \cdot T_c}{P_c} \quad (11)$$

$$\alpha(T, \omega) = \left(1 + m \left(1 - \sqrt{\frac{T}{T_c}} \right) \right)^2 \quad (12)$$

$$m = 0.379642 + 1.48503\omega + 0.164423\omega^2 + 0.016667\omega^3 \quad (13)$$

5. PIPELINE HEAT TRANSFER DESCRIPTION

While transporting a cryogenic fluid, e.g. liquefied natural gas, it is crucial to accurately determine heat exchange taking place between ambient air and the fluid transmitted through the pipeline. Excessive inflow of heat to the transmitted LNG may result in an increase of its temperature, and consequently presence of vapor phase in the pipeline. During a typical operation of LNG unloading at a terminal, the BOR may range between 1100 do 11000 kg/h per 1 km of the unloading pipeline. An exemplary dependence of participation of vapor phase versus temperature for a few pressure values of an LNG composition taken from Table 2, is presented in Figure 4.

The control and ability to control the conditions in which LNG will be evaporated are crucial for safe exploitation of LNG terminal as far as storage tanks and LNG reloading lines are concerned. The presence of vapor phase in the stream of running LNG (two-phase system) negatively influences the entire unloading process and its safety. One of the key factors influencing the amount of boiling-off LNG are the type, quality and thickness of applied thermal insulation [7, 8, 9].

The changes of molar fraction of particular components of analyzed natural gas in liquid and vapor phases in a function of temperature at 1 bar pressure are presented in Figure 5. For thus assumed composition of liquefied natural gas and at a pressure of 1 bar the evaporation process was initiated at a temperature of 111.84 K – in these conditions the vapor phase

constitutes only 0.02% of the entire system with the dominating role of methane (~95%) and nitrogen (~5%); the molar fraction of the remaining components is negligible. With the increasing temperature at a pressure of 1 bar, the vapor methane content increases and nitrogen decreases, which owing to its characteristic boils off first. With the further temperature growth the participation of ethane and propane also slightly increases in the vapor phase. With the growing temperature in the vapor phase the participation of boiling-off methane decreases, whereas the molar fraction of ethane, propane and heavy hydrocarbons, which evaporate in much higher temperatures, increases. When the evaporation begins it is nitrogen which boils off first. This results in a temporary drop of density of liquid phase and is a negative effect in the process of LNG storing (Fig. 6).

The key value determining the ability of a specific cylindrical membrane to transfer heat is the overall heat transfer coefficient U . For a line having complex parameters (see Tab. 1 and Fig. 2) the heat transfer coefficient is determined with a formula [1]:

$$U = \frac{1}{\frac{1}{\alpha_{in}} + \frac{\ln\left(\frac{D_{out}}{D}\right) \cdot D_{in}}{2 \cdot k_{pipe}} + \frac{\ln\left(\frac{D_{ins}}{D_{out}}\right) \cdot D_{in}}{2 \cdot k_{ins}} + \frac{D_{in}}{\alpha_{out} \cdot D_{ins}}} \quad (14)$$

In equation (14) α_{in} is the convective heat transfer coefficient. In the case of turbulent flow, when $Re > 10000$ in the first approximation, the Dittus-Boelter equation can be used for determining the heat transfer inside the pipeline [3]

$$\alpha_{in} = 0.023 \frac{k^{1-n} \cdot Ms^{0.8} \cdot C_p^n}{\mu^{0.8-n} \cdot D_{in}^{0.2}} \quad (15)$$

where $n = 0.4$ for fluids which are cooler than their environment.

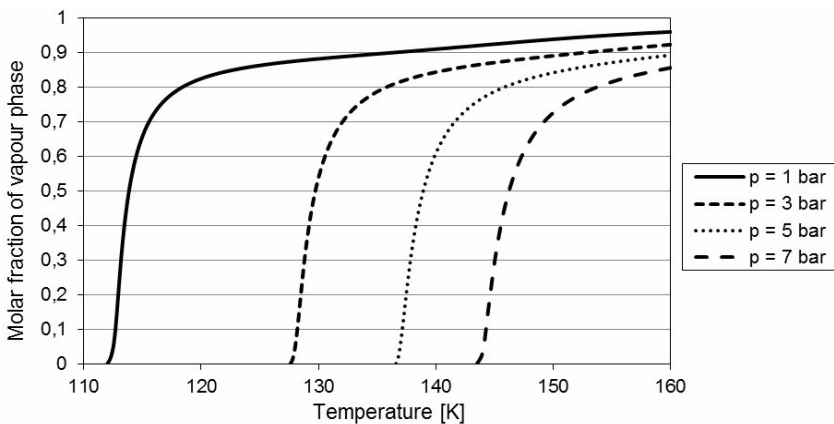


Fig. 4. The molar ratio of the vapor phase in the system in the function of temperature for the LNG composition shown in Table 2 (also for chosen pressures)

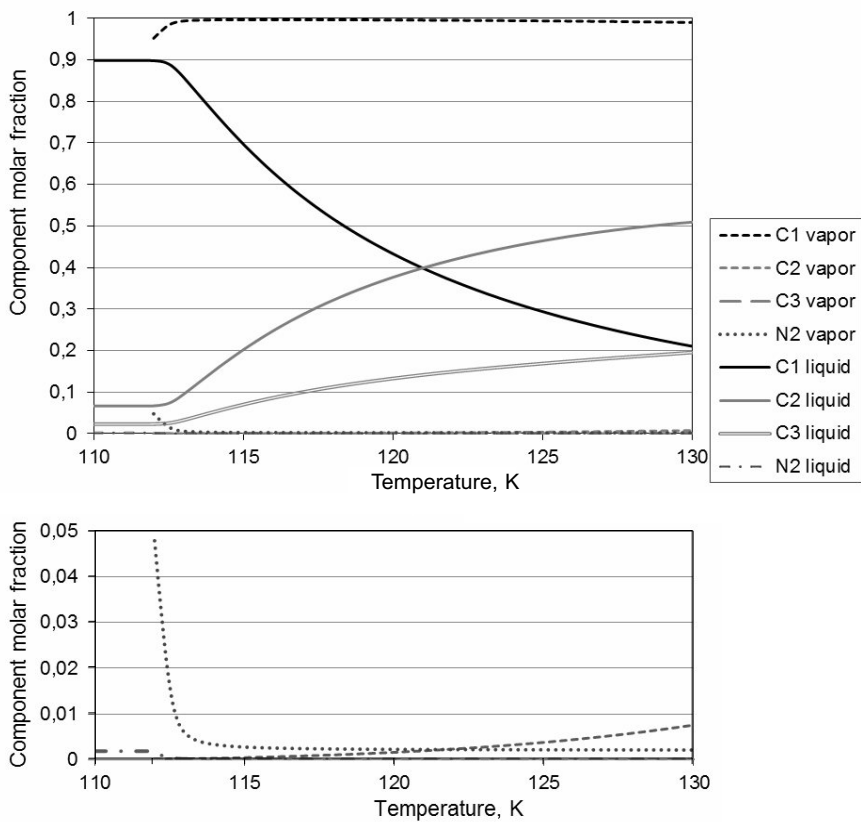


Fig. 5. Molar fraction of LNG components in liquid and vapor phase. Bottom chart shows detailed molar fraction range between 0 and 5%

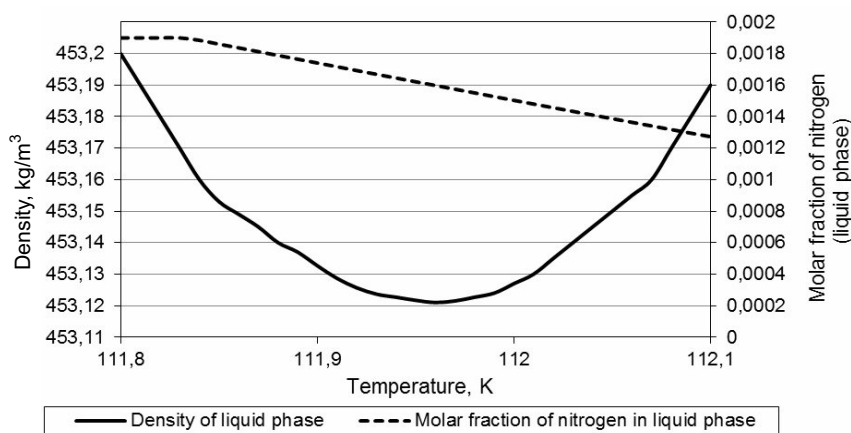


Fig. 6. Changes in the density of the liquid phase during the evaporation of nitrogen from LNG as a function of temperature

6. CALCULATIONS ALGORITHM

The proposed calculation algorithm is devised for a static model and can be used for determining changes of basic thermodynamic parameters when LNG flows in the pipeline (Fig. 7).

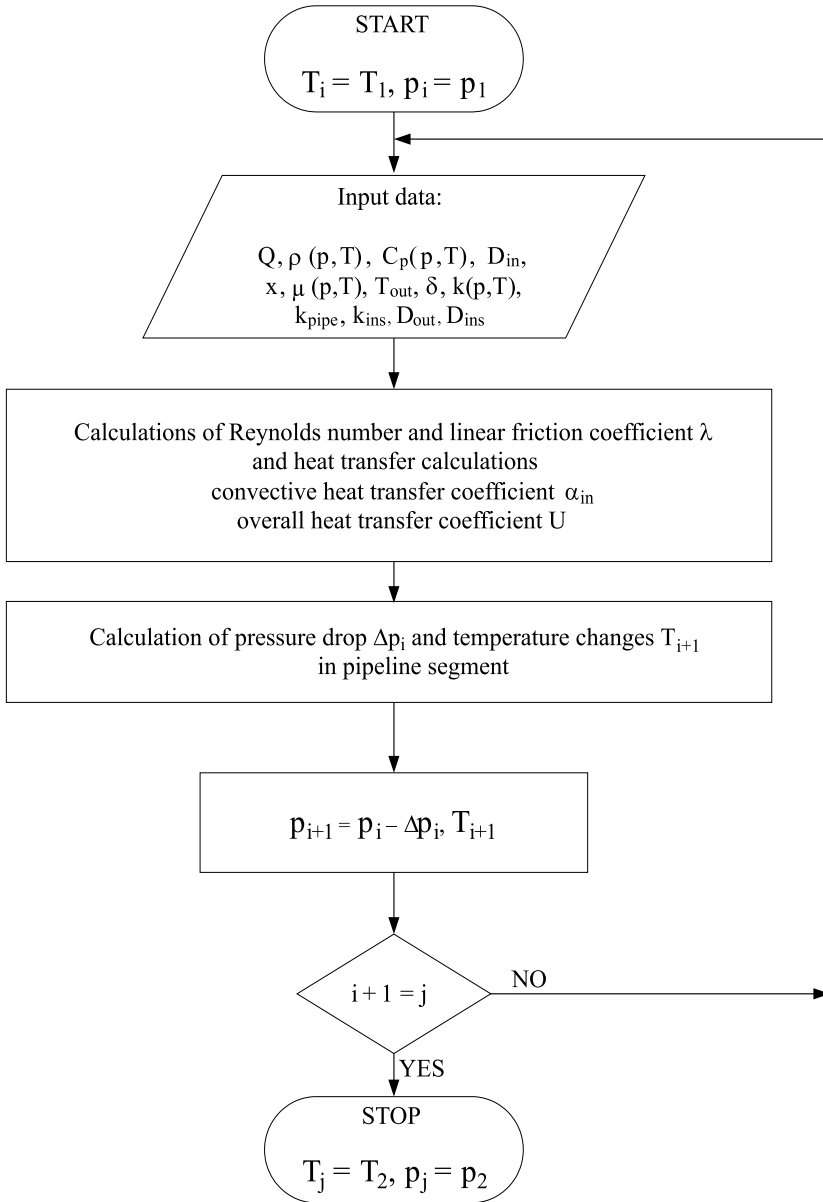


Fig. 7. Calculations algorithm

The calculations can be done for the successive segments of the pipeline. The following parameters were assumed in the model: first of all inlet pressure p_i , inlet temperature T_i and parameters characterizing the pipeline, i.e. diameter, thickness of the pipe wall, thickness and properties of the applied thermal insulation. Then follow density, viscosity and other parameters of the analyzed gas which depend on p_i and T_i . The successive step lies in determining parameters on the basis of which the drops of pressure (e.g. linear friction coefficient) and temperature (heat transfer coefficient) can be defined. After performing all preliminary calculations for each segment we obtain output pressure (p_{i+1}) and output temperature (T_{i+1}). The dependences used for determining the drop of pressure and temperature allow for conducting calculations simultaneously. On this basis the entry parameters are calculated for each pipeline section with the Peng–Robinson equation of state. These calculations are repeated for the successive pipeline segments (j – number of pipeline segments).

7. CALCULATION RESULTS

The basic parameters characterizing the process of LNG unloading is the time of unloading. A typical time of unloading for a methane ship equals to 12 to 24 hours; for economy reasons this time should be shorter and attempts are frequently made to shorten the time of all unloading operations to 12–16 hours. The standard capacity of methane ships equals to about 150,000 m³; Q-flex methane ships have capacity of 215,000 m³, and the biggest Q-max ones even to 260,000 m³ [7]. Depending on the ship, the total flow rate in the unloading pipelines is 300,000 to 520,000 m³/day during 12 hours of unloading, and 150,000 to 260,000 m³/day during 24 hours of unloading. The 24-hours variant was assumed in the calculations for a methane ship of 200,000 m³ capacity. The inlet pressure of the LNG pumped into the pipeline was assumed at a level of 5 bar, and its temperature at a level of 111 K. In such conditions the density of liquefied natural gas equaled to 454.46 kg/m³. Heat overtaken by LNG during operation of pumps was ignored in the calculations. Pressure and temperature changes in a function of pipeline length are presented in Figure 8. Owing to a very large mass flow rate (1050 kg/s) the observed temperature increase in the assumed section of the transmission pipeline was low, i.e. about 0.36 K (almost a linear function).

The density and viscosity changes of the liquefied natural gas in the unloading pipeline are presented in Figure 9. These values may slightly vary and the liquefied natural gas remains in the liquid phase in the assumed range of pressure and temperature values.

The simplified model of the pipeline does not account for local pressure losses due to the changes of direction of the unloading pipeline. The developed variant of this model should account for the losses due to the cryogenic fluid flow through subs, elbows, valves and compensators.

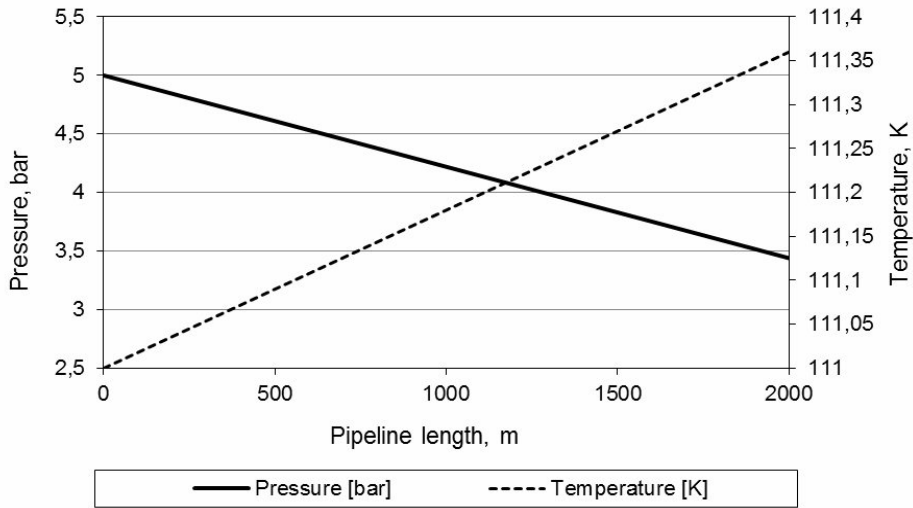


Fig. 8. Pressure and temperature changes versus unloading pipeline length

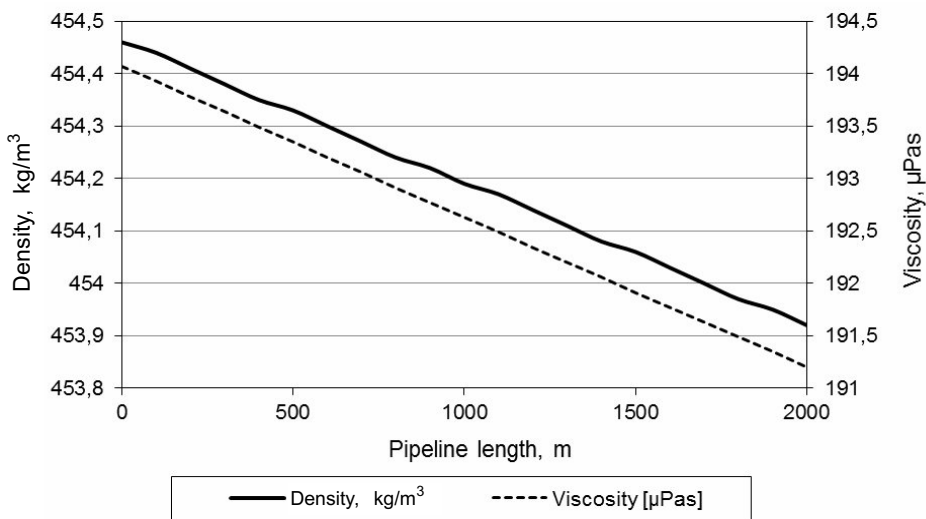


Fig. 9. Density and viscosity of liquefied natural gas versus unloading pipeline length

8. CONCLUSIONS

The presented model describes changes of basic thermodynamic parameters of liquefied natural gas (LNG) during its flow through the unloading pipeline between a methane ship and the storage tank on the terminal. The calculations were based on the Peng–Robinson

equation of state commonly applied for determining phase equilibria for liquid/vapor of hydrocarbon mixtures. The obtained results proved the applicability of the Peng–Robinson equation to the calculation of thermodynamic parameters of cryogenic fluids, e.g. LNG. The pressure drop was determined on the basis of the Darcy–Weissbach equation; it can be applied for one-phase flow of liquid phase. In the presence of vapor phase (two-phase system) other correlations should be used, e.g. Lockhart–Martinelli correlation, Friedel correlation or other. Calculations can be also based on other empirical correlations. For determining temperature changes in a function of pipeline length, the Schorres model was used. This model was modified by other authors and used for calculating temperature changes in pipelines transmitting hydrocarbons, including two-phase systems. Owing to the short unloading time, the mass flow rate of transported LNG is high in the analyzed case, therefore the calculated increase of LNG temperature in a short pipeline section was small and the liquefied natural gas of assumed composition remained in a liquid phase. The correct determining of the heat transfer coefficient, particularly the heat penetration coefficient are especially important in the assumed model of heat flow.

The proposed model can be successfully applied for calculating changes of thermodynamic parameters for a single-phase liquefied natural gas flow (LNG). The presented model also is a good starting point for further analysis of the process of unloading liquefied natural gas (LNG), especially taking into account the variability of the composition of the unloaded LNG (impact of composition changes on limit pressure and temperature parameters of two phase system emergence) and the heat delivered to the LNG during the pumping process and its impact on growth temperature and the evaporation process in unloading pipelines. The successive modifications of the proposed analytical model shall account for the process of filling storage tanks, analysis of pressure losses for local resistances and changes of height at which the pipeline has been disposed.

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