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PHASE EQUILIBRIA FOR LIQUEFIED NATURAL GAS (LNG) AS A MULTICOMPONENT MIXTURE**

1. INTRODUCTION

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. Diversification of supplies of this ecologic fuel is the key element for the energy security in the economy of each country. 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 a gas phase and causes changes in the composition of stored liquid LNG. The bubble temperature of liquefied natural gas at atmospheric pressure, depending on the composition is about −162°C (111 K). The main component of LNG is methane, the remaining components are primarily ethane, propane, butane and nitrogen. Depending on the participation of these components the basic thermodynamic parameters of LNG can significantly change. Changes in the composition of the stored LNG may lead to stratification and instability called roll-over. LNG is also a product sensitive to changes of temperature. An increase in its temperature leads to rapid evaporation and sudden increase of pressure in the storage tank [1, 2]. In order to better prediction the changes of individual parameters of stored LNG caused by changes of temperature and LNG composition vapor-liquid equilibrium (VLE) calculations are performed for cryogenic conditions using modified equations of state (EOS).

2. EQUATIONS OF STATE USED IN CRYOGENIC CONDITIONS

To describe the equilibrium phenomena of gas-liquid system in cryogenic conditions several equations of state can be used successfully. The most commonly used equations for

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liquefied natural gas or natural gas in cryogenic conditions are [3]: the classic model of Peng––Robinson (PR) EOS and its modifications; the Benedict–Webb–Rubin (BWR) equation of state and its modifications (i.e. by Starling); the Lee–Kesler–Prausnitz equation of state (LKP).

The Peng–Robinson classic model is used for calculations in this work. Also, the forms of other two equations are presented below.

Peng–Robinson EOS

The Peng–Robinson (PR) equation of state [2] is one of the most popular equations for describing the PVT (Pressure, Volume, Temperature) behavior of real pure substances and mixtures, in particular of liquid and gaseous hydrocarbons and common inorganic gases such as oxygen, nitrogen, and hydrogen sulfide. The Peng–Robinson equation has the following form [4]:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

where:

$$a(T) = a \cdot \alpha(T, \omega) \tag{2}$$

$$a = 0.45724 \frac{R^2 \cdot T_c^2}{p_c} \tag{3}$$

$$b = 0.07780 \frac{R \cdot T_c}{p_c} \tag{4}$$

$$\alpha(T, \omega) = \left[1 + m \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \tag{5}$$

$$m = 0.379642 + 1.48503 \cdot \omega + 0.164423 \cdot \omega^2 + 0.016667 \cdot \omega^3 \tag{6}$$

The Peng–Robinson equation is intended for a description of the PVT behavior of pure components. However, it can also be used for mixtures by using "mixture-averaged" values for the equation parameters. Peng–Robinson EOS is commonly used for determining phase equilibria of liquid/vapors of hydrocarbon mixtures. The mixing rules of PR EOS have the following form:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i z_j a_{ij} \tag{7}$$

$$b = \sum_{i=1}^{N} (z_i \cdot b_i) \tag{8}$$

$$a_{ij} = (1 - \delta_{ij}) \cdot \sqrt{a_i \cdot a_j} \tag{9}$$

The PR EOS can be written in polynomial form:

$$Z^3 + (B-1) \cdot Z^2 + (A - 3 \cdot B^2 - 2 \cdot B) \cdot Z + B^3 + B^2 - A \cdot B = 0 \qquad (10)$$

where:

$$A = \frac{a \cdot p}{(RT)^2} \qquad (11)$$

$$B = \frac{b \cdot p}{RT} \qquad (12)$$

And the compressibility factor can be written as:

$$z = \frac{pv}{RT} \qquad (13)$$

The fugacity coefficient of i component in the mixture for cubic PR EOS can be calculated from equation:

$$\ln(\phi_i) = \ln\left(\frac{f_i}{z_i \cdot p}\right) = -\ln(Z - B) + (Z - 1) \cdot \frac{b_i}{b} -$$
$$- \frac{A}{2\sqrt{2} \cdot B} \cdot \left[\frac{1}{a} \cdot \left[2 \cdot \sum_j (z_j \cdot a_{ij}) \right] - \frac{b_i}{b} \right] \cdot \ln\left[\frac{Z + \left(\sqrt{2} + 1\right) \cdot B}{Z - \left(\sqrt{2} - 1\right) \cdot B} \right] \qquad (14)$$

Benedict–Webb–Rubin EOS

The Benedict–Webb–Rubin (BWR) equation of state is used in fluid dynamics. The original model has the following form [3, 5]:

$$p = \frac{RT}{v} + \frac{B}{v^2} + \frac{C}{v^3} + \frac{D}{v^6} + \frac{E}{v^3}\left(1 + \frac{F}{v^2}\right)\exp\left(\frac{-F}{v^2}\right) \qquad (15)$$

where B, C, D, E, F are BWR EOS parameters determined by PVT experimental data.

Lee–Kesler–Prausnitz EOS

Lee–Kesler–Prausnitz (LKP) equation of state has a general form [3, 6]:

$$Z = \frac{p_r \cdot V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 \cdot V_r^2} \cdot \left(\beta + \frac{\gamma}{V_r^2}\right) \cdot \exp\left(\frac{-\gamma}{V_r^2}\right) \qquad (16)$$

where B, C, c_4, D, β, γ are constants which can be obtained in the API Databook and $V_r = p_c v / RT_c$.

3. VAPOR-LIQUID EQUILIBRIA (VLE) CALCULATIONS IN CRYOGENIC CONDITIONS

Four different natural gas mixtures (simulating LNG compositions) were assumed for vapor-liquid equilibrium calculations. These compositions are characterized by the diversity of molar fractions of hydrocarbons (C_2–C_4) and nitrogen (Tab. 1).

Table 1
Exemplary compositions of natural gas mixtures used for VLE calculations

Component	Short Symbol	Composition 1 [% mol]	Composition 2 [% mol]	Composition 3 [% mol]	Composition 4 [% mol]
Methane	C_1	96.0	92.0	87.0	92.0
Ethane	C_2	2.5	5.0	8.0	4.0
Propane	C_3	0.75	1.5	3.5	0.6
n-Butane	nC_4	0.25	0.5	0.5	0.2
Isobutane	iC_4	0.25	0.5	0.5	0.2
Nitrogen	N_2	0.25	0.5	0.5	3.0

Chosen mixture components have a different physical properties which are presented in Table 2.

Table 2
Physical properties of mixture components

Component	Critical temperature [K]	Critical pressure [MPa]	Acentric factor [–]	Bubble point temperature at atmospheric pressure [K]
Methane	190.6	4.59	0.011	111.5
Ethane	305.3	4.85	0.098	184.2
Propane	369.8	4.21	0.149	231.2
n-Butane	425.1	3.77	0.197	272.5
Isobutane	408.1	3.58	0.177	261.6
Nitrogen	126.2	3.39	0.037	77.4

Calculations for this paper were made using the classic Peng–Robinson equation of state. There is no precisely defined boundary for cryogenic conditions. Currently, cryogenic conditions are usually assumed for temperatures below 120 K (−153°C). The International Congress of Refrigeration in 1971 established the bubble point of methane 111,5 K (−162°C) as the boundary of cryogenic conditions [13]. However, in some sources higher temperatures can be found as boundary of cryogenics i.e.: 123 K (−150°C) [7] or 143 K (−130°C) [8].

The dimensionless equilibrium ratio of mixture component i is described as a quotient of molar fraction of component i in vapor phase by a molar fraction of this component in liquid phase [5, 11]:

$$K_i = \frac{y_i}{x_i} \tag{17}$$

With using the Raoult–Dalton law it can be written as:

$$K_i(p,T) = \frac{p_i^{sat}}{p} = \frac{y_i}{x_i} \tag{18}$$

The definition equation (17) can be used in the general equation:

$$z_i = L\,x_i + V\,y_i \tag{19}$$

From equation 19 the molar fractions of i component in the liquid phase and gas phase can be obtained:

$$x_i = \frac{z_i}{1 + V(K_i - 1)} \tag{20}$$

$$y_i = \frac{z_i \cdot K_i}{1 + V(K_i - 1)} \tag{21}$$

Sum of molar fractions of all components in each phase is equal to 1, hence it is possible to get the Rachford–Rice equation using previous equations [5, 11]:

$$f(V) = \sum_i \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \tag{22}$$

This equation is used to determine of vapor phase molar fraction in the two-phase system.

The equilibrium ratio (K_i) can be calculated from the semi-empirical Wilson equation and used for a numerical solution of the Rachford–Rice equation. Then, using an appropriate equation of state, it is possible to determine the fugacity coefficients and compressibility factor for vapor and liquid phases. As a result of these flash calculations we can obtain the compositions of liquid and vapor phases in defined conditions of pressure and temperature (Fig. 1). Also, other parameters of vapor and liquid phase can be calculated (i.e. compressibility factor, density).
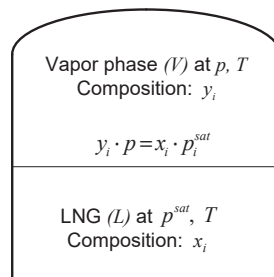

Fig. 1. Description of vapor-liquid equilibrium for Liquefied Natural Gas (LNG) as a multi-component mixture

4. RESULTS

The results of VLE calculations are shown below on p-T phase envelopes for these four liquefied natural gas compositions (Fig. 2–5). The position of bubble point is essential for the stability of the LNG storage processes. Higher molar fraction of hydrocarbons C_2–C_4 does not have a significant impact on the position of the bubble point under constant pressure, a higher molar fraction of nitrogen causes a decreased of bubble point temperature (Fig. 6).
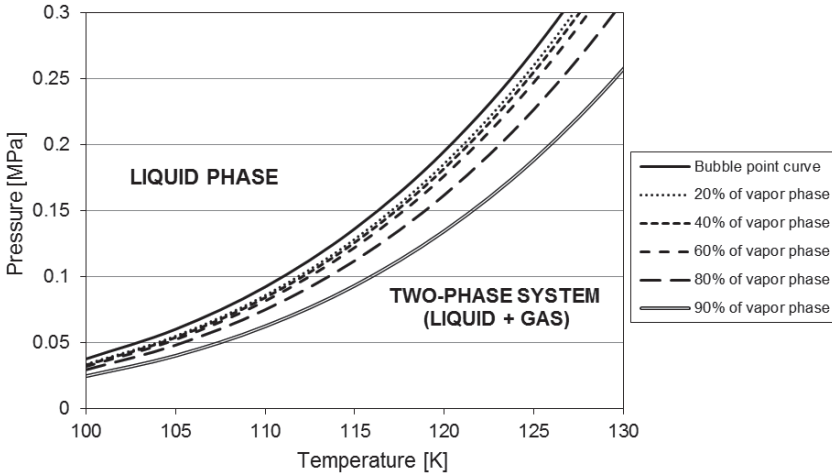

Fig. 2. p-T phase envelope of natural gas composition 1 with molar fraction of the vapor phase in the two-phase system
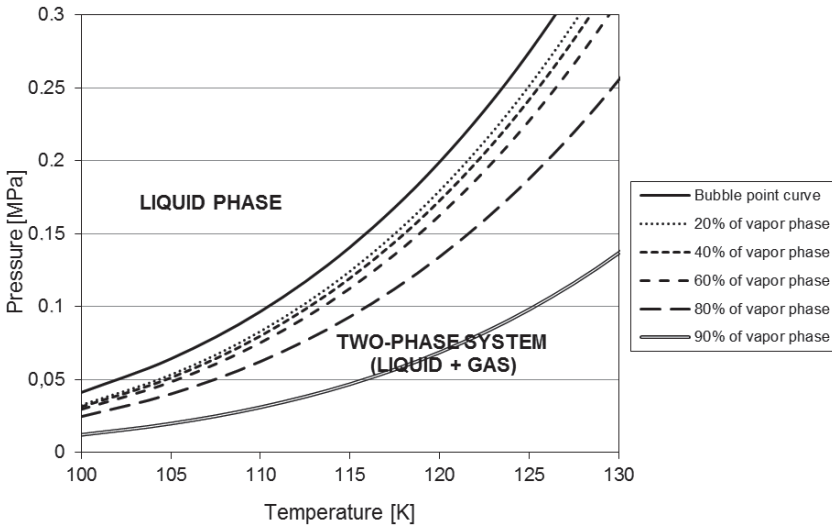

Fig. 3. p-T phase envelope of natural gas composition 2 with molar fraction of the vapor phase in the two-phase system
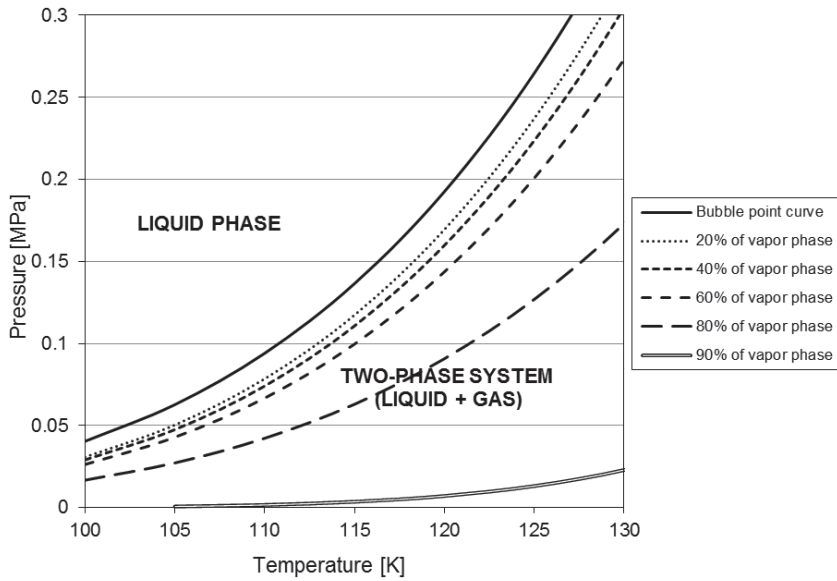
Fig. 4. p-T phase envelope of natural gas composition 3 with molar fraction of the vapor phase in the two-phase system
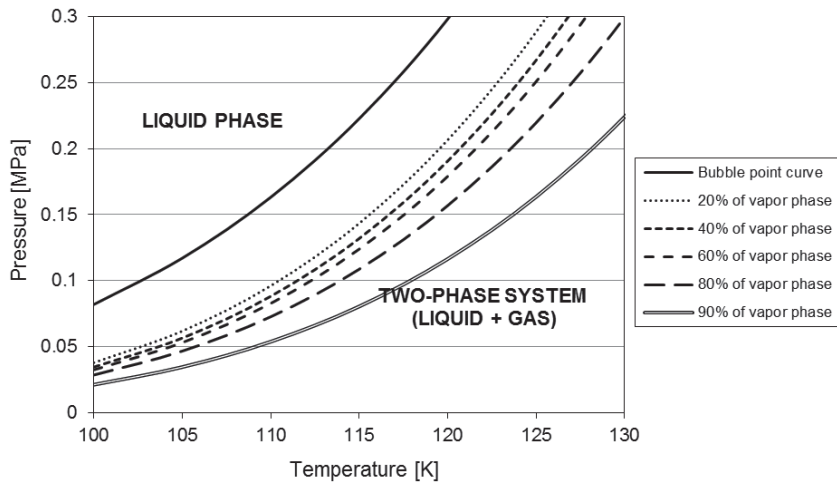

Fig. 5. p-T phase envelope of natural gas composition 4 with molar fraction of the vapor phase in the two-phase system
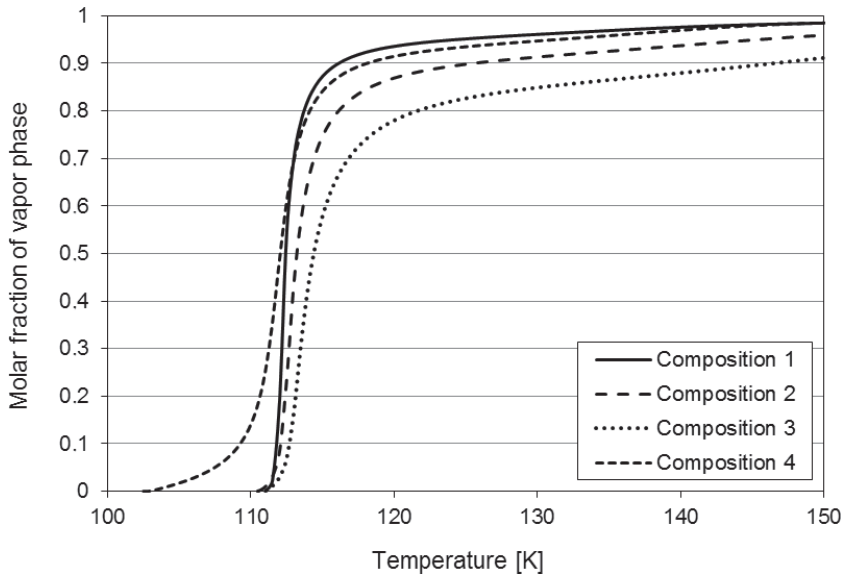
Fig. 6. The molar ratio of the vapor phase in the two-phase system versus the temperature for exemplary compositions

The composition changes of liquid and gas phases in function of temperature at atmospheric pressure are shown in Figures 7–8. An analysis of phase composition changes is one of the most important factors of the liquefied natural gas storage process. The sudden change in the composition (due to the evaporation process or unloading new supply of LNG with other composition to terminal) may cause instability of stored LNG and threaten the safety of the storage process [1, 2, 9]. The evaporation process is initiated at a specific temperature for each composition (Tab. 3). In all composition cases nitrogen evaporates first because of its lower bubble point temperature. With temperature increasing at constant pressure, the vapor methane molar fraction increases and nitrogen decreases. The molar fraction of hydrocarbons (C_2–C_4), which evaporates in much higher temperatures, increases slowly with temperature increase.

For natural gas mixtures in cryogenic conditions the most important factor is the nitrogen molar fraction. Nitrogen which has the lowest bubble point temperature among assumed components significantly changes the parameters of the entire mixture, especially for mixture 4, where the nitrogen molar fraction is equal to 3%. After the initialization of the evaporation process, nitrogen constitutes more than 50% of the vapor phase, resulting in a significant change in the density of the liquid phase.

The density of the liquid phase (for composition 4 with high molar fraction of nitrogen) decreases more rapidly because nitrogen has a higher molar mass than methane [10]. The dependence of liquid phase density in function of temperature at a constant barometric pressure and for constant total composition is presented in Figure 9. Density changes of the liquid phase in the storage tank may initiate the process of dissection and consequently lead to roll-over instability. For a more detailed analysis of the potential for roll-over phenomenon the dynamics of the process including the changes of the liquid phase composition and density should be considered for the next time steps.

Table 3

Bubble point temperatures for exemplary compositions
at atmospheric pressure and pressure of 0.5 MPa

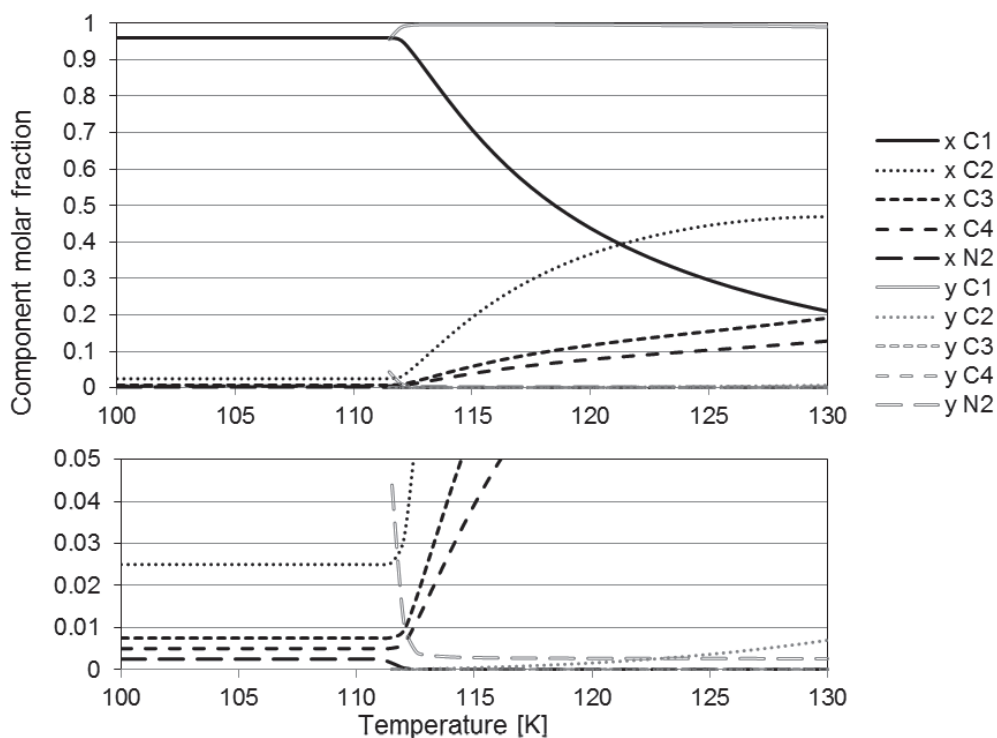| Composition	Atmospheric pressure (0.101325 MPa)	0.5 MPa
	[K]	[K]
1	111.18	135.44
2	110.62	135.49
3	110.98	136.27
4	102.94	129.73

Fig. 7. Molar fraction components in the liquid and vapor phase (Composition 1).
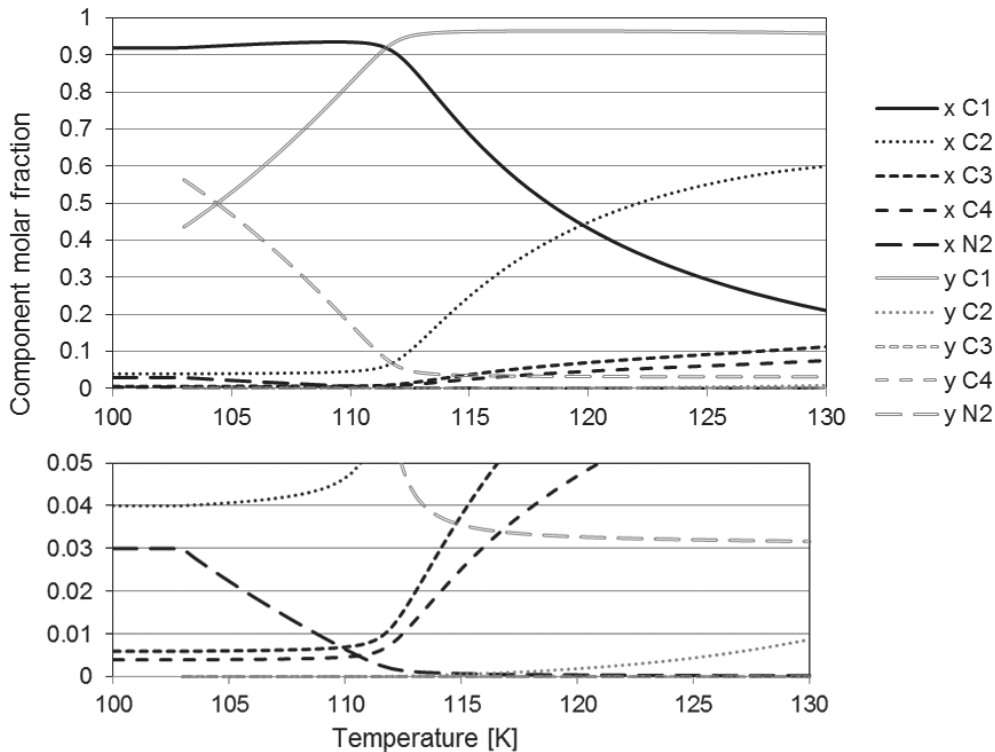Bottom chart shows a detailed molar fraction range between 0 and 5%

Fig. 8. Molar fraction of components in the liquid and vapor phase (Composition 4).
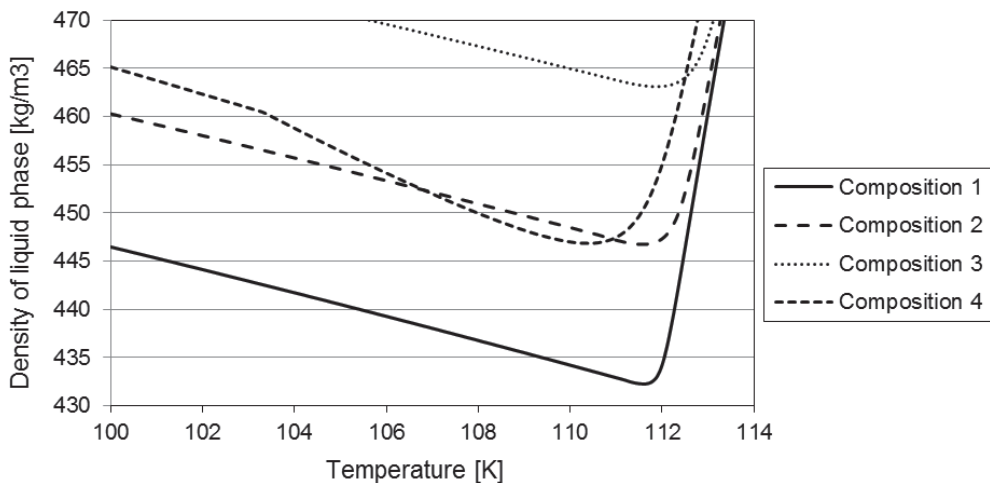Bottom chart shows detailed molar fraction range between 0 and 5%

Fig. 9. Density changes of the liquid phase for exemplary compositions versus temperature
(obtained from VLE calculations)

5. CONCLUSIONS

In this paper the basic vapor-liquid equilibrium calculations for natural gas mixtures (simulating liquefied natural gas compositions) in cryogenic conditions have been performed. The research of phase equilibrium for natural gas at low temperature ranges are important for industrial applications, particularly in the natural gas liquefaction technology and the processes of LNG pipeline transportation and storage. The Peng–Robinson equation of state was used for all calculations. A simple form of this equation is commonly used to determine the vapor-liquid equilibrium calculations for hydrocarbons mixtures. Calculations were made for four exemplary compositions of natural gas in which the dominant component is methane. Increasing the molar fraction of hydrocarbons (C_2–C_4) does not have a significant impact on changing the bubble point temperature. It significantly increases the molar fraction of the liquid phase in the two-phase system. The most significant change entails increasing the molar ratio of nitrogen. Increased molar ratio of nitrogen causes decreasing of the bubble point temperature of natural gas (to 102.94 K) and the density of the liquid phase. For the composition with higher molar fraction of nitrogen the first stage of the evaporation process is slower than for other mixtures. It is caused by the evaporation of nitrogen in lower temperatures in which other components are in liquid phase. Real time control of LNG composition, especially nitrogen molar fraction is significantly important for the stability and safety of liquefied natural gas storage processes.

NOMENCLATURE

a, b – Peng–Robinson EOS parameters
A, B – dimensionless Peng–Robinson EOS parameters
f_i – fugacity [Pa]
L – molar fraction of liquid phase [–]
p – pressure [Pa]
p_c – critical pressure [Pa]
p_r – reduced pressure: $p_r = p/p_c$ [–]
p^{sat} – saturation pressure [Pa]
R – ideal gas constant [J/mol·K]
T – temperature of fluid [K]
T_c – critical temperature [K]
T_r – reduced temperature: $T_r = T/T_c$ [–]
v – molar specific volume [m³/mol]
V – molar fraction of vapor phase [–]
x_i – i component molar fraction in liquid phase [–]
y_i – i component molar fraction in liquid phase [–]
z_i – i component molar fraction [–]
Z – compressibility factor [–]
α, m – Peng–Robinson EOS parameters
δ_{ij} – binary interaction coefficient
ρ – molar density [mol/m³]
φ_i – fugacity coefficient of i component [–]
ω – acentric factor

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