



## CO<sub>2</sub>-CH<sub>4</sub> mixtures phase equilibrium analysis

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### ABSTRACT

Carbon dioxide removal is crucial step during natural gas processing, as CO<sub>2</sub> is highly corrosive in presence of water. There are natural gas sources around the world with very high carbon dioxide content that cannot be developed. In order to design the effective CO<sub>2</sub> removal process, properties of methane-carbon dioxide mixtures has to be determined. Authors have investigated thermodynamic properties of CH<sub>4</sub>-CO<sub>2</sub> mixtures. Extended Peng-Robinson equations were used to determine the phase equilibrium of CH<sub>4</sub>-CO<sub>2</sub> systems of different compositions.

**KEYWORDS:** *natural gas, mixtures, phase equilibrium*

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### 1. INTRODUCTION

Natural gas becomes more and more popular as a clean and efficient fuel. The main advantages of natural gas usage are rapid increase of demand for low-carbon energy sources (*decarbonisation*), wide range of applications (heating and domestic use, electricity generation, fuel for transportation, etc.), convenience and reliability [10]. Also recent progress in development of storage technologies like CNG (*Compressed Natural Gas*) and LNG (*Liquefied Natural Gas*) has impact on popularity of natural gas. Pipeline natural gas and LNG consist mostly of methane and smaller amount of higher hydrocarbons, while composition of unprocessed natural gas varies significantly depending on the source (Table 1). The major impurities are water, mercury, sulfur species, nitrogen, helium and carbon dioxide.

This paper will focus on carbon dioxide. The amount of carbon dioxide in unprocessed natural gas varies largely - from CO<sub>2</sub>-free natural gas sources in Siberia [12]

to even 92% of CO<sub>2</sub> (Colorado, [5]). Large gas fields in Southeast Asia are unexplored due to very high carbon dioxide content: Natuna Field in Indonesia ( $1.3 \cdot 10^{12}$  m<sup>3</sup> of reserves and CO<sub>2</sub> content up to 71%) or gas fields in Malaysia (up to  $3.7 \cdot 10^{11}$  m<sup>3</sup>, CO<sub>2</sub> content between 28% and 87%) [12]. CO<sub>2</sub> forms highly corrosive carbonic acid in presence of water (moisture) and may lead to destruction of the pipelines and other equipment. At low temperatures, high content of carbon dioxide can cause clogging of delivery pipelines [8]. CO<sub>2</sub> also decreases the heating value of fuel and wastes capacity of pipelines [12]. Therefore, carbon dioxide removal process is crucial for the improvement of natural gas quality.

**Table 1:** Composition of natural gas (% vol.) from different underground sources [6]

Source	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	CO <sub>2</sub>	H <sub>2</sub> S	N <sub>2</sub>	He
Lubaczów	89.9	1.6	0.9	0.7	-	0.3	-	6.5	-
Tarchały	50.37	0.22	0.01	0.02	-	-	-	47.8	0.003
Nowa Sól	38.67	16.09	8.35	2.71	0.48	0.5	-	23.2	-
Daszawa	97.8	0.5	0.2	0.1	0.05	0.05	-	1.3	-
Romaszkino	47.4	21.4	14.4	4.5	3.3	0.5	-	8.6	-
Panhanle	73.2	6.1	3.2	1.6	0.6	0.3	-	14.3	0.7
Texas	39.56	6.17	2.89	2.2	2.28	4.5	42.4	-	-
Alaska	95.5	0.05	0.01	-	-	0.01	-	0.43	-
Wyoming	28.8	6.35	3.35	2.84	3.4	42	1.11	4.09	-
Venezuela	70.9	8.2	8.2	6.2	3.7	2.8	-	-	-
Canada	71.8	-	13.9	13.94	-	0.3	-	12.4	0.6
Libya	70	15	9	3.5	1	-	-	2	-
Algeria	86.9	9	2.6	1.2	-	-	-	0.3	-

Conventional methods of carbon dioxide removal (*gas sweetening*) are absorption in amine (or other suitable chemical solution) and membrane separation. However in case of high CO<sub>2</sub> content natural gas, the mentioned methods may become too expensive to use. One of the alternative methods of CO<sub>2</sub> separation is the cryogenic distillation method. The cryogenic separation technologies may be divided into the following categories which are [3]:

- Conventional cryogenic methods which are liquid-vapor distillation and extractive distillation.
- Nonconventional method which include solid vapor desublimation separation, condensed centrifugal separation and cryocoolers based separation.

The CO<sub>2</sub> capture efficiency for the above mentioned techniques varies. For the cryogenic packed beds method which are based on the desublimation concept it is possible to capture 99% of CO<sub>2</sub> [8]. However, condensed rotational separation idea proposed by [15] catches only 72% of CO<sub>2</sub>. Energy required for the operation differs depending on the method chosen from 0.842 MJ/kg of CO<sub>2</sub> for condensed contaminant centrifugal separation [13] up to 1.8 MJ/kg of CO<sub>2</sub> for the desublimation concept [8].

In small scale CO<sub>2</sub> removal installation the high performance Joule-Thomson coolers fed with gas mixtures can be used [2]. In order to understand the mechanisms of cryogenic gas sweetening technologies and to design properly gas purification system, the knowledge of phase equilibrium of natural gas-carbon dioxide mixture is needed. Thermodynamic analysis presented in this article will be performed for binary mixture of methane and carbon dioxide, other natural gas ingredients are neglected in order to simplify the calculations.

## 2. CALCULATION METHOD WITH PENG-ROBINSON EOS

To solve the phase equilibrium of a binary carbon dioxide-methane mixture one of equation of state (EoS) should be used. As it was mentioned in [7] the highest accuracy is achieved for Peng-Robinson EoS (P-R EoS) [9]. The following calculations were carried out basing on available literature regarding binary mixtures ([1], [4], [14], [16]). For the phase equilibrium calculations the P-R EoS can be written as:

$$p = \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m) + b_m(v - b_m)} \quad (1)$$

For mixtures of the gases, the van der Waals mixing rules were used to calculate the  $a_m$  and  $b_m$  coefficients.

$$a_m = \sum_{i=1}^N \sum_{j=1}^N z_i z_j (a_i a_j)^{0,5} (1 - k_{ij}) \quad (2)$$

$$b_m = \sum_{i=1}^N z_i b z_i \quad (3)$$

where:

$$a_i = 0,45724 \frac{R^2 T_{ci}^2}{p_{ci}} \left[ 1 + m_i \left( 1 - \left( \frac{T}{T_{ci}} \right)^{0,5} \right) \right]^2 \quad (4)$$

$$b_i = 0,0778 \frac{RT_{ci}}{p_{ci}} \quad (5)$$

$$m_i = 0,37464 + 1,54226\omega_i + 0,26992\omega_i^2 \quad (6)$$

where  $N$  is the number of components in the mixture,  $z_i$  is the mole fraction of each component in the mixture and  $k_{ij}$  is the binary interaction coefficient which describes the molecular interaction between the molecules of gases in the mixture.

As far as is known the pure carbon dioxide during cooling in ambient pressure do not liquefy. It changes from a gas to a solid in the resublimation process. To determine the solid vapour equilibrium the fugacity of the two phases must be calculate. In equilibrium there is a fugacity balance and the fugacity of the gas phase must equal fugacity of solid phase, eq. (7),

$$f_2^v(x_2, T, p) = f_2^s(T, p) \quad (7)$$

where  $f$  is the fugacity.

The solid and gas phase fugacity can be calculated by eq.(8) and eq. (9) respectively. The solid phase consists mainly of carbon dioxide and to simplify the equations it was assumed that there is only carbon dioxide in the solid phase. Therefore the fugacity of solid phase can be described by eq. (9).

$$f_2^v(x_2, T, p) = x_2 \varphi_2^v p \quad (8)$$

$$f_2^s(T, p) = p_{2\text{ Solid}}^{\text{sat}} \varphi_2^{\text{sat}} \exp \left( \frac{V_{2\text{ Solid}} (p - p_{2\text{ Solid}}^{\text{sat}})}{RT} \right) \quad (9)$$

Comparing eq. (8) and eq. (9) and assuming that the values of fugacities are equal the solid-vapour equilibrium can be expressed as:

$$x_2 \varphi_2^v p = p_{2\text{ Solid}}^{\text{sat}} \varphi_2^{\text{sat}} \exp \left( \frac{V_{2\text{ Solid}} (p - p_{2\text{ Solid}}^{\text{sat}})}{RT} \right) \quad (10)$$

where  $p_{2\text{ Solid}}^{\text{sat}}$  is the pure carbon dioxide vapour pressure and can be calculated with exponential eq. (11):

$$p_{2\text{ Solid}}^{\text{sat}} = 9,44 \cdot 10^8 \exp \left( -\frac{3108,2}{T} \right) \quad (11)$$

Equation (11) can be used if the following condition is met:  $T < T_{TP}$ , where  $T_{TP}$  is the triple point temperature of pure CO<sub>2</sub> and equals 216,55 K.

To solve the eq. (10) the fugacity coefficient  $\varphi_i$  must be calculated (given in eq. (12))

$$\varphi_i = \exp \left( \frac{b_i}{b_m} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left( \frac{2 \sum_j z_j (a_i a_j)^2 (1 - k_{ij})}{a_m} - \frac{b_i}{b_m} \right) \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \right) \quad (12)$$

where  $Z$  is compressibility factor and the parameters  $A$  and  $B$  are given in eq. (13) and eq. (14) respectively.

$$A = \frac{a_m p}{R^2 T^2} \quad (13)$$

$$B = \frac{b_m p}{RT} \quad (14)$$

where  $R$  is universal gas constant equals  $8.314 \text{ J/mol}^{-1} \text{ K}^{-1}$ .

The above considerations concern the solid-vapour equilibrium. The scheme of determining the solid-liquid equilibrium is analogous. Assuming that the solid phase consists of pure carbon dioxide, the solid and liquid phase fugacities can be described by eq. (15) and eq. (16)

$$f_2^l(x_2, T, p) = x_2 \varphi_2^l p \quad (15)$$

$$f_2^s(T, p) = p_{2\text{ Solid}}^{\text{sat}} \varphi_2^{\text{sat}} \exp \left( \frac{V_{2\text{ Solid}} (p - p_{2\text{ Solid}}^{\text{sat}})}{RT} \right) \quad (16)$$

and liquid-solid equilibrium of CO<sub>2</sub>-CH<sub>4</sub> mixture can be described as:

$$x_2 \varphi_2^l p = p_{2\text{ Solid}}^{\text{sat}} \varphi_2^{\text{sat}} \exp \left( \frac{V_{2\text{ Solid}} (p - p_{2\text{ Solid}}^{\text{sat}})}{RT} \right) \quad (17)$$

The solubility of CO<sub>2</sub> can be calculated by modification of the eq. (17) and given as:

$$x_2 = \frac{p_{2\text{ Solid}}^{\text{sat}} \varphi_2^{\text{sat}} \exp \left( \frac{V_{2\text{ Solid}} (p - p_{2\text{ Solid}}^{\text{sat}})}{RT} \right)}{\varphi_2^l p} \quad (18)$$

To calculate the equilibrium the fugacity coefficient can be calculated with the PREoS as follows:

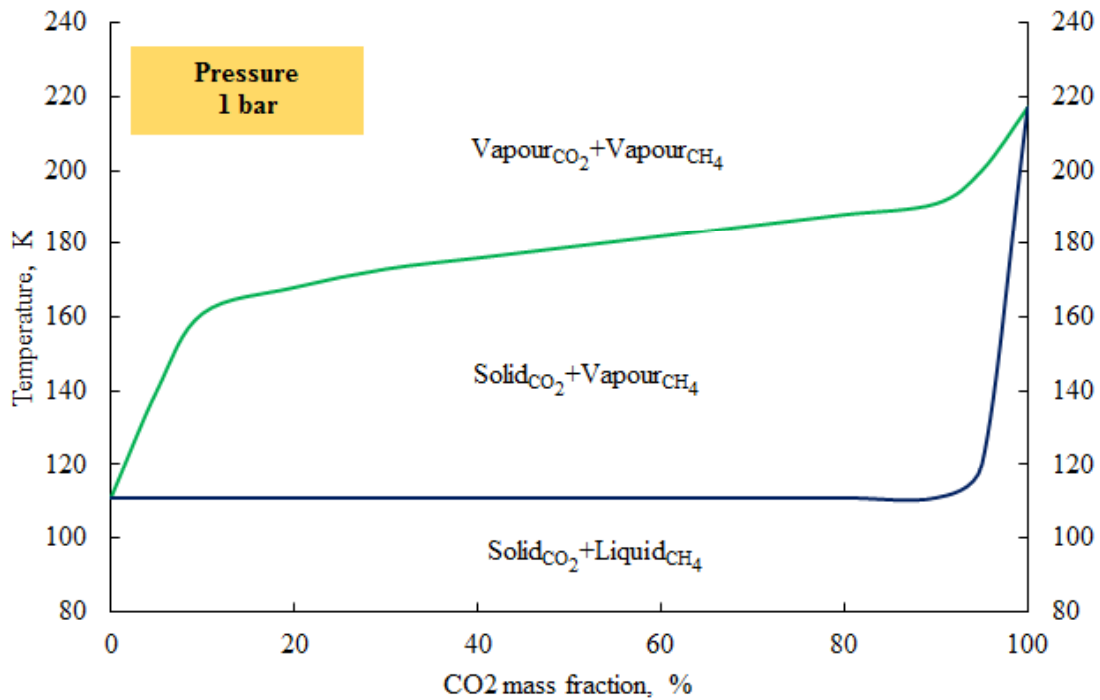
$$\varphi_i = \exp \left( \frac{b_i}{b_m} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left( \frac{2\sum_j z_j (a_i a_j)^2 (1 - k_{ij})}{a_m} - \frac{b_i}{b_m} \right) \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \right) \quad (19)$$

To analysis the binary mixture of CO<sub>2</sub> and CH<sub>4</sub> was taken and the calculations were made for different mass fractions of these components. Based on the Peng-Robinson equation of state the solid-liquid and solid-vapour equilibrium has been determined.

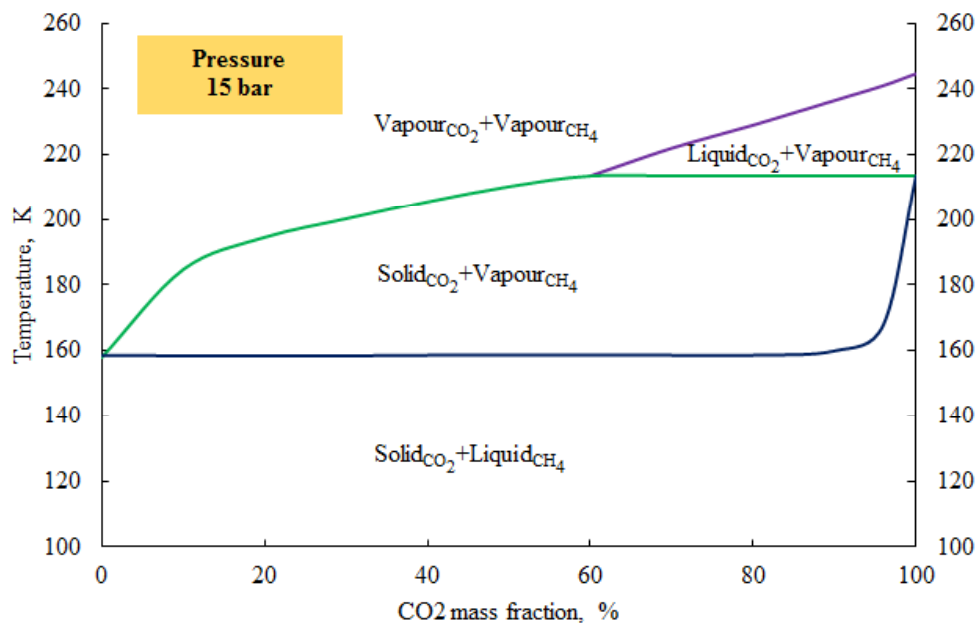
### 3. RESULTS

Proper design of cryogenic CO<sub>2</sub> separation processes requires prediction of solid phase transition that may occur in CH<sub>4</sub>-CO<sub>2</sub> mixtures at cryogenic temperatures. To predict the occurrence of solid CO<sub>2</sub> phase, graphs of phase equilibrium of mixtures were generated and examined. Figures 1-3 show behavior of the mixture for chosen pressures of 1 bar, 15 bar and 30 bar. Increase of the pressure causes the liquefaction of CO<sub>2</sub>. The CH<sub>4</sub>-CO<sub>2</sub> phase equilibrium diagrams were evaluated for the different pressure levels. For the pressure of 1 bar there is no chance of liquid CO<sub>2</sub> occurrence (Fig. 1). For the two remaining pressures, depending on CO<sub>2</sub> concentration, it is possible for CO<sub>2</sub> to condensate (Fig. 2 and Fig. 3). Figure 2 shows behavior of the mixture held at 15 bar pressure. It may be seen that the CO<sub>2</sub> starts to condensate when its concentration is around 60% for the temperatures higher than 213 K.

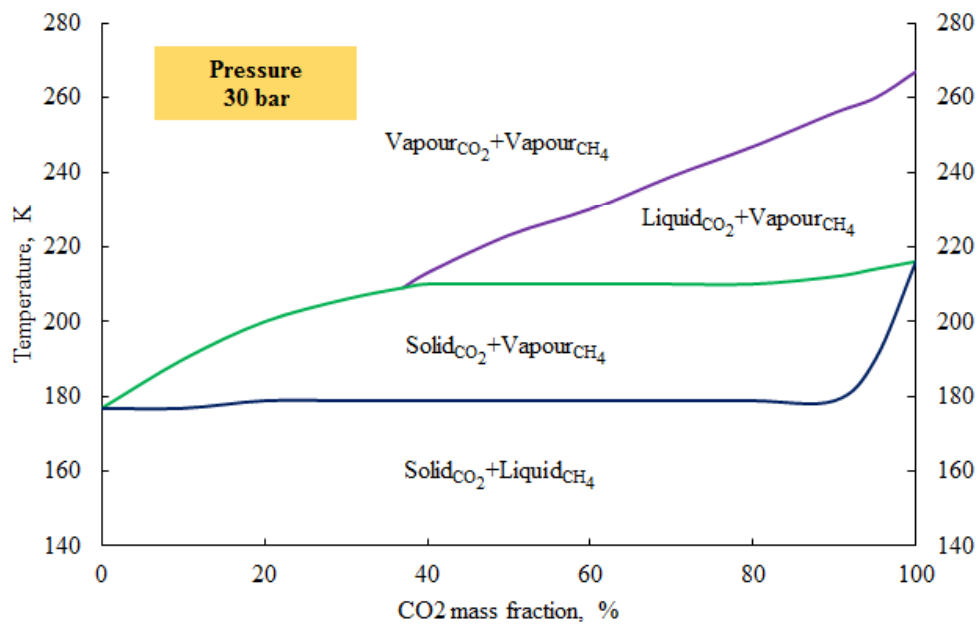
In figure 3 is shown behavior of the mixture at 30 bar pressure. It may be seen that the CO<sub>2</sub> starts to condensate when its concentration is above 37% for the temperatures around 210 K.



**Fig. 1:** A temperature and CO<sub>2</sub> mass concentration dependent behavior of the CH<sub>4</sub>-CO<sub>2</sub> mixture at 1 bar pressure

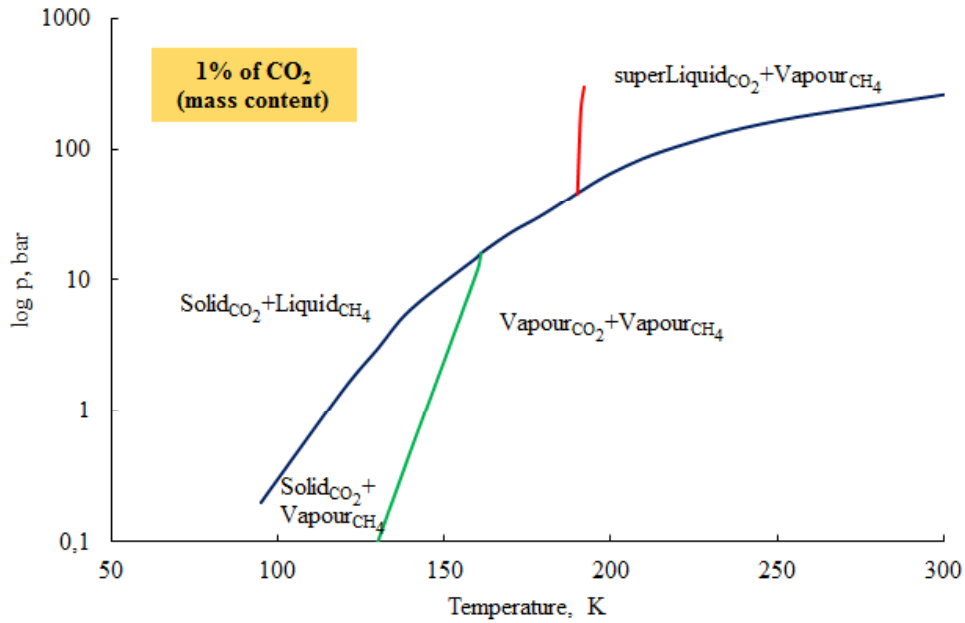


**Fig. 2:** A temperature and CO<sub>2</sub> mass concentration dependent behavior of the CH<sub>4</sub>-CO<sub>2</sub> mixture at 15 bar pressure

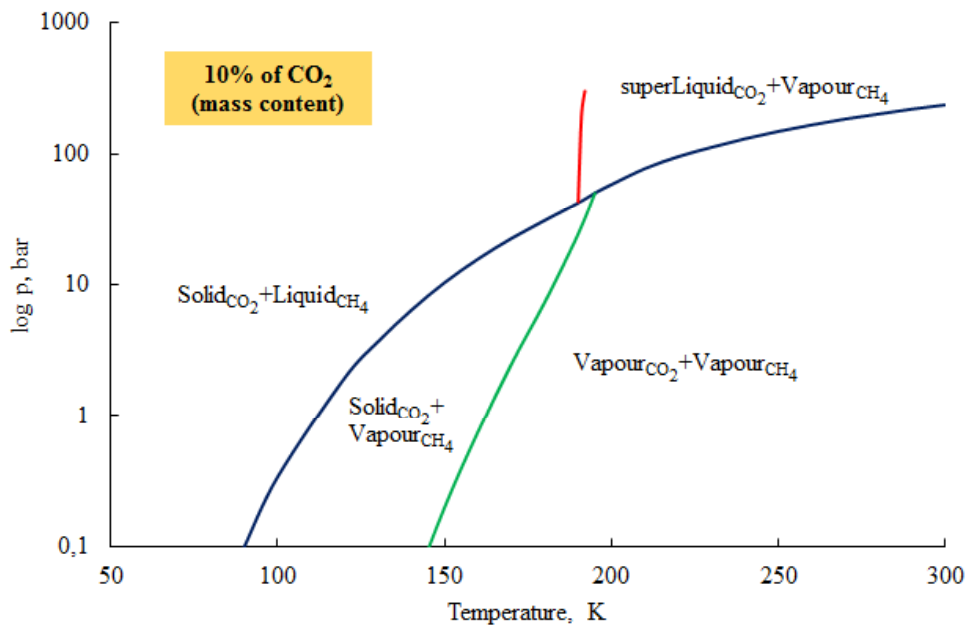


**Fig. 3:** A temperature and CO<sub>2</sub> mass concentration dependent behavior of the CH<sub>4</sub>-CO<sub>2</sub> mixture at 30 bar pressure

For few chosen CO<sub>2</sub> mass concentrations  $p - T$  plots were prepared and showed in Figs 4-7. When content of CO<sub>2</sub> is significant (e.g. 50%) the possibility of carbon dioxide condensation may be expected to take place (Fig. 7). From the graphs comparison, the temperature and the pressure growth of CO<sub>2</sub> gas-solid transition with the rise of content is seen. For above 60 bar gas-supercritical fluid transition occurs. Additionally, for smaller CO<sub>2</sub> concentrations, around 1%, and high process pressures, above 25 bar, natural gas components may liquefy (Fig. 4). Obtained results indicate what are the process parameters at which the condensation or solidification of carbon



**Fig. 4:** A pressure and temperature dependant behaviour of the CH<sub>4</sub>-CO<sub>2</sub> mixture for 1% CO<sub>2</sub> mass concentration

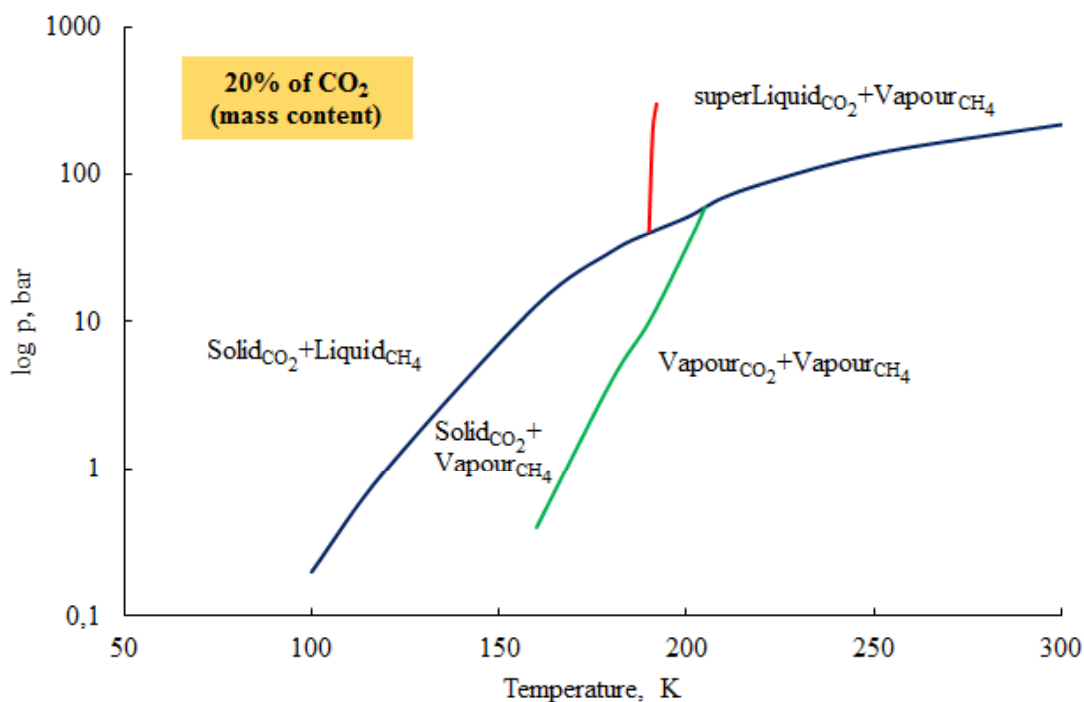


**Fig. 5:** A pressure and temperature dependant behaviour of the CH<sub>4</sub>-CO<sub>2</sub> mixture for 10% CO<sub>2</sub> mass concentration

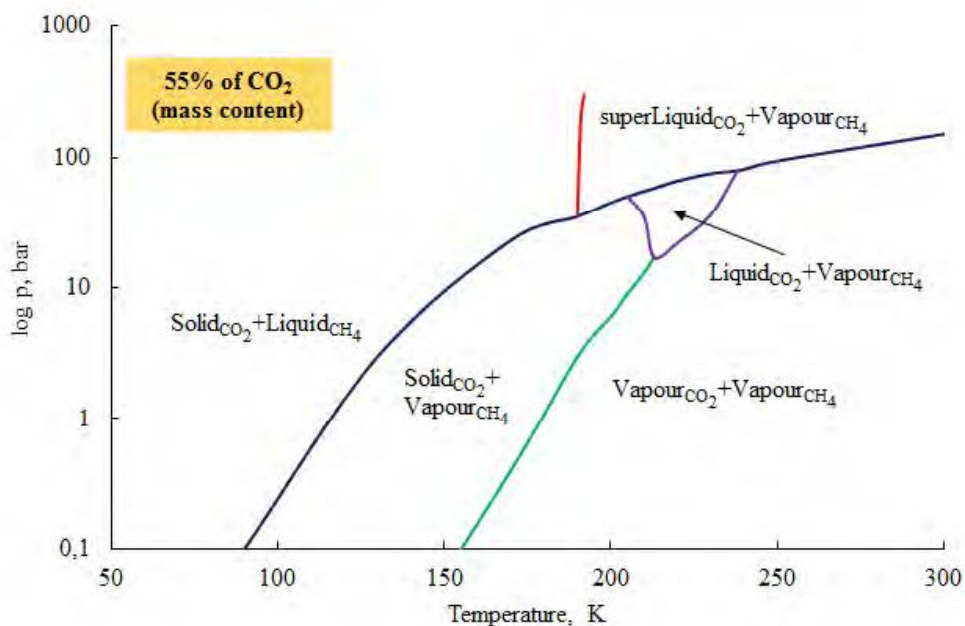
dioxide occurs for a given CO<sub>2</sub> mass fraction. That information is necessary to choose between CO<sub>2</sub> liquefaction and CO<sub>2</sub> solidification methods and predict the permissible range of process pressures.

#### 4. CONCLUSIONS

Understanding of the mechanisms of cryogenic natural gas sweetening methods requires a deep look into thermodynamic analysis of CH<sub>4</sub>-CO<sub>2</sub> phase equilibrium.



**Fig. 6:** A pressure and temperature dependant behaviour of the  $\text{CH}_4\text{-CO}_2$  mixture for 20%  $\text{CO}_2$  mass concentration



**Fig. 7:** A pressure and temperature dependant behaviour of the  $\text{CH}_4\text{-CO}_2$  mixture for 55%  $\text{CO}_2$  mass concentration

The thermodynamic properties of  $\text{CH}_4\text{-CO}_2$  mixtures have been investigated using Peng-Robinson equations of state and the phase diagrams for several different  $\text{CO}_2$  concentrations were prepared. Predicted behaviour of  $\text{CO}_2$  - natural gas mixtures varies largely depending on carbon dioxide mass fraction and the process pressure. Therefore choice of the  $\text{CO}_2$  capture technology and process parameters should be analysed individually for each natural gas source.



Future work should focus mostly on confirmation of the obtained results by comparison with experimental data.

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