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CONFINED PHASE ENVELOPE OF GAS-CONDENSATE SYSTEMS IN SHALE ROCKS**KRZYWA NASYCENIA UKŁADÓW GAZOWO-KONDENSATOWYCH
W NANOPOROWYCH SKALACH**

Natural gas from shales (NGS) and from tight rocks are one of the most important fossil energy resource in this and next decade. Significant increase in gas consumption, in all world regions, will be marked in the energy sector. The exploration of unconventional natural gas & oil reservoirs has been discussed recently in many conferences. This paper describes the complex phenomena related to the impact of adsorption and capillary condensation of gas-condensate systems in nanopores. New two phase saturation model and new algorithm for search capillary condensation area is discussed. The algorithm is based on the Modified Tangent Plane Criterion for Capillary Condensation (MTPCCC) is presented. The examples of shift of phase envelopes are presented for selected composition of gas-condensate systems.

Keywords: unconventional natural gas, shale gas, gas condensate, capillary condensation, adsorption, phase envelope, nanopores, Blue Gas

Gaz ziemny z łupków (NGS) oraz z ze złóż niskoprzepuszczalnych (typu 'tight') staje się jednym z najważniejszych zasobów paliw kopalnych, w tym i następnym dziesięcioleciu. Znaczący wzrost zużycia gazu we wszystkich regionach świata zaznacza się głównie w sektorze energetycznym. Rozpoznawanie niekonwencjonalnych złóż gazu ziemnego i ropy naftowej w ostatnim czasie jest omawiane w wielu konferencjach. Niniejszy artykuł opisuje złożone zjawiska związane z wpływem adsorpcji i kapilarnej kondensacji w nanoporach w złożach gazowo-kondensatowych. Pokazano nowy dwufazowy model równowagowy dwufazowy i nowy algorytm wyznaczania krzywej nasycenia w obszarze kondensacji kapilarnej. Algorytm bazuje na kryterium zmodyfikowanym płaszczyzny stycznej dla kapilarnej kondensacji (MTPCCC). Przykłady zmiany krzywych nasycenia są przedstawiane w wybranym składzie systemów gazowo- kondensatowych

Słowa kluczowe: gaz niekonwencjonalny, gaz z łupków, gaz kondensatowy, kondensacja kapilarna, adsorpcja, krzywa nasycenia, Blue Gas

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Acronyms

PVT	– Pressure-Volume-Temperature,
VLE	– Vapor Liquid Equilibria,
PR CEOS	– Peng-Robinson Cubic Equation of State,
VTPR EOS	– Volume Translated Cubic Equation of State,
CEOS	– Cubic Equation of State,
IFT	– Interfacial Tension.

Nomenclature

A, B, C	– coefficients in Peng-Robinson EOS,
a, b, t	– coefficients in Peng-Robinson EOS,
f	– fugacity,
k	– binary interaction constant,
n	– number of components,
p	– pressure,
T	– temperature,
R	– universal gas constant,
x	– mole fraction of component in liquid phase,
y	– mole fraction of component in vapor phase,
x	– mole fraction of component in liquid or vapor phase,
v	– molar volume,
w	– Pitzer's acentric factor,
z	– mole fraction of component in system,
\hat{R}	– fugacity coefficient,
β	– phase mole fraction,

indexes

c	– critical parameter
i	– i -component,
j	– j -component
l	– liquid phase
n	– standard condition
v	– vapor phase.

1. Introduction

Extraction of natural gas from shale rocks, tight rocks (also production of coal bed methane) – successfully implemented in the USA in the last two decades stimulate the American economy (IEA (2011, 2012), EIA 2013). The low cost of fuel and low carbon emission during combustion of natural gas induce high gas demand in the World in the next 30 years (IEA (2011, 2012)). Natural gas is also an important energy source for the transition time towards a low-carbon economy in the World (IEA, 2011, 2012; MIT, 2011; Siemek et al., 2009; Nagy & Siemek, 2011; Siemek & Nagy 2012). The small European Union gas production and the high gas import dependency of

Poland (Siemek et al., 2009; Nagy et al., 2009) is a motivation to search own way to increase country energy safety in next twenty years. The first results of exploration suggest wet/condensate or light oil systems in Baltic Basin as well as in the Lublin basin (Poprawa, 2010; Siemek & Nagy, 2012; PGI, 2012). This is also motivation to research potential efficiency of extraction dry shale gas (Klimkowski & Nagy, 2014) and to know thermodynamics and flow mechanism in two phase shale/tight systems. Large part of this paper has been presented in last year (Nagy & Siemek, 2013)¹. The entire thermodynamic analysis of the reservoir hydrocarbon system is impossible because of the large influence of factors (see e.g. Nagy, 2002, 2003). The reservoir engineering models of shale/light gas extraction usually omitt the condensation in parous media, focuset on “dry” gas (e.g. Rubin, 2010; Klimkowski & Nagy, 2014) The traditional attitude to flat vapor-liquid thermodynamics may be extended to curved surfaces with gravity and adsorption/capillary condensation components and with new nano-effects in case of mezzo- and micropore reservoirs. The new effects related to critical phenomena in narrow pores will be significant for vapor- liquid equilibrium in tight and shale rocks.

2. State of the art of research of VLE in the porous media

The interface between phases (i.e. gas, condensate, brine) in a porous media is not flat. The capillarity and gravity segregation effects on the PVT and VLE properties of reservoir fluid are omitted In the classical thermodynamic analysis, which one may find in many works – see e.g. Ahmed (1989), Pedersen et al. (1989), Firoozabadi (1999), Whitson & Brule, 2000). In the range of laboratory PVT-VLE research an additional effect of capillarity is omitted in the case of saturation phase envelope. The pioneered Russian authors Trebin and Zadora (1968) reported a strong influence of the porous media on the dew point pressure and VLE of condensate system. The observed effect was about 10-15% increase of dew point pressure in this system. A similar observation was recorded by Sadyk and Zade (1963) and Tindy and Raynal (1966). The other American and Canadian research (Smith, Yarborough (1968), Sigmund et al. (1973)) suggest that there is no evident impact of capillarity on the saturation pressure. Smith and Yarborough (1968) indicate in their paper about wettability that the porous structure has little impact on the vaporization process of the liquid phase in the rock. Sigmund and al. (1973) have analysed of laboratory works and concluded that the main reason of the hypothetical impact of porous structure on the saturation pressure was the lack of fluid circulation in the cell. More interesting discussion related to impact of porous media properties on VLE is presented in a paper of Ping et. al. (1996), Brusilovsky (1990), Firoozabadi (1999), Shapiro & Stanby (1996), Nagy (2002), Didar & Akkutlu (2013), Pang et al. (2012), Devegowda et al. (2012), Firincioglu et al. (2012).

TABLE 1

IUPAC classification of pores (Everett, 1972)

	Pore width	Major process
Micropore	Less than 20 Å	Monolayer adsorption and volume filling
Mesopore	Between 20 and 500 Å	Multilayer adsorption and capillary condensation
Macropore	Larger than 500 Å	Multilayer adsorption and capillary condensation

¹ The part of this paper has been presented in last year in: ICEE/ICIT-2013 conference Cape Town, South Africa: Nagy, Siemek (2013).

In authors opinion the condition of necessary to form continuous liquid phase is oil wettability. The other papers see e.g. Cao Minh et al. (2012) confirm the existence of such type of wettability in the unconventional reservoirs, where up to 50% of pores are located in organic matrix (kerogen). The opinion of Lee (1989), Brusilovsky (1990), and Guo (1996), Firoozabadi (1999), Nagy (2002, 2003), Elamin et al. (2013), Didar & Akkutlu (2013), Whitson & Sunjerga (2012), Orangi (2011), Hartman et al. (2011), Pang et al (2012), Honarpour et. al. (2012), Kuppe F. et al., 2012. Some of the confirm necessary to include the capillary effects in the deep reservoir with the low permeability and oil-wet wettability. Additionally new effect is considered – shift of critical parameters (Didar & Akkutlu (2013), Elamin et al. (2013)). The range of pore diameters in the shale gas reservoir is between 1.5-100 nm (Clarkson & Haghshenas (2012), Kang (2011), Diaz et al. (2009). Kang (2011), Clarkson et al. (2012) Diaz et al. (2009), Zhang et al. 2013, Sanaei et al. 2013. Firincioglu et al. (2012) have analysed porosity and pore structure of several shale reservoir. A molecular layer density for methane at 80°C across of a 3.6 nm organic slit-pore is given based on Diaz et al. (2009) work (Fig. 1). The Figure 1 has been obtained by Diaz et al. using molecular dynamics simulation carried out in the canonical (NVT) ensemble.

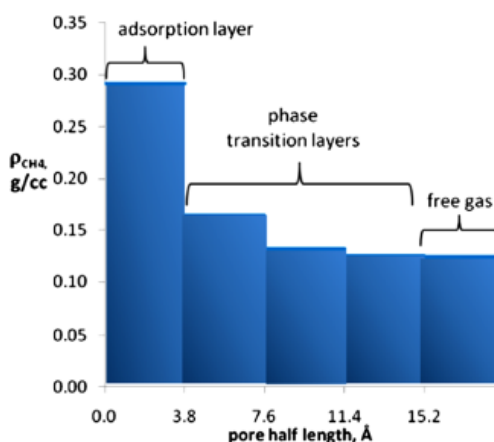


Fig. 1. Molecular density of methane across the organic silt-pore (Kang, 2011 – cited from Campos et al. 2010)

The estimated pore pressure for the bulk phase measurements of methane is 4,413 psi. Similar analysis is presented in Ma & Jamili (2014). The example of histogram of pore diameter from MICP experiment in the shale rock is given also in the Figure 2 (Clarkson & Haghshenas (2012)), similar histogram associated to different shale rock is given in Figure 3 (Dhanapal et al., 2014). The mentioned papers presented more detailed possible distribution of porous structures in shale and tight rocks. Based on IUPAC pore size distribution Alharthy et al (2013) proposed three different thermodynamic phase behaviours' paths related to VLE conditions in porous media:

1. **Unconfined** pore phase behaviour, which is mainly the unshifted phase behaviour in macropores or what would be in a PVT cell with no pore confinement effects. These occupy majority of the macro and mesopores (60-80%).

2. **Mid-confined** pore phase behaviour, which is the partially shifted phase behavior in mesopores and is considered to be between unconfined and confined pore phase behaviors. This category occupies about 10-15% of the pores.
3. **Confined** pore phase behavior, which is the shifted phase behavior in nanopores where the pore size is less than 3 nm and these occupy about 3-5% of pores and is dependent on the mineralogy (clay content).

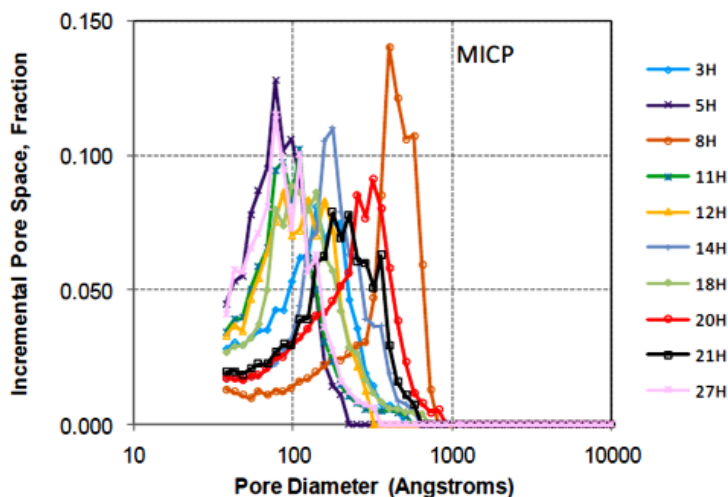


Fig. 2. Nano-pore size distributions using MICP from one of the shale rocks after Clarkson et al. (2012)

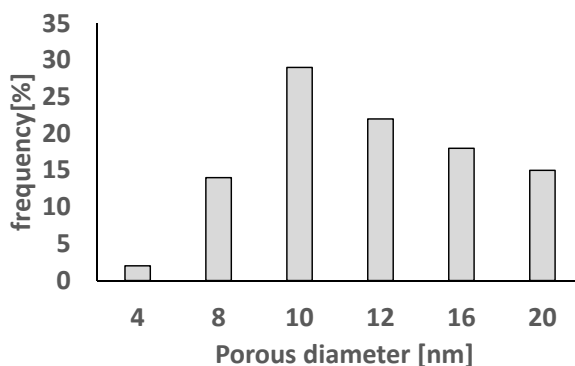


Fig. 3. Example of size pore distribution taken from Dhanapal at al (2014)

The paper of Alharthy et. la (2013) also discussed two possible scenario relevant to condensation of hydrocarbon in dew phase envelope (Figs 4 & 5):

1. scenario without phase envelope shift: inside the nanopores, the capillary pressure is high and the gas phase pressure is higher than the original dew point pressure which causes

the fluid condense sooner (capillary condensation (see Nagy, 2002)). This is in contrast to the meso and macro pores where at high pressures the supercritical fluid condenses the normal condensation path.

- scenario with shift of phase envelope (shift of dew pressure): in case of favorable phase envelope shift, the process of condensation does not occur. The fluid in nanopores stays in the supercritical state with minimum liquid dropout. In the meso and macropores the fluid will condense sooner.

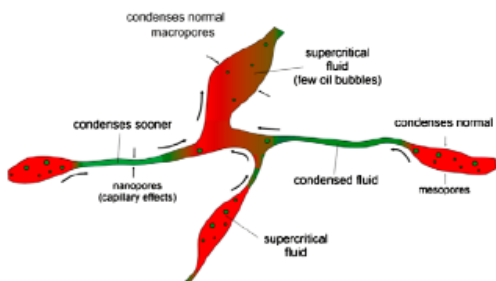


Fig. 4. Beginning of condensation process in nanopores for case “without phase envelope shift” (Alharthy et al., 2013)

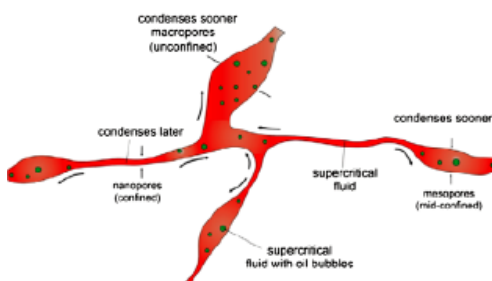


Fig. 5. Beginning of condensation process in nanopores for case “with phase envelope shift” (Alharthy et al., 2013)

2.1. Hydrocarbon adsorption phenomena in the porous rocks in the near of saturation curve

The adsorption phenomena in the porous media may have a significant impact on the reserve distribution of tight, shale and coal-bed methane reservoirs. The adsorption process may largely distinguish from surface adsorption observed in the chemical labs. The main two differentiating reasons are: existence of capillary condensation phenomena in the narrow pores and possibility of flow access blocking in the porous network. The progress in the fundamentals of adsorption theory one may find in the Dąbrowski (2001) paper. The adsorption phenomena related to the porous media are discussed in many textbooks (ie. Defay, Prigogine (1966), Adamson (1990), Dullien (1992)). The advances in the adsorption process in the high pressure porous media may be found in Shapiro, Stenby (1996, 2000, 2001), Guo et al., (1996) and Satik, Horne, Yortsos, (1995), Kang (2011) Altman et al. (2014), Travalloni et al. (2013) papers. In this paper the conservative model of adsorption has been used with the single molecular layer. The maximum thickness of adsorption film found in the real mesopore system is 23 Å (Adamson, 1990), but in this work very conservative film of adsorption 4 Å is assumed. The possible selective molecule adsorption to the kerogene in a shale gas condensate system is presented in Fig. 6 after Altman et al. (2014).

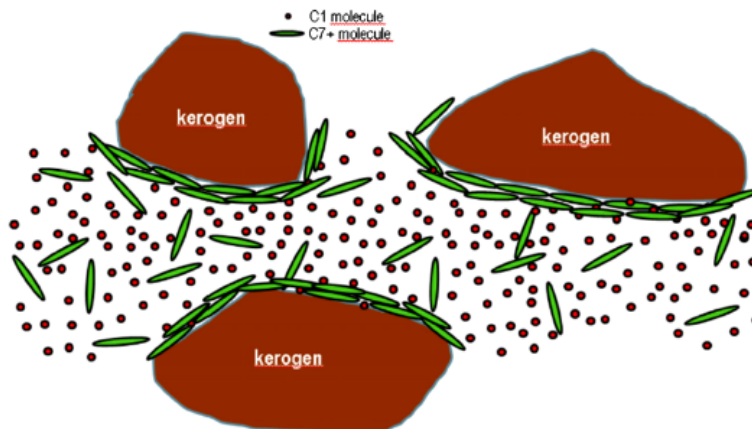


Fig. 6. Example of selective molecule adsorption to the kerogen in a shale gas condensate system (Altman et al., 2014)

2.2. Capillary-adsorption vapor-liquid equilibrium (VLE) model

On the curved surface inside of porous media for the stationary state of the second kind (based upon Prigogine definition) following set of equation is valid (neglecting gravity force):

$$p_v(T_v, \mu_1, \mu_2, \dots, \mu_{nc}) - p_l(T_l, \mu_1, \mu_2, \dots, \mu_{nc}) = \frac{2 \cdot \sigma(p_v, T_v, \mu_1, \mu_2, \dots, \mu_{nc})}{r_e - t} \quad (1)$$

$$T_v = T_l \quad (2)$$

where T — temperature and m — chemical potential of i — component can be varied independently, that r is allowed to vary at the same time, t — i the critical adsorption film. At the dew point of capillary condensation phenomena exist three types of chemical potential:

$$\mu_i^L = \mu_i^V = \mu_i^{Vad}, \quad i = 1, \dots, nc \quad (3)$$

or

$$f_i^L(p_v - p_c, T, x_1, x_2, \dots, x_{nc}) - f_i^V(p_v, T, x_1, x_2, \dots, x_{nc}) = 0, \quad i = 1, \dots, nc \quad (4)$$

$$z_i - y_i = 0, \quad i = 1, \dots, nc \quad (5)$$

$$\sum_{i=1}^{nc} x_i - 1 = 0, \quad \sum_{i=1}^{nc} y_i - 1 = 0 \quad (6)$$

Laplace equation (another proposal for modification of Laplace equation is presented in paper of Firincinoglu et al. (2012), in this work only classic equation has been used):

$$p_v - p_l - \frac{2 \cdot \sigma}{r_e - t} = 0 \quad (7)$$

Interfacial multicomponent surface tension is calculated using (8) equation:

$$\sigma^{l/E} = \frac{p_v}{Z^v RT} \sum_{i=1}^{nc} \left[\left(\frac{Z^v}{Z^L} \right) \cdot x_i - y_i \right] \cdot \pi_i \quad (8)$$

where σ — interfacial tension (IFT), Z^V , Z^L — vapor and liquid phase compressibility factors, E — empirical dimensionless constant, π_i — parachor of i -component (Danesh, 1991; Weinaug & Katz, 1943)).

The set of nonlinear equations may be modified by expanding using Taylor series and taking into consideration only first term, the chemical potential of i -component in the liquid phase may be calculated:

$$\begin{aligned} \mu_i^L(p_v - p_c(r, t), T, x_1, x_2, \dots, x_{nc}) = \\ = \mu_i^L(p_v, T, x_1, x_2, \dots, x_{nc}) - \frac{\partial \mu_i^L(p_v, T, x_1, x_2, \dots, x_{nc})}{\partial p_v} p_c(r, t) \end{aligned} \quad (9)$$

or using fugacity of i -component for isothermal conditions:

$$\begin{aligned} \ln f_i^L(p_L, T, x_1, x_2, \dots, x_{nc}) = \\ = \ln f_i^L(p_v, T, x_1, x_2, \dots, x_{nc}) - \frac{\partial \ln f_i^L(p_v, T, x_1, x_2, \dots, x_{nc})}{\partial p_v} p_c(r, t) \end{aligned} \quad (10)$$

The derivative on the right side is a molar partial component volume:

$$\frac{\partial \ln f_i^L(p_v, T, x_1, x_2, \dots, x_{nc})}{\partial p_v} = \frac{\bar{V}_i^L}{RT} \quad (11)$$

where \bar{V}_i^L is partial liquid molar volume of i -component. Equation (10) may be rewritten to the form:

$$\ln f_i^v(p_v, T, y_1, y_2, \dots, y_{nc}) = \ln f_i^L(p_v, T, x_1, x_2, \dots, x_{nc}) - \bar{V}_i^L \frac{p_c(r, t)}{RT} \quad (12)$$

Based upon the above derivation difference between bulk and capillary condensate dew point equations may be formulated:

$$F(N_v = 1, p_c(r, t) \neq 0) \equiv 1 - \sum_{i=1}^{nc} \frac{z_i}{K_i^\infty} \cdot \exp(\varepsilon_i p_c(r, t)) = 0 \quad (13)$$

where: $\varepsilon_i = \frac{V_i^L}{R \cdot T}$ — component Poynting factor, V_i^L — partial molar liquid component volume.

Based upon equation the new capillary condensation equilibrium constant may be introduced:

$$K_i = K_i^\infty \cdot \exp\left(\int_0^{p_c(r, t)} \varepsilon_i dp\right) \quad (14)$$

or after simplification based of constant partial molar volume:

$$K_i = K_i^\infty \cdot \exp(\varepsilon_i p_c(r, t)) \quad (15)$$

The proposed algorithm for calculation of the capillary condensation dew pressure is given in the paper of Nagy (2002) together with new form of Rachford_Rice equation and modified modified tangent plane criterion for capillary condensation (MTPCCC) based upon the fundamental work of Michelsen (1982a, 1982b). Generally, our use of stability proposed test (MTPCCC) to direct computation of vapor liquid equilibrium in the capillary condensation area without necessity to compute saturation pressure of flat and curved system.

2.3. The nano impact on the critical parameters of natural gas components

A very interesting discussion of the phase nanopore effects is presented in the paper of Devogowda et al. (2012). This paper discusses such change of critical parameters in micro- and meso-pores – so called “confinement effect”. The authors discuss the Monte Carlo simulations Hamach et al. (2007), Sing et al. (2009), Travalloni et al. (2012), Ortiz et al. (2005). Numerical study of Sing et al. (2009) experiment being used by the Devogowda et al. in the construction of function of the critical pressure and temperature as a function of molecular weight.

Devogowda et al. (2012) shows the possible impact of the curvature coefficient of porous media to compressibility factor Z , phase PVT properties (without capillary effects, and without adsorption). This work discusses the influence of parameters on the viscosity of the pore gas as a function of the Knudsen number. The present work uses data of Sing et al. (2009) for correlating the critical temperature as a function of the effective pore radius (or diameter).

$$\frac{T_{cc}}{T_c} = 0.1126 \ln(r / r_0) + 0.8057 \quad (16)$$

where T_{cc} — confined critical temperature, T_c — critical temperature, r_0 — reference pore diameter (1.5 nm), r — actual pore diameter (nm). The critical pressure has been estimated on the basis of Sing et al. (2009) as a function similar to the correlation equation Antoione for vapor pressure:

$$\ln\left(\frac{P_{cc}}{P_c}\right) = 6.4265 - \frac{6.3709}{\frac{T_{cc}}{T_c}} \quad (17)$$

where P_{cc} — confined critical pressure, P_c — critical pressure. Both equations are valid only for 1.5-5 nm radius (or 3-10 nm pore diameter).

A similar correlation functions for the critical pressure also suggested Didar & Akkutlu (2013). The relative shift of critical parameters (after Sing(2009) may be defined as:

$$\Delta T_c = \frac{T_c - T_{cc}}{T_c} \quad (18)$$

$$\Delta P_c = \frac{P_c - P_{cc}}{P_c} \quad (19)$$

The second correlation relevance to dimensionless shift of critical parameters pressure and temperature is presented in Ma et al. (2013), Ma & Jamili (2014) paper:

$$\Delta T_c = \frac{T_c - T_{cc}}{T_c} = 0.8493 \left(\frac{D_p}{\sigma} \right)^{-1.241} + 0.015 \quad (20)$$

$$\Delta P_c = \frac{P_c - P_{cc}}{P_c} = 1.8 \left(\frac{D_p}{\sigma} \right)^{-0.775} \quad (21)$$

where ΔT_c , ΔP_c — dimensionless shift of critical temperature and pressure relevant to confinement phenomena.

$D_p = 2 r_p$ — porous diameter, σ — effective particle diameter based on the formula:

$$\sigma = \sqrt[3]{1.15798 \frac{b}{N_{av}}} \quad (22)$$

where: b — volume parameter from van der Waals equation of state, N_{av} — Avogadro number.

2.4. Phase envelope algorithm (classical bulk – hydrocarbon dew pressure case)

The algorithm of calculation of bulk phase envelope in gas condensate system is shown in figure 9 (Nagy, 1992). standard Tangent Criterion (Michelsen, 1982a, 1982b) is used in calculation. The presented algorithm is not sensitive to selection of Equation of State. In this scheme two solution method are preferable, simple successive substitution ($\lambda = 1$) or GDEM (General Dominant Eigenvalue Method) where λ -acceleration exponent (Crowe & Nishio, 1975). The method has been tested in several papers (e.g. Nagy, 1992a, 1992b, 2002, 2003).

2.5. An algorithm for the calculation of the capillary condensation dew pressure

In the presence of transition region (gas-oil) in the tight/shale rock (where average capillary radius is below 1 μm – see Nagy 2002, 2003) we should include the additional terms related to adsorption and capillary condensation process. The proposed algorithm for calculation of the capillary condensation dew pressure consists of the following steps:

1. Compute set of initial equilibrium constants K_i^∞ ,
2. Compute thickness (t) of the adsorption film using any meso-pores adsorption model (i.e. Frankel-Halsey-Hill, simplified de Boer et al., etc.),
3. Compute the interfacial tension (IFT) (σ) using scale or parachor model,
4. Compute capillary pressure p_c ,
5. Compute the set of liquid partial volume of components \bar{V}_i^L and Pointing factors (ε_i),
6. Compute new-corrected equilibrium constants using equation
7. Compute the newly-corrected condensate capillary equilibrium composition of the liquid phase,
8. Perform saturation pressure correction for capillary/bulk vapour/liquid equilibria using,
9. Repeat steps 2-7 until convergence is reached.

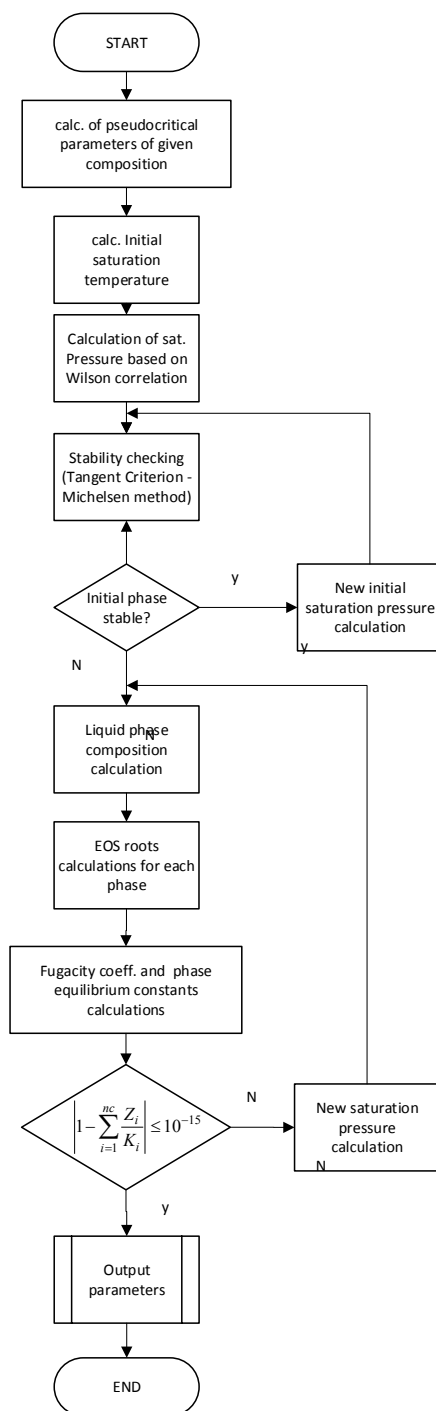


Fig. 7. Saturation (Dew) pressure calculation scheme (modified after Nagy, 1992a; Warowny et al., 2004)

3. Application of theory to possible reservoir gas-condensate systems

The selection of proper Equation of State for VLE is important. Although there is a hot discussion related to new EOS designated to description of nano confinement phenomena (Zarragoicoechea & Kuz, 2004; Derouane, 2007; Travalloni et al., 2010, 2013) – this paper is focused on classical EOS. The computation procedure in this work has been done using volume translated version of Peng-Robinson equation. From among a lot of versions of PR CEOS (Peng-Robinson, 1976; Peneloux et al., 1982; Stryjek & Vera, 1986; Jhaveri & Youngren, 1988; Patel & Teja, 1982, Stamatakis & Magoulas, 2001; Lin & Duan, 2005). The Tsai and Chen (1998) VT-PR EOS version have been chosen. The mentioned Tsai Chen VT-PR EOS and VT-PR in the form of being in the opinion of the authors most versatile EOS for high pressure vapor liquid equilibria. The original Tsai and Chen (1998) form of the equation is given below:

$$p = \frac{RT}{v+t-b} - \frac{a}{(v+t)(v+t+b)+b(v+t-b)} \quad (23)$$

where t — the translated volume parameter, with the volume calculated by the CEOS approaches the experimental value (see Nagy, 2002; Tsai & Chen, 1998).

The most important parameter which is needed in this algorithm is proper evaluation of surface tension oil/condensate-gas in the high pressure VLE. The presented computation is re-

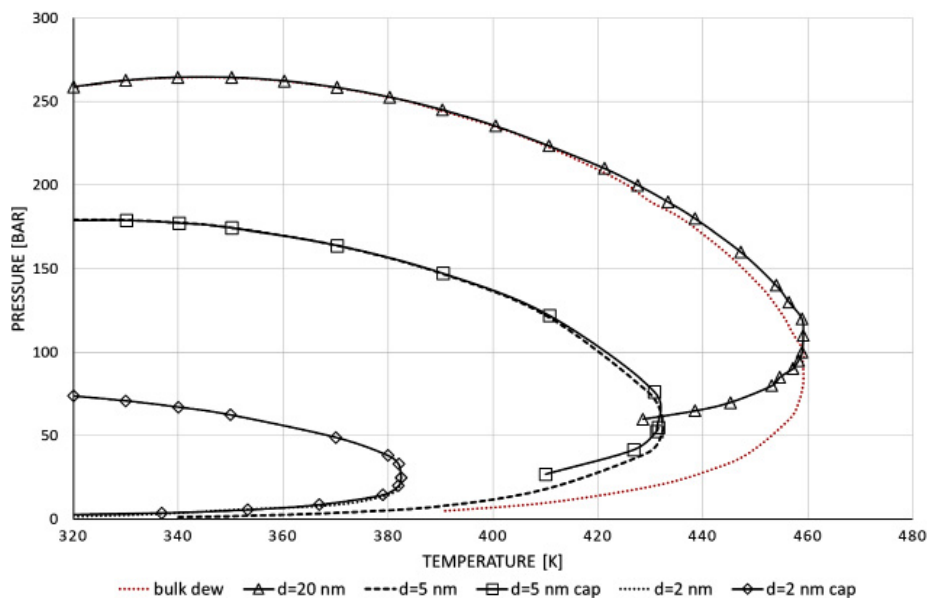


Fig. 8. Phase envelope of gas condensate system (gas condensate composition of Brusilovsky (1990) with capillary-adsorption effects and impact of confinement phenomena of critical parameters using Tsai & Chen VT-PR EOS

lated to new papers Fanchi (1990), Danesh et al. (1991). The data from this paper has been used in computations. The models of Fanchi and Danesh et al. are related to critical parameters. The solution procedure is similar as presented by Nagy (1992, 2002) using classical critical properties taken from Reid, Prausnitz (1977) and using confined parameters (eq. 16-17 or 20-21). The confined critical parameters have been used in this calculation for case of 5 and 2 nm pore diameters. The mole composition of gas condensate mixture has been taken from Brusilovsky (1990): methane 0.7643; ethane 0.0746; propane 0.0312; i-butane 0.0059; n-butane 0.0121; i-pentane 0.005; n-pentane 0.0059; n-hexane 0.0079; n-heptane 0.01; n-octane 0.01; n-nonane 0.01; n-decane 0.037; CO₂ 0.0249; N₂ 0.0012). Results of computation are given in Figure 8. The capillary-adsorption impact on the vapor phase fraction near flat upper part dew point line is small except near cricondenterm point – above 420 K. The cricondenterm pressure calculated with the set of equation (4-8) is located 30 bars above “flat surface” cricondenterm pressure. The largest impact of capillary effects is observed in the lower part of the curve, where the difference in increase of pressure is close to 40 bars. The capillary effects are much smaller in case of use of confined critical parameters, but are still important in the lower part of the phase envelope. The confined parameters (eq. (16-17)) are used for calculation of IFT. The effect of capillarity is very small for pore diameter 2 nm in the case of use of confined critical parameters. The impact of new confined critical parameters for calculation of phase equilibria of rocks with 2, 5 20+ nm pore diameter is large, as you may observe in the Figure 8. In case of the reservoir temperature higher than 385 K, the process of condensation of the heavy component (C₂-C₁₀) is stopped for 2 nm pore diameter. In this case the saturation pressure of 5 nm pores is lower up to 150 bars – difference (80 bars). In such example the condensation process is expected in the pores of diameter 100-20 nm. This may be important in the deep shale gas structures, below 3000 m, where the shift of average pore diameters of structure may be valid.

Similar impact of nano-porosity on bubble and dew curve is presented on figure 9 for ternary oil-like composition (CH₄ – 10%) – nC₄H₁₀ (25%) – nC₈H₁₈ (65%) using TC TVPR EOS. This calculation is done without adsorption and capillary pressure modification, but with the shift of critical parameters for confined conditions (eq. 20-21). In this situation we observe lowering of bubble pressure in confinement pores ($D_p = 4$ nm). An important problem relevant to calculation of the compressibility factor of single phase – like methane – has to be additional research (see Fig. 10). The observed isotherm at 85°C shows different shapes and values in case of confinement pore structure. This may influence significant on estimation Gas In Place Resources.

4. Conclusions

The porous media dew pressure of gas condensate in this paper shows mixed impact in case of capillary/adsorption effects. The impact of porous media in near critical condition is small. It is a low probability to expect of any capillarity effect in the high permeability rock. The new numerical experiments may be very useful in understanding of VLE phenomena, but should be verified in the future. The shift of phase envelope in the nano-porous structure should be still investigated. Because only part of the shale gas reservoir has a nanopore structure of 2-5 nm diameter, probably the shift of phase envelope parameters must be addressed only to those elements of structure. The rest of the reservoir, which have a pore diameter larger than 10 nm should be described using classical tools with capillary correction as presented in this paper.

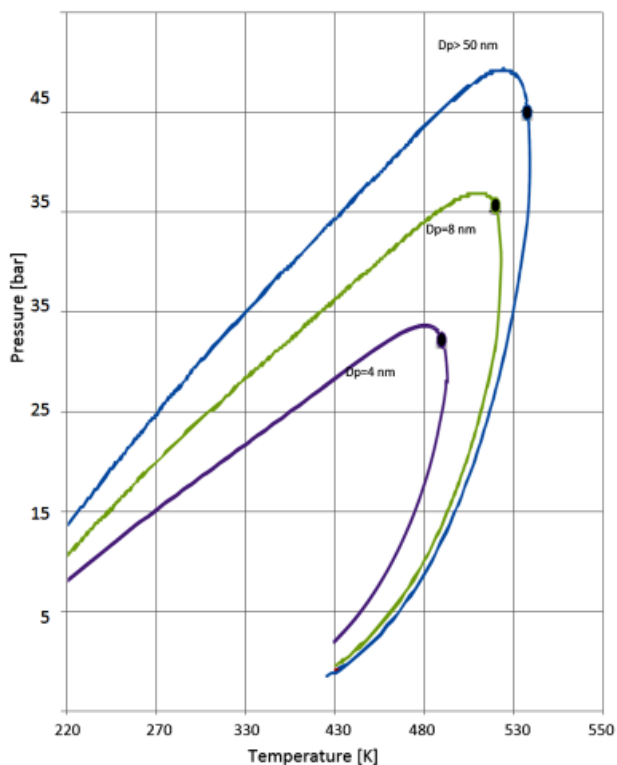


Fig. 9. Phase envelope for pseudo light oil mixture at different pore diameters

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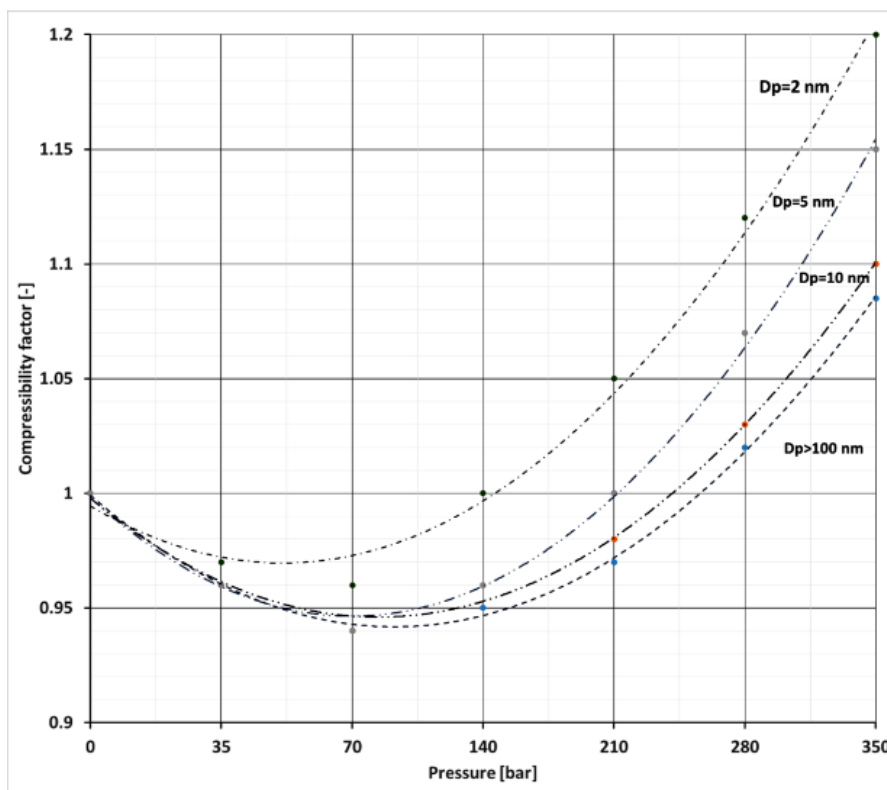


Fig. 10. Compressibility factor of pure methane in bulk ($D_p > 100$ nm) and confined conditions ($D_p = 2, 5, 10$ nm) at constant temperature 85°C (equivalent to 2700 m depth at geothermal gradient $3.3^\circ/100$ m) using TsaiChen PR EOS with modified critical parameters

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