Calculation of maximum water content in gas phase for selected natural gases

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Abstrakt During the expansion of natural gas in the pipeline transportation, the gas cools down due to the Joule-Thomson effect and due to the interaction between pipeline system and its surroundings to the conditions at which gas is saturated by water vapors, and gas is not able to keep excess humidity and its condensation and hydrate formation will occur. For that reason it is necessary to identify the critical parts of the pipeline systems, maximum water content in the gas, to choose appropriate physical model. For the physical model development, method based on equality of fugacity concept with modified Peng-Robinson equation of state and Rachford-Rice appropriate solution algorithm are used to develop the model estimating the water content in equilibrium with natural gas. The results of the presented method are compared with selected experimental data (methane-water and natural gas - water systems) from the literature. Selected natural gases are compared from maximum water content point of view.

1 Introduction

During the expansion of natural gas in the pipeline transportation, the gas cools down due to the Joule-Thomson effect and due to the interaction between pipeline (and pipeline system equipments) and its surroundings (heat transfer processes) to the conditions at which different phase formation as water liquid, condensates and other solid materials (hydrates) might occur [1]. NG hydrates are crystalline solids composed of the water and the gas. The gas molecules (guest) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules [2]. Typical NG hydrate molecules include methane, ethane, propane, and carbon dioxide. Both hydrates and liquid slugs are damaging the gas pipeline system operation by corrosion, valve seat erosion, clogging and the mechanical stress to the system [3]. In gas distribution systems, the main precaution that can eliminate these problems is the gas heating before its throttling in pressure reduction stations. The maximum water content in NG (or dew point) considerably influences energy consumption requirements due to dependence on intensity of gas heating before NG throttling. Based on presented information, appropriate equation of state for maximum water content in NG calculation is used (compared with selected experimental data available from literature) and also selected natural gases are compared from maximum water content point of view.

2 Methods and model

The starting point for vapor-liquid equilibrium is the equality of fugacity coefficient of each component in each phase. In order to solve the problem and to approach the real behavior of water-gas system modified Peng-Robinson equation of state (PR EoS) is used. This equation using GERG water model is published as part of the ISO 18453, proposed by the European Gas Research Group GERG (Group Européen de Recherche Gazière), see [4], [5]. Phase equilibrium calculations with equation of state are iterative and in this case the isothermal flash calculation is used [6]. The flash method is the type of calculation where the objective is to calculate the amount of phases present in an equilibrium mixture and to determine the composition of the coexisting phases. The temperature, pressure, and initial compositions are the input parameters. The objective function is solved by using Rachford-Rice algorithm. Then it uses the Newton-Rapson method for the correction steps.

3 Results and discussion

Comparing the results of calculations of maximal water content in the gas of the methane-water and various NG-water systems are together with the comparison of experimental values defined in **Tab. 2** and compositions of selected gas mixtures are showed in **Tab. 1**.

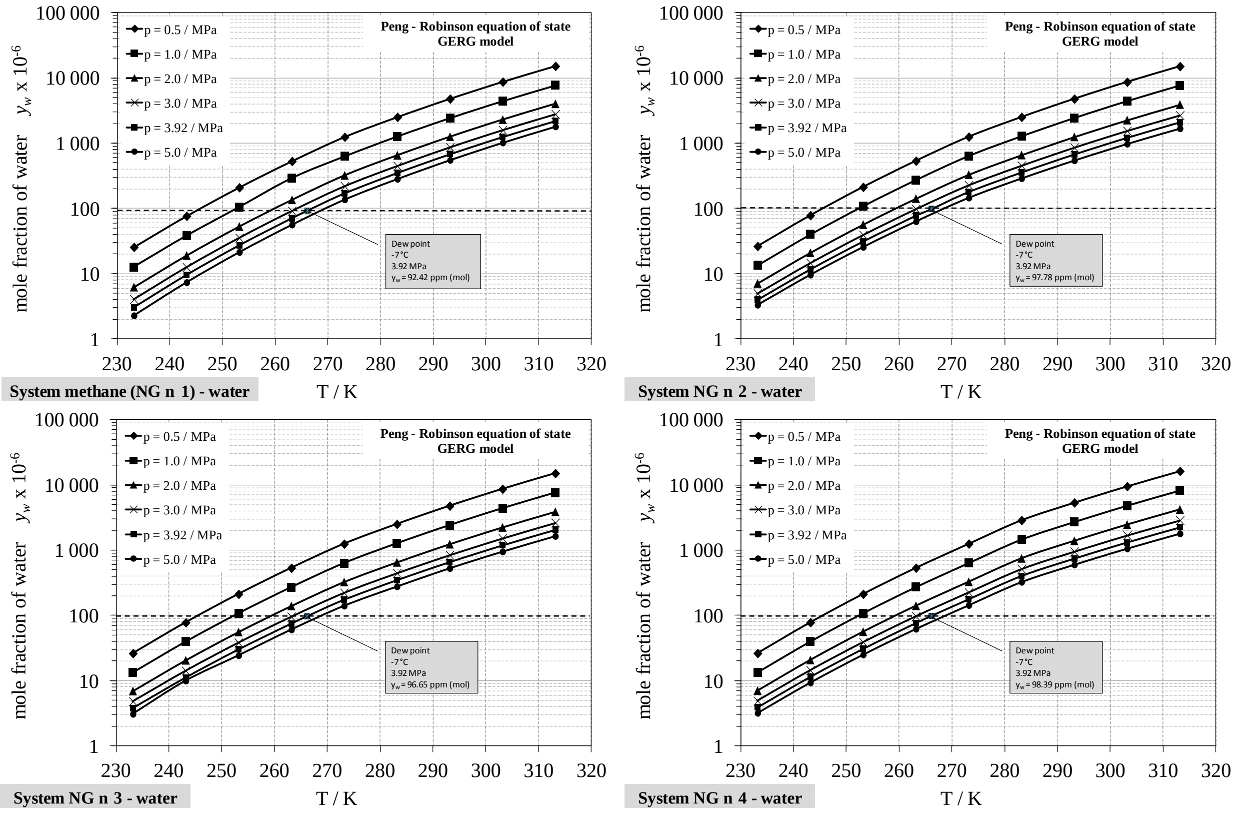
Tab. 1 Compositions of selected natural gases

Component name	**NG n°1**	**NG n°2**	**NG n°3**	**NG n°4**
	Methane	Laboratory synthetic gas	Laboratory synthetic gas	Laboratory synthetic gas
	Composition [mol %.]			
methane	100.0000	94.0000	89.0000	84.4000
ethane	–	4.0000	7.0000	10.0000
propane	–	–	–	4.0000
n-butane	–	2.0000	4.0000	1.0000
iso-butane	–	–	–	0.6000
n-pentane	–	–	–	–
iso-pentane	–	–	–	–
n-hexane	–	–	–	–
n-heptane	–	–	–	–
n-octane	–	–	–	–
hydrogen	–	–	–	–
helium	–	–	–	–
nitrogen	–	–	–	–
ox. uhličitý	–	–	–	–

The experimental and calculated data shows that the maximal water content ($y_{w,exp}$ and $y_{w,calc}$) decreases with the decreasing temperature and rising pressure. In **Tab. 2**, presented results especially for temperature range 250.95 ≤ T ≤ 273.09 K present not accepTab. agreement between the experimental and calculated results by using modified PR EoS (GERG model) and various areas of improvements should be applied, specially below the temperature 273 K. Very high deviations from experimental values are in selected range of temperatures and pressures for all NG which are not characteristics for the area of vapour-liquid equilibrium (VLE) but for the zone of hydrate formation. The selected ranges of temperatures and pressures are showed due to application of presented PR EoS (GERG model) for calculation especially for the critical parts of pressure reduction valve (valve seats) and pipelines where the temperatures goes below 273 K. Originally, GERG model was proposed for VLE applications but for (ice, hydrate)-vapor equilibria was extrapolated PR EoS by fitting binary interaction coefficient (temperature dependent) of PR EoS to experimental data and by using different function for the energy term. But as it is evident from **Tab. 2**, these actions for PR EoS are not sufficient and some improvement should by proposed for another modification of PR EoS or by using three different types of phase equilibria and models to cover the actual temperature and pressure ranges (vapor-liquid, vapor-ice, vapor-hydrate), [10]. As it is showed in **Obr. 1**, for example the dew point for selected NG varies for temperature – 7 °C and pressure 3.92 MPa for maximum water content 92.42 ppm (mol) to 98.39 ppm (mol) as a function of various NG compositions. The major changes in water content are due to the changes of ethane component, but detail analysis should be applied also to *other hydrocarbons as propane and butane. The differences between presented NG are not so evident because “laboratory synthetic gas” (see **Tab. 1**) was without presence of other components as nitrogen, carbon dioxide hydrogen and helium which can influence considerable maximum water content in NG and hydrate formation region. These components are natural part of commercially distributed gases, e.g. Russian, Norwegian or domestic NG as ZPS Senné and ZPS Prieskum.

Tab. 2 Experimental and calculated water content (mole fractions) of the various NG-water systems

Experimental data					Calculations		Experimental data					Calculations	
NG n°	T	p	Data source	$y_{w,exp}$ x 10^6	$y_{w,calc}$ x 10^6	error	NG n°	T	p	Data source	$y_{w,exp}$ x 10^6	$y_{w,calc}$ x 10^6	error
	K	MPa		mol	mol	%		K	MPa		mol	mol	%
1	250.95	3.440	[7]	32.300	24.628	-23.75	3	250.92	0.491	[9]	120.000	169.918	41.60
1	255.35	3.440	[7]	47.700	38.175	-19.97	3	256.64	1.000	[9]	120.000	144.383	20.32
1	260.05	3.440	[7]	71.400	59.866	-16.15	3	260.07	1.490	[9]	120.000	132.973	10.81
1	264.75	3.440	[7]	105.000	92.215	-12.18	3	264.15	2.011	[9]	120.000	141.863	18.22
1	266.75	3.440	[7]	123.000	110.247	-10.37	3	266.87	2.509	[9]	120.000	143.945	19.95
1	271.05	3.440	[7]	171.200	160.218	-6.41	3	269.04	2.994	[9]	120.000	144.981	20.82
1	271.95	3.440	[7]	183.300	172.960	-5.64	3	255.37	0.477	[9]	210.000	268.432	27.82
1	250.55	6.890	[7]	14.800	11.693	-20.99	3	261.80	0.998	[9]	210.000	232.088	10.52
1	253.25	6.890	[7]	19.000	15.546	-18.18	3	266.92	1.557	[9]	210.000	233.279	11.09
1	255.55	6.890	[7]	23.200	19.698	-15.10	3	269.42	2.025	[9]	210.000	221.855	5.65
1	259.15	6.890	[7]	33.600	28.233	-15.97	3	256.53	0.498	[9]	310.000	286.769	-7.49
1	260.65	6.890	[7]	38.300	32.683	-14.67	3	263.15	0.968	[9]	310.000	269.890	-12.94
1	264.15	6.890	[7]	51.700	45.621	-11.76	3	268.11	1.536	[9]	310.000	261.834	-15.54
1	269.15	6.890	[7]	74.900	72.116	-3.72	3	270.54	1.991	[9]	310.000	247.899	-20.03
2	268.15	1.020	[8]	4.514	4.053	-10.21	4	263.15	1.500	[10]	159.700	175.413	9.84
2	273.09	1.063	[8]	6.857	5.874	-14.34	4	263.15	6.000	[10]	50.600	43.347	-14.33
2	278.15	1.007	[8]	8.884	8.875	-0.10	4	273.15	1.500	[10]	365.100	410.979	12.57
2	283.14	1.018	[8]	13.715	12.341	-10.02	4	273.15	4.000	[10]	129.700	154.799	19.35
2	288.15	1.012	[8]	17.925	17.234	-3.86	4	273.15	6.000	[10]	102.100	102.539	0.43
2	288.15	6.017	[8]	3.460	3.223	-6.86	4	283.15	6.000	[10]	226.300	207.474	-8.32



Obr. 1 Water content calculations of the methane - water and NG n° 2, 3, 4 - water systems using modified PR EoS (GERG model)

4 Conclusion

Following presented results, in future work the analyses of various gas compositions will be based on PR EoS based on using CPA (Cubic Plus Association) method which combines the classical simple PR EoS with an advances association term. Associating system are those which contain compounds capable of hydrogen bonding (e.g. water or some inhibitors for gas hydrate prevention. etc.). The scope is to describe better the dense phases (i.e. the gas phase or the liquid water phase) coupled a solid phase model, which can be an ice or hydrate model.

Due to the recent events in supplying middle European region with NG it is a hot issue to analyze in details examples, when the NG will be distributed through gas pipeline systems from various suppliers, i.e. NG of different composition with different physical and chemical parameters and water content, those substantially affect capacity of gas system and energy intensity of transmission and distribution. For various components of NG the sensitivity analysis of monitored parameters on energy intensity should be applied for EoS model calibration.

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