THE EQUATION OF STATE OF BIOGAS

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Abstract

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The presented work deals with a state behavior of real gas, biogas. Theoretical approach was utilized for processing of this work. Compressibility factor was calculated with help of two equation of state – Van der Waals equation and Redlich-Kwong equation. Constants *a* and *b* of both equations were calculated using geometric average of the constants of pure substances. On the basis of calculated data charts showing the dependence of compressibility factor and the pressure were created. These charts were created for temperatures 20 ℃ and 40 ℃. Statistical analyses of data were carried out. The results showed that compressibility factor reached value from 0.997 to 0.97 (20 ℃) and from 0.997 to 0.974 (40 ℃) in the case Van der Waals equation and in the range of pressure from 100 kPa to 1000 kPa. In the case of Redlich-Kwong equation these values were from 0.997 to 0.967 (20 ℃) and from 0.997 to 0.974 (40 ℃) in the same range of pressures.

Keywords: biogas, equation of state, Redlich-Kwong, Van der Waals

INTRODUCTION

Generally, the equations of state play an important role in industry. The knowledge of the state behaviour of gases is used in chemical, petrochemical, food and energy industries as well as in agriculture. The knowledge of the state behaviour of gases is applied in the field of thermodynamic analysis, in technical calculations of the device for transport and heat transfer, and in calculations of piping systems (Grigor'ev *et al.*, 2016). In agriculture, the knowledge of the behaviour of the thermodynamic system is used mainly in drying and cooling. More often it is also used in technologies designated for the biogas production – biogas stations.

Biogas is a mixture of two major gases, carbon dioxide (CO_2) and methane (CH_4). However, biogas contains other gases as well, for example hydrogen (H_2), carbon monoxide (CO), nitrogen (N_2), water vapour (H_2O), hydrogen sulfide (H_2S) or ammonia (NH_3) (Straka *et al.*, 2006). The final composition of biogas depends on the technology of the biogas station and primarily on input material, which is processed in biogas station. The usual concentrations of gases in biogas produced in agricultural biogas stations are the following. Methane up to 60 %$_{vol}$, carbon dioxide up to 40 %$_{vol}$, hydrogen up to 5 %$_{vol}$ and nitrogen ranged from 1 to

2 %$_{vol}$ (Mohammadi *et al.*, 2013). But in general, the concentration of methane in biogas is variable and can reach value up to 75% (Vitázek *et al.*, 2011).

The knowledge of the state behaviour of biogas is particularly important in terms of operation and safety of devices installed at biogas stations. Specifically, this includes for example the calculation of the amount of biogas in the gasholder of a biogas station at various state conditions or behaviour of biogas in internal combustion engine of cogeneration unit.

In the simplest case, to calculate the state behaviour of a gas, an equation of state for an ideal gas according to the Boyle-Mariotte a Gay-Lussac laws can be used. However, real gases are not governed by these laws. For real gases, there are a lot of equations of state, both empirical as well as derived on the basis of concepts about behaviour of molecules, their movements and the forces between them (Pavelek, 2013).These equations include virial equations, Van der Waals, Berthelot, Redlich-Kwongand many other equations. The Redlich-Kwong equation of state was formulated in 1948. This equation is consideredto be the most accurate two-constant equation of state of a real gas (Novák *et al.*, 1972). It has undergone many modifications. The Redlich-Kwong-Soave equation
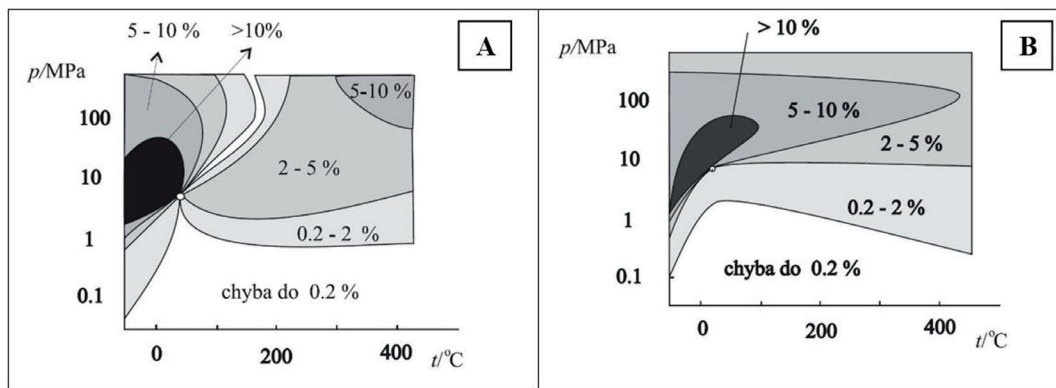
1: *Percent deviation of the compressibility factoror volume of CO2 according to A) Redlich-Kwongequation, B) Redlich-Kwong-Soave equation (Novák et al., 2007).*

is one of the numerous modifications (Novák *et al.*, 2007). Percent deviations at the Redlich-Kwong and Redlich-Kwong-Soave's equations are shown in Fig 1. From the figure 1, it is obvious that at temperatures around 40 °C (temperature at which biogas is produced in most biogas stations) and gauge pressure up to 500kPa (pressure of a gas in the gasholder) the percent deviation at carbon dioxide is up to 0.2 %. This deviation applies even to higher pressures than 1MPa.

In practice, gas mixtures are much more common than just pure gases. Several methods are used for the calculation of thermodynamic quantities of real gas mixtures. A traditional application of equations of state can be used, classical methods based on theorem of corresponding states, an application of empirical laws at mixtures, etc. (Novák *et al.*, 2007). However, it appears that the achieved results using the methods using qualities of pure substances are often not very satisfactory. Then, it is necessary to use methods in which experimental findings from the behaviour of gas mixtures are used. However, for its simplicity, the methods using qualities of just pure substances are a very useful tool.

The aim of this paper is to apply selected equations of state to the calculation of the compressibility factor z depending on the pressure of biogas. For this purpose, a mixture of gases (60 %$_{vol}$ of CH$_4$ and 40 %$_{vol}$ of CO$_2$) was chosen.

MATERIAL AND METHODS

Material

For the purposes of this paper, biogas (60 %$_{vol}$ CH$_4$ and 40 %$_{vol}$ CO$_2$) was used. Physical properties of pure gases were taken from other scientific papers. The dependence of the compressibility factor on pressure was carried out at 20 °C and 40 °C separately for CH$_4$ and CO$_2$ gases, followed by the mixture of these two gases.

Equations of state

For the calculation of state quantities, two equations were chosen. The Van der Waals and the Redlich-Kwong equations. Calculated values were compared to each other.

The Van der Waals equation is formulated as:

$$p = \frac{r \cdot T}{v - b} - \frac{a}{v^2} \tag{1}$$

Where:
p ....is the gas pressure[Pa]
r ....is the gas constant[J·kg^{-1}·K^{-1}]
v ....is the molar volume[m^3·kg^{-1}]
a, b ....are constants [−]

The Redlich-Kwong (Redlich *et al.*, 1949) equation is formulated as:

$$p = \frac{r \cdot T}{v - b} - \frac{a}{v^2} - \frac{a}{\left[\sqrt{T} \cdot v \cdot (v + b) \right]} \tag{2}$$

Where:
p ....is the gas pressure [Pa]
r ....is the gas constant [J·kg^{-1}·K^{-1}]
v ....is the molar volume [m^3·kg^{-1}]
a, b ....are constants [−]

The calculation of the mixture

For such calculation, the classical method using equations of state were used. For this purpose, constants a and b were calculated using geometric average of the constants of pure substances. The used relationship can be described as follows:

$$A = \left(\sum_{i=1}^{N} x_i A_{ii}^{1/2} \right)^2 \tag{3}$$

This relationship uses the Redlich-Kwong and Van der Waals equations for the calculation of the constant a (Novák *et al.*, 2007).

Statistical analysis

For statistical analysis of the calculated values, software Statistica 12 was used. Levene's test was used to assess the homogeneity of variance of data files. Autocorrelation was tested by Von Neumann test and the comparison of two dependent variables was assessed using the Wilcoxon paired difference test. A regressive model for the dependence of pressure and the compressibility factor at CH_4 and CO_2 mixture according to the Redlich-Kwong and Van der Waals equations was used. All the tests were performed at the significance level of $\alpha = 0.01$.

RESULTS AND DISCUSSION

It is necessary to determine the values of critical parameters of gases in the mixture for the calculation of the state behaviour of gases using the Redlich-Kwong and Van der Waals equations. The basic physical properties of gases, which were also used in the calculation, are shown in Tab. I, from which it can be clearly seen that the critical parameters (especially critical temperature and pressure) of CH_4 and CO_2 are very different.

An important part of the calculation is to determine the constants a and b, which are a part of both equations. In the calculations, recommended relationships of Novák *et al.* (1972) were used. They make use of state parameters in the critical point. The relationships for the constants used in the Redlich-Kwong equation are the following:

$$a = \Omega_A \left(RT_K \right)^2 \cdot \frac{\sqrt{T_k}}{p_k} \tag{4}$$

$$b = \Omega_B \cdot \frac{RT_K}{p_k} \tag{5}$$

For the constants Ω_A and Ω_B, the following values were used in the calculations (Chueh *et al.*, 1967): for methane $\Omega_A = 0.4278$ and $\Omega_B = 0.0867$, for carbon dioxide $\Omega_A = 0.447$ and $\Omega_B = 0.0911$. Generally, the constants can be calculated using various methods (Novák *et al.*, 2007). The relationships mentioned in the work of Soave are used for the modified Redlich-Kwong equation according to Soave (1971).

For the calculation of the constants a and b according to the Van der Waals equation, the following relationships was used (Novák *et al.*, 2007):

$$a = \frac{27}{64} \cdot \frac{R^2 T_c^2}{p_c} \tag{6}$$

$$b = \frac{1}{8} \cdot \frac{RT_c}{p_c} \tag{7}$$

The results of the calculation are shown in Figs. 2–5. Figures describe the dependence of the compressibility factor on pressure, both for pure gases and mixtures of gases. The dependence was determined for 20 °C and 40 °C. The temperature 20 °C is the temperature at normal conditions (NTP), the temperature 40 °C is approximately the temperature of biogas at its production at biogas stations operating within the mesophilic regime.

The diagram clearly shows that the compressibility factor is very close to 1 in case of low absolute pressures. We can therefore assume that biogas has similar state behaviour as an ideal gas at low pressures. If we assume that the absolute pressure in the gasholder is 200 kPa, the compressibility factor of biogas calculated using the Van der Waals equation is $z = 0.994$ at 20 °C, and $z = 0.995$ at 40 °C. The compressibility factor calculated according to the Redlich-Kwong is $z = 0.993$ at 20 °C and $z = 0.995$ at 40 °C.

The difference between state quantities calculated according to the equation of state for an ideal gas and state quantities calculated according to the Redlich-Kwong and Van der Waals equations is approximately 0.5 %. As expected, the higher the pressure, the higher the deviation will be (Figs. 2–5).

Calculated data (for pressure 100–1000 kPa) was statistically evaluated. Tab. II shows basic results of the exploratory data analysis. The standard deviation of all calculated data reached very small values. The variable coefficient reached the maximum value of 1.7 %. The Shapiro-Wilk test was used to assess the normality of particular data files and the *p*-value ranged in the interval of 0.891–0.898. It follows that at the significance level of $\alpha = 0.01$, the distribution of the calculated values is in all cases normal.

Figs. 6 and 7 show box plots, from which we can clearly see that there was no remote or extreme values in assessed data. According to these figures, the calculated values of the compressibility factors for carbon dioxide at the temperature of 20 °C show the largest variability according to both the Redlich-Kwong and the Van der

I: *Basic physical properties of gases*

| Properties	Unit	CH$_4$	CO$_2$	References
T$_c$	K	190.9	304.13	CH$_4$ (Korsten, 1998), CO$_2$ (Janeček *et al.*, 2015)
p$_c$	MPa	4.501	7.3773	CH$_4$ (Korsten, 1998), CO$_2$ (Janeček *et al.*, 2015)
v$_c$	dm³·mol⁻¹	0.0986	0.0941	CH$_4$ (Janeček *et al.*, 2015), CO$_2$ (Janeček *et al.*, 2015)
ρ$_c$	mol·dm⁻³	10.1390	10.6247	CH$_4$ (Janeček *et al.*, 2015), CO$_2$ (Janeček *et al.*, 2015)
T$_v$	K	111.66	194.674	CH$_4$ (Vohlídal *et al.*, 1999), CO$_2$ (Vohlídal *et al.*, 1999)
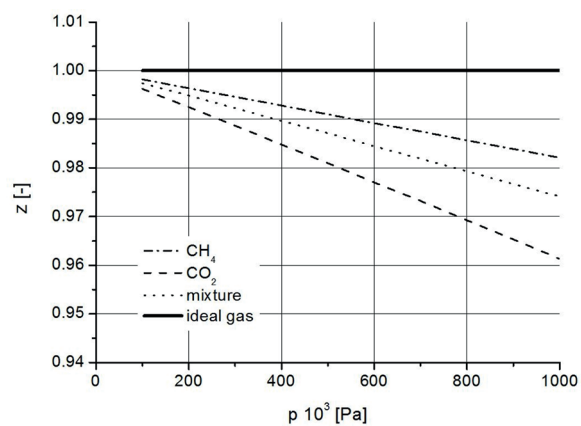
2: *The dependence of the compressibility factor z on pressure at 20 °C (Van der Waals)*
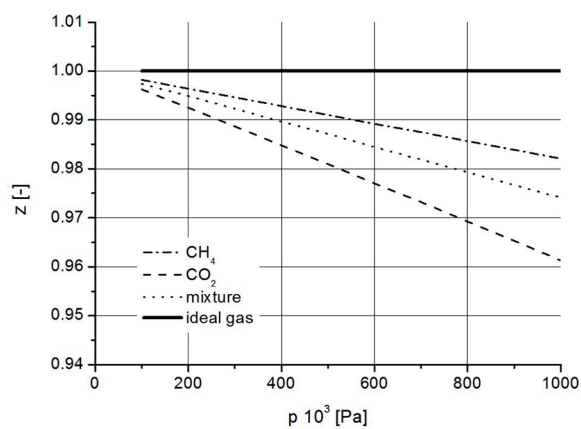
3: *The dependence of the compressibility factor z on pressure at 40 °C (Van der Waals)*
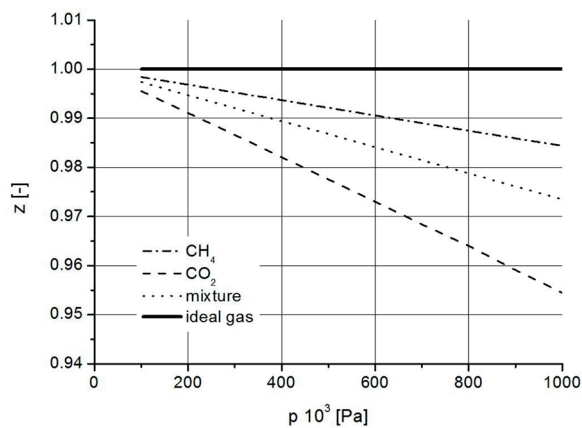
4: *The dependence of the compressibility factor z on pressure at 20 °C (Redlich-Kwong)*
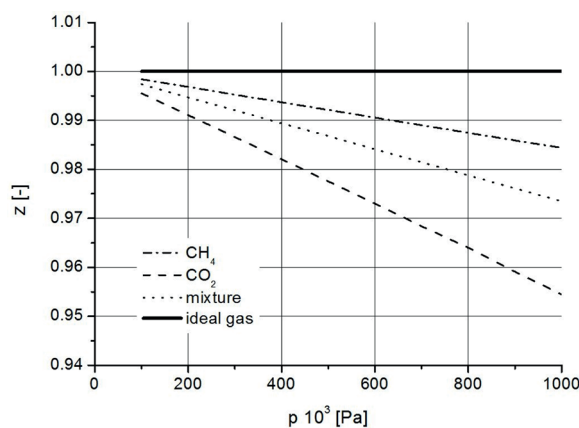
5: *The dependence of the compressibility factor z on pressure at 40 °C (Redlich-Kwong)*

II: *Exploratory data analysis*

Equat.	Temp.	Gas	Median	SD	S-W test p-value	Skewness	Kurtosis
Redlich-Kwong	20 °C	Mixture	0.982	0.00996	0.891	−0.012	−1.20374
		CO_2	0.970	0.0169	0.891	−0.028	−1.19976
		CH_4	0.989	0.00598	0.893	0.004	−1.19909
	40 °C	Mixture	0.985	0.00804	0.892	0.0002	−1.20205
		CO_2	0.975	0.01380	0.898	−0.025	−1.18654
		CH_4	0.991	0.00472	0.892	0.0109	−1.20029
Van der Waals	20 °C	Mixture	0.983	0.00940	0.898	−0.0196	−1.18986
		CO_2	0.975	0.01391	0.895	−0.035	−1.19269
		CH_4	0.988	0.00658	0.897	−0.014	−1.19322
	40 °C	Mixture	0.986	0.00785	0.887	−0.009	−1.20787
		CO_2	0.979	0.01176	0.890	−0.024	−1.20176
		CH_4	0.990	0.00541	0.893	0.003	−1.20027

Waals equations. On the contrary, the values of the calculated compressibility factor for methane show the smallest variability of the data. This results is also evident from Figs. 2–5.

Subsequently, an analysis of variance was performed. The analysis of variance focused on the comparison of the data calculated according to the Redlich-Kwong and the Van der Waals equations. For this purpose, it was investigated whether there is a statistically significant difference between the calculated data according to the Redlich-Kwong and Van der Waals equations for the pressures ranged from 100 kPa to 1000 kPa. For this reason, the Von Neumann test of data dependence was performed first. The values of Von Neumann testing criteria were in all cases more than 15. For this reason, the hypothesis about the independence of elements was denied at the level of significance $\alpha = 0.01$. The Levene's and the Brown-Forsyth tests were used afterwards for the homogeneity of variance. As we can see in Tab. III, the p-value is in both cases close to 0. It follows that the data files show heteroscedasticity at the level of significance of $\alpha = 0.01$.

Based on the information obtained from the survey analysis of the data, it was decided to use the Wilcoxon test to compare two dependent variables. Tab. III shows the p-values of the Wilcoxon test. Based on the values, we can see that at the significance level $\alpha = 0.01$, there is a statistically significant difference between the data calculated according to the Redlich-Kwong and Van der Waals for pressure ranged from 100 kPa to 1000 kPa.

Finally, the regression analysis was used to evaluate the dependence of the compressibility factor on pressure. For this analysis data for mixtures (biogas) at 20 °C and 40 °C was used. Tab. IV shows proposed regression models determining the dependence of the compressibility factor and the pressure at mixtures for the temperatures of 20 °C and 40 °C. The Shapiro-Wilk test was used to assess the normality of residues. It is clear from the table that all the residues showed a normal distribution. The evaluation of autocorrelation came negative only for the proposed regression model for a temperature of 40 °C calculated from the data according to the Redlich – Kwong equation. Other proposed regression models can be considered valid.
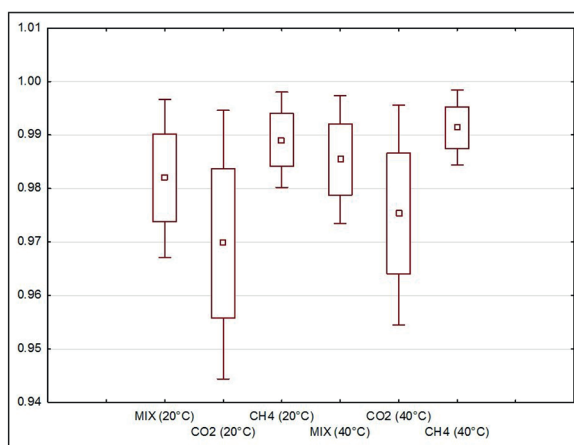
6: *Box-plot of calculated values by Redlich-Kwong*
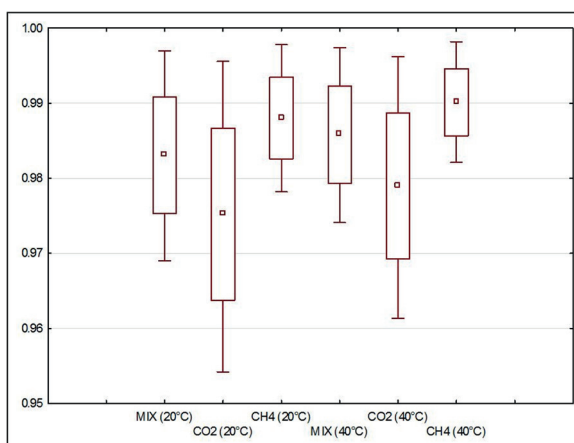
7: *Box-plot of calculated values by Van der Waals*

III: *The test results of the homogeneity of variance and the comparison of two dependent variables*

Test type	*p*-value
Levene's	0.0000
Brown-Forsyth	0.0000
Wilcoxon (20 °C)	0.0051
Wilcoxon (40 °C)	0.0077

IV: *The results of the regression analysis*

Equat.	Temp.	Proposed regression model	Pearson coefficient *r*	Normality of residues *p*-value (S-W test)	Durbin Watson *d*	Autocorrelation of the residues
Redlich-Kwong	20 °C	$y = 1.0001 - 3.2891 \cdot 10^{-5}x$	0.999	0.19	1.496	NO
	40 °C	$y = 1 - 2.6557 \cdot 10^{-5}x$	0.999	0.897	3.302	YES
Van der Waals	20 °C	$y = 1.0002 - 3.1048 \cdot 10^{-5}x$	0.999	0.21	0.681	NO
	40 °C	$y = 1.0001 - 2.593 \cdot 10^{-5}x$	0.999	0.532	1.535	NO

CONCLUSION

The calculations of the compressibility factors according to the Redlich-Kwong and Van der Waals equations showed that the deviation from an ideal gas, as expected at low pressures and at monitored temperatures, is around 0.5 %. In case of higher pressures, the deviation increases and so does the difference between the values calculated by the Redlich-Kwong and Van der Waals equations. In case of the calculation of state properties of biogas stored in low pressure gas holders, it is possible to use also the basic equation of state. It is more suitable to use the more accurate Redlich-Kwong equation for higher pressures. The dependence of the compressibility factor on pressure was described by the regression model. All the proposed regression models had a high value of the determination coefficient.

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