

Simulation of condensation in biogas containing ammonia

Lars Erik Øi¹ Terje Bråthen¹ Jon Hovland²

¹Department of and Process, Energy and Environmental Technology, University of South-Eastern Norway

²SINTEF Tel-Tek, SINTEF Industry, Porsgrunn, Norway

lars.oi@usn.no

Abstract

Condensation in raw biogas during compression is a problem because the CO₂ and water in the liquid phase is very corrosive. Raw biogas typically contains 60 mol-% methane, 40 mol-% CO₂, is saturated with water and may contain contaminants as ammonia (NH₃). In case of NH₃, it is of interest whether it has influence on the dew point (condensation) temperature. The aim of this work is to calculate the dew point under different conditions using different equilibrium models. Phase envelopes showing the two-phase area are also calculated. For dry mixtures of methane and CO₂ with up to 1 mol-% NH₃ (a high value for biogas), the different models gave similar results. When the NH₃ increased from 0 to 1 mol-%, the dew point temperature increased with approximately 3 K. When water was included, the amount of calculated NH₃ dissolved in water varied considerably with the model. The electrolyte based models Sour PR, Sour SRK and Electrolyte NRTL did not calculate reasonable dew point temperatures, but the dissolved amounts of NH₃ and CO₂ were more reasonable using the electrolyte models compared to using PR or SRK. For biogas simulation including NH₃, a simple equation of state as PR or SRK can be recommended to determine the dew point. If accurate composition of the condensed liquid is to be calculated, an electrolyte based model like Sour PR, Sour SRK or the Electrolyte NRTL is recommended.

Keywords: CO₂, methane, water, biogas, phase envelope, Aspen HYSYS, Aspen Plus

1 Introduction

Condensation in biogas containing water is a challenge because the CO₂ and water in the liquid phase is very corrosive. Raw biogas typically contains 60 mol-% methane, 40 mol-% CO₂, is saturated with water and may contain contaminants as H₂S and NH₃. Under compression up to 300 bar, it is a question whether condensation will occur. NH₃ is very soluble in water, and the solubility increases in the presence of CO₂

because the liquid becomes acidic. When the biogas contains NH₃, it is of interest whether it has influence on the dew point temperature. It is also of interest how much CO₂ and NH₃ will condense in the liquid phase.

This work is a continuation of the work from Øi and Hovland (2018), Bråthen et al. (2019) and Bråthen et al. (2020) which did not consider NH₃.

Traditionally, gas mixture properties of methane, CO₂ and water are calculated in a process simulation program with standard models like PR (Peng and Robinson, 1976) and SRK (Soave, 1972). There is traditionally only one constant binary parameter for each component pair, but in the process simulation tools Aspen HYSYS and Aspen Plus, the binary parameter for e.g. water/CO₂ can be made temperature dependent. Other models including electrolyte models are also available in Aspen HYSYS and Aspen Plus. Properties of mixtures of the biogas components have been studied extensively in natural gas processing where the methane concentration is very high (Kunz and Wagner, 2012). The same components have also been studied in the development of CO₂ injection into different hydrocarbon reservoirs (Ziabakhsh-Ganji and Kooi, 2012). There have been found few articles about process simulation of biogas (Tan et al., 2017; Pellegrini et al., 2015; Ahmad et al., 2018). The articles Nabgan et al. (2016) and Sotof et al. (2015) are about simulation of ammonia stripping in biogas production reactors and processes.

When using fitted binary parameters (k_{ij} parameters) these models simulate the gas phase and the condensation point reasonably accurately (within a few degrees) at least below the critical point which is 46 bar for methane and 74 bar for CO₂ (Øi and Hovland 2018; Bråthen et al., 2019; Bråthen et al., 2020).

Studies of models for vapour/liquid equilibrium in the methane/CO₂/water-system have been performed by Jarne (2004), Austegard et al. (2006), Privat and Jaubert (2014), Al Ghafri et al. (2014), Legoix et al. (2017) and Bråthen et al. (2019). Austegard et al. (2006) concluded that a simple equation of state like SRK is satisfactory to describe the vapour phase, but more complex models are necessary to describe the liquid phase.

Several authors have studied models for the system CO₂/water (Spycher et al., 2003; Longhi, 2005; Aasen et al., 2017). Bråthen et al. (2019; 2020) concluded that

PR and SRK with a standard k_{ij} value were able to simulate this system satisfactory, at least for the vapour phase up to the critical point (40-70 bar).

There are much available literature on data, thermodynamics and simulation of mixtures of NH_3 . Neumann et al. (2020) present an equation of state for many components. It is based on a Helmholtz energy model similar to the Gerg-2008 model (Kuntz and Wagner, 2012) which is a standard model in natural gas simulation.

The $\text{NH}_3/\text{CO}_2/\text{water}/\text{system}$ is extensively studied (Ayers, 1985; Kurz et al., 1995; Jilvero et al., 2015). Gudjonsdottir et al. (2016) discuss models also including solid formation of different salts from concentrated solutions of NH_3 and CO_2 in water. This is typical conditions for ammonia based processes for CO_2 capture.

In this work, the emphasis is on the standard PR and SRK methods available in the process simulation programs Aspen HYSYS and Aspen Plus. In the case of calculation of the liquid composition after condensation, the electrolyte based models Sour PR, Sour SRK and Electrolyte-NRTL are evaluated.

The aim of this work is to calculate the dew point or condensation of biogas containing NH_3 under different conditions with varied temperature, pressure and gas composition and using different equilibrium models.

2 Simulation Programs and Models

2.1 Available models in Aspen HYSYS and Aspen Plus

Øi and Hovland (2018) and Bråthen et al. (2019) simulated dry biogas (CH_4 and CO_2) and mixtures also containing water using the process simulation programs Aspen HYSYS and Aspen Plus. The equilibrium models SRK (Soave, 1972), PR (Peng and Robinson, 1976) and also other models were used.

The reason why the simple models PR and SRK are selected, is that the models and fitted binary parameters are usually available in different process simulation programs. Other commercial process simulation programs are ProMax, ChemCad and ProTreat.

In Aspen HYSYS and Aspen Plus the PR and SRK models have only one adjustable parameter for each binary component pair, but for some components, and especially water/ CO_2 and water/ H_2S , this parameter may be temperature dependent.

2.2 Description of the PR Equation of state

Equations for the SRK equation of state are shown in (1) to (8) from Aspen HYSYS Version 10. Aspen HYSYS and Aspen Plus Version 10 were used in the simulations. More details are discussed in Bråthen et al. (2019).

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

$$b = \sum_{i=1}^N x_i b_i \quad (2)$$

$$b_i = \frac{0,08664RT_c}{p_c} \quad (3)$$

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j (a_i a_j)^{0,5} (1 - k_{ij}) \quad (4)$$

$$a_i = a_{ci} \alpha_i \quad (5)$$

$$a_{ci} = \frac{0,42748R^2 T_c^2}{p_c} \quad (6)$$

$$\alpha_i = \left[1 + m_i \left(1 - T_r^{1/2} \right) \right]^2 \quad (7)$$

$$m_i = 0,48 + 1,574\omega_i - 0,176\omega_i^2 \quad (8)$$

P, T, v and R are the pressure, temperature, molar volume and the universal gas constant. T_c is the critical temperature, ω is the acentric factor and T_r is the reduced temperature (the ratio between T and T_c). The binary interaction parameter k_{ij} ($= k_{ji}$) is a constant for a binary component pair and x_i is the mole fraction for component i. In the PR equation, equation 1, 3, 6 and 8 are replaced by equation 9, 10, 11 and 12.

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (9)$$

$$b_i = \frac{0,077796RT_c}{p_c} \quad (10)$$

$$a_{ci} = \frac{0,457235R^2 T_c^2}{p_c} \quad (11)$$

$$m_i = 0,37464 + 1,54226\omega_i - 0,26992\omega_i^2 \quad (12)$$

2.3 Recommended Binary Parameters

The binary parameter k_{ij} is normally a constant for each binary pair. When utilizing the default k_{ij} values in Aspen HYSYS and Aspen Plus, the k_{ij} values are constant for all component pairs except for water/ CO_2 and water/ H_2S where it is a temperature dependent function. Different optimized values for the k_{ij} values can be found because the parameters may be optimized for different conditions, e.g. for accurate prediction of either the gas phase or the condensate phase. For the calculation of dew points, it is reasonable to use binary interaction coefficients optimized for the gas phase (Bråthen et al., 2019).

The PR and SRK versions used in Aspen Plus are equal to the Aspen HYSYS versions shown in (1) to (12), except that some of the numerical values are slightly different. Especially the coefficients in the m_i expressions (8) and (12) are slightly different.

The parameters in (1) to (12) may be slightly different in different process simulation programs. The alfa (α_i) parameter in equation (7) is calculated

differently in the PR-Twu and SRK-Twu models (Twu et al., 1991).

A k_{ij} value for water/ CO_2 close to 0.19 is suggested by Ziabakhsh-Ganji and Kooi (2012), Li et al. (2014) and Bråthen et al. (2019). Some recommends different k_{ij} values dependent on emphasis on the vapour or liquid phase (Austegard et al., 2006).

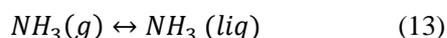
The standard k_{ij} value in Aspen HYSYS and Aspen Plus for water/ NH_3 is -0.253 for PR and -0.273 for SRK. Skogestad (1980) states that the value -0.28 for SRK gives a good fit to experimental data.

2.4 Electrolyte models in Aspen HYSYS and Aspen Plus

Traditional equations of state are not taking ions in solution into account. Aspen HYSYS and Aspen Plus have two models Sour PR and Sour SRK which are based on electrolyte calculations. The Sour PR model is using PR for the gas phase and a Wilson equation (API, 1980) for the liquid phase. It is developed for stripping components like CO_2 , H_2S and NH_3 from water in hydrocarbon processing. More complex models are also available. In Aspen Plus, the Electrolyte NRTL model is available. The standard Electrolyte NRTL in Aspen Plus use the Redlich Kwong equation of state for the vapour phase. Que and Chen (2011) have combined Electrolyte NRTL in Aspen Plus with the SAFT model for the vapour phase. Gudjonsdottir et al. (2016) compare different models including the extended UNIQUAC equation and is also including solid salt simulation and non-ideality in the liquid phase.

The most important equations in electrolytic calculations of the CO_2 /carbonate and NH_3 /ammonium systems are based on the solubility of the gases in water and on the ion equilibriums of the ionization step for NH_3 and two ionization steps for CO_2 . The equations (15 to 24) are from Øi (2012) with equations for solubility and ionization of NH_3 included. These are similar to equations found in API (1980) and Gudjonsdottir et al. (2016). One challenge with these models in a process simulation tool is that the electrolyte models normally use concentrations in e.g. (mol/liter) while process simulation tools like Aspen HYSYS and Aspen Plus use calculations based on mole fractions.

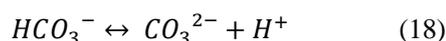
Equation (13) and (14) shows solubility and ionization of NH_3 . The “g” and “liq” in equation (13) and (15) indicate the gas and liquid phase. All the other equations are indicating concentrations in the liquid phase.



In the liquid phase, CO_2 reacts with hydroxide to bicarbonate according to Equation (16).



The fast proton transfer reactions (17 and 18) also occur. Equation (17) is the water self-ionization reaction and (18) describes the deprotonation of the bicarbonate ion to carbonate ion:



The reactions in Equations (13 to 18) can be described with equilibrium constants. The equilibrium in Equations (13 and 15) is normally described by a temperature dependent Henry's constant which connects the partial pressure of the CO_2 in the gas with the concentration of CO_2 in the liquid.

$$p_{\text{CO}_2} = H_{e\text{CO}_2} \cdot C_{\text{CO}_2} \quad (19)$$

$$p_{\text{NH}_3} = H_{e\text{NH}_3} \cdot C_{\text{NH}_3} \quad (20)$$

Equations (21 to 24) represent the equilibrium constants for the reactions in Equations (14) and (16 to 18).

$$K_{14} = \frac{C_{\text{NH}_4^+} \cdot C_{\text{H}^+}}{C_{\text{NH}_3} \cdot C_{\text{H}_2\text{O}}} \quad (21)$$

$$K_{16} = \frac{C_{\text{HCO}_3^-}}{C_{\text{CO}_2} \cdot C_{\text{OH}^-}} \quad (22)$$

$$K_{17} = \frac{C_{\text{H}^+} \cdot C_{\text{OH}^-}}{C_{\text{H}_2\text{O}}} \quad (23)$$

$$K_{18} = \frac{C_{\text{CO}_3^{2-}} \cdot C_{\text{H}^+}}{C_{\text{HCO}_3^-}} \quad (24)$$

In addition an equation for the charge balance is needed, e.g. by setting the sum of concentrations for the negative ions equal to the sum of concentrations for positive ions. To solve this equation set, component material balances for the total of nitrogen containing components and for the total of carbon containing components can be included. This is traditional if only the liquid phase is simulated.

If the gas composition, pressure and the temperature dependent equilibrium constants are known, this equation set can be used to calculate the dew point temperature and all the liquid concentrations including the ion concentrations.

3 Process Description and Simulation Specifications

3.1 Process description of raw biogas compression

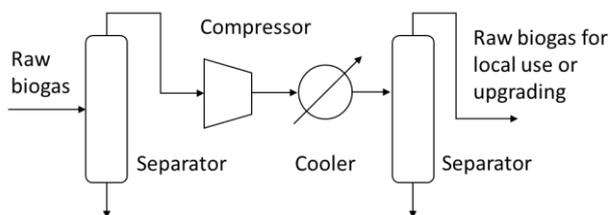


Figure 1. A raw biogas compression process

The principle for a traditional raw biogas compression process is shown in Figure 1. The compression can be up to 300 bar.

The actual process is discussed in more detail in Hovland (2017), Øi and Hovland (2018) and Bråthen et al. (2019). Bråthen et al. (2020) used the same approach for dew point calculations of biogas mixtures containing H_2S .

In Øi and Hovland (2018), Bråthen et al. (2019; 2020) it is stated that condensation during compression is a problem that should be avoided.

3.2 Simulation specifications

In earlier work, process simulations have been performed for different conditions relevant for biogas production as in Øi and Hovland (2018) and Bråthen et al. (2019; 2020). The models PR, SRK, PRSV (Stryjek-Vera, 1986), TST, PR-Twu and SRK-Twu were used. The default parameters (especially the k_{ij} for water/ CO_2) were used. Phase envelopes showing the dew and bubble point curve for a temperature and pressure range have been calculated. In the dry gas cases, the HYSYS 2-phase option was selected for phase envelope calculations. In the cases including water and NH_3 , the ComThermo 3-phase option was selected.

Calculations have been performed with both Aspen HYSYS and Aspen Plus. In Aspen Plus the Peng-Robinson and RKSoave models were selected. The B and D cases are referring to Øi and Hovland (2018) and simulated in Bråthen et al. (2019; 2020).

In earlier simulations (Case B) dry biogas with 40 mol-% methane and 60 mol-% CO_2 starts at 37 °C and 1 bar, is cooled to 10 °C and is compressed to 64 bar. In this work, 1 mol-% NH_3 is added, and the mol-% methane is reduced to 39.

In earlier simulations (Case D), 59.9 kmol/h methane, 40 kmol/h CO_2 and 0.1 kmol/h water is mixed at 37 °C and 1 bar, cooled to 10 °C, and then compressed to 64 bar. In this work, 1 mol-% NH_3 is added, and the mol-% methane is reduced to 58.9.

4 Process Simulation, Results and Discussion

4.1 Simulation of dry methane/ CO_2 mixture including H_2S/NH_3 (Case B)

An Aspen HYSYS flow-sheet model of the process for the base case simulation is presented in Figure 2.

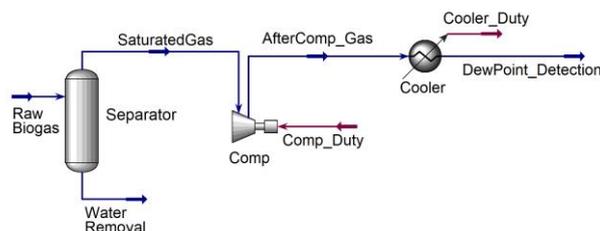


Figure 2. Aspen HYSYS flow-sheet for compression and cooling

In earlier calculations, Case B was of interest because a 40 % methane and 60 % CO_2 has a dew point close to 0 °C. Earlier evaluations from Øi and Hovland (2018) and Bråthen et al. (2019) have shown that below 60 mol-% CO_2 , no condensation should appear if the temperature is kept above -3 °C.

Table 1. Dew point at 64 bar, cricondenterm and cricondenbar for a mixture of 39 mol-% methane, 60 mol-% CO_2 and 1 mol-% NH_3 (Case B)

Model	T_{DEW}	T_{CRIC} (°C)	P_{CRIC} (bar)
PR Hysys	-2.8	1.0	91.0
SRK Hysys	-2.7	1.3	89.8
TST Hysys	1.6	2.0	83.9
PR-Twu Hysys	-3.7	0.1	91.6
SRK-Twu Hysys	-3.2	0.8	92.2
Sour PR Hysys	-2.8	1.0	91.0
Sour SRK Hysys	-2.7	1.4	90.0
PR Aspen Plus	-2.9	-0.9	90.0
SRK Aspen Plus	-1.2	-0.9	89.9

The results in Table 1 are similar to the results from Øi and Hovland (2018) and Bråthen et al. (2019), and also similar to the results with 1 % H_2S (Bråthen et al., 2020). The results in Aspen HYSYS and Aspen Plus are not identical due to slightly different model parameters. The dew points are typically 2-4 K less than the calculations for mixtures without NH_3 . These deviations are in the same order of magnitude compared to the deviation in calculated dew point between different models used. The dew point change was slightly higher when adding NH_3 compared to the change when H_2S was added (Bråthen et al., 2020).

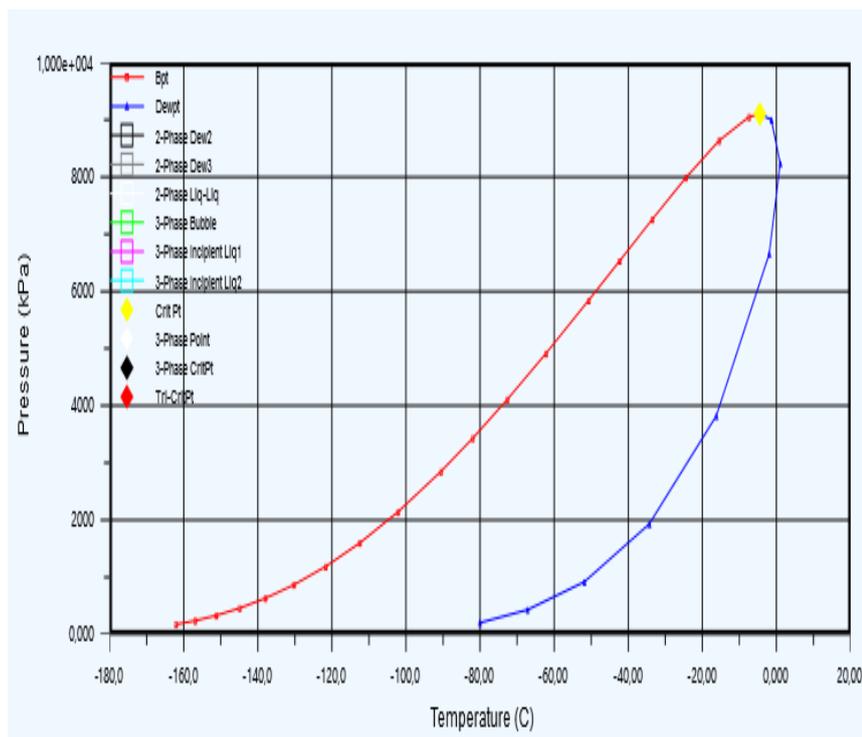


Figure 3. Phase envelope, Peng-Robinson, $\text{CH}_4=0.39$, $\text{CO}_2=0.6$, $\text{NH}_3=0.01$. PR with default k_{ij} values.

Also when NH_3 is included, the calculated cricondenters with different models have a deviation of typically 2-4 K. It is concluded that the results can be expected to be fairly accurate for all the models evaluated. Even with 1 mol-% NH_3 , very little condensation will appear above 0°C in a dry biogas with more than 40 mole-% CH_4 . This was also the conclusion without H_2S from Hovland (2017), Øi and Hovland (2018) and Bråthen et al. (2019; 2020).

The phase envelope from Aspen HYSYS is shown in Figure 3. The dew point curve is to the right. The point with the highest temperature is the cricondenterm. The point with the highest pressure is the cricondenbar. In the critical point for the mixture, the compositions in both phases are equal.

The phase envelope in Figure 3 is very close to the phase envelope in Bråthen et al. (2019) which was calculated without NH_3 . But the cricondenterm is 3 K higher. This is the same comparison as the comparison in Table 1 which was also compared with simulations without NH_3 . The deviation in temperature seems to be less than 4 K. According to Figure 3, there should not occur any condensation (two-phase) between 90 and 300 bar.

These simulations indicate that the calculated dew points and phase envelopes for dry biogas including up to 1 mol-% NH_3 are reasonably accurate for all the models tested.

4.2 Simulation of compression of a raw biogas including water and NH_3 , Case D

The process (Case D) was simulated with water and NH_3 included. The simulations are similar to the simulations in Bråthen et al. (2019; 2020) and in this work 1 mol-% NH_3 is added, and the mole fraction of methane is reduced correspondingly. The results are shown in Table 2.

Table 2. Dew point at 64 bar, cricondenterm and pressure at cricondenterm for 58.9 mol% CH_4 , 40 mol% CO_2 , 1 mol% NH_3 , 0.1 mol% water, Case D

Model	T_{DEW} ($^\circ\text{C}$)	T_{CRIC} ($^\circ\text{C}$)	P_{CRIC} (bar)
PR	30.4	-18.6	86.3
SRK	31.1	-19.5	85.5
PRSV	30.9	-19.7	85.9
PRTwu	21.4	-22.1	86.1
SRKTwu	22.5	-18.9	86.8

Compared to the dew point temperatures without NH_3 (Bråthen et al., 2019), the dew point was 4-6 K higher. The deviation between the models were small. The TST model was also tried (as in earlier work), but the deviation in dew point temperature was considerable compared with the other models (about 10 K). The dew point temperatures in Table 2 were also calculated in Aspen Plus with PR and SRK and that gave as expected similar results.

The calculated cricondenterm values in Table 2 are very much lower than the values in Bråthen et al. (2019) but similar to the values calculated by Bråthen et al. (2020). The reason for the difference is probably because the values in Aspen HYSYS Version 10.0 and later are calculated without taking water into account. This is a problem also when calculating a phase envelope as in Figure 4. The phase envelope in the figure is without NH₃.

The dew point temperature was also calculated with the electrolyte models Sour PR and Sour SRK (in Aspen HYSYS) and with the Electrolyte NRTL model (Electro-NRTL in Aspen Plus). When using the Sour PR model, the dew point was calculated to 37.7 °C without NH₃, and it gave unreasonable values for gas streams with NH₃. When the Electrolyte NRTL model was used, the dew point temperature increased slightly from 51.4 °C without NH₃ to 53.0 °C with 1 mol-% NH₃. This indicates that the simple PR and SRK models give more accurate dew point temperatures than the electrolyte based models, at least for low NH₃ content.

The challenge with combining an electrolyte model with a gas phase model is well known. In the Aspen HYSYS user guide, it is stated that the flash calculation for Sour PR is much slower than the standard EOS because the method performs an ion balance for each calculation of the electrolyte model. Que and Chen (2011) have combined Electrolyte NRTL in Aspen Plus with the SAFT model for the vapour phase.

4.3. Calculation of dew point and liquid composition at different NH₃ levels in gas

In Table 3, the calculated liquid composition is shown for different NH₃ compositions for the traditional PR equation and for the electrolyte Sour PR model.

Table 3. Dew point at 64 bar and liquid composition for different NH₃ concentrations in gas and for the PR and Sour PR models of 59.9 mol% CH₄, 40 mol% CO₂, 0.1 mol% water, Case D

Model	y _{NH₃=0}	0.01%	0.1%	1%
T _{DEW} (PR)	26.5	26.8	27.3	30.4
x _{CO₂} (PR)	0.009	0.0085	0.0086	0.0092
x _{NH₃} (PR)	0	0.0032	0.027	0.14
T _{DEW} (SOUR PR)	37.7	-3.51	-1.60	-19.5*
x _{CO₂} (SOUR PR)	0.009	0.108	0.266	0.7709*
x _{NH₃} (SOUR PR)	0	0.0848	0.263	0.0791*

As commented in the previous subsection, the Sour PR model calculates unreasonable dew points (which decrease with increasing NH₃ amount) for these conditions, even without NH₃. The PR model calculates a slight increase in dewpoint, which is reasonable.

The PR equation calculates too low solubilities of CO₂ and NH₃ in the liquid. This is expected because PR and SRK are not electrolyte based models. Non-electrolyte models calculate the dissolved NH₃ and CO₂ only based on equation (19 and 20).

Because NH₃ makes the water phase less acidic, the CO₂ concentration is expected to increase when the NH₃ concentration increases. This is the case for the electrolyte model Sour PR. It is also seen that the amount of CO₂ and NH₃ is about equal for the case of 0.01 % and 0.1 % NH₃. This is reasonable because that gives a close to neutral water solution. Equation (21) shows that the ratio between the NH₄⁺ and NH₃ concentrations increases when the H⁺ concentration (or pH) increases. Equation (22) shows that the ratio between the HCO₃⁻ and CO₂ concentrations increases when the OH⁻ concentration increases.

For the case of 1 % NH₃ in the gas, the concentrations of CO₂ and NH₃ become very large, and this is probably outside the reasonable range for the Sour PR model. Similar calculations have also been performed using the Electrolyte NRTL model. That gave more CO₂ and less NH₃ in the solution compared to the Sour PR model. For NH₃ values typically for biogas which are lower than 0.1 %, the calculated liquid compositions using the Sour PR model are reasonable.

4.4. Phase envelope calculations

The phase envelope for PR with $k_{ij}=0.19$ from Table 2 is shown in Figure 4. The phase envelope in Figure 4 is from Bråthen et al. (2019) without NH₃. Based on the results in Table 2, the dew point line to the right in the figure will deviate (increase) with order of magnitude 3 K. For reasonable NH₃ levels in biogas below 0.1 mol-%, the deviation compared to the phase envelope is expected to be less than 1 K. For pressures above the critical point (about 90 bar), the dewpoint is expected to decrease slightly according to Figure 4.

As stated in earlier work, it is expected that the uncertainty in dew point calculations increases when the pressure increases and the mixture is close to the critical point which is about 70 bar (Øi and Hovland, 2018; Bråthen et al., 2019).

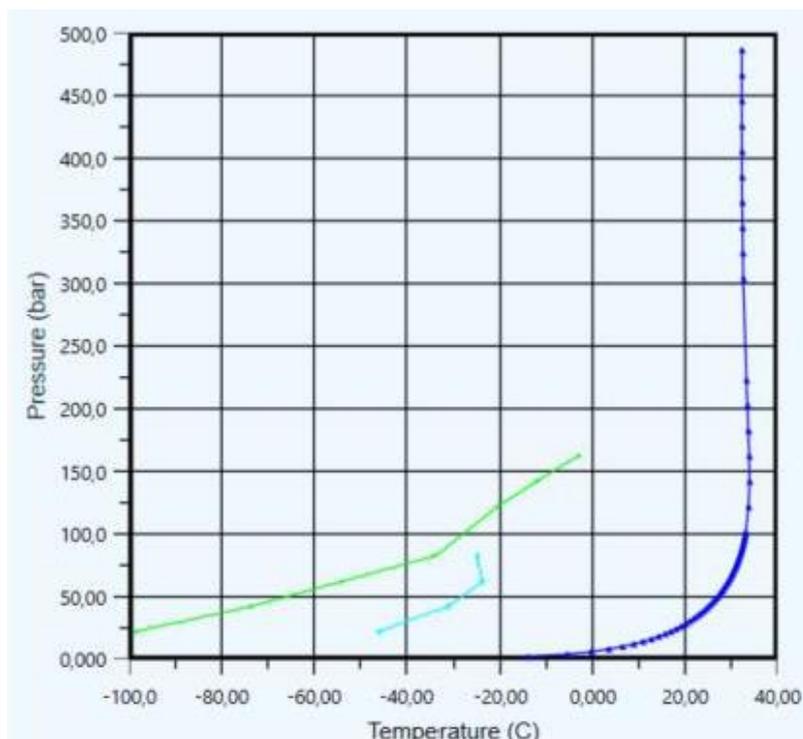


Figure 4. Phase envelope for PR model, 59,9 mol% CH₄, 40 mol% CO₂, 0.1 mol% water: $k_{ij}=0.19$ for water/CO₂ (Bråthen et al., 2019)

5 Conclusion

Specified mixtures of raw biogas with and without water have been simulated at different temperatures and pressures. The effect of adding up to 1 mol-% NH₃ to the mixtures have been evaluated. For some conditions, phase envelopes have been calculated and different models have been compared.

For mixtures of methane and CO₂ with up to 1 mol-% NH₃ (a high value for biogas), the different models gave similar results. Under normal ambient temperatures (above 0 °C), a mixture with more than 40 mol-% methane will not give any condensation. When the NH₃ increased from 0 to 1 mol-%, the dew point temperature increased with 3.0 K. A phase envelope for biogas with 1 mol-% NH₃ is only slightly different from an earlier calculated phase envelope for biogas without NH₃.

When raw biogas is cooled or compressed, water will condense first. NH₃ will dissolve in the water, and the amount of calculated NH₃ dissolved in water varied significantly with the model.

For biogas simulation including NH₃, a simple equation of state as PR or SRK can be recommended to determine the dew point. If accurate composition of the condensed liquid is to be calculated, an electrolyte based model like Sour PR or Electrolyte NRTL is recommended.

References

- A. Aasen, M. Hammer, G. Skaugen, J. P. Jakobsen and Ø. Wilhelmsen. Thermodynamic models to accurately describe the PVTxy-behaviour of water/carbon dioxide mixtures, *Fluid Phase Equilibria*, 442:125-139, 2017.
- N. E. Ahmad, M. Mel and N. Sinaga. Design of Liquefaction Process of Biogas using Aspen HYSYS Simulation. *Journal of Advanced Research in Biofuel and Bioenergy*, 2:10-15, 2018.
- API (American Petroleum Institute). A New Correlation of NH₃, CO₂ and H₂S Volatility Data from Aqueous Sour Water Systems. EPA report 600/2-80-067, 1980.
- S. Z. S. Al Ghafri, E. Forte, G. C. Maitland, J.J. Rodriguez-Henriquez and J. P. M. Trusler. Experimental and Modeling Study of the Phase Behaviour of (Methane + CO₂ + Water) Mixtures. *Journal of Physical Chemistry*, 118:14462-14478, 2014.
- G. P. Ayers. Solubility of ammonia in water in the presence of atmospheric CO₂. *Tellus*, 37B:35-40, 1985.
- A. Austegard, E. Solbraa, G. de Koeijer and M. J. Mølnvik. Thermodynamic models for calculating mutual solubilities in H₂O-CO₂-CH₄ mixtures. *Trans IChemE, Part A, Chem. Eng. Res. Des.*, 84(A9):781-7946, 2006.
- T. Bråthen, L. E. Øi and J. Hovland. *Simulation of Dew Points in Raw Biogas Using PR and SRK Equations of State*. In Linköping Electronic Conference Proceedings SIMS 60, pp. 31-36, 2019. doi: 10.3384/ecp20170112.
- T. Bråthen, L. E. Øi and J. Hovland. *Simulation of condensation in Raw Biogas containing H₂S*. In Linköping Electronic Conference Proceedings SIMS 61, pp. 300-305, 2020. doi.org/10.3384/ecp20176300.

- V. Gudjonsdottir and C. I. Ferreira. Comparison of Models for Calculation of the Thermodynamic Properties of $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ Mixture. *International Refrigeration and Air Conditioning Conference*. Paper 1641 (2016).
- J. Hovland. *Compression of raw biogas – A feasibility study*. Tel-Tek report 2217020-1, 2017. Available on <https://www.biogas2020.se/wp-content/uploads/2017/06/2217020-1compressionrawbiogas.pdf>
- C. Jarne, S. T. Blanco, M. A. Gallardo, E. Rauzi, S. Otin and I. Valesco. Dew Points of Ternary Methane (or Ethane) + Carbon Dioxide + Water Mixtures: Measurements and Correlation. *Energy & Fuels*, 18:396-404, 2004.
- H. Jilvero, K. J. Jens, F. Normann, K. Andersson, M. Halstensen, D. Eimer and F. Johnsson. Equilibrium measurements of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system – measurements and evaluation of vapor-liquid equilibrium data at low temperatures. *Fluid Phase Equilibria*, 385:237-247, 2015.
- O. Kunz and W. Wagner. The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004. *J. Chem. Eng. Data*, 57:3032-3091, 2012.
- F. Kurz, B. Rumpf and G. Maurer. Vapor-liquid-solid equilibria in the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ from around 310 to 470 K: New experimental data and modeling. *Fluid Phase Equilibria*, 104:261-275, 1995.
- L. N. Legoix, L. Ruffine, J. P. Donval and M. Haeckel. Phase Equilibria of the $\text{CH}_4\text{-CO}_2$ Binary and the $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ Ternary Mixtures in the Presence of a CO_2 -Rich Liquid Phase. *Energies*, 10(2034):1-11, 2017. Doi:10.3390/en10122034.
- J. Li, L. Wei and X. Li. Modeling of $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S}$ -brine based on cubic EOS and fugacity-activity approach and their comparisons. *Energy Procedia*, 63:3598-3607, 2014.
- J. Longhi. Phase equilibria in the system $\text{CO}_2\text{-H}_2\text{O}$ I: New equilibrium relations at low temperatures. *Geochimica et Cosmochimica Acta*, 69(3): 529-539, 2005.
- B. Nabgan, T.A.T. Abdullah, W. Nabgan, A. Ahmad, I. Saeh and K. Moghadamian. Process Simulation for Removing Impurities From Wastewater Using Sour Water 2-Strippers system via Aspen Hysys. *Chem. Prod. Process Model*, 11(4):315-321, 2016.
- T. Neumann, M. Tho, I. H. Bell, E. Lemmon and R. Span. Fundamental Thermodynamic Models for Mixtures Containing Ammonia. *Fluid Phase Equilibria*, 511:112496, 2020.
- D. Peng and D. B. Robinson. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, 15(1):59-646, 1976.
- L. Pellegrini. Biogas to liquefied biomethane via cryogenic upgrading technologies. *Renewable Energy*, 124:75-83, 2018.
- R. Privat and J. N. Jaubert, *Predicting the Phase Equilibria of Carbon Dioxide Containing Mixtures Involved in CCS Processes Using the PPR78 Model*. InTech, 2014. Available on <http://dx.doi.org/10.5772/57058>.
- H. Que and C.C. Chen. Thermodynamic Modeling of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system with Electrolyte NRTL Model. *Ind. Eng. Chem. Res.*, 50(19):11406-11421, 2011.
- S. Skogestad. Experience in Norsk Hydro with cubic equations of state. *Fluid Phase Equilibria*, 67:179-188 1983.
- G. Soave. Equilibrium constants from a modified Redlich Kwong equation of state. *Chemical Engineering Science*, 27:1197-1203, 1972.
- L F. Sotoft, M. B. Pryds, A. K. Nielsen and B. Norddahl. Process Simulation of Ammonia Recovery from Biogas Digestate by Air Stripping with Reduced Chemical Consumption, 37:2465-2470, 2015.
- N. Spycher, K. Pruess and J. Ennis-King. $\text{CO}_2\text{-H}_2\text{O}$ mixtures in the geological sequestration of CO_2 . I. Assessment and calculation of mutual solubilities from 12 to 100 °C and up to 600 bar. *Geochimica et Cosmochimica Acta*, 67 (16):3015-3031, 2003.
- R. Stryjek and J. H. Vera. PRSV – An Improved Peng-Robinson Equation of State with New Mixing Rules for Strongly Nonideal Mixtures. *The Canadian Journal of Chemical Engineering*, 64:334-340, 1986.
- Y. Tan, W. Nookuea, H. Li, E. Thorin and J. Yan. Cryogenic technology for biogas upgrading combined with carbon capture – a review of systems and property impacts. *Energy Procedia*, 142:3741-3746, 2017.
- C. H. Twu, D. Bluck, J. R. Cunningham and J. E. Coon. A Cubic Equation of State with a New Alpha Function and a New Mixing Rule. *Fluid Phase Equilibria*, 69:33-50, 1991.
- Z. Ziabakhsh-Ganji and H. Kooi. An Equation of State for thermodynamic equilibrium of gas mixtures and brines to allow simulation of the effects of impurities in subsurface CO_2 storage. *International Journal of Greenhouse Gas Control*, 11(Supplement):S21-S34, 2012.
- L. E. Øi and J. Hovland. *Simulation of Condensation in Compressed Raw Biogas Using Aspen HYSYS*. In Linköping Electronic Conference Proceedings SIMS 59, pp. 31-36, 2018. doi: 10.3384/ecp1815331.
- L. E. Øi. *Removal of CO_2 from exhaust gas*. PhD Thesis, Telemark University College, Porsgrunn. (TUC 3: 2012)