



GHGT-12

Thermal effects in a depleted gas field by cold CO₂ injection in the presence of methane

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Abstract

Depleted gas fields are seen as promising options for geological storage of CO₂. The advantage of hydrocarbon fields are that the characteristics, such as the storage capacity and the proven sealing capacity are known. This means that only limited uncertainty remains after a technical feasibility study. One important issue with depleted gas reservoirs is the low pressure, at the onset of injection. This may lead to adiabatic cooling (Joule-Thomson cooling or JTC). The temperature reduction associated with this JTC can lead to hydrate formation and freezing of the residual pore water, especially the injected fluid also has a low temperature. In a related paper, we report on the development of a simulator, which is capable of predicting the fate of transport of a CO₂ in either the liquid gaseous and supercritical phase. The model only contains CO₂ besides the aqueous phase. One of the remaining challenges is to predict the impact of the methane, which is still present in a depleted gas reservoir, on the phase behavior of CO₂ and the thermal aspects.

In this study simulations were performed on the P18-4 depleted gas field. The CO₂ was injected at a minimum temperature of 12 °C into the reservoir formation with a temperature of 120 °C. The average injection rate during the demonstration phase was modelled with 1.1 Mton/yr over a period of 5 year.

The injection of cold CO₂ into P18-4 was modelled in TOUGH2 and a new module, which can handle not only the behaviour of CO₂ but also of CH₄. The original ECO2M module was initially designed for CO₂ behaviour in gas reservoir and aquifers for brine-CO₂ mixtures, including all possible phase transitions, in the absence of any other gas. The new TOUGH2 module, which we gave the name ECO2MG module, was extended in such a way that compositional flow simulations of two different gases can be modelled, namely CO₂ and CH₄. The ECOMG module can not only model the behaviour brine CO₂ mixtures but also the behaviour of brine-CO₂-CH₄ mixtures including phase changes from gas to liquid and from super- and sub-critical conditions. Density, viscosity and enthalpy of the CO₂-CH₄ mixture is based on NIST data.

The new TOUGH2 module was used to model the thermal aspects of CO₂ injection including the presence of brine and CH₄ initially in the reservoir. The reservoir model was initialized with a brine-methane mixture at 20 bar, which is the expected abandonment pressure of the reservoir.

The prediction of thermal effects of this new tool were compared with those of the earlier version (CO₂ only) for several times during the projected 5 year injection period.

The thermal effects investigated in this study were the JTC and also the effect of evaporation of the aqueous phase. The heat of evaporation of the brine is very significant and cools down the near well area significantly depending on the initial water saturation and the injection temperature of the CO₂ itself.

In the new module we saw that after the CO₂ injection was started at first instance an uniform front of CO₂/CH₄ was formed. After a few years gravity override of the still gaseous CO₂ becomes visible, which became stronger after the phase transition to liquid CO₂. A free CH₄ phase moved during the simulation in front of the CO₂ plume.

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1. Introduction

Depleted gas fields are seen as a promising option for geological storage of CO₂. The advantage of hydrocarbon fields is that the characteristics, such as storage capacity and proven sealing capacity are known (e.g. Oldenburg et al 2001, Hughes, 2009), which is not the case for saline aquifers. Furthermore these reservoirs have existing gas production infrastructure which can possibly be converted for CO₂ injection. This results into a limited uncertainty after a technical feasibility study. An important issue with depleted gas reservoirs is the low pressure, at the onset of injection. This may lead to adiabatic cooling also known as the Joule-Thomson cooling (JTC).

The temperature reduction associated with JTC can lead to hydrate formation and freezing of the residual pore water, especially the injected CO₂ also has a temperature close to the average sea temperature [1,2]. A worst-case scenario is that the formation of hydrates or ice would impair the CO₂ injectivity. In most studies performed the JTC in and around the well was analyzed by reservoir simulations, or analytic methods, which only contained pure CO₂ beside the aqueous phase [2,3].

One of the remaining challenges was to predict the impact of the methane, which is still present in a depleted gas reservoir, on the phase behavior of CO₂ and the thermal aspects around the well. A candidate reservoir for CO₂ storage in the Netherlands is the P18 offshore gas field, which was investigated in the Dutch national CO₂ research program research program [4,5]. The P18 reservoir consists of three different compartments. P18-2, P18-4 and P18-6. The total storage capacity is 40Mton of CO₂. In the ROAD project (Dutch acronym for Rotterdam storage and capture demonstration project) is the focus on the P18-4 reservoir with a storage capacity of 8 Mton.

In previous studies of Oldenburg the effect of the presence of methane in a depleted gas field is investigated. However only in one phase (gas phase or supercritical phase) this effect could be modelled, due to the restrictions of the TOUGH2/EOS7c module [7,8].

In the current study, simulations of CO₂ injection into the P18-4 reservoir was applied not only in the gaseous phase, but also a phase transition into the liquid phase is investigated. The CO₂ was injected at a minimum temperature of 12 °C into the formation with a temperature of 120 °C. The planned average CO₂ injection rate during the demonstration project is 1.1 Mton/yr over a period of 5 year.

The injection of cold CO₂ into P18-4 is modelled in TOUGH2/ECO2M simulator [9,10]. The ECO2M module is designed to model the CO₂ properties only. By extending the ECO2M module into a new module called ECO2MG, we are able to model the thermodynamic behaviour of the mixtures between CO₂ and CH₄ in the gaseous phase and the liquid phase.

The next section describes the new ECO2MG module and the setup of the P18 reservoir. In Section 3 the results and the impact presence of methane on the thermodynamic behaviour is investigated. In the last two section the results are discussed and the conclusion of this study are presented

2. Method

The new ECO2MG module is an extension of the fluid property module ECO2M of the numerical simulator TOUGH2 [9]. The original ECO2M module was initially designed for CO₂ behavior, in the presence of brine, in gas reservoir and aquifers, including all possible phase transitions, in the absence of any other gas. This ECO2MG module, is extended in such a way, that compositional flow simulations of two gases (namely CO₂ and CH₄) can be performed. The ECO2MG module allows not only for the modelling of the behavior brine of CO₂ mixtures but also

the behaviour of brine-CO₂-CH₄ mixtures (including phase changes from gas to liquid and from super- and sub-critical conditions).

In the new ECO2MG module a new method is implemented to describe the thermophysical behavior of the mixture of CO₂-CH₄. This method includes a new algorithm, which handles the multi-component and multi-phase behaviour of the fluid.

In the ECO2M module the thermophysical properties (e.g. viscosity, density, specific enthalpy) of pure CO₂ are based on the Altunin [11] correlations. These correlations are presented in a tabular format. In this table the thermophysical properties of CO₂ properties are presented on a regular temperature and pressure grid.

The thermophysical properties needed in the simulations can be calculated at any pressure a temperature by using an interpolation algorithm. The saturation line (Figure 1) is used to determine the phase of CO₂ at actual conditions (e.g. fluid, gas, subcritical). This state of the fluid is important for assigning the correct relative permeability's.

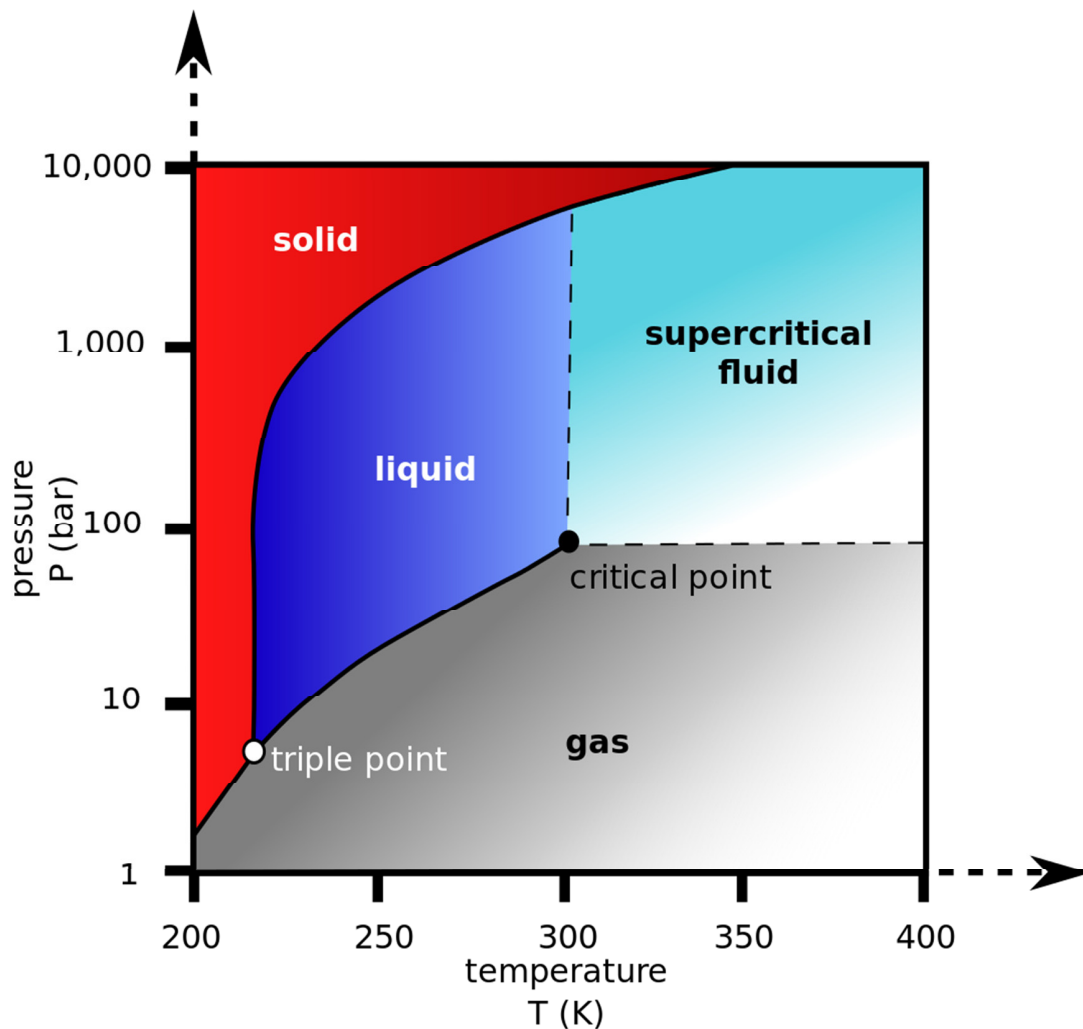


Figure 1. Phase states of CO₂ [13].

The approach to improve the ECO2M module is by expanding the 2-dimensional table representing the thermophysical properties (density, viscosity, specific enthalpy) into a 3-dimensional table. The 2-dimensional table,

called CO2TAB, has a regular grid with pressure and temperature on both axes, while in the new 3-dimensional table, the CO₂-CH₄ mixture composition added to the new axis.

In this study a new 3-dimensional table of density, viscosity and specific enthalpy is generated based on National Institute of Standards and Technology (NIST) data. This new thermophysical table consist of a mixture composition of 0 % CO₂ (which means: 100% CH₄), 20% CO₂, 33% CO₂ and 100% CO₂ (see Figure 2).

The original phase envelopes are not monotonically ascending to the critical point, which is needed in the adjusted interpolation algorithm. To avoid this complication, a modification was made by defining pseudo critical point in such a way the bubble point line is monotonically increasing until the critical point. This modification established only one temperature value can be found by one single pressure value. This is obviously important for simulator as it is designed right now. Although introducing an error around the critical point by using the pseudo pressures, however the thermophysical behaviour away from the critical point is correct.

The algorithm which determines the thermophysical properties (e.g. density) at specific pressure, temperature and mixture conditions is upgraded to handle the new 3-D thermophysical table. The ECO2MG module is now able to estimate the required property by the main TOUGH2 program using this upgraded algorithm, more details about the procedure can be found in Appendix A.

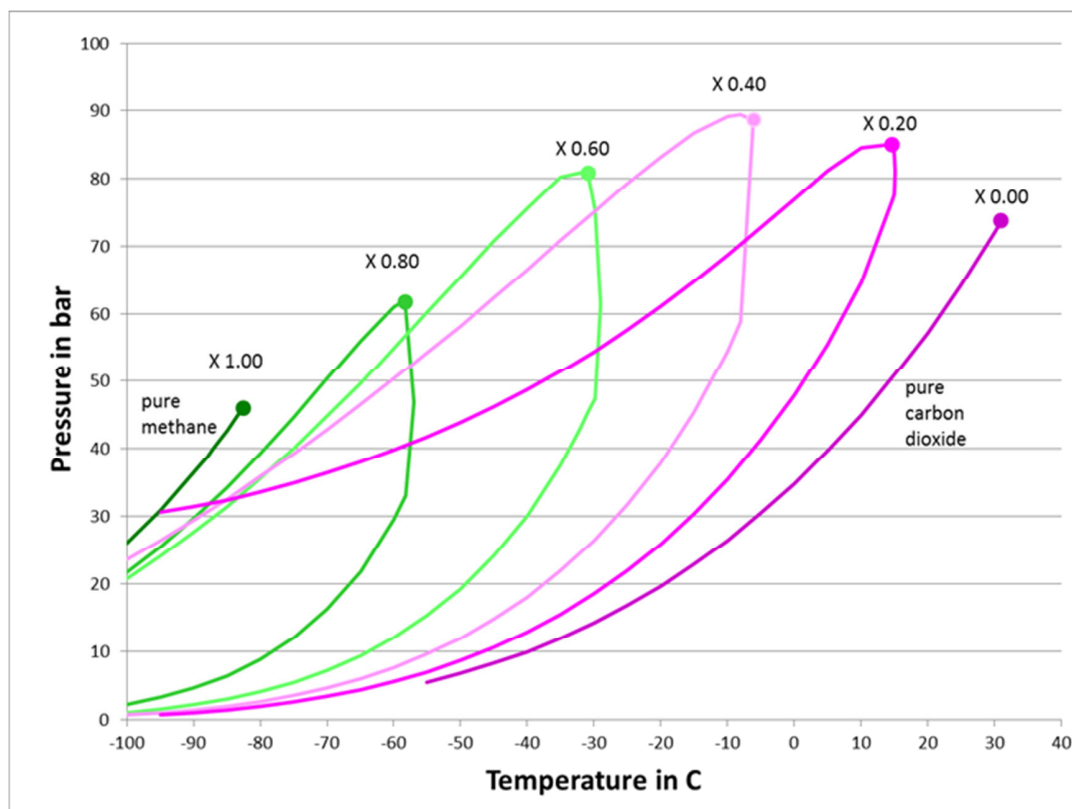


Figure 2: Pressure temperature of the different phase envelopes. The critical points are modified to pseudo critical points in order to change the bubble point curve to monotonic ascending curve (see appendix A)

In addition, a new description of the relative permeability's and capillary pressure was added to ECO2MG. In this new description the relative permeability and capillary pressure are only dependent on their own specific phase saturation, as can be seen in Equation (1)

$$Kr_i = \left(\frac{(S_i - Sr_i)}{(1 - Sr_i)} \right)^n \quad (1)$$

Where:

i is the particular phase (aqueous, gas or liquid)

Kr_i is the relative permeability of the phase i

Sr_i is the residual saturation of the phase i

S_i is the saturation of the phase i

n is the Corey coefficient

The endpoints in this Corey formulation are assumed to be equal to 1.

3. Model setup

A 20 layered radial model was created to analyze the temperature distribution and the dry out zone around the injector. This radial model is based on the P18-4 reservoir properties. The two most important formations in the P18 reservoir are the Hardegsen and the Detfurth formation (Figure 3).

The 2-D model has 87 grid-cells in horizontal direction, with grid refinement in the vicinity of the well. The radius of the model is 700m and with closed boundaries

The injection well, which is situated at the left hand site of the reservoir is constrained at an injection rate of 1.1 Mton/yr for a period of 5 years. The injection temperature is set at 12°C, which is chosen as a lower limit to avoid hydrate formation [5].

The initial reservoir pressure and temperature is 20 bar and 100 °C. Note that the real reservoir temperature is 120 °C but the thermodynamic tables in the simulator are limited to a temperature between 0°C of 103°C. Other properties of the P18 reservoir model is given in Appendix B.

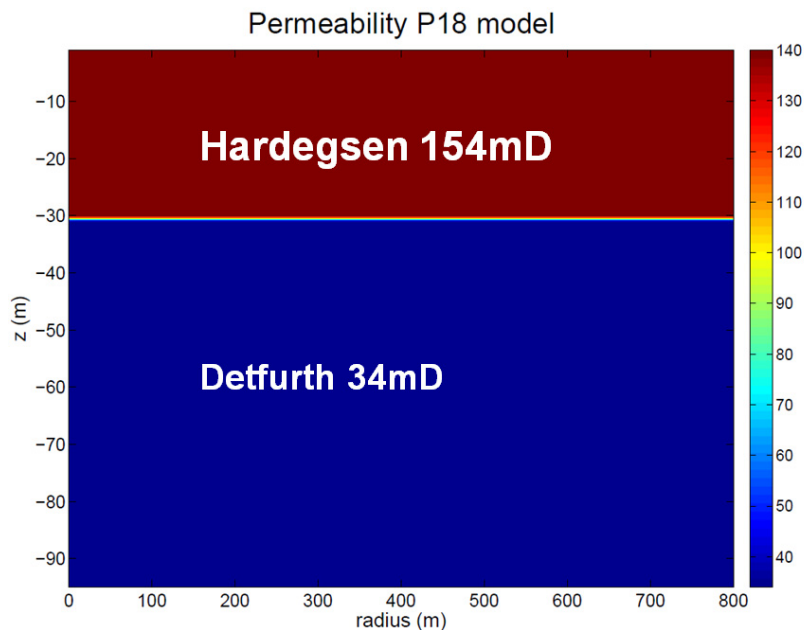


Figure 3: 2D-P18 Reservoir model

4. Results of the ECO2M module

First the results of the original ECO2M module are presented in Section 4.1 and 4.2. This are the simulations without the presence of methane in the reservoir, instead the reservoir is initialized with CO₂. In Section 4.3 and 4.4 the results of the simulations are compared to the ECO2MG module, where methane is present from the start.

4.1. Joule Thomsen effect at low temperature injection

CO₂ injection at 12°C in a 100°C reservoir results in a cold front around the well. In the figure 4 the injection well is located at the left hand side of the image, while the CO₂ propagated to the right into the reservoir. Figure 4 shows that the CO₂ progressed more rapidly in the Hardegsen formation, which can be attributed to its higher permeability. A clear gravity override is observed in the Hardegsen formation as well, caused by the higher CO₂ density within the cold front. In the Detfurth formation the temperature front is more uniform during the 5 years of injection. The maximum extend of the cold front is about 110 meters in the Detfurth formation while 230 in the Hardegsen formation. After 1.5 year the pressure in the reservoir exceeds the critical pressure and the CO₂ undergoes a transition from a low density gaseous phase into a high density liquid phase.

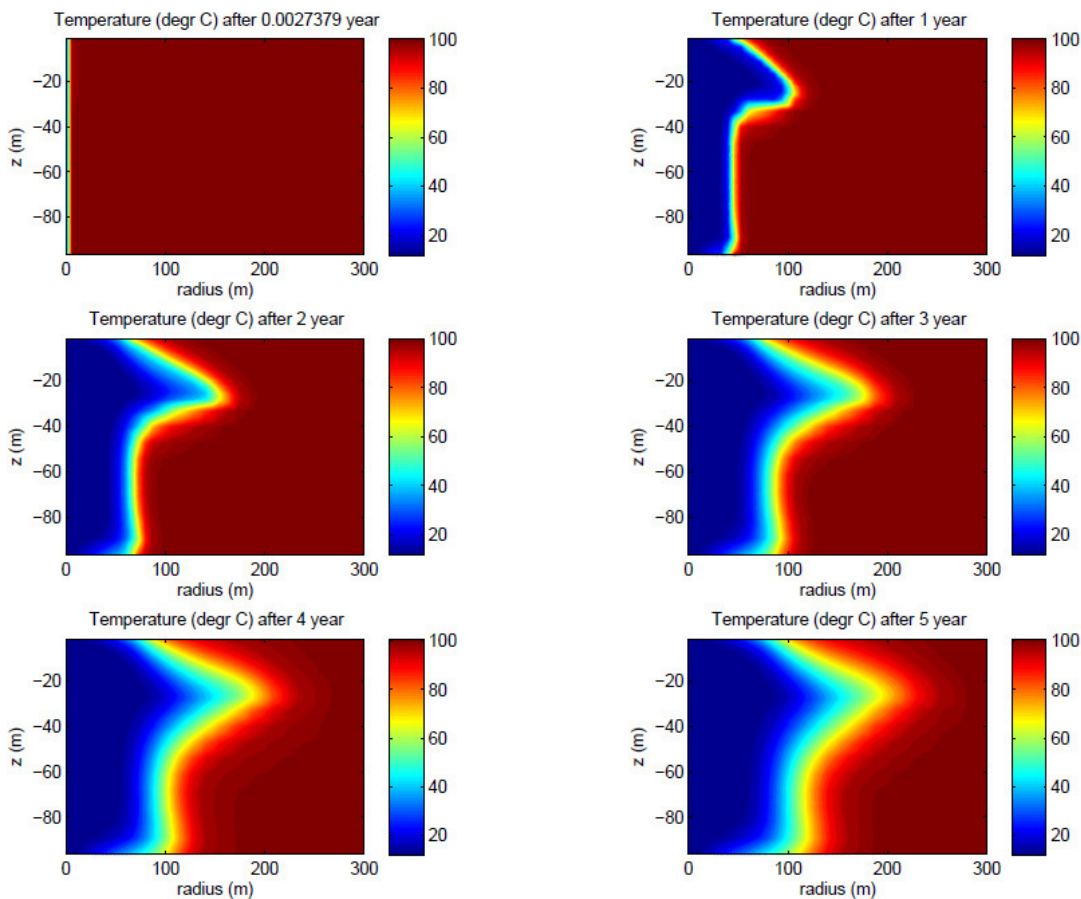


Figure 4: Temperature profile in the P18-4 reservoir during the 5 years of cold CO₂ injection of 1.1 Mton/yr.

One of the uncertainties in the P18 reservoir is the actual value of the initial aqueous phase. Therefore a sensitivity analysis is performed with the value of the initial aqueous phase. Figure 5 shows the effect of an initial aqueous phase of 0.01 and 0.2, respectively. The cold front propagated faster throughout the reservoir at an initial aqueous phase of 0.2 compared to 0.01.

The dry-out zone (up to 5 meters after 146 days) around the injection well is relatively small at the high initial brine saturation, compared to the low initial saturation, where the dry-out zone progressed up to 180 m (Figure 4).

The minimum temperature predicted in the P18 reservoir simulation are 6.3°C and 7.0 °C for high and low initial saturation, respectively. These temperatures are well within the range, where hydrate formation temperature may occur.

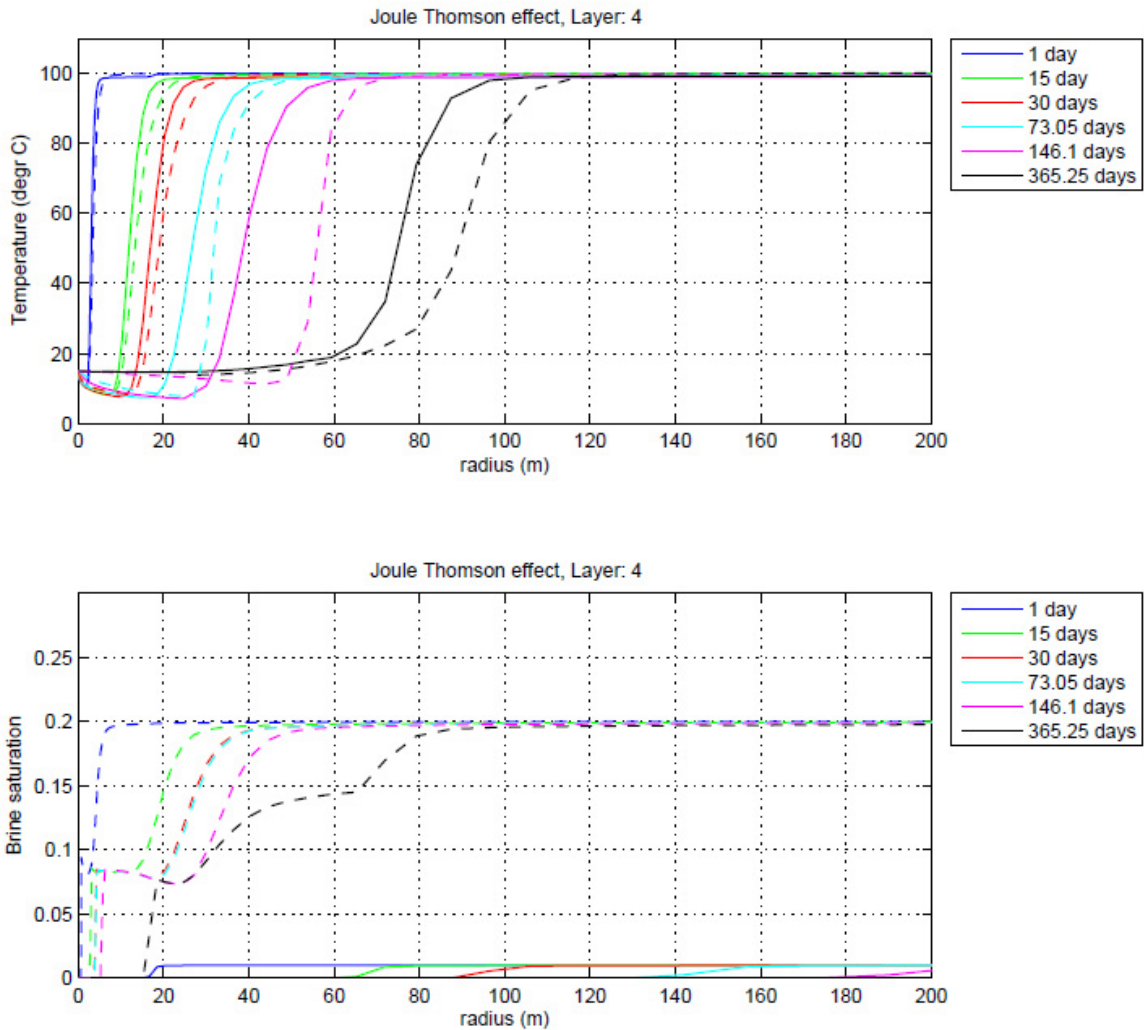


Figure 5: Joule Thomson effect in Layer 4 for low temperature injection. The hard line is the Joule Thomson effect with an initial aqueous saturation of 0.01 and the dashed line is the Joule Thomsen effect with an initial aqueous saturation of 0.20.

4.2. Joule Thomson effect at high temperature injection

The Joule Thomson effect at higher temperature injection, which is 99°C, is presented in Figure 6. At high temperature injection the Joule Thomson effect is much evident compared to the low temperature injection. This effect is very strong especially with an initial brine saturation of 0.2, in this scenario the temperature of the reservoir decreased approximately 25 °C. The minimum temperatures observed in the simulations are 74.7°C and 91.5°C for high and low initial brine saturation, respectively.

The dry out zone for the low brine saturation is similar to the low temperature injection scenario (see Figure 4 and 5). However for the high brine saturation scenario the dry out front propagates faster throughout the reservoir than in the lower injection temperature.

In case of the high brine saturation the cold front covers only a small area around 5m after one day, but after 5 years an larger area between 40m and 100 m has a significant lower temperature (dashed lines). In case of the low initial brine saturation there is small cold front observed at the start of injection. But after 5 years of injection there is not a real cold front anymore, the temperature is 1-2 °C degrees lower than the reservoir temperature and gradually increases to the original reservoir temperature at 200 m from the injection well.

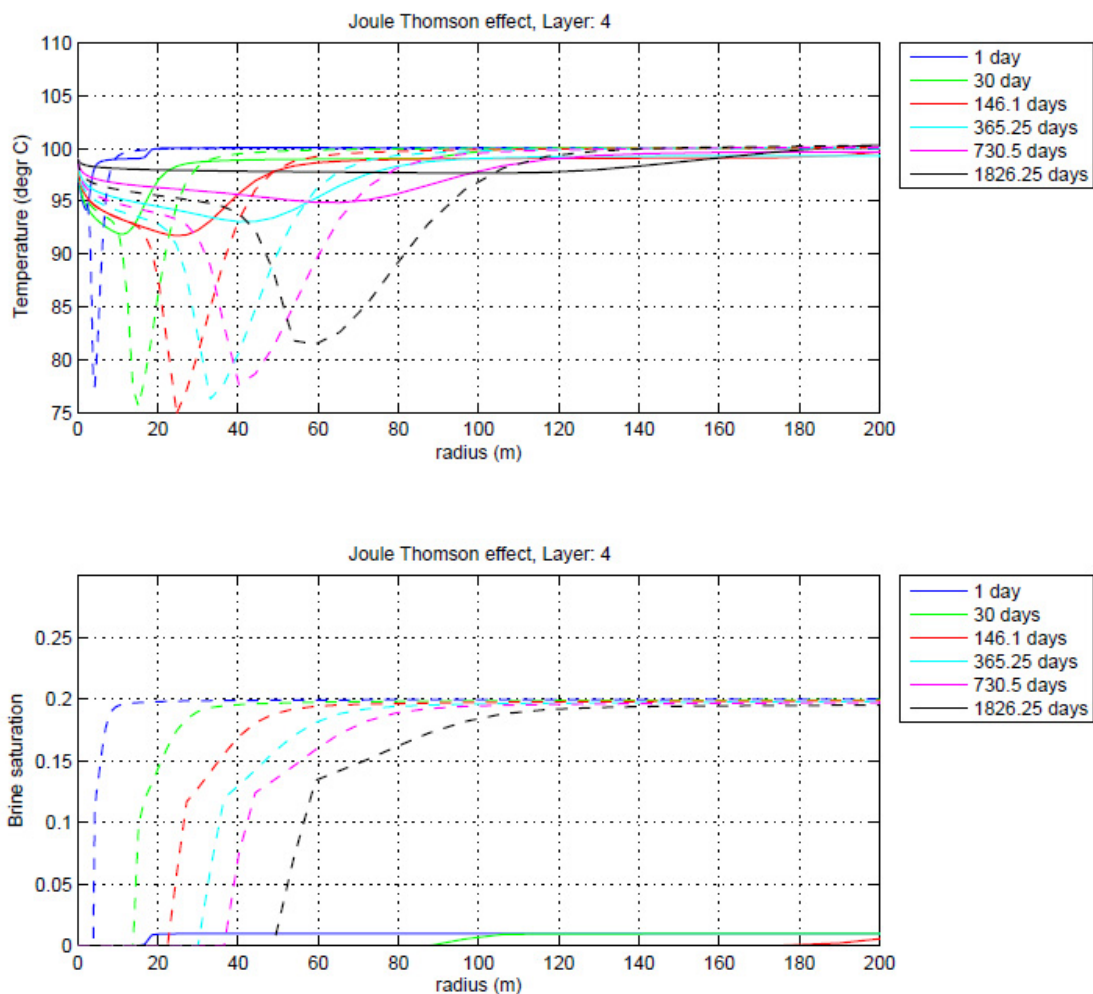


Figure 6: Joule Thomson effect in Layer 4 for high temperature injection. The hard line is the Joule Thomson effect with an initial aqueous saturation of 0.01 and the dashed line is the Joule Thomson effect with an initial aqueous saturation of 0.20.

4.3. Results of the ECO2MG module

The results for the ECO2MG module are similar for high temperature injection and therefore not shown here. However, for low temperature injection the temperature front propagated faster into the reservoir as presented in Figure 7. Furthermore the Joule Thomson cooling is less pronounced in the ECO2MG simulation compared to the ECO2M simulation, which is best visible in Figure 7 after 146.1 days. On the other hand the front is progressing faster into the P18 reservoir.

Figure 8 shows the composition of the gas in the reservoir. As expected, the methane is pushed away from the injection well, in the top formation the process is faster. After one year almost all methane is accumulated at the border of the reservoir and the CO₂ becomes dominant gas in the reservoir.

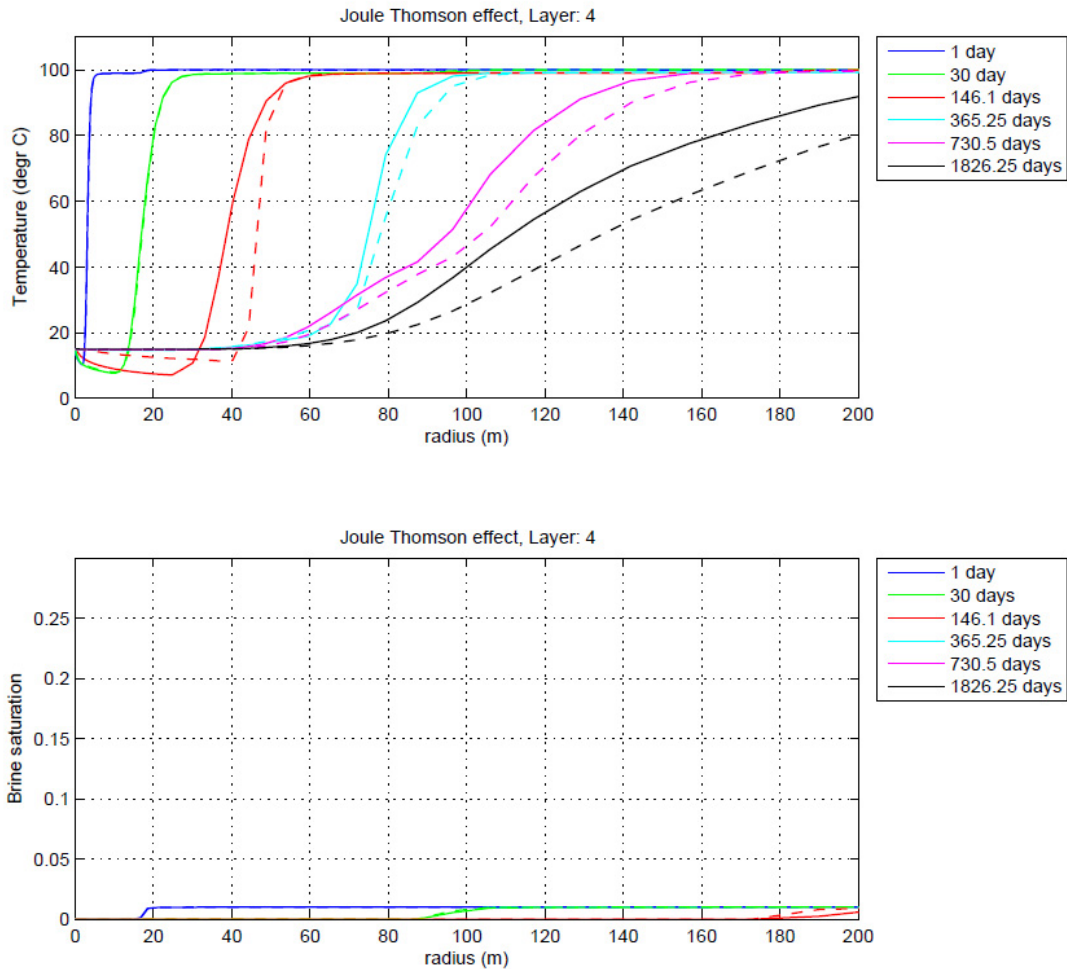


Figure 7: Joule Thomson effect in layer 4 for low temperature injection. The hard line is the Joule Thomson effect with the ECO2M module and the dashed line is the Joule Thomsen effect with the ECO2MG module.

5. Discussion

The results showed that independent of the presence of methane that by cold CO₂ injection the cold front propagated faster throughout the reservoir with an initial aqueous phase of 0.2 compared to 0.01. The reason for this is that the heat of evaporation (the energy required to transform water from liquid to gas) leads to an extra cooling on top of the JTC. The heat of evaporation is around 40-44KJ/mol [12] in the temperature range of 12 °C to 100 °C, which is a relative high number compared to the specific heat of water (energy needed to raise the temperature of one mole by 1 degree Kelvin) which is 75,3 J/Mol/K. Therefore it will take more energy to evaporate a higher initial aqueous phase and therefore the cooling effect will be greater as well.

The effect of heat of evaporation is even stronger during injection at high temperature The vapor pressure of water is a measure for the inter molecular forces within liquid water. By increasing temperature obviously the vapor pressure will decrease, which means more water can exist in the gaseous phase which consist of CO₂. In other words the solubility of water into the CO₂ is higher at higher temperatures, which obviously means more water can evaporate and therefore more energy is needed, which results in a additional decrease is temperature.

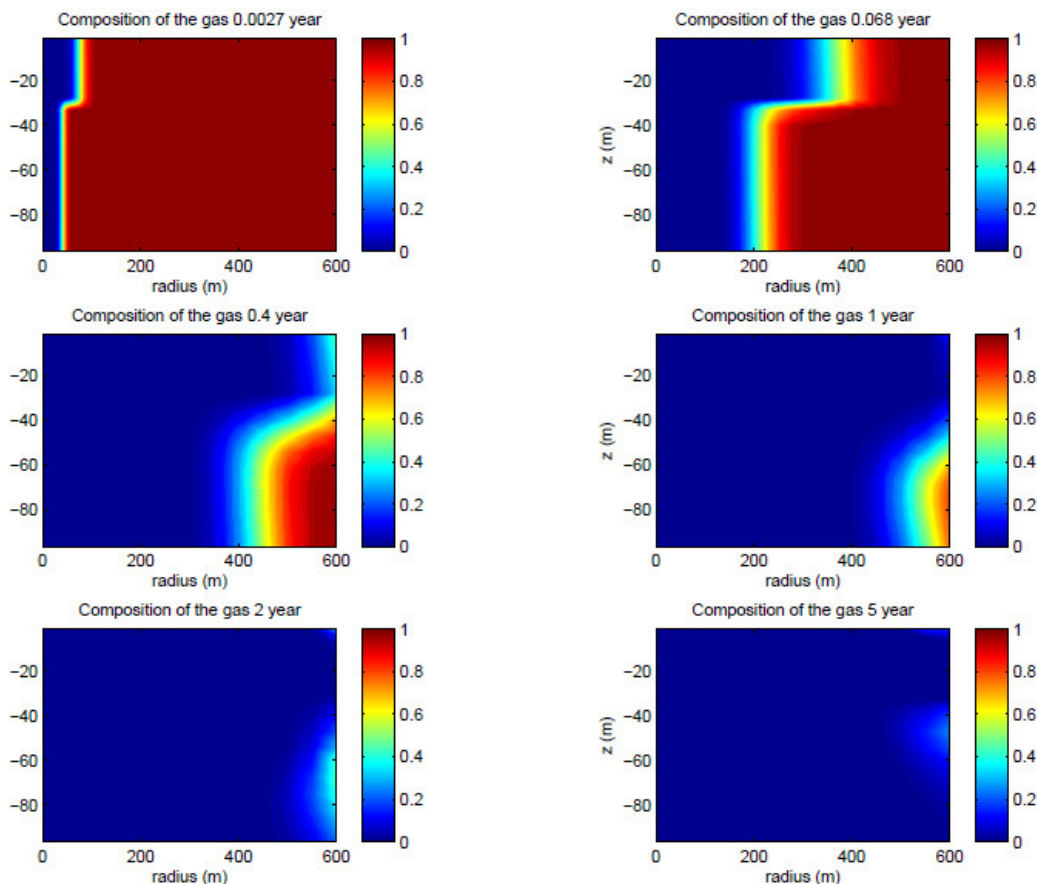


Figure 8: Composition of the gas in for low temperature injection. The value 1 (red) represent 100% methane and te value 0 (blue) represents 100% CO₂ composition.

In the ECO2MG module the Joule Thomson effect is less pronounced compared to ECO2M module. The explanation for this observed effect is the presence of methane. The methane lowers the compressibility of the gas (the mixture of CO₂ and CH₄) in the reservoir, which results in higher pressures around the well. At higher pressures the Joule Thomson coefficient is smaller and therefore the cooling effect as well.

6. Conclusion

- A new TOUGH2 module called ECO2MG was developed to model gaseous and liquid CO₂ in the presence of methane
- The presence of methane reduced the Joule Thomson cooling effect
- The observed cooling in the depleted gas field is a combination of Joule Thomson cooling and energy required to evaporate the aqueous phase.
- CO₂ injection in P18 close to reservoir temperature condition can have a cooling effect around the well up to 25 °C, which is mainly caused by the energy required to evaporate the aqueous phase.
- Cold CO₂ injection in P18 can have cooling effect around the well up to 9 °C.

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8. Appendix A

The procedure to calculate the thermophysical properties (e.g. density, viscosity, specific enthalpy) at a known molfraction CO₂-CH₄ (x), pressure (P) and temperature (T) is added to the ECO2MG module.

In order to explain the procedure an example is used. In the example below we show the procedure to estimate the specific enthalpy (H), but the computational scheme is the same for other properties like density and viscosity. .

In a 2 dimensional table (named CO2TAB) the thermophysical properties are stored, which are needed for ECO2M module. The axes of the table represent pressure and temperature, respectively.. In the ECO2MG this table is extended into a 3-dimensional table, with on the 3rd axis the CO₂-CH₄ mixture composition. The composition axis is defined at the following mixture fractions: 0% CH₄ (so 100% CO₂), 20% CH₄, 33%CH₄ and 100% . In the new module an advanced algorithm is developed to determine the thermophysical properties for all mixture fractions , temperatures and pressures configurations. The main TOUGH2 program can request all type of mixture fractions, temperature and pressure values which are not equal to the values within the CO2TAB table. Therefore a special interpolation procedure is performed to obtain the thermophysical property in at the requested conditions.

Assume the main program requested for the specific enthalpy of CO₂ at 80 bar and 10 ° C, which is mathematical expressed as: $H(P=80, T=10, x=0.1)$.

The following procedure of 6 separate steps will start to determine the value of the specific enthalpy, note that for other properties like viscosity and density this procedure is the same.

1. The dew point and bubble point line for $x=0.1$ are not known. But these points are known at mixture fraction $x=0.0$ and $x=0.2$ are known (Figure 1). At 100% CO₂ or at $x=0.0$ the dew point line and the bubble point line are the same. The first step to calculate these dew point and bubble point at mixture fraction $x=0.1$ is to find the critical point of this mixture by linear interpolation, because the saturation line (and therefore the dew point and bubble point) do scale very well with the critical point:

$$Pc(x) = wPc(x^+) + (1 - w)Pc(x^-) = 0 \quad (8-2)$$

$$Tc(x) = wPc(x^+) + (1 - w)Tc(x^-) = 0 \quad (8-3)$$

Where:

W: The weights used for a correct interpolation (molfraction weighted average).

Pc: The critical pressure.

Tc: The critical temperature.

X: The fraction CO₂.

x^+ : The known mixture of CO₂-CH₄ a level above the requested fraction x .

x^- : The known mixture of CO₂-CH₄ a level below the requested fraction x .

In our example this means:

$$Pc(x = 0.1) = wPc(x = 0.2) + (1 - w)Pc(x = 0) \quad (8-4)$$

$$Tc(x = 0.1) = wTc(x = 0.2) + (1 - w)Tc(x = 0) \quad (8-5)$$

2. Next step is to check in whether the required property is in a single-phase region or two-phase region (see figure 9)
 - 2.1. In case the $T > T_c \rightarrow$ you are in the one phase region, by definition the area where $P > P_c$ we call a liquid phase and $P < P_c$ we call a gaseous phase. This last definition is important for assigning the correct type of relative permeability.
 - 2.2. In case $T < T_c$ then you are possibly in a two phase region, which depends on the values of the dewpoint pressure $P_d(T, x)$ and bubble point pressure $P_b(T, x)$.
 - 2.2.1. If $P > P_b \rightarrow$ liquid phase
 - 2.2.2. If $P_d < P < P_b \rightarrow$ two phase
 - 2.2.3. If $P < P_d \rightarrow$ gas phase

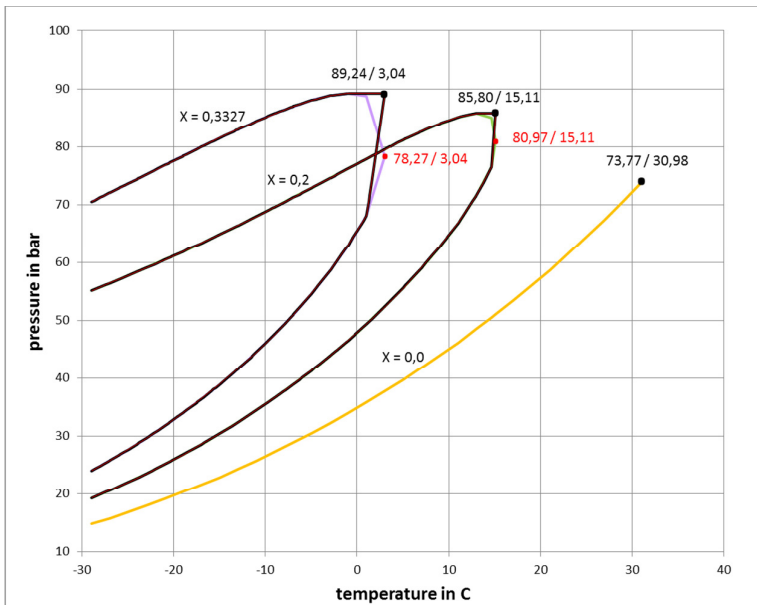
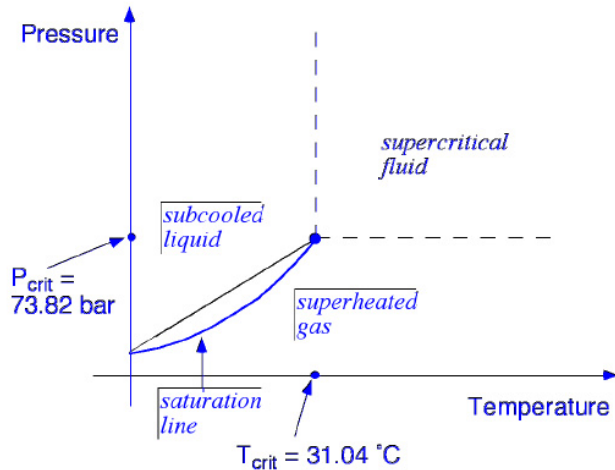


Figure 9: Pressure temperature of the different phase envelopes. The critical points (red) are modified to pseudo critical point (black) in order to change the bubble point curve to monotonic ascending curve

Figure 10: Phase states of CO₂ [10]

3. To apply the criteria defined in 2.2 we first have to determine the dewpoint pressure $P_d(T,x)$ and bubble point pressure $P_b(T,x)$. In order to determine $P_b(T=10,x=0.1)$ and $P_d(T=10,x=0.1)$ an interpolation between the known saturation curves next to the mixture fraction $x=0.1$ is needed:

$$P_b(T,x) = wP_bT'(x^+) + (1-w)P_bT'(x^-) \quad (8-6)$$

$$P_d(T,x) = wP_dT'(x^+) + (1-w)P_dT'(x^-) \quad (8-7)$$

Where:

W: The weights used for a correct interpolation (molfraction weighted average).

T': Scaled temperature which is equal to: $T'(x^+) = \alpha(x)T_c(x^+)$ and $T'(x^-) = \alpha(x)T_c(x^-)$

$\alpha(x)$: Dimensionless or reduced temperature equal to: $\alpha(x) = (T_o + T)/(T_o + T_c(x))$

Where T_o is the absolute minimum temperature = -273.15°C

In our example the reduced temperature is equal to $\alpha(x=0.1) = (T_o + 10)/(T_o + T_c(x=0.1))$

Now we know in which area the requested property is (one phase or two phase)

4. The dewpoint and the bubble point are known now an interpolation or extrapolation is needed at the level above (x^+) and below (x^-) the known CO₂-CH₄ mixture fraction (x) in order to estimate the property at the requested mixture fraction, pressure and temperature. In the known mixture of CO₂-CH₄. The interpolation in the level above and below is done with a scaled pressure, which is defined in step 5.
- 4.1. If $P > P_b$ then extrapolation is needed
 - 4.2. If $P_d < P < P_b$ then interpolation between the two points is needed
 - 4.3. If $P < P_d$ then extrapolation is needed

5. Case 4.2 is done by linear interpolation between Pd(T,x) and Pb(T,x) in the property table (e.g. specific enthalpy)

$$H(P, T, x) = wH[P'(x^+), T'(x^+), (x^+)] + (1-w)H[P'(x^-), T'(x^-), (x^-)] \quad (8-8)$$

Where:

$$P'(x^+) = Pd(x^+) + \beta(x)P(x^+) \quad (8-9)$$

$$P'(x^-) = Pd(x^-) + \beta(x)P(x^-)$$

$$\beta(x) = [P(x) - Pb(x)] / (Pb(x) - Pd(x)) \quad (8-10)$$

P' is the scaled pressure and $\beta(x)$ is the dimensionless pressure.

6. Case 4.1 is calculated also with equation 8.7, however $\beta(x)$ is defined different:

$$P'(x^+) = Pb(x^+) + \beta(x)P(x^+) \quad (8-11)$$

$$P'(x^-) = Pb(x^-) + \beta(x)P(x^-)$$

$$\beta(x) = Pb(x) + [P(x) - Pb(x)] / Pd(x) \quad (8-12)$$

7. Case 4.3 is calculated also with equation 8.7, however $\beta(x)$ is defined different:

$$P'(x^+) = Pb(x^+) + \beta(x)P(x^+) \quad (8-13)$$

$$P'(x^-) = Pb(x^+) + \beta(x)P(x^-)$$

$$\beta(x) = Pd(x) + [P(x) - Pd(x)] / Pb(x) \quad (8-14)$$

9. Appendix B

Table 1: P18 reservoir properties:

Property	Value	Unit
Cells horizontal	87	
Cells vertical	20	
Radius	700	m
Temperature	100	°C
Initial Pressure	20	Bar
Kv/Kh	0,1	
Injection rate	1,1	Mton/yr
Relative permeability	Corey	
Residual water saturation	0,3	
Residual gas saturation	0,01	
Corey coefficient aqueous, gas, liquid phase	3	
Capillary pressure	No capillary pressure	
Permeability of the Hardegsen	154	mDarcy
Porosity of the Hardegsen	0,11	
Thickness of the Hardegsen	26	m
Permeability of the Dethfurt	34	mDarcy
Porosity of the Dethfurt	0,08	
Thickness of the Dethfurt	72	m