Simulation of the production and storage of natural gases - Influence of thermodynamic quantities and phase equilibria

Wolfgang Littmann

Consulting Reservoir Engineering, Wunstorf Conference Paper - Translation of German Text – DGMK Celle Frühjahrstagung 2022

Abstract

Simulation programs such as Eclipse® for the production or storage of natural gases often do not sufficiently take into account the thermodynamic behavior of the gases. The simulation is usually carried out under isothermal conditions. However, practice shows both during storage in caverns and in porous media that in addition to pressure changes, measurable temperature shifts also occur, which in turn change the PVT behavior of the gas and thus the phase equilibria, e. g. between gas, water and condensate.

To simulate such processes, a program has been developed that makes it possible to take such thermodynamic processes into account for caverns and porous media.

In this way, the pressure conditions for reservoirs or caverns can be calculated with sufficient precision. This modeling also takes into account the hysteresis between injection and withdrawal in porous media storage, whereby the well head pressures and temperatures are calculated.

Another advantage lies in the calculation of the amount of water dissolved in the gas and also in the determination of the amount of condensate produced. The calculations can be easily extended to the thermodynamic states in surface systems such as compressors or separators.

On the basis of practice-relevant examples, simulation results of a condensate reservoir, a natural gas storage facility and a compressed air storage power plant are presented and discussed in detail.

Introduction

The field of reservoir engineering deals with the flow of gas and liquids in porous rock under the influence of pressure changes. This concerns the flow in the reservoir itself, but also the inflow into a borehole and the flow in the borehole. The pressure changes that occur during extraction from a reservoir can also lead to changes in the state of the substances involved. In the case of a gas, the density mainly changes, in the case of oil, for example, the content of gas dissolved in the oil. The behavior of the substances is described by its *PVT* properties. *P* stands for the pressure, *V* for the volume and *T* for the temperature. The volume is determined by the size of the reservoir, the pressure changes due to the production or injection of substances, the temperature is determined by the geological depth of the formation. This means that the temperature is assumed to be constant for all reservoir engineering calculations, i.e. it does not appear in most equations. This also applies to most numerical reservoir models, which are created with great effort and level of detail.

To assume the temperature in all areas of a reservoir and in all parts of the production flow as constant may still be correct for oil and water in the first approximation, but this is no longer

the case with the extraction of gas and especially in natural gas storage. In the following, the influence of temperature and its change in the production and storage of natural gas is discussed and explained using practical examples.

Thermodynamics

Some thermodynamic terms are briefly explained below to shed light on the subject, but a complete derivation at this point is not possible.

The law of conservation of energy

The 1. law of thermodynamics describes the equivalence of heat and work.

$$\Delta U = q + w \tag{1}$$

Here, U is the internal energy, w is the mechanical work and q is the heat.

If no energy is supplied from the outside during a change of state, then ΔU is equal to zero and

$$q = -w \tag{2}$$

This approach shows the equivalence of work and heat. The 1st law further states that it is impossible to construct a perpetual motion machine. This means that when a system is transferred from a state A to state B and then back to state A, the change in internal energy is zero.

The equation of state

The equation of state for an ideal gas is

$$p \cdot V = nRT \tag{3}$$

p is the pressure, V is the volume, n is the amount of substance in moles, R is the gas constant, and T is the absolute temperature. When using SI units, the product pV gets the unit Joule (J). The unit of absolute temperature is Kelvin (K).

The product of pressure and volume has the unit of energy. The gas constant R has the unit of a specific heat namely J/(mol K). So the right side of the equation of state (3) has the dimension of heat in J and the left side the dimension of work in J. If 3 parameters are specified in the equation of state, such as the amount of substance *n*, the pressure *p* and the volume *V*, then the temperature *T* is clearly determined.

Real gases

The equation of state (3) applies to ideal gases. An ideal gas in thermodynamics does not consist only of a mass-free idealized point cloud, as is often assumed, but actually of real molecules. These molecules have a mass, e.g. nitrogen the molecular weight 28 g/mol. Furthermore, these molecules have several degrees of freedom in which the energy or heat of the gas is stored. A nitrogen molecule has e.g. 5 degrees of freedom, 3 of the translation (in all 3 spatial directions) and 2 of the rotation. In each of these degrees of freedom, heat with the amount 1/2 R is stored.

For real gases, it was found that the PVT behavior deviates from this ideal behavior depending on the molecular structure. Further forces occur within the gas, so that the equation of state (3) must be corrected by a factor *z*. This *z*-factor or compressibility factor is a function of pressure and temperature.

$$z = z(p, T) \tag{4}$$

The equation of state for real gases is then:

$$p \cdot V = znRT \tag{5}$$

The z-factor can be calculated from the critical data (critical pressure, critical temperature) and other properties. Known algorithms for this are Hall-Yarborough, Peng-Robinson, Soave-Redlich-Kwong, GERG, AGA-GRI.

Expansion and compression of gases

When handling gases, there are often changes in state, such as compression and expansion. For example, in compressors, expansion turbines, expansion and compression in a storage cavern. These state changes often take place adiabatic, i.e. no heat is supplied from the outside. The gas must therefore do the expansion work itself.

According to the 1st law and a little more vividly according to the equation of state, heat is extracted from the gas during an adiabatic expansion and the temperature of the gas changes. In the case of compression, this is analogously reversed.

For reversible-adiabatic expansion from state 1 to state 2:

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\kappa - 1} \tag{6}$$

where is:

$$\kappa = \frac{c_p}{c_v} \tag{7}$$

Furthermore, the following applies:

$$\frac{T_1}{T_2} = \left(\frac{p_2}{p_1}\right)^{\frac{\kappa-1}{\kappa}} \tag{8}$$

and

 $(p \cdot V)^{\kappa} = const. \tag{9}$

For an ideal 2-atomic gas, such as nitrogen with 5 degrees of freedom, the following would apply:

$$\kappa = \frac{c_p}{c_v} = \frac{\frac{5}{2}R + R}{\frac{5}{2}R} = \frac{\frac{7}{2}}{\frac{5}{2}} = 1.4$$
 (10)

Figure 1 shows the temperature change as a function of the compression ratio. The initial temperature T_1 is 300 K. It can be seen that, for example, with a compression from 1 bar to 100 bar, temperature changes of about 800 °C occur.

Figure 1: Temperature change depending on the compression ratio (p_1/p_2) for a 2-atomic ideal gas.

Phase equilibria

Another aspect of oil and gas production is the balance between liquid and gaseous phases. There is, except perhaps in the case of heavy oil production, no oil production that does not also produce gas and, on the other hand, no natural gas production without water or condensates, although usually in small quantities.

An extension of the equation of state (3) is, for example, the *van der Waals* equation for real gases (11).

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{11}$$

or in another notation

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \tag{12}$$

Here, a/V^2 means the so-called internal pressure and b the van der Waals co-volume, which corresponds approximately to 4 times the intrinsic volume of the molecules.

An extension of van der Waal's equation is, for example, the equation of state of Soave-Redlich-Kwong (13).

$$p = \frac{RT}{V-b} - \frac{a(T)}{\left[\frac{V}{V-b}\right]}$$
(13)

The constants a(T) and b can be calculated for the individual components of a gas mixture or a crude oil from the critical data (temperature and pressure).

A liquid is in balance with its vapor. The equilibrium pressure at a certain temperature is the vapor pressure. The liquid has a higher density than the vapor. As the temperature increases, the density of the liquid decreases and that of the vapor increases. Above a certain temperature, the densities of the liquid and the vapor are the same, this temperature is the critical temperature, the associated pressure is the critical pressure. These values are documented for many substances. For example, the critical pressure for CO_2 is 50.4 bar and the critical temperature is 304.2 K (31 °C).

With the help of an equation of state, all thermodynamic quantities and phase equilibriums can then be calculated.



Figure 2: Phase diagram for a natural gas calculated with GERG-2008

Figure 2 shows a phase diagram for a natural gas with 80 % C_1 , 10 % N_2 , 2 % CO_2 , 5 % C_2 and 3 % C_3 . The calculations here were carried out with the software GERG-2008. The critical point is particularly marked, to the left of the critical point is the bubble point curve above which the gas is liquid, within the phases envelopes there are 2 phases (liquid, vapor). To the right of the critical point is the dew point curve below which the gaseous phase is present.

Reservoir and storage simulation

Thermodynamics are very often ignored in simulation of natural gas production and gas storage processes. The simulation, e.g. in programs such as Eclipse[®], is isothermal. As shown above, this is rarely the case, because with every pressure change of a gas is also associated with a change in temperature, or heat must be added or dissipated in the event of an isothermal pressure change.

Furthermore, considerable amounts of water and condensate can also be dissolved in natural gas, which is often not taken into account. To take these processes into account, a simple material balance program has been developed that takes into account the temperature changes in an adiabatic state change of a gas and continues to take into account phase equilibria between gas and water as well as higher hydrocarbons.

Surface systems such as compressors, water separators, heaters or coolers can also be included in the simulation.

Below are some practical examples of cavern storage, pore storage and natural gas fields.

Cavern storage

For natural gas storage in salt caverns, storage and withdrawal takes place at very high rates, so that temperature changes in the caverns are not negligible, which means that the storage

pressure can only be correctly calculated by taking thermodynamic processes into account.

Figure 3 shows the well head pressure of a storage cavern and Figure 4 shows its temperature. The simulation was carried out using daily average values for the rates, so that the dynamics in the head pressure development in the representations are smoothed. The measured values for well head pressure and temperatures were recorded only once a day.

The cavern temperature is 40 °C. The cooling from 40 °C to a head temperature of 20 - 25 °C is caused by the expansion of the gas and results from equation 8. The gas has to do work and this is extracted from the gas as heat.

For example, at a rate of 100 000 $m^3(V_n)/h$, approximately 70 tonnes of natural gas per hour must be transported to the surface. This corresponds approx. to 700 10^6 J or 200 kWh for a depth of 1 000 m.



Figure 4, corresponds very well with the measured values especially with regard to dynamics.

Figure 3: Head pressure development of a storage cavern [4]. Points: Measured values, Line: Simulation



Figure 4: Simulation of the head temperature of a storage cavern [4]

Pore storage

The pressure and temperature behavior of a borehole during a production test is shown in Figure 5 for pore storage facilities or natural gas deposits. At a flow rate of around 20 000 m³(V_n)/h, a pressure reduction of 15.5 bar results in a temperature change of 7 °C. It is also noteworthy that the temperature build-up is significantly slower than the pressure build-up, which is important e. g. for scale formation processes.



Figure 5: Temperature change during a production test in a storage well [5]

The following example looks at the simulation of an aquifer storage. The simulation was carried out with the simulation program Eclipse[®] and with the material balance program. Figure 6 and Figure 7 show the results for the well head pressure. The calculations with the material balance program naturally show less dynamics, but match the measured values just as well as the much more detailed Eclipse model. It should be noted that in order to get a satisfying match in Eclipse, about 120 runs were necessary and this can only be obtained with a hysteresis model for the relative permeability. A total of 6 sets of relative permeability were used for imbibition and drainage for the individual layers as well as one set for the wells. These relative permeabilities had to be elaborately adjusted in the approximately 120 history match runs, whereas only about 10 simulation runs were required to adapt the tank model.



Figure 6: Simulation (line) and measured values (triangles) of the storage pressure (head pressure of a hole) with a Black Oil Model (Eclipse®)



Figure 7: Simulation (line) and measured values (points) of the storage pressure with a "thermodynamic" material balance program.

Figure 8 shows the calculated average gas temperature in the tank model. The temperature changes of about 10 °C around the reservoir temperature of 50 °C are the result of the pressure changes during injection and production. They are of the same order of magnitude as the temperature changes in the Figure 5.



Figure 8: Calculated gas temperature during simulation with the material balance program

Another difference between the two simulation models is the calcuation of water production. The relative permeabilities required for the pressure match in the Eclipse simulation resulted in a relatively poor match of water production (Figure 9). The calculated values for the production of water were initially too high for many wells, after each storage cycle the water production decreased until after about 7 cycles no more water was produced.



Figure 9: Simulation (line) and measured values (points) of the water production of a borehole with a Black Oil Model (Eclipse®).

Figure 10 shows the production of water dissolved in the gas as calculated with the thermodynamic material balance program. This corresponds well to the measured values. Initially, the measured amount of water is slightly above the simulation, which indicates that in addition to the dissolved water, free water was also produced. Over time, the proportion of mobile reservoir water became lower, so that the calculated values corresponded well with the measured values.



Figure 10: Simulation (line) and measured values (points) of water production with the "thermodynamic" material balance program.

Reservoirs

For a condensate reservoir, the pressure curve and the production of water and condensate were calculated using the material balance program. The pressure curve is shown in Figure 11, while Figure 12 shows water production. The reservoir has a temperature of 100 °C, so that relatively much water is dissolved in the gas.

The production therefore shows from the beginning (1993) a water production that corresponds to the dissolved proportion of water. After about 10 years of production (2003) the production of free reservoir water of a well is added, after another 5 years (2008) the water breakthrough of another well takes place.

The simulation with the material balance program reflects very well the proportion of water production that is solely due to the solubility of the water in the gas.



Figure 11: Reservoir pressure, simulation with material balance program (line: simulation, points: measured values)



Figure 12: Water production, simulation with material balance program (line: simulation, points: measured values)

Figure 13 the measured and simulated condensate production. Simulation and measured values also match very well here. The dispersion of the measured values at the end (from 2017) is due to the inaccuracy of the measurements due to low production rates.



Figure 13: Condensate accumulation, simulation with material balance program (line: simulation, points: measured values)

Compressed air energy

As part of the energy transition, energy storage using compressed air is also being discussed. With the compression of air in a cavern, heat is generated, which is stored in the concept of the so-called adiabatic compressed air energy storage and is added again during the expansion of the compressed air.



Figure 14: Principle sketch of an adiabatic compressed air storage

With the thermodynamic simulation program described here, it is also possible to calculate such processes.

With a compressed air storage, the compressed air is stored at a high rate. The air is first brought to the temperature of the heat storage tank in a heat exchanger connected to a heat reservoir, then expanded via a turbine and returned to the atmosphere.

Figure 14 schematically shows the principle of an adiabatic compressed air energy storage. Figure 15 shows this flow diagram for simulation, showing flow rate, pressure, and temperature at the input and output for each module. The calculations did not take into account whether the intended units, such as compressors or turbines, can be technically designed to meet pressures or temperatures.

Withdrawal / Discharge

Initially, a cavern (CAES) filled with air at a pressure of 150 bar was assumed. The air is stored via the Well1 borehole and then heated to the temperature stored in a heat reservoir. Here it is taken into account that the stored amount of heat is finite and thus the temperature decreases in the course of storage. The heated air is then expanded via a turbine and thus generated electricity. Via the unit Well2, the air is released back into the atmosphere.

Injection / Charge

In the diagram shown in Figure 16, air is sucked in via the Well2 unit, then compressed and then cooled to the instantaneous temperature of the heat reservoir. Before the air is released into the cavern, it is cooled down to the ambient temperature.

Module	CAES Welll		Heater3	Turbine3	Well2	ATM
In.Rate Out.Rate	0.0 -2600000.0	-2600000.0 2600000.0	2600000.0 2600000.0	2600000.0 2600000.0	2600000.0 2600000.0	2600000.0 0.0
In.Pressure Out.Pressure	1.0 146.9	146.9 125.5	125.5 125.5	125.5 10.0	10.0 10.0	10.0 1.0
In.Temp. Out.Temp.	0.0 48.3	48.3 28.2	28.2 490.0	490.0 105.9	105.9 105.9	105.9 30.0

Figure 15: Flow diagram storage / discharge (rate in $m^3(V_n)/h$, pressure in bar, temperature in °C).

Module	: ATM	: Well2	: Comp03	Heater3	AirCooll	Welll	CAES
In.Rate Out.Rate	0.0 -2600000.0	-2600000.0 2600000.0	2600000.0 2600000.0	2600000.0 2600000.0	2600000.0 2600000.0	2600000.0 2600000.0	2600000.0 0.0
In.Pressure Out.Pressure	10.0 1.0	1.0 1.0	1.0 74.8	74.8 74.8	74.8 74.8	74.8 86.1	86.1 82.4
In.Temp. Out.Temp.	-28.3 30.2	30.2 30.2	30.2 711.2	711.2 277.1	277.1 20.0	20.0 34.9	34.9 14.4

Figure 16: Flow diagram storage / charging (rate in $m^3(V_n)/h$, pressure in bar, temperature in °C).

The stored energy and the storage capacity are shown in Figure 17 over time. With the shown mode of operation, approx. 2.7 GWh can be stored, the storage capacity is on average 200 MW.



Figure 17: Storage performance and storage energy (storage positive, storage negative)

As shown in Figure 18, a storage cycle is performed in such a way that at the end there is the same gas content in the storage cavern as at the beginning. However, this means that at the end of a storage cycle, the temperature is higher and so is the pressure.



Figure 18: Gas content, withdrawal - injection



Figure 19: Cavern pressure and temperature (discharge - charge)

In the shown mode of operation for the compressed air energy storage, it is not possible to completely return the heat stored during charging to the process. It would be necessary to use this heat to keep the gas within the cavern at the most constant temperature possible, but this is not technically feasible. Therefore, significant temperature changes occur in the cavern during removal. Figure 19 shows the temperature curve and pressure in the cavern in time. A temperature change during storage from 50 °C to -20 °C and a subsequent temperature increase to about 100 °C is certainly problematic for rock mechanical reasons.

The efficiency of the storage cycle shown here is 30 % with a mode of operation that would be necessary for rock mechanical reasons if the efficiency were even lower.

Summary

With the presented thermodynamic material balance program, the behavior of cavern storage, aquifer storage and natural gas deposits can be simulated. By taking into account the thermodynamic behavior of gases, some processes in natural gas storage and production can be better described than with an isothermal numerical reservoir simulation.

The program can also be used to simulate the behavior of a compressed air energy storage. The design of such a storage with regard to the mode of operation and heatstorage can thus be optimized in a simple way.

The advantages of including thermodynamics in the simulation are:

- A better description of the pressure behavior of cavern and pore storage.
- More accurate calculation of the pressure loss in wells and calculation of well head temperature.
- Calculation of water production in gas storages and reservoirs, especially at high reservoir temperatures.
- Calculation of condensate production.
- Calculation of hysteresis in storage operations.

- Simulation of compressed air energy storage.
- Simulation of surface facilities, such as:
 - Compressors / Expansion Turbines
 - Pipe lines
 - Water separators
 - Heaters
 - o Dryers

Thus, with the thermodynamic program, even complex processes in the behavior of a natural gas reservoir, a pore storage or a cavern storage can be calculated quickly and reliably in a simple way. Furthermore, the condensate content or the proportion of free and dissolved water in gas can be calculated and this also in the above-ground facilities of a storage. This facilitates the planning of surface systems and the operation of a storage facility.

Literature:

- [1] Cengel BD, Boles MA: Thermodynamics—an engineering approach, 6th edn. Tata McGraw Hill, New Delhi (2008)
- [2] Lübbers, B., Rehmer, Abdelhaq, A.: "Construction of the world's first helium cavern storage facility in Germany", Erdöl Erdgas Kohle 2018, 4
- [3] Pedersen, K. S., Fredenslund a., Thomassen, P.: "Properties of Oils and Natural Gases",, Gulf Publishing Company, (1989), p. 88
- [4] Littmann W., Brodersen F., Krieter M., Zwiggelaar O.:" The Debriningand Operation of a Gas Cavern with Variable Cushion Gas du to Adjustable Gas Brine Contact" ERDÖL ERDGAS KOHLE 131. Jg. 2015, Heft 4
- [5] Littmann W.: "Gas Flow in Porous Media Turbulence or Thermodynamics", Oil Gas European Magazine, 2004 p. 166