

# The Advantages of Equations of State in Form of the Helmholtz Energy for the Design of CCS-Relevant Processes

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## ABSTRACT

Based on an isentropic adiabatic compression of pure CO<sub>2</sub> typical approaches using the isentropic relation are compared with properties calculated from a fundamental equation of state in form of the Helmholtz energy. The comparisons focus on the estimated energy consumption of the compression, the estimated end temperature, and a reasonable thermodynamic behavior.

**Keywords:** carbon capture and storage, isentropic adiabatic compression, thermodynamic properties, fundamental equations of state

## NOMENCLATURE

### Abbreviations

CCS	Carbon capture and storage
CO <sub>2</sub>	Carbon dioxide
const.	Constant
EOS	Equation of state
ref.	Reference

### Symbols

$c$	Heat capacity
$\Delta$	Difference
$g$	Gramm
$h$	Enthalpy
$i$	Index
$J$	Joule
$k$	Kilo
$K$	Kelvin
$\kappa$	Isentropic exponent
$M$	Mega

$o$	Ideal
$p$	Pressure / Isobaric
Pa	Pascal
$\rho$	Density
$s$	Entropy
$T$	Temperature
$v$	Specific volume / Isochoric
$w$	Speed of sound

## 1. INTRODUCTION

The present climate change is caused by increasing temperatures due to global warming as a result from greenhouse gases accumulating in the atmosphere. If the global temperature increase exceeds 1.5 °C [1] the climate will most likely be irreversibly changed resulting in major negative consequences for the environment. To prevent this, the emission of the most abundant greenhouse gas, carbon dioxide (CO<sub>2</sub>), has to be decreased. A key technology is carbon capture and storage (CCS), which is based on the separation of CO<sub>2</sub> for example from the flue gas of power plants burning fossil fuels or cement factories. Consequently, the CO<sub>2</sub> is transported to a safe and permanent storage side, like depleted gas fields or saline aquifers. Since these processes require additional energy, which is directly related to higher costs, an efficient process design is highly aspired.

After capturing the CO<sub>2</sub>, it is typically at atmospheric conditions in a gaseous state, which necessitates a compression into the liquid state for a more efficient transport. The compression to the phase change is usually estimated with the isentropic relation and the assumption of a temperature independent ideal isentropic exponent. However, comparing the ideal and

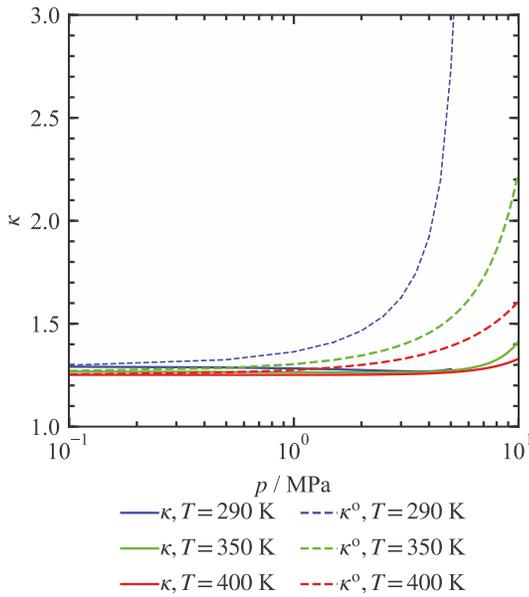


Fig. 1. The ideal and real isentropic exponents calculated with the reference equation of state for CO<sub>2</sub> [2] for different temperatures plotted over pressure.

real isentropic exponent of CO<sub>2</sub> for various temperatures over pressure, as shown in Fig. 1, indicates the defectiveness of this assumption. To avoid problems, fundamental equations of state (EOS) in terms of the Helmholtz energy can be used instead of simple relations derived for ideal gases. These EOS allow for the accurate calculation of all thermodynamic properties, e.g. densities, enthalpies, or heat capacities in all fluid regions covering vapor, liquid, and supercritical states. Thus, a more precise and efficient process design can be directly developed. In this work, comparisons of a simple isentropic twofold compression of pure CO<sub>2</sub> calculated with the reference EOS for CO<sub>2</sub> [2] and various ways using the isentropic relation are presented.

## 2. THEORY AND CALCULATIONS

The comparisons in this work are based on calculations with a Helmholtz energy EOS and with the isentropic relation with an isentropic exponent. The following sections provide the background for the acquired results.

### 2.1 Theoretical background

The isentropic relation for an isentropic adiabatic change of state reads

$$p_i v_i^\kappa = \text{const.} \quad (1)$$

with the pressure  $p$ , the specific volume  $v$ , and the isentropic exponent  $\kappa$ . It is constant for all states  $i$ .

The isentropic exponent is defined as

$$\kappa = -\frac{v}{p} \left( \frac{\partial p}{\partial v} \right)_s, \quad (2)$$

in which  $s$  is the entropy.

For the assumptions of an ideal gas and that the ideal isobaric heat capacity  $c_p^0$  and consequently also the ideal isochoric heat capacity  $c_v^0$  are temperature independent, the ideal isentropic exponents can be written as:

$$\kappa^0 = \frac{c_p^0}{c_v^0}. \quad (3)$$

For an ideal gas, Eq. (1) can also be rewritten to a temperature relation which reads

$$T_{i+1} v_{i+1}^{\kappa^0-1} = T_i v_i^{\kappa^0-1}. \quad (4)$$

On the contrary, the evaluation of Eq. (2) for a real gas results in

$$\kappa = \frac{\rho \cdot w^2}{p} \quad (5)$$

with the density  $\rho$  and the speed of sound  $w$ . To calculate the isentropic exponent in a specific state, the required thermodynamic properties are calculated with a fundamental EOS. In this work, the reference EOS for CO<sub>2</sub> by Span and Wagner [2] in terms of the Helmholtz energy is used. The independent variables of the EOS are temperature and density. The EOS is valid in all fluid states covering the vapor, liquid, and supercritical regions. Because of the fundamental nature of the EOS, the calculation of all thermodynamic properties is possible by combinations of its derivatives. For more details about these relations see Span [3]. In this work, the EOS was applied for the calculation of densities, ideal isobaric as well as ideal isochoric heat capacities (calculated as real gas properties in the limit of zero density), entropies, and speeds of sound at a specified temperature and density or pressure using the thermodynamic property software TREND 5.0 [4]. The iterative routines implemented in TREND also support various other input combinations, e.g. pressure and entropy.

### 2.2 Calculations of changes of state

In the following, four different exemplary cases of calculation of an isentropic adiabatic compression are discussed. There are no differences with regard to the computational simplicity between the different cases.

The reference case is calculated with the EOS with given temperature and pressure at the starting point of the compression. This allows for the calculation of the entropy at this state. The entropy in the next state point

is identical because the process is considered isentropic. Since the higher pressure is known in this state, the temperature can be calculated with entropy and pressure as input variables. For both states the ideal and real isentropic exponent can be calculated.

In the second case, ideal gas behavior is assumed for the whole gaseous region so that Eq. (1) and Eq. (4) can be applied to compress the gas from one state to another. A further assumption is a constant ideal isentropic exponent, which is calculated with the EOS at the starting point (cf. Table 1). With the calculated temperature and density, the entropy and enthalpy can be calculated using the EOS. This case represents the typical approach.

The third case still assumes an ideal gas behavior and Eq. (1) and Eq. (4) are used. However, the ideal isentropic exponent is not assumed constant. Since temperature and density are dependent on  $\kappa^0$  and the ideal isentropic exponent itself is also dependent on temperature and density,  $\kappa^0$  had to be iterated. This results in

$$p_2 v_2^{\kappa_2^0} = p_1 v_1^{\kappa_1^0}. \quad (6)$$

The last case is the same as the third case except for the use of the real isentropic exponent calculated with the EOS according to Eq (5). Still Eq. (1) and Eq. (4) were applied.

### 3. RESULTS AND DISCUSSION

The four different cases were applied to a typical twofold compression of gaseous CO<sub>2</sub>, which is assumed to be a pure substance (typical impurities of captured CO<sub>2</sub> are neglected). The compression starts in state 1 at a temperature of 290 K and a pressure of 0.1 MPa. The intermediate pressure level is 0.7 MPa and the final pressure is 4.9 MPa. From this point on the CO<sub>2</sub> is typically liquified and further pumped to higher pressures required for the CO<sub>2</sub> transport. However, at liquid states Eq. (1) is not applicable anymore.

The ideal and real isentropic exponents for all four cases in all three states are listed in Table 1.

Table 1: Ideal and real isentropic exponents for all cases in all state points.

State point	$\kappa^0$	$\kappa$
<b>Case 1 (isentropic with EOS)</b>		
1	1.298	1.291
2	1.254	1.243
3	1.238	1.231
<b>Case 2 (<math>\kappa^0 = \text{const.}</math>)</b>		
1	1.298	1.291

2	1.249	1.239
3	1.229	1.227
<b>Case 3 (<math>\kappa^0</math> (iterative))</b>		
1	1.298	1.291
2	1.256	1.244
3	1.239	1.231
<b>Case 4 (<math>\kappa</math> (iterative))</b>		
1	1.298	1.291
2	1.258	1.245
3	1.242	1.233

Since state 1 is the starting point,  $\kappa^0$  and  $\kappa$  are the same for all cases.

The isentropic exponents shown in Table 1 deviate slightly from the reference case 1. The maximal relative deviation is 0.8 %. Nevertheless, state 3 of cases 2 and 4 differs in absolute terms of the enthalpy from the reference case as visible in Fig. 2. with significant amounts of around 6 % (cf. Table 2). In particular in case 2, the needed amount of energy to compress the CO<sub>2</sub> to the desired pressure is overestimated resulting in higher estimated costs.

To validate the isentropic behavior of the changes of state as well as the temperatures at the end of the analyzed compression, a temperature over entropy

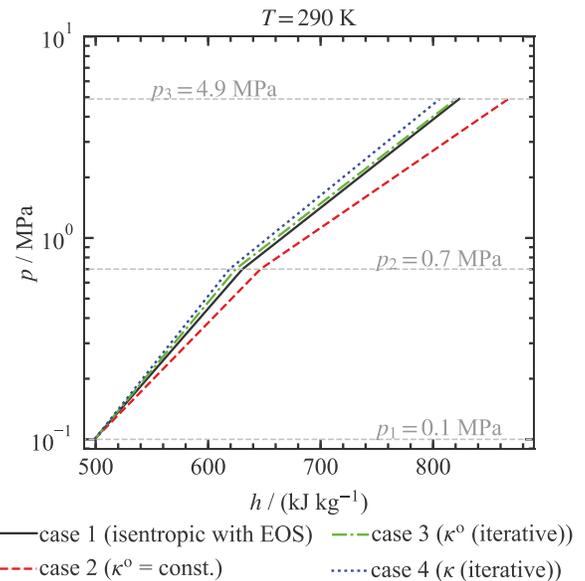


Fig. 2. Pressure over enthalpy diagram for the changes of state for all four cases.

diagram is presented in Fig. 3.

Cases 2 and 3 follow physically unreasonable paths for the change from state 1 to 2 because the entropy decreases. Contrary, the change from state 2 to 3 is almost isentropic in case 3. However, case 3 is quite close to the reference case in terms of temperature and enthalpy. Case 2 exhibits the highest deviation in terms

of entropy and temperature from the reference case. Especially, the higher temperature in state 3 of almost 40 K will influence the process development because more cooling will be needed for the liquefaction.

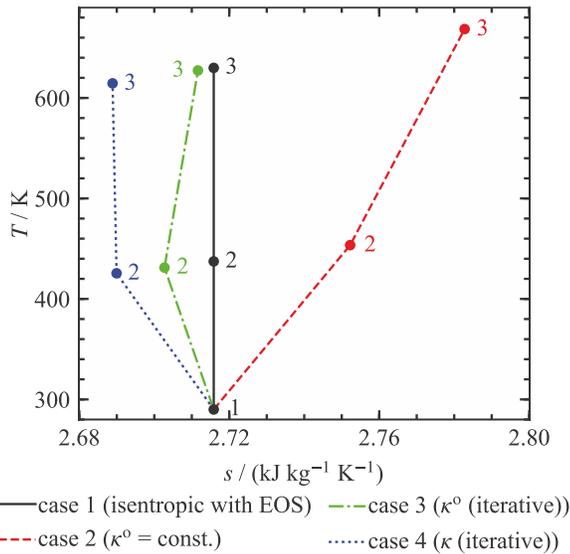


Fig. 3. Temperature over entropy diagram for the changes of state for all four cases.

The absolute enthalpy and temperature differences at the end of the compression compared to the reference case 1 are listed in Table 2.

Table 2: The absolute and relative enthalpy as well as absolute temperature differences from the reference case 1 according to  $\Delta h = h_i - h_{\text{ref.}}$  and  $\Delta T = T_i - T_{\text{ref.}}$ .

Case $i$	$\Delta h / (\text{kJ kg}^{-1})$	$(100 \cdot \Delta h) / h_{\text{ref.}}$	$\Delta T / \text{K}$
2	43.73	5.31	38.6
3	-2.886	-0.33	-2.58
4	-17.23	-2.10	-15.4

If the CO<sub>2</sub> is in a transcritical state, similar results are expected as the ideal assumptions cannot be applied in this state region.

#### 4. CONCLUSION

The comparisons for a compression of gaseous CO<sub>2</sub> presented in this work show the advantages of fundamental EOS in form of the Helmholtz energy versus typical approaches using the isentropic relation. The typical approaches either lead to thermodynamic unreasonable behavior or overestimate the energy needed for the compression as well as the end temperature. The higher end temperature also results in a slightly higher estimated cooling water demand for downstream liquefaction by cooling. Contrary, the fundamental EOS is able to accurately and reliably

calculate all thermodynamic properties for an efficient process design.

Further interesting aspects to investigate are the influence of the different state points 3 on the density. In particular, if the density is calculated with a cubic EOS in contrast to the reference EOS this adds another source of deviation. Different densities directly affect the estimation of the volume flow through the compressor. This can lead to wrongly designed compressor blades, which then will not work at their optimum.

The same calculations can be carried out with a multicomponent mixture containing CO<sub>2</sub> and typical impurities. The EOS-CG-2021 [5] mixture model, which is also formulated in terms of the Helmholtz energy, can be used to calculate the required thermodynamic properties. This would allow for an analysis of the effect of impurities because it is known that these can significantly affect for example the phase behavior.

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