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Phase diagrams of CO₂ and CO₂-N₂ gas mixtures and their application in compression processes

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Abstract

Phase diagrams of carbon dioxide, nitrogen and their mixtures with different amounts of nitrogen (e.g. 5 mol%, 10 mol% N₂) were calculated with high accuracy with the NIST Reference Fluid Thermodynamic and Transport Properties database program REFPROP® for up to 200 bar, as well as density-pressure diagrams.

Beside the use of carbon dioxide as a solvent for supercritical fluid extraction, increasing interest in physical chemical properties of CO₂ exists as Carbon dioxide Capture and Storage (CCS) starts to play an important role to limit anthropogenic emissions of CO₂ into the atmosphere. Therefore CO₂ processing and pipeline technologies became of considerable commercial importance, especially in the context of future underground storage of CO₂.

As example the CO₂ compression process with gas separation membrane in post-combustion capture was simulated with PRO/II® software. Through adopting several different equations of states, phase diagrams of different CO₂ - N₂ gas mixtures were calculated and compared with the aforementioned accurate thermodynamic and transport properties calculation results. This type of validation is very useful for process engineering analysis.

Further investigations related to the compression process were carried out for the different CO₂ gas mixtures, which are generated from the gas separation membrane capture process. Specific energy of the compression process was analysed for each gas mixture. The energy consumption and the state of the compressed compounds are strongly influenced by the N₂ composition in the mixture.

The impurities in multi-component CO₂ mixtures vary strongly depending on the different capture technologies. The calculation of reliable phase diagrams of CO₂ mixtures provides guidelines for optimization of compression, pipeline transport, and storage processes.

Keywords: thermodynamic properties; thermophysics; transport properties, phase diagrams CO₂ N₂ mixtures, CO₂ compression

1. Introduction

Carbon dioxide Capture and Storage (CCS) is playing an important role to limit anthropogenic emissions of carbon dioxide into the atmosphere causing global warming. CCS is a process consisting of the separation of CO₂ from industrial and energy-related sources, transport to the storage location and long-term isolation from the atmosphere [1]. The four main steps are: capture, compression, transport and storage. Therefore, there is increasing interest in the properties of carbon dioxide for scientific reasons and also for industrial applications. Beside the use of carbon dioxide as a solvent for supercritical fluid extraction, carbon dioxide processing and pipeline technologies became of considerable commercial importance, especially in the context of future underground storage of carbon dioxide.

Owing to the different capture processes in power plants, the captured CO₂ mixtures have diverse compositions. An example given here is the gas separation membrane process in post-combustion capture [2,3]. Some different CO₂ and N₂ mixtures are generated from the process, e.g. 95 mol% CO₂, 5 mol% N₂ and 90 mol% CO₂, 10 mol% N₂. As a key step in a CCS process, it is important to transport the

captured CO₂ safely and economically from the point of capture to a storage site. In order to reduce the costly transport volume, CO₂ and CO₂/N₂ mixtures should be in dense liquid, supercritical or solid state.

Pipelines today operate as a mature market technology and are the most common method for transporting CO₂ [4,5]. These pipelines operate in the 'dense phase' mode (in which there is a continuous progression from gas to liquid, without a distinct phase change), and at ambient temperature and high pressure. CO₂ compression, a joint junction between the capture and transport process, will be investigated here. The investigation of the phase diagrams of these CO₂/N₂ mixtures is an important prerequisite to quantify the relevant energy consumption and to identify promising capture strategies.

2. Phase diagrams of Carbon Dioxide, Nitrogen and its mixtures

Phase diagrams, as well as density-pressure diagrams, of carbon dioxide, nitrogen and their mixtures with different amounts of nitrogen (e.g. 5 mol%, 10 mol% N₂) were calculated with NIST Reference Fluid Thermodynamic and Transport Properties database program REFPROP® [6] for up to 200 bar.

2.1. Carbon Dioxide properties

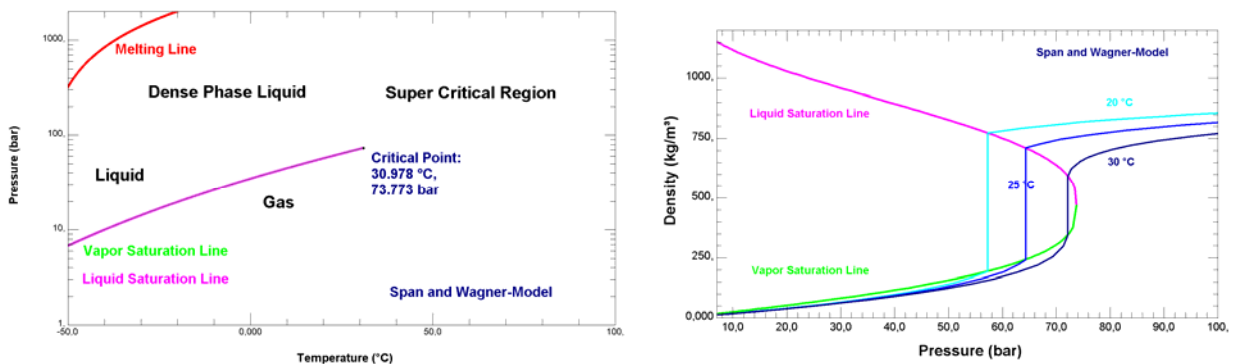


Fig. 1: Carbon dioxide phase diagram [7]

For pure CO₂ the critical point [7] is defined through its critical temperature of 30.978 °C (304.1282 K ± 0.015 K), its critical point pressure of 73.773 bar (7.377 3 MPa ± 0.003 MPa) and its critical point density of (467.6 ± 0.6) kg/m³. The triple-point temperature is 216.592 K ± 0.002 K and the triple-point pressure (0.517 95 ± 0.00010) MPa.

The very accurate Helmholtz energy equation of state of Span and Wagner [7] (Model FEQ in NIST REFPROP®-Software) was used within the limits: -56,558 °C to 1726,9 °C, $p < 8000$, bar, density lower than 1638,9 kg/m³ to calculate the density-pressure and pressure-temperature diagrams. For technical processes most important conditions with pressures up to 30 MPa and temperatures up to 523 K, the estimated uncertainties are up to ±0.05% in density, up to ±1% in the speed of sound and up to ±1.5% in isobaric heat capacity. Special emphasis has been put on the description of the critical region.

Additionally the Peng-Robinson (PR) method [8] was used within REFPROP for calculation of CO₂ properties, because the simulation PRO/II® software used later on for calculation of compression processes does not include the accurate equation of states. Large differences can be seen in the densities, which were calculated in 50 kg/m³ steps.

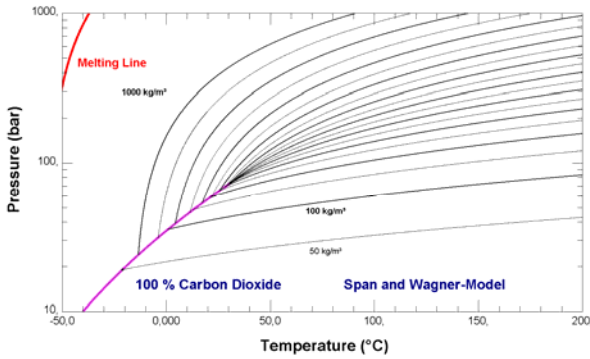


Fig. 2a: Carbon Dioxide phase diagram: Accurate Model [7] RFPROP [8]

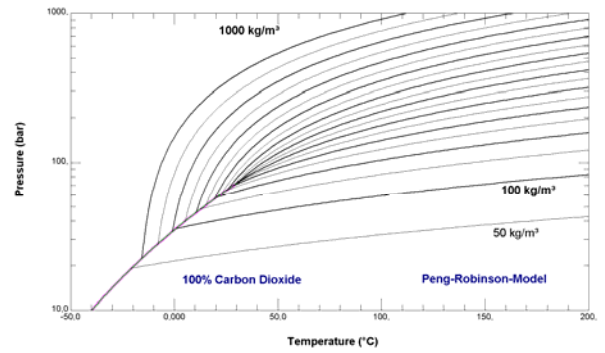


Fig. 2b: CO₂ phase diagram calculated with NIST

2.2. Nitrogen properties

For Nitrogen a corresponding accurate description by Span, Lemmon, Jacobsen, Wagner and Yokozeki [9] was used for the equation of states. This equation describes the density-pressure-temperature surface with high accuracy. Based on comparisons of calculated properties to available experimental data, the estimated uncertainty in density is $\pm 0.02\%$ (at the 95% confidence level) from the triple point up to temperatures of 523 K and pressures up to 12 MPa and from temperatures of 240 to 523 K at pressures less than 30 MPa. The uncertainty in pressure in the critical region is estimated to be 0.02%. The estimated uncertainties of vapor pressure, saturated liquid density, and saturated vapor density are in general $\pm 0.02\%$ for each property.

2.3. CO₂-N₂ mixture properties

For calculation of the phase diagrams and density-pressure-temperature dependencies as well as vapor liquid equilibrium of CO₂-N₂ mixtures with good accuracy the GERG 2004 equations of O. Kunz, R. Klimeck, W. Wagner and M. Jaeschke [10] were used.

For derivation of the GERG 2004 equation of states for the thermodynamic properties of carbon dioxide, nitrogen, natural gases and binary mixtures the measured densities of Nitrogen - Carbon dioxide mixtures (CO₂ fraction: 0.1 to 0.98, pressure range from 0.1 to 274.0 MPa, temperature range of 209K to 673 K) and vapor liquid equilibrium (VLE) data ($1.0 \leq p/\text{MPa} \leq 21.4$, CO₂ mole fractions in the liquid phase in the range of 0.4 - 1.0 and in the vapor phase of 0.14 - 1.0) were used. The equations uncertainty in gas phase density is less than 0.1% within the temperature range from 250 K to 450 K and pressures up to 35MPa, which is about a factor of 5 to 10 worse than for the pure compounds N₂ and CO₂, but still accurate enough for most technical applications.

Using the accurate GERG 2004 equation of state, it can be observed (Fig. 1 and Fig. 3 a) - c)) that with increasing the N₂ content from 0 mol% to 20 mol% the critical point shifts to lower temperature and higher pressure. The density increases and the liquid saturation line moves to higher pressure with increasing amount of Nitrogen within the mixture.

For the mixture of 90 Mol% Carbon Dioxide and 10 Mol% Nitrogen the large differences in densities between the accurate GERG-2004 equation of state [10] (Figure 3b on the upper right side) and the Peng-Robinson-Model [8] (Figure 3d on the lower right side) can be seen through comparison of these diagrams, as well as the difference in the critical point conditions.

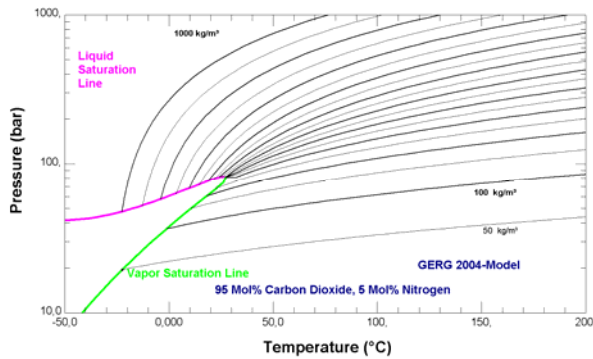


Fig. 3a. Phase diagram 95 Mol% Carbon Dioxide 5 Mol% Nitrogen calculated with accurate GERG 2004 equation [10] Critical Point: 27.12 °C, 81.13 bar [10]

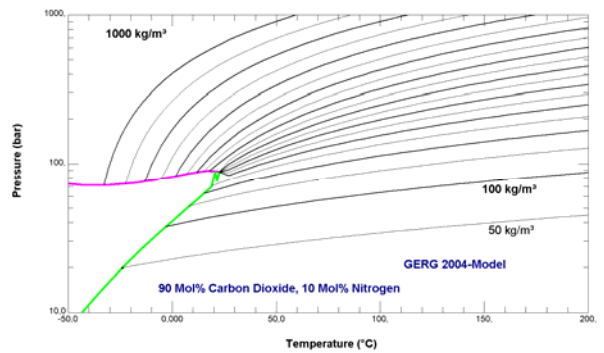


Fig. 3b. Phase diagram 90 Mol% Carbon Dioxide 10 Mol% Nitrogen calculated with accurate GERG 2004 equation [10] Critical Point: 22.51 °C, 87.70 bar [10]

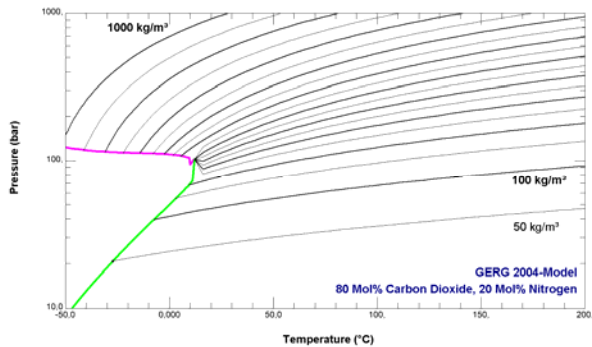


Fig. 3c. Phase diagram 80 Mol% Carbon Dioxide 20 Mol% Nitrogen calculated with accurate GERG 2004 equation [10] Critical Point: 12.00 °C, 102.24bar [10]

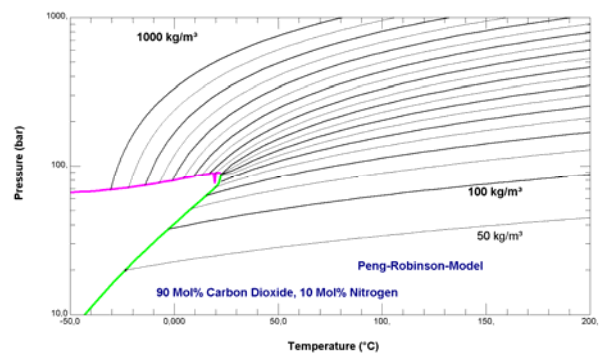


Fig. 3d. Phase diagram 90 Mol% Carbon Dioxide 10 Mol% Nitrogen calculated with Peng-Robinson-model from NIST REFPROP [8] Critical Point: 31°C, 74 bar [8]

3. Simulation of CO₂ compression processes

To simulate the capture process, the software PRO/II® [11] was used and phase envelopes for multi-component streams were generated (program module “phase envelope”). The algorithm can easily generate points in the retrograde condensation region (where at constant temperature, the vapor phase in contact with the liquid may be condensed by a decrease in pressure; or at constant pressure, the vapor is condensed by an increase in temperature). The calculations are limited to the Soave-Redlich-Kwong (SRK) [12] and Peng-Robinson (PR) [8] methods, and work best for mixtures of non-polar hydrocarbons. The Michelsen method [13] is used to compute the true critical point, cricondentherm, cricondenbar, and other points on the envelope. The reference state for both liquid and vapour is the ideal gas and deviations from ideal behaviour are determined by calculation of the fugacity coefficients for both phases. For SRK and PR the liquid density is determined using the American Petroleum Institute (API) method [14]. Owing to the limitation of the PRO/II® software, the phase diagram of pure CO₂ can not be generated. So a mixture composed of 99.99 mol% CO₂ and 0.01 mol% N₂ was simulated as a reference to compare with the other mixtures. In the pipeline the transported medium should have very good fluidity; the above mentioned “dense phase” exists over the critical point. The phase diagrams of different mixtures are shown in Fig. 4 a) - d), the critical points are signed.

It can be observed (Fig. 4 a) - d)) that with increasing the N₂ content from 0.01 mol% to 20 mol% the critical point shifts from 31.06 °C, 73.84 bar to 14.55 °C, 105.47 bar. In the defined temperature and pressure range, SRK and PR methods have no evident deviation, especially in c) and d), the two curves overlap themselves completely.

Comparing with the accurate results of GERG-2004 equation of state calculated by REFPROP® (Figures 1, 2a and 3a-3c) it is shown, that the critical points are reproduced by the SRK and PR method calculated with PRO/II® within 2.5°C ($\pm 22\%$) for the critical temperature and within 2.5 bar ($\pm 5\%$) for the critical pressure.

However from comparison of the calculation results for 90%CO₂ and 10%N₂ it can be observed, that the implementation and/or the used parameter for the Peng-Robinson method are different in the 2 programs (Figure 3d and 4c). Differences between the results of accurate GERG-2004 equation of state with RP-method calculation results in PRO/II® are smaller than the differences with the RP-calculation results from REFPROP.

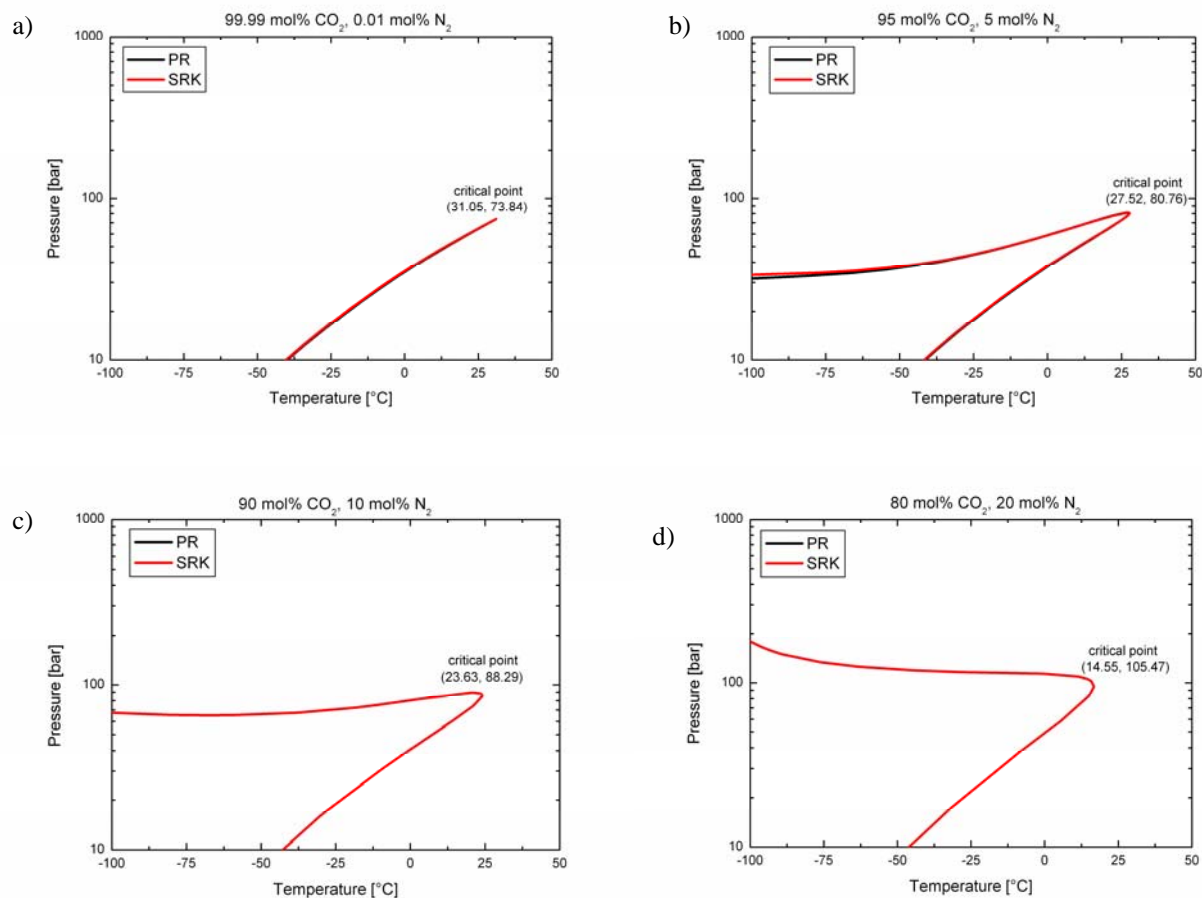


Fig. 4 Phase diagrams generated by PRO/II® for different mixtures with Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) method
a.) 99.99 mol% CO₂, 0.01 mol% N₂; b.) 95 mol% CO₂, 5 mol% N₂; c.) 90 mol% CO₂, 10 mol% N₂; d.) 80 mol% CO₂, 20 mol% N₂.

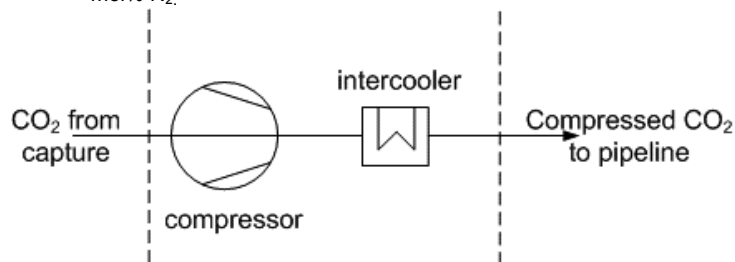


Fig. 5 shows a schematic illustration of the CO₂ compression process. The captured CO₂ will be compressed in a stage-arranged CO₂ compressor, and then led to the pipeline transport. Intercooling is an important measure to lower the electrical energy for compression.

Fig. 5 Schematic illustration of the CO₂ compression process

In our case, the captured CO₂ at 50°C and 1 bar [3] with the flow rate of 1000 kmol/h is compressed by an 8-stage CO₂ compressor [15]. The adiabatic efficiency of the compressor is assumed to be 85%; a uniform pressure ratio is adopted for each stage. The intercooling temperature is defined as 30 °C. The end condition of the compression is assumed here to be 110 bar, 30°C. Table 1 lists the compression energy consumption of the above mentioned mixtures, which is calculated by referring to the total CO₂ amount in the mixture.

Gas mixture	Composition	Specific energy [kWh/t CO ₂]	Density [kg/m ³] (GERG 2004)
1	100 mol% CO ₂	86	792
2	95 mol% CO ₂ , 5 mol% N ₂	87	681
3	90 mol% CO ₂ , 10 mol% N ₂	88	536
4	80 mol% CO ₂ , 20 mol% N ₂	89	343

Table 1 Compression specific energy for different gas mixtures, the end condition 110 bar, 30°C

Fig. 6 shows the compression in P-T diagram, a) for the mixture 2 (95 mol% CO₂, 5 mol% N₂) and b) for the mixture 4 (80 mol% CO₂, 20 mol% N₂).

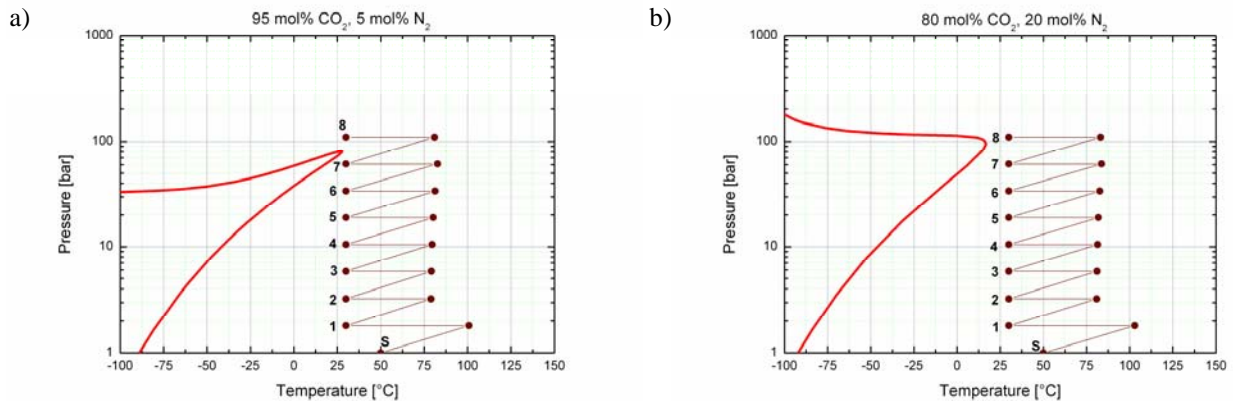


Fig.6: CO₂ mixtures compression in P-T diagram, a) the mixture of 95 mol% CO₂, 5 mol% N₂ and b) the mixture of 80 mol% CO₂, 20 mol% N₂; “S” represents “starting point”, “1-8” for 8 compression stages.

From these results it can be seen that with increasing the impurity of N₂ in the stream the specific energy to drive the compressor to reach the end condition will be enhanced. From the table 1 it can be seen that the density of the mixture 2 (95 mol% CO₂, 5 mol% N₂) at the stage 8 (110 bar, 30°) is 681 kg/m³ (GERG 2004 model) and that of mixture 4 (80 mol% CO₂, 20 mol% N₂) is 343 kg/m³ (GERG 2004 model). Then, these data help to understand the final state of these two mixtures listed in Table 1.

Obviously, owing to the diverse capture processes, the impurities in the captured stream vary significantly, which strongly influences the compression process. Here, ideal mixtures only composed of CO₂ and N₂, worked out by gas separation membrane process, were analyzed and the influence on energy consumption for compression was analyzed.

4. Conclusions

- The critical points and the vapor-liquid and liquid-solid line of the density-pressure-temperature diagrams of CO₂, N₂ and its mixtures calculated by PRO/II® with Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations are in sufficient agreement with the accurate diagrams calculated by REFPROP® using a.) Span and Wagner; Span b.) Lemmon, Jacobsen, Wagner and Yokozeki c.)

and Oliver Kunz, Reinhard Klimeck, Wolfgang Wagner, Manfred Jaeschke GERG 2004- equations. This verification is very useful for further process engineering analyses.

- In order to reduce the costly transport volume, CO₂ and CO₂/N₂ mixtures should be in dense liquid, supercritical or solid form. So the compression to a high pressure is necessary and very important for the following transport. Most important criteria for transportation of CO₂ mixture are 1) no free water; 2) limited concentration of contaminants (like SO₂, H₂S, O₂); 3) limited concentration of non-condensable gases (N₂, NO_x, CH₄, Ar and H₂).
- The impurities in multi-component CO₂ mixtures vary strongly according to different capture technologies: Reliable phase diagrams of different CO₂-N₂ mixtures like the ones presented above provide valuable guidelines for the selection and adjustment of the parameters of compression processes, pipeline transport processes and storage processes.

5. Acknowledgements

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References

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- [1] B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer (Eds.), IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage, Prepared by Working Group III of the Intergovernmental Panel on Climate Change, Cambridge University Press, United Kingdom & New York, NY, USA, available at http://www.ipcc.ch/publications_and_data/publications_and_data_reports_carbon_dioxide.htm.
- [2] L. Zhao, E. Riensche, R. Menzer, L. Blum, D. Stolten, A parametric study of CO₂/N₂ gas separation membrane processes for post-combustion capture, *J. Membr. Sci.*, 325 (2008) 284-294.
- [3] L. Zhao, E. Riensche, L. Blum, D. Stolten, Multi-stage gas separation membrane processes with post-combustion capture: energetic and economic analyses, *J. Membr. Sci.*, 359 (2010) 160-172.
- [4] M. Conturie, Reduction of Carbon Dioxide Emissions by Capture and Re-injection, *Renewable Energy Sources and Environment*, Vrnjacka Banja, Serbia, 17th-24th October, 2006.
- [5] E. deVisser, C. Hendriks, M. Barrio, M.J. MØlsvik, G. deKoeijer, S. Liljemark, Y. LeGallo, Dynamis CO₂ quality recommendations, *International Journal of Greenhouse Gas Control*, 2 (2008) 478-484.
- [6] NIST Reference Fluid Thermodynamic and Transport Properties - REFPROP, NIST Standard Reference Database 23, Version 8.0, E.W. Lemmon, M.L. Huber, and M.O. McLinden, Physical and Chemical Properties Division, 2007.
- [7] Span, R. and Wagner, W., "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa," *J. Phys. Chem. Ref. Data*, 25(6):1509-1596, 1996.
- [8] D.-Y. Peng, D.P. Robinson, A new two-constant equation of state, *Ind. Eng. Chem. Fundam.*, 15 (1976) 59-64.
- [9] Roland Span, Eric W. Lemmon, Richard T Jacobsen, Wolfgang Wagner, Akimichi Yokozeki, A Reference Equation of State for the Thermodynamic Properties of Nitrogen for Temperatures from 63.151 to 1000 K and Pressures to 2200 MPa, *J. Phys. Chem. Ref. Data*, Vol. 29, No.6, 2000 p1361-1433.
- [10] Oliver Kunz, Reinhard Klimeck, Wolfgang Wagner, Manfred Jaeschke, The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures, GERG TM15 2007, VDI Fortschritt-Berichte Nr. 557 (2007), ISBN: 978-3-18-355706-6 ISSN: 0178-9414.
- [11] PRO/II, Simulation Science Inc.(SimSci), <http://www.simsci.com>.
- [12] G. Soave, Equilibrium Constants from a Modified Redlich-Kwong Equation of State, *Chem. Eng. Sci.*, 27 (1972) 1197-1203.
- [13] M.L. Michelsen, Calculation of phase envelopes and critical points for multicomponent mixtures, *Fluid Phase Equilibria*, 4 (1980) 1-10.
- [14] API technical data book.
- [15] C. Holdack, Turbomaschinen für CCS-Prozesse, Kraftwerkskomponenten 2010 – Capture Ready? 4. Workshop Kraftwerkskomponenten, Gelsenkirchen, Germany, March 2nd, 2010.