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Evaluation of SPUNG[#] and other Equations of State for use in Carbon Capture and Storage modelling

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Abstract

In this work, Equations of State (EoS) relevant for carbon capture and storage modelling have been evaluated for pure CO_2 and CO_2-mixtures with particular focus on the extended corresponding state approach, SPUNG/SRK. Our work continues the search of an EoS which is accurate, consistent and computationally fast for CO_2-mixtures. These EoS have been evaluated: Soave-Redlich-Kwong (SRK), SRK with Peneloux shift, Peng-Robinson, Lee-Kesler, SPUNG/SRK and the multi-parameter approach GERG-2004. The EoS were compared to the accurate reference EoS by Span and Wagner for pure CO_2. Only SPUNG/SRK and GERG-2004 predicted the density accurately near the critical point (< 1.5 % Absolute Average Deviation (AAD)). For binary mixtures, Lee-Kesler and SPUNG/SRK had similar accuracy in density predictions. SRK had a sufficient accuracy for the gas phase below the critical point (<2.5%), and Peng Robinson had a decent accuracy for liquid mixtures (<3%). GERG-2004 was the most accurate EoS for all the single phase density predictions. It was also the best EoS for all the VLE predictions except for mixtures containing CO_2 and O_2, where it had deviations in the bubble point predictions (~20 % AAD). Even though multi-parameter EoS such as GERG-2004 are state-of-the-art for high accuracy predictions, this work shows that extended corresponding state EoS may be an excellent compromise between computational speed and accuracy. The SPUNG approach combines high accuracy with a versatile and transparent methodology. New experimental data may easily be taken into account to improve the predictive abilities in the two phase region. The approach may be improved and extended to enable applications for more difficult systems, such as polar mixtures with CO_2 and H_2O.

Keywords: SPUNG, Equation of State, extended corresponding state, GERG-2004, SRK, thermodynamics, PR, CO_2, CCS

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[#] State R&D Program for Utilization of Natural Gas (1987-1993)

Nomenclature

Symbols

α	Dimensionless Helmholtz energy [-]
a	Helmholtz energy [J/mol]
C	Arbitrary variable [-]
f	Compressibility function [-]
k_{ij}	Binary interaction parameter between component i and j [-]
N	Number of experimental points used in the regression
N_{exp}	Total number of experimental points
P	Pressure [MPa]
R	Universal gas constant [J/K mol]
T	Temperature [K]
V	Volume [m^3]
ω	Acentric factor [-]
x	Bubble point composition [-]
Y	Function to minimize in regression [-]
y	Dew point composition [-]
z	Composition [-]
Z	Compressibility factor [-]
θ	Temperature shape factor [-]
ϕ	Volume shape factor [-]

Subscripts/Superscripts

0	Standard conditions
exp	Experimental data
I	Component i
J	Component j
M	Mixture
R	Reduced variable
sat	Saturated pressure

1. Introduction

The focus on CO_2 capture, transport and storage (CSS) has not only increased in the general population, but also in the industry according to a survey by Hendriks et al [1]. Theoretical models predicting thermodynamic and transport properties are the fundament for most modelling of industrial processes. Choice of models and proper inclusion of interaction parameters for multicomponent mixtures may have a large impact on higher level modelling and thus on decisions about issues such as: process design, energy efficiency, economy and safety.

This work focuses on the study of Equations of State (EoS) applied for both pure CO_2 and multicomponent mixtures important for CCS. An EoS suitable for use in all the parts of the CCS-chain (capture, conditioning, transport and storage) should have accurate predictions with temperatures from 218 to 1620 K and pressures from ~ 0 to 50 MPa according to Li et al. [2,3]. Possible impurities in the CO_2 are: Ar, H_2O, H_2S, N_2, O_2, SO_2, NO_2, CH_4, CO, H_2 and amines. Depending on the process, many compositions are possible, and the impurities in the CO_2 may amount to a total of 25 mol % [2]. In this work, we will focus on the following impurities: CH_4, N_2 and O_2. These impurities are commonly encountered in CCS, and since CH_4 and N_2 are relevant components in gas processing, much thermodynamic data is available.

1.1. Equations of State

Several EoS have been evaluated for CO_2 rich mixtures in the literature, for instance cubic EoS such as Soave-Redlich-Kwong (SRK) and Peng-Robinson, corresponding state methods like Lee-Kesler and multiparameter wide range EoS like GERG-2004 and EoS with a theoretic foundation from statistical mechanics such as SAFT [2]. Cubic EoS have a simple structure and are still capable of giving reasonable results for the thermodynamic properties. They are known to have poor accuracy for liquid phase density calculations and for heats of evaporation and heat capacities in the vicinity of the critical point. It is common to use a correction factor to improve the density calculations of cubic EoS in the liquid-phase. For SRK, this correction factor is called Peneloux shift. More complex EoS typically give better results for the density, but not necessarily the Vapour-Liquid Equilibrium (VLE) where the cubic EoS are considered quite good. None of the EoS evaluated in the literature so far show any clear advantage in CCS applications for the calculation of all thermodynamic properties. This work continues the search for a proper EoS for CCS applications, with particular focus on the (State R&D Program for Utilization of Natural Gas) SPUNG EoS, and the concept of extended corresponding state methods [4].

The principle of corresponding states suggests that all substances display the same behaviour at the reduced state. A corresponding state EoS typically has one or more reference components described by very accurately reference equations. How various fluids and mixtures are related through the reference fluids in corresponding state EoS is typically described as a function of the compressibility factor through the following relation:

$$Z = f(V_R, T_R, \omega, \dots) \qquad \text{Eq.1}$$

Here, subscript R denotes reduced conditions, V is the volume and T is the temperature. Additional variables are the acentric factor, ω, and other parameters. Extended corresponding state EoS are recognized by the way they are formulated:

$$Z = f\left(\frac{V_R}{\phi}, \frac{T_R}{\theta}\right) \qquad \text{Eq. 2}$$

Here, ϕ and θ are the shape factors which take into account how the mixture in consideration differs from the reference fluid(s). EoS using the principle of extended corresponding states may differ in several ways, such as in the choice of reference components and reference EoS. Another major difference within the class of extended corresponding state methods is in the description of the shape factors. Several approaches have been suggested. Generalized formulas for the shape factors were for instance derived by Leach [5] and Rowlinson and Watson [6]. Later, Ely and co-workers developed the so called: "exact shape factor concept" in 1990 [7], where reference EoS could be used for each component to map the exact deviation between an arbitrary component and the reference component represented by the shape factors. Mixture rules were developed for various mixtures, also with complex dependencies. The advantage of using exact shape factors is that the best accuracy of any extended corresponding state approach could be obtained. One disadvantage however, is that a two-dimensional Newton-Raphson iteration has to be applied for each component to map the thermodynamic space onto the space of the reference component. Another challenge when reference EoS with different functional forms are used, is that the derived properties may be quite complex. For very accurate descriptions of fluids, the state-of-the-art approach today is to use a multi-fluid approximation such as in the reference EoS for natural gas, GERG-2004 [8]:

$$\frac{a_M(T,V,z)}{RT} = \alpha_M^0(T,V,z) + \sum_{j=1}^{C} z_j\, \alpha_{j,R}(T_R,V_R) + \Delta\alpha_{M,R}(T_R,V_R,z) \qquad \text{Eq. 3}$$

Here, a denotes the Helmholtz energy, α the dimensionless Helmholtz energy and subscript M denotes the mixture. $\Delta\alpha_{M,R}$ is the departure function which accounts for non-idealities of the mixture. A Challenge with a formulation such as the one above is that reference EoS for all the involved components are necessary. For some components, such as H_2S, SO_2 and NOx, reference EoS may not be available, and the formulation is thus limited. Another challenge is the range of validity of the reference EoS. For some components, for instance CO_2, the temperature range may be 216-900 K [8], while for O_2 on the other hand, the reference EoS in GERG-2004 is only valid from 54 - 300 K which may be too small for CCS applications. Even if the extrapolative properties of the reference equations are good, decent performance for mixtures requires experimental data. The industry has identified extrapolative abilities and relatively transparent implementations as important features for future EoS [1]. In this work, we will investigate the SPUNG EoS, which uses an alternative extended corresponding state approach less complex than the methodology which uses exact shape factors. The methodology is also less complex and computationally demanding than the multi-fluid approximation (Eq. 3).

If cubic EoS are used to calculate the shape factors, one may combine the strength of cubic EoS observed in VLE calculations with improved prediction of bulk properties obtained from a very accurate reference EoS. The initial work with the methodology leading to the SPUNG EoS was presented by Mollerup in 1980 [9]. Here, several two-constant EoS were used to obtain both shape factor correlations and reference potentials. The SPUNG EoS is based on an extended corresponding state principle using a very accurate MBWR EoS for the reference fluid and shape factors calculated by a cubic EoS [2]. The approach was presented in the PhD thesis by Jørstad in 1993 [4], and later published independently by Mollerup in 1998 [10]. The methodology has a foundation in statistical mechanics and the shape factor correlation may be easily obtained in a computer implementation, if the cubic EoS has already been implemented. Any mixing rules may be applied, such the mixing rules for polar mixtures presented by Huron and Vidal [11] which showed a promising performance for CO_2-H_2O-CH_4 mixtures in a study by Austegard et al [12]. In the SPUNG approach, any reference fluid and reference equation may be chosen. In this work, propane has been used as reference fluid as described by the very accurate MBWR equation by Younglove and Ely [13]. The SPUNG EoS with methane as the reference fluid is identical to the CSP/cubic EoS explained in the book by Michelsen and Mollerup [14].

In this work, several EoS will be compared to the accurate reference EoS by Span and Wagner [15] for pure CO_2 and experimental data for mixtures. Based on this, an assessment will be made of the ability of the different EoS to predict important properties for mixtures relevant for CCS.

2. Methodology

A regression of interaction parameters was conducted before the comparison to compare all the EoS on equal terms. The regression was based on VLE data for binary CO_2-rich mixtures found and evaluated in the paper by Li et al. [2]. Before the regression, the VLE data were carefully evaluated by comparing similar data and also comparing the data to the performance of SRK. If experimental points displayed inconsistent behaviour, or large deviations from SRK, which could not be properly explained, the experimental points were removed. The following objective function, Y, was minimized to obtain the binary interaction parameters:

$$Y(k_{ij}) = \sum_{ij} \sum_{r=1}^{N} (x_r - x_{exp,r})^2 + (y_r - y_{exp,r})^2 \qquad \text{Eq. 4}$$

Here, x denotes the liquid mole fraction and y denotes the mole fraction in the vapour phase. The mean square deviation between the bubble and dew points was summarized for all the involved components i and j and all the most accurate experimental points, N. Binary interaction parameters were regressed for all components investigated in this paper. No regression was necessary for GERG-2004. After the regression, the performance of the EoS was tested with the available experimental data collected and evaluated by Li et al [2]. The deviation between the experiments and the predictions will be evaluated based on the Absolute Average Deviation (AAD) defined as:

$$AAD(C, \%) = \frac{100}{N_{exp}} \sum_{r=1}^{N_{exp}} \frac{|C_r - C_{exp,r}|}{C_{exp,r}} \qquad \text{Eq. 5}$$

3. Results for pure CO_2, a comparison with the reference EoS by Span and Wagner

Since mixtures in CCS will have CO_2 as the main component, an EoS for CCS applications must be able to give accurate predictions also for pure CO_2. To assess the performance of the EoS investigated in this work, they have thus been compared to the very accurate pure component EoS by Span and Wagner first presented in 1996 (SW) [15], which replaced the earlier IUPAC equation for CO_2 by Angus et al [16] as the reference EoS. SW is explicit in the Helmholtz free energy, and has been optimized both with respect to parameters and mathematical form. The EoS is valid for temperatures from 216 - 1100 K and pressures up to 800 MPa, covering almost the entire CCS region. The estimated uncertainties of the SW equation range from ± 0.03 % to ± 0.05 % in the density and ± 0.15 % to ± 1.5 % in the isobaric heat capacity in the region with pressures up to 30 MPa and temperatures up to 523 K. Table 1 shows a comparison of several EoS with SW. 1000 random temperature/pressure points in the liquid, supercritical, vapour and critical region have been generated and the density and isobaric heat capacity have been compared. The regions chosen for the comparison tests have been defined as:

Supercritical region:	$223 < T < 423$ K and $7.4 < P < 15.0$ MPa, critical region omitted
Vapour region:	$223 < T < 423$ K and $1.0 < P < 7.4$ MPa, critical region omitted, $P < P_{sat}$
Liquid region	$223 < T < 304$ K and $1.0 < P < 7.4$ MPa, critical region omitted, $P > P_{sat}$
Critical region	$300 < T < 308$ K and $7.0 < P < 7.8$ MPa

Table 1 shows that SRK and PR are reasonable for predictions of the density and the specific heat capacity in the vapour region whereas deviations above 10 % should be expected in the liquid and super critical regions for the density. The Peneloux shift improves the density of SRK in all regions, but the deviations are still above 10% in the critical region. SPUNG/SRK and Lee-Kesler display similar performance for density predictions in the liquid phase and supercritical area (< 2), but only GERG-2004 and SPUNG/SRK manage to give accurate density predictions in the vicinity of the critical point. GERG-2004 is as expected very accurate for pure CO_2, since the same experimental data were used in the regression of GERG-2004 as for SW. GERG-2004 and SPUNG/SRK are the most accurate EoS for predictions of the specific heat capacity in the supercritical and the vapour phase area, but SRK is surprisingly accurate for heat capacity predictions in the liquid phase area. Up to 6 % deviations should be expected for SPUNG/SRK, PR and Lee-Kesler here. The specific heat capacity in the liquid phase depends on the accuracy of the ideal gas heat capacity contribution. Both a third degree polynomial in the temperature [17] and the hyperbolic DIPPR expression [18] were tried without any improvement in the liquid phase predictions of the specific heat capacity with neither SPUNG/SRK nor Lee-Kesler. The performance of the density calculations of all the EoS for pure CO_2 is displayed in Figure 1(A).

Table 1 Comparison with the Span and Wagner reference EoS for pure CO_2

	AAD Density				**AAD Specific heat capacity**			
EoS	**Super**	**Vapour**	**Liquid**	**Critical**	**Super**	**Vapour**	**Liquid**	**Critical**
SRK	7.58	1.01	8.09	14.96	4.48	1.79	2.45	21.00
SRK Peneloux	3.88	0.40	0.82	11.34	4.48	1.79	2.45	21.00
Peng Robinson	2.71	1.44	4.08	7.84	5.06	1.91	5.35	20.28
Lee-Kesler	1.07	0.46	1.99	3.67	4.99	2.64	6.49	10.92
SPUNG/SRK	1.27	0.20	1.70	1.00	1.95	0.62	5.93	3.57
GERG-2004	0.01	0.01	0.00	0.05	0.11	0.07	0.34	0.68

4. Results for CO_2 with impurities

CO_2 captured from an energy conversion process will always contain impurities and even small amounts of impurities (< 5 %) may affect the thermodynamic properties of the CO_2 mixture substantially [2,3]. To use the reference EoS for pure CO_2 discussed in the previous section, SW, will thus be insufficient for mixtures. In this section, the predictive ability of several EoS will be discussed for the density and VLE properties of mixtures. All the experimental data used in this work have been collected, evaluated and presented previously by Li et al. in 2011 [2].

4.1. Densities of CO_2 with impurities

Accurate density predictions are important in most parts of the CCS chain. An inaccurate prediction of the density may for instance give deviations in the estimation of pressure drops in pipeline-transport, which again may lead to the wrong design of pumps and compressors. Figure 1(B) shows how predicted densities compare to gas phase experiments for CO_2-CH_4 mixtures close to and above the critical point. GERG-2004 is the most accurate EoS and forms an almost straight line with a 2.5 % outlier at ~10500 mol/m^3. SPUNG/SRK scatters somewhat more around the line and reproduces the outlier by GERG-2004, which means that the outlier is most likely an experimental point with poor accuracy. The figure also shows that SRK underpredicts the density, in particular above the critical point. Table 2 gives the AAD of SRK, Lee-Kesler, SPUNG/SRK and GERG-2004 for multiple mixtures with CO_2, N_2, CH_4 and O_2. For these mixtures, typical AAD for gas phase predictions with cubic EoS is 1 - 3 %, 0.5 - 1.6 for Lee-Kesler, 0.5 - 0.8 for SPUNG/SRK and 0.1 - 0.4 for GERG-2004. For density calculations, GERG-2004 predicts within the limits of the experimental accuracy. Consider for instance the highly accurate experimental data by Seitz et al. [19]. Here, the author has reported uncertainties in the densities which are in general less than 10 - 3 cm^3/m^3.

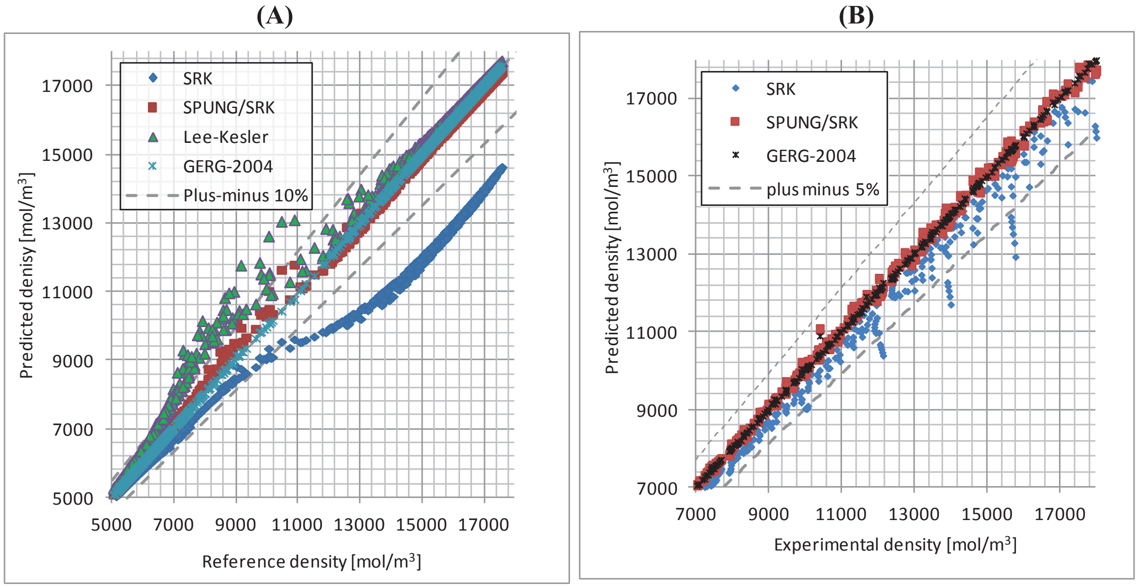

Figure 1 Comparison of density predictions of different EoS with: (A): The reference EoS by Span and Wagner for pure CO_2 and (B): Experimental data for CO_2-CH_4 mixtures [2]

If all the experimental data by Seitz et al. deviated with 10^{-3} cm^3/m^3, the calculated AAD would be 0.34 %, which is close to the AAD of GERG-2004 of 0.38 %. The AAD of SPUNG/SRK is also very low (0.68 %). The regression of GERG-2004 already contains binary data by Seitz et al. [8], and many other sources [8]. Except for the ternary mixture CO_2-CH_4-N_2, SPUNG/SRK shows little advantage over Lee-Kesler for binary mixtures and density calculations. The liquid phase predictions are less accurate than the gas phase predictions for all the EoS, with SRK being least accurate with an AAD of 11 - 12 %.

A comparison of Table 1 and 2 shows that the improvement in the liquid phase density predictions with SRK + Peneloux shift is smaller for mixtures than for pure CO_2. PR is surprisingly accurate for the liquid phase densities of the mixtures, but displays larger deviations at high pressures (P>20 MPa).

4.2. Vapour liquid equilibrium of CO_2 mixtures with impurities

VLE calculations are important in two phase flow simulations, both to quantify how much gas and liquid there is, and the composition of the respective phases. Prediction of the density in the two phase area for instance, requires both accurate VLE and density predictions. The VLE predictions by SRK and SPUNG/SRK depend largely on a proper regression of interaction parameters. This regression has thus been carried out before the evaluation as outlined in Section 2. Figure 2 shows the phase envelopes of the CO_2-N_2 mixture (A) and the CO_2-O_2 mixture (B). Here, GERG-2004 is the best EoS for the CO_2-N_2 mixture (Figure 2 (A)), followed closely by SRK and SPUNG/SRK, whereas it fails to predict the bubble points of the CO_2-O_2 mixture accurately (Figure 2 (B)).)

Table 2 The AAD of several EoS compared with experimental density data from [2].

	AAD of EoS [%]					
Mixtures:	**SRK**	**SRK + Peneloux**	**Lee-Kesler**	**Peng Robinson**	**SPUNG /SRK**	**GERG -2004**
CO_2-CH_4 gas	2.58	1.43	0.51	2.01	0.55	0.23
CO_2-CH_4 liquid	11.00	6.86	3.44	2.48	2.89	1.67
CO_2-N_2-gas	1.34	0.81	0.66	1.63	0.76	0.15
CO_2-N_2-liquid	12.37	8.00	2.91	2.88	3.44	2.97
CO_2-N_2-CH_4 gas	2.12	1.88	1.63	4.57	0.68	0.38

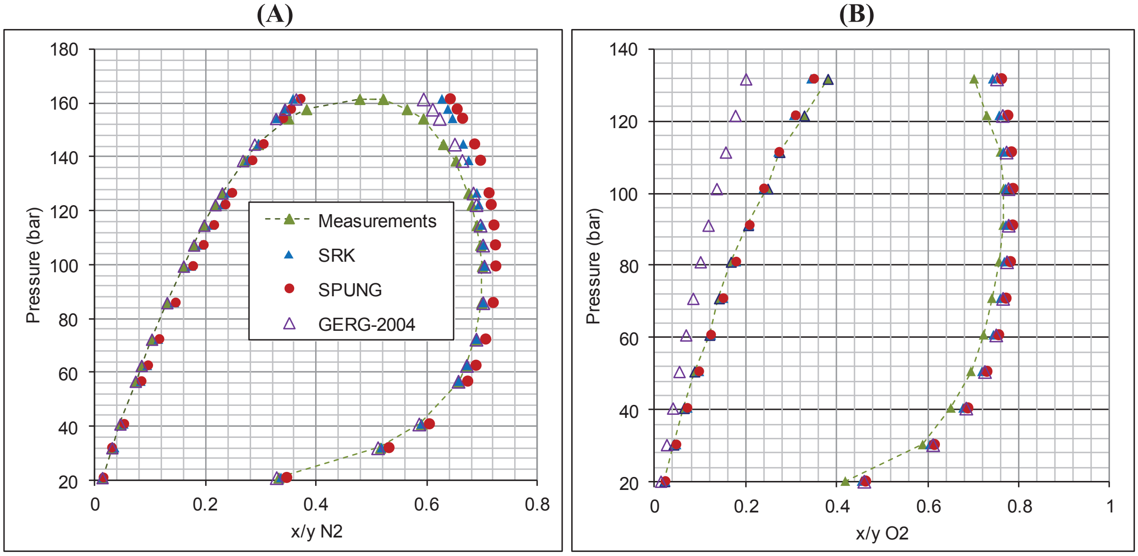

Figure 2 Comparison of the VLE predicted by several EoS with experimental data for (A): CO_2-N_2 at 240 K and (B): CO_2-O_2 at 233.15 K

Table 3 shows how accurately the EoS predict the bubble point compositions, x, and the dew point compositions, y, at a specified temperature and pressure. The AAD of these predictions is an average for all involved components. PR is omitted from the table because the performance is almost identical to the performance of SRK. Because some compositions may be very small (~0.001), a small absolute deviation may lead to a large deviation in %. The numbers in Table 3 should therefore be used only to compare the different EoS, and not as a stated accuracy. GERG-2004 is by far the best EoS for CO_2-CH_4 and CO_2-N_2. All the EoS display similar performance for N_2-O_2. GERG-2004, however, fails to predict the bubble-points of CO_2-O_2 mixtures accurately according to the bold numbers in Table 3. This is seen in comparisons with independent experimental data for both binary and ternary mixtures. All experimental data which deviate more than 20 % from GERG-2004 are classified as secondary data and rejected in the regression algorithm [9]. This is the reason why the dataset by Fredenslund and Sather [20] has been included in the evaluation, but none of the data has been used in the regression of GERG-2004. If GERG has no regressed interaction parameters or complementary experimental data for the CO_2-O_2 mxiture, we question the use of GERG-2004 as a performance indicator for these experimental data. Due to a rejection of the only binary VLE experiments for the CO_2-O_2 mixture, GERG-2004 will have inaccurate predictions of other mixtures with substantial amounts of CO_2 and O_2 in the two phase area. A comparison of density predictions in the two phase area for the CO_2-N_2-O_2 mixture with the experimental data by Muirbrook and Prausnitz [21] shows an AAD in the gas/liquid phase area of (2.7/12.2) for SRK, (2.0/1.3) for SPUNG/SRK and (50.9/36.1) for GERG-2004. Here, a weakness of the multi-parameter EoS methodology becomes visible. GERG-2004 will be accurate for the mixtures and components where there is experimental data available. What about the mixtures without any decent experimental data? What if new experimental data is available in two years? To implement these data into the GERG-2004 equation, requires additional regression, which is typically too complex to carry out for the industry and most research institutes. The advantage with the other EoS investigated is that they may easily be updated to take into account new VLE data.

Table 3 The AAD of several EoS compared with experimental VLE data from [2].

	AAD of EoS [%]					
Mixtures:	**SRK**		**SPUNG/SRK**		**GERG-2004**	
	x	y	x	y	x	y
CO_2-CH_4	8.3	7.3	8.1	9.0	6.0	4.4
CO_2-N_2	6.5	3.9	6.8	9.3	2.9	2.1
CO_2-O_2	6.9	7.3	6.3	8.6	**23.7**	7.3
N_2-O_2	3.7	3.6	3.3	2.7	3.1	2.8
CO_2-N_2-O_2	5.33	1.92	5.7	5.1	**18.4**	2.6

5. A comparison of runtime speed for the EoS

In has been shown in the previous section that for most mixtures and properties investigated in this work, GERG-2004 is the most accurate EoS followed by SPUNG/SRK, Lee-Kesler and then the cubic EoS. Another important property is the runtime speed. The runtime speed will of course depend on the implementation, but to have a coarse comparison, the implementations available at SINTEF Energy Research have been compared. For 10 000 random calculations of density, enthalpy and entropy in the liquid, vapour and the supercritical regimes of a three component mixture with CO_2, SRK used a total of 0.3 sec, Lee-Kesler 1.0 sec, SPUNG/SRK 1.3 sec and GERG-2004 12.1 sec. This shows that if the thermodynamic calculations are the time limiting factors of a model, the runtime may in the worst case scenario be increased by 40 times if GERG-2004 is used in stead of SRK.

6. Conclusions and future work

In this work, it has been shown that the SPUNG methodology is applicable for the prediction of density and VLE properties of both pure CO_2 and mixtures encountered in the CCS-chain, also in the vicinity of the critical point. GERG-2004 was, however, the most accurate EoS for all the investigated mixtures except those containing CO_2-O_2 in the two-phase area, where it displayed an AAD of ~20%. Other popular EoS such as SRK, PR, SRK+ Peneloux shift and Lee-Kesler failed to predict the CO_2 density to a decent accuracy near the critical point (AAD>3.5%). Except for GERG-2004, more work should be done to resolve the inaccurate heat capacity predictions of many of the EoS in the liquid phase area of pure CO_2 (>5%). For the SPUNG approach, other reference fluids and more accurate reference EoS than the MBWR equation should be evaluated. An advantage with the SPUNG/SRK approach is that the Huron-Vidal mixing rules may be applied, which have shown to be very promising for polar CO_2 mixtures with water. The multi-parameter approach has been generally accepted as the state-of-the-art methodology for thermodynamic calculations with high accuracy. This work shows that the extended corresponding state methodology is still valuable. It combines high accuracy with a versatile and transparent methodology. The computational speed is acceptable and it predicts accurately, also in vicinity of the critical point. In contrast to the multi-parameter approach, new VLE-data and new components may easily be taken into account.

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