Accurate and Predictive Mixture Models Applied to Mixtures with CO₂

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ABSTRACT
Supercritical CO₂ as a working fluid offers distinct advantages for power cycles, such as a comparably low critical temperature and pressure. However, the favorable properties of supercritical CO₂ could potentially be enhanced by blending CO₂ with suitable additives. In order to find promising additives for CO₂, a theoretical screening seems to be most feasible, as extensive experimental studies would be very time-consuming. For this purpose, a mixture model is needed that on the one hand yields good predictive results and on the other hand should be as accurate as possible. Therefore, in this work the performance of the multi-fluid mixture model combined with UNIFAC and with different versions of COSMO-SAC is evaluated for mixtures containing CO₂. The results are compared to results calculated with accurate multi-fluid mixture models. It is demonstrated that the predictive results for phase equilibria as well as for homogeneous densities of the multi-fluid mixture model combined with UNIFAC and COSMO-SAC are superior to the results of the multi-fluid mixture model with standard mixing rules. However, it can also be seen that the parameters of UNIFAC and COSMO-SAC should be readjusted in order to further improve the results.

INTRODUCTION
Thermophysical properties of pure components and mixtures are important for the design and optimization of various processes in power and process engineering. The most accurate source of thermophysical property data are highly-accurate multiparameter equations of state. These equations of state are capable of representing all experimental data within the experimental uncertainty. The reference equation of state for carbon dioxide (CO₂) [1] is an example for such an equation of state.

If properties of mixtures are required, the multi-fluid mixture model [2–4] can be used. This model allows for a very accurate representation of experimental data for mixtures, if the model parameters are fitted to experimental data. However, the predictive capabilities of this model are rather limited. Therefore, Jäger et al. [5,6] have developed a theoretically based departure function for the multi-fluid mixture model, which allows for the combination of the multi-fluid mixture model with the predictive excess Gibbs energy models UNIFAC and COSMO-SAC.

The basic idea of the UNIFAC model [7] is to describe the interactions of structural groups of molecules instead of modeling molecule-molecule interactions. In this way, the interactions of structural groups can be fitted to experimental data for well-studied mixtures and then be transferred to mixtures for which no experimental data exist. While UNIFAC is capable of describing fluid mixtures well and yields good predictive results, it also has some shortcomings. Many adjustable parameters need to be fitted to experimental data. Furthermore, it might happen that molecules cannot be subdivided into structural groups that exist in UNIFAC. In these cases, UNIFAC cannot be applied.

In order to overcome these shortcomings, the more predictive model COSMO-SAC [8], which only has a few substance-independent parameters, has been combined with the multi-fluid mixture model [6]. COSMO-SAC depends on quantum mechanical calculations, which need to be performed in order to calculate the screening charge densities on the molecular surface.

Hence, COSMO-SAC considers the interactions of charged surface segments instead of modeling the interactions of structural groups of molecules. Processes with supercritical CO₂ in thermal power generation offer some distinct advantages over currently used technologies, see, for example, Gampe et al. [9]. The favorable properties of supercritical CO₂ can potentially be further improved by considering mixtures of CO₂ with other substances as working fluid.

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fluids instead of using CO$_2$ as a pure substance.

As an example, the critical point can be shifted to other temperatures and pressures by mixing CO$_2$ with other substances. By this, the supercritical state could already be reached at lower temperatures and pressures compared to the critical temperature $T_c = 304.128$ K and critical pressure $p_c = 7.3773$ MPa of pure CO$_2$ (values taken from the reference equation of state for CO$_2$ by Span and Wagner [1]). Figure 1 shows parts of the vapor pressure curve of pure CO$_2$ calculated with the reference equation of state for CO$_2$ by Span and Wagner [1]. For comparison, Figure 1 shows parts of the bubble and the dew line for a binary mixture of $x_{CO_2} = 0.9$ and $x_{C_2H_6} = 0.1$ calculated with the mixture model for CO$_2$ and C$_2$H$_6$ by Kunz and Wagner [4].

![Figure 1](https://via.placeholder.com/150)

**Figure 1:** Calculated vapor pressure curve and critical point of pure CO$_2$ (solid blue line) in comparison to calculated dew and bubble lines and the mixture critical point of a binary mixture of 90% CO$_2$ with 10% C$_2$H$_6$ (dashed red line).

This indicates that the performance of power processes (thermal efficiency, net power etc.) could be optimized by finding suitable additives for CO$_2$. Since a lot of different substances can be considered as additives and various mixture compositions need to be investigated, an extensive experimental investigation for suitable additives does not seem feasible. Therefore, promising additives could be identified by a theoretical screening. For this purpose, mixture models will be needed which on the one hand allow for the use of reference equations of state (such as the reference equation of state for CO$_2$ by Span and Wagner [1]) and on the other hand can be used well predictively.

The multi-fluid mixture model originally proposed by Lemmon and Tillner-Roth [2] (which will be introduced in more detail in the next section) allows for the use of reference equations of state in order to model pure fluids. The model is also capable of representing experimental data for mixtures well if the adjustable parameters of the model are fitted to experimental data. However, the predictive capabilities of the multi-fluid mixture model are very limited, which has been shown by Jäger et al. [5] and will be discussed in more detail later in this work.

Other equations of state with good predictive capabilities for modeling thermophysical properties of mixtures (vapor-liquid equilibria, liquid-liquid equilibria, excess enthalpies, etc.) are the well-known combinations of cubic equations of state with excess Gibbs energy models ($g^E$-models). Sophisticated examples for combinations of cubic equations of state with the $g^E$-model UNIFAC [7] are the predictive Soave-Redlich Kwong equation of state (PSRK) [10–12] and the volume-translated Peng-Robinson group contribution equation of state (VTPR) [13–15]. The disadvantage of these models is that only cubic equations of state can be used to model pure fluids and mixtures, which significantly limits the achievable accuracy. This is illustrated in Figure 2 by comparing highly-accurate experimental data on saturated liquid densities by Duschek et al. [16] (overall combined standard uncertainty smaller than 0.015% for temperatures below 295 K. The uncertainty rises to 0.2% close to the critical temperature) to calculated saturated liquid densities from different models.

![Figure 2](https://via.placeholder.com/150)

**Figure 2:** Deviations of experimental saturated liquid density data for CO$_2$ (symbols, Duschek et al. [16]), of the PSRK (solid black line), of the PR (dashed red line), and of the VTPR (dash-dotted blue line) from the reference equation of state for CO$_2$ [1]. The reference equation for CO$_2$ is the zero line and deviations of the experimental data and the other models from the reference equation of state are displayed.

The reference equation of state for CO$_2$ is capable of representing the experimental data within the experimental uncertainty, while the PSRK, the original Peng-Robinson [17], and the Peng-Robinson with volume-translation applied at the triple point temperature of CO$_2$ yield maximum deviations from the experimental data of about $-23.5\%$, $-16\%$, and $-18\%$, respectively (see Figure 2). Deviations of the PSRK and volume-translated Peng-Robinson to experimental data are especially high in the vicinity of the critical point of CO$_2$.

In order to overcome the shortcomings of the aforementioned models, we recently proposed a combination of the multi-fluid
mixture model with the $g^E$-models UNIFAC [5] and COSMO-SAC [6]. In this work, we extend this model by combining the multi-fluid mixture model with improved versions of the COSMO-SAC model, which consider different types of hydrogen-bonding interactions [18] and dispersive interactions [19]. Furthermore, the predictive capabilities of the combination of the multi-fluid mixture model with $g^E$-models with regard to the description of properties in the homogenous phase are investigated for the first time in this work.

**MODEL DESCRIPTION**

Lemmon and Tillner-Roth [2] proposed the multi-fluid mixture model in 1999. Subsequently, the model was further developed and applied to typical natural gas mixtures by Kunz and Wagner [4] and to typical mixtures relevant for carbon capture and storage (CCS) by Gernert and Span [20]. This model is an extended corresponding states model and reads

$$\alpha(\tau, \delta, \bar{x}) = \sum_{i=1}^{N-1} x_i \left[ \alpha_{\text{ref}}^0(\rho, T) + \ln(x_i) + \alpha_{\text{ref}}^0(\delta, \tau) \right] + \sum_{i=1}^{N} x_i x_j F_{ij} \beta_{ij}^*(\tau, \delta).$$  

(1)

The meaning of the symbols in Equation (1) is explained in the nomenclature. The reduced density $\delta$ can be written as

$$\delta = \rho / \rho_r$$  

(2)

and the inverse reduced temperature is defined as

$$\tau = T_r/T.$$  

(3)

The quantity $\rho_r$ is the reducing density and the quantity $T_r$ is the reducing temperature. These reducing functions are defined in the following way [4]:

$$T_r = \sum_{i=1}^{N} x_i x_j \beta_{ij} \gamma_{ij} \rho_{T,ij}^{\frac{1}{2}} x_i \gamma_{ij} \left( T_{c,ij} \cdot T_{c,ij} \right)^{0.5}$$  

(4)

and

$$\frac{1}{\rho_r} = \sum_{i=1}^{N} x_i x_j \beta_{ij} \gamma_{ij} \rho_{T,ij}^{\frac{1}{2}} \frac{x_i + x_j}{\rho_{c,ij} x_i + x_j} \left( \frac{1}{\rho_{c,ij} + \rho_{c,ij}} \right)^{3}.$$  

(5)

The reducing temperature $T_r$ contains the two adjustable parameters $\beta_T$ and $\gamma_T$ and the reducing density $\rho_r$ contains the two adjustable parameters $\beta_c$ and $\gamma_c$ for each combination of components $i$ and $j$. Typically, these four parameters of the mixture model are fitted to experimental data. If sufficient experimental data of good quality are available, additionally the binary departure function $\alpha_{ij}^*$ (see Equation (1)) can be established. This function does not have a fixed structure but consists of combinations of polynomial, exponential, and special terms that have to be determined during the fitting procedure, see [4]. If no experimental data exist for a mixture of interest, the multi-fluid mixture model according to Equation (1) can be used predictively by neglecting the binary departure function ($\alpha_{ij}^* = 0$) and applying standard mixing rules for the reducing functions, such as linear mixing rules for the reduced temperature

$$T_r = \sum_{i=1}^{N} x_i T_{c,ij}$$  

(6)

and the reduced density

$$\frac{1}{\rho_r} = \nu_r = \sum_{i=1}^{N} x_i \nu_{c,ij} = \sum_{i=1}^{N} x_i \frac{1}{\rho_{c,ij}}.$$  

(7)

This predictive mixture model will be referred to as “LIN-MOD” in the following.

It has been demonstrated in our previous work [5,6] that the multi-fluid mixture model with linear mixing rules for the reducing functions (LIN-MOD) does not yield good predictive results for phase equilibria of binary mixtures. Therefore, we have proposed a combination of the multi-fluid mixture model with excess Gibbs energy models, which reads

$$\alpha(\tau, \delta, \bar{x}) = \sum_{i=1}^{N} x_i \left[ \alpha_{\text{ref}}^0(\rho, T) + \ln(x_i) + \alpha_{\text{ref}}^0(\delta, \tau) \right]$$

$$+ \ln(1 + b \rho_p) \left[ \frac{g_{\text{ref}}^E}{RT} \right]$$

$$- \sum_{i=1}^{N} x_i \left[ \alpha_{\text{ref}}^* \left( \delta_{\text{ref}}, \tau \right) - \alpha_{\text{ref}}^* \left( \delta_{\text{ref}}, \tau \right) \right].$$

(8)

with

$$\frac{1}{\rho_{\text{ref}}} = \sum_{i=1}^{N} x_i \nu_{\text{ref}}^{\frac{1}{3}} p_0,$$  

(9)

with $\nu_{\text{ref}}^{\frac{1}{3}}$ denoting the molar volume of the saturated liquid of component $i$ at the reference pressure $p_0$.

In this work, the residual excess Gibbs energy $g_{\text{ref}}^E$ is either calculated from UNIFAC [5,7] or different versions of COSMO-SAC [6,8]. While in our previous work [6] only the original version of COSMO-SAC [8] has been combined with the multi-fluid mixture model, in this article we investigate the performance of improved versions of COSMO-SAC [18,19] when combined with the multi-fluid mixture model. The combination of the multi-fluid mixture model with UNIFAC will be referred to as “UNI-MOD” and the combination with the original version of COSMO-SAC [8] will be referred to as “COS1-MOD”. The combinations with the modification of COSMO-SAC considering different strengths of donor-acceptor surface segments [18] will be referred to as “COS2-MOD”. Finally, the combination with the COSMO-SAC model considering dispersive interactions [19] will be referred to as “COS3-MOD”.

For all calculations presented in this work, the reference equations of state for pure components have been used. For carbon dioxide (CO$_2$), the multiparameter equation of state by Span and Wagner was used [1]. For ethane (C$_2$H$_6$), the multiparameter equation of state by Bücker and Wagner was applied [21] and for methane (CH$_4$) the multiparameter equation of state by Setzmann and Wagner [22] was used. The database of Mullins et al. [23] containing COSMO calculations for 1432 components has been used to calculate sigma-profiles needed for
COS1-MOD, COS2-MOD, and COS3-MOD. For UNI-MOD, the UNIFAC parameters of the VTPR have been used.\[13,14\]. The multi-fluid mixture model (Equations (1) and (8)) is a fundamental equation formulated in the dimensionless Helmholtz energy $\alpha$. Therefore, thermophysical properties can be calculated from this model by combining derivatives of the model with respect to its independent variables \[4,24\]. For example, the pressure can be calculated from this model in the following way

$$p = \rho RT \left( 1 + \delta \left( \frac{\partial K}{\partial \delta} \right) \right)$$

(10)

All of the described mixture models are implemented in the thermophysical property software TREND \[25\]. The necessary derivatives for the theoretically based departure function in combination with UNIFAC are supplied in the supplementary material of the article by Jäger et al. \[5\]. The required derivatives for the models “COS1-MOD”, “COS2-MOD”, and “COS3-MOD” have been calculated numerically by the central difference scheme. Phase equilibrium calculations have been performed in TREND \[25\] with the algorithms described by Gernert et al. \[26\] and Jäger \[27\].

**PREDICTIVE RESULTS FOR PHASE EQUILIBRIA**

In our previous works \[5,6\], we have investigated the representation of phase equilibria of binary mixtures of CO$_2$, ethane, propene, ethanol, and benzene over a broad temperature range. It was found that the combination of the multi-fluid mixture model with $g^p$-models yields better predictive results for phase equilibria than the multi-fluid mixture model with standard mixing rules (LIN-MOD). In this work, the predictive capabilities of the models will be evaluated exemplarily for a binary mixture of CO$_2$ + C$_2$H$_6$ on an isotherm of $T = 253$ K. Figure 3 shows the experimental vapor-liquid equilibrium (VLE) data of Nagahama et al. \[28\] (symbols) for a binary mixture of C$_2$H$_6$ + CO$_2$ in comparison to the multi-fluid mixture model with adjusted reducing function parameters by Kunz and Wagner \[4\] (solid blue line, no binary specific departure function was fitted for this binary mixture by Kunz and Wagner \[4\], i.e., $\alpha_{ij}^i = 0$). Furthermore, Figure 3 shows the results of the predictive multi-fluid mixture model with linear mixing rules according to Equations (6) and (7) without a departure function (dashed red line, LIN-MOD). It can be seen that the multi-fluid mixture model with adjusted parameters is capable of describing the azeotropic behavior of the binary mixture CO$_2$ + C$_2$H$_6$ correctly, while LIN-MOD is not capable of qualitatively correctly describing the behavior of this mixture. Note that Kunz and Wagner have adjusted the reducing function parameters for the binary mixture of CO$_2$ + C$_2$H$_6$ to experimental VLE data.

Figure 3: Experimental VLE data (symbols, Nagahama et al. (1974) \[28\]) for a binary mixture of CO$_2$ + C$_2$H$_6$ on an isotherm of $T = 253$ K and vapor-liquid equilibria calculated with the empirical multi-fluid mixture model by Kunz and Wagner \[4\] (GERG-2008, solid blue line) and with LIN-MOD (dashed red line).

COS3-MOD combines the multi-fluid mixture model with the improved version of COSMO-SAC considering dispersive interactions \[19\]. Hsieh et al. \[19\] proposed to consider the contribution to the activity coefficient due to dispersive forces with a one-constant Margules equation, depending on a molecular dispersion parameter $\varepsilon_{\text{molecule}}$. The dispersion parameters for methane and ethane ($\varepsilon_{\text{CH}_4}/k_B = \varepsilon_{\text{C}_2\text{H}_6}/k_B = 115.7023$ K) can be calculated from the atomic contributions provided by Hsieh et al. \[19\] in Table 2 of their article. The dispersion parameter for CO$_2$ can in principle also be calculated from these atomic contributions. However, Hsieh et al. \[19\] have not considered CO$_2$ in their fitting procedure and the resulting $\varepsilon_{\text{CO}_2}/k_B = 14.6531$ K does not yield good results for phase equilibria of mixtures with CO$_2$. Therefore, in this work $\varepsilon_{\text{CO}_2}/k_B$ has been manually adjusted (by trial-and-error) to the phase equilibria of the binary CO$_2$ + C$_2$H$_6$ mixture in order to obtain a value for $\varepsilon_{\text{CO}_2}/k_B$ which allows for a better representation of phase equilibria of mixtures of CO$_2$ with hydrocarbons. It was found that $\varepsilon_{\text{CO}_2}/k_B = 85$ K yields a good representation of phase equilibria for the binary mixture of CO$_2$ + C$_2$H$_6$.

Figure 4 shows the predictive results of the models UNI-MOD (using the VTPR parameters of UNIFAC, see \[13,14\]), COS1-MOD, COS2-MOD, and COS3-MOD. LIN-MOD is also shown for comparison.
While LIN-MOD is not capable of representing the azeotropic behavior of the binary mixture of CO$_2$ + C$_3$H$_6$ correctly, all of the combinations of the multi-fluid mixture model with $g^E$-models predict the mixture behavior qualitatively correctly. UNI-MOD with VTPR parameters for UNIFAC ([13,14]) slightly overpredicts the bubble and dew point pressures as well as the pressure at the azeotropic point. A clear improvement can be seen for the different versions of COSMO-SAC combined with the multi-fluid mixture model. COS1-MOD qualitatively correctly describes the azeotropic behavior of the mixture, however, the calculated dew and bubble point pressures are underestimated by this model. COS2-MOD yields slightly better results than COS1-MOD. COS3-MOD describes the experimental data quantitatively well, however, note that $\epsilon_{CO_2}/k_B$ has been adjusted by trial-and-error in order to improve the description of the experimental VLE data for this mixture. However, this demonstrates that the performance of COS3-MOD could be significantly improved by fitting the molecular dispersion parameters to experimental data.

**PREDICTIVE RESULTS FOR DENSITIES**

Predictive results of the combination of multi-fluid mixture models with $g^E$-models for properties in the homogeneous phase have not been investigated in our previous works. Therefore, here we present calculated densities in the homogeneous phase for different predictive and empirical models for the binary mixtures of CO$_2$ + CH$_4$ and CO$_2$ + C$_3$H$_6$. Accurate experimental density data in the homogeneous phase for these mixtures by Jaeschke et al. [29,30] are available and have been used for the development of the GERG-2004 and GERG-2008 equation of state, see Kunz et al. [3] and Kunz and Wagner [4], respectively. Figure 5 shows relative deviations of the experimental density data by Jaeschke et al. [29,30] for a binary mixture of CO$_2$ + CH$_4$ on an isotherm of $T = 290$ K from calculated data with different models.

While LIN-MOD is not capable of representing the azeotropic behavior of the binary mixture of CO$_2$ + C$_3$H$_6$ correctly, all of the combinations of the multi-fluid mixture model with $g^E$-models predict the mixture behavior qualitatively correctly. UNI-MOD with VTPR parameters for UNIFAC ([13,14]) slightly overpredicts the bubble and dew point pressures as well as the pressure at the azeotropic point. A clear improvement can be seen for the different versions of COSMO-SAC combined with the multi-fluid mixture model. COS1-MOD qualitatively correctly describes the azeotropic behavior of the mixture, however, the calculated dew and bubble point pressures are underestimated by this model. COS2-MOD yields slightly better results than COS1-MOD. COS3-MOD describes the experimental data quantitatively well, however, note that $\epsilon_{CO_2}/k_B$ has been adjusted by trial-and-error in order to improve the description of the experimental VLE data for this mixture. However, this demonstrates that the performance of COS3-MOD could be significantly improved by fitting the molecular dispersion parameters to experimental data.

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Figure 4: Experimental VLE data (symbols, Nagahama et al. (1974) [28]) for a binary mixture of CO$_2$ + C$_3$H$_6$ on an isotherm of $T = 253$ K and vapor-liquid equilibria calculated with the predictive models LIN-MOD (dashed red line), UNI-MOD (solid blue line), COS1-MOD (dotted black line), COS2-MOD (dashed-dotted black line), and COS3-MOD (dashed black line).

Figure 5: Relative deviations of experimental density data by Jaeschke et al. [29,30] for a mixture of $x_{CH_4} = 0.6855$ and $x_{CO_2} = 0.3145$ on an isotherm of $T = 290$ K from calculated results of the reference model by Kunz and Wagner (GERG-2008), and calculated results of the predictive models LIN-MOD, UNI-MOD, and COS3-MOD.

The reference model of Kunz and Wagner (GERG-2008) which was fitted to the experimental data and contains an empirical departure function represents the data with the least deviation. The predictive model LIN-MOD deviates up to 6% from the data, while the predictive models UNI-MOD and COS3-MOD deviate significantly less from the data. In order to assess this in more detail, the average absolute relative deviations (AARD) for all models have been calculated. The AARD is defined according to

$$\text{AARD} = \frac{1}{N_p} \sum_{i=1}^{N_p} \frac{|\rho_{\text{exp},i} - \rho_{\text{calc},i}|}{\rho_{\text{calc},i}},$$

with $N_p$ being the number of data points. The AARDs of the different models for the experimental densities of Jaeschke et al. [29,30] are: $\text{AARD}_{\text{GERG-2008}} = 0.047\%$, $\text{AARD}_{\text{LIN-MOD}} = 2.993\%$, $\text{AARD}_{\text{UNI-MOD}} = 0.666\%$, and $\text{AARD}_{\text{COS3-MOD}} = 0.201\%$. Kunz and Wagner [4] estimate the combined standard uncertainty of the data to be 0.1 % in density. The GERG-2008 is capable of representing the experimental data within the measurement uncertainty. The predictive models do not represent the experimental data within the measurement uncertainty (which is to be expected); however, there are distinct differences between the performances of the predictive models. While LIN-MOD exhibits large deviations up to $-6\%$, the
predictive models UNI-MOD and COS3-MOD deviate less from the experimental data and have a significantly lower AARD.

In order to further investigate this phenomenon, deviations of these models to accurate experimental density data by Jaeschke et al. [29,30] for a binary mixture of CO$_2$ + C$_2$H$_6$ have been calculated. Figure 6 shows deviations of the experimental data in a temperature range from $T = 293.1$ K to $T = 313.1$ K from calculated data with different models.

![Figure 6](image)

Figure 6: Relative deviations of experimental density data by Jaeschke et al. [29,30] for a binary mixture of $x_{C_2H_6} = 0.2267$ and $x_{CO_2} = 0.7733$ in a temperature range from $T = 293.1$ K to $T = 313.1$ K from calculated results of the reference model by Kunz and Wagner [4] (GERG-2008), and calculated results of the predictive models LIN-MOD, UNI-MOD, and COS3-MOD.

Again, the GERG-2008 represents the experimental data well. For this binary mixture, Kunz and Wagner fitted only the four parameters of the reducing functions ($\beta_r, \gamma_r, \beta_i$, and $\gamma_i$) to the experimental data and have not developed an empirical departure function. The AARDs of the different models for the experimental densities of Jaeschke et al. [29,30] are: AARD$_{GERG-2008}$ = 0.007%, AARD$_{LIN-MOD}$ = 1.299%, AARD$_{UNI-MOD}$ = 0.0967%, and AARD$_{COS3-MOD}$ = 0.165%. Among the predictive models, again LIN-MOD deviates the most from the experimental data with deviations up to more than 3%. UNI-MOD and COS3-MOD represent the experimental densities significantly better.

**CONCLUSIONS**

In our recent work [5,6], we demonstrated that the combination of the multi-fluid mixture model with $g^E$-models yields good predictive results for the calculation of phase equilibria for various mixtures, while the multi-fluid mixture model with linear mixing rules for the reducing functions and without a departure function cannot be used well predictively. In this work, we extended our previous work by investigating the model performance for mixtures with CO$_2$ with special focus on the representation of densities in the homogeneous phase. While in our previous work [6], only the original version of the COSMO-SAC model by Lin and Sandler [8] has been combined with the multi-fluid mixture model (COS1-MOD), in this work two improved models of COSMO-SAC [18,19] have been combined with the multi-fluid mixture model (COS2-MOD and COS3-MOD). It was found that COS2-MOD and COS3-MOD are capable of describing phase equilibria more accurately than COS1-MOD. Especially COS3-MOD could be significantly improved by fitting molecular dispersion parameters to experimental data.

For the investigated mixtures with CO$_2$, the combinations of the multi-fluid mixture model with UNIFAC and COSMO-SAC (UNI-MOD, COS1-MOD, COS2-MOD, and COS3-MOD) yield better predictive results regarding accurate experimental density data in the homogeneous phase. UNI-MOD and COS3-MOD represent the experimental densities by Jaeschke et al. [29,30] significantly better than LIN-MOD. However, the representation of experimental densities could still be improved, as the experimental data are not represented within the experimental uncertainties by the predictive models.

From these findings, it can be concluded that the combinations of multi-fluid mixture models with $g^E$-models yield good predictive results for properties of mixtures containing CO$_2$. Hence, these models could be employed to find suitable additives to CO$_2$ in order to improve the performance of power cycles with supercritical CO$_2$.

So far, the investigations have been restricted to mixtures of CO$_2$ with CH$_4$ and C$_2$H$_6$ for which accurate experimental data and multi-fluid mixture models exist. In future work, this study can readily be extended to mixtures of other components with CO$_2$.

**NOMENCLATURE**

**Symbols**

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<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$b$</td>
<td>co-volume of a cubic equation of state (m$^3$ mol$^{-1}$)</td>
</tr>
<tr>
<td>$\partial$</td>
<td>partial derivative</td>
</tr>
<tr>
<td>$F$</td>
<td>parameter of the departure function (-)</td>
</tr>
<tr>
<td>$i$</td>
<td>index of summation</td>
</tr>
<tr>
<td>$j$</td>
<td>index of summation</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant ($k_B = 1.380649 \cdot 10^{-23}$ J K$^{-1}$)</td>
</tr>
<tr>
<td>$N$</td>
<td>number of components in the mixture</td>
</tr>
<tr>
<td>$N_p$</td>
<td>number of experimental points</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure (Pa)</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant ($R = 8.3144598$ J mol$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>$x$</td>
<td>mole fraction (-)</td>
</tr>
<tr>
<td>$\vec{x}$</td>
<td>vector of mole fractions (-)</td>
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**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>dimensionless Helmholtz energy (-)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>model parameter (-)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>reduced density (-)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>model parameter (-)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>molar density (mol m$^{-3}$)</td>
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\( \tau \) reduced temperature (-)

**Subscripts**
- c property at the critical point
- calc calculated property
- exp experimentally measured property
- GE property calculated from an excess Gibbs energy model
- i property of component \( i \)
- j property of component \( j \)
- o property of a pure fluid
- r reducing property
- s property at saturation (at vapor-liquid equilibrium)
- ref property at reference pressure

**Superscripts**
- 0 ideal gas property
- E excess property
- L property of a liquid phase
- r residual property

**Chemical Formulas**
- \( \text{CH}_4 \) methane
- \( \text{C}_2\text{H}_6 \) ethane
- \( \text{CO}_2 \) carbon dioxide

**Abbreviations**
- AARD average absolute relative deviation
- CCS carbon capture and storage
- COS2-MOD multi-fluid mixture model combined with COSMO-SAC by Hsieh et al. [18] using a theoretically based departure function.
- COS3-MOD multi-fluid mixture model combined with COSMO-SAC by Hsieh et al. [19] using a theoretically based departure function.
- COSMO-SAC conductor-like screening model - segment activity coefficient
- LIN-MOD multi-fluid mixture model with linear mixing rules for the reducing functions and no departure function
- PSRK predictive Soave-Redlich-Kwong equation of state
- UNI-MOD multi-fluid mixture model combined with UNIFAC (with VTPR parameters) using a theoretically based departure function.
- UNIFAC UNIQUAC Functional-group Activity Coefficients
- VLE vapor-liquid equilibrium
- VTPR volume-translated Peng-Robinson group contribution equation of state

**REFERENCES**


