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The impact of thermo-physical properties of CO₂ mixtures in the flow assurance

L'impatto delle proprietà termo-fisiche delle miscele di CO₂ nella gestione del flusso

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Abstract

Le tecnologie di *Carbon Capture and Storage*, generalmente indicate con l'acronimo *CCS*, rappresentano uno dei temi di maggiore interesse scientifico quale strumento per contrastare l'effetto antropico della produzione di CO_2 sul clima. Nella consapevolezza che per molti anni ancora i combustibili fossili giocheranno un ruolo fondamentale come principale fonte di energia per il pianeta, le CCS costituiscono un insieme di tecnologie di estrema utilità nella riduzione delle percentuali di CO_2 immessa nell'atmosfera con l'effetto di limitare le inevitabili ricadute sull'intero assetto climatico.

Le tecnologie CCS costituiscono un sistema di produzione dell'energia a ciclo chiuso. Il carbonio, inizialmente estratto dal sottosuolo sotto forma di gas, petrolio o carbone, viene utilizzato per la produzione di energia. Poi, una volta separato dai fumi delle centrali o degli impianti industriali, il flusso ad alta concentrazione di CO_2 così ottenuto viene disidratato e compresso, al fine di rendere più efficienti il trasporto e lo stoccaggio in appositi siti geologici. La disidratazione è necessaria per evitare la corrosione delle attrezzature e infrastrutture mentre la compressione è utile per trasformare la miscela ricca di CO_2 in un fluido denso che occupa molto meno spazio rispetto alla forma gassosa.

Il trasporto fino alla sede di stoccaggio può essere effettuato via nave o attraverso condutture (*pipelines*).

Le navi attualmente utilizzate per trasportare gas petroliferi liquefatti (GPL) sono adatte anche per il trasporto della CO₂. Tuttavia, il trasporto via nave non garantisce un flusso continuo tra la fonte ed il sito di stoccaggio, occorre quindi impiegare dei serbatoi intermedi a terra.



Il trasporto in condutture è attualmente impiegato per trasportare le grandi quantità di CO_2 usate dalle compagnie petrolifere nel recupero assistito di petrolio (Enhanced Oil Recovery, EOR). Questo tipo di trasporto ha un costo più competitivo rispetto a quello via nave e offre anche il vantaggio di fornire un flusso continuo di CO_2 dall'impianto di cattura al sito di stoccaggio. Tutte le condutture esistenti operano ad alte pressioni ed in questo modo la CO_2 è in stato supercritico per cui si comporta come un gas, ma ha la densità di un liquido.

Gli obiettivi della R&D (*Research and Developement*) degli ultimi dieci anni si sono concentrati principalmente sul raggiungimento dell'efficienza energetica, dell'ottimizzazione dei costi e della massima sicurezza.

Tuttavia, la realizzazione di un impianto efficiente, economicamente conveniente e sicuro dipende in gran parte dalla corretta progettazione del sistema stesso. Ciò è possibile solo a seguito di una profonda comprensione delle proprietà termofisiche

delle miscele di CO₂ utilizzate così da poter effettuare il giusto dimensionamento delle apparecchiature e stabilire le condizioni operative ottime dei diversi processi. Le proprietà chiave da studiare nell' ambito della progettazione delle *pipelines* per il trasporto della CO₂ includono le proprietà termodinamiche come l'equilibrio liquido-vapore (VLE), la densità ma anche la viscosità e la conducibilità termica.

Bisogna poi aggiungere che a seconda del metodo di cattura della CO₂ usato presso l'impianto di produzione di energia (Post-Combustione, Pre-Combustione o Ossicombustione), l'anidride carbonica catturata contiene sempre una percentuale di impurità come azoto, idrogeno, ossigeno, metano e molte altre sostanze che alterano in maniera non trascurabile le caratteristiche della miscela rispetto alla CO₂ pura.

Grazie al progresso delle tecnologie di misura, alla maggiore consapevolezza riguardo l'importanza della corretta stima delle proprietà fluidodinamiche delle miscele ricche di CO₂ sono stati condotti e pubblicati recentemente nuovi studi sperimentali che hanno permesso di colmare molte lacune conoscitive e di conseguenza di perfezionare le equazioni di stato che nel tempo sono state modellate per la descrizione di suddette miscele multicomponente.

Lo scopo di questa tesi è quello di mettere in luce i progressi fatti negli ultimi 10 anni nello studio delle proprietà termodinamiche e delle proprietà di trasporto in relazione ai nuovi dati sperimentali trovati in letteratura.

Inoltre, la comprensione dell'impatto delle proprietà termofisiche sulla progettazione e sul funzionamento dei diversi processi di CCS è essenziale per capire le priorità da assegnare alla R&D. Pertanto, in conclusione, viene riportato un breve studio sull'impatto che le proprietà termodinamiche hanno sul trasposto della CO₂ tramite pipelines.

L'analisi dei dati ha mostrato che tra i modelli termodinamici esistenti, le equazioni di stato cubiche hanno la struttura più semplice e sono in grado di dare risultati ragionevoli per le proprietà PVTxy delle miscele di CO₂ ma solo se i parametri di interazione binaria k_{ij} sono calibrati. Equazioni di stato con strutture più complicate, come la Benedict-Webb-Rubin e le SAFT, hanno dimostrato di dare una migliore precisione rispetto nel calcolo di volume, ma le cubiche, d'altra parte, mostrano un vantaggio nei calcoli dell'equilibrio liquido-vapore. La GERG, a fronte della sua dichiarata precisione, dovrebbe dare i migliori risultati tuttavia essendo stata sviluppata per i gas naturali, e non per le miscele ricche di CO₂ le sue applicazioni sono limitate a determinate impurità.

Attualmente, nessuna delle EoS valutate in letteratura mostra un chiaro vantaggio nelle applicazioni CCS per i calcoli VLE e altre proprietà termodinamiche.

Inoltre, ci sono ancora alcune lacune nei dati di letteratura raccolti. Ad esempio, non sono ancora disponibili dati sull'equilibrio di fase di $CO_2/COS e CO_2/NH_3$, sulla densità di CO_2/NH_3 , $CO_2/O_2 e CO_2/NO_2 e$ le non si hanno informazioni sulle proprietà di trasporto di CO_2/H_2S , $CO_2/COS e CO_2/NH_3$.

Le ricerche precedenti si sono concentrate sulle principali impurità. Tuttavia, per ottenere proprietà più accurate, è necessario prestare maggiore attenzione anche ai componenti minori.

Introduction

Carbon capture and storage (CCS) refers to a set of technologies designed to reduce carbon dioxide emissions from large industrial point sources of emission, such as coal-fired power stations, in order to mitigate greenhouse gas production. The technology involves capturing CO_2 and then storing it in a reservoir, instead of allowing its release to the atmosphere, where it contributes to climate change.

 CO_2 transportation is an integral part of the CCS chain. After capture, CO_2 needs to be transported to locations whereby it is stored or alternatively used in various processes. Different transport solutions are available, the main ones being pipelines and ships, for which high density and purity are recommended. Furthermore, for safe final storage a CO_2 concentration > 95,5% is required. Transport can also influence the choice of the capture technology in terms of CO_2 concentration and the kind of impurities it contains.

 CO_2 can be transported in pipelines in all of its physical states. However, its gas density is very low, and the gas phase needs equipment capable of carrying large volumes, which is not very convenient. Thus, CO_2 transport in a liquid or supercritical phase is preferable, in particular at a pressure greater than critical pressure (*Pc*) and at room temperature (lower than *Tc*). Under these conditions the CO_2 is in a "dense" phase and exhibits a low viscosity and a density similar to a liquid. In every case, in order to avoid pipeline stress, the pressure should not be too high. CO_2 will most likely be transported in the range of (8–30) MPa, depending on the distance and intended disposal or use of CO_2 . Moreover, to avoid two-phase flow, it is necessary to repump the CO_2 whenever the pressure falls to near critic pressure. Therefore, it is essential to study the pressure drop and the density variation along the pipeline.

As mentioned earlier, in the context of combustion gases, the CO_2 gas stream is not pure and contains numerous impurities so it is clear the thermodynamic properties required for CCS-processes should not be calculated for pure CO_2 but for CO_2 -rich mixtures with various components. It is expected that some of these impurities have a significant impact on the fluid behaviour.

The main impurities that can be found in CO₂ mixtures as a result of different capture technologies are summarised in Table 1.

	Oxyfuel combustion	1	Pre-	Post-	
	Raw/dehumidified	Double	Distillation	Combustion	Combustion
CO _{2%} v/v	78.8-87.0	95.84-96.7	99.3-99.95+	95-99	99.6-99.8
O2% v/v	3.21-6.0	1.05-1.2	0.0014	0	0.015-0.0035
N2% v/v	4.0-16.6	1.6-2.03	Trace-0.2	0.0195-1	0.045-0.29
Ar% v/v	2.3-4.47	0.4-0.61	Trace-0.1	0.0001-0.15	0.0011-0.021
NO _x ppmv	100-709	0-150	3-100	400	20-38.8
SO ₂ ppmv	36-800	0-4500	0.1-50	25	0-67.1
SO3 ppmv	20	-	0.1-20	-	N.I.
H ₂ O ppmv	100-1000	0	0-100	0.1-600	100-640
CO ppmv	50-162	-	<2-50	0-2000	1.2-10
H ₂ S/COS				0.2-34,000	
ppmv					
H ₂ ppmv				20-30,000	
CH4 ppmv				0-112	

Table 1

|--|

Some of them are the results of combustion like NO_x, SO₂, Ar, O₂, N₂O, CO and N₂. We can have also some hydrocarbons, traces of H₂S, traces of solvent, H₂ in the case of pre-combustion process, water, etc... During the transportation of CO₂, in all the cases it is important to know the thermodynamic behaviour in the presence of these impurities and the impact of them on the thermophysical properties of the fluid. The objective is to guaranty a safe design of transportation process. In effect, in case of problem during the transportation, for example a leakage, the presence of the impurities may lead to the apparition of a 2 phases region which can modify the flow and so increase the cost of fluid transportation.

Several thermophysical properties of interest need to be known in the context of CO_2 transportation by pipeline or vessels. The design of process for CO_2 transportation requires thermodynamic models. Consequently, the knowledge of phase diagram of CO_2 gas stream with the presence of impurities is essential. Equations of state require parameters, so it is important to determine phase diagram of each binary system between CO_2 and impurities and between impurities themselves. Densities and speed of sound are also important properties that can be used to test the accuracy of equations of state and to determine compressibility factor. Moreover, density is an essential property for the design of the compressors and pumps, which in turn, also requires the knowledge of transport properties like viscosity.

The aim of the present work is to highlight the progress made over the last 10 years in the study of thermodynamic and transport properties in relation to new experimental data found in the literature. Furthermore, understanding the impacts of properties on the design and operation of different CCS processes is essential to prioritize the objectives of R&D. Therefore, in conclusion, a brief study is also included to examine the impact of thermophysical properties on CO_2 transport by pipelines.

1 Equations of State

Equations of State (EoS) are commonly classified into thermal and fundamental formulations. Thermal EoS describe the relation between the three thermal properties: pressure p, molar or specific volume v (or density ρ), and temperature T. Over the centuries, a variety of different approaches for thermal EoS was developed and published in the literature. Cubic EoS represent the most prominent group of thermal EoS. Although they are still widely used, thermal EoS have lost relevance for formulations with reference quality. The main reason for this is that the calculation of caloric (energy related) properties from thermal EoS requires additional correlations for the properties of the ideal-gas state and furthermore potentially complex integrations. This problem significantly increases the computing time in both fitting and employing these formulations. Besides, many thermal (in particular cubic) EoS provide quite reliable results for phase-equilibria but do not represent accurate homogeneous densities or other data for homogeneous state properties within their experimental uncertainties. Especially in the liquid phase, calculated values might deviate considerably from experimental results.

Fundamental EoS are explicitly formulated in a caloric property such as the internal energy u, enthalpy h, Helmholtz energy a, or Gibbs Energy g. This functional form allows for the calculation of all thermal and caloric properties through combinations of partial derivatives. Conversely, it is also possible to use all types of thermodynamic property data to fit these equations. Most state-of-the-art reference EoS are written in terms of the Helmholtz energy. A particular challenge in the

development of Helmholtz-energy explicit EoS for mixtures is posed by the poor data situation for many of these systems. Fitting the adjustable parameters of this type of EoS requires a certain amount of reliable experimental or molecularsimulation data. If no or no reliable data are available, combining rules still allow for the calculation of results, but the predictive potential of these rules is limited.

Every equation of state that has been proposed through the years has more or less severe limitations with regard to the kinds of substances that it could represent, or the range of operating conditions, or the phases. Some equations are better for PVT, others for phase equilibria, and still others for enthalpy or entropy deviations. There is little hope that a universal equation of state of moderate complexity ever will be discovered.

A brief summary of the main state equations found in the literature to this date is given in the next sections.

1.1 Cubic EoS

Due to their large range of validity and their comparably simple mathematical structure, cubic EoS are widely used in technical applications. Over the years, a variety of cubic functions were proposed in order to improve the representation of experimentally obtained thermophysical property data; however, all these approaches are in principle modifications of the well-known functional form introduced by van der Waals in 1873² This functional form reads:

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

with R being the universal gas constant. The van der Waals equation itself is a modification of the ideal-gas equation, which is the simplest model for the description of pure gases and gaseous mixtures. The ideal-gas equation is based on the assumption that the gas molecules have no volume and that the thermodynamic behaviour is not influenced by interactions between molecules. Van der Waals corrected these two assumptions by introducing the parameter b taking into account the volume of the molecules and the additional parameter a that considers attractive forces between molecules. For the first time, this modification allowed the whole fluid surface including the gas phase, liquid phase, and supercritical states to be described with one single EoS. The van der Waals equation was the starting point for the development of many other cubic EoS available in the literature.

1.1.1 The Soave-Redlich-Kwong

One of the most famous enhancements is the EoS of Redlich and Kwong³ that was further modified by Soave⁴. The Soave-Redlich-Kwong, or short "SRK", EoS reads:

$$P = \frac{RT}{v-b} - \frac{\alpha a}{v(v+b)}$$

Compared to the basic functional form of van der Waals, one of the most significant modifications is the introduction of a temperature dependency in the interaction parameter a. Considering a mixture of N fluid components, the full expression for a(T) is:

$$a(T) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j \sqrt{a_i(T)a_j(T)} (1 - k_{ij})$$

which corresponds to a quadratic mixing rule for the arithmetic mean values of the pure-fluid interaction parameters a_i extended by the binary interaction parameter k_{ij} . This interaction parameter is fitted to experimental data available for a binary mixture. The most accurate description of a multi-component mixture is achieved by fitting k_{ij} values for every possible binary combination of the pure components. The standard value of k_{ij} without fitting it to experimental data is zero. Of course, the SRK EoS is also valid for pure fluids. In this case, k_{ij} and the mole fractions are meaningless ($k_{ij} = 0$ and $x_i = x_j = 1$), which leads to $a(T) = a_i(T) = a_j(T)$.

1.1.2 The Peng-Robinson

The Peng Robinson cubic Eos or short "PR" is another important variation of the van der Waals EoS that was introduced in 1976 by Peng and Robinson⁵. Although this equation refines on the liquid density prediction and the representations of vapour-liquid equilibrium (VLE) for many mixtures, it cannot describe volumetric behaviour around the critical point. The PR is perhaps the most popular and widely used EoS. In terms of the molar volume v, Peng and Robinson proposed the following two-constant EoS:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (1.1)$$

where, at critical point:

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c}$$
$$b(T_c) = 0.07780 \frac{RT_c}{P_c}$$
$$Z_c = 0.307$$

The generalised expression for the temperature-dependant parameter of the eq. (1.1) is given by:

$$a(T) = a(T_C)\alpha(T)$$

Where:

$$(T) = \left[1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2$$

With:

$$m = 0.3746 + 1.5423\omega - 0.2699\omega^2$$

1.2 Virial EoS

Another widely used type of thermal EoS is based on a virial expansion of the compressibility factor Z. The compressibility factor quantifies the deviation of the real fluid behaviour from the hypothetical ideal gas. The simplest form of the virial EoS reads:

$$Z = \frac{\rho RT}{p} = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots,$$

with the molar density ρ , the second virial coefficient *B*, the third virial coefficient *C*, and the fourth virial coefficient *D*. Adding additional higher order virial coefficients increases the accuracy of the EoS; nevertheless, the expansion is frequently truncated after the third coefficient *C*. Various modifications of the virial expansion approach can be found in the literature.

1.2.1 Benedict–Webb–Rubin

The celebrated equation of Benedict, Webb, & Rubin (1940, 1942, 1951) was devised as an improvement on the Beattie-Bridgeman equation. Some steps in the evolution of these equation are summarize below:

Beattie-Bridgeman equation (1927)⁶:

$$P = RT\rho + \left(B_0RT - A_0 - \frac{Rc}{T^2}\right)\rho^2 + \left(-B_0bRT + A_0a - \frac{RB_0c}{T^2}\right)\rho^3 + \frac{RB_0bc}{T^2}\rho^4$$

Benedict-Webb-Rubin equation (1940)⁷ or short "BWR":

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c}{T^2}\rho^3(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

Starling (1970)⁸ or short "BWRS":

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c}{T^2}\rho^3(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

The BWR equation defines the pressure or compressibility as a polynomial in terms of density with coefficients that are dependent on temperature, with an exponential term tacked on to compensate for the higher-power terms of the virial equation. The defect of the Beattie-Bridgeman equation that the BWR equation was intended to rectify was an inability to represent behaviour of liquids and of gases above the critical density.

Because of its high degree of nonlinearity, the BWR equation is more difficult to use than are cubic equations for which analytical solution for the volume or compressibility is possible.

1.2.2 Lee-Kesler-Plöcker

Various modifications of the virial expansion approach can be found in the literature. One of the most well-known modifications apart of the Benedict-Webb-Rubin EoS is the Lee and Kesler ⁹ developed in 1975 that was further modified by

Plöcker et al.¹⁰ 1978. The Lee-Kesler-Plöcker or short "LKP", EoS describes the compressibility factor by:

$$Z = Z^0 + \frac{\omega}{\omega^{ref}} (Z^{ref} - Z^0) \quad (2.1)$$

with the acentric factor of the investigated fluid ω and the compressibility factor Z defined as:

$$Z = \frac{\pi \Psi}{\vartheta}$$

including the reduced pressure π , the reduced volume Ψ , and the reduced temperature ϑ according to:

$$\pi = \frac{p}{p_r}, \quad \Psi = \frac{p_r v}{RT_r}, \quad and \ \vartheta = \frac{T}{T_r},$$

with the reducing temperature T_r and the reducing pressure p_r .

Eq. (2.1) includes the special compressibility factors Z^0 and Z^{ref} . The first one represents the compressibility factor of a "simple fluid" (such as argon or methane) with an almost spherical molecule (acentric factor $\omega = 0$), whereas Z^{ref} is the compressibility factor of a "reference fluid" (n-octane) with the acentric factor ω^{ref} .

The calculation of the reduced properties π , Ψ , and ϑ is straightforward for pure fluids because the critical-point parameters $p_{c,i}$ and $T_{c,i}$ are used as the reducing temperature T_r and the reducing pressure p_r . For mixtures, pseudo-critical parameters are obtained from combining rules for the critical parameters of the pure components. The pseudo-critical temperature of a mixture with N components is defined as:

$$T_{c,mix} = \frac{1}{v_{c,mix}^{\eta}} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j v_{c,ij}^{\eta} T_{c,ij} \qquad (2.2)$$

The equation contains, among other quantities, the pseudo-critical volume $v_{c,mix}$ of the mixtures, which is calculated from the simple quadratic combining rule:

$$v_{c,mix} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j v_{c,ij}$$

With the binary pseudo-critical volume $v_{c,ij}$ according to:

$$v_{c,ij} = \frac{1}{8} (v_{c,i}^{1/3} + v_{c,j}^{1/3})^3.$$

Because for many pure fluids the critical molar volume (or density) is not accurately known, it is determined from the critical temperature and pressure and the acentric factor:

$$v_{c,i} = (0.2905 - 0.085\omega_i) \frac{RT_{c,i}}{p_{c,i}}$$

The calculation of the pseudo-critical temperature also requires the binary pseudocritical temperature $T_{c,ij}$, which is defined as:

$$T_{c,ij} = k_{i,j} (T_{c,i} T_{c,j})^{1/2}$$
,

which includes the binary interaction parameter k_{ij} . As discussed for the SRK EoS, this parameter can be fitted to experimental data in order to improve the accuracy of the EoS. The standard value is applied by setting k_{ij} to unity.

In Eq. (2.2) the exponent η is an adjustable parameter. The standard value $\eta = 0.25$ was given by Plöcker et al.¹⁰.

In order to calculate the reduced pressure \mathcal{P} , the pseudo-critical pressure of the mixture is needed. This pseudo-critical pressure is calculated as:

$$p_{c,mix} = (0.2905 - 0.085\omega_{mix}) \frac{RT_{c,mix}}{v_{c,mix}}$$

with the acentric factor of the mixture ω_{mix} according the simple linear combining rule:

$$\omega_{mix} = \sum_{i=1}^{N} x_i \omega_i.$$

For mixture calculations, this acentric factor ω_{mix} also needs to be used as the acentric factor in Eq. (2.1) ($\omega = \omega_{mix}$).

1.3 Multi-Parameter Helmholtz-Energy EoS

Multi-Parameter Helmholtz-Energy is a fundamental EoS, which allows for the calculation of all thermodynamic properties by combining derivatives of its functional form. This aspect is not only relevant to computing time, but also allows simultaneous fitting of the EoS to all types of experimental thermodynamic property data. In general, EoS explicit in the Helmholtz energy a can be formulated as:

$$a(T,\rho) = a^{o}(T,\rho) + a^{r}(T,\rho).$$
 (3.1)

The independent variables temperature and molar density enable a clear description of the whole fluid surface, including the vapor-liquid equilibrium region. The function a^o describes the behaviour of the hypothetical ideal gas, whereas a^r represents the residual Helmholtz energy that results from molecular interactions in the real fluid. Usually, the Helmholtz free energy is used in its dimensionless form $\alpha = \frac{a}{RT}$. Thus, Eq. (3.1) becomes:

$$\alpha(\delta,\tau) = \alpha^0(\delta,\tau) + \alpha^r(\delta,\tau),$$

Where $\delta = \rho/\rho_c$ is the reduced density and $\tau = T_c/T$ is the inverse reduced temperature with ρ_c as the critical density and T_c as the critical temperature of the considered fluid.

1.3.1 GERG-2008

The GERG-2008 EoS^{11} is an expansion of the GERG-2004 EoS previously proposed by Kunz et al.¹² in 2007.

The GERG-2008 EoS for natural gases and other mixtures of natural gas components is based on a multi-fluid approximation explicit in the reduced Helmholtz free energy.

$$\alpha(\delta, T, \bar{x}) = \alpha^0(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x})$$

where the α° part represents the properties of the ideal-gas mixture at a given mixture density ρ , temperature *T*, and molar composition \overline{x} according to

$$\alpha^{o}(\rho, T, \bar{x}) = \sum_{i=1}^{N} x_{i} [\alpha^{o}_{oi}(\rho, T) + lnx_{i}] \qquad (4.1)$$

The residual part α^r of the reduced Helmholtz free energy of the mixture is given by:

$$\alpha^{r}(\delta, T, \bar{x}) = \sum_{i=1}^{N} x_{i} \alpha_{oi}^{r}(\delta, \tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_{i} x_{j} F_{ij} \alpha_{ij}^{r}(\delta, \tau) \quad (4.2)$$

where δ is the reduced mixture density and τ is the inverse reduced mixture temperature according to:

$$\delta = \frac{\rho}{\rho_r(\bar{x})} \text{ and } \tau = \frac{T_r(\bar{x})}{T}$$
 (4.3)

and N = 21 is the total number of components in the mixture. Since the mixture model is not limited to the currently considered 21 components, the summation variable N is continuously used in this work to denote the maximum number of components.

Eq. (4.2) takes into account the residual behaviour of the mixture at the reduced mixture variables δ and τ . The first sum in this equation is the linear contribution of the reduced residual Helmholtz free energy of the pure substance equations of state multiplied by the mole fractions x_i . The double summation in Eq. (4.2) is the departure function $\Delta \alpha^r(\delta, \tau, \bar{x})$ which is the summation over all binary specific and generalized departure functions $\Delta \alpha^r_{ij}(\delta, \tau, \bar{x})$ developed for the respective binary mixtures.

In Eq. (4.2), the dimensionless form of the Helmholtz free energy in the ideal-gas state of component i is given by:

$$\alpha_{oi}^{o}(\rho,T) = \ln\left(\frac{\rho}{\rho_{c,i}}\right) + \frac{R^{*}}{R} \left[n_{oi,1}^{o} + n_{oi,2}^{o} \frac{T_{c,i}}{T} + n_{oi,3}^{o} ln\left(\frac{T_{c,i}}{T}\right) + \sum_{K=4.6} n_{oi,k}^{o} ln\left(\left|\sinh\left(\vartheta_{oi,k}^{o} \frac{T_{c,i}}{T}\right)\right|\right) - \sum_{k=5.7} n_{oi,k}^{o} ln\left(\cosh\left(\vartheta_{oi,k}^{o} \frac{T_{c,i}}{T}\right)\right) \right]$$
(4.4)

Where $\rho_{c,i}$ and $T_{c,i}$ are the critical parameters of the pure components and R is the molar gas constant.

The values of the coefficients $n_{oi,k}^o$ and the $\vartheta_{oi,k}^o$ parameters of Eq. (4.4) for all of the considered 21 components considered in the development of the GERG-2008 are listed in the work of Kunz et al.¹¹.

In Eq. (4.2), the residual part of the reduced Helmholtz free energy of component i is given by:

$$\alpha_{oi}^{r}(\delta,\tau) = \sum_{k=1}^{K_{Pol,i}} n_{oi,k} \delta^{d_{oi,k}} \tau^{t_{oi,k}} + \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{oi,k} \delta^{d_{oi,k}} \tau^{t_{oi,k}} e^{-\delta^{c_{oi,k}}}$$
(4.5)

The respective values for the coefficients $n_{oi,k}$ and the exponents $d_{oi,k}$, $t_{oi,k}$ and $c_{oi,k}$ for all considered components and the critical parameters are given by Kunz et al.¹¹

For the simultaneously optimized equations of state of Span and Wagner¹³, the old molar gas constant was substituted with the recent one without any other conversion. This change can be neglected with regard to the accuracy of the equations of state. The mathematical structure of Eq. (4.5) is identical for all components in GERG-2008.

The function $\alpha_{ij}^r(\delta, \tau)$ of Eq. (4.2), which is the part of the departure function $\Delta \alpha_{ij}^r(\delta, \tau, \bar{x})$ that depends only on the reduced mixture variables δ and τ , is given by

$$\alpha_{ij}^{r}(\delta,\tau) = \sum_{k=1}^{K_{Pol,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} exp \left[-\eta_{ij,k} \left(\delta - \varepsilon_{ij,k} \right)^{2} - \beta_{ij,k} \left(\delta - \gamma_{ij,k} \right) \right]$$
(4.5)

where $\alpha_{ij}^r(\delta, \tau)$ was developed for either a specific binary mixture (a binary specific departure function with binary specific coefficients and parameters) or a certain group of binary mixtures (generalized departure function with a uniform structure for the group of binary mixtures considered). For a binary specific departure function, the adjustable factor F_{ij} in Eq. (4.2) is set to unity. The factor F_{ij} is fitted to binary specific data for each mixture in the group of generalized binary mixtures. The values for the coefficients $n_{ij,k}$ and the exponents $d_{ij,k}$, $t_{ij,k}$, $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ for all binary specific and generalized departure functions considered in the GERG-2008 equation of state are given by Kunz et al.¹¹.

The reduced mixture variables δ and τ are calculated from Eq. (4.3) by means of the composition-dependent reducing functions for the mixture density:

$$\frac{1}{\rho_r(\bar{\mathbf{x}})} = \sum_{i=1}^N x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{\nu,ij} \gamma_{\nu,ij} \frac{x_i + x_j}{\beta_{\nu,ij}^2 x_{ii} + x_j} \frac{1}{8} (\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}})^3$$

and the mixture temperature:

$$T_r(\bar{x}) = \sum_{i=1}^N x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{c,i} T_{c,j})^{0.5}$$

The binary parameters $\beta_{\nu,ij}$ and $\gamma_{\nu,ij}$ and $\beta_{T,ij}$ and $\gamma_{T,ij}$ are fitted to data for binary mixtures.

1.3.2 Equation of State for Combustion Gases and Combustion Gas like Mixtures (EOS-CG)

The mixture model EOS-CG developed by Gernet et al.¹⁴ adopts the functional form introduced by Lemmon and Tillner-Roth¹⁵, which was further developed in the GERG-2008 equation of state. It is a fundamental equation of state explicit in the Helmholtz energy *a* with the independent variable's density ρ , temperature *T*, and molar composition \bar{x} . Written in the dimensionless reduced form $\alpha = a/(RT)$, where R represents the universal gas constant, the basic structure of the model reads:

$$\frac{\alpha}{RT} = \alpha(\delta, T, \bar{x}) = \alpha^0(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x})$$

For pure fluids, temperature and densities are reduced with the critical-point parameters. For mixtures, this method is not feasible because the critical-point parameters are different for each component. Besides, the critical point of the mixture is, if existing, composition dependent and therefore quite complex to determine. The reduced mixture density δ and the inverse reduced mixture temperature τ are therefore calculated with composition-dependent "reducing functions":

$$\delta = \frac{\rho}{\rho_r(\bar{x})}$$
 and $\tau = \frac{T_r(\bar{x})}{T}$

while the residual α^r part of the reduced Helmholtz energy model is evaluated at reduced mixture parameters using composition-dependent reducing functions $\rho_r(\bar{x})$ and $T_r(\bar{x})$, the ideal-gas part α^o is given as:

$$\alpha^{o}(\rho,T,\bar{x}) = \sum_{i=1}^{N} x_{i} [\alpha_{oi}^{o}(\delta_{o,i},\tau_{o,i}) + lnx_{i}],$$

where N is the number of components in the mixture, α_{oi}^{o} is the dimensionless idealgas part of the Helmholtz energy, and x_i is the mole fraction of component *i* in the mixture. The sum over $x_i \ln x_i$ accounts for the entropy of mixing in the ideal mixture. The contributions of the pure components to the ideal-gas Helmholtz energy are evaluated at their component-specific reduced parameters $\delta_{o,i}$ and $\tau_{o,i}$ that are usually given by:

$$\delta_{o,i} = \frac{\rho}{\rho_{c,i}}$$
 and $\tau_{o,i} = \frac{T_{c,i}}{T}$

The residual part of the Helmholtz energy of the mixture is given by:

$$\alpha^{r}(\delta,T,\bar{x}) = \sum_{i=1}^{N} x_{i} \alpha^{r}_{oi}(\delta,\tau) + \Delta \alpha^{r}(\delta,\tau,\bar{x})$$

where α_{oi}^{r} is the residual part of the reduced Helmholtz energy of component *i*, δ and τ are the and $\Delta \alpha^{r}$ is the so-called *departure function*, which is given by:

$$\Delta \alpha^r(\delta,\tau,\bar{x}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_o^r(\delta,\tau)$$

with the binary specific departure function α_{ij}^r for the components *i* and *j* and the weighing factor F_{ij} introduced for the use of generalised departure functions for a group of binary systems. This weighting factor enables the use of "generalized

binary departure functions" for a group of chemically similar binary systems. If a departure function specific for a binary mixture is developed, F_{ij} is set to unity.

The reducing functions $\rho_r(\bar{x})$ and $T_r(\bar{x})$ are:

$$\frac{1}{\rho_r(\bar{x})} = \sum_{i=1}^N x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{\nu,ij} \gamma_{\nu,ij} \frac{x_i + x_j}{\beta_{\nu,ij}^2 x_{i_i} + x_j} \frac{1}{8} (\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}})^3$$
$$T_r(\bar{x}) = \sum_{i=1}^N x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_{i_i} + x_j} (T_{c,i} T_{c,j})^{0.5}$$

These functions form a composition-dependent surface between the critical parameters for density and temperature (indices c) of the pure components in the mixture. The binary parameters β_T , β_v , γ_T , and γ_v allow for almost arbitrary symmetric and asymmetric shapes of the functions and are fitted to experimental data.

The departure function $\Delta \alpha^r$ is introduced for the description of residual mixing effects that cannot be described accurately enough only by the use of the adjusted reducing parameters β and γ . This additional empirical correlation function is based on binary departure functions α_{ij}^r and fitted to experimental data of binary mixtures. The mathematical structure is similar to the structure of the established Helmholtz energy models for pure fluids, with the exception of the third term type, which was introduced exclusively for mixtures in Kunz et al¹¹.

$$\alpha_{ij}^{r}(\delta,\tau) = \sum_{k=1}^{K_{Pol,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{exp,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left(-\delta^{l_{ij,k}}\right)$$
$$+ \sum_{k=K_{Pol,ij}}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left[-\eta_{ij,k} \left(\delta - \varepsilon_{ij,k}\right)^{2} - \beta_{ij,k} \left(\delta - \gamma_{ij,k}\right)\right].$$

The coefficients n_{ij} and the exponents d_{ij} , t_{ij} , l_{ij} , ε_{ij} , β_{ij} and γ_{ij} are adjustable parameters and were fitted to experimental thermodynamic properties for each binary mixture.

1.4 Predictive Eos

As mentioned before, the development of Helmholtz-explicit EoS for mixtures as introduced in the previous section is challenging, if scarce or no reliable experimental or molecular-simulation data are available to fit the adjustable parameters. This problem is not only relevant to Helmholtz-explicit EoS; other approaches such as SRK or LKP also yield the most reliable results if a binary interaction parameter was fitted to accurate data. The development of less empirical and more "physically based" EoS is consequently the focus of many scientific works.

1.4.1 Predictive Soave-Redlich-Kwong

A widely used approach is the "Predictive Soave-Redlich-Kwong" EoS of Holderbaum and Gmehling¹⁶. As evident from its name, this EoS is a modification of the SRK EoS of Soave⁴. The main modification concerns the interaction parameter *a*. Instead of calculating *a* from combining rules and critical-point constraints, the parameter is obtained from a correlation that includes the excess Gibbs energy g^E described by the UNIFAC method of Fredenslund et al.¹⁷. The basic idea of this method is to split molecules into functional groups that interact with other functional groups present in a mixture; a mixture of groups rather than a mixture of molecules. Following this approach allows for the description of a mixture that is not experimentally investigated as long as the interactions between the present functional groups can be quantified. This restriction highlights that the PSRK EOS is only to a certain extent "physically based". The accurate description of a mixture still requires UNIFAC interaction parameters to be fitted for every binary combination of the relevant functional groups. Fitting these parameters, again, requires experimental data. Nevertheless, it should be noted that this fitting process is not restricted to experimental information on one binary mixture. Instead, the interaction parameters can be fitted to experimental data for various different mixtures containing the specific binary combination of functional groups.

1.4.2 SAFT-like EoS

Another concept of describing the thermodynamic properties of a fluid by modeling intermolecular forces is the "Statistical Associating Fluid Theory", or in short "SAFT", originally published by Chapman et al.¹⁸ in 1989. Within the SAFT approach, the complex shape of molecules is modelled through a chain of single spherical segments. The EoS is explicit in the Helmholtz energy, containing an ideal part and a residual part that is described through three physical contributions: repulsive dispersion of the spherical segments, the formation of chains, and association interactions such as hydrogen bonding. The SAFT approach was modified by many authors.

One of the most well-known modifications is the "Perturbated-Chain Statistical Associating Fluid Theory", or in short "PC-SAFT", by Gross and Sadowski¹⁹ that considers dispersive forces as a perturbation to a chain of spherical segments. The concept of adding perturbation terms was further pursued by Gross²⁰ and Gross and Vrabec²¹, who presented the "PCP-SAFT" EoS that also allows for the description of dipolar or quadrupolar substances. For the description of mixtures, the

perturbation theory applied uses an average radial distribution function with van der Waals one-fluid mixing rules. With regard to the description of experimentally less investigated mixtures, it should be noted that although PC(P)-SAFT describes the fluid behaviour from a molecular perspective, it still includes an interaction parameter that is meant to be fitted to experimental data for a binary mixture. The predictive potential of this approach is consequently limited.

Many other modifications of the SAFT-based EoSs were suggested over the years, such as CK-SAFT²², Lennard-Jones SAFT (LJ-SAFT)²³, variable range SAFT (SAFT-VR)²⁴, soft-SAFT²⁵.

Each SAFT version is different depending on the interaction pair potential between the segments (square-well, Lennard-Jones, Mie, etc) and the approach used to calculate the contributions (hard sphere, chain, association, etc).

2 CO₂ mixtures: progress on modeling

Recently, with the advancement of measuring technologies and the increasing attention on the fundamental properties, many new experimental data have been published about thermo-physical properties of CO₂-rich mixture at given pressure and temperature, which have bridged some of the knowledge gaps identified in the past. Meanwhile, with the development of computer technologies, new models are also emerging. The objective of this chapter is to update and review the status regarding the studies on thermodynamic and transport properties of CO₂ mixtures developed since the last 10 years with special attentions paid to the development of property models. The available models about thermodynamic properties and transport properties are summarized and compared in Table 2 and Table 3.

Mixtures	Models	year	T and P		Accuracy (Absolute		
					average relative deviation%)		tive
							6)
			T (K)	P (MPa)	VLE	v^G	v^L
CO_2/N_2	PR	1990	220.00-	<15.800	2.1-	-	-
			270.00		3.3		
		2009	193.00-	0.100-14.300	1.22-	1.58-	1.74-
			363.00		6.04	13.02	9.43
		2014	273.00-	1.000-20.000	-	2.0	2.0
			293.00				
	BWR	2007	216.00-	0.520-14.500	2.7-	0.8-	>9
			363.00		9.7	9.2	
	PT	1990	220.00-	<15.800	1.6-	-	-
			270.00		3.2		
		2009	193.00-	0.100-14.300	2.32-	0.98-	1.77-
			363.00		10.82	13.06	9.28
	LK	1983	220.00-	0.600-16.700	3-3.9	-	-
			270.00				

TABLE 2

Available models for thermodynamic properties summarized and compared by Li et al.²⁶
$\begin{array}{cccccccccccccccccccccccccccccccccccc$							
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1994	220.00-	2.000-12.000	-	<5(10	<5(10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			273.00			-20)	-20)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SRK	2009	193.00-	0.100-14.300	1.32-	1.5-	4.18-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			363.00		11.28	14	10.84
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	RK	2009	193.00-	0.100-14.300	5.25-	1.47-	4.86-
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			363.00		14.17	14.26	11.96
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Predictive	2007	216.00-	0.520-14.500	1.4-	0.6-	>9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SRK	2007	363.00	0.020 1.0000	16.2	9.2	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3P1T	2000	103.00	0.500-14.000	3 32	5.2	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5111	2009	262.00	0.300-14.000	25 75	-	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	GERG 2004	2004	00.00	<25 000	102	0.2	0.1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	UEKU-2004	2004	90.00- 450.00	<33.000	1.0-5	0.2-	0.1-
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		2007	450.00	0.500 14.500		0.5	0.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2007	216.00-	0.520-14.500	2.2-	0.5-	3.8-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			363.00		10.4	5.7	18.4
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Duan 96	1996	<2000.	<2500.000	-	<2	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			00				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PR-Penelousx	2009	220.00-	0.100-14.300	-	2.85-	3.79-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			347.00			11.64	10.51
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	SRK-Peneloux	2009	220.00-	0.100-14.300	-	2.59-	4.97-
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			347.00			12.76	12.15
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Improved	2009	220.00-	0.100-14.300	-	5.17-	4.64-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SRK		347.00			8.83	13.21
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	RKS	2014	273.00-	1.000-20.000	-	1.5	10.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			293.00				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	RKSP	2014	273.00-	1.000-20.000	-	1.5	5.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			293.00				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BWRS	2014	273.00-	1.000-20.000	-	1.7	2.1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			293.00				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	LKP	2014	273.00-	1.000-20.000	-	1.4	0.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			293.00				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SAFT-VR Mie	2017	225.00-	4.000-800.000	0.99-	1.18	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			673.00		5.43		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PC-SAFT	2014	273.00-	1.000-20.000	-	1.9	0.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-011	293.00	10000 200000			0.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2017	225.00	4 000-800 000	1 73-	3 10	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2017	673.00	4.000-000.000	7 32	5.17	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	FOS CG	2015	208 15	11 000 31 000	1.52	<0.1	<01
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	EOS-CO	2013	290.15- 422.15	11.000-31.000	-	<0.1	<0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2016	425.15	<19.000	0.04		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2010	223.00-	<18.000	0.04-	-	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0010	303.00	5 0.000	0.63	0.1	0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	GERG-2008	2012	60.00-	0.000</td <td>1.0-</td> <td>0.1</td> <td>0.1-</td>	1.0-	0.1	0.1-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		• • • •	/00.00		3.0		0.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2014	273.00-	1.000-20.000	-	1.3	0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			293.00				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2015	298.15-	11.000-31.000	-	< 0.1	< 0.1
PR+EOS/ 2016 213.00- 1.0003-19.900 0.76- - - a _{res} ^{E,γ-Wilson} 473.00 2.85 - - -			423.15				
a _{res} ^{E,γ-Wilson} 473.00 2.85	PR+EOS/	2016	213.00-	1.0003-19.900	0.76-	-	-
	$a_{res}^{E,\gamma-Wilson}$		473.00		2.85		

		2017	218.00-	1.000-16.700	0.08-	-	-
			303.00		4.22		
	Demetriades	2016	273.00-	<16.000	-	-	-
	and Graham		304.00				
	EOS						
CO_2/O_2	PR	2009	193.00-	0.100-14.300	1.22-	1.58-	1.74-
			363.00		6.04	13.02	9.43
		2014	273.00-	1.000-20.000	-	1.6	2.1
			293.00			-	
	BWR	2007	216.00-	0.520-14.500	2.7-	0.8-	>9
	2011	,	363.00	0.020 1.0000	9.7	9.2	-
	РТ	2009	193.00-	0 100-14 300	2 32-	0.98-	1 77-
		2009	363.00	0.100 11.200	10.82	13.06	9.28
	SRK	2009	193.00-	0 100-14 300	1 32-	1 5-	2.20 4.18-
	SIGK	2007	363.00	0.100-14.500	11.52-	1.5-	10.84
	DV	2000	103.00	0 100 14 300	5 25	14	10.04
	ΛK	2009	262.00-	0.100-14.300	5.25- 14.17	1.47-	4.00-
	Duadiativa	2007	216.00	0 520 14 500	14.1/	14.20	>0
	CDV	2007	210.00-	0.320-14.300	1.4-	0.0-	~9
	SKK	2000	363.00	0.500.14.000	16.2	9.2	
	3P11	2009	193.00-	0.500-14.000	3.32-	-	-
	OFD C 2004	2007	363.00	0.520.14.500	25.75	0.5	2.0
	GERG-2004	2007	216.00-	0.520-14.500	2.2-	0.5-	3.8-
		• • • • •	363.00	• • • • • •	10.4	5.7	18.4
		2004	90.00-	<35.000	1.0-3	0.2-	0.1-
			450.00			0.5	0.5
	Duan96	1996	<2000.	<2500.000	-	<2	-
			00				
	RKS	2014	273.00-	1.000-20.000	-	2.0	9.4
			293.00				
	RKSP	2014	273.00-	1.000-20.000	-	2.4	5.3
			293.00				
	BWRS	2014	273.00-	1.000-20.000	-	1.6	2.1
			293.00				
	LKP	2014	273.00-	1.000-20.000	-	2.1	0.2
			393.00				
	GERG-2008	2014	273.00-	1.000-20.000	-	2.4	0.1
			293.00				
	PR+EOS/	2016	213.00-	1.000-19.900	0.76-	-	-
	$a_{res}^{E,\gamma-Wilson}$		473.00		2.85		
		2017	218.00-	0.900-14.200	0.08-	-	-
			293.00		4.22		
	Demetriades	2016	273.00-	<16.000	-	-	_
	and Graham	2010	304.00	10.000			
	FOS		50 1.00				
	PC-SAFT	2014	273.00	1 000-20 000	_	2.2	1 8
	I U-DAP I	2014	273.00-	1.000-20.000	-	2.2	1.0
			202.00				
		2017	293.00	0 555 15 000	7.60		

	E-PPR78	2017	213.10-	0.555-15.000	6.36	-	-	
CO_2/Ar	PR	2009	298.33 193.00-	0 100-14 300	1 22-	1 58-	1 74-	
002/11	T IX	2009	363.00	0.100 11.500	6.04	13.02	9.43	
		2014	273.00-	1.000-20.000	-	1.8	2.2	
		-01.	293.00	1.000 200000		110		
	BWR	2007	216.00-	0.520-14.500	2.7-	0.8-	>9	
			363.00		9.7	9.2		
	РТ	2009	193.00-	0.100-14.300	2.32-	0.98-	1.77-	
			363.00		10.82	13.06	9.28	
	SRK	2009	193.00-	0.100-14.300	1.32-	1.5-	4.18-	
			363.00		11.28	14	10.84	
	RK	2009	193.00-	0.100-14.300	5.25-	1.47-	4.86-	
			363.00		14.17	14.26	11.96	
	Predictive	2007	216.00-	0.520-14.500	1.4-	0.6-	>9	
	SRK		363.00		16.2	9.2		
	3P1T	2009	193.00-	0.500-14.000	3.32-	-	-	
			363.00		25.75			
	GERG-2004	2007	216.00-	0.520-14.500	2.2-	0.5-	3.8-	
		• • • • •	363.00	• • • • • •	10.4	5.7	18.4	
		2004	90.00-	<35.000	1.0-3	0.2-	0.1-	
		1000	450.00	-2500.000		0.5	0.5	
	Duan 96	1996	<2000.	<2500.000	-	<2	-	
	DD D	2000	220.00	0 100 14 200		2.95	2 70	
	PR-Penelousx	2009	220.00-	0.100-14.300	-	2.85-	5./9- 10.51	
	SPK Danaloux	2000	220.00	0 100 14 300		2 50	10.31	
	SKK-Felleloux	2009	220.00-	0.100-14.300	-	2.39-	4.97-	
	Improved	2009	220.00-	0 100-14 300	_	5 17-	4 64-	
	SRK	2009	347.00	0.100 11.500		8.83	13 21	
	RKS	2014	273.00-	1.000-20.000	-	1.8	7.4	
			293.00				,	
	RKSP	2014	273.00-	1.000-20.000	-	1.7	3.3	
			293.00					
	BWRS	2014	273.00-	1.000-20.000	-	1.6	2.1	
			293.00					
	LKP	2014	273.00-	1.000-20.000	-	1.6	0.6	
			293.00					
	PC-SAFT	2014	273.00-	1.000-20.000	-	2.3	0.6	
			293.00					
	An improved	2018	213.00-	0-16.000	0.042	0.016	1.052	
	Hemholtz-		299.00		-		-	
	Energy-				3.270		1.570	
	explicit							
	mixture model							
	EOS-CG	2015	298.15-	11.000-31.000	-	<0.5	< 0.5	
			423-15					
		2016	273.15-	<9.000	-	0.18	-	

		2017	257.00-	2.400-6.000	0.35	0.37	-
			291.00				
	GERG-2008	2014	273.00-	1.000-20.000	-	1.8	0.5
			293.00				
		2015	298.15-	11.000-31.000	-	< 0.5	< 0.5
			423.15				
		2016	273.15-	<9.000	-	0.95	-
			323.15				
	PR+EOS/	2016	213.00-	1.000-19.900	0.76-	-	_
	ares ^{E, γ-Wilson}		473.00		2.85		
	105	2017	223.00-	1.500-14.700	0.08-	_	_
			299.00		4.22		
CO_2/SO_2	PR	2009	193.00-	0.100-14.300	1.22-	1.58-	1.74-
			363.00		6.04	13.02	9.43
	BWR	2007	216.00-	0.520-14.500	2.7-	0.8-	>9
	2	,	363.00	0.020 1.0000	97	9.2	-
	РТ	2009	193.00-	0 100-14 300	2.32-	0.98-	1 77-
		2009	363.00	0.100 1 1.500	10.82	13.06	9.28
	SRK	2009	193.00-	0 100-14 300	1 32-	1 5-	4 18-
	SIGC	2007	363.00	0.100 14.500	11.52	1.5	10.84
	RK	2009	193.00-	0 100-14 300	5 25-	1 47-	4 86-
	i i i i i i i i i i i i i i i i i i i	2007	363.00	0.100-14.500	14.17	14.26	11.06
	Predictive	2007	216.00	0 520 14 500	1 4	0.6	_0
	SPV	2007	210.00-	0.320-14.300	1	0.0-	~)
	301T	2000	103.00	0 500-14 000	3 32	9.2	
	51 1 1	2009	262.00	0.300-14.000	25.75	-	-
	DD Danalousy	2000	220.00	0 100 14 300	25.15	2.85	3 70
	T K-T CHClousx	2009	220.00-	0.100-14.500	-	2.65-	5.79- 10.51
	SDV Danalouv	2000	220.00	0 100 14 200		2 50	10.31
	SKA-Felleloux	2009	220.00-	0.100-14.300	-	2.39-	4.97-
	T	2000	347.00	0 100 14 200		12.70	12.15
	Improved	2009	220.00-	0.100-14.300	-	5.17-	4.04-
	SKK	2017	347.00	0.000.0000	2 (1	8.83	13.21
	PC-SAF1	2017	263.15-	0.200-9.060	3.61	-	-
		2017	333.21	0.000.0000	2.05		
	E-PPK/8	2017	203.15-	0.200-9.060	5.05	-	-
	<u> </u>	2015	333.21	.40.000		1 (0.0
	An improved	2017	273.00-	<42.000	-	1.6	0.2
	Hemholtz-		353.00				
	Energy-						
	explicit						
	mixture model						
	EOS-CG	2017	313.15-	<30.000	1.67-	8.25	5.33
			373.15		6.30		
		2018	263.15-	<20.000	0.88-	2.91	0.73
			304.21		2.07		
$\mathrm{CO}_2/\mathrm{H}_2\mathrm{S}$	PR	2002	250.00-	0-20.000	-	1.26(2.81
			450.00			2.76)	
		2009	193.00-	0.100-14.300	1.22-	1.58-	1.74-

	BWR	2007	216.00-	0.520-14.500	2.7-	0.8-	>9
			363.00		9.7	9.2	
	РТ	2002	250.00-	0-20.000	-	1.02(2.16
			450.00			2.26)	
		2009	193.00-	0.100-14.300	2.32-	0.98-	1.77-
			363.00		10.82	13.06	9.28
	SRK	2002	250.00-	0-20.000	-	0.51(9.23
			450.00			2.79)	
	SRK	2009	193.00-	0.100-14.300	1.32-	1.5-	4.18-
			363.00		11.28	14	10.84
	RK	2009	193.00-	0.100-14.300	5.25-	1.47-	4.86-
			363.00		14.17	14.26	11.96
	Predictive	2007	516.00-	0.520-14.500	1.4-	0.6-	>9
	SRK		363.00		16.2	9.2	
	3P1T	2009	193.00-	0.500-14.000	3.32-	-	-
			363.00		25.75		
	Duan 96	1996	<2000.	<2500.000	-	<2	-
			00				
	PR-Penelousx	2002	250.00-	0-20.000	-	1.39(3.53
			450.00			3.24)	
	PR-Penelousx	2009	220.00-	0.100-14.300	-	2.85-	3.79-
			367.00			11.64	10.51
	SRK-Peneloux	2002	250.00-	0-20.000	-	0.65(5
			450.00			2.89)	
		2009	220.00-	0.100-14.300	-	2.59-	4.97-
			347.00			12.76	12.15
	Improved	2009	220.00-	0.100-14.300	-	5.17-	4.64-
	SRK		347.00			8.83	13.21
	SAFT-VR Mie	2017	249.00-	1.500-60.000	0.99-	1.18	-
			500.00		5.43		
	PC-SAFT	2017	249.00-	1.500-60.000	1.73-	3.19	-
			500.00		7.32		
	GERG-2008	2012	60.00-	<70.000	1.0-	0.1	0.1-
			700.00		3.0		0.5
		2016	273.00-	<41.000	-	1	1
			353.00				
CO ₂ /CH ₄	PR	1990	220.00-	<15.800	2.1-	-	-
			270.00		3.3		
		2009	193.00-	0.100-14.300	1.22-	1.58-	1.74-
			363.00		6.04	13.02	9.43
		2018	293.13-	5.720-7.930	0.34-	-	-
			303.15		0.55		
	РТ	1990	220.00-	<15.800	1.6-	-	-
			270.00		3.2		
		2009	193.00-	0.100-14.300	2.32-	0.98-	1.77-
			363.00		10.82	13.06	9.28
	LK	1983	220.00-	0.600-16.700	3-3.9	-	-
			370.00				

		1994	220.00-	2.000-12.000-	/	<5(10	<5(10
			273.00			-20)	-20)
	SRK	2009	193.00-	0.100-14.300	1.32-	1.5-	4.18-
			363.00		11.28	14	10.84
		2018	293.13-	5.720-7.930	0.38-	-	-
			303.15		0.58		
	RK	2009	193.00-	0.100-14.300	5.25-	1.47-	4.86-
			363.00		14.17	14.26	11.96
	3P1T	2009	193.00-	0.500-14.000	3.32-	-	-
			363.00		25.75		
	SRK-HV	2006	245.00-	0.100-350.000	3-9.3	-	-
			383.00				
	PR-Penelousx	2009	220.00-	0.100-14.300	-	2.85-	3.79-
			347.00			11.64	10.51
	SRK-Peneloux	2009	220.00-	0.100-14.300	-	2.59-	4.97-
			347.00			12.76	12.15
	Improved	2009	220.00-	0.100-14.300	-	5.17-	4.64-
	SRK		347.00			8.83	13.21
	UMR-PRU	2018	293.13-	5.720-7.930	0.18-	-	-
			303.15		0.43		
	PR-SAFT	2018	293.13-	5.720-7.930	0.42-	_	-
			303.15		0.52		
	GERG-2008	2012	60.00-	<70.000	1.0-	0.1	01-
	CERC 2000	2012	700.00	, 0.000	3.0	0.1	0.5
		2013	304 21	0 100-20 000	-	04-	0.4-
		2015	504.21	0.100 20.000		1.1	1.1
	PR+FOS/	2017	219.00-	1 100-8 500	0.08-	1.1	-
	$E.\gamma$ -Wilson	2017	219.00-	1.100-0.500	4.22	-	-
CO./H.	GEDC 2004	2004	00.00	<35.000	1.0.3	0.2	0.1
CO_2/Π_2	UEKU-2004	2004	90.00-	<33.000	1.0-5	0.2-	0.1-
	Durin 06	1006	430.00	<2500.000		0.5	0.5
	Duan 96	1990	<2000.	<2300.000	-	<2	-
	CEDC 2000	2012	00	<70.000	1.0	0.1	0.1
	GERG-2008	2012	60.00-	0.000</td <td>1.0-</td> <td>0.1</td> <td>0.1-</td>	1.0-	0.1	0.1-
		2017	700.00		3.0	0.4	0.5
		2017	2/3.15-	<6.000	-	0.4	-
			323.15				
	PR+EOS/	2017	220.00-	0.900-93.000	0.08-	-	-
	ares ^{E,γ-wilson}		280.00	4 6 9 9 6	4.22		
	Demetriades	2016	273.00-	<16.000	-	-	-
	and Graham EOS		304.00				
CO ₂ /CO	GERG-2004	2004	90.00-	<35.000	1.0-3	0.2-	0.1-
			450.00			0.5	0.5
	Duan 96	1996	<2000.	<2500.000	-	<2	/
			00				
	EOS-CG	2018	253.00-	<13.000	-	1.4	-
			298.00				
	GERG-2008	2012	60.00-	<70.000	1.0-	0.1	0.1-
			700.00		2.0		0.5

		2013	304.21-	0.100-20.000	-	0.4-	0.4-
			308.15			1.1	1.1
	PR+EOS/	2017	223.00-	0.800-14.200	0.08-	-	-
	$a_{res}^{E,\gamma-Wilson}$		283.00		4.22		
CO ₂ /n-	GERG-2004	2004	90.00-	<35.000	1.0-3	0.2-	0.1-
alkanes			450.00			0.5	0.5
	GERG-2008	2012	60.00-	<70.000	1.0-	0.1	0.1-
			700.00		3.0		0.5
CO_2/H_2O	PR-HV	2017	273.00-	0.100-60.800	4.5	-	2.8
			478.00				
	EOS-CG	2017	273.00-	0.100-60.800	8.0	-	0.6
			478.00				
CO ₂ /NO	PC-SAFT	2017	232.93-	1.483-11.486	7.82	-	-
			273.02				
	E-PPR78	2017	232.93-	1.483-11.486	4.84	-	-
			273.02				
$CO_2/NO_2(N_2$	SAFT	2008	298.00-	-	0.003	-	-
O ₄)			328.00		-2.2		
CO ₂ /Ar/N ₂	EOS-CG	2017	268.00-	<23.000	0.5-	0.5	0.5
			303.00		3.5		
	GERG-2008	2017	268.00-	<23.000	0.5-	0.5	0.5
			303.00		3.4		
CO ₂ /Ar/H ₂	EOS-CG	2017	268.00-	<23.000	0.5-	0.5	0.5
			303.00		3.5		
	GERG-2008	2017	268.00-	<23.000	0.5-	0.5	0.5
			303.00		3.4		
$CO_2/N_2/O_2$	PR+EOS/	2017	233.00-	4.000-15.000	1.0-	-	-
	$a_{res}^{E,\gamma-Wilson}$		273.00		4.4		
$CO_2/CH_4/N_2$	PR+EOS/	2017	233.00-	4.000-15.000	1.0-	-	-
	$a_{res}^{E,\gamma-Wilson}$		273.00		4.4		

TABLE 3

Available models for transport properties summarized and compared by Li et al.²⁶

Mixtures	Models	year	Phase	Туре	T and P		Accuracy (AARD%)
					T (K)	P(MPa)	-
Viscosity							
Pure CO ₂	Vesovic et al.	1990	L.+G.	Empirical	200.00-	0.100-	G.:5
				(Emp)	1500.00	100.000	
							L.:7
	Fenghour and	1998	L.	Emp.	200.00-	<300.00	$\pm 0.3 - \pm 5.0$
	Wakeham				1500.00	0	
	Bahadori and	2010	L.	Emp.	260.00-	10.000-	1.1
	Vuthaluru				450.00	70.000	
	Heidaryan et	2011	Sc.	Emp.	310.00-	7.500-	1.7
	al.			_	900.00	101.400	
CO_2/N_2	Hirschfelder	1948	G.	Chapman-	293.00-	-	0.1
				Enskog (CE)	303.00		

	337'11	1050	C	<u>CE</u>	20(00		0.5
	Wilkes	1950	G.	CE	296.00-	-	0.5
	equation				303.00		1.7
		2017			293.00	-	1./
		2017			298.00-	0.100-	2.0
	D 1011	10/7	~	-	8/3.00	6.000	1.2.2.4
	Dean and Stiel	1965	G.	Emp.	-	-	1.3-3.6
		2017			298.00-	0.100-	2.8
			_		873.00	6.000	
	KRW law	1972	G.	Corresponding	298.00-	-	1.0
				State (CS)	873.00		
		2017			298.00-	0.100-	1.3
			_		873.00	6.000	
	Hanley	1976	G.	CS	289.00	2.000-	0-7.8
						12.000	
	EH	2017	G.	Helmholtz free	298.00-	0.100-	1.4
				energy theory (HE)	876.00	6.000	
CO_2/O_2	Wilkes	1950	G.	CE	296.00-	-	1.9
	equation				303.00		
		2017			298.00-	0.100	2.0
					674.00		
	Boltzmann	1977	G.	CE+CS	298.00-	-	0.3
					674.00		
	DS	2017	G.	Emp.	298.00-	0.100	2.8
				1	674.00		
	KRW			CS			1.3
	EH			HE			1.4
CO ₂ /Ar	Hirschfelder	1948	G.	CE	293.00-	-	0.1
					303.00		
	KRW law	1972	G.	CS	298.00-	-	1.0
					873.00		
		2017			293.00-	0.100-	1.3
					303.00	2.600	
	Wilke	2017	G.	CE	293.00-	0.100-	2.0
					303.00	2.600	
	DS			Emp.			2.8
	EH			HE			1.4
CO_2/SO_2	Herning-	1936	G.	Emp.	298.00-	-	3.5
	Zipperer			1	353.00		
	Chapman-	1939	G.	CE	298.00-	-	2
	Enskog				353.00		
	Hirschfelder	1948	G.	CE	238.00-	-	<1
					308.00		-
	Wilkes	1950	G.	CE	298.00-	-	3.5
	equation				353.00		
	- 1	2017			217.00-	1.000-	2.0
		2017			500.00	15.000	210
	Brokaw	1965	G.	CE	298.00-	-	<2
					353.00		-
	Canonically	1971	G	CE	289.00	0.100	1.8-3.0
	angle-average	17/1	5.		209.00	0.100	1.0 5.0
	pair potential						
	enerov						
	function						
	Tunction						

CO ₂ /H ₂ O	Runberg and	1949	L.	Emp.	273.00-	0- 30.000	<1
	NISSan	1007	т	Г	278.00	50.000	1
	Arrnenius type function	1996	L.	Emp.	293.00-	-	1
	DS	2017	G	Emp	217.00-	1.000-	2.8
	05	2017	0.	Emp.	500.00	15 000-	2.0
	KDW			CS	500.00	15.000	13
							1.3
	Willes			IIL CE			1.4
CO./CIL	Williag	1050	C	CE	208.00		2.0
CO ₂ /CH ₄	equation	1930	U.	CE	298.00	-	< <u>1</u>
	Dean and Stiel	1965	G.	Emp.	-	-	1.3-3.6
	DeWitt and	1966	G.	Emp.	323.00-	-	1.8
	Thodos				473.00		
	KRW law	1972	G.	CS	298.00-	-	1
					873.00		
CO_2/H_2	Hirschfelder	1948	G.	CE	299.00-	-	2-3
					550.00		
					288.00	0.100	<1
	Wilkes	1950	G.	CE	296.00-	-	0.6
	equation				303.00		
	1				500.00-	0.300	<8
					1100.00		
CO ₂ /H ₂ O/	Kumagai and	1999	L.	Emp.	273.00-	0.100-	1.3
NaCl	Yokovama			r	278.00	30.000	
11001	Bando	2004	L	Emp	303.00-	10 000-	5
	Dundo	2001	д.	Emp.	333.00	20,000	J
MDEA	NRTL-DVIS	2017	L	Excess Gibbs	293.00-	-	<5-6
DMEA.	correlation		2.	energy (GE)	353.00		00
DEEA	••••••				200100		
MAPA/C							
O_2/H_2O							
021120		1950	G	CE	296 00-	_	18
$CO_2/H_2/H$	Wilkes		<u> </u>	CE .	200.00		1.0
CO ₂ /H ₂ /H	Wilkes	1750			303.00		
$CO_2/H_2/H$ 2 $CO_2/O_2/N$	Wilkes equation Wilkes	1950	G	CF	303.00 296.00-	_	0.8
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N	Wilkes equation Wilkes equations	1950	G.	CE	303.00 296.00- 303.00	-	0.8
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N 2	Wilkes equation Wilkes equations	1950 1950 2017	G.	CE	303.00 296.00- 303.00 317.00-	-	0.8
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N 2	Wilkes equation Wilkes equations	1950 1950 2017	G.	CE	303.00 296.00- 303.00 317.00- 1161.00	-	0.8 2.0
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N 2	Wilkes equation Wilkes equations	1950 1950 2017 2017	G.	CE	303.00 296.00- 303.00 317.00- 1161.00 317.00-	-	0.8
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N 2	Wilkes equation Wilkes equations KRW	1950 2017 2017	G. G.	CE CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00	- -	0.8 2.0 1.3
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N 2	Wilkes equation Wilkes equations KRW	1950 1950 2017 2017	G. G.	CE CS HE	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00	- -	0.8 2.0 1.3
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N 2	Wilkes equation Wilkes equations KRW EH DS	1950 1950 2017 2017	G. G.	CE CS HE	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00		0.8 2.0 1.3 1.4 2.8
CO ₂ /H ₂ /H 2 CO ₂ /O ₂ /N 2	Wilkes equation Wilkes equations KRW EH DS KRW law	1950 1950 2017 2017	G. G.	CE CS HE Emp. CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00	-	0.8 2.0 1.3 1.4 2.8
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ /	Wilkes equation Wilkes equations KRW EH DS KRW law	1950 1950 2017 2017 1972	G. G.	CE CS HE Emp. CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00	-	0.8 2.0 1.3 1.4 2.8 1
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N	Wilkes equation Wilkes equations KRW EH DS KRW law	1950 1950 2017 2017 1972	G. G. G.	CE CS HE Emp. CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 283.00	-	0.8 2.0 1.3 1.4 2.8 1
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law	1950 1950 2017 2017 1972 1972	G. G. G.	CE CS HE Emp. CS CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 283.00	-	0.8 2.0 1.3 1.4 2.8 1 1
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law	1950 1950 2017 2017 1972 1972 2017	G. G. G.	CE CS HE Emp. CS CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 873.00 298.00-	-	0.8 2.0 1.3 1.4 2.8 1 1
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law KRW law	1950 1950 2017 2017 1972 1972 2017	G. G. G.	CE CS HE Emp. CS CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 873.00 298.00- 873.00	- - -	0.8 2.0 1.3 1.4 2.8 1 1 1.3
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law KRW law	1950 1950 2017 2017 1972 1972 2017 2017	G. G. G.	CE CS HE Emp. CS CS	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 873.00 298.00- 873.00	-	0.8 2.0 1.3 1.4 2.8 1 1 1.3
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law KRW law	1950 1950 2017 2017 1972 1972 2017 2017	G. G. G. G.	CE CS HE Emp. CS CS HE	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 873.00 298.00- 873.00 298.00- 873.00	-	0.8 2.0 1.3 1.4 2.8 1 1 1.3 1.4
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law KRW law EH	1950 2017 2017 2017 1972 1972 2017 2017	G. G. G. G.	CE CS HE Emp. CS CS HE	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 873.00 298.00- 873.00 298.00- 873.00	-	0.8 2.0 1.3 1.4 2.8 1 1 1.3 1.4 2.8
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law KRW law EH EH	1950 2017 2017 2017 1972 1972 2017 2017	G. G. G. G.	CE CS HE Emp. CS CS HE Emp.	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 873.00 298.00- 873.00 298.00- 873.00	-	0.8 2.0 1.3 1.4 2.8 1 1 1.3 1.4 2.8 2.0
CO ₂ /H ₂ /H ² CO ₂ /O ₂ /N ² CO ₂ /CH ₄ / N ₂ CO ₂ /Ar/N ²	Wilkes equation Wilkes equations KRW EH DS KRW law KRW law EH EH DS Wilkes	1950 2017 2017 2017 1972 1972 2017 2017	G. G. G. G.	CE CS HE Emp. CS CS HE HE Emp. CE	303.00 296.00- 303.00 317.00- 1161.00 317.00- 1161.00 298.00- 283.00 298.00- 873.00 298.00- 873.00 298.00- 873.00	-	0.8 2.0 1.3 1.4 2.8 1 1 1.3 1.4 2.8 2.0

CO ₂ /O ₂ /N 2/Ar CO ₂ /Alka ne CO ₂ /O ₂ /N 2/Ar/H ₂ /C O/CH ₄	CO ₂ - SUPERTRAP P, CO ₂ - Pedersen, CO ₂ -CS2, CO ₂ -LBC	2018	L.+ G.+ Sc.	Extended corresponding states (ECS), CS, CS2, Residual viscosity theory	243.00- 423.00	1000- 150.000	3.8, 4.6, 5.3, 9.2
Thermal Co	nductivity						
Pure CO ₂	Jarrahian and Heidaryan	2012	Sc.	Emp.	310.00- 960.00	7.400- 210.000	2.7
	Amooey	2014	Sc.	Emp.	290.00- 800.00	-	2.7
	CSA-LSSVM model	2015	G.+L.	Emp.	293.50- 474.31	0.100- 93.100	0.8
	ANFIS model	2016	G.+L. +Sc.	Emp.	293.65- 961.50	0.100- 127.800	2.6
	GP	2017	Sc.	Emp.	293.65- 961.05	0.100- 127.800	2.3
CO ₂ /N ₂	Wassiljewa+L indsaiy- Bromley Aij	1950	G.	Semi-Emp.	642.00- 961.00	-	-3~-1
					348.00	0.100- 300.000	<30
	Enskog	1951	G.	Rigorous Kinetic thory (RKT)	323.00- 623.00	0.100	3.4
	Hirschfelder	1957	G.	RKT	294.00- 1000.00	-	10.0
					323.16	-	6.4-7.8 4
	Mason and Saxena	1658	G.	RKT	323.00- 961.00	-	4.6
		2017	_		273.00- 2000.00	0.100- 300.000	5.4
	Mochick	1964	G.	RKT	300.00- 1000.00	-	2(≤500K)
	Hanley	1985	G.	CS Eme	302.00- 470.00	30.800	5
	WD	2017	G.	Emp. Hirschfelder's	470.00 273.00-	30.800 0 100-	73
	KM	2017	0.	equation Wassiliewa's	2000.00	300.000	5.4
	Cheung			equation Emp.			4.9
	EH		_	HE			3.5
CO ₂ /O ₂	Cheung	1962	G.	Emp.	273.00- 1047.00	-	2.1
	WD	2017	G	TT' 1011 -	370.00	-	4.9
	WD	2017	G.	Hirschfelder's equation	369.00- 370.00	-	7.3

	KM			Wassiljewa's			5.4
				equation			
	EH			HĒ			3.5
	MS			RKT			5.4
CO_2/SO_2	Wassiliewa	1940	G.	Semi-Emp.	323.00-	-	0.5
	···j-···-				373.00		
	Wassiliewa +	1950	G.	Semi-Emp.	323.00-	-	-1.2-2.5
	Lindsay-	1900	0.	Seini Emp	373.00		112 210
	Bromley Aii				575.00		
	Hirschfelder	1957	G	RKT	323.00	_	0-3
	imsemender	1757	0.	iuri	\$25.00 &		0.5
					373.00		
CO_2/H_2	Wassiliewa +	1950	G	Semi-Emp	273.00-	_	-0 2-8 4
002/112	Lindsay-	1750	0.	Seini Emp.	298.00		0.2 0.1
	Bromley Aii				270.00		
	Hirschfelder	1057	G	DKT	273 16		2225
	mischielder	1957	U.	KK1	275.10	-	2.2-3.3 5 9
					238.00- 472.00	-	5-8
					200.00	0.850	>0.2
					300.00	0.850-	-0.3
	A J	1075	C	F	272.00	7.300	1
	Andreev and	1975	G.	Emp.	2/3.00	-	1
	Mai ter				& 802.00		
	М	1079	C	DIZT	893.00		5
	Mason	1978	G.		-	-	5
	Kestin	1983	G.	Emp.	300.00	-	0.4
CO_2/H_2O	Wassiljewa +	1950	G.	Semi-Emp.	338.00	-	1.4
	Lindsay-						
	Bromley Aij	1050	C	a i F	200.00		10
		1950	G.	Semi-Emp.	298.00-	-	10
		40.00	~	D.117	333.00		10
	Mason and	1958	G.	RKT	298.00-	-	10
	Saxena		_	_	333.00		
	Tondon and	1968	L.	Emp.	338.00	-	2.2
	Saxena						
CO ₂ /CH ₄	Wassiljewa +	1958	G.	Semi-Emp.	298.00-	0-9.000	<5
	Mason-				308.00		
	Saxena						
	Rosenbaum	1969	G.	Emp.	333.00-	3.300-	2
	and Thodos				433.00	6.900	
	Hellmann and	2016	G.	Improved	293.00-	-	<1.2
	Bich			kinetic theory	303.00		
CO ₂ /Ar	Wassiljewa +	1658	G.	Semi-Emp.	298.00-	0-9.000	<5
	Mason-				308.00		
	Saxena						
	Hirschfelder	1957	G.	RKT	273.00-	-	3
					473.00		
	Kestin	1982	G.	Emp.	300.00	-	0.5
	WD	2017	G.	Hirschfelder's	273.00-	0.100-	7.3
				equation	473.00	11.000	
	KM			Wassiljewa's			5.4
				equation			
	EH			HE			3.5
	MS			RKT			5.4
	Cheung			Emp.			4.9
CO_2/N_2O	Kestin	1984	G.	Emp.	300.00	-	0.7

	Hirschfelder	1957	G.	RKT	300.00- 750.00	-	-2-9
CO_2/O_2N_2	Cheung	1962	G.	Emp.	273.00- 1047.00	-	2.1
Diffusivity							
CO ₂ /Ar	RKT	1954	G.	Modified- Buckingham potential	276.00- 317.00	-	inconsisten
		1964		Lennard-Jones potential			
	Fuller- Schettler- Giddings	1966	G.	Emp.	194.80- 1200.00	0.100	-3.3-14.4
CO ₂ /O ₂	RKT	1960	G.	Lennerd-Jones potential Exponential Repulsion Point center of repultion	273.00- 293.00	0.100	Within th experiment l error
		1954		Modified- Buckingham			
	Fuller- Schettler- Giddings	1966	G.	Emp.	300.00- 1500.00	0.100	-2.4-4.7
CO ₂ /N ₂	Fuller- Schettler- Giddings	1966	G.	Emp.	194.80- 1200.00	0.100	-3.3-14.4
	-				300.00- 1500.00	0.100	-2.4-4.7
CO ₂ /CO	RKT	1964	G.	Lennard-Jones potential	296.10	-	1.3
	Fuller- Schettler- Giddings	1955 1966	G.	Wilke-Lee Emp.	300.00- 1500.00	0.100	7.3 -2.4-4.7
CO ₂ /H ₂ O	Wilke-Chang	1955	L.	Semi-Emp.	279.00- 338.00	-	<11
					291.00- 348.00	-	-20
					298.00- 328.00	0.400	5
	Othmer- Thakar	1960	L.	Semi-Emp.	279.00- 338.00	-	<11
	Stokes- Heinstein	1960	L.	Hydrodynamic theory	298.00- 328.00	0.400	5
	Fuller- Schettler- Giddings	1966	G.	Emp.	194.80- 1200.00	0.100	-3.3-14.4
	6				300.00- 1500.00	0.100	20.9
	Arrhenius- type	1986	G.	Emp.	298.00- 328.00	0.400	1.7
	-78-	1996			220.00		1.0

	A generalized	2016	L.	Emp.	323.15-	200.000	2.6
	speedy-angle				1023.15	-	
	correlation					1000.00	
	Fuller-	1966	G.	Emp.	194.80-	0.100	-3.3-14.4
	Schettler- Giddings	1,000	0.	2	1200.00	0.100	
	C				300.00-	0.100	-2.4-4.7
					1500.00		
					315.20-	0.100	< 0.5
					343.90		
CO_2/SO_2	RKT	1971	G.	Canonically	263.00-	0.100	3
				angle-average	473.00		
				pair potential			
				energy function			
CH ₄ /CO ₂	Hellmann and	2016	G.	Improved	293.00-	-	<1.2
	Bich			Kinetic theory	303.00		
H ₂ S/CO ₂	Hellmann and	2016	G.	Improved	293.00-	-	<1.2
	Bich			Kinetic theory	303.00		

2 Thermodynamic property models

2.1.1 Newly developed models

- GERG-2008

GERG-2008 is an updated version of GERG-2004¹¹, which was proposed by Kunz and Wagner (2012)¹². Compared to GERG-2004, three new components, n-nonane, n-decane and hydrogen sulphide are added. The validity range has extended to temperatures from 60K to 700 K and pressures up to 35 MPa. However, the development of a generalized departure function about GERG-2008 is based on several important main and secondary natural gas components, which may not result in a good prediction for key mixtures related to CCS.

 Equation of State for Combustion Gases and Combustion Gas like Mixtures (EOS-CG)

Equation of State for Combustion Gases and combustion gas like mixtures (EOS-CG) ¹⁴, has been developed in 2016 specifically for CO₂-rich mixtures typical for CCS processes. It has been implemented in TREND software package of Ruhr-University Bochum. EOS-CG uses the mathematical approach of GERG-2008 and obtains new mixing parameters against a significantly wide literature database with a full composition range. It is proved that the EoS presents a significant improvement for thermodynamic properties of mixtures in CCS compared to Cubic EoS and GERG. The validity of EOS-CG was further investigated and extend to additional components by Rurh-University in 2018²⁷.

Peng-Robinson + residual Helmholtz energy-based model (PR+EOS/ a_{res}^{E,γ-}
^{Wilson})

Peng-Robinson (PR)+residual Helmholtz energy-based model is an advanced cubic EoS that was developed based on the combination of standard PR and the residual part of the Wilson excess Helmholtz energy model²⁸. This combination of the strengths of Cubic EoS and activity-coefficient models (g^E) has shown clear superiority in the critical region, which is particularly suitable for VLE of polar and non-polar mixtures at low and high pressures.

- E-PPR78 (Enhanced Predictive Peng-Robinson, 1978)

The E-PPR78 proposed by Quian²⁹ for natural gas and petroleum mixtures, can be seen as the combination of PR EoS and a Van Laar type activity coefficient (g^E) model under infinite pressure. Its applicability range was further extended to SO₂, O₂ and NO, and COS, NH₃, NO₂, N₂O₄ and N₂O, which covered the main components of mixtures involved CCS.

- Pressure-explicit EOS by Demetriades and Graham (2016)

A pressure-explicit EoS was derived by Demetriades et al. ³⁰ from the pure fluid fugacity and mixing rules without further integration, which was obtained to generalize an EoS for pure CO₂ to binary mixtures with N₂, O₂ and H₂. It was found that this EoS had a comparable or superior performance to GERG-2008 for those three CO₂ mixtures. Further, an expression for the mixture fugacity for an arbitrary EoS with arbitrary mixing rules could also be deduced.

2.1.2 Models evaluation

As shown in Table 1, many models have been evaluated for predicting the thermodynamic properties of CO_2 mixtures.

Even though the evaluation results about the performance of different EOSs have not pointed to one EoS, which is superior to others, the evaluated accuracy provides a good guideline regarding model selection.

Petropoulou et al.³¹ compared Redlich-Kwong-Soave (SRK), Peng Robinson (PR), Perturbated-Chain SAFT (PC-SAFT) and PR EOS with Universal Mixing Rule (UMR-PRU) for the VLE of CO₂/CH₄ mixture at (293.13, 298.14 and 303.15) K, with emphasis on the mixture critical area.

Results showed that UMR-PRU has the lowest deviation with an absolute average relative deviation (AARD) of 0.18% for the bubble point pressure and 0.43% for CO₂ mole fraction of the vapor phase. The accuracy of the models has been also evaluated in the prediction of the critical point of the mixture, where PR, SRK and PC-SAFT yield similar results, while UMR-PRU predicts slightly better the critical point both in terms of critical point pressure and critical point composition with an overall deviation equal to 1.15% and 0.99% respectively.

Diamantonis et al.³² evaluated Redlich-Kwong (RK), SRK, PR, SAFT and PC-SAFT for VLE of CO₂ mixtures including CH₄, N₂, O₂, SO₂, Ar, and H₂S. PC-SAFT was, on average, more accurate than the others. Extensive comparison between cubic and the more-complex PC-SAFT EoS reveals that there is no increased accuracy for the latter when a binary interaction parameter is used. In

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other words, one may prefer to use a relatively simpler and computationally faster EoS when some experimental data are available, and the binary parameter can be optimized. On the other hand, in the absence of experimental data, PC-SAFT is the model of choice for CO₂-gas mixture phase equilibria.

Mazzoccoli et al.³³ compared both cubic and non-analytical equations. The cubic equations chosen were PR and RKS, the non-analytical equations considered were the Benedict-Webb-Rubin-Starling (BWRS), Lee-Kesler-Plöcker (LKP) and GERG-2004/2008. In addition, a perturbation model was tested: Perturbated-Chain SAFT (PC-SAFT).

Those models were compared for the density of CO_2/N_2 , CO_2/O_2 and CO_2/Ar mixture under pipeline transport conditions: temperatures (273.15 K, 283.15 K and 293.15) K and for the pressure range of (1-20) MPa.

The highest differences were noticed increasing the pressure and the impurity concentration. Moreover, these differences increased further when the temperature was high (293 K). In such cases, the mixtures come close to the mixture critical temperature (T_{Cm}), in fact the T_{Cm} decreased compared to the T_C of pure CO₂ (\approx 304 K) with increasing concentration of impurities which had a lower T_C than CO₂.

The PR equation tends to overestimate the density value at lower temperature and to underestimate it at higher temperature, however it overestimates the density value for every temperature considered when the CO_2 concentration is lower in the CO_2/O_2 mixture. The RKS equation significantly underestimates the value of the liquid density, showing AARDs often above 10%. A lower deviation was observed

for the RKSP equation compared to the RKS, as expected, because the RKSP model contains the volume translation, a concept introduced by Peneloux, which improves the prediction of molar liquid volumes. The BWRS equation generally overestimates the density value; the deviation increased when the temperature increased, and the pressure decreased. The GERG model, the LKP and PC-SAFT equations seemed to predict better the liquid density showing AARDs below 2%.

In the vapour region, the density prediction was quite similar for every EoS studied and the deviation with the experimental data was not significant; AARDs were always lower than 5.0% and often lower than 2.5%. The highest differences continued to be noticed when increasing the pressure and the impurity concentration. However, it is important to take into account that CO₂- mixture will very likely be transported as a "dense" liquid phase in CCS process.

Perez et al.³⁴ investigated SRK, PR, PC-SAFT and SAFT-VR Mie for VLE and density of 108 binary mixtures mainly including CO₂, CH₄, C₂H₆, N₂, and H₂S. Results showed that SAFT-VR Mie had the best performance for both the VLE and density. The work of Diamantonis et al.³² made similar conclusion that the performances of the four studied EoSs were close for VLE when the regressed binary interaction parameter was used

Xu et al. ³⁵ compared E-PPR78 and PC-SAFT for VLE of 77 binary mixtures containing CO₂, SO₂, O₂, NO, H₂O and hydrocarbons. Both models show very good modeling phase equilibrium capability of the phase-equilibrium properties of most of the studied CCS mixtures. It was however necessary to adjust one binary

interaction parameter ($k_{ij,PC-SAFT}$) within the PC-SAFT model to improve its accuracy.

For CO₂/SO₂, CO₂/O₂ and CO₂/NO, the AARDs of PC-SAFT and E-PPR78 are 3.61%, 7.60%, 7.82% and 3.05%, 6.36%, 4.84% respectively.

GERG-2008 was used to calculate the density of CO_2/N_2 and CO_2/Ar . The AARD against the data measured by Yang et al.³⁶ were smaller than 0.1% and 0.5%. It is mainly because no binary specific departure function was available for the (CO₂/Ar) system in the GERG-2008. GERG-2008 was also tested for the phase equilibrium of CO_2/Ar and results showed that in general, the calculated results agreed well with the measured data at high CO_2 mole fractions. However, it predicted a significantly higher critical pressure and lower CO_2 mole fraction at and above 243 K.

GERG-2008 has been compared with classical Cubic EoSs (PR, SRK and VPT) for the density of CO₂/H₂S by Nazeri et al.³⁷. Densities of the 95.05 mol% CO₂ + 4.95 mol% H₂S binary system were measured at pressures up to 41 MPa at five different temperatures, (273, 283, 298, 323 and 353) K in gas, liquid and supercritical regions. The specific heat capacity, compressibility factor, dew point and bubble point of the system have also been derived from the measured density data. The results showed that GERG-2008 had the best accuracy with the AARD of 1.1%. High accuracy was also obtained for the derived properties. For instance, the AARDs were 1.1% and 4.8% for compressibility factor and isobaric heat capacities of CO₂/ H₂S, respectively. GERG-2008 was also compared with EOS-CG by Yang et al. for the density of CO_2/Ar^{38} at temperatures T = (273.15, 283.15, 293.15, 308.15, and 323.15) K with pressures up to the dew-point pressure or 9.0 MPa, whichever was lower. Results showed that the AARDs were around 0.95% and 0.18% for GERG-2008 and EOS-CG respectively. It was concluded that the improvement of EOS-CG is attributed to the employment of a binary specific departure function.

GERG-2008, EOS-CG, PR and gSAFT were evaluated for VLE and density of two ternary systems (CO₂ + Ar + N₂ and CO₂ + Ar + H₂) at temperatures between 268K and 303K by Ke et al.³⁹. CO₂, which is the major component, has a mole fraction ranging from 0.90 to 0.98 in both systems. The molar ratio of the two minor components is Ar:N₂ = 1:1 and Ar:H₂ = 2:3, respectively for the two ternary systems. Among these equations, EOS-CG exhibits the best predictions on both the p-T phase diagrams and densities of CO₂ + Ar + N₂; and gSAFT gives the lowest average absolute deviation between the predicted and the measured bubble-point pressures of CO₂ + Ar + H₂.

EOS-CG has also been used to calculate the VLE and density of CO₂/SO₂. The results showed that the AARD for density, dew point and bubble point were 0.54%, 2.07% and 0.88% in the temperature range of (263-304) K. However, high deviations (25.6% for vapor density and 9.46% for liquid density) were found at 304.21 K, which was due to the close proximity to the critical point of the mixture.

PR+EOS/ $a_{res}^{E,\gamma-Wilson}$ was compared with the corresponding standard cubic EoS by Lasala et al.²⁸ for the VLE of some binary mixtures like: CO₂/N₂, CO₂/O₂ and

CO₂/Ar. Results showed that PR highly over-predicted the critical point, while PR+EOS/ $a_{res}^{E,\gamma-Wilson}$ can accurately capture it.

In a study carried out in 2017, Lasala et al.⁴⁰, despite the scarcity of data available in literature, further investigated the reliability of the PR+EOS/ $a_{res}^{E,\gamma-Wilson}$ also with regard to the two ternary CO₂+N₂+O₂ and CO₂+CH₄+N₂.

The results of the comparison of the standard PR and the PR+EOS/ $a_{res}^{E,\gamma-Wilson}$ have shown that the PR+EOS/ $a_{res}^{E,\gamma-Wilson}$ model is much more accurate than the optimized standard-PR equation of state in computing multicomponent VLE data, as already attested in modeling VLE properties of the binary mixtures. The lower capability of the standard-PR in calculating bubble and critical points is also attested, especially in mixtures (in this case the ternary CO₂+N₂+O₂) of components which binary combinations lead to systems that are inaccurately modelled by the standard PR-equation of state (in this case the binaries CO₂/N₂ and CO₂/O₂).

Moreover, CO₂-water mixtures are of particular importance because these mixtures exist commonly in the range of processes in CCS industry. Additionally, they are very challenging mixtures due to the polar nature.

The study conducted in 2013 by Ibrahim et al.⁴¹ aims mainly to investigate the capabilities of SPUNG EoS when dealing with CO₂-water. The evaluation was done by comparing the behaviour of SPUNG equation of state to experimental data, and two other EoSs of a different class: SRK with van der Waals mixing rules, and SRK with Huron-Vidal mixing rules (SRK-HV).

About the CO₂-rich supercritical phase density prediction, results shown that at lower temperatures, the predictions of SPUNG EoS were substantially better than those of the SRKs, especially in capturing the steep change in density over the pressures between 5 and 10 MPa at about 308K and between 5 and 15 MPa at about 323K. In these two cases, the errors of SRKs jumped to around 15 and 13%, while the SPUNG errors were below 1.3%. Furthermore, the errors of the SRKs were reduced gradually as the density to pressure curve started saturating, while the errors of SPUNG remained low over the entire interval.

At the two evaluated high temperatures (363-383) K, the errors were similar to those of the lower temperatures and the RE distribution in general had a more flattened profile as the density increase with pressure was much more gradual at high temperatures than at the low temperature cases.

Aasen et al.⁴² conducted a much more comprehensive comparison of models for describing densities and phase compositions of CO₂/H₂O, including Cubic EoSs (PR and SRK), PC-SAFT, Perturbed-chain polar SAFT (PCP-SAFT), Cubic plus association SRK (CPA-SRK), corresponding states models with various reference fluids, GERG-2008 and EOS-CG. All the thermodynamic models were fitted with the same experimental data and compared on the same basis, facilitating a general discussion about their strengths and weaknesses. They limitated the domain of the literature survey to temperatures in the range (274-478) K and pressures below 60.8 MPa, both to cover the entire domain for CCS operating conditions, and to avoid regions where reliable measurements are scarce.

At least three fitting parameters are needed to represent the PVTxy behavior of CO₂/H₂O mixtures within an accuracy of 10%. By including a fourth parameter, it is possible to significantly improve the accuracy for phase compositions, where the Peng Robinson cubic EoS (with the Huron Vidal mixing rule and volume shift) gives the best results with an average accuracy of 4.5% and 2.8% for phase compositions and densities respectively. In comparison, the most accurate multiparameter EoS, EoS-CG, exhibits an average accuracy of 8.0% and 0.6% for phase compositions and densities respectively.

Generally speaking, EOS-CG has a better performance on both VLE and density than GERG and Cubic EOSs except for the critical region.

Compared to Cubic EOSs, PR+EOS/ $a_{res}^{E,\gamma-Wilson}$ shows a significant improvement in the critical region on VLE. When the binary interaction parameters are welltuned, Cubic EOSs can show accuracy like those models with complicated structures, such as PC-SAFT.

2.2 Transport property models

The study on transport properties is still far behind that on thermodynamic properties, in fact not many data are available; and even though some data exist for a couple of CO₂ mixtures, they are in narrow temperature and pressure ranges. For example, the thermal conductivity and diffusivity data are not yet available for most liquid CO₂ mixtures and there are no data about any transport property for CO₂/H₂S, CO₂/COS and CO₂/NH₃. For multi-component CO₂ mixtures, only some data are available for CO₂/N₂/Ar/H₂/CO/CH₄.

The slow progress in the experimental study of transport properties is mainly due to the difficulty of measurements caused by the wide ranges of temperature and pressure. New techniques may be needed to have a breakthrough.

Further, we should add that the properties of CO_2 are considerably different from other fluids commonly transported by pipeline, such as natural gas. Thus, it is necessary to use accurate representations of the phase behaviour, density, thermal conductivity and viscosity of CO_2 in the design of the pipeline.

In view of the above, there is an essential need for developing an accurate method in order to appropriately determine the transport properties of CO_2 especially in high pressures.

2.2.1 Newly developed models

- Viscosity

Bahadori and Vuthaluru⁴³ proposed a new empirical correlation for the viscosity of pure CO₂, which was an exponential function of pressure and temperature. With simple algebraic equations and few parameters, the AARD was found to be 1.1% against the reported data. The empirical coefficients could be easily tuned when new and more accurate measurements are available, which may serve as a convenient tool for engineers.

Lohrenz-Bray-Clark (LBC), originally developed for modeling natural gas and hydrocarbons mixtures, was tuned by Nazeri et al.⁴⁴ to predict the viscosity of CO₂-rich mixtures based on the residual viscosity theory (CO₂-LBC). The empirical correlative model was a fourth-order polynomial equation in the reduced density, and PR with the CO₂ volume correction (PR-CO₂ EOS) was used to calculate the mixture density.

It has been concluded that CO₂-LBC shows better prediction than original LBC, especially for density correction.

Nazeri and Chapoy ⁴⁴ proposed three predictive models for the viscosity of CO₂rich mixtures based on the corresponding states (CS) theory by using new reference fluids. CO₂-Pedersen model (CS model with one reference fluid), originally developed by Pedersen, was modified by changing the reference fluid from methane to CO₂. Similarly, CO₂-CS2 model (CS model with two reference fluids) was modified by changing the reference fluids from methane and n-decane to methane and CO₂. Moreover, the SUPERTRAPP model was modified by changing reference fluid from propane to CO₂.

The NRTL-DVIS correlation was proposed by Pinto and Svendsen⁴⁵ to calculate the liquid viscosity of mixtures. The adopted mixing rule was a function of excess Gibbs energy, which was specifically represented using the NRTL model. The adjustable parameters were fitted by the particle swarm optimization (PSO) algorithm and they had a temperature dependency.

- Thermal conductivity

Many empirical models are developed for the thermal conductivity of pure CO₂.

The correlation by Jarrahian and Heidaryan⁴⁶ was a function of the pressure and temperature based on the multiple regression analysis technique.

Amooey⁴⁷ correlated thermal conductivity as a function of density and temperature by minimizing the sum of square of errors.

A novel correlation by Rostami et al.⁴⁸ served as a powerful equation generator based on genetic programming (GP) mathematical strategy and it provided much flexibility. They are all simple without a large number of parameters.

Shams et al.⁴⁹ proposed an intelligent modeling approach, Least-Square Support Vector Machine modeling with Coupled Simulated Annealing (CSA- LSSVM), which set linear equations using support vectors. Another predictive model by Tatar et al.⁵⁰ was based on Adaptive Neuro-Fuzzy Inference System (ANFIS) and trained by the combination of Hybrid and Particle Swarm Optimization (PSO) methods. It was found to be accurate for the prediction of 1042 experimental data from the literature.

For CO₂ mixtures, the classical trajectory method was used by Hellmann et al.⁵¹ for dilute gas thermal conductivity of CH₄/CO₂, CH₄/H₂S and H₂S/CO₂. The latest intermolecular potential energy surfaces based on highly accurate quantum-chemical were employed in the calculation. The deviation reported on thermal conductivity is 2.0% for 300K < T< 700K, 2.5% for 200K < T< 300K and 700K < T/< 1200K, and 3.5% for 150K < T < 200K.

- Diffusivity

The model of Hellmann can also be applied for the calculation of diffusivity of CH_4/CO_2 , CH_4/H_2S and H_2S/CO_2 . For diffusivity, the deviation reported is 2.0% for 300K < T < 700K, 2.5% for 200K < T < 300K and 700K < T < 1200K, and 3.5% for 150K < T < 200K too.

Moultos et al.⁵² proposed a new phenomenological equation, a generalized form of the Speedy–Angel relationship, for correlating the diffusivity of CO_2/H_2O based on atomistic molecular dynamics (MD) simulations. It was a function of pressure and temperature and was found to be in good agreement with experimental data either at 283.15 K < T < 623.15 K (0.1 MPa < P < 100.0 MPa) or at 323.15 K < T < 1023.15 K (200 MPa < P < 1000 MPa) through the combination of specific force fields. The correlation can be useful for engineering calculations by extrapolating experimental data outside the measurement range.

2.2.2 Models evaluation

Wilke, Kestin-Ro-Wakeham model (KRW), Dean-Stiel model (DS), and Ely-Hanley model (EH) were evaluated by Tan et al.⁵³ for viscosity of binary and multicomponent CO₂ mixtures with non-condensable gas impurities N₂, O₂ and Ar in cryogenic process, and the AARDs were 2.0%, 1.3%, 2.8% and 1.4% respectively.

The predicted values and deviations of viscosity of CO_2/N_2 from 1 to 21 bar at X_{CO2} = 37.52 mol% at 293K have shown that the accuracies on viscosity of all models are not affected clearly by pressures except DS model. Compared to other models, DS has the worst performance and the deviation becomes larger with the increment in pressure, reaching -6.7% at pressure of 21 bar.

On average, KRW showed a better performance than the others. However, different models showed different capabilities under different working conditions.

For the operating temperature and pressure of cryogenic process (217K < T < 500 K, 1 bar < P < 150 bar), specifically, DS model is recommended to use when temperature is lower than 283 K with AAD of 1.0%. In addition, for temperature higher than 283 K at atmospheric pressure, KRW model is the first choice to calculate the viscosity of CO₂ mixtures with non-condensable impurities with AAD of 1.3%. For pressures higher than atmospheric pressure, EH model is recommended.

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Under the conditions of CO₂ cryogenic process, Tan et al.⁵³ also compared Westenbery-Dehaas model (WD), Keyes-Mass model (KM), Mason-Saxena model (MS), Cheung and Ely-Hanley model (EH) for thermal conductivity of CO₂/N₂, CO₂/O₂ and CO₂/Ar and the AARDs were 7.3%, 5.4%, 5.4%, 4.9% and 3.5%, respectively. In general, EH should be recommended for predicting thermal conductivity. Cheung model was recommended for temperature higher than 273 K at atmospheric pressure. For pressures higher than atmospheric pressure, KM model was preferred at pressure lower than 3 MPa, and EH should be employed at pressure higher than 3 MPa.

CO₂-Pedersen, CO₂-SUPERTRAPP, CO₂-CS₂ and CO₂-LBC were compared by Nazeri et al.⁴⁴ for the viscosity of CO₂/O₂/N₂/Ar, CO₂/O₂/N₂/Ar/H₂/CO/CH₄ and $CO_2/C_2H_6/C_3H_8/C_4H_{10}$, of which the experiment was conducted at temperatures from 243 to 423 K and pressures from 1 to 155 MPa in gas, liquid and supercritical regions.

The AARDs were 3.8%, 4.6%, 5.3% and 9.2% respectively for the three multicomponent CO₂-rich mixtures. Overall, CO₂-Pedesen showed the best accuracy, especially with an AARD of 2.8% for binary CO₂ mixtures containing O₂, Ar, N₂, H₂, CO and CH₄.

The performances of transport property models are more dependent on the mixtures and T and P conditions, compared to the thermo-dynamic property models. The newly developed viscosity models, such as CO₂-LBC and CO₂-Pedersen, are superior to others due to their good accuracy and wide application ranges.

3 CO₂ properties in pipeline transport

 CO_2 is transported from capture plants to storage sites by pipelines or ships, with the selection of transport method based mainly on the distance. Pipelines today operate as a mature market technology and are the most common method for transporting CO_2 .

A CO₂ stream is typically pumped to a pressure greater than 8 MPa to increase the density of CO₂ and to avoid two-phase flow regimes, thereby making it easier and less costly to transport.

The pipeline transport capacity is one of the first design criteria required for CO_2 transport cost estimation. Pipeline capacity is a function of both pipeline diameter and operating pressure, and pipelines must be appropriately sized based on corresponding CO_2 emission sources. The diameter calculation method specified by the MIT Carbon Capture and Sequestration Program shows that the pipeline diameter is a function of maximum allowable pressure drop, the CO_2 mass flow rate and the CO_2 density. Therefore, the key properties for determining the pipeline diameter are density and viscosity. For steady-state flow processes, the pressure and temperature profile are important for transporting CO_2 in its dense phases. Therefore, the most important parameters are pressure loss and temperature drop, which are related to momentum and heat transfer processes. The key properties are the phase characteristic, density, viscosity, thermal conductivity and heat capacity. The phase characteristic is one of the important properties because CCS streams are designed to be transported in their liquid or dense phases; therefore, knowledge of

the phase enveloping the CO₂ mixture is essential. Thermal conductivity and heat capacity are physical properties that govern heat diffusion in the steady state and are important for temperature drop estimation. In addition to heat transfer effects in the pipe flow, the main properties in pressure calculations are the fluid viscosity and the fluid density. For the transient transport processes, in addition to the properties mentioned in steady flow process, other properties including the speed of sound, diffusivity, and the Joule-Thomson inversion curve are significant. The speed of sound is used for the prediction of wave propagation in a pipeline, leakage tests, monitoring compositional changes, as well as 4D seismic studies. Diffusivity is a physical property governing transient heat diffusion. The Joule-Thomson inversion curve is important for hazard assessment studies of pipeline depressurization because it indicates whether the outflow stream will follow a cooling or a heating path upon pressure drops.

The next sections provide an analysis of the existing studies of the property impacts on the transport process by pipelines.

3.1 Density

Chapoy et al.⁵⁴ studied the effect of multicomponent impurities on the density and the impact on the transportation cost. The results showed that the density of the mixtures can be as much as 35% lower than that of pure CO₂ at the same temperature and pressure, which can have a significant impact on transportation costs.

Zhao and Li⁵⁵ investigated the impacts of nonpolar and polar impurities on the mass density at critical and supercritical temperatures and the property impact on pipeline transportation. It was found that higher transport temperatures and pressures will minimize the chance that the density changes abruptly for supercritical-phase CO₂ pipeline transportation.

Nookuea et al.⁵⁶ used the REFPROP model to calculate the density and varied the value from -20% to +20% to perform the sensitivity analysis. It was shown that overestimating the density increases the pressure loss and decreases the temperature drop, whereas underestimating the density decreases the pressure loss and increases the temperature drop. The maximum modeling deviations for density were found to be 18%, and, correspondingly, a maximum deviation of approximately 16% and 20% was found for the pressure loss and temperature drop, respectively. From the perspective of property modeling, this behaviour shows that developing more accurate density models should be prioritized.

3.2 Viscosity

The viscosity impacts on column diameter, packing height and annual capital cost were studied by Nookuea et al. for the absorber in chemical absorption⁵⁶. It was found that a 10% underestimation of liquid phase viscosity can result in 0.34%, 7.06% and 5.3% underestimations of the column diameter, packing height and AC respectively. The AC of the absorption tower was affected by the viscosity of liquid phase more obviously than that of the gas phase.

Tan et al.⁵⁷ investigated the impacts of viscosity on pressure loss and temperature drop in CO₂ pipeline transport. A sensitivity analysis was conducted by varying the value of viscosity from -20% to +20%. The results showed that overestimating the viscosity increases the pressure loss, whereas underestimating viscosity decreases it. In fact, it is easy to understand that a higher viscosity will increase frictional force between fluid and pipe, resulting in the rise of pressure loss. In addition, pressure loss and temperature drop are shown to not be sensitive to viscosity, and an overestimation of the viscosity by 20% leads to an increment in pressure loss of approximately 3% and a negligible variation in the temperature drop.

Moreover, the impact of viscosity on the volume and AC of the multi-stream heat exchanger in the cryogenic separation process was evaluated by Tan et al.^{53,58}. It was found that the overestimation of viscosity led to the overestimation of the volume. That is because heat transfer coefficient decreases and pressure drop increases when viscosity increases, both resulting in the increase of volume.

3.3 Phase Characteristic

Mazzoccoli et al.⁵⁹ compared the P- ρ -T experimental data of CO₂ binary mixtures with different EoS. Based on that comparison, pipelines were simulated to illustrate the impacts of the predicted properties on the pressure drop.

The pressure drops for transportation in the supercritical region, in the dense region and as a subcooled liquid were compared by using different EoS as Redlich-Kwong-Soave (RKS) and GERG. In the supercritical region, the difference in pressure drop calculated by RKS and GERG is from 10.5% to 43.8%, in the dense region, the difference is from 11.8% to 22.9% and in subcooled liquid, the difference is from 1.7% to 3.3%.

3.4 Heat capacity

Tan et al. ⁵⁷ evaluated the impact of heat capacity on the transport process and calculated the temperature drop by varying the value of heat capacity. The accuracy of the existing models of heat capacity was reviewed to study the real deviation of the temperature drop. The value was varied from -20% to +20% for the sensitivity analysis. The overestimation of the heat capacity leads to a lower temperature drop, whereas the underestimation of the heat capacity results in a higher temperature drop. For predicting the heat capacity, the maximum modeling deviation is 5%; correspondingly, the maximum deviation leads to the variation of the temperature drop of 3%.

3.5 Thermal conductivity

Tan et al.⁵⁷ conducted a sensitivity analysis on the influence of the thermal conductivity on the temperature drop in a pipeline for the transport of CO_2 mixtures by varying the thermal conductivity from -20% to +20%. It was shown that the impacts of the thermal conductivity on the temperature drop are small and can be neglected.
Discussion and conclusion

This work pictures the progress in studies on thermodynamic and transport properties of CO_2 mixtures, including vapor-liquid equilibrium, density, viscosity and thermal conductivity. Thanks to the new experimental data a more consistent comparison of the performance of the available thermodynamic models has been possible.

Among the existing thermodynamic models, cubic equations of state have the simplest structure and are capable of giving reasonable results for the PVTxy properties of CO₂ mixtures, if the binary interaction parameters k_{ij} are calibrated. EoS with complicated structures, such as BWR and SAFT, have shown to give a better accuracy than cubic EoS for volume calculations, but cubic EoS on the other hand, show an advantage in VLE calculations. GERG, according to its claimed accuracy, should give the best results. The equation is however intended for natural gas components, and not CO₂ rich mixtures and its applications are limited to certain impurities.

Currently, none of the EoS evaluated in the literature show any clear advantage in CCS applications for VLE and other thermodynamic property calculations.

In addition, there are still some gaps in the literature data collected. For example, no data are available yet about the phase equilibrium of CO_2/COS and CO_2/NH_3 , the density of CO_2/NH_3 , gaseous CO_2/O_2 and CO_2/NO_2 (N₂O₄), and transport properties of CO_2/H_2S , CO_2/COS and CO_2/NH_3 . Previous works have mainly

focused on the major impurities. However, in order to obtain more accurate properties, more attention needs to be paid to the minor components.

Because of this situation, more experimental measurements about the PVTxy properties of CO₂-rich mixtures should be conducted, including both binary and multi-component mixtures in order to ensure sufficient data for proper development of future EoS. In addition, it is also of importance to identify the accepted accuracy according to the demands of process design and operation before a proper model could be developed for CCS applications. A reference EoS for CCS should be a goal for the future.

Regarding the recent development on modeling, new models and methods were proposed. Methods of data analysis, such as machine learning and artificial neural network, have been adopted. Such methods, which do not rely on a deep understanding of the fundamental theory, can make the model development easier.

Nevertheless, data processing techniques require more experimental data about the properties of CO₂ mixtures, especially the multicomponent mixtures.

For the transport process, existing studies mainly focused on property impacts on the performance of pipeline steady flow processes. The studied parameters include pressure loss, temperature drop and transport safety. Among the properties, density and heat capacity are the most important in the pipeline steady flow process. For other properties, including viscosity and thermal conductivity, the property impacts are much smaller. In addition, the phase characteristics were studied mainly from the aspect of avoiding two-phase flow and securing transport safety; these phase characteristics are also very important in pipeline transport.

To improve the property models, the existing models which have the potentials to give accurate results can be modified, otherwise the new models should be developed if the existing models with modifications cannot satisfy the requirements.

Because of this situation, much more experimental measurements about the PVTxy properties of CO₂-rich mixtures should be conducted, including both binary and multi-component mixtures in order to ensure sufficient data for proper development of future models. In addition, it is also of importance to identify the accepted accuracy according to the demands of process design and operation before a proper model could be developed for CCS applications. A reference EoS for CCS should be a goal for the future.

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