CHEMICAL ENGINEERING TRANSACTIONS
VOL. 32, 2013
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791
DOI: 10.3303/CET1332311

CO_2-mixture Properties for Pipeline Transportation in the CCS Process

Michela Mazzoccoli[a], Giorgia De Guido[b], Barbara Bosio[a], Elisabetta Arato[a], Laura A. Pellegrini*[b]

[a] Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova, Via Opera Pia 15, 16145 Genova, Italy
[b] Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy
laura.pellegrini@polimi.it

Transport is an essential feature of the CCS process as the CO_2 quality required for transport may influence the choice of the capture technology and impose limits on the performance requirements. Therefore, to design CO_2 transport networks, it is important to have an accurate knowledge of the thermodynamic properties of CO_2-mixtures. In this paper the results of different EOS (both cubic equations as Peng-Robinson or Redlich-Kwong-Soave and non-analytical equations as Benedict-Webb-Rubin-Starling, Lee-Kesler or GERG model) have been compared with *P-ρ-T* experimental data obtained by the authors. The Lee-Kesler equation and the GERG model showed a good prediction of CO_2-mixture density in the working conditions of the pipeline transport. Finally, simulations of pipelines that transport pure CO_2 and CO_2-mixtures have been performed and discussed.

1. Introduction

Reducing the emissions of greenhouse gases is one of the most important challenges to be faced. CO_2 emissions must be reduced by 50 - 85% by 2050 (compared to 2000 levels) (IPCC, 2011).
Carbon Capture and Storage (CCS) could be a good option in a portfolio of technologies with the potential to cut the CO_2 emissions and allow continued use of fossil fuels (IPCC, 2005; Pellegrini et al., 2011).
Transportation is an essential component of the CCS process. Power and industrial plants where CO_2 is captured are usually located at long distances from the storage locations, requiring the transportation of CO_2 from the point of capture to the storage site. For the purpose of transportation, the CO_2-mixture must have high density and purity levels, thus the requirement for transportation may also influence the type of capture technology to be chosen.
Once CCS develops to a large industry, the main transport solution will be via pipelines where the CO_2-rich streams will likely be transported in the supercritical, "dense" or subcooled liquid conditions as indicated in Figure 1, so that the volumes to be transported are not large, in contrast to the gas phase where the density is low. This working condition will also reduce the work required in the pumping stations.
It is extremely important to know the thermodynamic properties of the different CO_2-mixtures to be transported under these conditions and the interactions between the pure carbon dioxide and other components that may be present in the streams (i.e. N_2, O_2, Ar, CH_4, H_2). Therefore, the study of Equations-of-State (EOS) that calculate the thermodynamic properties of different CO_2-rich mixtures could be of great interest in the CCS process.

Please cite this article as: Mazzoccoli M., De Guido G., Bosio B., Arato E., Pellegrini L., 2013, Co2-mixture properties for pipeline transportation in the ccs process, Chemical Engineering Transactions, 32, 1861-1866 DOI: 10.3303/CET1332311

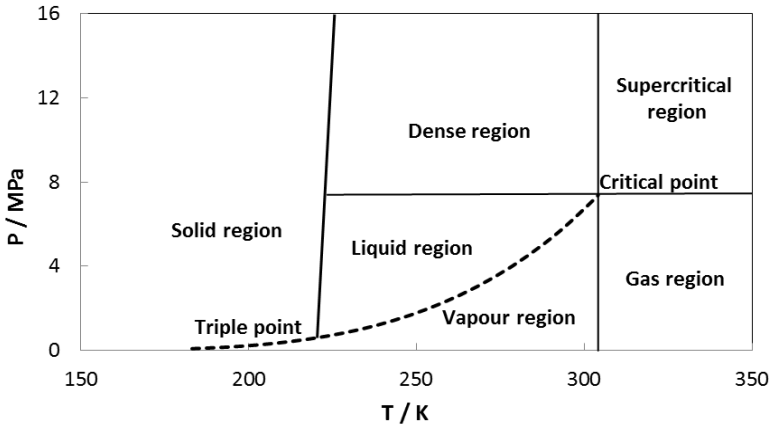

Figure 1: PT diagram of pure CO_2.

In this work the results of different EOS (both cubic equations and non-analytical equations) will be compared with *P-ρ-T* experimental data of binary mixtures of carbon dioxide with nitrogen, oxygen and argon obtained by the authors at the Energy and Environmental Laboratory of Piacenza (LEAP) using a vibrating tube densimeter (Anton Paar DMA 512-HPM). These mixtures, in particular CO_2-O_2 and CO_2-Ar binary mixtures, have been selected because very few volumetric experimental data are available at the CCS transport conditions (Mazzoccoli et al., 2012).
Finally, simulations of pipelines that transport pure CO_2 and CO_2-mixtures will be discussed.

2. Comparison between experimental data and EOS results

The *P-ρ-T* experimental data of CO_2-rich mixtures (Mazzoccoli et al., 2012) obtained at the LEAP have been compared with different EOS included in the commercial simulation software Aspen Plus V7.3.
The EOS analyzed were both cubic and non-analytical equations. Among the former ones, Peng-Robinson (PR) (Poling et al., 2001), Redlich-Kwong-Soave (RKS) (Poling et al., 2001) and Redlich-Kwong-Soave with volume translation, that is a concept introduced by Peneloux and Rauzy to improve molar liquid volume calculation (RKSP) (Peneloux et al., 1982), have been chosen.
The non-analytical equations considered were the Benedict-Webb-Rubin-Starling (BWRS) (Starling and Han, 1972), Lee-Kesler-Plöcker (LKP) (Knapp et al., 1982) and GERG model (Kunz et al., 2007; Kunz and Wagner, 2012).
The molar fractions of the binary mixtures considered are reported in Table 1.
The Data Regression System implemented in Aspen Plus V7.3 with the Britt-Luecke algorithm was used to compare the EOS results with the experimental data and to make the regression of the binary interaction parameters, k_{ij}.
All the EOS considered have been calibrated with respect to k_{ij}, except for the GERG model due to the complexity of its binary mixture models that require a large number of experimental data in order to achieve statistical significance in the derived interaction parameters.
The k_{ij} obtained for each mixture studied are reported in Table 2.
To compare the different EOS the percentage absolute average deviation (AAD), represented in Eq(1), was taken into account:

$$AAD = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|y_{calc,i} - y_{\exp,i}\right|}{y_{\exp,i}} \cdot 100 \qquad (1)$$

where $y_{calc,i}$ is the variable calculated by EOS, $y_{exp,i}$ is the experimental variable and N is the number of experimental data.
Figure 2 reports the AAD obtained for the liquid density of the binary mixtures studied for the different EOS.
In general the cubic equations showed higher errors, in particular the RKS equation. Cubic EOS were developed originally to describe the non-ideal behaviour in the vapour region and have been extended to

describe also the liquid region, but without volume translation the prediction of liquid density can lead to significant deviations.
Among the non-analytical EOS, the BWRS equation showed an higher AAD. The LKP equation and the GERG model seemed to better predict the liquid density, in particular in the conditions typical for transport in pipelines where the CO_2-mixture should be characterised by a CO_2 molar concentration above 95%.

Table 1: Molar fraction of the binary mixtures considered

	Mix1	Mix2	Mix3	Mix4	Mix5	Mix6
CO_2	0.9605	0.9276	0.9873	0.8785	0.9558	0.8512
Ar	0.0395	0.0724	-	-	-	-
N_2	-	-	0.0127	0.1215	-	-
O_2	-	-	-	-	0.0442	0.1488

Table 2: Regressed k_{ij} using the Britt-Luecke algorithm

	PR	RKS	RKSP	BWRS	LKP
CO_2-Ar	0.086	-0.627	-0.339	0.076	0.008
CO_2-O_2	0.192	-0.186	0.009	0.077	-0.045
CO_2-N_2	-0.069	-0.347	-0.297	-0.082	0.081

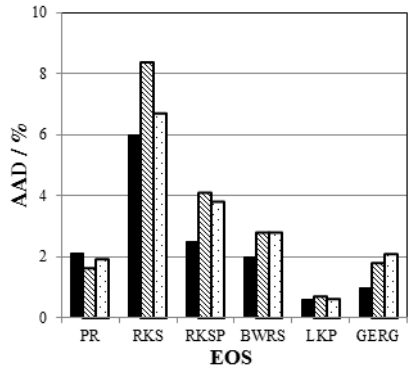

Figure 2: The AAD between the experimental liquid density and the density calculated by EOS with regressed k_{ij} for different binary mixtures: CO_2-Ar (■), CO_2-N_2 (▨) and CO_2-O_2 (⊡).

3. Simulations of pipelines

To illustrate the impact of the differences between predicted properties using different EOS, the pressure profile along a horizontal pipeline transporting streams with different compositions is presented. The software program used for CO_2 transport simulations is again Aspen Plus V7.3. For the purpose of illustration, a simplified case study has been considered: 4.519×10^6 Sm^3/d transported by a 160.9 km long pipeline, with an inside diameter of 395 mm and a thickness of 6 mm (Moshfeghian, 2012). Thermal losses have been neglected.
Five systems have been chosen for the simulations: one consisting of pure CO_2 and the other ones represented by a binary mixture of CO_2 with Ar, O_2, N_2 and CH_4, respectively. Internationally accepted standards for the specification of CO_2 mixtures for pipeline transmission systems do not exist. Thus, based on the fluid specification for Kinder Morgan operated pipelines in the USA and on those proposed by the Ecofys study (Oosterkamp and Ramsen, 2008), a molar composition of 96% CO_2 and 4% of the other component has been considered for the CO_2-Ar, CO_2-O_2 and CO_2-N_2 system and a molar composition of 95% CO_2 and 5% CH_4 has been assumed for the CO_2 binary mixture with methane. The non-CO_2 component molar fraction in the binary mixtures is the maximum allowed by the previously cited literature in order to emphasize its influence on the system behavior.
Technically, CO_2 can be transported through pipelines in the form of a gas, of a supercritical fluid or as a subcooled liquid. Operationally, most CO_2 pipelines used for enhanced oil recovery transport CO_2 as a

supercritical fluid. In the literature (Zhang et al., 2006) mainly supercritical fluid and subcooled liquid transport modes are compared, examining their impact on energy efficiency and costs.
In order to analyze how the thermodynamic package affects the simulation results, three sets of inlet operating conditions are studied: the supercritical conditions of 316.15 K and 18.6 MPa, corresponding to the design conditions of the Cortez pipeline (Oosterkamp and Ramsen, 2008), the dense region conditions of 293.15 K and 14 MPa (average conditions for the Cortez pipeline) and the subcooled liquid conditions of 273.15 K and 6.0 MPa for pure CO_2 and 7.5 MPa for the studied binary mixtures (conditions chosen to avoid two-phase flow).
To further compare the previously mentioned EOS, the PT-envelopes for the four binary mixtures CO_2-Ar, CO_2-O_2, CO_2-N_2 and CO_2-CH_4 have been constructed using the Aspen Plus software. For the former three mixtures the regressed binary interaction parameters k_{ij} shown in Table 2 have been used. For the CO_2-CH_4 mixture the binary interaction parameters available in Aspen Plus have been adopted. The PT-envelopes for the four binary mixtures are reported in Figure 3: some differences are evident near the critical point, especially for the CO_2-Ar, CO_2-O_2 and CO_2-N_2 systems, for which the BWRS equation tends to give a value of the mixture critical pressure which is higher than that provided by the other EOS. Differences among the considered EOS can also be noticed at low temperatures when the most volatile components are present in mixture with CO_2 (Figure 3a, b and c), although the transportation by pipelines at such low temperatures is not usually carried out.

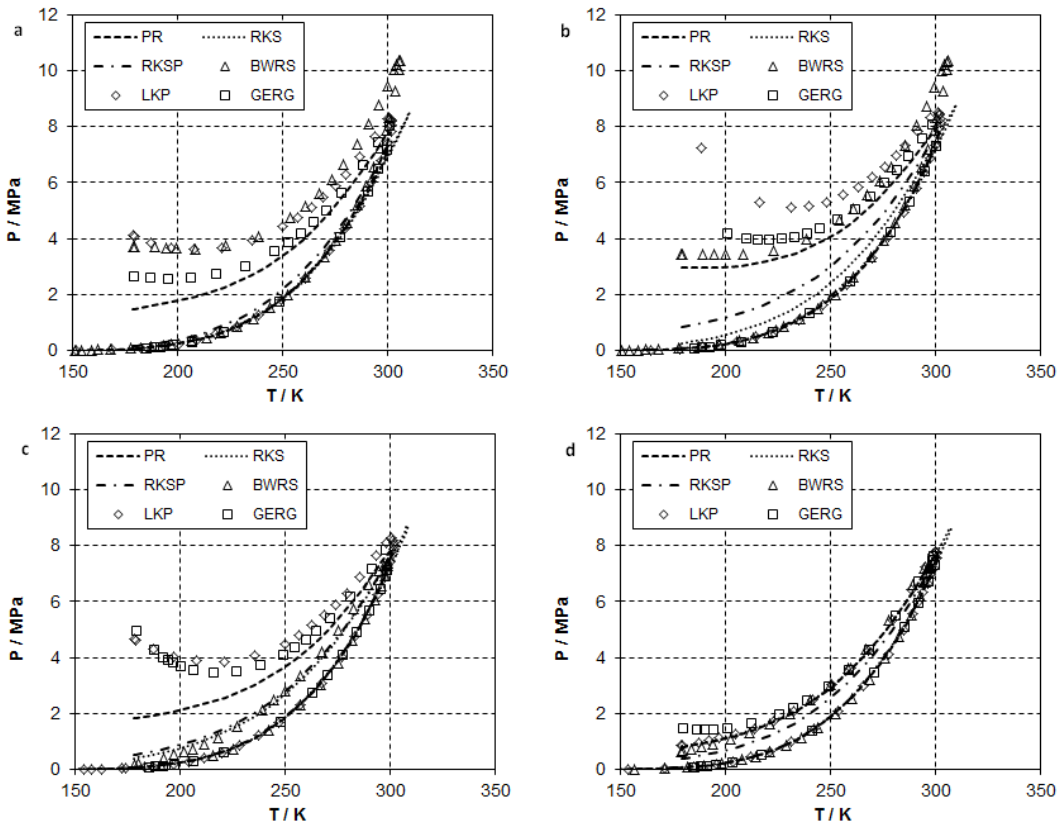

Figure 3: PT-envelopes for the CO_2-Ar (96% - 4%) mixture (a), the CO_2-O_2 (96% - 4%) mixture (b), the CO_2-N_2 (96% - 4%) mixture (c) and the CO_2-CH_4 (95% - 5%) mixture (d).

The results obtained from the pipeline simulations using the RKS and GERG equations of state are shown in Table 3. The two EOS have been selected since they are representative of models with a high and low AAD, respectively (Figure 2). The results reported in Table 3 confirm how the use of different thermodynamic models affects pressure drop calculations. The greatest differences in the values obtained with the two EOS are observed for the operating conditions in the supercritical and in the dense regions. On the contrary, modest changes in pressure drop calculations are observed for the subcooled liquid. This

behavior can be easily explained: it is well known that the cubic EOS, at least when classical mixing rules are applied (Pellegrini et al., 2010), fail in predicting the system thermodynamic behavior at the supercritical conditions (Pellegrini et al., 2012a; Pellegrini et al., 2012b).

Table 3: Pressure drop [MPa] calculation results for transportation in the supercritical region, in the dense region and as subcooled liquid

	Supercritical region		Dense region		Subcoooled liquid	
	RKS	GERG	RKS	GERG	RKS	GERG
CO_2	1.971	1.751	1.787	1.598	1.551	1.525
CO_2-Ar	2.603	1.810	1.908	1.636	1.568	1.540
CO_2-O_2	1.992	1.803	1.900	1.628	1.570	1.531
CO_2-N_2	2.079	1.817	2.016	1.641	1.594	1.543
CO_2-CH_4	2.116	1.781	1.908	1.612	1.553	1.519

The operation profile of the pipelines in the three different operating conditions is shown in Figure 4 for pure CO_2 and for the four CO_2-mixtures, when the GERG model is used: in all the cases the stream remains outside the phase envelope. However, in the case of subcooled liquid stream, attention must be paid to avoid the onset of a two-phase flow when the pressure decreases because of pressure losses.

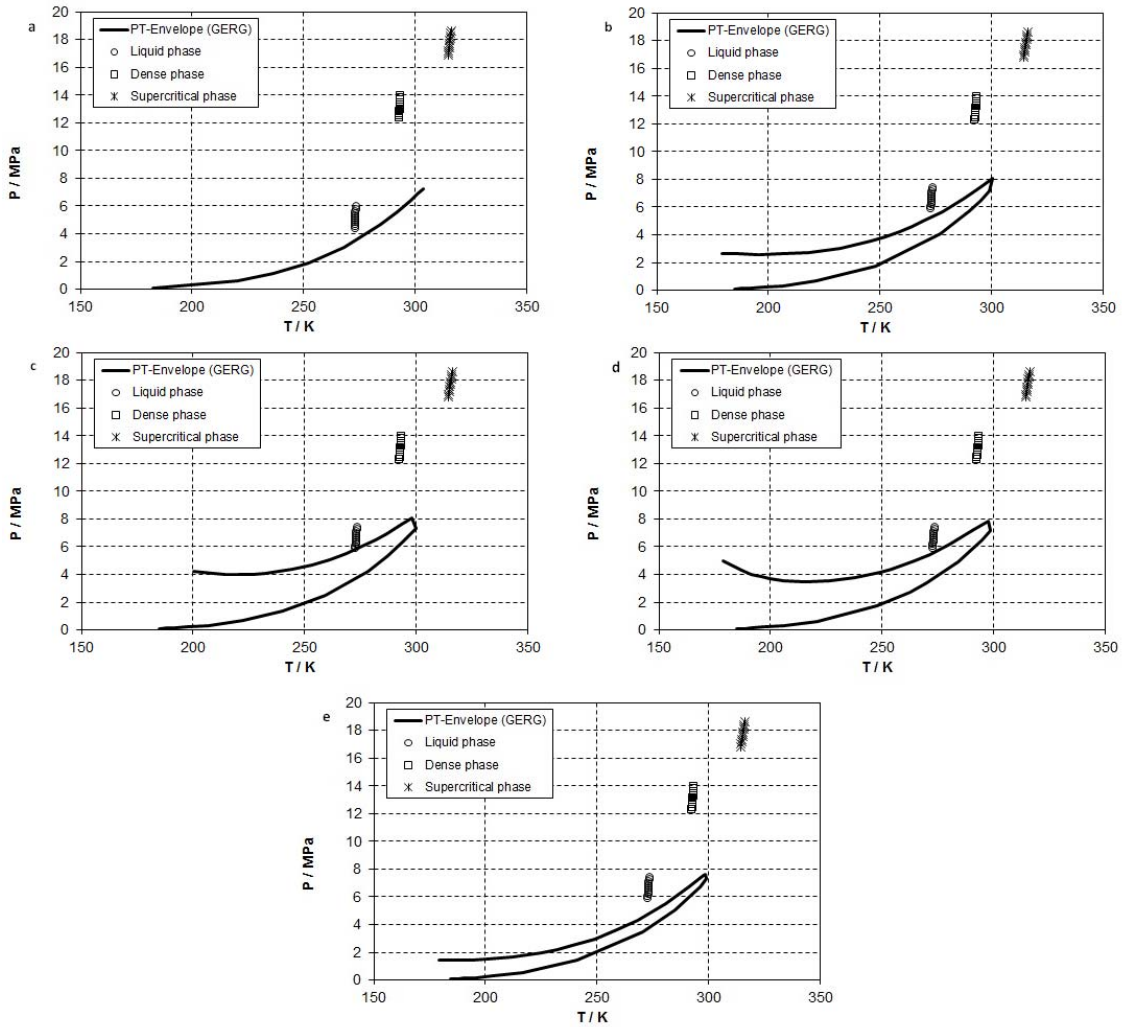

Figure 4: PT profile along the pipeline for pure CO_2 (a), the CO_2-Ar (96% - 4%) mixture (b), the CO_2-O_2 (96% - 4%) mixture (c), the CO_2-N_2 (96% - 4%) mixture (d) and the CO_2-CH_4 (95% - 5%) mixture (e).

4. Conclusions

Carbon Capture and Storage is increasingly promoted as a solution to global warming. An important step in this process is the transportation of CO_2 from the point of capture to the storage site. The most efficient way to transport CO_2 is in the supercritical phase (WRI, 2008) or in the dense phase. The performances of different equations of state have been analyzed according to their capability to predict the supercritical and dense phase behavior. This paper reports the results of the comparison between experimental data and the most used EOS predictions. It shows that the Lee-Kesler-Plöcker (LKP) equation and the GERG model predict the liquid density better than the other equations of state. The simulations of pipelines transporting pure CO_2, CO_2-Ar, CO_2-O_2, CO_2-N_2 and CO_2-CH_4 mixtures confirm that differences in pressure drop calculations are observed when different EOS are used. The greatest differences in the calculated values are found for the supercritical and the dense region flow, while in the case of subcooled liquid also the RKS with classical mixing rules presents good performances.

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