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Analysis and comparison of Equations-of-State with p-ρ-T experimental data for CO_2 and CO_2-mixture pipeline transport

Michela Mazzoccoli*, Barbara Bosio, Elisabetta Arato

Department of Civil, Enviromental and Architectural Engineering, University of Genoa,via Opera Pia,15, 16145 Genoa, Italy

Abstract

Transport is an important feature of the CCS process as the CO_2 quality requested by pipelines may influence the choice of the capture technology and its limit performance requirements. So, the knowledge of the thermodynamic properties of CO_2-mixtures has an important role, however a suitable equation of state under the appropriate conditions for pipeline transport has not been clearly defined yet.
In this paper different equations of state for predicting densities of CO_2 and CO_2 mixtures have been analyzed and compared with experimental data found in literature or obtained by authors performing specific laboratory p-ρ-T measurements.

Keywords:CO_2 mixtures; Transport; Pipelines; Thermodynamics; Equation of State; Simulation.

1. Introduction

Transport is important in the framework of the CCS process, which, indeed, is sometimes indicated as the CCS&T (Carbon Capture, Storage and Transportation) process. In fact, the power and industrial production plants that are large producers of CO_2 are normally located a long distance from the CO_2 storage locations and the captured CO_2 has to be transported from the point of capture to the storage site.

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

* Corresponding author. Tel.: +39-010-3532588; fax: +39-010-3532589.
E-mail address: michela.mazzoccoli@dicat.unige.it.

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required [1]. Therefore transport can also influence the choice of the capture technology in terms of CO_2 concentration and the kind of impurities it contains.

In this work our attention was focused on pipelines, where CO_2 will most likely be transported in the "dense" phase (above the critical pressure and under the critical temperature).

To understand the thermodynamic properties of different CO_2-mixtures and the interactions between the CO_2 and other components which can be present in the gaseous stream (i.e. N_2, H_2, O_2, CH_4), the study of the Equations of State (EOS) is extremely important.

In literature many references are available on CO_2 and CO_2 mixture EOS [2,3,4,5], nevertheless a suitable equation of state for mixtures in appropriate conditions for pipeline transport, in particular with a high CO_2 concentration, has not been clearly defined yet as reported in [6].

The aim of this work is to highlight the crucial working conditions necessary for CO_2 transport by pipeline and compare the reliability of different EOS for predicting the densities of the CO_2 and binary CO_2 mixtures in such conditions.

In particular, we have compared the cubic equations (Peng Robinson and Redlich-Kwong-Soave) and more complex equations (Benedict-Webb-Rubin-Starling, Wagner models) with p-ρ-T experimental data (see Table 1).

The comparison has been made with the commercial simulation software Aspen Plus©.

2. CO_2 conditions for transport by pipelines

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 (P_c) and at room temperature (lower than T_c). Under these conditions the CO_2 is in a "dense" phase (see Fig. 1) and exhibits a low viscosity and a density similar to a liquid.

In order to avoid pipeline stress, the pressure should not be too high. Therefore CO_2 will most likely be transported in the range of 80-130 bar.

Moreover, to avoid two-phase flow, it is necessary to repump the CO_2 whenever the pressure falls to near P_c. Therefore, it is essential to study the pressure drop and the density variation along the pipeline.

In order to evaluate the above-mentioned stream characteristics, pipeline simulations have been made with different commercial softwares: Aspen Plus and Aspen Hysys licensed by AspenTech and Olga licensed by SPTgroup.

The density results obtained with Aspen Plus (using the Peng-Robinson equation and the Span-Wagner equation [2]) and Olga (using the Span-Wagner equation) for pure CO_2 were similar.

With regards the CO_2-mixtures, some convergence problems were encountered using the AspenTech softwares assuming different EOS.

Therefore a comparison of different EOS with experimental data was necessary to identify which equations better predicted the CO_2 and CO_2-mixture density under pipeline-transport working conditions, to overcome the problems previously described.

3. EOS comparison with literature experimental data

The experimental data reported in Table 1 were compared with the density value calculated by different EOS included in the Aspen Plus database [7].

The equations of state analyzed for pure CO_2 and for CO_2-mixtures are reported in Table 2.

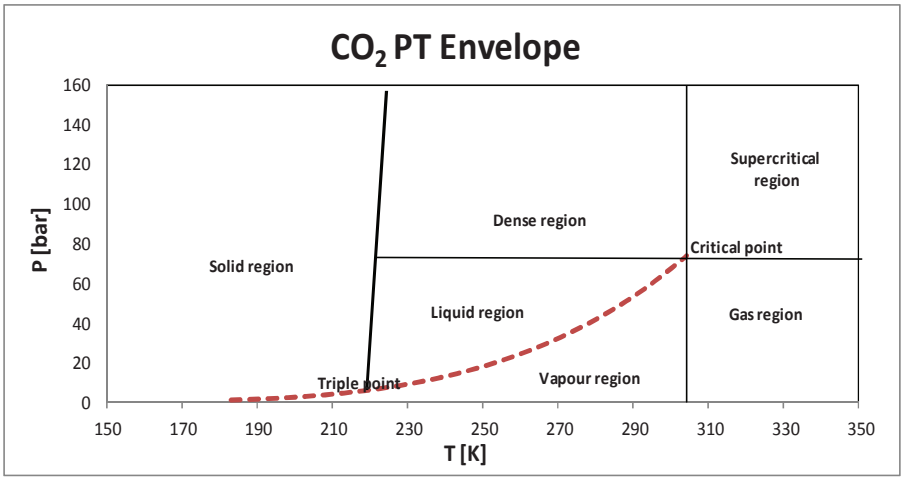

Fig. 1 CO_2 PT envelope

To better compare the different models, some dimensionless parameters were taken into account: the relative deviation (RDρ), the average deviation (Biasρ), the absolute average deviation (AADρ), and the maximum deviation (MAXDρ):

$$RD\rho = \frac{\rho_{calc} - \rho_{\exp}}{\rho_{\exp}} \qquad Bias\rho = \frac{1}{N}\sum_{i=1}^{N} RD_{\rho}$$

$$AAD\rho = \frac{1}{N}\sum_{i=1}^{N}\left|RD_{\rho}\right| \qquad MAXD\rho = \max\left|RD_{\rho}\right|$$

where ρ_{calc} is the calculated density by EOS, ρ_{exp} is the experimental density and N is the number of experimental data.

3.1. Results and discussion

3.1.1. Pure CO_2

On the basis of the available data, the EOS comparison was made for different regions (see Fig. 1): the vapour region [11,13], gas region [10,11,12], dense region [11], supercritical region [10,11,12] and phase equilibrium [9,13].

Each EOS showed similar behaviour in the vapour and in the gas region, even if the relative deviation in the latter region was slightly higher.

The RKS and its modifications exhibited the same behaviour and tended to underestimate the experimental value, while the PR and its modifications, BWRS and LK tended to overestimate it. Furthermore, the two latter equations had a higher relative deviation near the critical point.

The REFPROP model had good accuracy in the density prediction; the relative deviation was lower than 0.5% in the vapour region and 1.2% in the gas region.

In the dense region, almost all equations predicted the density with significantly less accuracy. The worst were the PR and its modifications (except PR-BM equation), the RKS and its modifications (except RKSP and RKSP-TWU equations) that often had errors higher than 10%, in particular near the critical temperature, where they even arrived at 25%. The PR-BM, RKSP and RKSP-TWU equations predicted

the experimental data better, in fact their AAD were around 3,5%. The LK equation and REFPROP model had the lowest relative deviation (<1.5% for the former and <0.5% for the latter).

On the contrary, the worst prediction of density in the supercritical region was reported by the RKSP and RKSP-TWU equations, while the PR and its modifications predicted the experimental data better (AAD < 3.8%). Again LK equation and the REFPROP model showed the lowest relative deviation.

The PR, PR-MC, PR-TWU, RKS, RKS-TWU and REFPROP fitted the experimental data on the saturated liquid density very well: the maximum deviation was 0,09% for the last one and 0,9% for the others. The LK showed a low deviation (AAD < 1.6%), except that for few data.

PR-BM, RKSM, RKSP, RKSP-TWU and BWRS, in particular near the critical point, predicted density with less accuracy.

The bias, the AAD and the maximum deviation of each EOS are displayed in Fig. 2 and it is evident that the REFPROP model, where the Span-Wagner equation for CO_2 is implemented, predicted the experimental data in a good way in every region analyzed. Considering the other equations, instead, there is no good global model and each EOS has regional advantages and disadvantages. In addition the different alpha function does not improve the behaviour of cubic equations, only the PR-BM showed a better density prediction respect to other PR equations, except in the phase equilibrium.

Table 1. Available p–ρ-T experimental data

Source	Year	N° of data	Mixture	T (K)	P (MPa)	Uncertainty
[9]	1976	29	CO_2	216-303	0.5-7.1	
[10]	1998	108	CO_2	304-320	1-10.5	P: ±2 kPa, T: ± 0.01 mK
[11]	2001	118	CO_2	240-470	0.5-30	P: ±0.05 kPa, T: ± 0.004 K
[12]	2004	11	CO_2	360	1-10.2	P: ±10 kPa, T: ± 0.01 mK
[13]	2005	61	CO_2	233-293	0.1-5.7	P: ±5.0 mbar, T: ± 0.02 K
[14]	1971	201	CO_2-N_2, CO_2-CH_4	253-288	2-15	P: ±0.01 atm, T: ± 0.01 K
[15]	1988	91	CO_2-CH_4	225-400	2-35	P: ±0.01%, T: ± 0.05 K
[16]	1997	747	CO_2-N_2	225-450	1-70	P: ±0.006 MPa, T: ± 0.005 K

Table 2. EOS analyzed

Equation	Abbreviation	Fluid
Peng Robinson with standard alpha function	PR	CO_2/CO_2-mixtures
Peng Robinson with Boston Mathias extrapolation	PR-BM	CO_2/CO_2-mixtures
Peng Robinson with Mathias Copeman alpha function	PR-MC	CO_2
Peng Robinson with TWU alpha function	PR-TWU	CO_2
Peng Robinson with modified Huron Vidal mixing rules	PR-MHV2	CO_2-mixtures
Peng Robinson with Wong Sandler mixing rules	PR-WS	CO_2-mixtures
Redlich Kwong Soave	RKS	CO_2/CO_2-mixtures
Redlich Kwong Soave with Mathias alpha function	RKSM	CO_2/CO_2-mixtures
Redlich Kwong Soave with TWU alpha function	RKS-TWU	CO_2
Redlich Kwong Soave with modified Huron Vidal mixing rules	RKS-MHV2	CO_2-mixtures
Redlich Kwong Soave with Wong Sandler mixing rules	RKS-WS	CO_2-mixtures
Redlich Kwong Soave with volume translation (Peneloux modification)	RKSP	CO_2/CO_2-mixtures
Redlich Kwong Soave - Peneloux with TWU alpha function	RKSP-TWU	CO_2
Benedict Webb Rubin Starling	BWRS	CO_2/CO_2-mixtures
Lee-Kesler- Plöcker	LK	CO_2/CO_2-mixtures
REFerence fluid PROPerties model (RefProp) developed by NIST (It includes the Span-Wagner [2] equation of state for CO_2).	S&W	CO_2
GERG-2008 model by the Groupe Européen de Recherches Gazières [8]	GERG2008	CO_2-mixtures

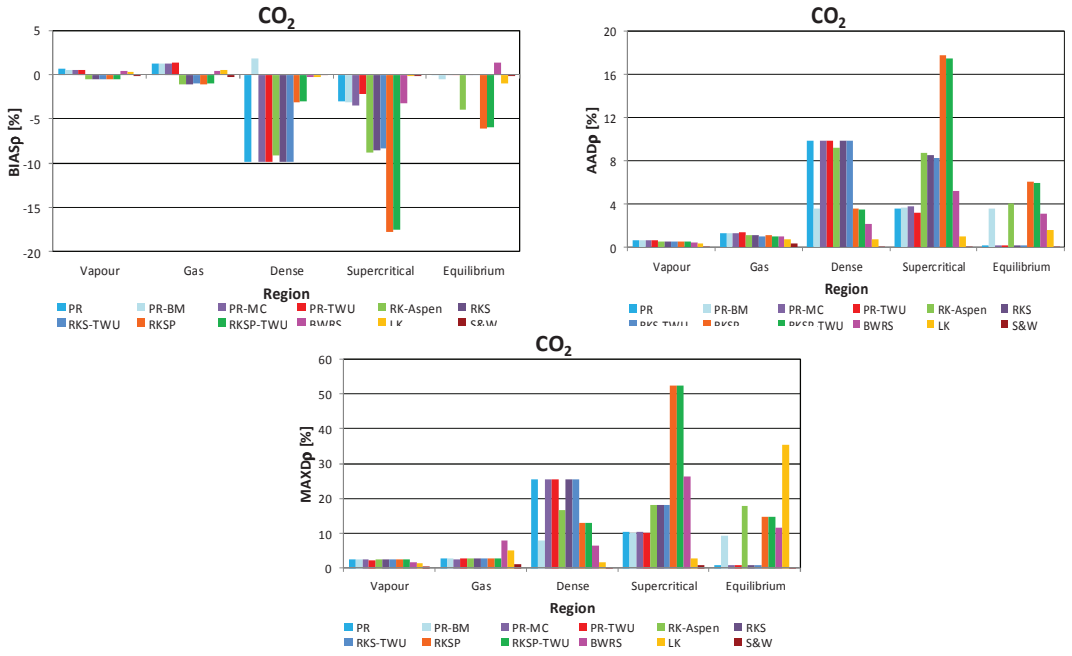

Fig. 2. (a) Bias; (b) Average absolute deviation; (c) Maximum deviation of CO_2 density in different regions

3.1.2. CO_2-mixtures

The available experimental data from literature are related to CO_2-N_2 and CO_2-CH_4 mixtures.

The comparison of the EOS was made considering different temperatures, pressures and compositions.

The interaction parameters used are that reported by default in the Aspen Plus database [7].

As regards the CO_2-N_2 mixture, comparing the EOS results with the experimental work of [16], almost all cubic equations and the LK equation showed a deviation increase when the CO_2 concentration (x_{CO2}) increases: for the PR the AAD was 3.8% at x_{CO2}=0.1 and 7.9% at x_{CO2}=0.9, for the RKS it was 1,4% and 10%, for the RKSM it was 2.8% and 6.7%, for RKS-MHV2 it was 1,8% and 5,2%, for the RKSP it was 1.4% and 3.8% and for LK it was 0,4% and 7%.

The other equations seemed less influenced by the composition changes and, in particular, BWRS and the GERG-2008 equations reported a better accuracy on density prediction, the former had an AAD between 1.5% and 2.5% and the latter between 0.1% and 0.3%.

However the EOS comparison with the experimental work of Arai et al. [14] did not indicate a similar composition influence for cubic equations, even if it was necessary to consider that the lowest CO_2 concentration was 0.4%. Furthermore, in this case, the GERG-2008 model exhibited a higher deviation: $Bias_\rho$ = -1.4%, AAD_ρ=1.5% and MAX_ρ=4.8%.

According to both experimental works, increasing the pressure increases the deviation, in particular operating over the critical pressure of pure CO_2. The mixtures (especially those with a high CO_2 concentration) are probably in the supercritical phase near this pressure value.

This deviation increase is significant for PR, RKS, RKSP and LK equations.

The results obtained from the different experimental works [14,15] for the CO_2-CH_4 mixture were comparable. The BWRS and GERG-2008 equations seemed to better predict the mixture density with, respectively, a bias of <3% and < 1%. However, the GERG-2008 model had a $MAXD_\rho$=3%, much lower than the other equations, but not negligible. Again, the deviation increased over the CO_2 critical pressure.

A separate analysis had to be done for the phase equilibrium. For CO_2-N_2 mixture the RKS and its modifications showed a lower accuracy, in particular RKS and RKSM, for the former AAD_ρ=7.6%, for the latter AAD_ρ =5.5%. For CO_2-CH_4 mixture, above all for the density prediction at the bubble point, the cubic equations with different mixing rules (PR-MHV2, PR-WS, etc.) showed the worst behaviour.

The GERG-2008 equation, although it gave better results than the others, exhibited much higher deviations than in the other regions with a $MAXD_\rho$= ~ 7% for CO_2-CH_4 and a $MAXD_\rho$= ~ 8% for CO_2-N_2.

This EOS comparison for CO_2-mixtures had showed that there does not seem to be an equation that can reliably predict the mixture density. The GERG-2008 model had the lowest deviations, however they were not negligible, in particular in the phase equilibrium.

The PR-BM equation and the RKSM equation predict the density better than the standard equations, except that in the equilibrium phase. The different mixing rules applied to cubic equations do not seem further improve the behaviour of the above mentioned equations.

The relative deviations of the experimental data at conditions that could easily be found in pipeline transport are reported in Figs. 3-4.

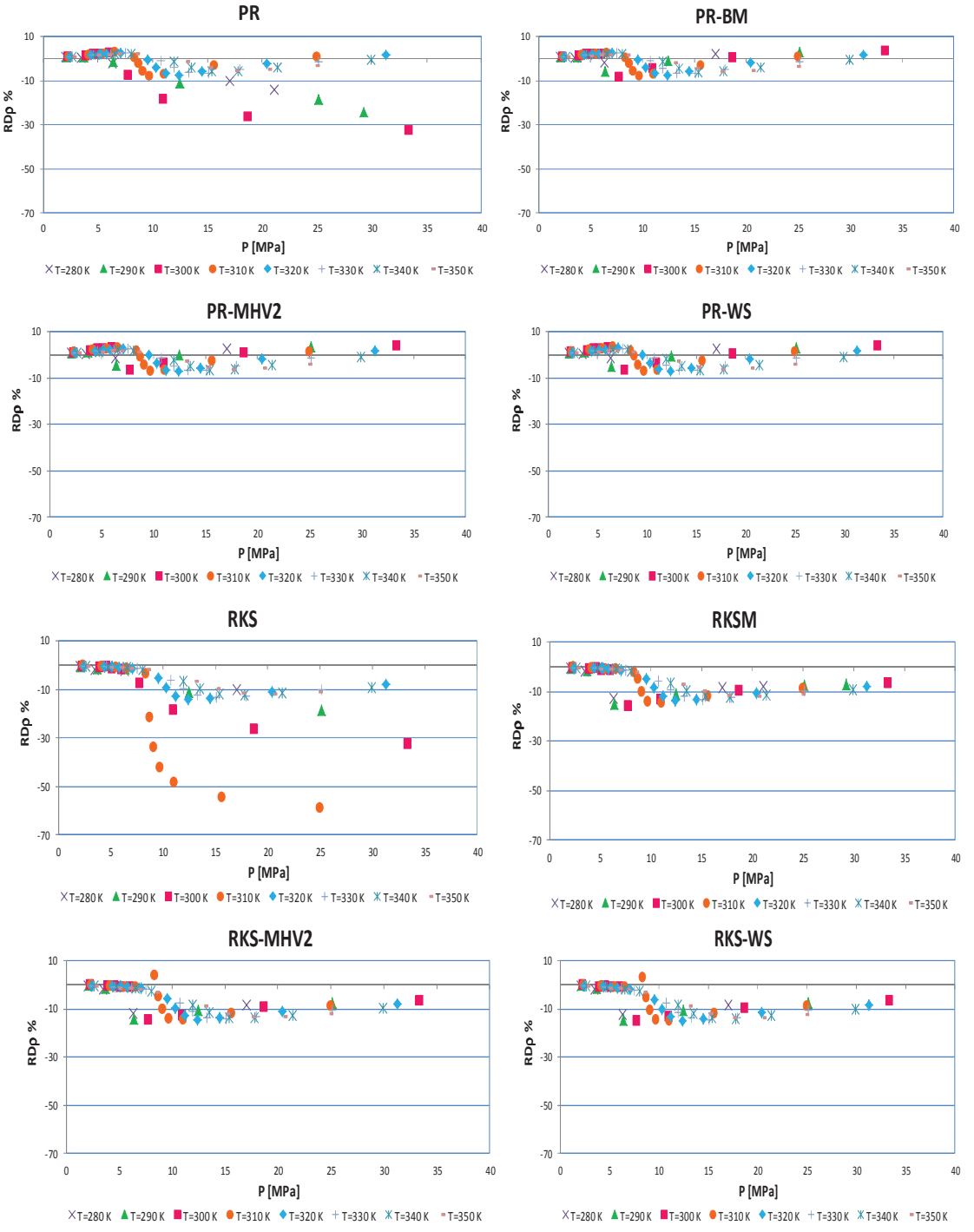

Fig. 3. Relative deviation of the CO_2-CH_4 mixture density at x_{CO2}=0.98 [15] for different cubic equations.

4. Experimental work

As the experimental data of the CO_2 mixtures containing O_2, Ar, SO_2, CO and H_2 are limited [6], even if such impurities can be present in the CCS processes, an experimental campaign has been organized in collaboration with LEAP (Energy and Environmental Laboratory of Piacenza).

Besides to obtain more experimental data on CO_2 mixtures, this experimental work aims to further investigate the ability of EOS to predict density of these kind of mixtures.

The experimental campaign provided to determine the p-ρ-T data of some CO_2 mixtures, in particular CO_2-O_2 mixtures with a CO_2 concentration of 85% and 95% at 273 K, 283 K and 293 K from 1 up to 20 MPa, with an Anton Paar DMA 512-HPM vibrating tube densimeter.

The obtained experimental data are reported in Table 3.

The EOS, among of those previously analyzed that, in general, seemed to better predict the CO_2-mixtures density, were chosen for the comparison with the experimental results: PR, PR-BM, RKSM, BWRS, LK, GERG-2008.

The comparison results evidenced that for all equations the deviation increased when the temperature increased and for PR, PR-BM and BWRS the deviations increased decreasing the CO_2 concentration.

In the vapour region the deviations were extremely lower (< 4%) than in the liquid phase for all equations (i.e. ≈ 10% for RKSM at T= 20°C and x_{CO2}=95%), except that for the GERG-2008 model which predicted the liquid density with the lowest AAD respect to other equations (< 1% at x_{CO2}=95% and < 4% at x_{CO2}=85%), .

LK, PR-BM and PR showed also a relatively good reliability. An example of the comparison of EOS with some experimental data are displayed in Fig. 5.

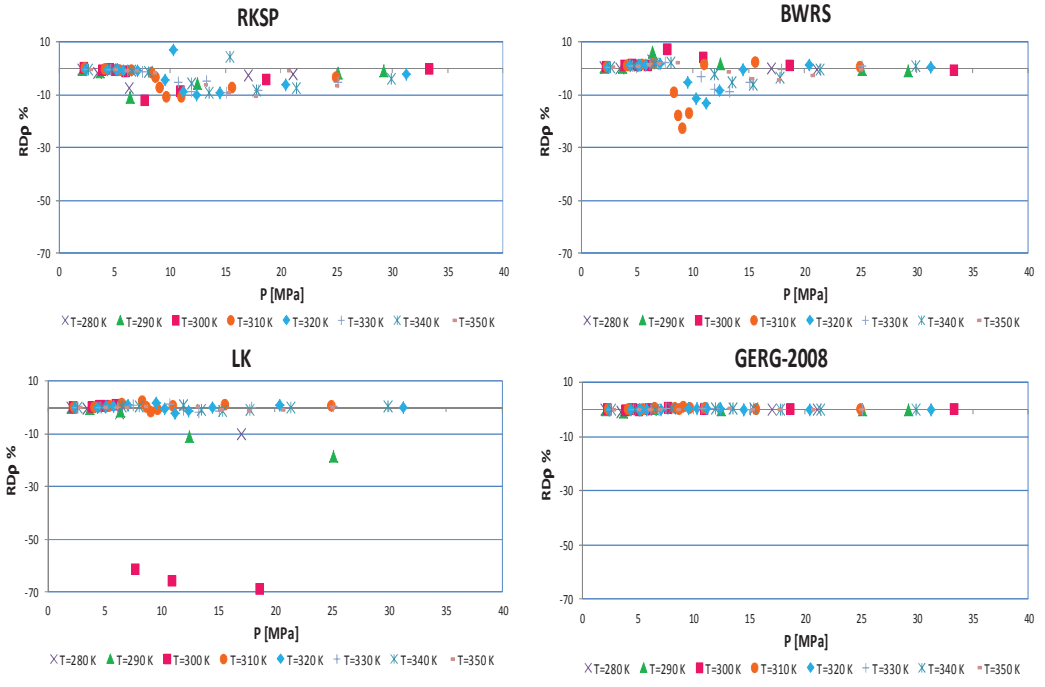

Fig. 4. Relative deviation of the CO_2-CH_4 mixture density at x_{CO2}=0.98 [15] for different equations.

Table 3. Experimental results of CO_2-O_2 mixtures

95% CO_2						85% CO_2					
0°C		10°C		20°C		0°C		10°C		20°C	
P [MPa]	ρ [kg/m^3]	P [MPa]	ρ [kg/m^3]	P [MPa]	ρ [kg/m^3]	P [MPa]	ρ [kg/m^3]	P [MPa]	ρ [kg/m^3]	P [MPa]	ρ [kg/m^3]
1,0	21,03	1,0	20,99	1,0	22,79	1,0	20,04	1,0	19,17	1,0	18,67
2,0	44,52	2,0	43,21	2,0	42,57	2,0	41,94	2,0	39,69	2,0	38,08
3,0	74,17	3,0	69,82	3,0	66,24	3,0	68,03	3,0	63,25	3,0	59,80
3,6	97,58	4,0	103,88	4,0	95,16	4,0	101,02	4,0	91,10	4,0	84,58
5,0	894,48	4,7	139,44	5,0	132,37	4,4	121,07	5,0	125,66	5,0	113,51
6,0	902,54	6,2	818,99	6,0	190,23	9,0	798,30	6,0	175,64	6,0	148,80
7,0	911,87	7,0	835,31	7,4	717,97	10,0	811,54	9,6	686,56	7,0	194,61
8,0	920,43	8,0	849,75	8,0	746,96	11,0	825,05	10,0	699,36	8,0	260,88
9,0	928,62	9,0	862,81	9,0	775,58	12,0	837,41	11,0	728,79	8,7	323,50
10,0	936,04	10,0	873,84	10,0	797,36	13,0	848,50	12,0	751,41	9,8	460,27
11,0	943,08	11,0	884,11	11,0	813,94	14,0	858,70	13,0	770,50	10,0	481,51
12,0	949,61	12,0	893,24	12,0	828,62	15,0	868,15	14,0	786,56	11,0	564,71
13,0	955,76	13,0	901,86	13,0	841,27	16,0	876,96	15,0	799,98	12,0	617,79
14,0	961,53	14,0	909,85	14,0	852,15	17,0	885,39	16,0	812,38	13,0	657,67
15,0	967,05	15,0	917,34	15,0	862,39	18,0	892,93	17,0	823,52	14,0	686,21
16,0	972,43	16,0	924,19	16,0	871,62	19,0	898,30	17,5	828,01	15,0	710,21
17,0	977,56	17,0	930,78	17,0	880,21					16,0	730,80
18,0	982,44	18,0	937,00	18,0	888,29					17,0	747,42
19,0	987,19	19,0	942,96	19,0	895,87						
20,0	991,68	20,0	948,66	20,0	902,81						

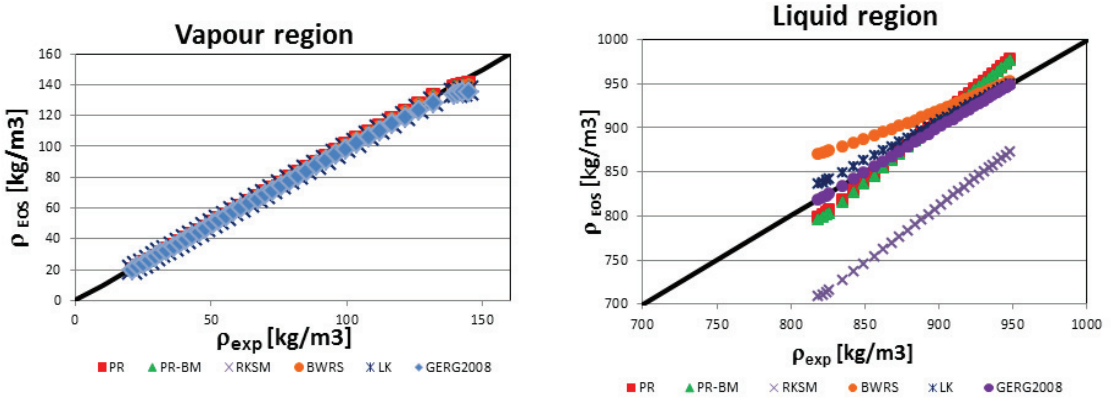

Fig. 5. EOS comparison with experimental data of CO2-O2 mixture (xCO2=0.95) at 10°C

5. Conclusion

Considering pure CO_2 the Span-Wagner equation showed the lowest error in the density prediction in every region analyzed. Considering CO_2-mixtures, the EOS comparison with literature experimental data showed that there is not an equation that can reliably predict the mixture density experimental data. The GERG-2008 model had the lowest deviations, however they were not negligible, in particular in the phase equilibrium.

Therefore to obtain more experimental data on CO_2 mixtures and to further investigate the ability of EOS to predict density, an experimental campaign has been organized in collaboration with LEAP.

In this paper the p-ρ-T experimental data of CO_2-O_2 mixtures obtained at different CO_2 concentrations and temperatures with an Anton Paar DMA 512-HPM vibrating tube densimeter were reported. In the vapour region the EOS showed a similar behaviour, whereas in the liquid region the density prediction was worse, except that for the GERG-2008 model. However also PR-BM equation reported a density prediction quite acceptable.

Acknowledgements

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References

[1] De Visser E, Hendriks C, Barrio M, Mølnvik MJ, De Koeijer G, Liljemark S, Le Gallo Y. (2008). Dynamis CO_2 quality recommendations. Int. J. Greenh. Gas Con 2008; 2: 478-484.
[2] Span R, Wagner W. A New Equation of State for Carbon Dioxide covering the fluid region from the triple –point temperature to 1100 K at pressures up to 800 MPa. J. Phys. Chem.1996; 25.
[3] Kunz O, Klimeck R,Wagner W, Jaeschke M. The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures; 2007.
[4] Li H, Yan J. Evaluating cubic equations of state for calculation of vapour-liquid equilibrium of CO_2 and CO_2-mixtures for CO_2 capture and storage processes. Applied Energy 2008; 86: 826-836.
[5] Li H, Yan J. Impacts of equations of state (EOS) and impurities on the volume calculation of CO_2 mixtures in the applications of CO_2 capture and storage (CCS) processes. Applied Energy 2009; 86: 2760-2770.
[6] Li H, Jacobsen J.P, Wilhelmsen O, Yan J. PVTxy properties of CO_2 mixtures relevant for CO_2 capture, transport and storage: Review of available experimental data and theoretical models.. Applied Energy 2011; 88: 3567-3579.
[7] Aspen Physical Property System. Physical Property Model. AspenTech; 2010.
[8] www.ruhr-uni-bochum.de
[9] Angus S, Armstrong B, de Reuck KM. International Thermodynamic Tables of the Fluid State. 3: Carbon Dioxide. International Union of Pure and Applied Chemistry, Division of Physical Chemestry; 1976.
[10] Tsuji T, Honda S, Hiaki T, Hongo M. J. Supercritical Fluids 1998; 13-15.
[11] Klimeck J, Kleinrahm R, Wagner W. Measurements of the (p,ρ,T) relation of methane and carbon dioxide in the temperature range 240 K to 520 K at pressures up to 30 MPa using a new accurate single-sinker densimeter. J. Chem. Thermodynamics 2001; 33: 251-267.
[12] Tsuji T, Tanaka S, Hiaki T. J. Supercritical Fluids 2004; 29: 215-220.
[13] Saleh B, Wendland M. Measurement of Vapor Pressures and Saturated Liquid Densities of Pure Fluids with a New Apparatus. J. Chem. Eng. Data 2005; 50: 429-437.
[14] Arai Y, Kaminishi G, Saito S. The experimental determination of the P-V-T-x relations for the Carbon Dioxide-Nitrogen and the Carbon Dioxide-Methane systems. J. Chem. Eng. of Japan 1971; 4(2): 113-122.
[15] Magee JW, Fly JF. Isochoric (p,v,T) measurements on CO_2 and (0.98 CO2+0.02CH4) from 225 to 400 K and Pressures to 35 MPa. Int. J. Thermophys 1988; 9(4):547-557.
[16] Brugge HB, Holste JC, Hall KR, Gammon BE, Marsh KN. Densities of Carbon Dioxide + Nitrogen from 225 K to 450 K at Pressures up to 70 MPa. J. Chem. Eng. Data 1997; 42: 903-907.