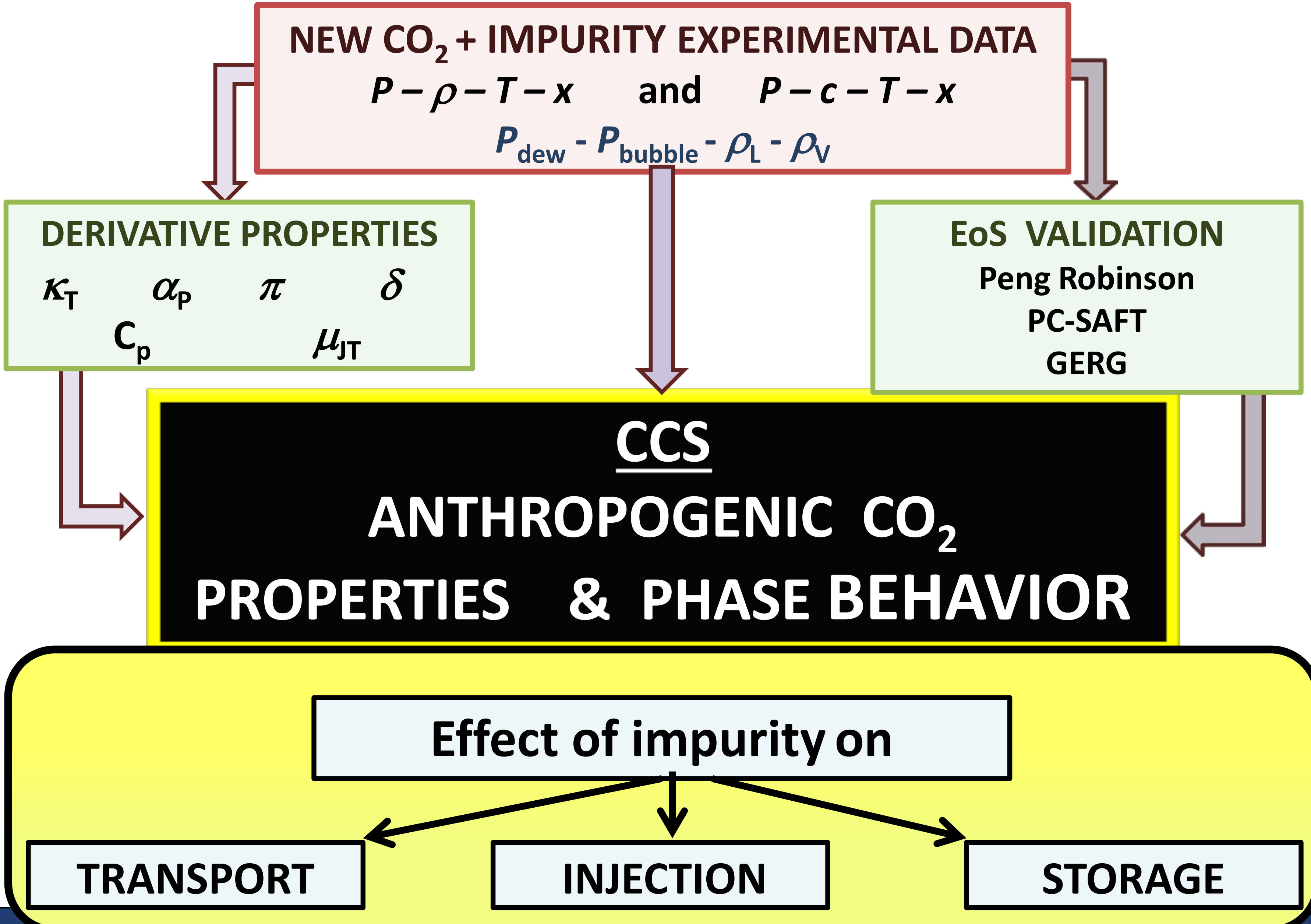
CO_2+SO_2 co-capture assessment. Part 1.

B. Gimeno, J. Fernández, M. Artal, S. T. Blanco*, I. Velasco

Department of Physical Chemistry, Faculty of Sciences , University of Zaragoza, Spain

***Presenting author's email: sblanco@unizar.es**


NEW CO_2 + IMPURITY EXPERIMENTAL DATA
$P-\rho-T-x$ and $P-c-T-x$
P_{dew} - P_{bubble} - ρ_L - ρ_V
DERIVATIVE PROPERTIES
κ_T α_P π δ
C_p μ_{JT}
EoS VALIDATION
Peng Robinson
PC-SAFT
GERG
CCS
ANTHROPOGENIC CO_2
PROPERTIES & PHASE BEHAVIOR
Effect of impurity on
TRANSPORT
INJECTION
STORAGE

Anthropogenic CO_2 quality; Concentration limits of impurities

✓ They must be established by analyzing two aspects:

- **Risks ↔ Safety**
- **Costs**

✓ When handling **compounds dangerous** for health or environment, for which the **total elimination can be expensive,**

an **alternative** may be the **co-capture**

Impact of anthropogenic CO_2 quality on CCS technology; Feasibility of co-capture CO_2/SO_2*

$CO_2 + SO_2$

In progress

$CO_2 + CH_4$

- ✓ Environ. Sci. Technol, 2012, 46, 13016
- ✓ IJGGC, 2013, 18, 264

$CO_2 + CO$

- ✓ IJGGC, 2013, 18, 264
- ✓ Environ. Sci. Technol, 2014, 48, 10984

Model Mixture

$CO_2 + CH_4 + CO + SO_2$

Final Goal

$CO_2 + CO + CH_4$

2015

$CO_2 + CO + SO_2$

2016

$CO_2 + CH_4 + SO_2$

2016

(*) Funding from Ministry of Economy and Competitiveness of Spain **ENE2013-44336-R**

Experimental thermodynamic data available in literature

CO_2+SO_2

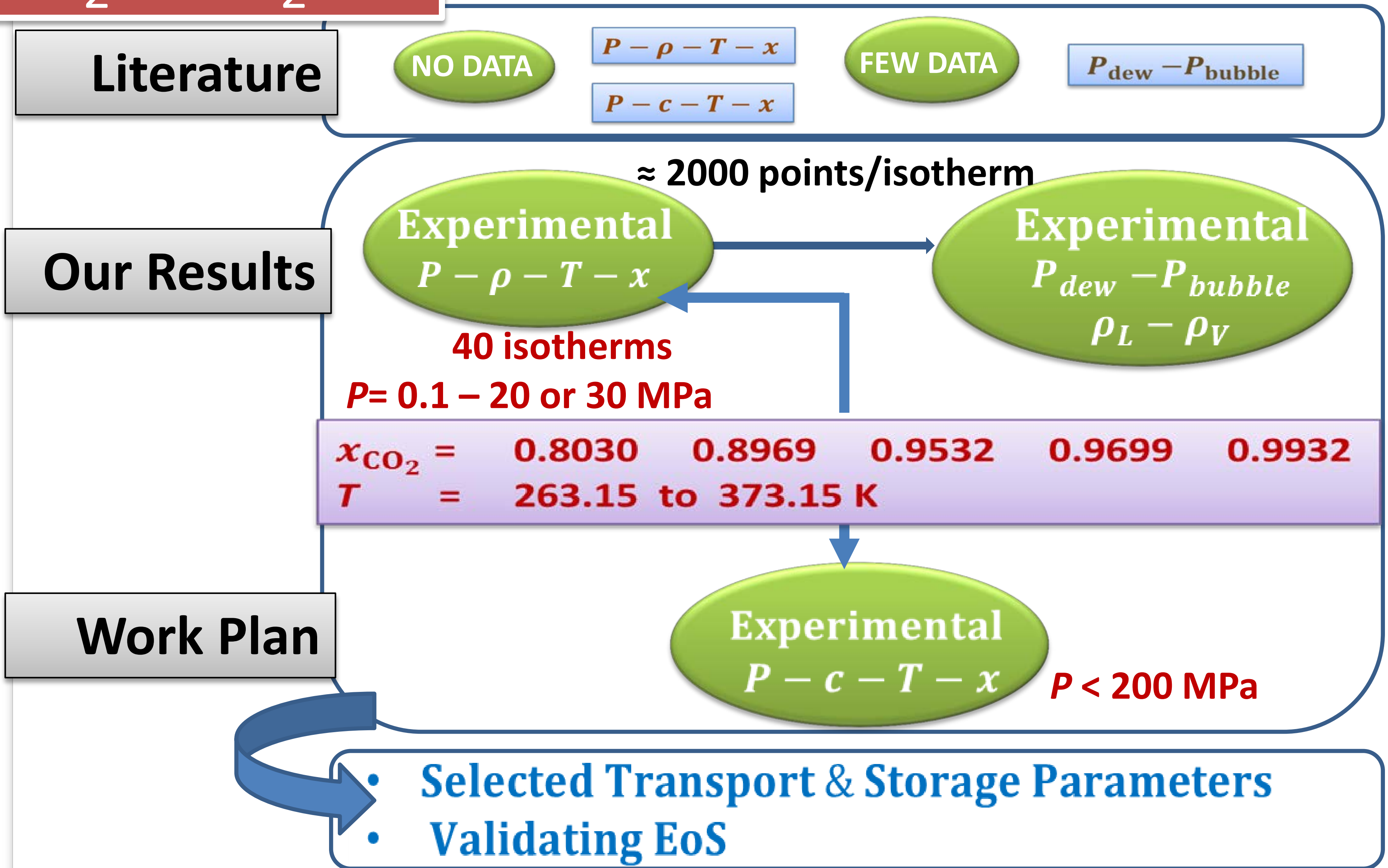
Prop.	x_{CO_2}	*T* / K	*P* / MPa	Reference
VLE	0-0.4	293-393	0.1-3.1	Blumcke, 1888
VLE	0.09-0.61	291-416	2.7-10.5	Caubet, 1904
VLE	0-1	263 and 333	0.1-9.0	Lachet et al., 2009

Neither density nor speed of sound data available

Outside the composition range of anthropogenic CO_2

Do not cover the *T*, *P* conditions of CCS technology

$CO_2 + SO_2$



ASSESSMENT OF CO_2 / SO_2 CO-CAPTURE

Concentration limits of SO_2 in anthropogenic CO_2 from literature

With SO_2 removal mol %	No contaminant control mol %
< 0.0001	1.5
0.076	1.5
0.03-0.2	0.4-3.1
	4

$x_{SO_2} \leq 0.04$

The experimental composition range must be wider for more accurate and useful models

We have studied $0.8030 \leq x_{CO_2} \leq 0.9932$

Experimental data acquisition

Technical specifications

- **Method: vibrating tube densimeter**
- ***T* range: 263 to 473 K**
  $u(T)$= 0.006 K
- ***P* range: 0.1 MPa to 70 MPa**
  $u(P)$= 0.008 MPa
- ***x* range: 0.0000 to 1.0000**
  $u(x)$= 0.0005
- **$U(\rho) = 0.4 – 0.7$ kg/m^3**

Measurements of thermodynamic properties

- Gas, liquid, critical and supercritical densities
- Vapour-liquid equilibrium

Calculated density derivative properties

- Isothermal compressibility
- Isobaric expansivity
- Internal pressure → Solubility parameter

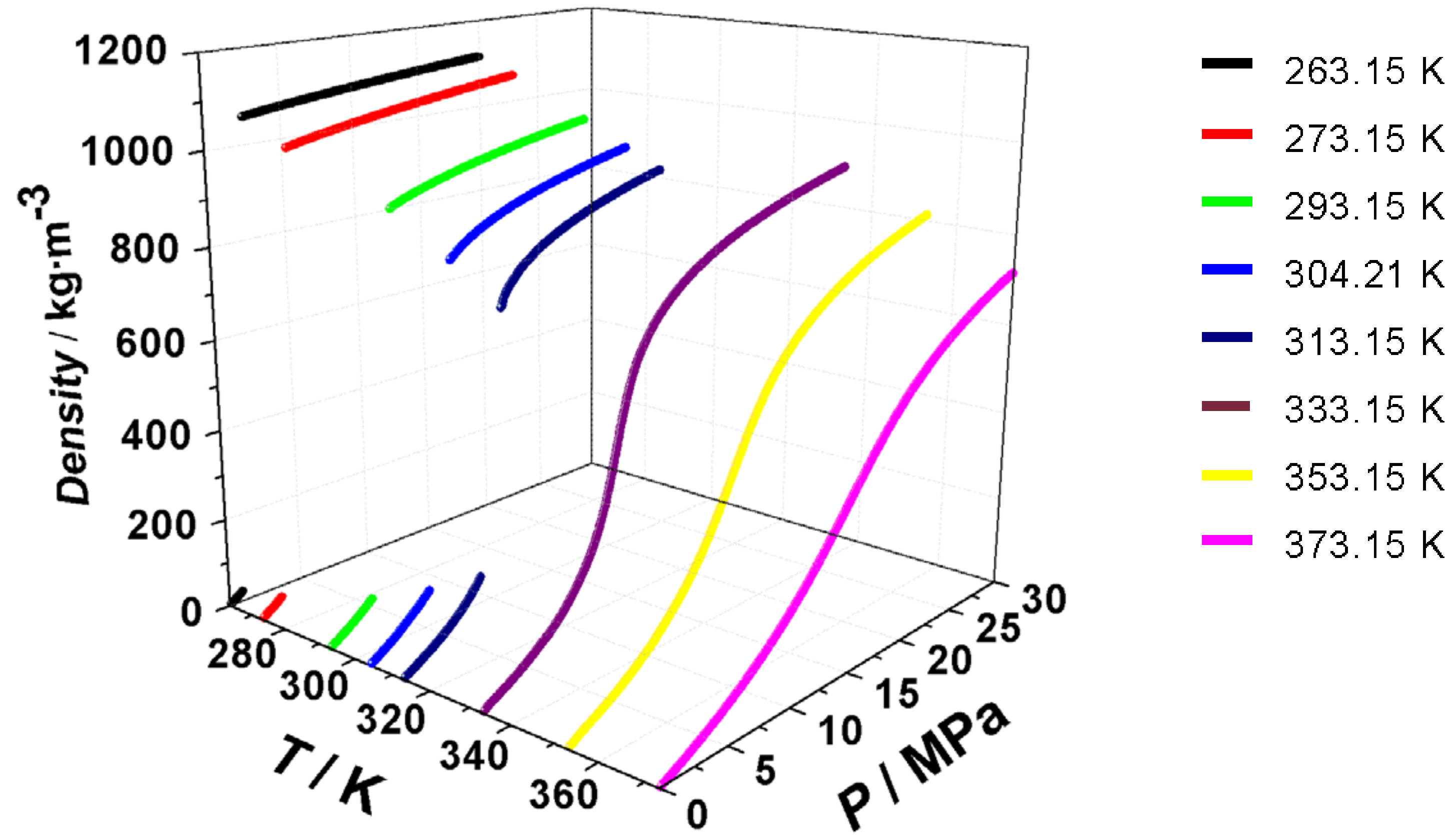
High pressure *PρT*- VLE laboratory, UZ, Spain

2000 points/isotherm→ Quasi-continuous data along subcritical, critical, and supercritical regions of pure fluids and mixtures allow us to determine the limits of VLE, and density derivative properties

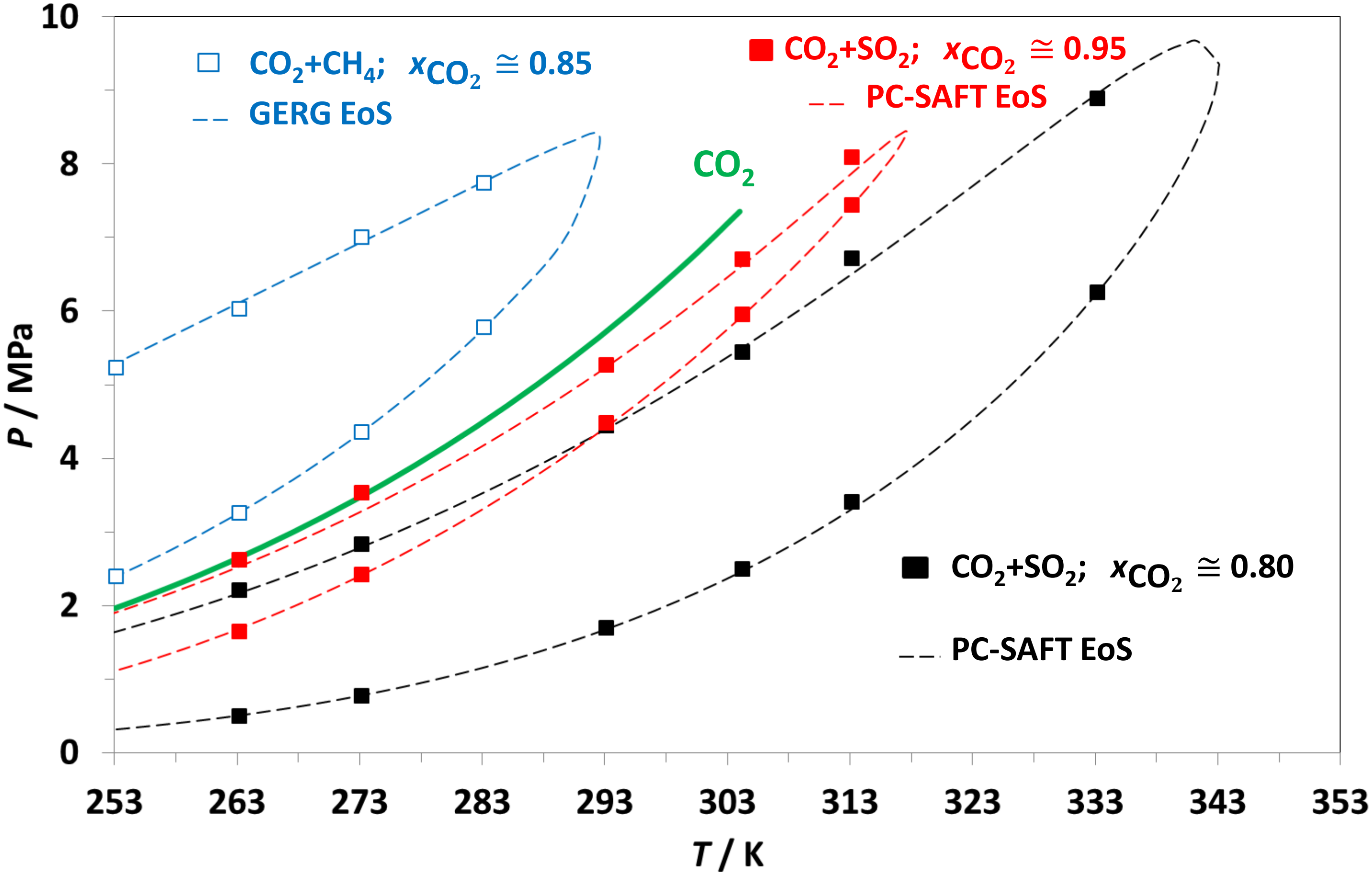
CO_2+SO_2

P –*ρ* –*T* – *x* experimental results

$x_{CO_2} \cong 0.90$



CO_2+SO_2
VLE experimental results



As the amount of SO_2 increases, the P_{bubble} of the mixtures reduces, then the minimal operational pressure decreases

Effect of SO_2 on Transport, Injection and Storage

- Study of the effect of SO_2 (condensable impurity) on transport, injection and storage of the anthropogenic CO_2
- Comparison of the behavior of the mixtures CO_2+SO_2 with those of pure CO_2 and CO_2+CH_4 (non-condensable impurity) mixtures

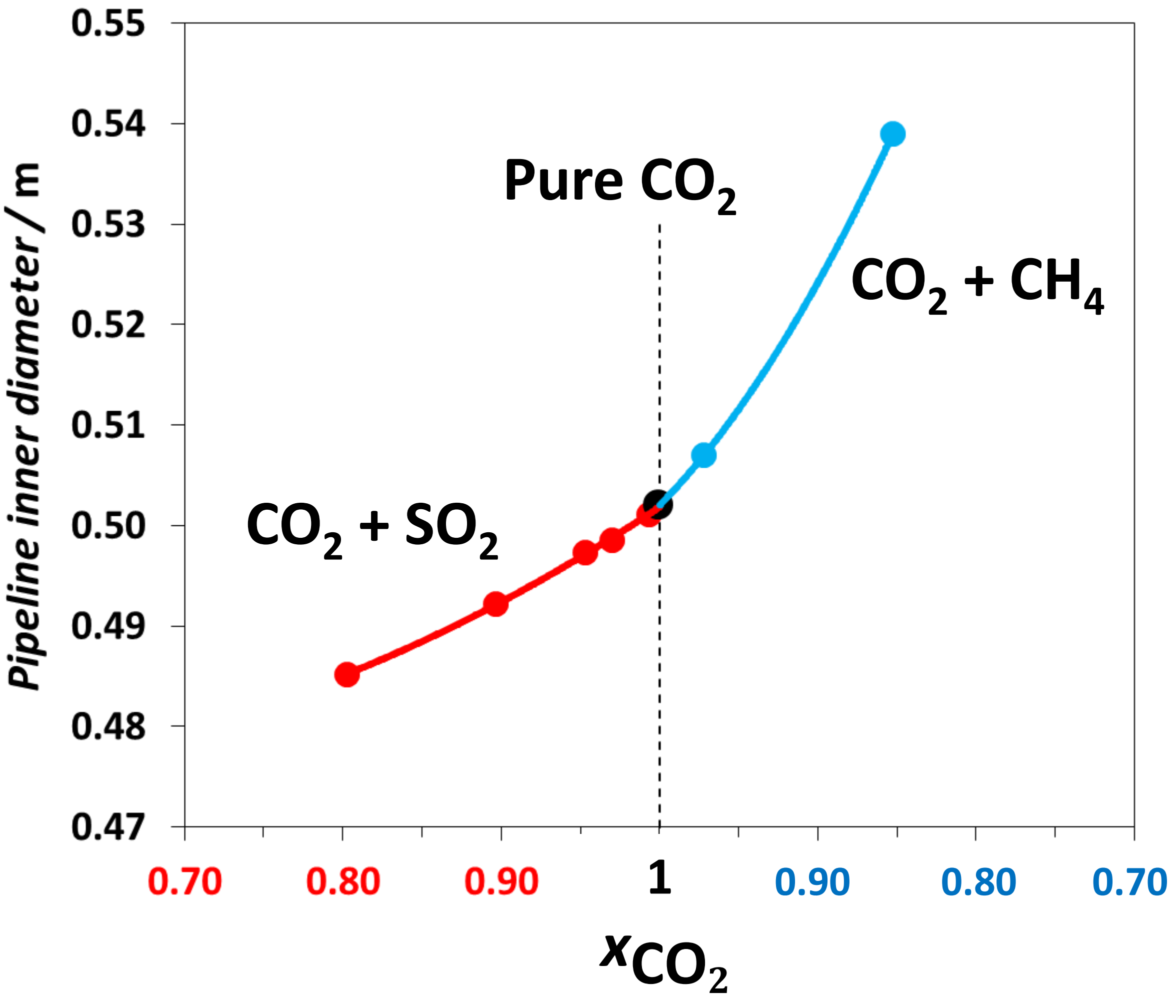
For all the systems:

- recommended equations
- using our experimental densities
- calculated viscosities with REFPROP 9.1.

Effect of SO_2 on Transport

Pipeline diameter to transport 10 Mt/year of fluid at 293.15 K and 10 MPa

($\Delta P/L$ = 36 Pa/m . Roughness height = 4.6×10^{-5} m)



Higher density of the CO_2+SO_2 mixtures

✓ higher mass flow through a given pipeline

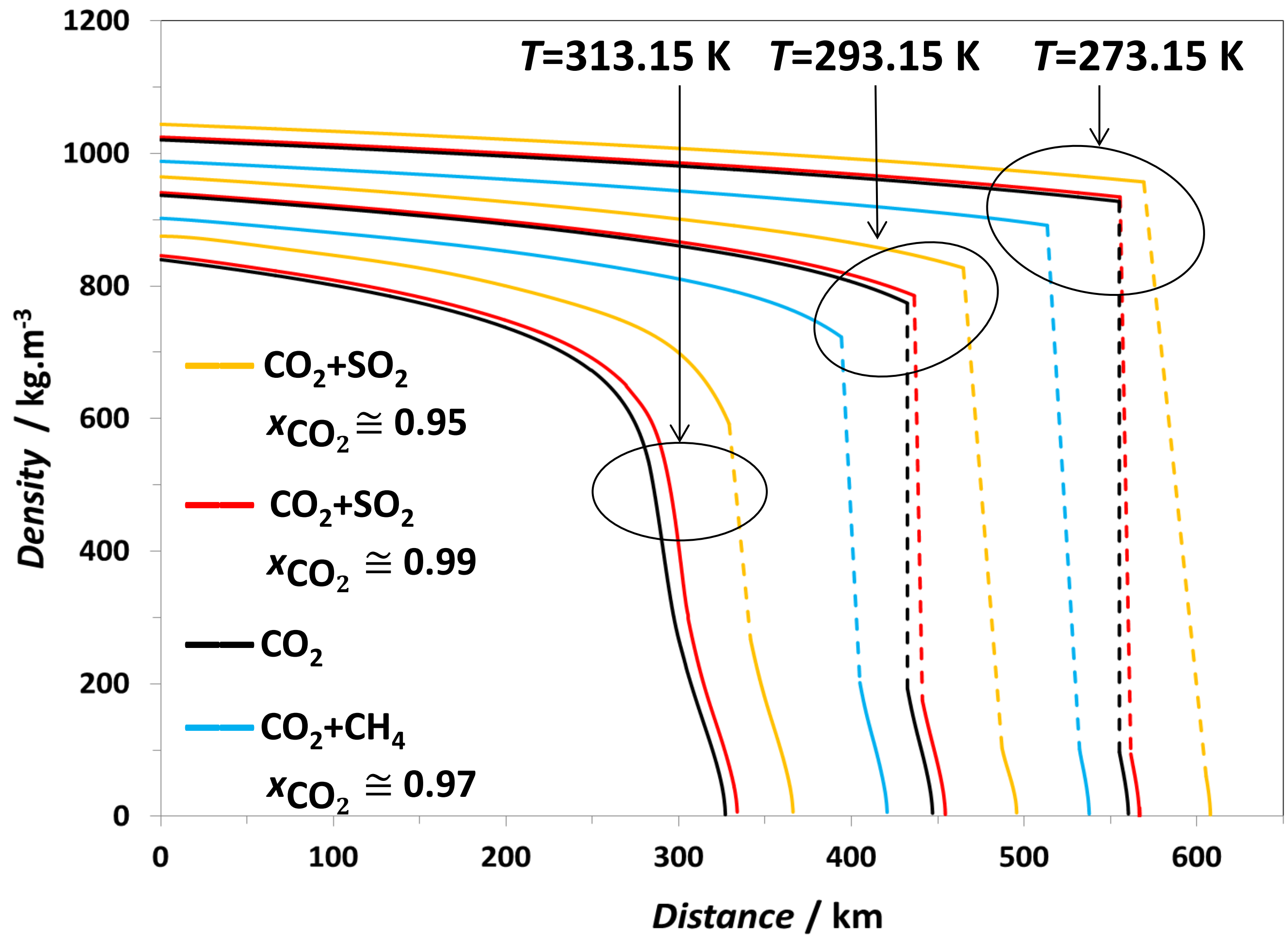
or

✓ smaller pipeline diameter needed for a given mass flow.

Effect of SO_2 on Transport

Density profile along a pipeline for CO_2+SO_2, pure CO_2 or CO_2+CH_4

(Diameter: 20 inch, mass flow: 10 Mt/year; inlet pressure: 20 MPa; roughness height: 4.5×10^{-5} m)



The density drop along the pipeline is lower for mixtures containing SO_2

- ✓ Higher SO_2 content

  and/or

- ✓ Lower temperature

⬇

- ✓ **Longer available operational distance**
- ✓ **Less boosters**

Effect of SO_2 on Injection and Storage

<u>The presence of SO_2</u> in the confined fluid causes the decrease of pH of the medium

Acidifying the medium increases the reactivity of the rock with the fluid

Greater dissolution of minerals causes an increase in the porosity of the rock

Increasing the porosity, <u>the rock permeability modified</u>

Effect of SO_2 on Storage

Other parameters must be studied to assess the convenience of storing CO_2 containing SO_2

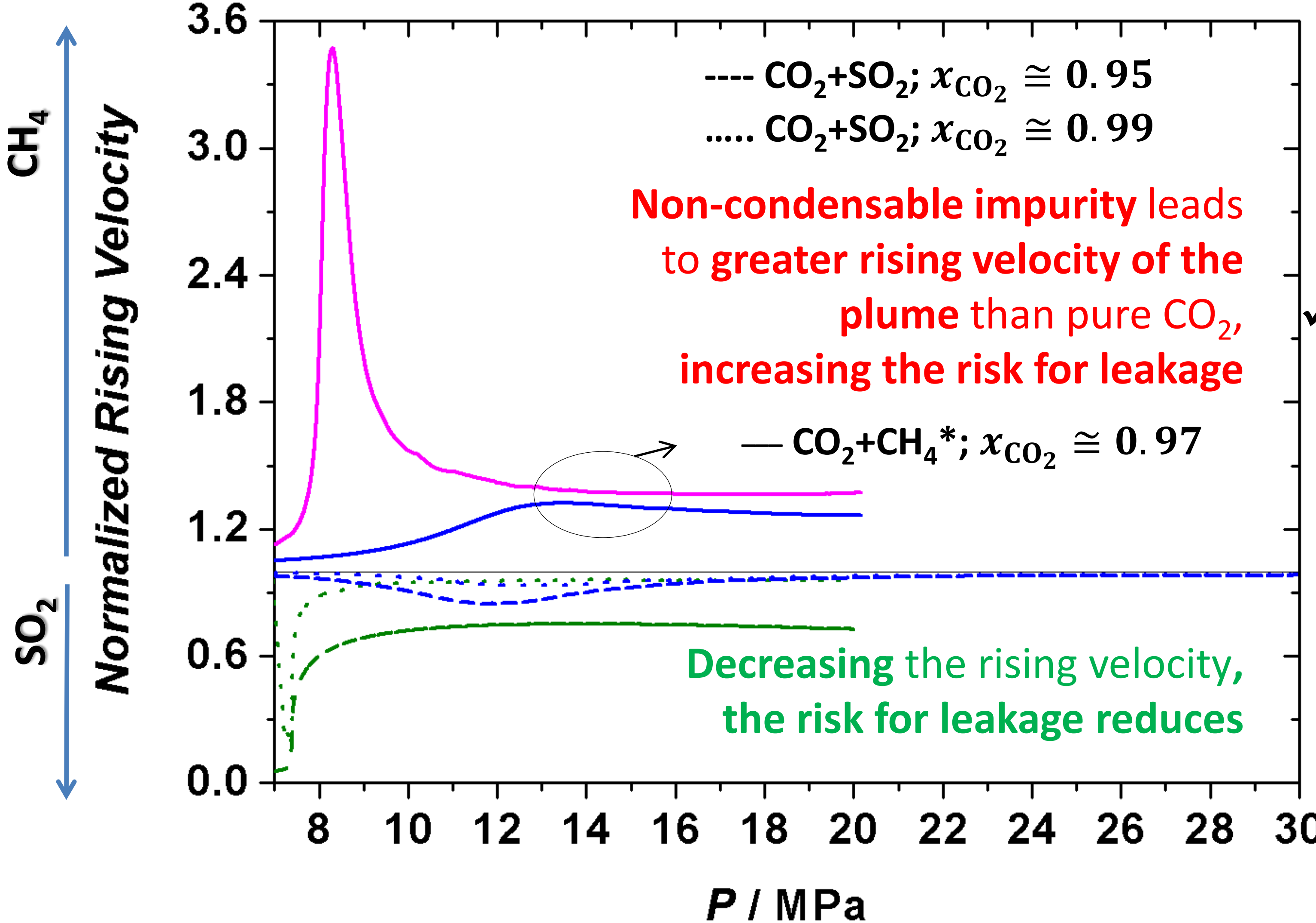
Selected parameters:

- ✓ **Normalized Storage Capacity** $\frac{M}{M_0} = \frac{\rho}{\rho_0\left[1 + \sum_i\left(\frac{m_i}{m_0}\right)\right]}$
- ✓ **Normalized Rising Velocity** $\frac{\nu}{\nu_0} = \frac{(\rho_{\text{brine}} - \rho)(\rho_0\eta_0)}{(\rho_{\text{brine}} - \rho_0)(\rho\eta)}$
- ✓ **Normalized Permeation Flux** $\frac{\dot{M}}{\dot{M}_0} = \frac{\rho\left(\frac{\eta_0}{\eta}\right)}{\rho_0\left[1+\sum_i\frac{m_i}{m_0}\right]}$

calculated disregarding the difference in reactivity with pure CO_2

Equations from Wang, J. et al. *Energy Procedia* **2011**, *4*, 3071-3078

Effect of SO_2 on Storage



The same amount of SO_2 affects:

- ✓ ν up to 40%
- ✓ *M* up to 5%

green *T*= 304.21 K
pink *T*= 308.15 K
blue *T*= 333.15 K

(*) S. T. Blanco et al. *Environmental Science & Technology* 48, pp. 10984-10992. 2014

PC-SAFT Validation

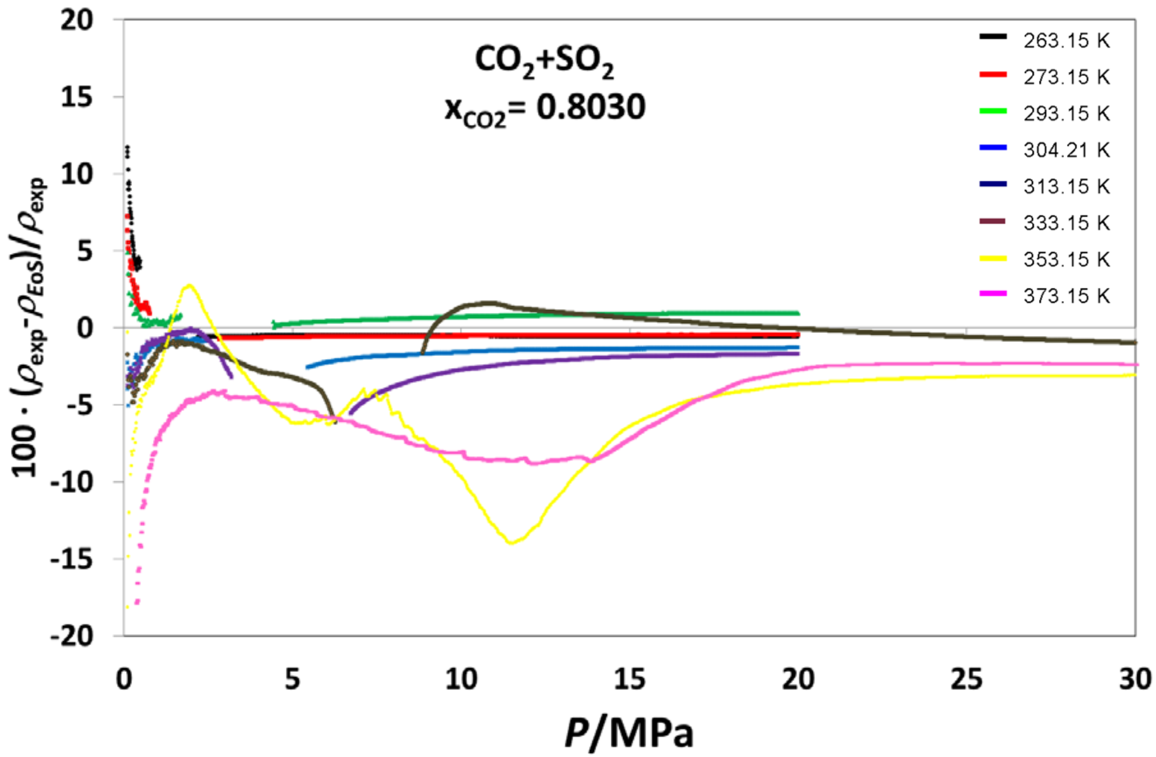
$P-\rho-T-x$

	x_{CO_2}					
	0.8030	**0.8969**	**0.9532**	**0.9699**	**0.9932**	$\overline{MRD}/\%$
MRD(ρ)/%	2.37	1.50	2.40	1.15	1.43	**1.76**

$$MRD\ (\rho) = \frac{100}{N}\sum_{i=1}^{N}\frac{|\rho_{i,exp} - \rho_{i,EoS}|}{\rho_{i,exp}}$$

Pure compounds parameters: Gross, J. and Sadowski, G. *Ind. Eng. Chem. Res.* 2001, **40**, 1244-1260.

Binary interaction parameter: Diamantonis et al. *Ind. Eng. Chem. Res*. 2013, **52**, 3933-3942.



PC-SAFT Validation

Property	$\overline{MRD}$ / %
P_{dew}	1.61
P_{bubble}	2.74
ρ_V	2.58
ρ_L	1.40

$$MRD\ (P) = \frac{100}{N} \sum_{i=1}^{N} \frac{|P_{i,exp} - P_{i,EoS}|}{P_{i,exp}}$$

$$MRD\ (\rho) = \frac{100}{N} \sum_{i=1}^{N} \frac{|\rho_{i,exp} - \rho_{i,EoS}|}{\rho_{i,exp}}$$

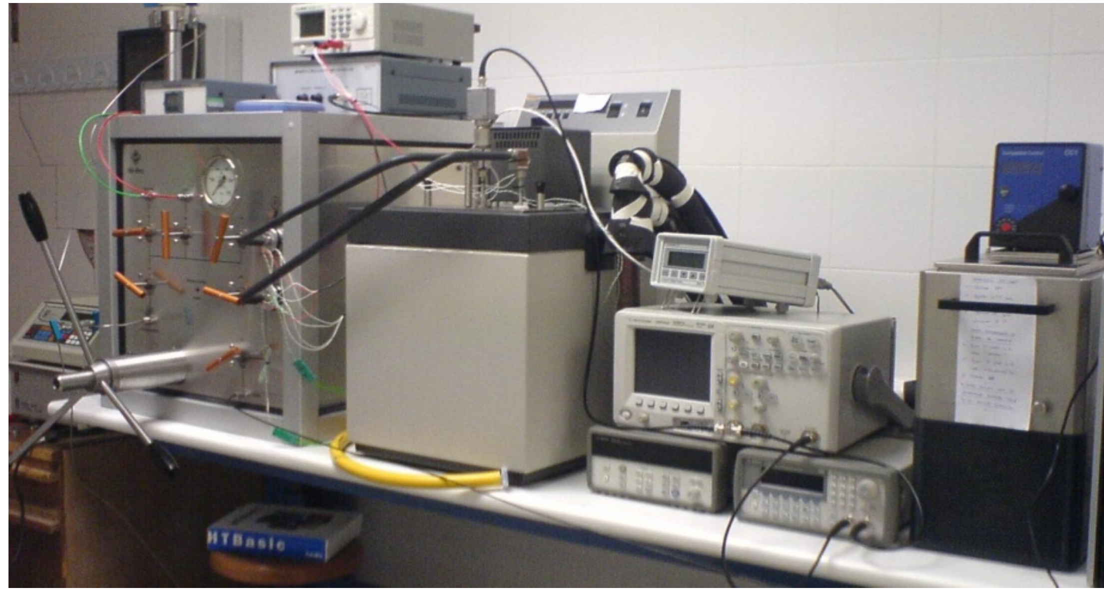
Pure compounds parameters : Gross, J. and Sadowski, G. *Ind. Eng. Chem. Res.* 2001, **40**, 1244-1260.
Binary interaction parameter: Diamantonis et al. *Ind. Eng. Chem. Res*. 2013, **52**, 3933-3942.

Experimental data acquisition

High Pressure Speed of Sound Laboratory, UZ, Spain

Technical specifications

- **Method: 5 MHz pulsed ultrasonic system**
- ***T* range: 253 to 473 K**
  ***u*(*T*)= 0.015 K**
- ***P* range: 0.1 MPa to 200 MPa**
  ***u*(*P*)= 0.02 MPa**
- ***x* range: 0.0000 to 1.0000**
  ***u*(*x*)= 0.0005**
- ***U* (*c*) = $1.6 \cdot 10^{-3} \cdot c$ m/s**



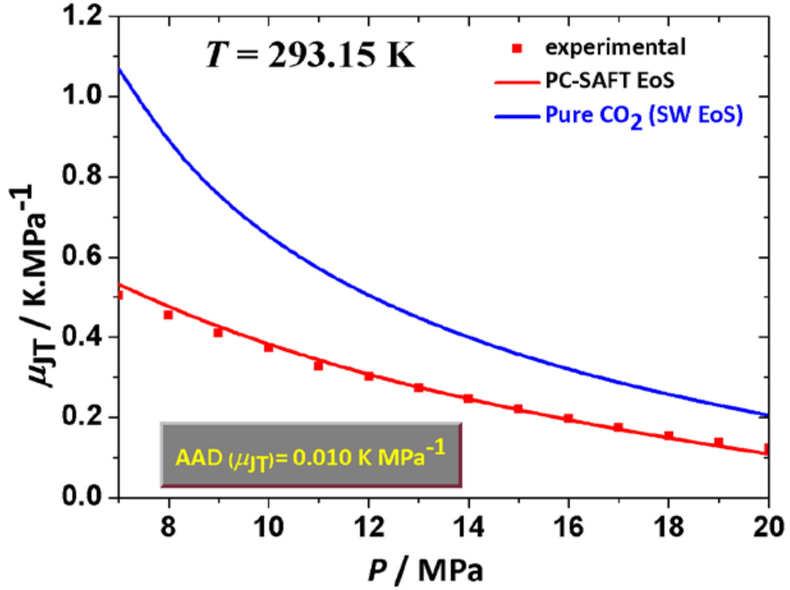
Measurements of thermodynamical properties

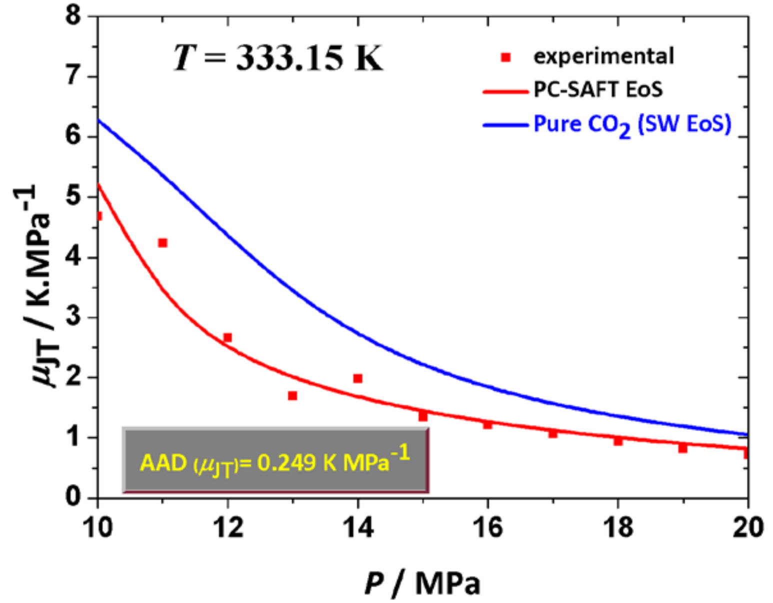
- **Liquid, compressed gases and supercritical speeds of sound**

- ❑ **Evaluation of fracture propagation**
- ❑ **Calculated derivative properties from speed of sound and density**
  - **Heat Capacity**
  - **Joule-Thomson Coefficient**

CO_2+SO_2 Joule-Thomson Coefficient, μ_{JT}

$x_{CO_2} \cong 0.90$





Conclusions

CO_2+SO_2

x_{CO_2} = 0.8030 – 0.9932

Operational *T* and *P* of pipeline transport and geological storage

- **40 experimental isotherms $P - \rho - T - x$**
- **VLE isopleths P_{dew}, P_{bubble}, ρ_V , ρ_L**
- **PC-SAFT validated under CCS conditions and wider:**

$$MRD_{density} = 1.76\%$$

- **Impact of SO_2 on transport, injection and storage from our experimental values**
- **8 experimental isotherms $P - c - T - x$ ($x_{CO_2} = 0.8969$)**
- **Joule-Thomson coefficients ($x_{CO_2} \cong 0.90$)**

$$\mu_{JT,mixtures} < \mu_{JT,CO_2} \text{ at studied } T \text{ and } P$$

Effect of SO_2 on CO_2 transport, injection and storage		CONCLUSIONS		
		CO_2+SO_2	CO_2	CO_2+CH_4
Pipeline Transportation	***Operational P***	—		+
	Diameter	—		+
	ΔP	—		+ +
	ΔDensity	—		+ +
	Less booster stations required			
Injection and Geological Storage	***Storage capacity***	—		— —
	Rising velocity	—		+ +
	Permeation flux	—		
	Headhole P	—		+
	No adverse effects (aside reactivity)			

— : decrease +: increase green: favorable blak: neutral red: adverse

Thank you for your attention

Acknowledgment: The research leading to these results has received funding from Ministry of Economy and Competitiveness of Spain **ENE2013-44336-R**