Department for
Science, Innovation
& Technology

TÜV SÜD

Thermophysical Properties of CO_2-rich Blends

Bridging Between Experimental and Modelling Studies

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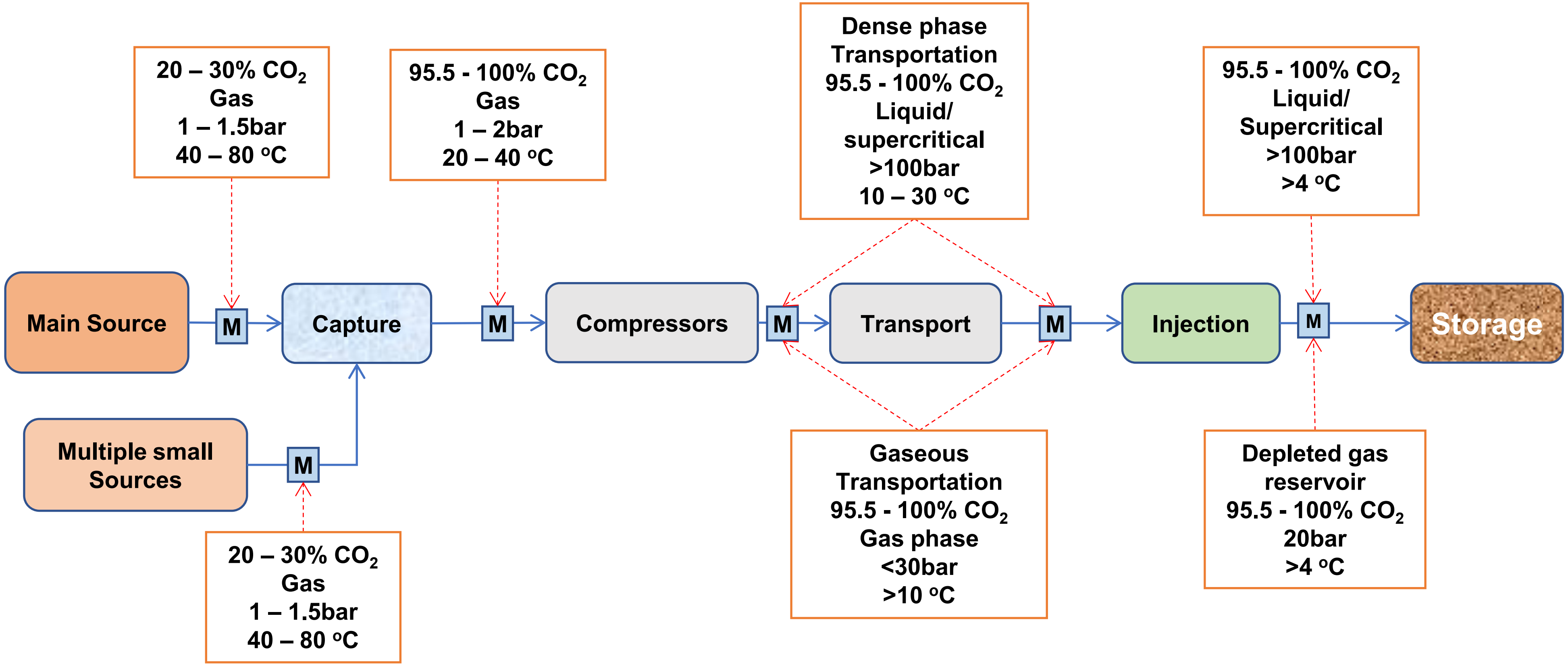
Measurement Focus Group Meeting
Birmingham, 2026-04-29

**Add value.
Inspire trust.**

CCS Flow Metering and Significant Role of Thermodynamic Properties



M – Measurement station (Fiscal accounting, Emission regulation and process monitoring)

Schematic representation of the CCS process, highlighting key stages, typical operating conditions, and locations of measurement stations.

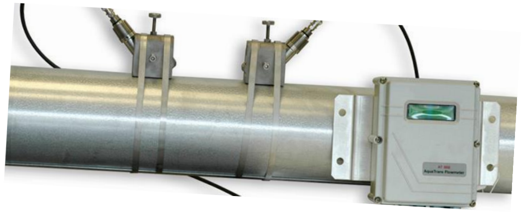
Why Determination of Thermophysical Properties Matters?

Density

- **Turbine Flow Meter**
  - Strong sensitivity near critical region
  - $\dot{m} = Q \times \boxed{\rho}$

$$u(\dot{m}) \uparrow \leftarrow u(\rho) \uparrow$$

Speed of Sound (SoS)



- **Ultrasonic Flow Meter**
  - Accurate $\boxed{\text{Speed of sound (SoS)}}$
  - Strong sensitivity near critical region

Phase Behaviour

- **Coriolis Flow Meter**
  - Measures $\dot{m}$
  - Operates at $\boxed{\text{single phase}}$
  - Strong sensitivity near critical region

How to Determine Thermophysical Properties?

Challenge: These properties are not measurable everywhere.

Thermodynamic Models or Equations of States

Aim: How do molecules interact under P–T conditions?

- **Ideal gas:**

$$P = nRT/V$$

- **Non-ideal gas:**

$$P = ZnRT/V$$

Z=1, Ideal gas
Z<1, Attraction forces
Z>1, Repulsion forces

Cubic Equations of State (EoSs)

- **Van der Waals**

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Attraction

Excluded volume

- **Soave–Redlich–Kwong (SRK)**

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + ubV + wb^2}$$

Temperature dependant attraction

Sphericity of molecules

- **Peng–Robinson (PR)**

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}$$

Improved attraction

Improved volume

- **Valderrama-Patel-Teja (VPT)**

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + c(V-b)}$$

Shape term

Thermodynamic Models (continued)

- **Cubic-Plus-Association (CPA)**

$$P = \underbrace{P_{cubic}}_{\text{Cubic EoS (SRK)}} + \overbrace{P_{association}}^{\text{Hydrogen bonding}}$$

- **Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT)**

$$\alpha = \alpha^{id} + \alpha^{res}$$

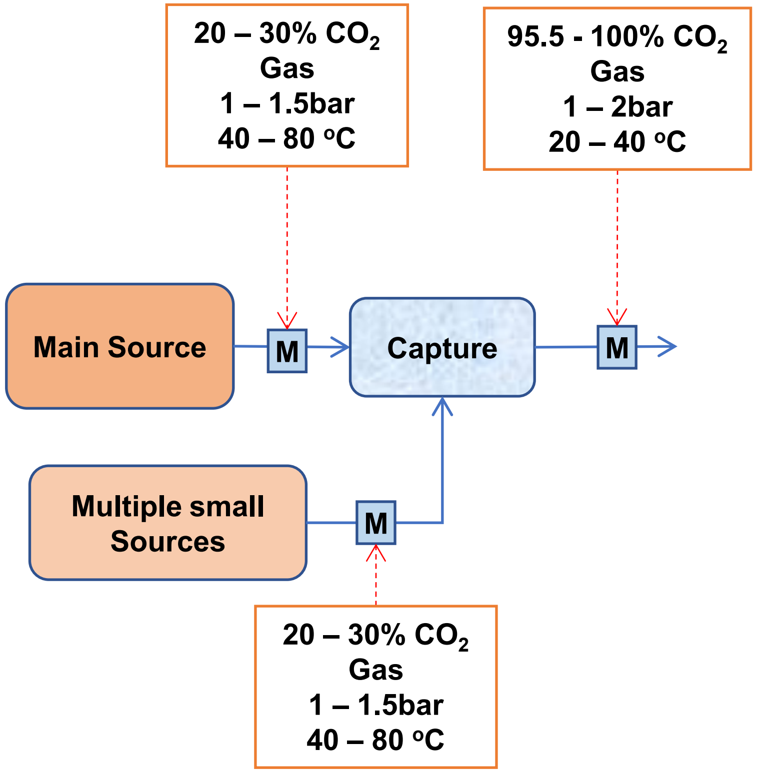
$$\alpha^{res} = \underbrace{\alpha^{hc}}_{\substack{\text{Hard chain:}\\ \text{Hard-sphere contribution}\\ \text{Chain connectivity}}} + \underbrace{\alpha^{disp}}_{\substack{\text{Dispersion:}\\ \text{Attractive (van der Waals) interactions}}} + \underbrace{\alpha^{assoc}}_{\substack{\text{Association:}\\ \text{specific interactions (Hydrogen bonding)}}}$$

- **European Gas Research Group (GERG)**

$$\underbrace{a(\rho, T)}_{\text{Helmholtz free energy}} = \underbrace{a^{ideal}(\rho, T)}_{\text{Ideal fluid contribution}} + \underbrace{a^{residual}(\rho, T)}_{\text{Intermolecular interactions}}$$

What is the Challenge?

- **Impurities:** N_2, O_2, H_2, CH_4, H_2S



20 – 30% CO_2
Gas
1 – 1.5bar
40 – 80 °C

95.5 - 100% CO_2
Gas
1 – 2bar
20 – 40 °C

Main Source

M

Capture

M

Multiple small Sources

M

20 – 30% CO_2
Gas
1 – 1.5bar
40 – 80 °C

Typical Impurities in CO_2-rich Streams

Component	Rationale	unit	Upper limit
CO_2	CCS Industry Standard	mol %	>95
N_2	Non-condensable gas, Two-phase zone	mol %	Combined total <5.0
H_2	Non-condensable gas, Lower recovery of oil, Two-phase zone	mol %	
Ar	Non-condensable gas, Two-phase zone	mol %	
CH_4	Non-condensable gas, Pipeline ductility issues, Flammable, Two-phase zone	mol %	
C_2H_6	Flammable, might cause asphyxiation at high temperatures, Two-phase zone	mol %	
C_3H_8		mol %	
H_2O	Reacts with sulphur to produce sulphuric acid which is corrosive	ppm mol	50
O_2	Non-condensable gas, thinning of pipeline, reacts with hydrocarbons, enhances growth of aerobic bacteria	ppm mol	10
NO	Toxic	ppm mol	10
SO_2		ppm mol	10
H_2S		ppm mol	5
NH_3	Toxic, Solid management	ppm mol	10
C_2H_7NO (MEA)	Liquid droplet	ppb mol	100

Mixing Rules in Equations of State

CO_2–CO_2 → ✓

H_2–H_2 → ✓

CO_2–H_2 → ❗

Mixing rules extend a pure-component EoS to mixtures by

1. Combine pure-component properties

Weighted by composition (mole fraction)

2. Account for cross-interactions

Between unlike molecules

- **Mixing equations:**

$$a_{mix} = \sum_j \sum_j x_i\, x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - \boxed{k_{ij}}\right)$$

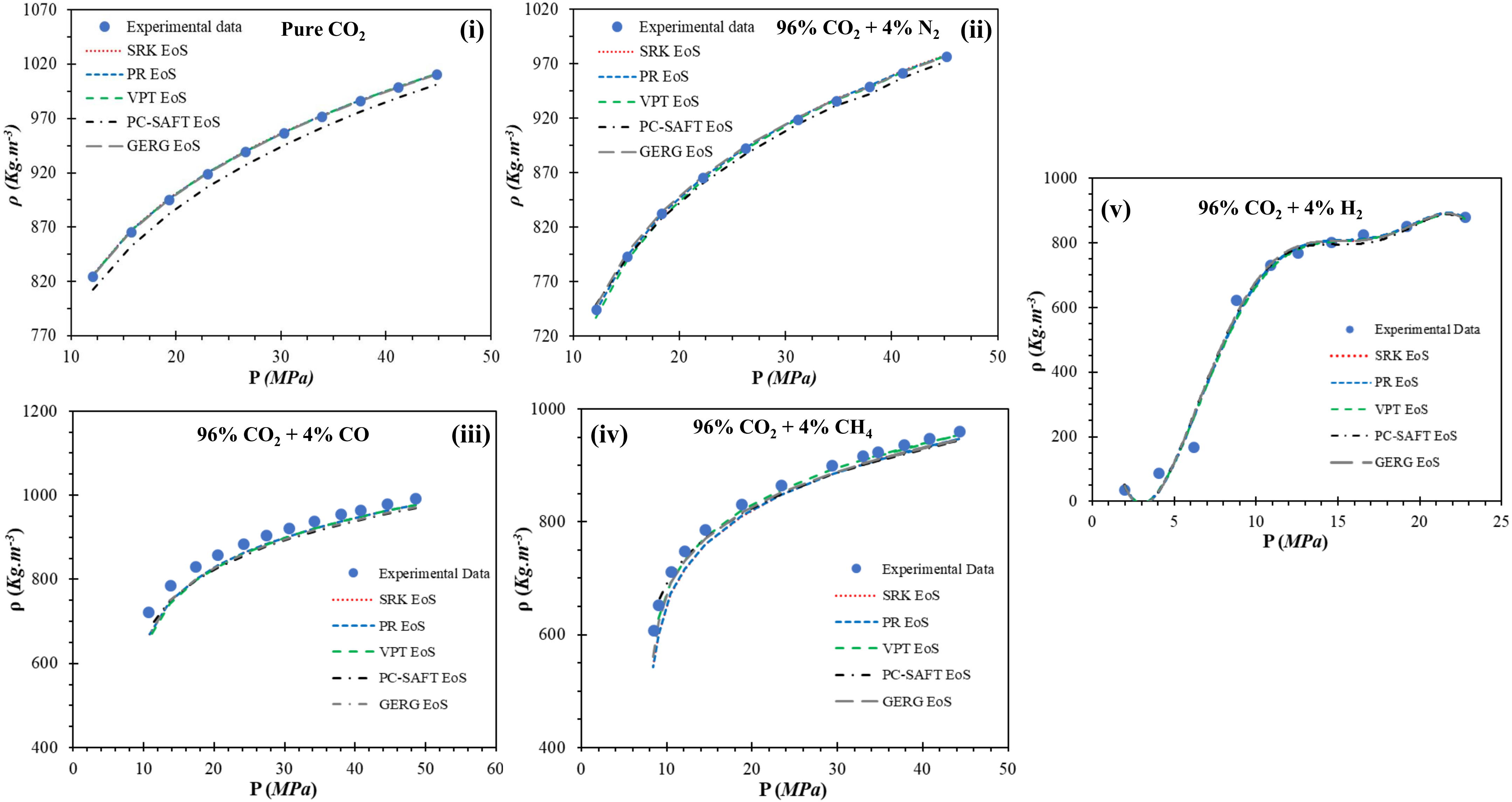
$$b_{mix} = \sum_i x_i\, b_i$$

a_{ij} →interaction between unlike molecules

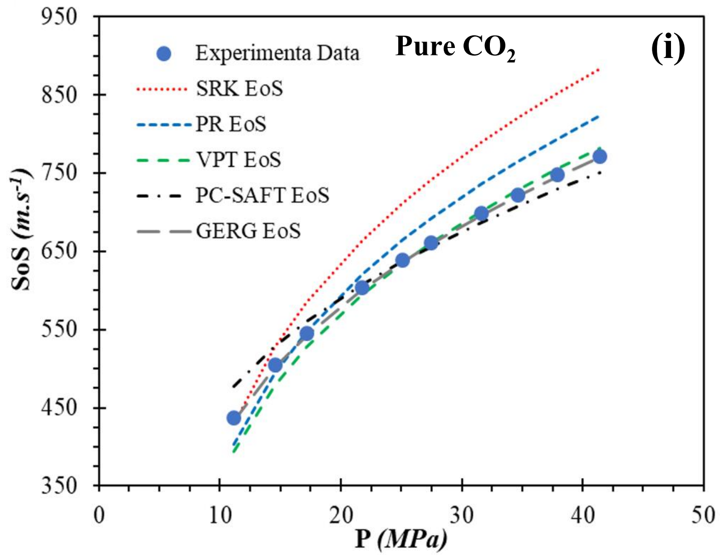
k_{ij} →binary interaction parameter (BIP)

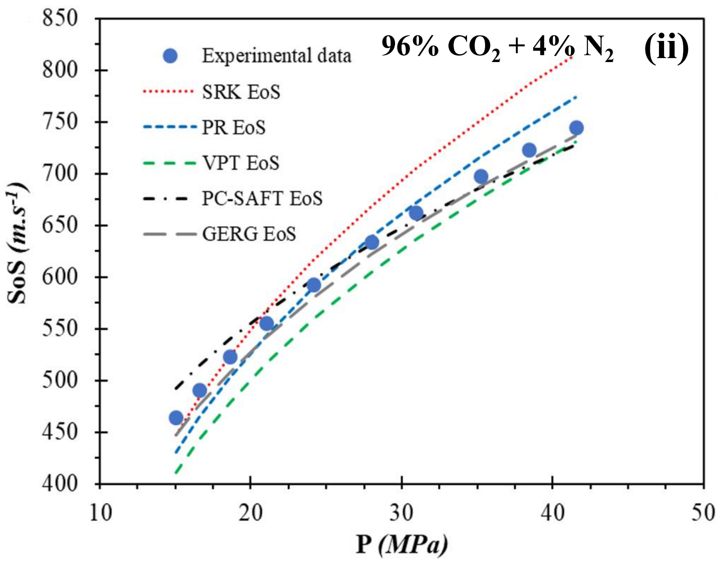
b→ molecular size (volume averaging)

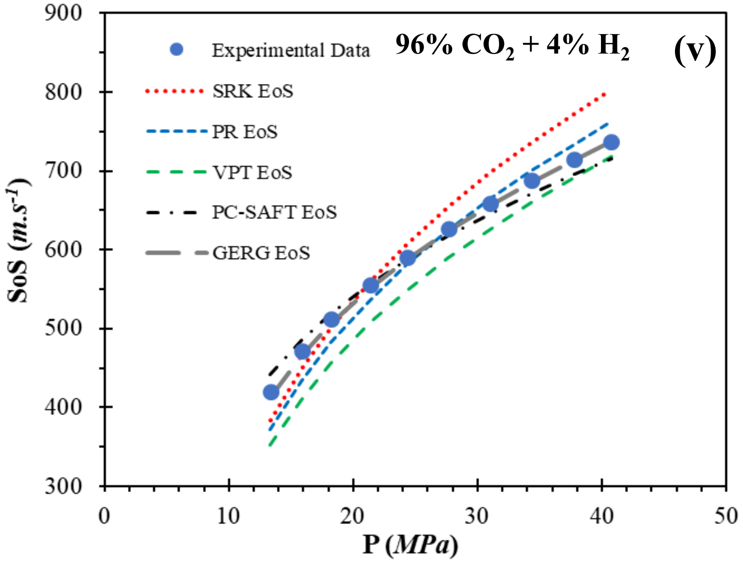
Effect on Density

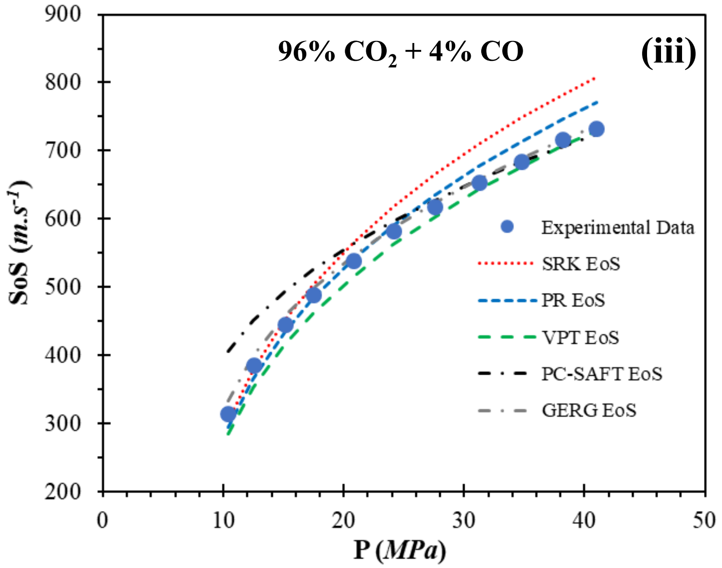


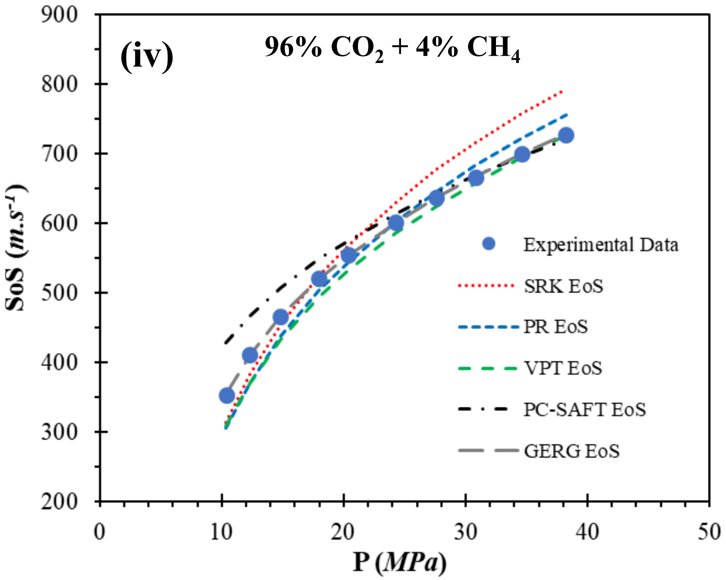
Effect on Speed of Sound



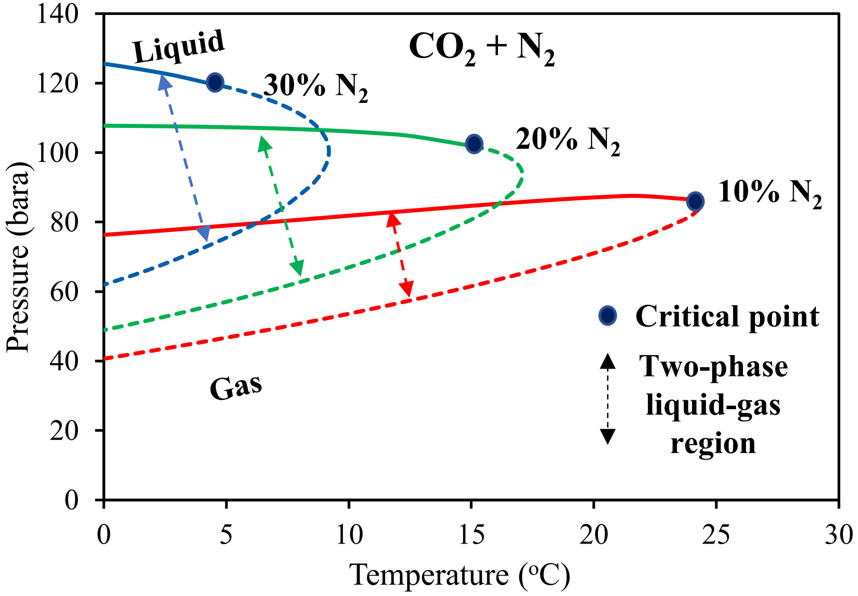


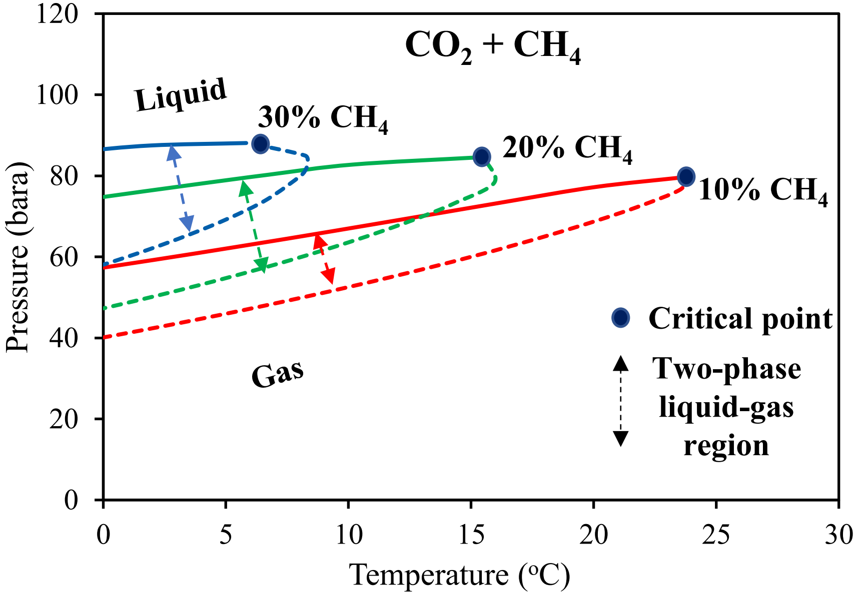


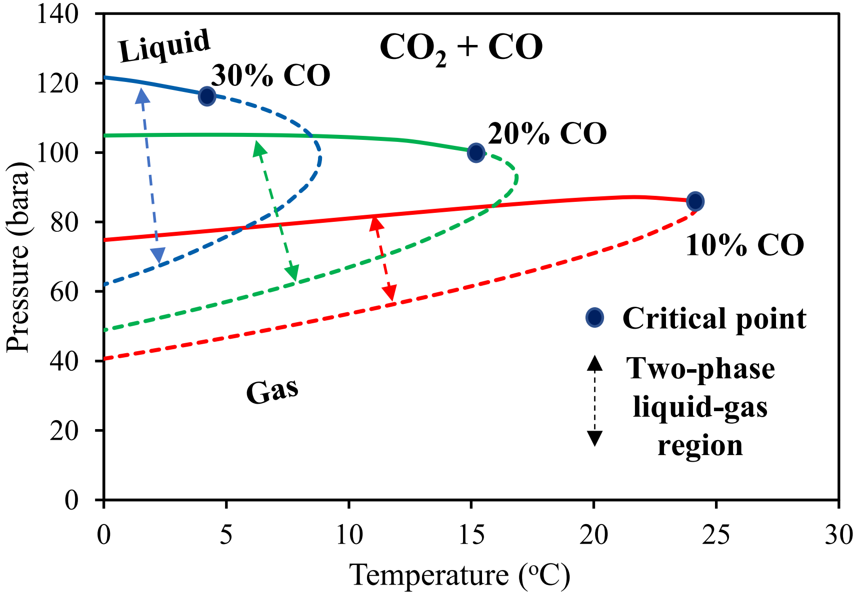


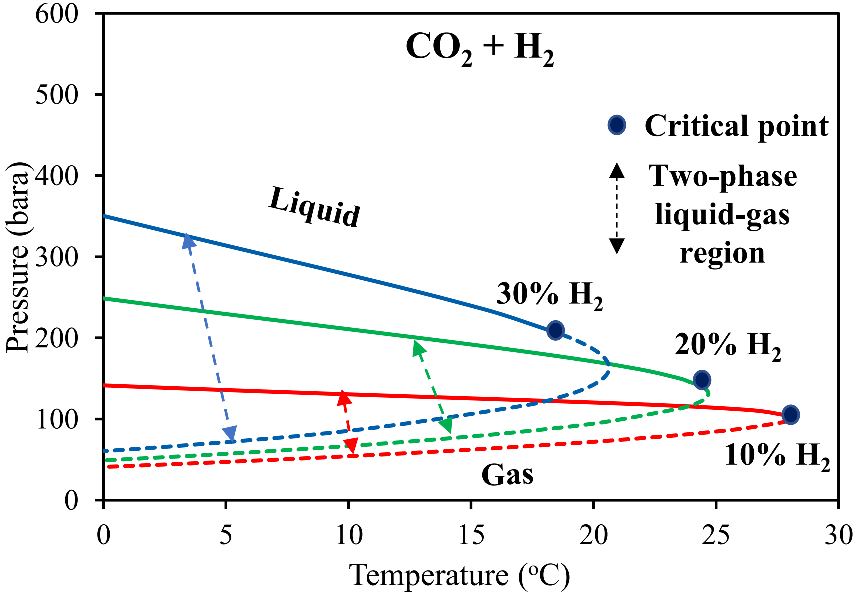


Effect on Phase Envelope









✓ Operating at **single phase** is desirable.

Effect of Impurities

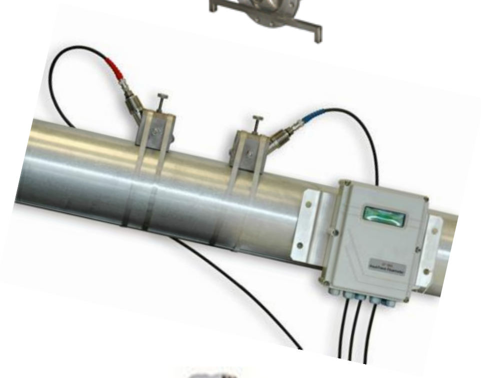
Solid Formation: A Hidden Risk in CO_2 Transport

- Strongly influenced by impurities
  - Solid CO_2
  - Ammonium Carbonate (CO_2, NH_3 and H_2O)
- Poorly predicted by standard EoSs
- Triggered by pressure drops and low temperatures
- Leads to:
  - Safety risks (blockage and erosion)
  - Flow meter malfunction

Impact on Flow Measurement

- **Coriolis meters:**
  - Assumes single-phase fluid
  - Vibration damping / signal distortion

- **Ultrasonic meters:**
  - Scatter acoustic waves
  - Signal attenuation



- **Differential pressure meters:**
  - Change in effective flow area
  - Unpredictable pressure drops

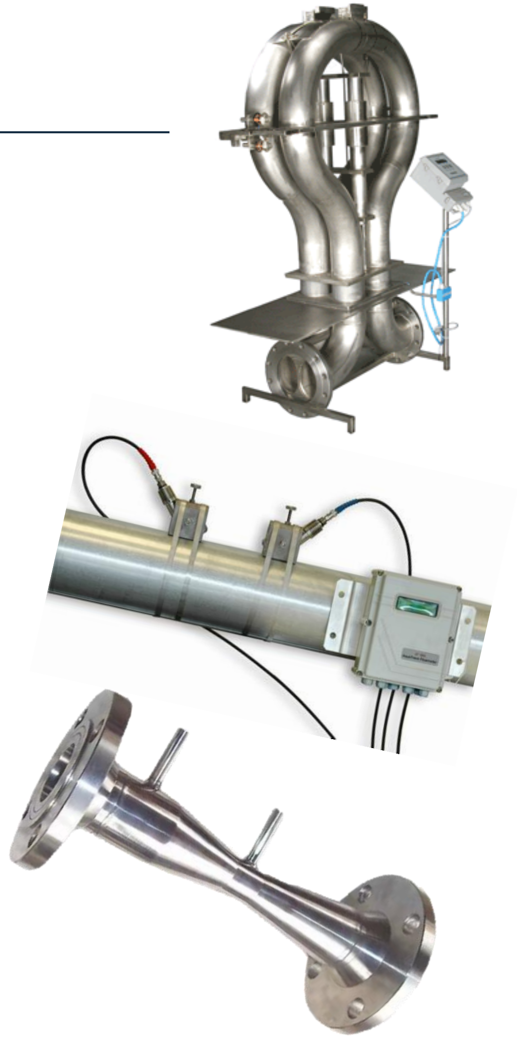
Effect of Impurities

Aqueous Phase Formation: A Critical Risk in CO_2 Transport

- Strongly influenced by impurities
  - Change water solubility
  - Promote phase separation
  - Hydrate formation
  - Acid formation (Corrosion)
- Flow assurance issues:
  - Slugging
  - Unstable flow regimes
  - Increased pressure drop

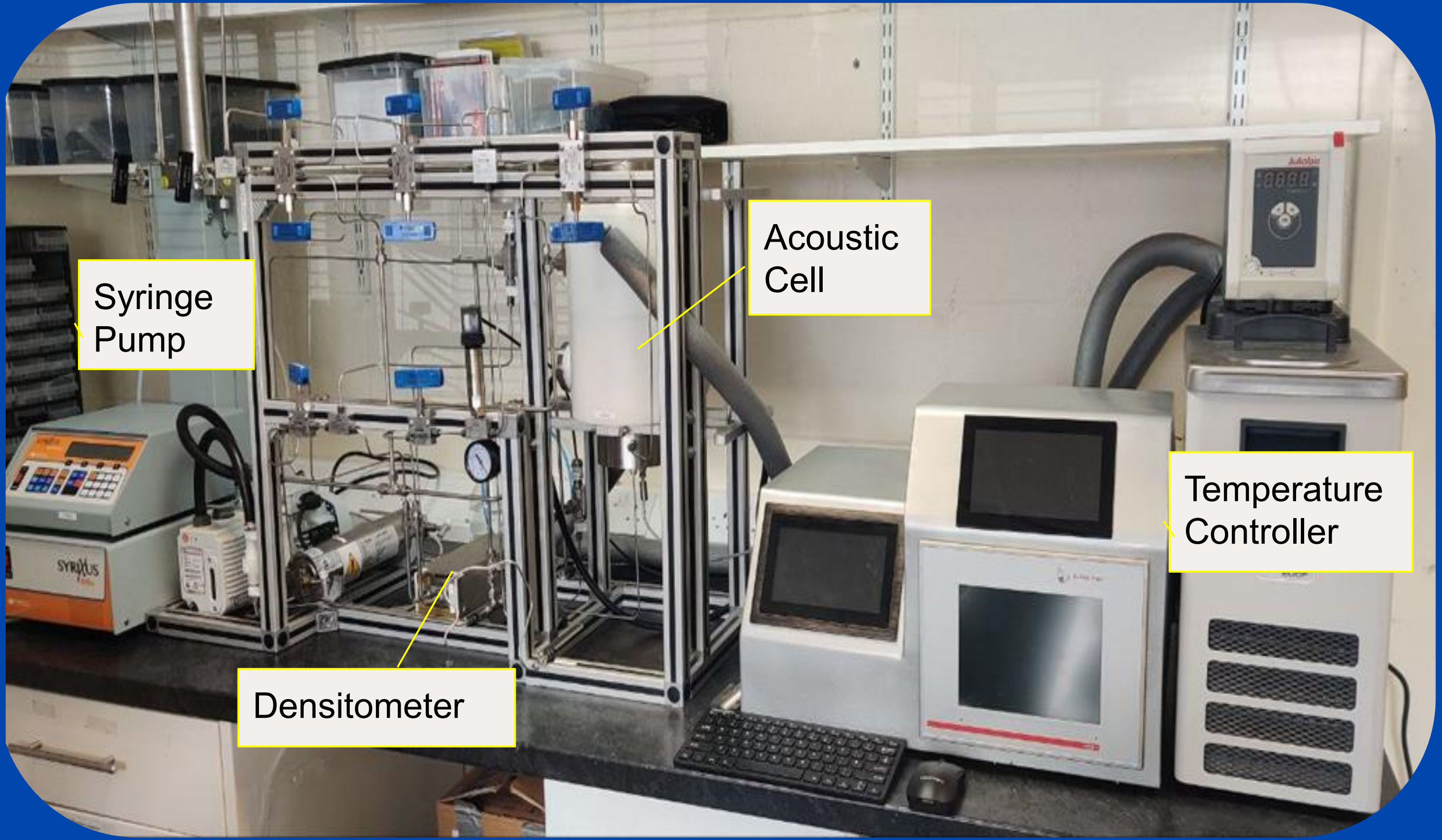
Impact on Flow Measurement

- **Coriolis meters:**
  - Assumes single-phase fluid
  - Signal instability
- **Ultrasonic meters:**
  - Scatter acoustic waves
  - Signal attenuation
- **Differential pressure meters:**
  - Invalid density assumption
  - Flow coefficients change

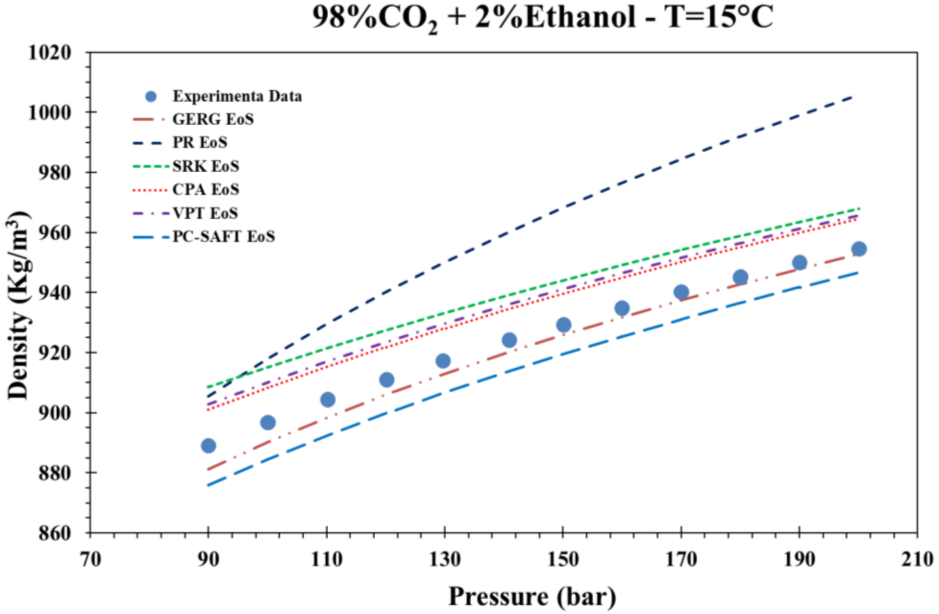


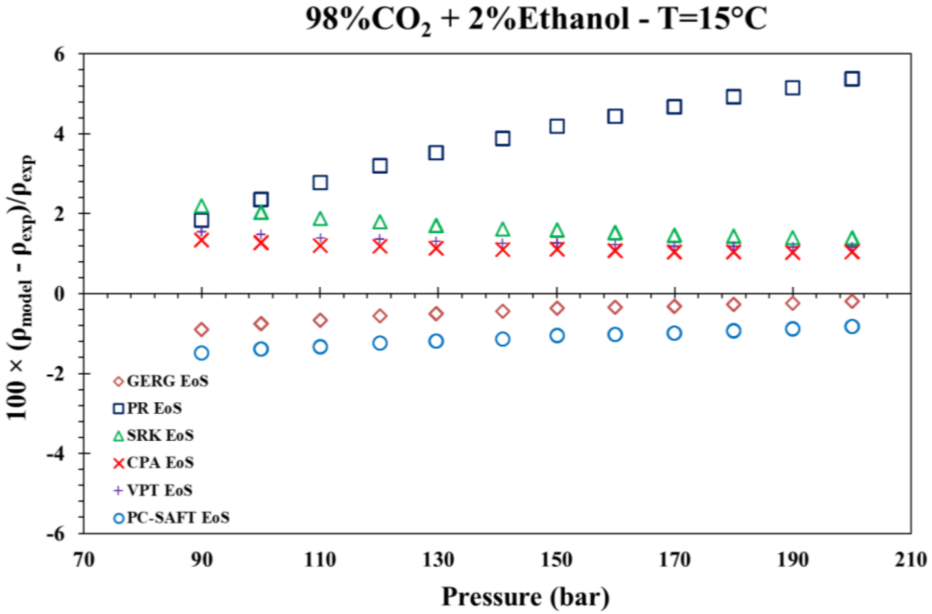
Fluid Properties Test Rig Facility at TÜV SÜD– NEL

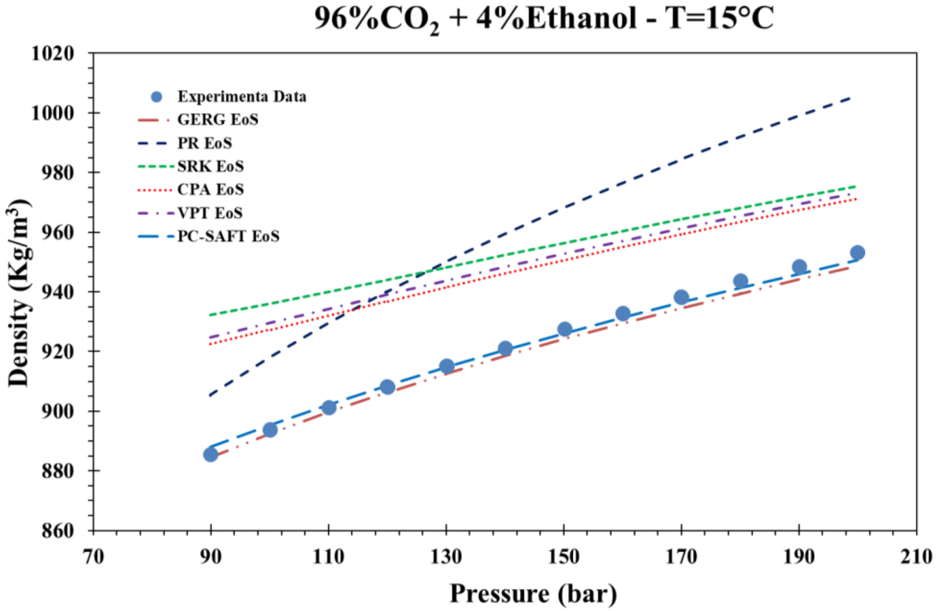
- **Density and speed of sound measurements.**
    - Pressure range: 0.1 to 400 bar
    - Temperature range: -10 to 100 °C (SoS up to 60 °C)
    - Phase: Gas, Liquid, Supercritical

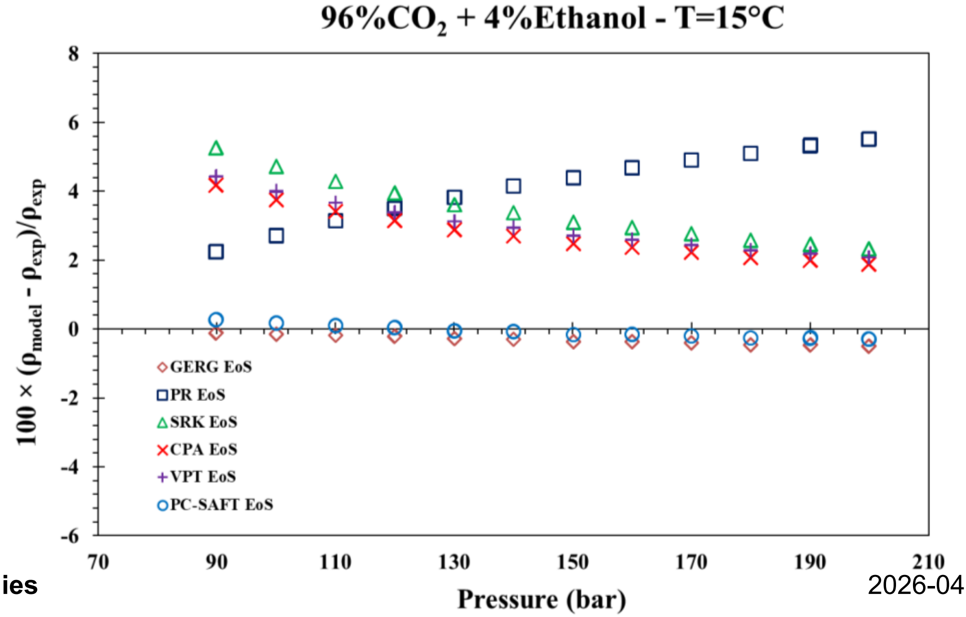


Experimental vs Modelling Results (Density)

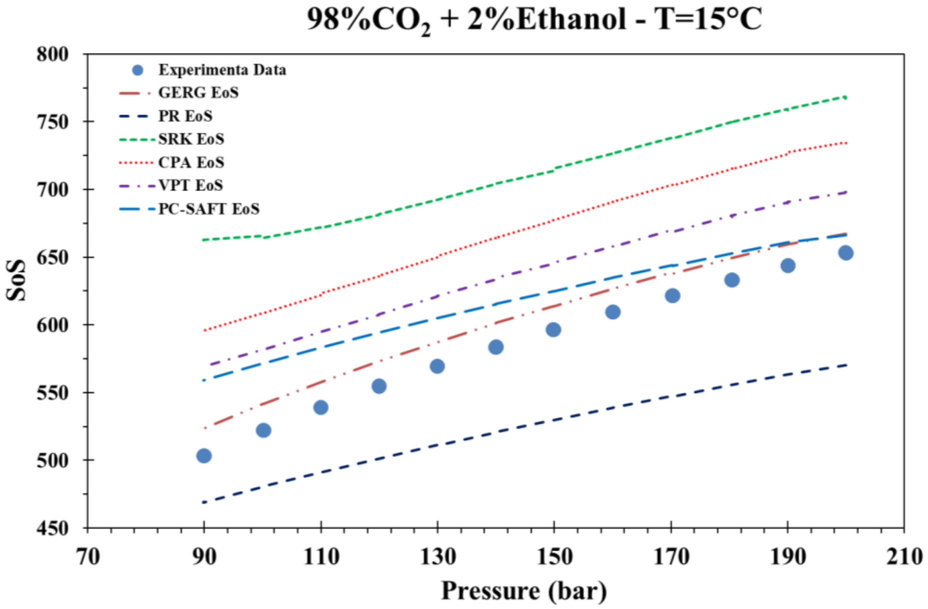


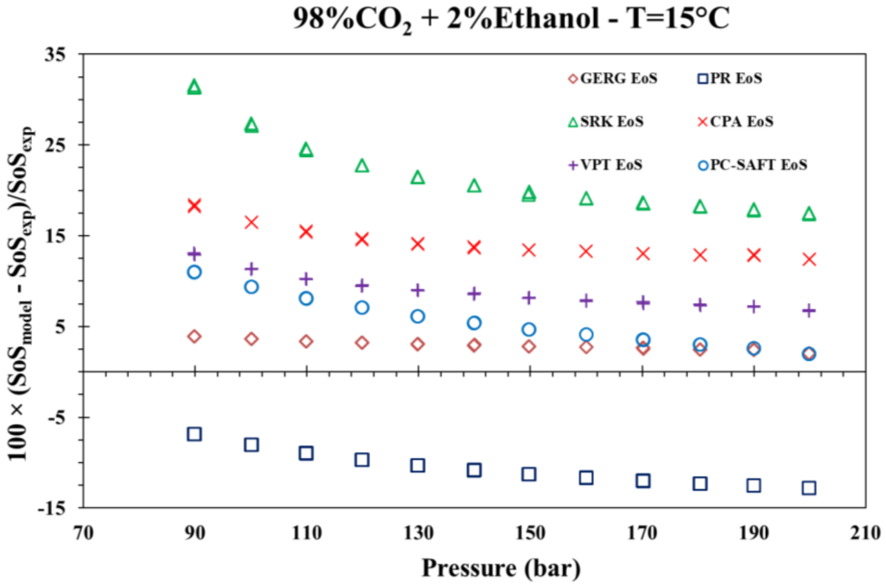


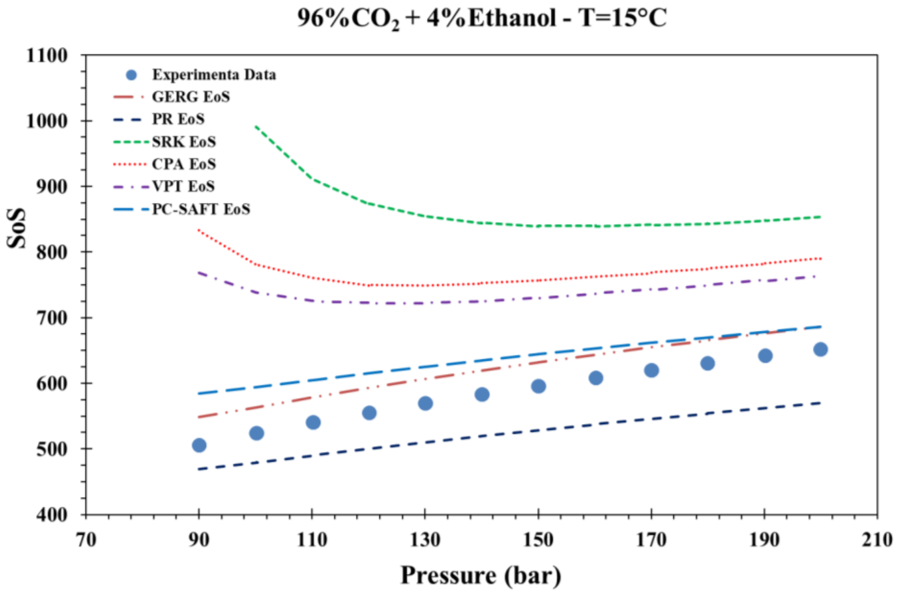


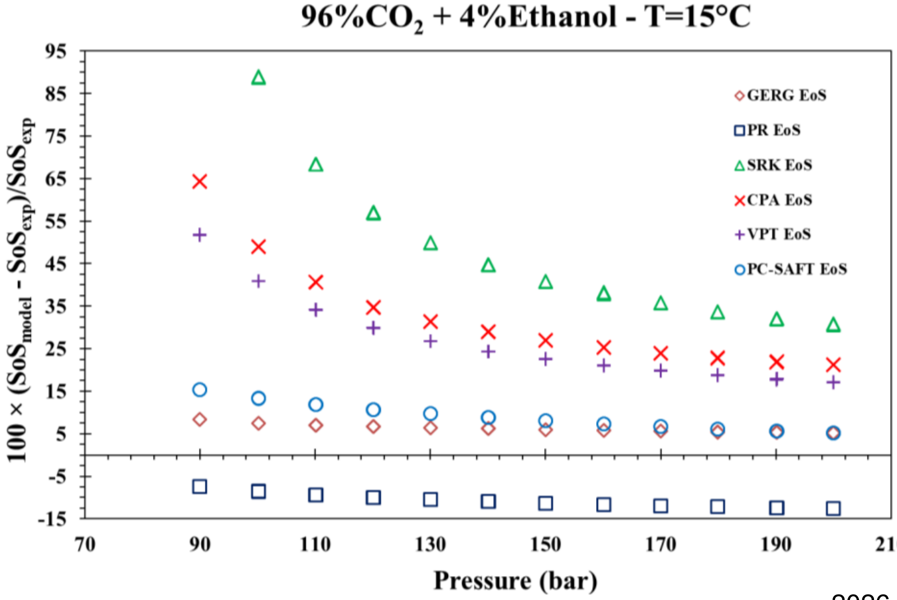


Experimental vs Modelling Results (SoS)





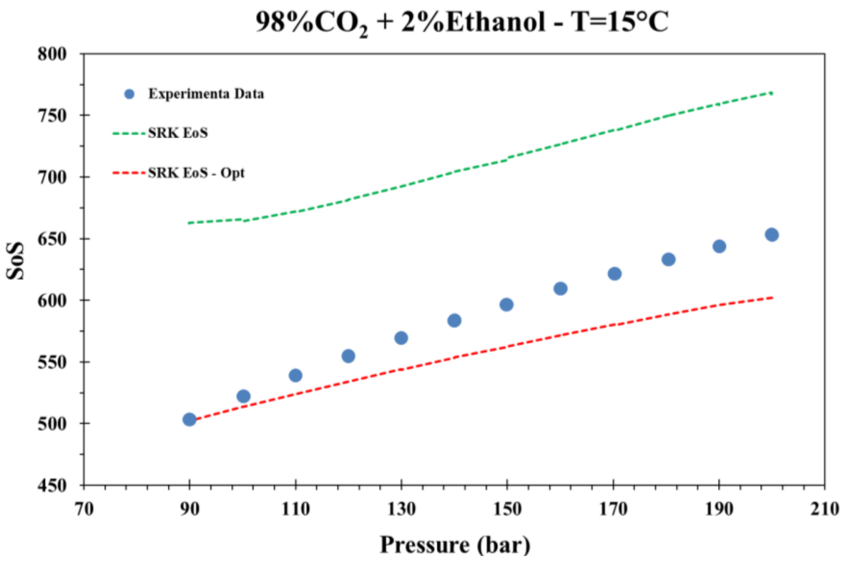




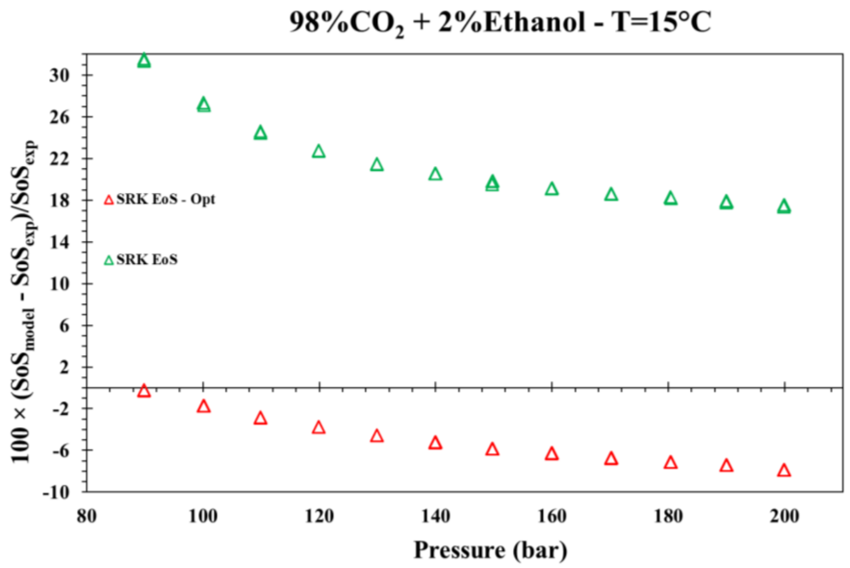
Optimised Binary Interaction Parameter (BIP)

$$a_{mix} = \sum_{j}\sum_{j} x_i\, x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - \boxed{k_{ij}}\right)$$



98%CO$_2$ + 2%Ethanol - T=15°C



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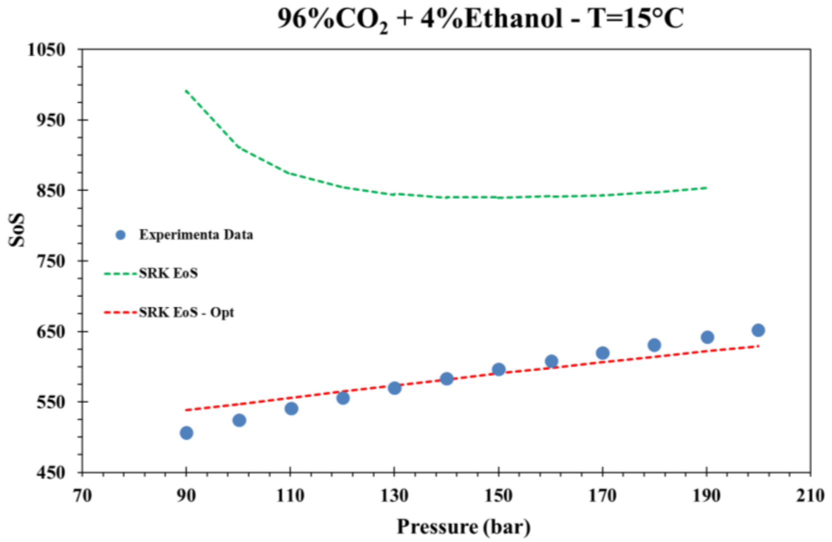
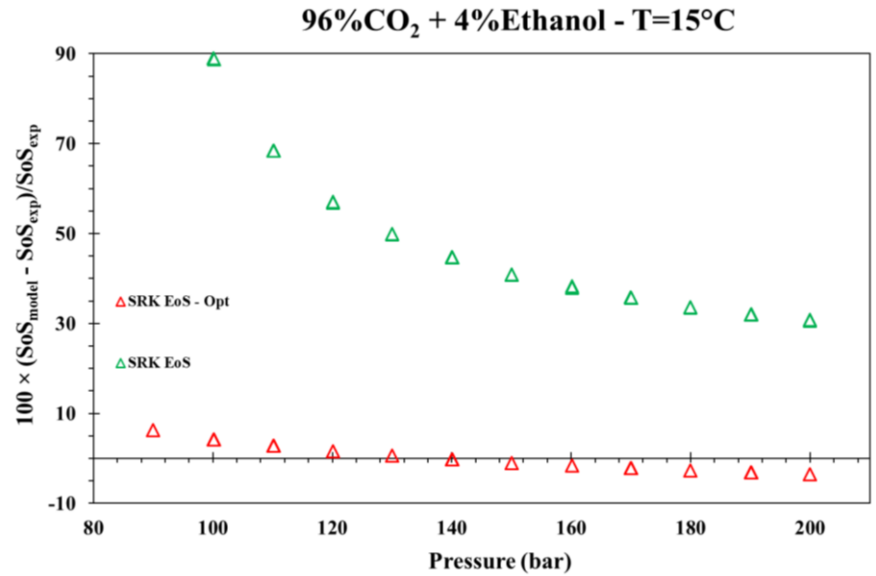


96%CO$_2$ + 4%Ethanol - T=15°C



96%CO$_2$ + 4%Ethanol - T=15°C

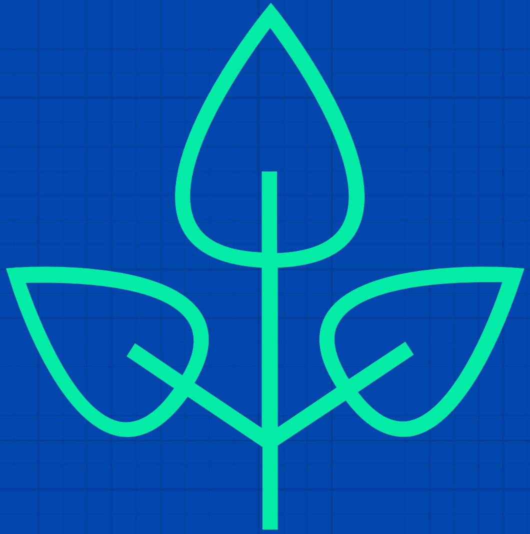
Conclusion

- The results demonstrate that impurities have a significant influence on both density and SoS, with their impact strongly dependent on molecular characteristics and operating conditions.
- Polar and associating components such as ethanol introduce more complex intermolecular interactions, leading to greater deviations in model predictions.
- GERG-2008 consistently provided the most reliable predictions for both density and SoS across the investigated conditions.
- Model performance can be significantly improved through the optimisation of BIPs.
- No single EoS is universally optimal for all CCS conditions.

Future Work

- Undertaking the experimental programme on phase behaviour/VLE of complex multi-component CO_2–rich fluids

Thanks for your attention



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