Vapour-liquid Equilibrium Data of Carbon Dioxide and Oxygen*

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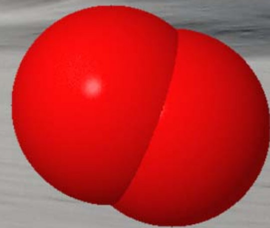

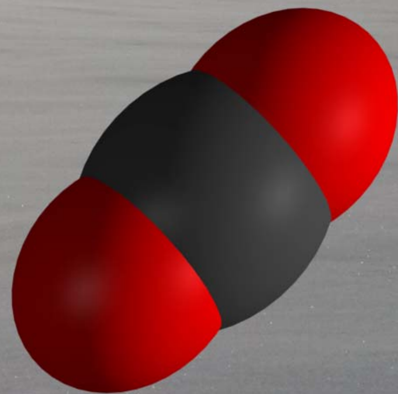

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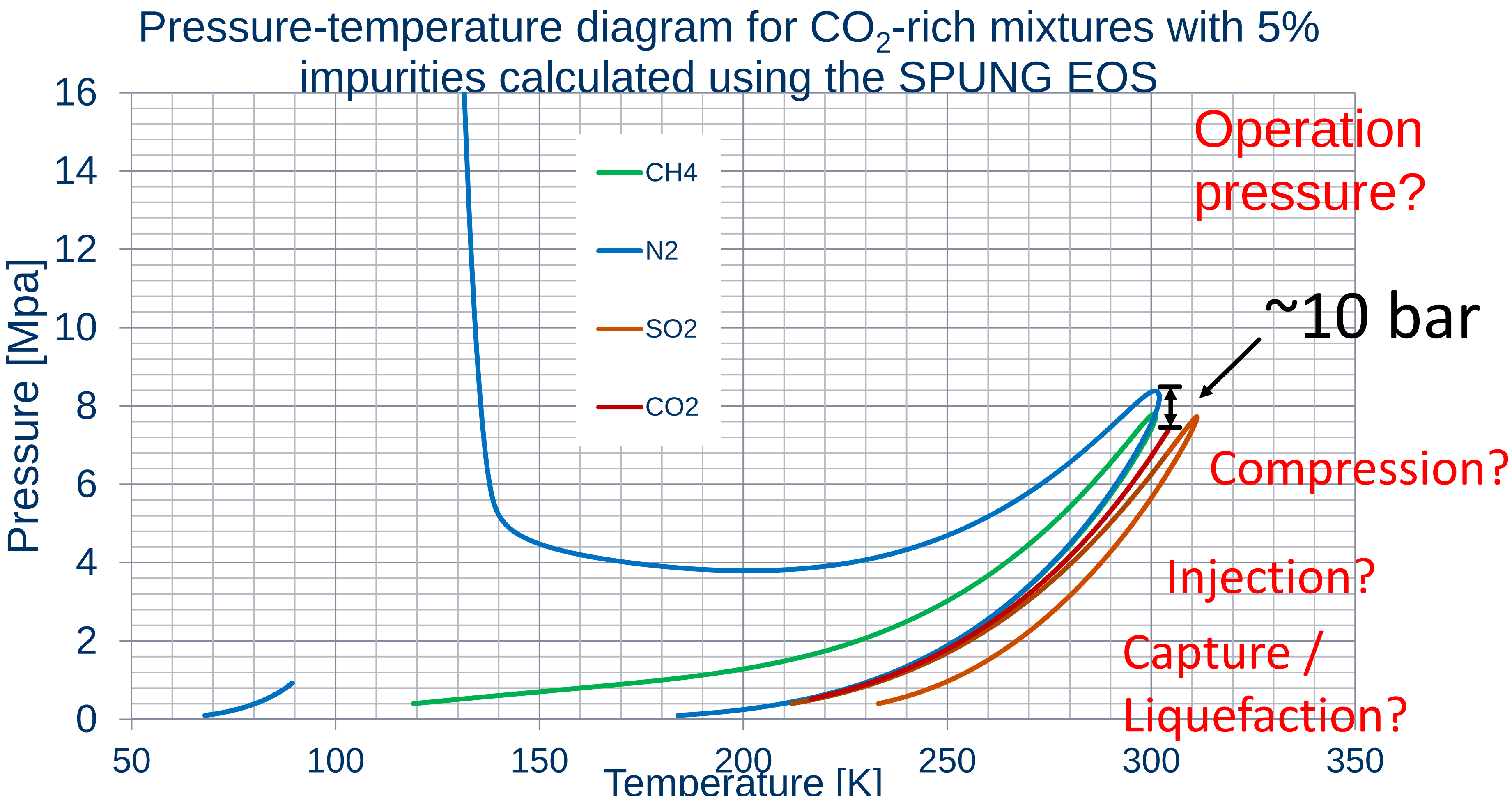
*Submitted to Fluid Phase Equilibria by Westman et al.

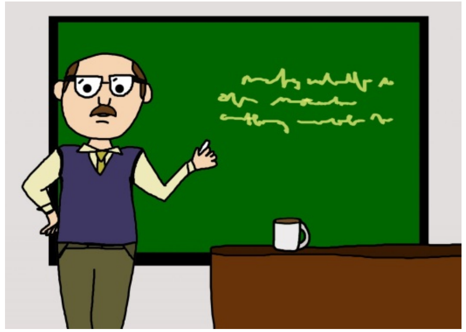
Influence of impurities on VLE

Water and corrosion?



Løvseth SW, Skaugen G, Jacob Stang HG, Jakobsen JP *et al.*. *Energy Procedia* 2013;**37**:2888-96.

All IMPACTS and CO2Quest people know that



- Impurities in CO_2 will be present in CCS
- The impurities could have large consequences
- Accurate and reliable models are required

Well behaved models and correlations for CCS

- Are easiest built with accurate data that are
  - on binary mixtures
  - w/ concentration ranges beyond the expected

But there are a lot of data, right?

VLE Binary Data Situation

- Systems relevant for natural gas covered with some gaps
  - CO_2 - N_2, - CH_4, - H_2O, - H_2
- Scarce / inconsistent,
  - CO_2 - O_2, - CO, - Ar, - NO_x, - H_2S
- No / little /very old data,
  - CO_2 - COS, - SO_2, many amines, trace comp
  - Most relevant mix. w/o CO_2

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PVTxy properties of CO_2 mixtures relevant for CO_2 capture, transport and storage: Review of available experimental data and theoretical models

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ABSTRACT

The knowledge about pressure–volume–temperature–composition (PVTxy) properties plays an important role in the design and operation of many processes involved in CO_2 capture and storage (CCS) sys-

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EOS–CG: A Helmholtz energy mixture model for humid gases and CCS mixtures

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Dissertation
zur
Erlangung des Grades
Doktor-Ingenieur

Munkejord et al., subm. Applied Energy

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- Scarce / inconsistent
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    - H_2S
- No / littl-
  - C-

  ...ce comp

  ...nt mix. w/o CO_2

Data improvement urgently needed

Munkejord et al., subm. Applied Energy

CO_2Mix and IMPACTS

- CO_2Mix
  - Late 2010 -2015
  - BIGCCS spin-off and funded by the CLIMIT/ Research Council of Norway
  - WP A: Experimental investigation of phase equilibria
    - SINTEF Energy Research and NTNU
    - Advanced experimental infrastructure established
  - WP B: Measurement of density and speed of sound
    - Headed by Prof. R. Span, Ruhr-University Bochum

- 2015 co-funding of VLE by CO_2Mix and IMPACTS
  - Analysis and documentation of CO_2-N_2 measurements
  - Measurements of CO_2-O_2 and CO_2-Ar

Phase Equlibrium Measurements: Basics

- Analytical method
  - Composition measurements of all fluid phases
  - Sampling and gas chromatograph (GC)
  - Total composition not critical for binary systems
- Temperature
  - Range: -60 to 150 °C
  - Combined accuracy, stability and uniformity of <5-10 mK
- Pressure:
  - Range: 4 to 200 bar
  - Accuracy better than 0.10 % (mostly <0.03 %)

Stang HGJ, et al., Energy Proc., 2013. **37**: p. 2897.
Westman SF, et al., Fluid Phase Equilib., 2016. **409**: p. 207.

Cell Design

- Volume 0.1 l
- Sapphire Tube / Titanium Flanges
- Separate valves and pumps for:
  - CO_2
  - Water
  - Other components / calibration mixture
  - N_2 – (flushing)
- Pressure measured using 4 sensors & differential pressure cell
- 25 Ω standard platinum resistance thermometers (SPRT / PT)
- Temperature control using thermostatic baths

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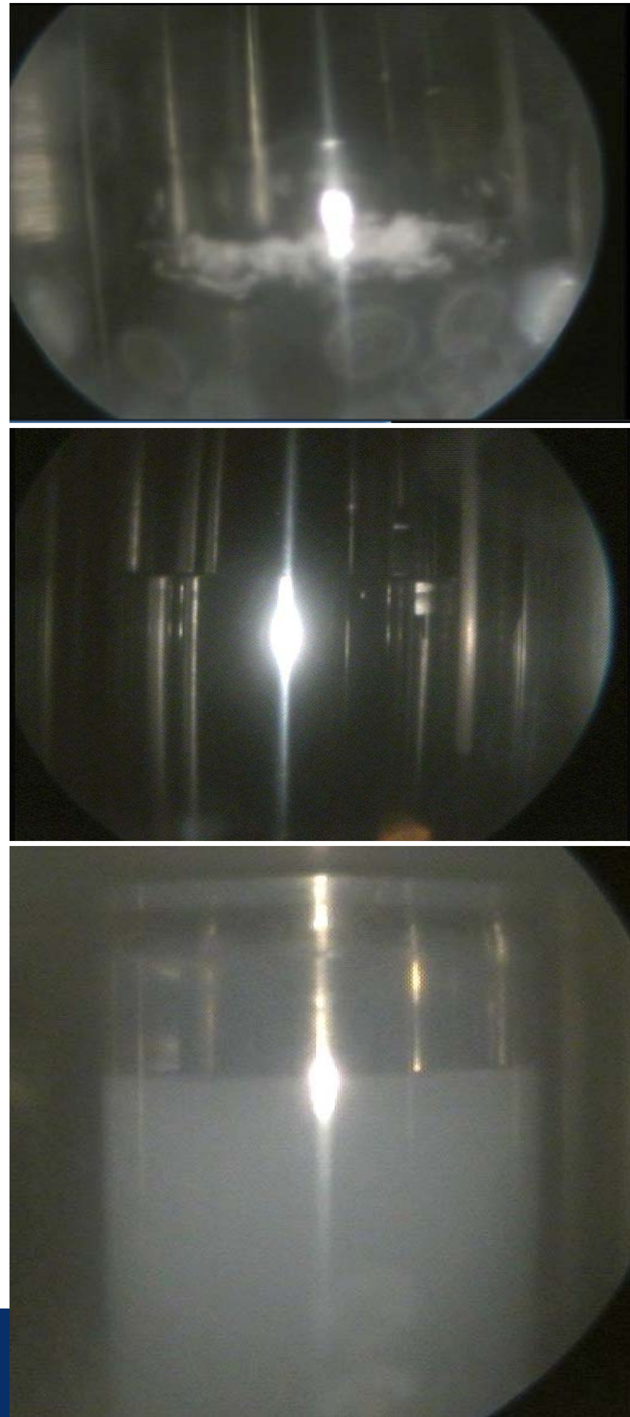
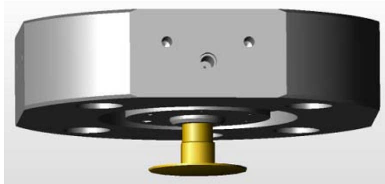
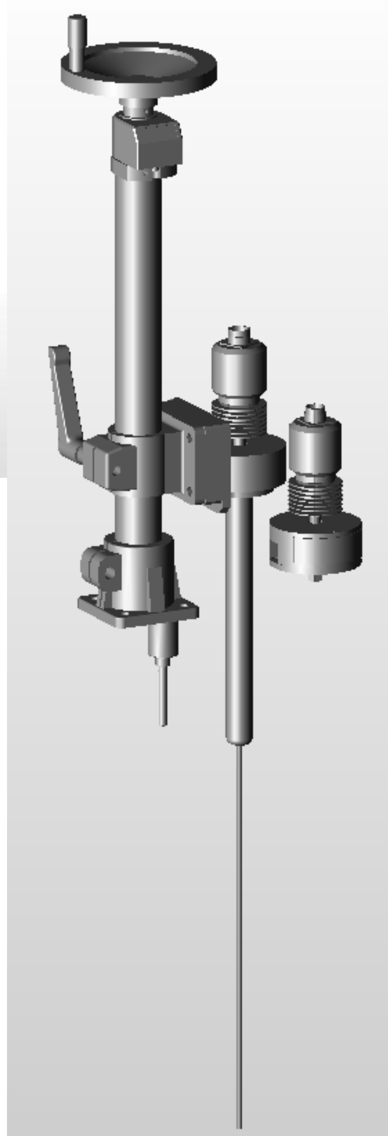


Analysis and Sampling

- Sampling volumes down to 3 μg
  - Fixed for gas phase
  - Movable for liquid phase
  - Heated lines
- Pressure cell compensation using bellows
- Gas Chromatograph
  - Agilent 7890A
  - Detection:
    - Flame ionization detector (FID) w/ methanizer
    - **Thermal conductivity detector (TCD)**
    - Flame-ionization detectors (FPD)





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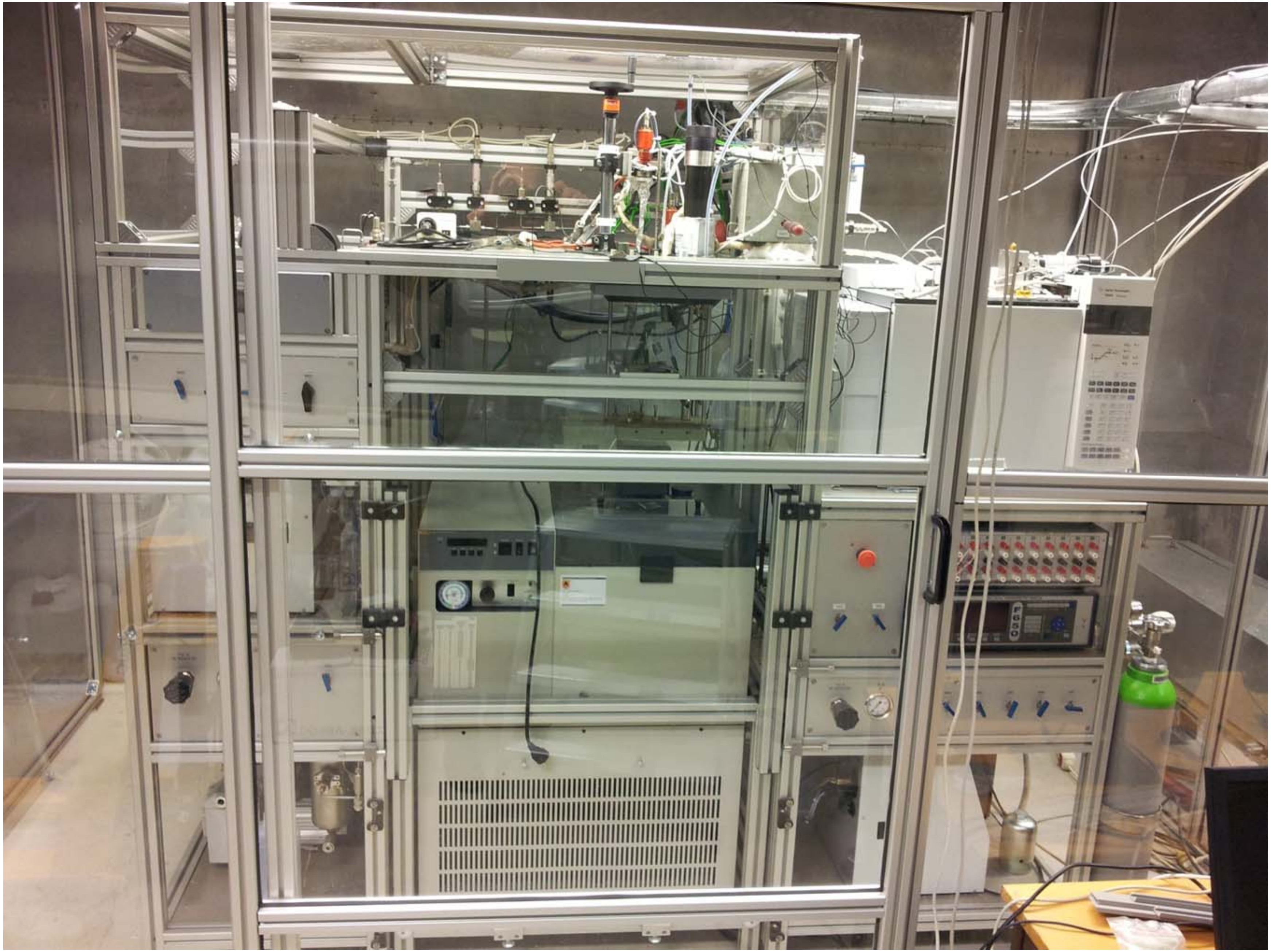
GC Calibration

- Accuracy $\lesssim$ 0.05 %
- In-house calibration gas prep
  - Accuracy <20 ppm absolute
- GC response dependent on
  - Sample composition
  - Sample size (optimized)
  - GC oven program
  - Integration method (improved!)
  - Calibration formula (improved!)

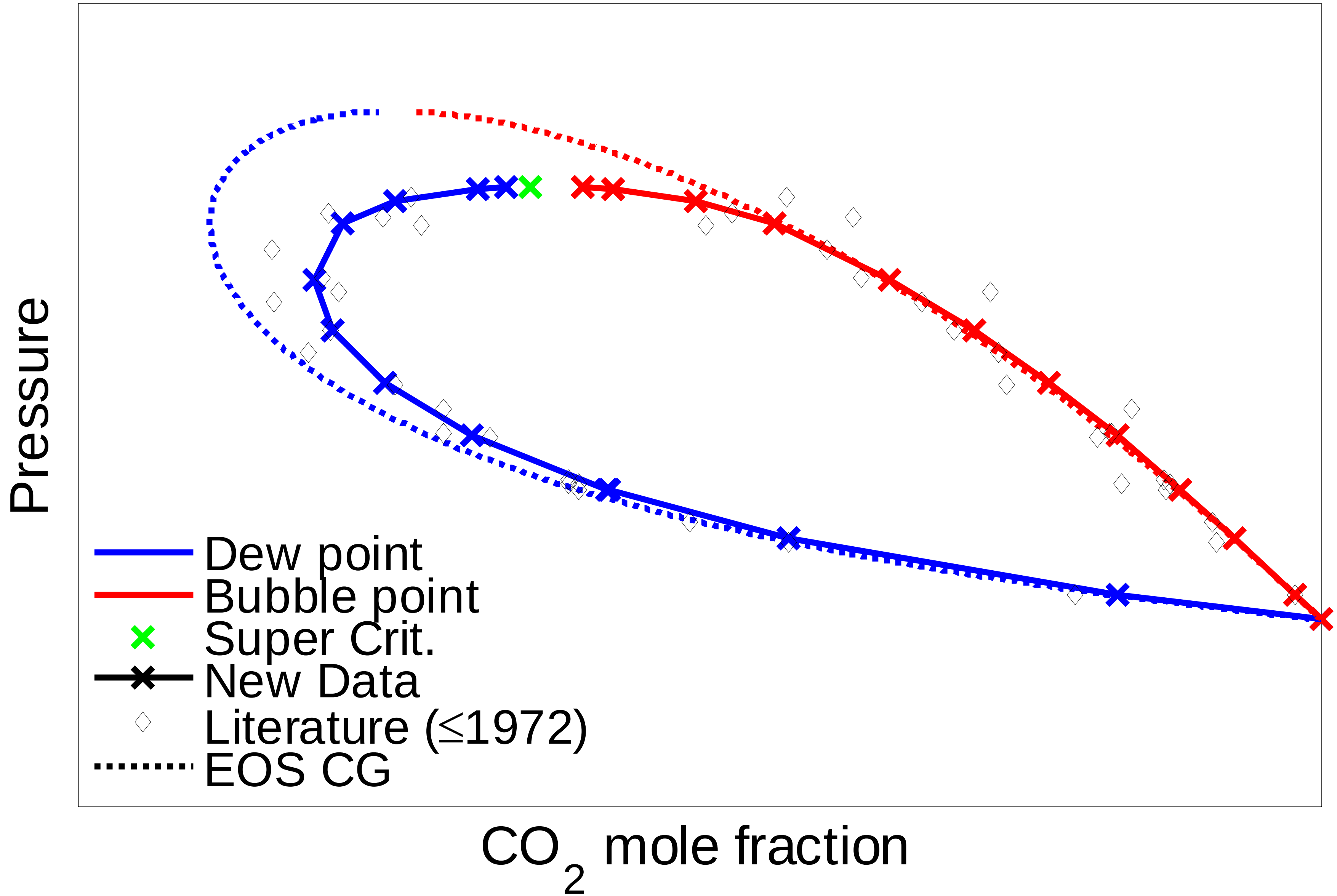
$$\hat{n}_{CO_2} \cdot k = A_{CO_2} + (A_{CO_2})^{c_1} + (A_{CO_2})^{c_2} ,$$

$$\hat{n}_{O_2} \cdot k = c_3 \cdot \left(A_{O_2} + (A_{O_2})^{c_4} + (A_{O_2})^{c_5}\right) ,$$

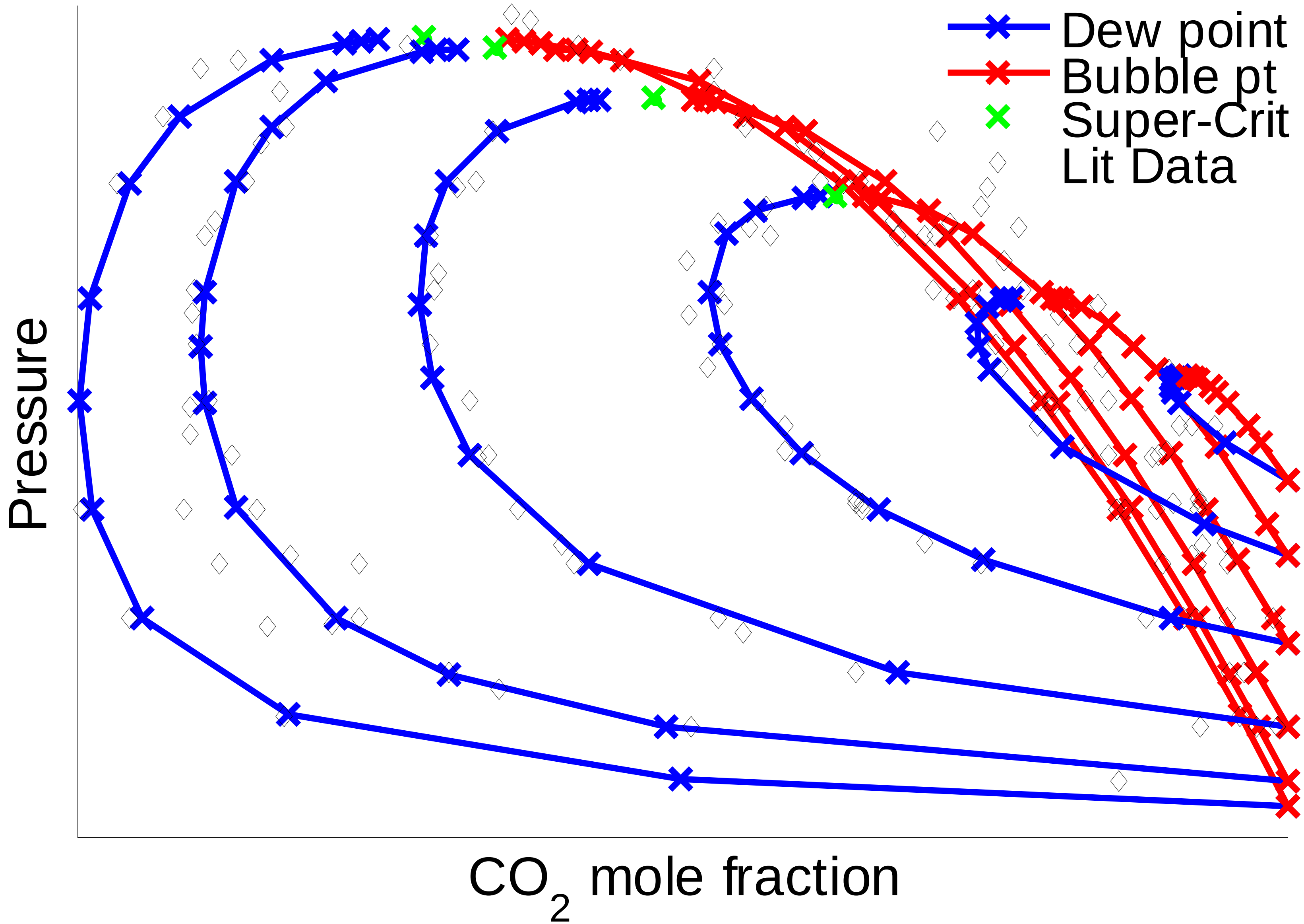
$$\hat{y}_{CO_2,cal} = \frac{\hat{n}_{CO_2}}{\hat{n}_{CO_2} + \hat{n}_{O_2}} ,$$



Phase equilibria CO_2-O_2 (~0 °C)



CO_2-O_2


Dew point
Bubble pt
Super-Crit
Lit Data
Pressure
CO2 mole fraction

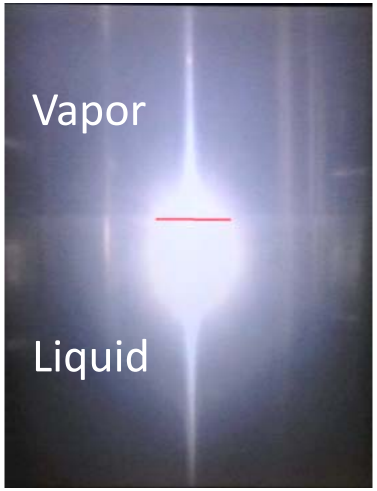
Critical region measurements: CO_2-O_2

- Using the bellows to tune pressure
- Scaling law regression to estimate the mixture critical point

$$z_{\mathrm{CO_2}} = \hat{z}_{\mathrm{CO_2,c}} + \left(\lambda_1 - \epsilon\frac{\lambda_2}{2}\right)(\hat{p}_\mathrm{c} - p) - \epsilon\frac{\mu}{2}(\hat{p}_\mathrm{c} - p)^\beta$$

- Overall fit using PR-MC-WS-NRTL represent data fairly well

Supercritical



Subcritical

Conclusions - General

- Good thermodynamic models are absolutely neccessary for robust and efficient CCS process design
- Models must be built by fitting binary interaction parameters to experimental data
- IMPACTS have worked together with the CO2Mix project to produce high quality phase equilibrium measurements

Conclusions – CO_2-O_2

- The data situation of this important binary system was poor
- 6 accurate isotherms from -55 to +25 °C have been measured
- The critical composition / pressure has been determined at each temperature
- Deviations with existing models have been found
- System is ripe for model improvements.

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Critical phase transition www.bigccs.no/co2mix