THE ADVANCED PROCESS MODELING COMPANY

gSAFT: advanced physical properties for carbon capture and storage system modelling

J. Rodriguez, M. Calado, E. Dias, A. Lawal, N. Samsatli, A. Ramos, T. Lafitte, J. Fuentes, C. Pantelides

CO_2 Properties and EoS for pipeline engineering
York
11 November 2014

Overview

- gCCS whole-chain system modelling environment
  - ETI's CCS system modelling tool-kit project
- Challenges in providing physical properties for the systems downstream of the capture plant
- gSAFT technology
  - Based on a predictive molecular equation of state
- gSAFT for the compression, transmission and injection subsystems within gCCS
- Application to typical CCS flowsheets
  - Using gCCS libraries
- Conclusions

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gCCS whole-chain system modelling environment

ETI’s CCS system modelling tool-kit project

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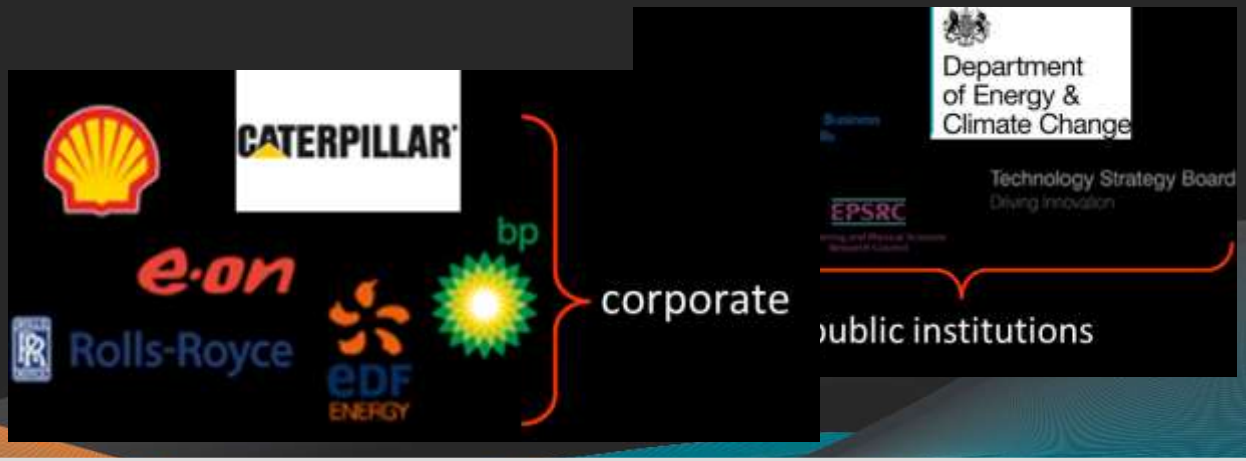
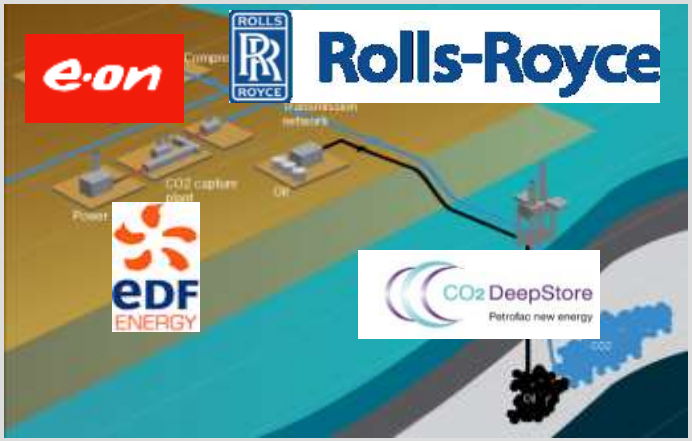
The CCS System Modelling Tool-kit Project

2011-2014

- **Energy Technologies Institute (ETI)**





- ~$5m project commissioned & co-funded by the ETI
- Objective: **“end-to-end” CCS modelling tool**

gCCS

PSE **gPROMS modelling platform & expertise**

E4tech Project Management

gCCS initial scope (2014/Q2)

- **Process models**
  - Power generation
    - Conventional: pulverised-coal, CCGT
    - Non-conventional: oxy-fuelled, IGCC
  - Solvent-based CO_2 capture
  - CO_2 compression & liquefaction
  - CO_2 transportation
  - CO_2 injection in sub-sea storage
- **Materials models**
  - cubic EoS (PR 78)
    - flue gas in power plant
  - Corresponding States Model
    - water/steam streams
  - SAFT-VR SW/ SAFT-γ Mie
    - amine-containing streams in CO_2 capture
  - SAFT-γ Mie
    - near-pure post-capture CO_2 streams

Open architecture allows incorporation of 3rd party models

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Physical properties for subsystems downstream of the capture plant

Challenges

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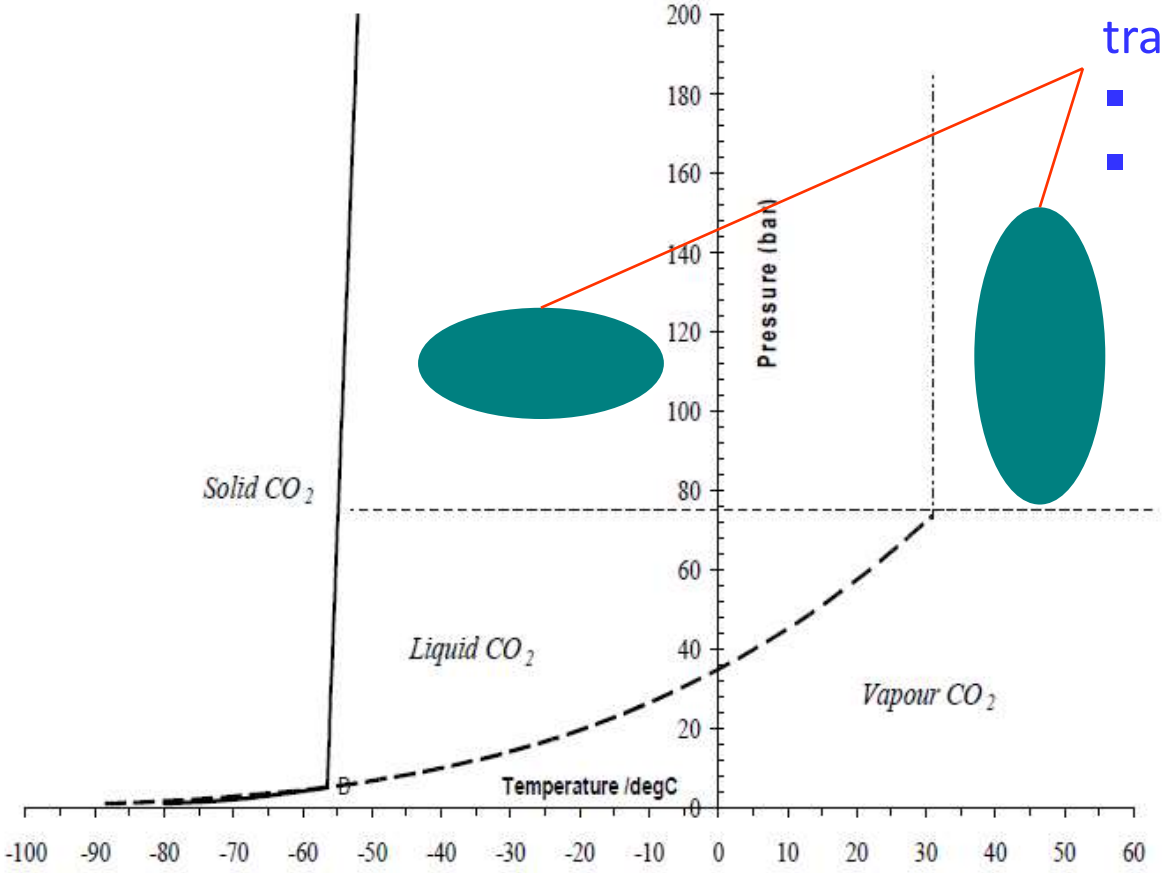
CO_2 phase diagram



Best choices for CO_2 transmission

- liquid-like density
- gas-like viscosity

Physical properties for pure CO_2 predicted very accurately by Span & Wagner EoS

Span, Wagner. "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."
Journal of physical and chemical reference data 25 (1996): 1509.

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Challenges I: Impurities

From post-combustion (dry basis):

CO_2 (>99%), N_2 (<0.17%), O_2 (<0.01%), SOx (10 ppmv), traces of Ar

From pre-combustion (dry basis):

CO_2 (>95.6%), H_2S (<3.4%), H_2 (<3%), N_2 (<0.6%), CO (<0.4%), Ar (<0.05%), CH_4 (350 ppmv)

From oxyfuel (dry basis):

CO_2 (>74.66%), N_2 (<15%), Ar (<2.5%), O_2 (<6.15%), SOx (<2.5%), traces of CO

…plus H_2O

The presence of impurities significantly affects physical properties (densities, phase envelope, critical temperature and pressure,…)

➔ impact on compressor/pump power, pipeline capacity, potential for hydrate formation & two phase flow, distance between booster stations…

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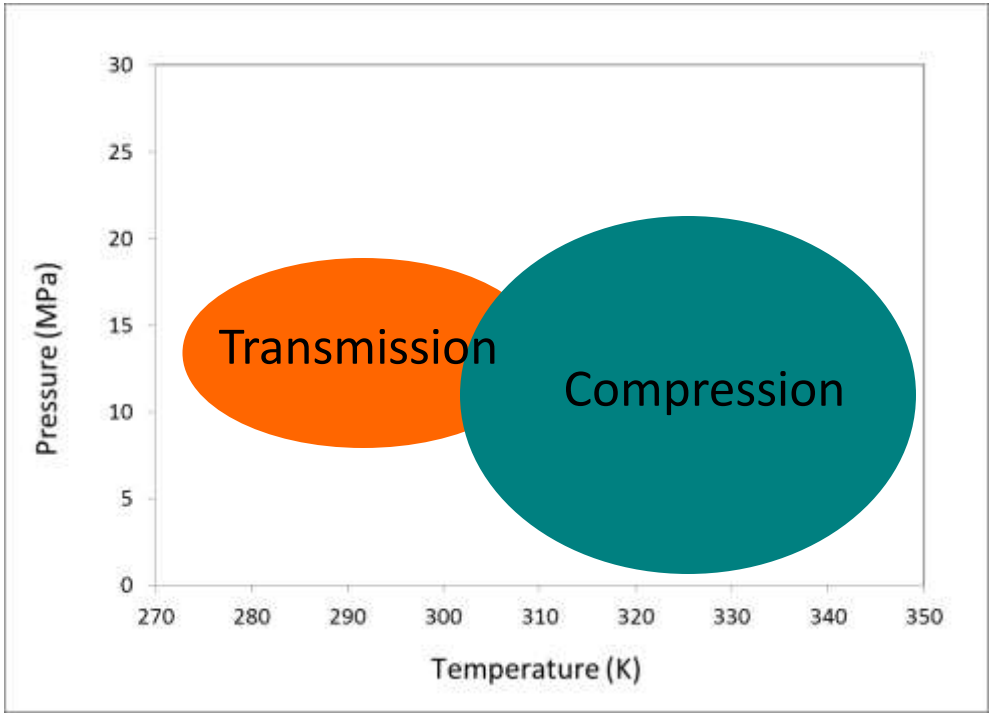
Challenges II: Wide range of conditions

- Compression subsystem
  - Pressures
    - Inlet 0.5 to 5 bara
    - Outlet 10 to 200 bara
  - Temperatures
    - Inlet 20-41 °C
    - Outlet 40-130 °C
- Transmission subsystem
  - Pressures
    - 50-200 bara
  - Temperatures
    - -5-40 °C



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Challenges III: Limited experimental data

- Recent literature review of experimental data
  - Li, Hailong, et al.
    "PVTxy properties of CO2 mixtures relevant for CO2 capture, transport and storage: Review of available experimental data and theoretical models."
    Applied Energy 88.11 (2011): 3567-3579.
- Limited range of conditions
- Gaps for several binary mixtures
  - some mixtures (e.g. CO_2-SO_2) are very corrosive
    ➔ experimentation problematic
- Very scarce data for ternaries and beyond

Working on solving this

- Release of experimental data from several projects
- Experimental plan at University of Nottingham for VLE measurements of near-pure CO_2 mixtures

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Challenges

- Impurities
- Wide range of conditions
- Limited experimental data

→ A predictive equation of state is required

gSAFT

- applied to mixtures of CO_2, CO, H_2O, Ar…..
- small molecules ➔ single group each

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gSAFT

A commercial implementation of the SAFT-γ Mie equation of state

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The Statistical Association Fluid Theory I

- Molecular-based EOS are a very appealing alternative to more classical approaches, such as cubic EOS

- The Statistical Association Fluid Theory (SAFT) is especially relevant for its ability to deal with complex fluids

- SAFT-based EOS are rooted on statistical mechanics, so
  - they involve a limited number of parameters
    - with a clear physical meaning
  - can be fitted to a limited amount of experimental data
    - can predict phase behaviour and physical properties for a wide range of conditions, including those far from the ones employed for parameter estimation

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The Statistical Association Fluid Theory II

- PSE's gSAFT is a commercial implementation of one of the most advanced SAFT-based EOS
  - SAFT-γ Mie, developed by Imperial College London

- **SAFT**: Chapman, Gubbins, Jackson, Radosz, *Ind. Eng. Chem. Res*., 29, 1709 (1990)
- **SAFT-VR**: Gil-Villegas, Galindo, Whitehead, Mills, Jackson, Burgess, *J. Chem. Phys*., 106, 4168 (1997)
- **SAFT-γ**: Lymperiadis, Adjiman, Jackson, Galindo, *Fluid Phase Equilib.*, 274, 85 (2008)
- **SAFT-γ Mie**: Papaioannou, Lafitte, Avendaño, Adjiman, Jackson, Muller, Galindo, *in preparation* (2014)

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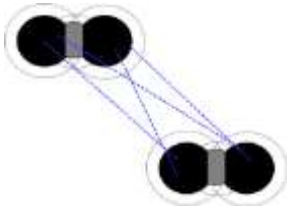
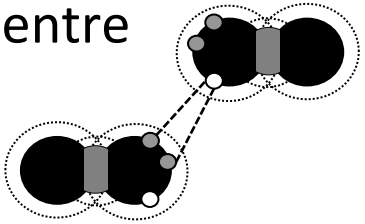
SAFT-γ Mie molecular model

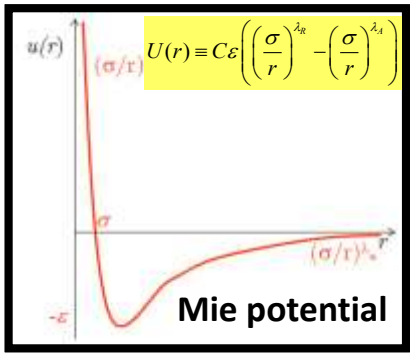
- Molecules are modelled as chains of spheres

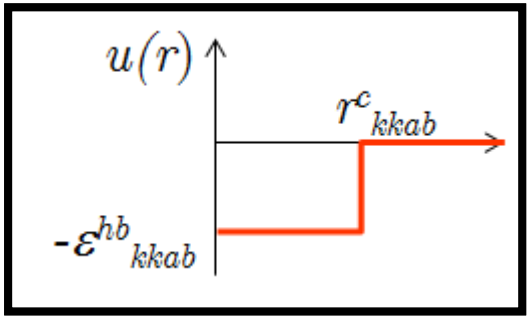
- Interactions
  - dispersion/repulsion (van der Waals) forces
  - hydrogen bonding via off-centre electron donor/acceptor ("association") sites
  - ionic (coulombic) forces

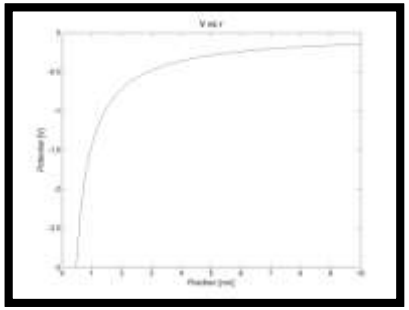
Increasing strength











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Transferability of parameter values

The values of the interaction parameters

are assumed to be constant across

different molecules and mixtures

in different phases

under different temperatures, pressures and compositions

An approximation

- based on SAFT-γ Mie's fundamental molecular basis
- supported by practical evidence

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gSAFT for near-pure CO_2 streams in gCCS

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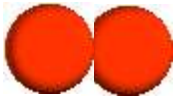
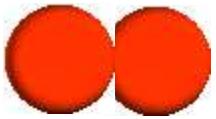
The gSAFT Databank

H_2O

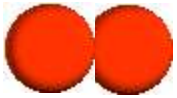


CO

CH_4

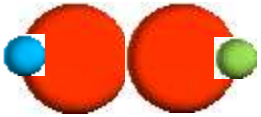


N_2



O_2

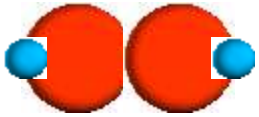
H_2S



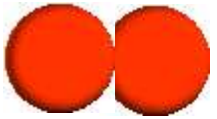
CH_3OH

Ar

H_2



CO_2



SO_2

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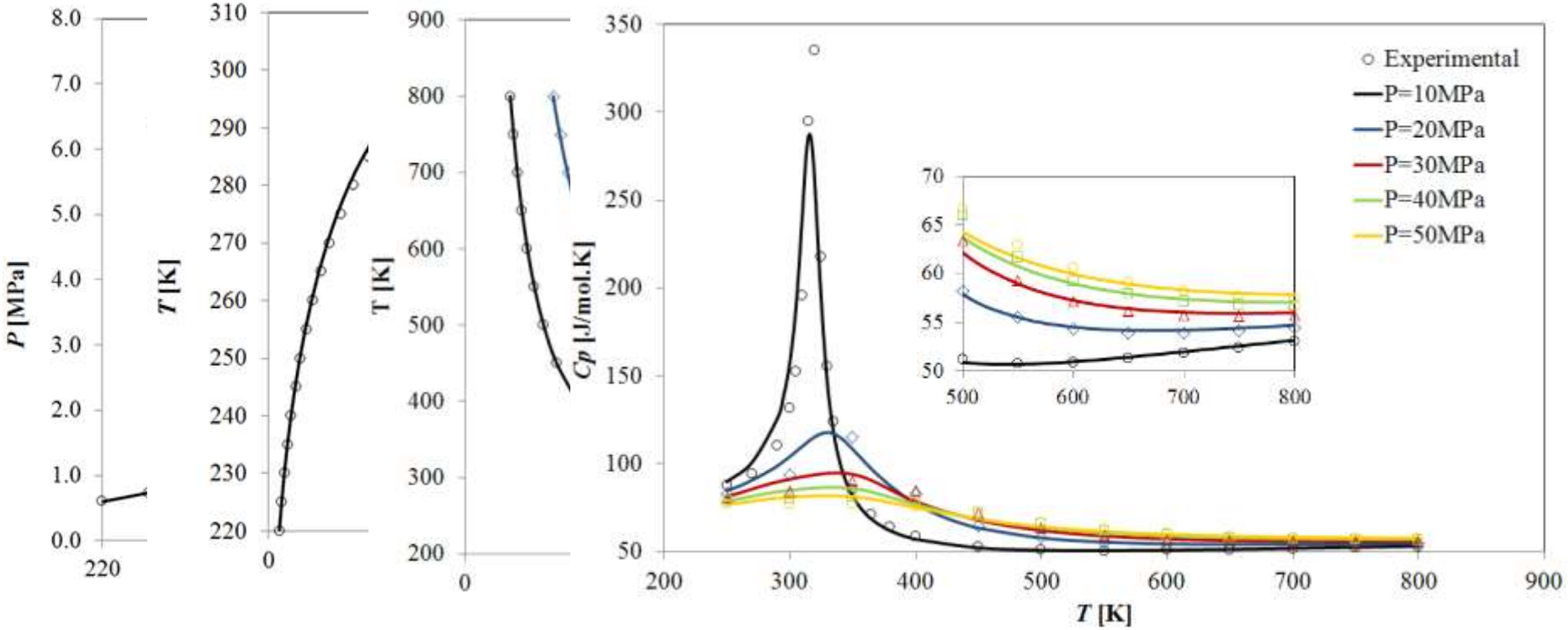
Comparisons: Pure CO_2

Physical property	AAD (%)	Trange [K]	No Data Points
Vapour pressure [MPa]	0.07	220.0 – 300.0	17
Saturated liquid density [kg/m³]	0.41	220.0 – 300.0	17
Density [kg/m³]	2.52	250.0 – 800.0	71
Isobaric Heat Capacity [J/mol.K]	3.73	250.0 – 800.0	71



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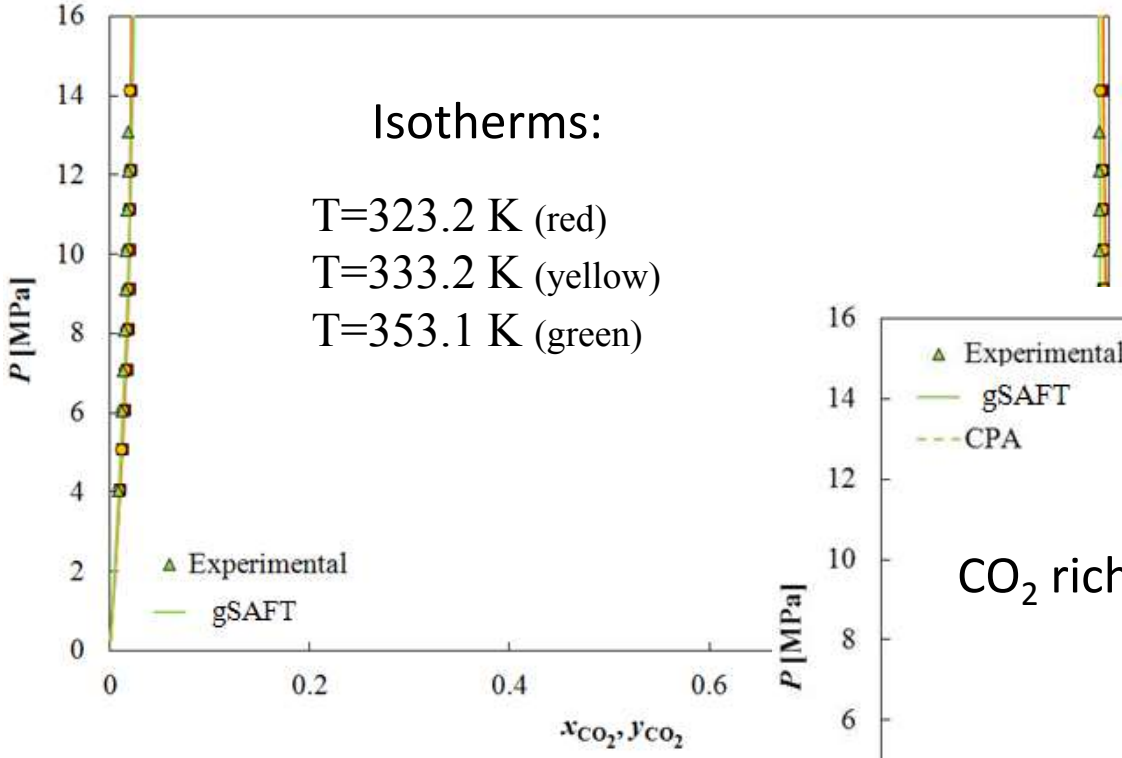
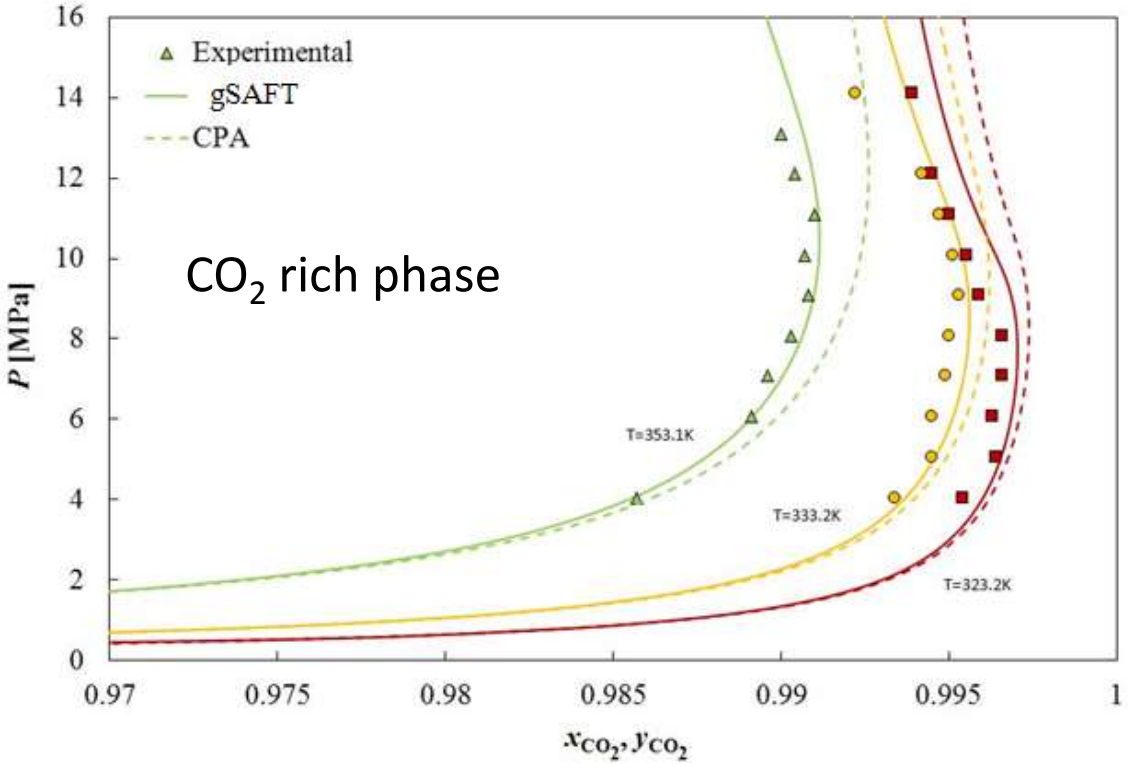
Comparisons: Binary mixture $H_2O + CO_2$



Isotherms:

T=323.2 K (red)
T=333.2 K (yellow)
T=353.1 K (green)

CPA: Cubic+Association EoS



CO_2 rich phase

Bamberger et al., 2000

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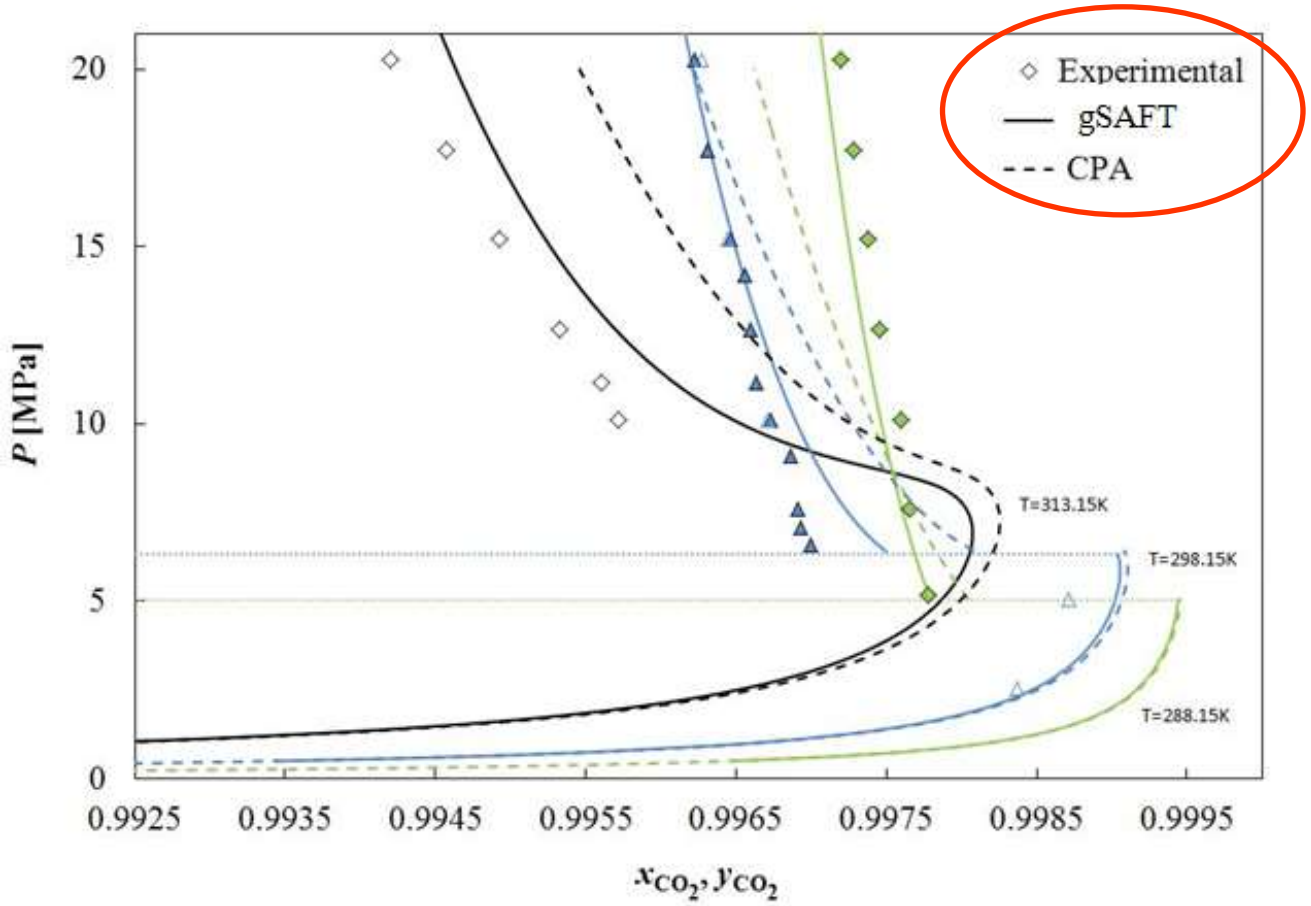
Comparisons: Binary mixture $H_2O + CO_2$

- CO_2 rich phase – low temperatures



King et al., 1992

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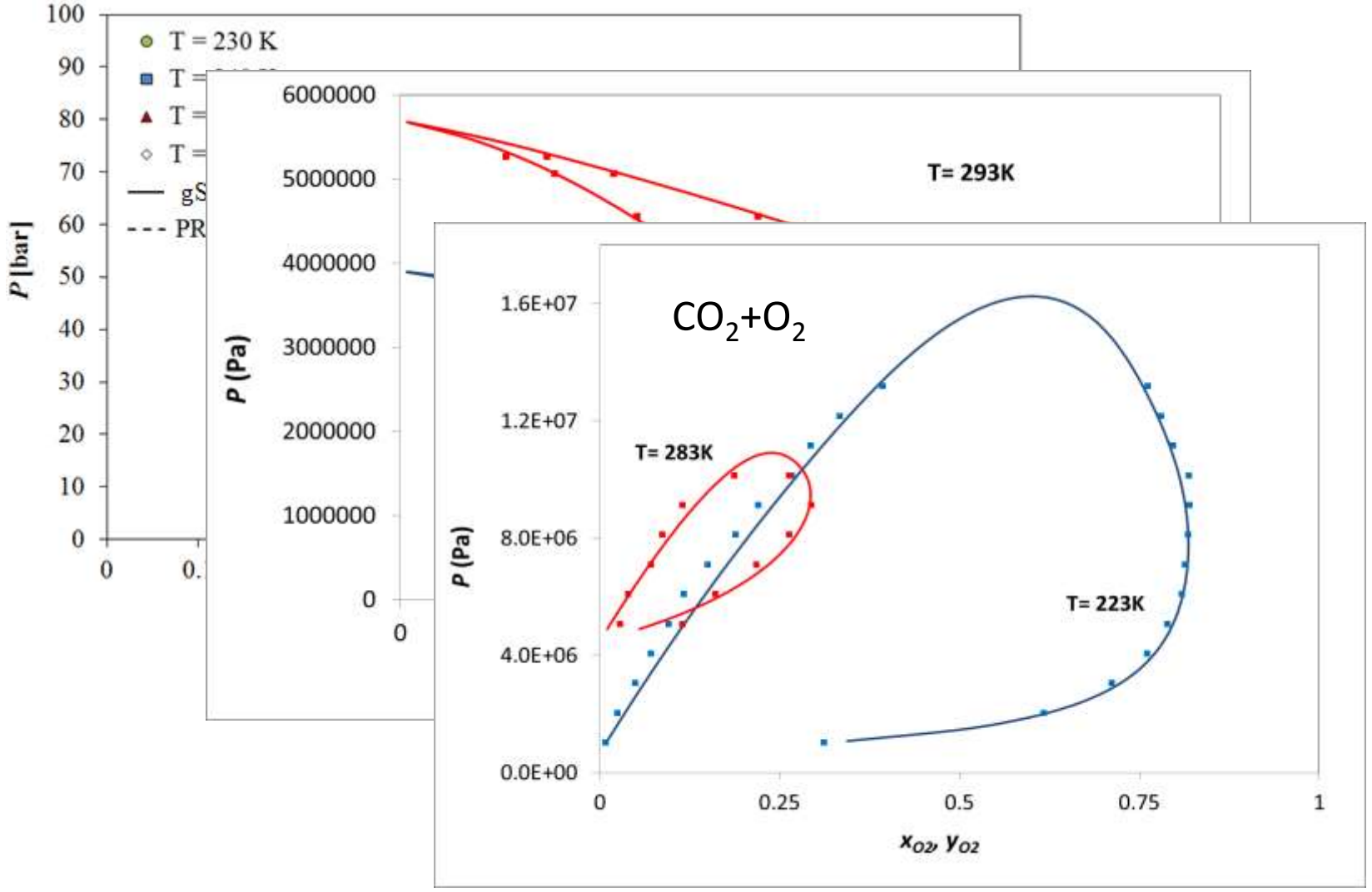
Comparisons: Binary CO_2 + impurities



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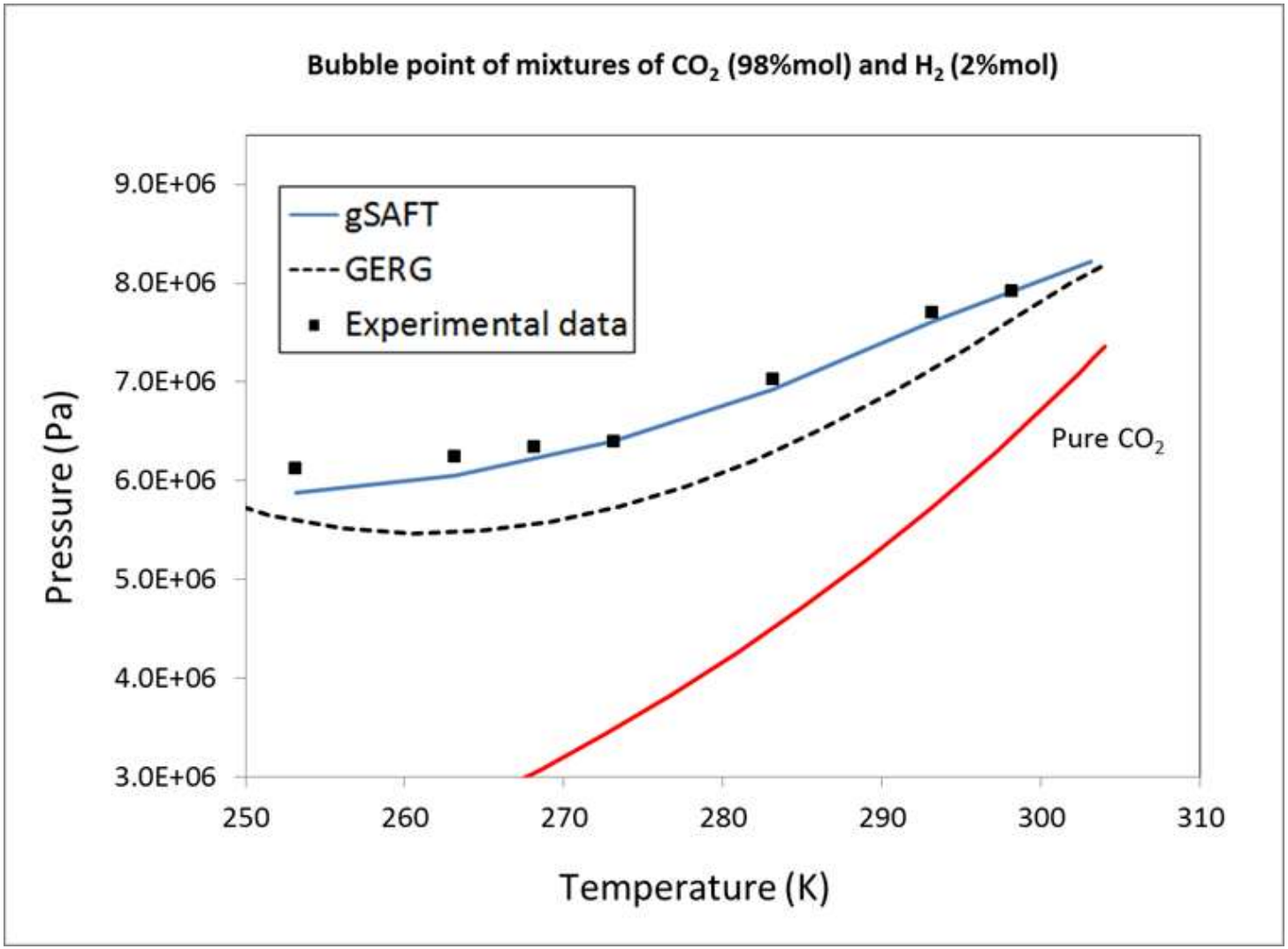
Predictions: Bubble point of CO_2+H_2



Chapoy et al., 2011

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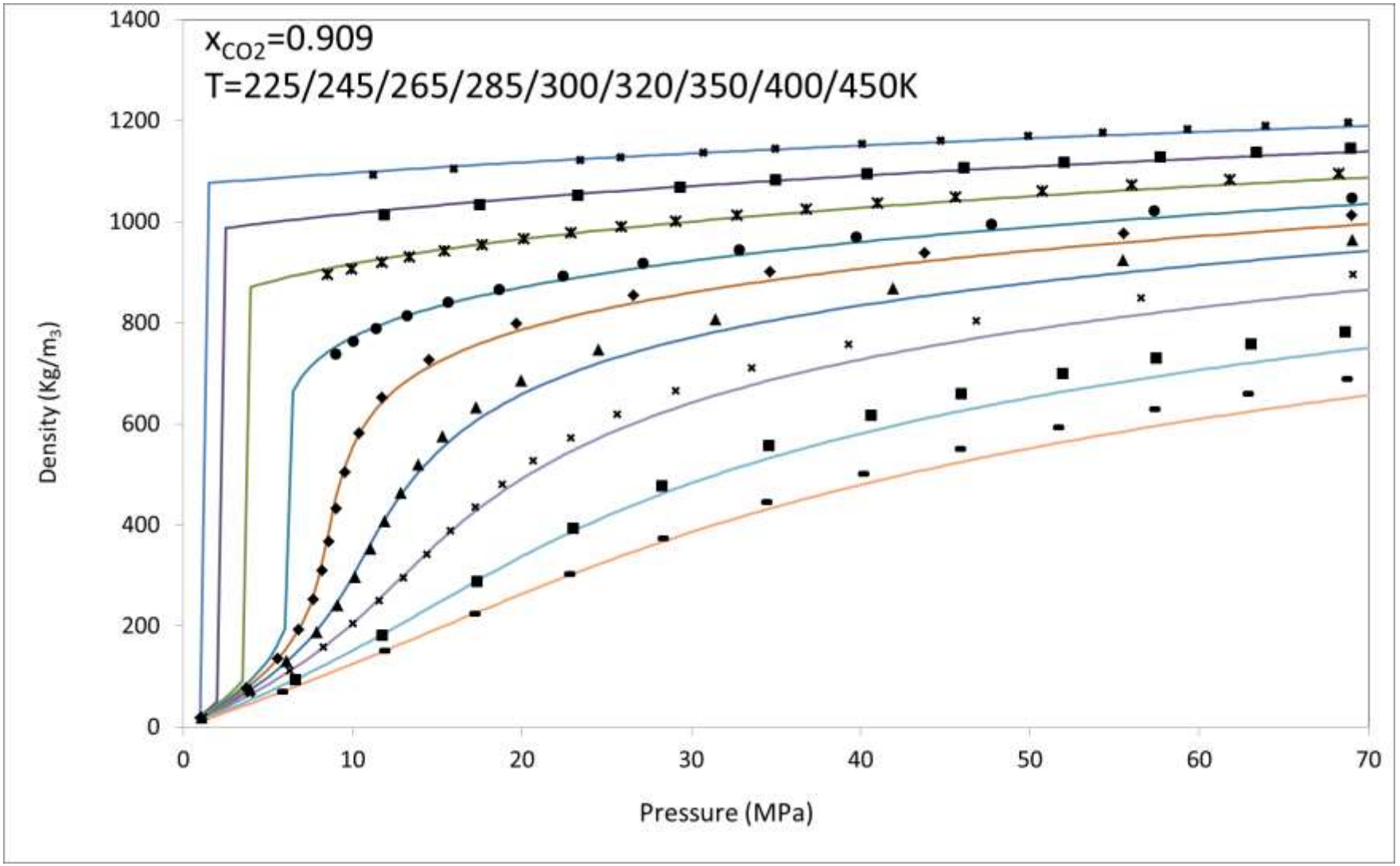
Predictions: CO_2+N_2 densities



Brugge et al., 1997

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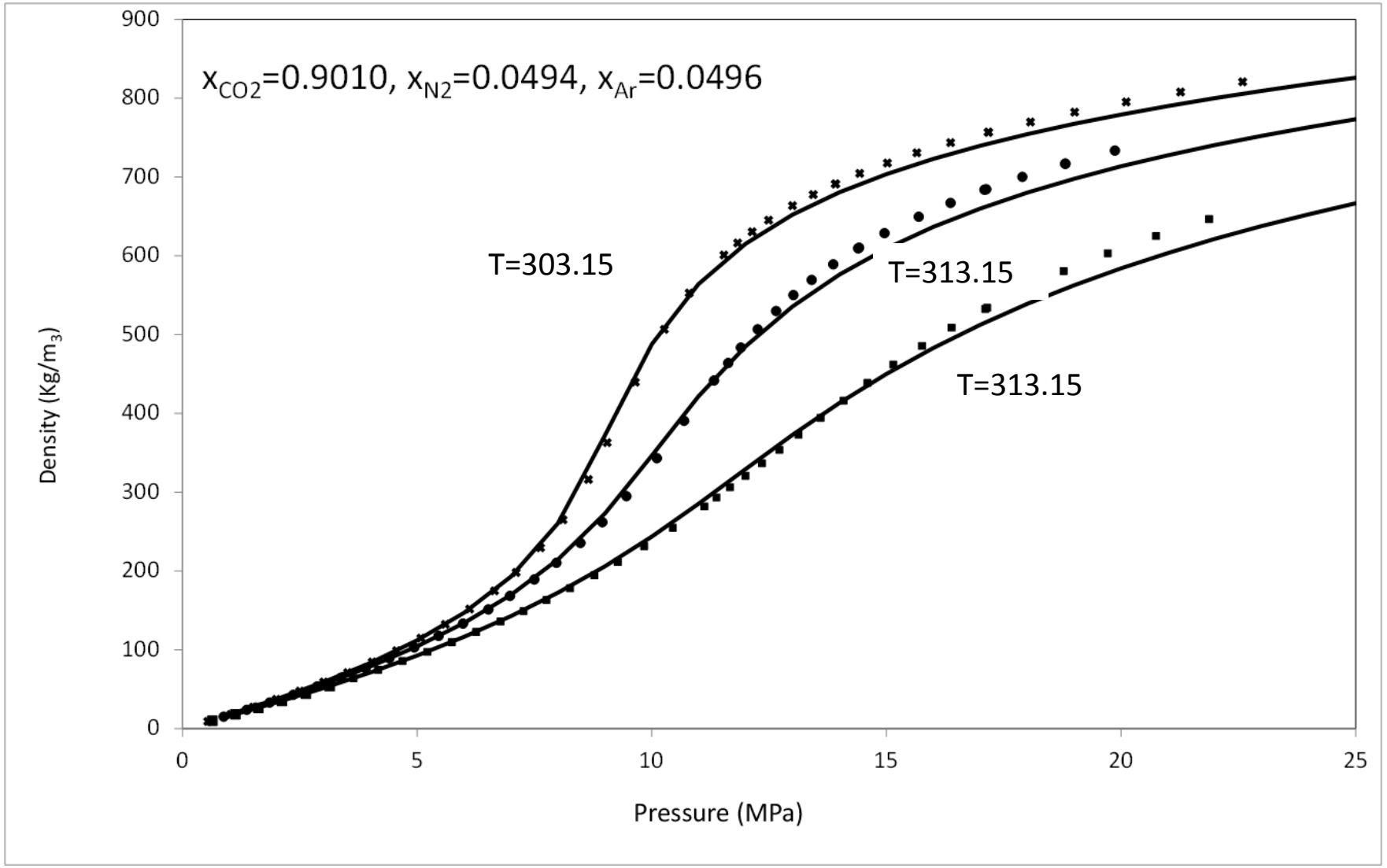
Predictions: CO_2+N_2+Ar densities



COZOC project, University of Nottingham

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Experimental plan

Dew-point and bubble-point lines for the following mixtures

Mixture Name	Component 1	Component 2	Component 3	x_1	x_2	x_3
E1	CO_2	N_2	Ar	0.90	0.05	0.05
E2	CO_2	N_2	Ar	0.98	0.01	0.01
E3	CO_2	Ar	H_2	0.95	0.02	0.03

- gSAFT predictive accuracy being tested
  - Specifically two-body interaction assumption
- gSAFT model parameters will be readjusted if necessary

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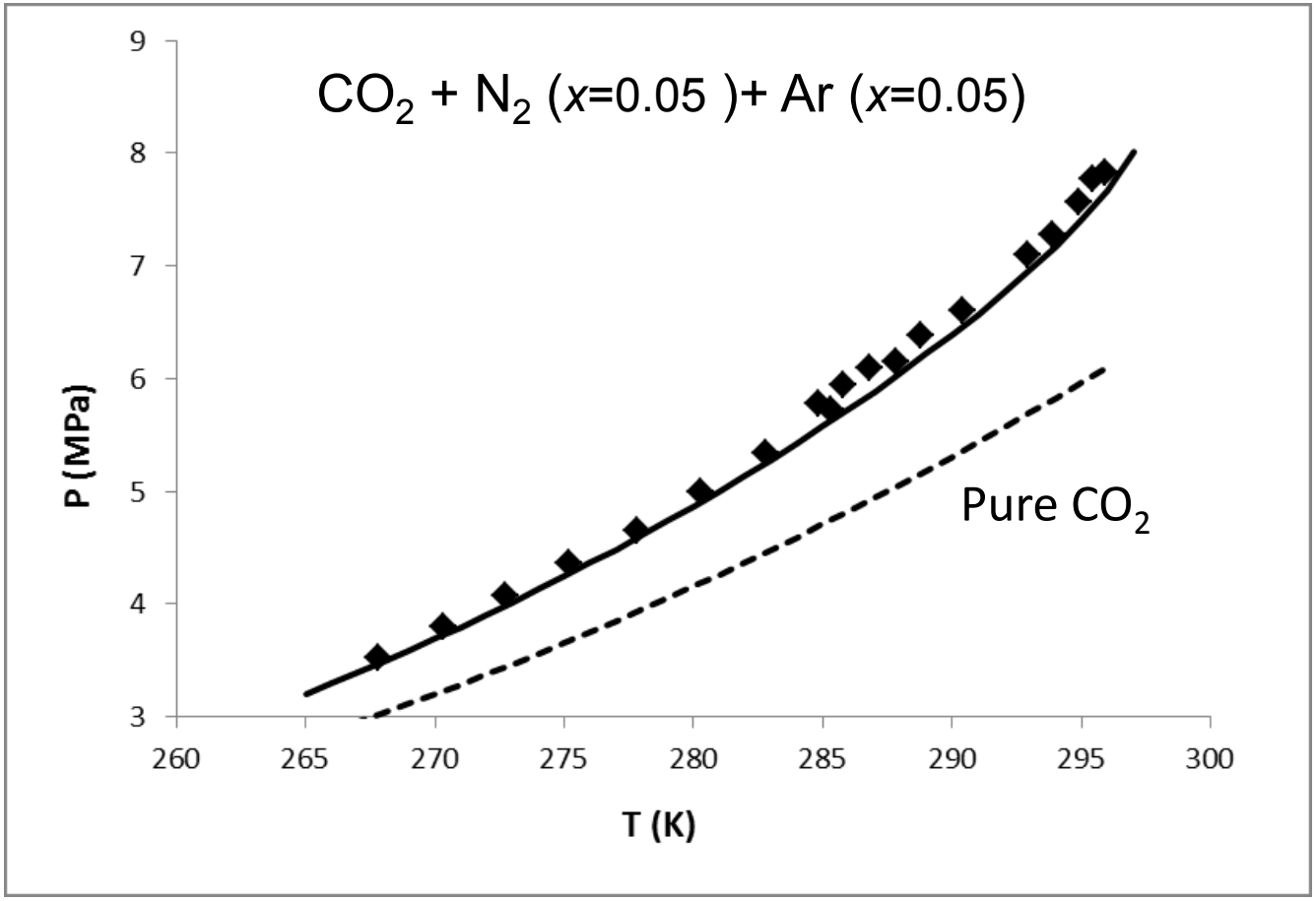
VLE predictions

Dew-point line



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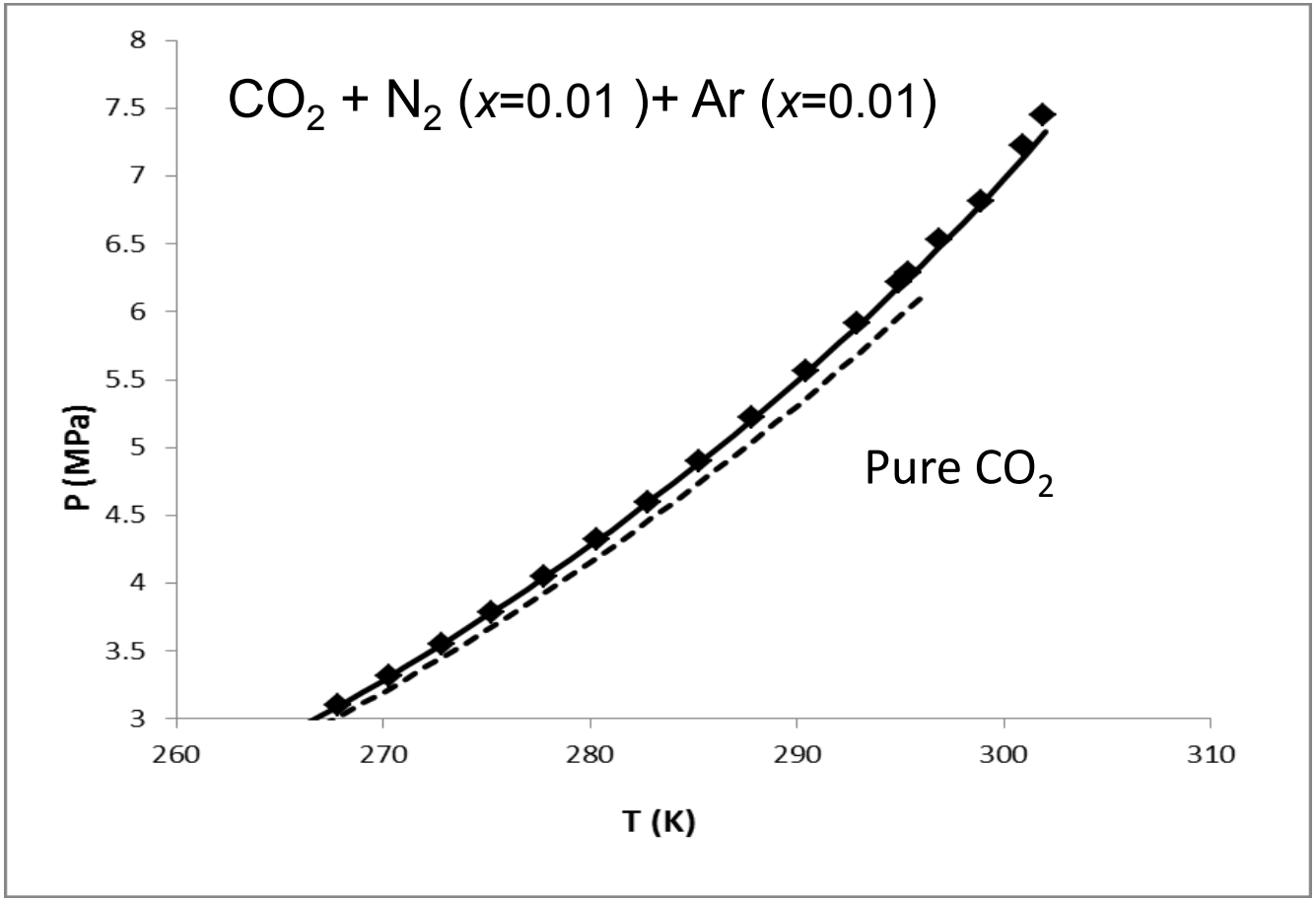
VLE predictions

Dew-point line



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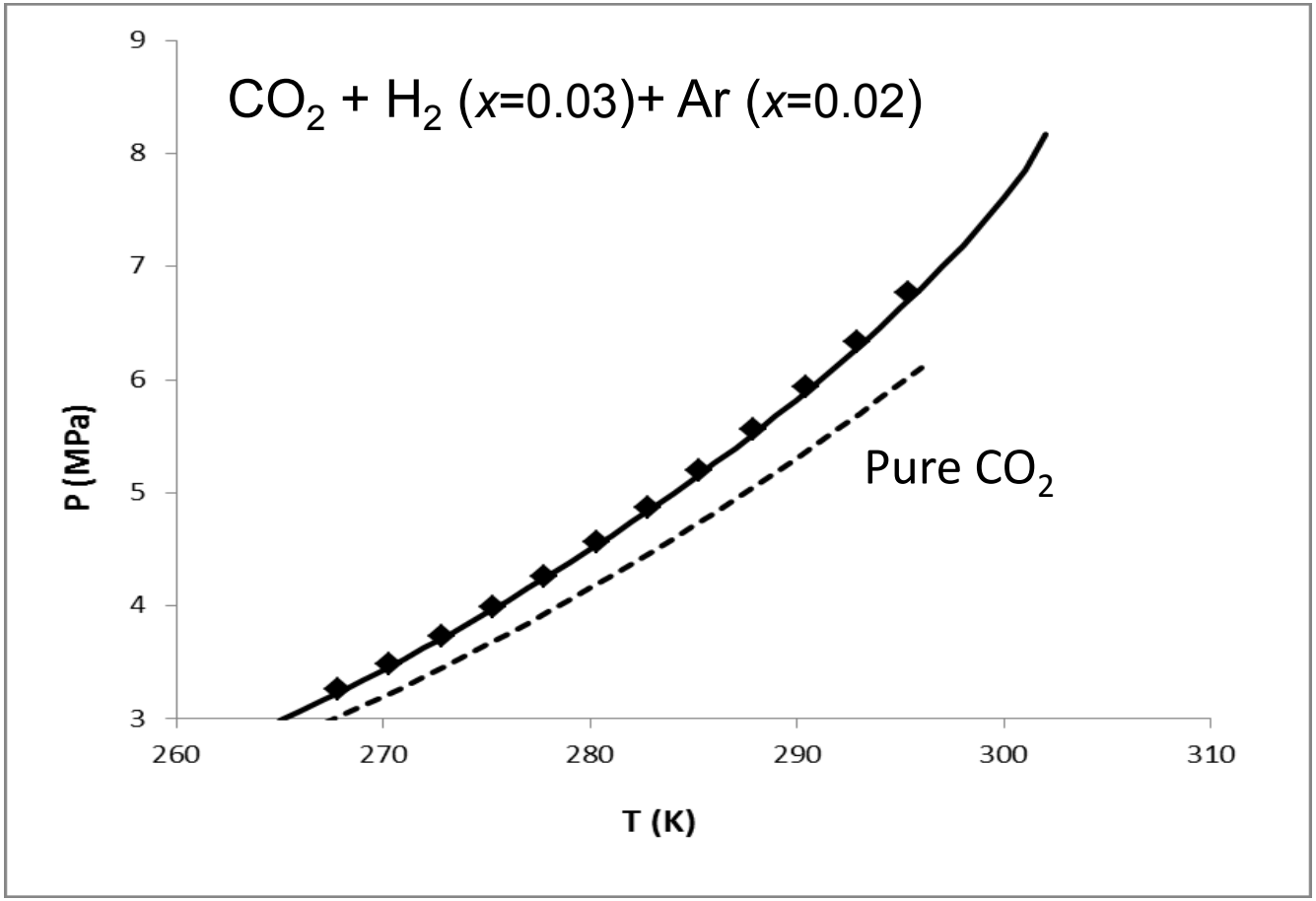
VLE predictions

Dew-point line



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Application to typical CCS compression, transmission and injection flowsheets

Using gCCS libraries

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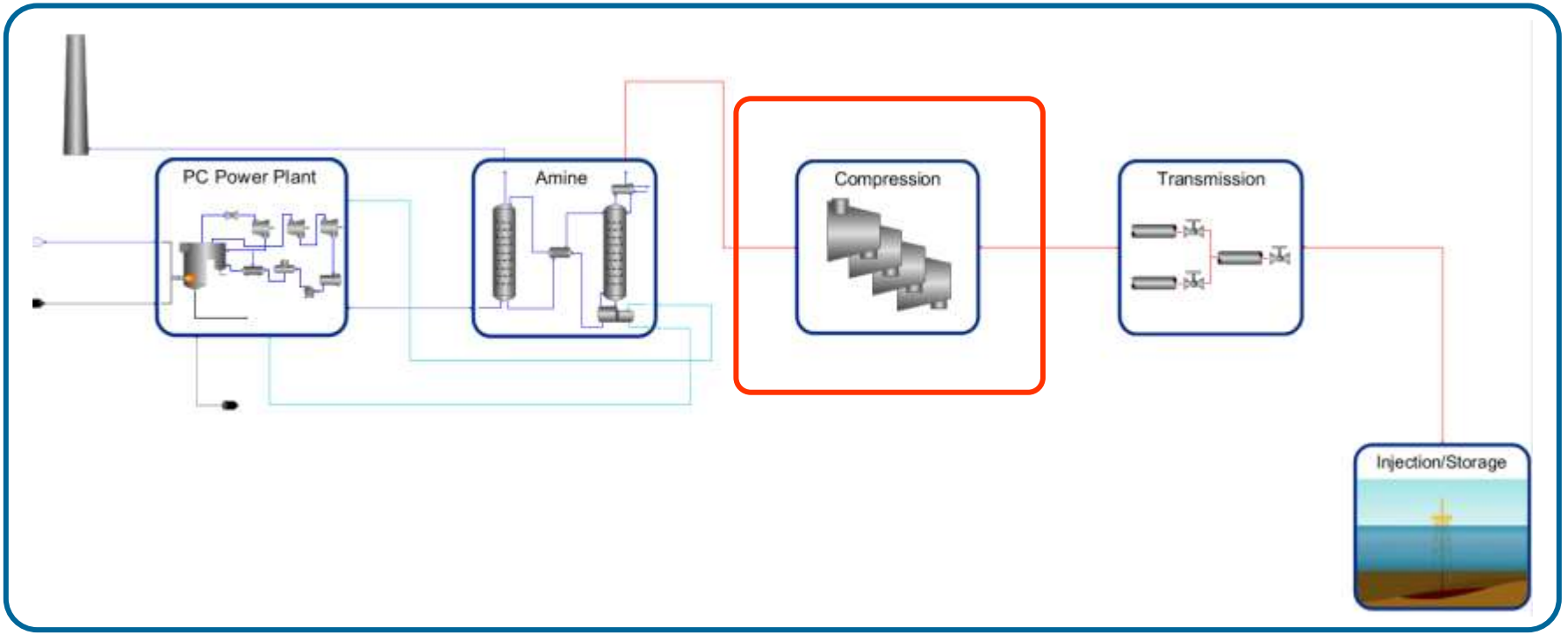
Compression



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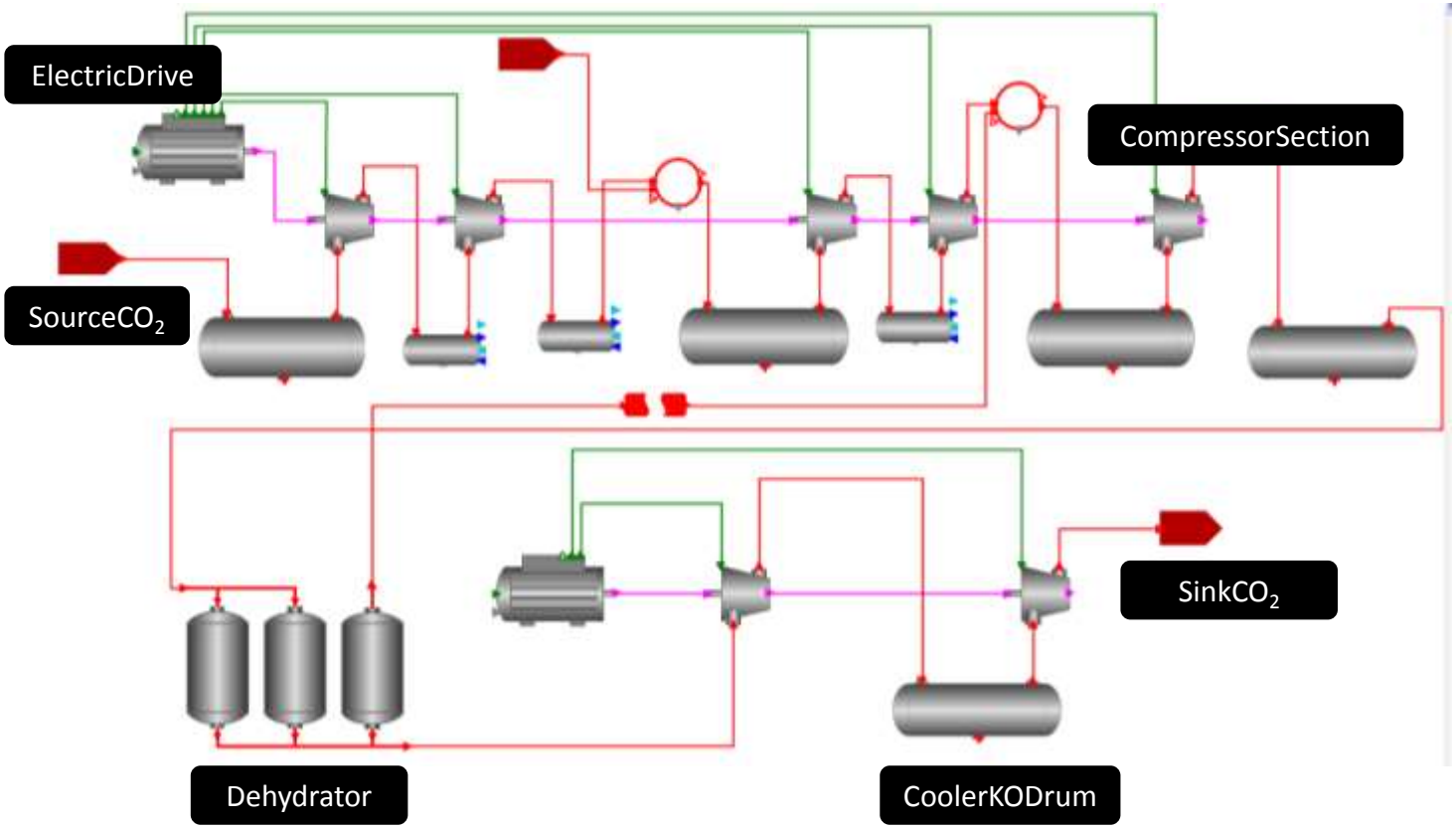

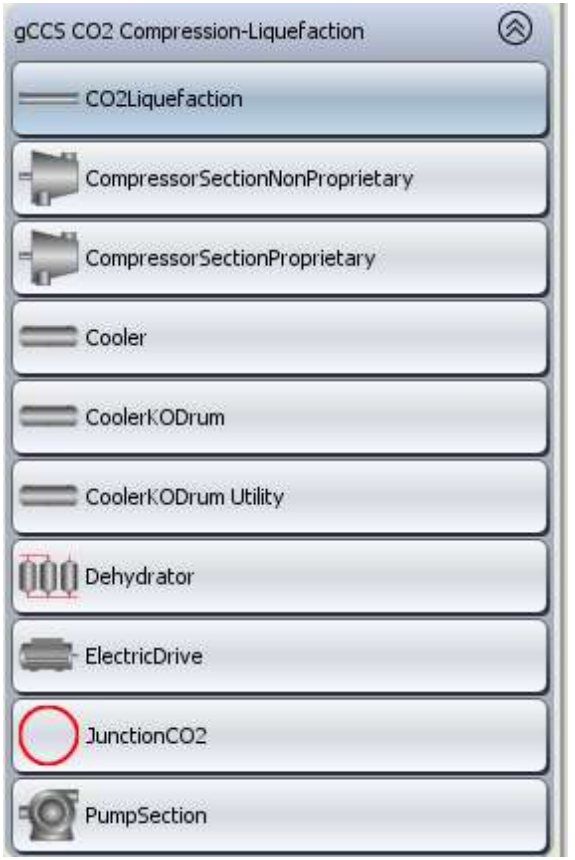

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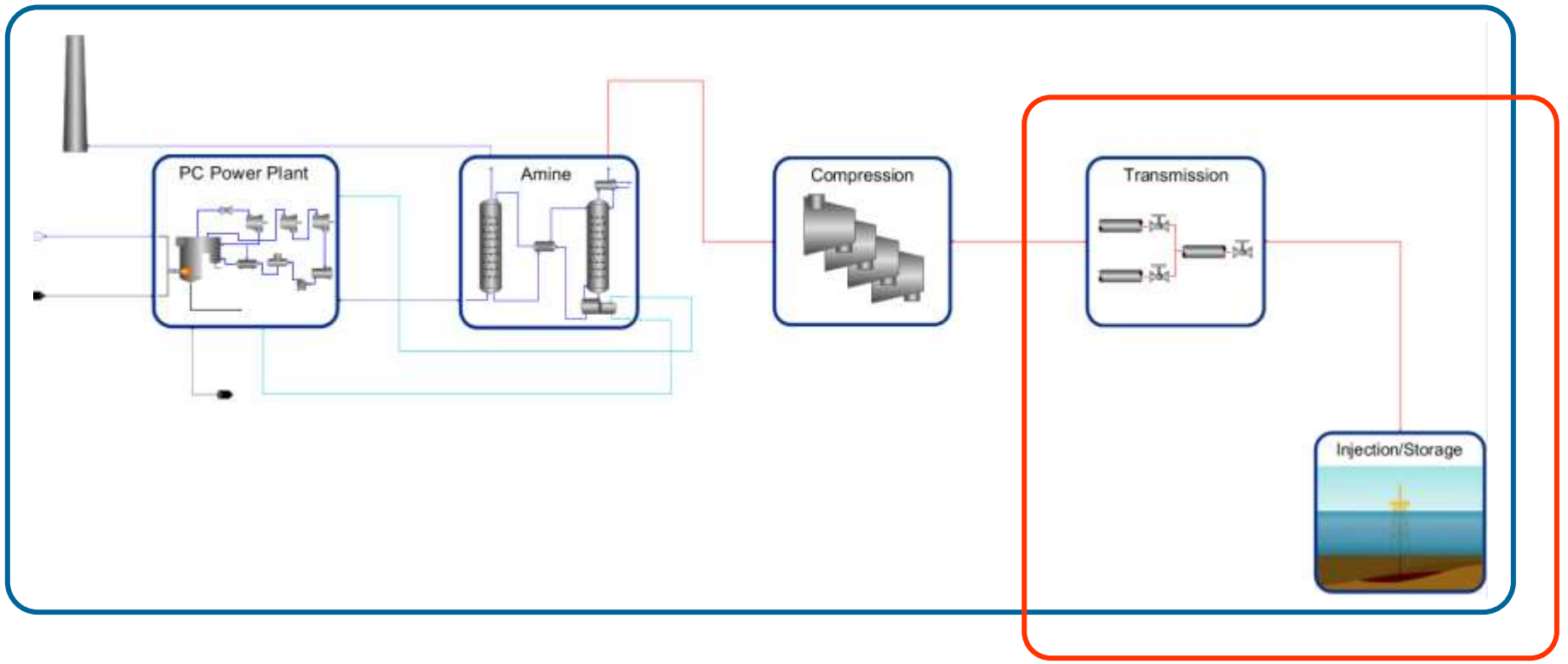
Transmission & injection



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Transmission and Injection

Emergency shutdown valve (ESD)

CO2 Flowmeter

Gate Valve

Distribution header

Vertical Riser

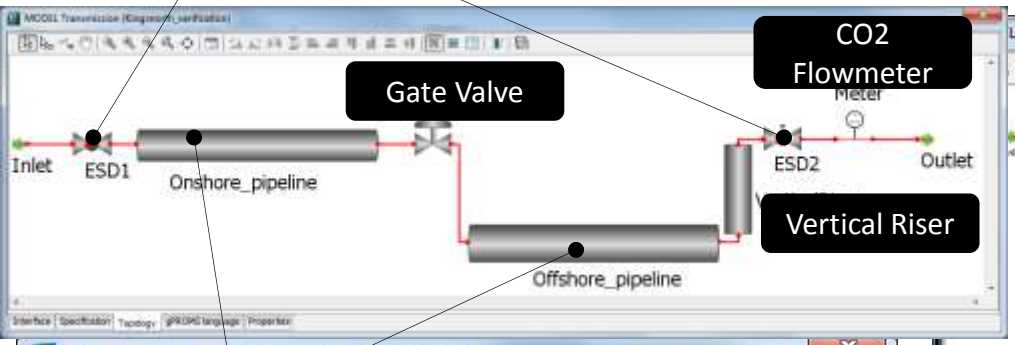
PipeSegment

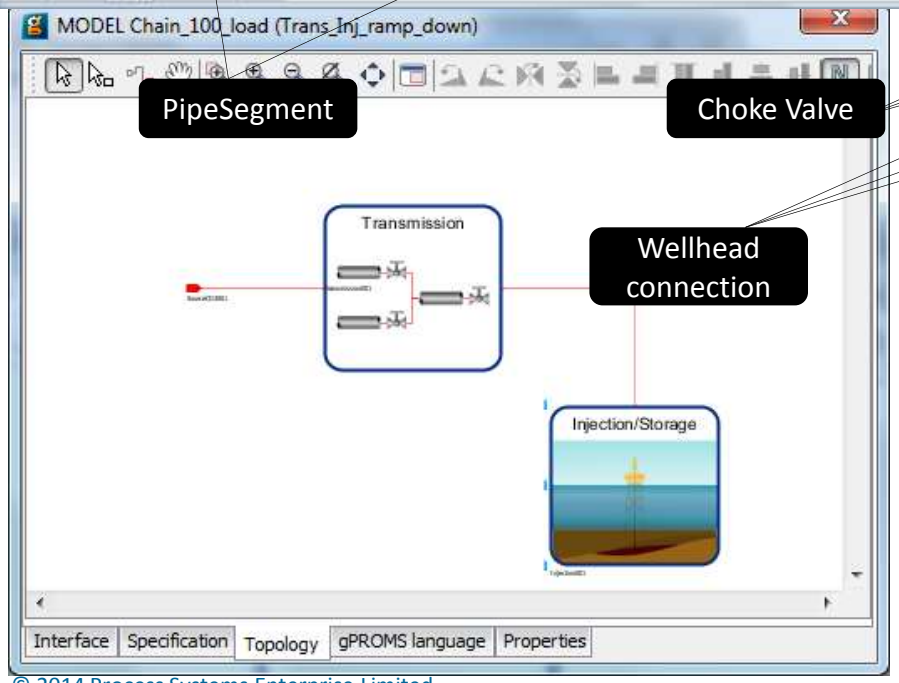
Choke Valve

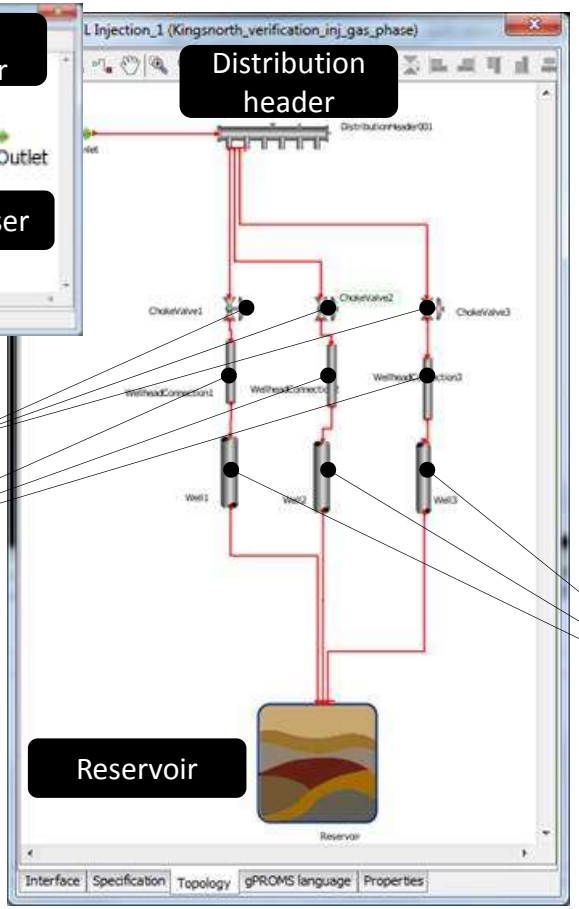
Wellhead connection

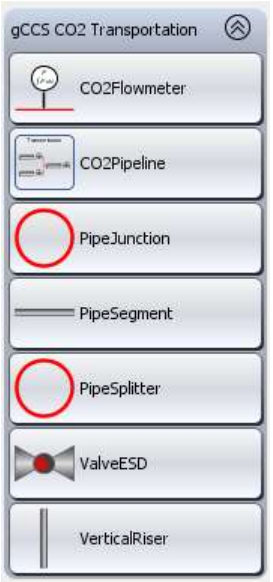
Reservoir

Well









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Line-packing operation

- System dynamics
  - Simulating **line-packing operation**: Sudden valve closure

- Assumed constant inlet flowrate at CO2Source (275tonnes CO_2 per day)
- Gas phase injection with discharge pressure in CO2 sink ~ 21bara
- Total pipeline length – 132.2km
- Pipeline is located offshore (in water)

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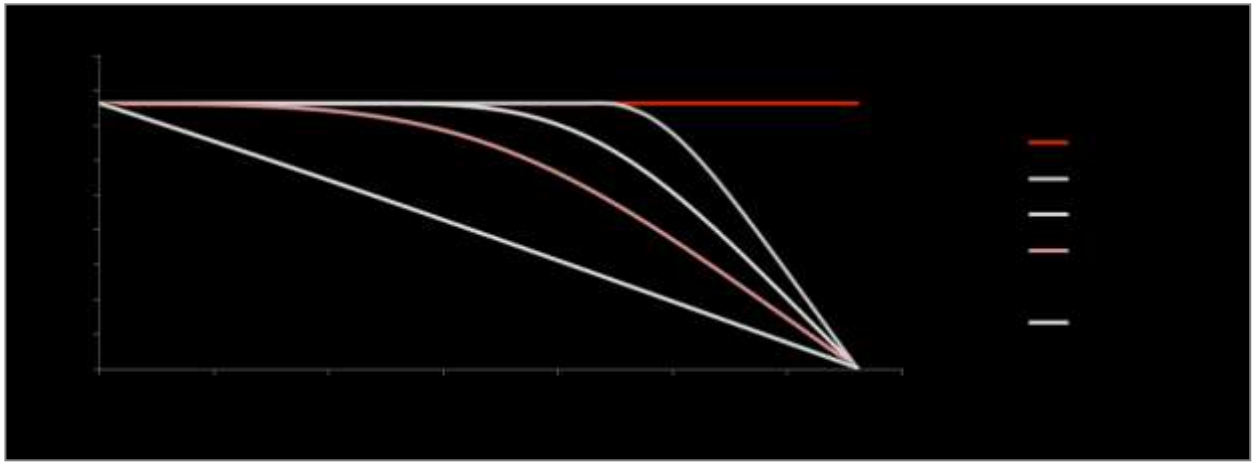
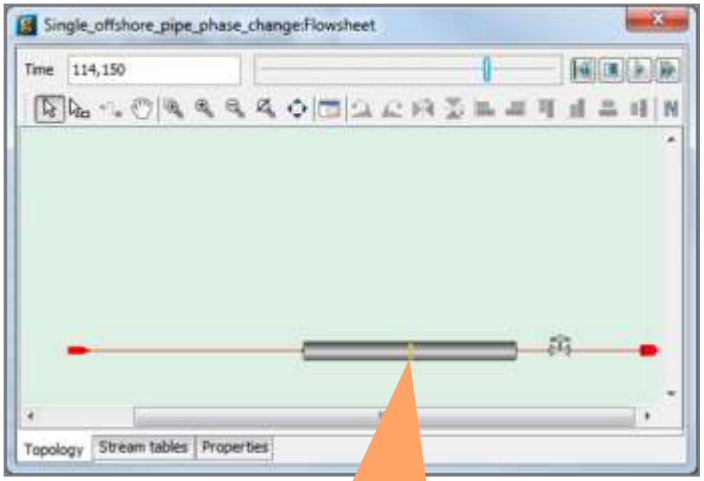
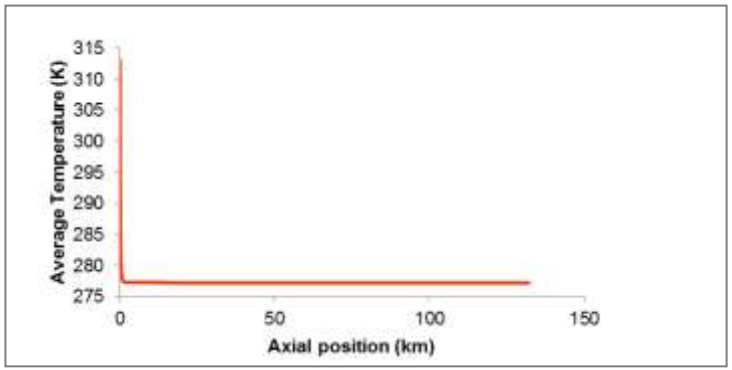
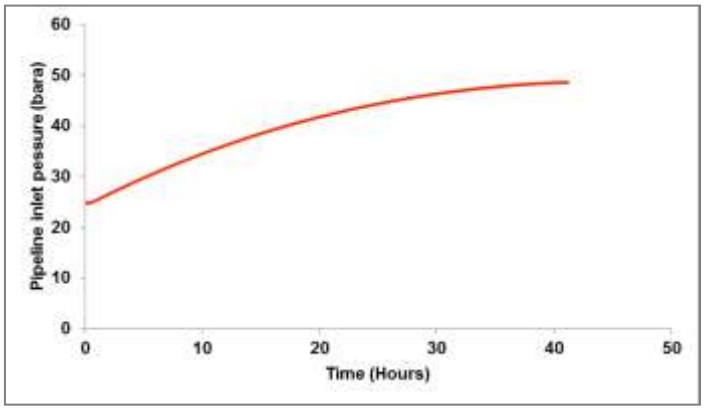
Line-packing operation

- System dynamics
  - Simulating **line-packing operation**: Sudden valve closure









***Warning**: Phase change identified!*

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Conclusions

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Conclusions

- Providing physical properties for a modelling tool for the systems downstream of the capture plant is challenging
  - Experimental data are limited
- gSAFT is an implementation of a SAFT equation of state, perfectly suited to address these challenges
  - a parameter databank for the relevant components has been developed
  - excellent correlations and predictions have been demonstrated
- gSAFT physical properties are already available within gCCS, an “end-to-end” modelling tool for CCS
  - for the simulation of compression/transmission/injection flowsheets

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