



Heriot-Watt University
Research Gateway

Hydrate Phase Equilibria of Natural Gas Mixture plus Carbon Dioxide in the Presence of Thermodynamic Inhibitors: Experimental Measurements and Modelling

Citation for published version:

Hajiw, M, Chapoy, A & Coquelet, C 2017, 'Hydrate Phase Equilibria of Natural Gas Mixture plus Carbon Dioxide in the Presence of Thermodynamic Inhibitors: Experimental Measurements and Modelling', 9th International Conference on Gas Hydrates, Denver, United States, 25/06/17 - 30/06/17.

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Other version

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

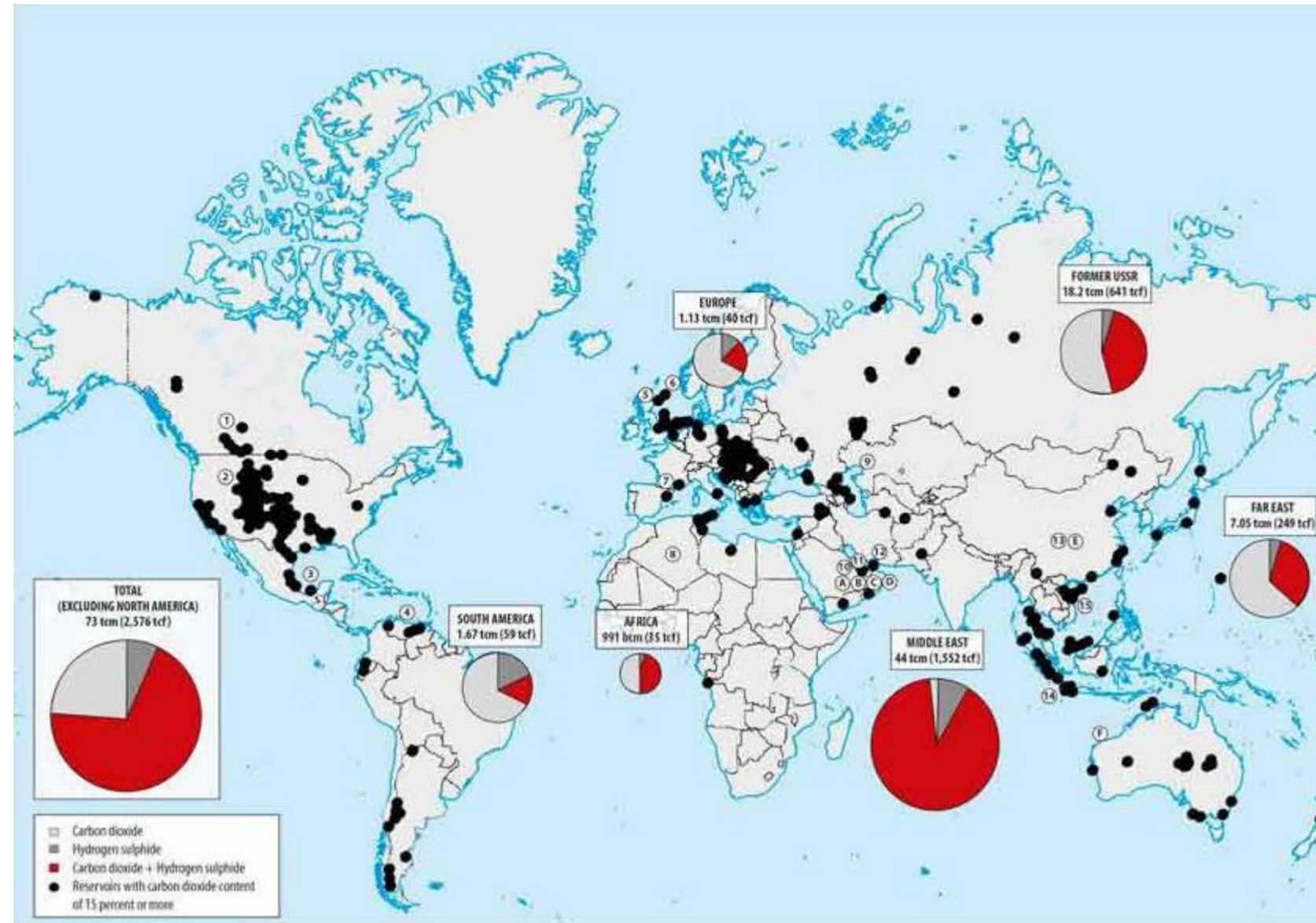
Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Hydrate Phase Equilibria of Natural Gas Mixtures Plus CO₂ in the Presence of Thermodynamic Inhibitors

Martha Hajiw, Antonin Chapoy, Christophe Coquelet

About **40% of natural gas fields are sour**, producing these reservoirs involves also low temperatures combined with high pressures working conditions, presence of water and transport times, leading to the possibility of gas hydrate formations in pipelines.



Sour gas fields (The Oil and Gas Year)

Hydrate dissociation points were measured for two systems **natural gas + CO₂**. These measurements were conducted in the presence of **25%wt and 50%wt** of thermodynamic inhibitors (**methanol, ethanol and ethylene glycol or MEG**).

Thermodynamic Modelling

To predict hydrate phase equilibria, the following models are used:

- ❖ **Hydrate Phase:** Van der Waals and Platteuw model (1959) as implemented by Parrish and Prausnitz (1979)
- ❖ **Fluid phase:**
 - **SRK-CPA** (Kontogeorgis et al., 1994) with adjusted binary interaction parameters (used for **systems with MEG**)
 - **GC-PR-CPA** (Hajiw et al., 2014): the PR-CPA equation of state is coupled with a **group contribution method** (modified PPR78 EoS), which calculates (in a predictive way) binary interaction parameters.

$$k_{ij}(T) = \frac{-\frac{1}{2} \text{Sum} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \frac{\sqrt{a_i(T)a_j(T)}}{b_i b_j}}$$

PPR78 EoS,
Jaubert et al. (2004)

$$\text{Sum} = \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T} \right)^{\left(\frac{B_{kl}-1}{A_{kl}} \right)}$$

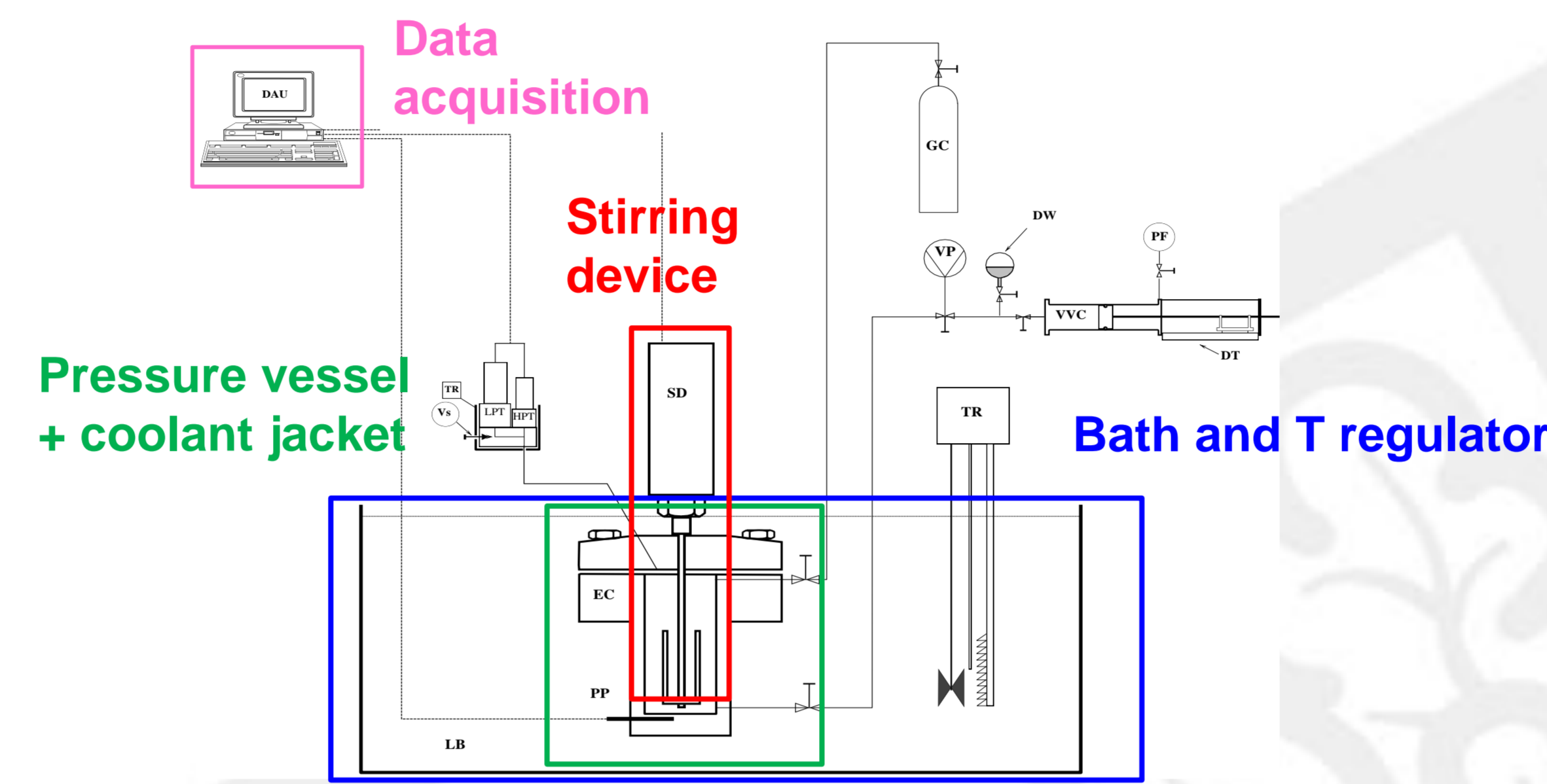
$$+ \sum_{k=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{i,ass} - \alpha_{j,ass})(C_{k,ass} T^2 + D_{k,ass} T + E_{k,ass})$$

$$+ \sum_{l=1}^{N_g} (\alpha_{il} - \alpha_{jl})(\alpha_{i,ass} - \alpha_{j,ass})(C_{kass,l} T^2 + D_{kass,l} T + E_{kass,l})$$

Modification for associating compounds (water, methanol and ethanol)

Device for hydrate dissociation point measurements

A **mixed autoclave rig** has been used for hydrate dissociation point measurements. The cell volume is about 500 mL and can operate **up to 400 bar** and between **-35°C and 50°C**.



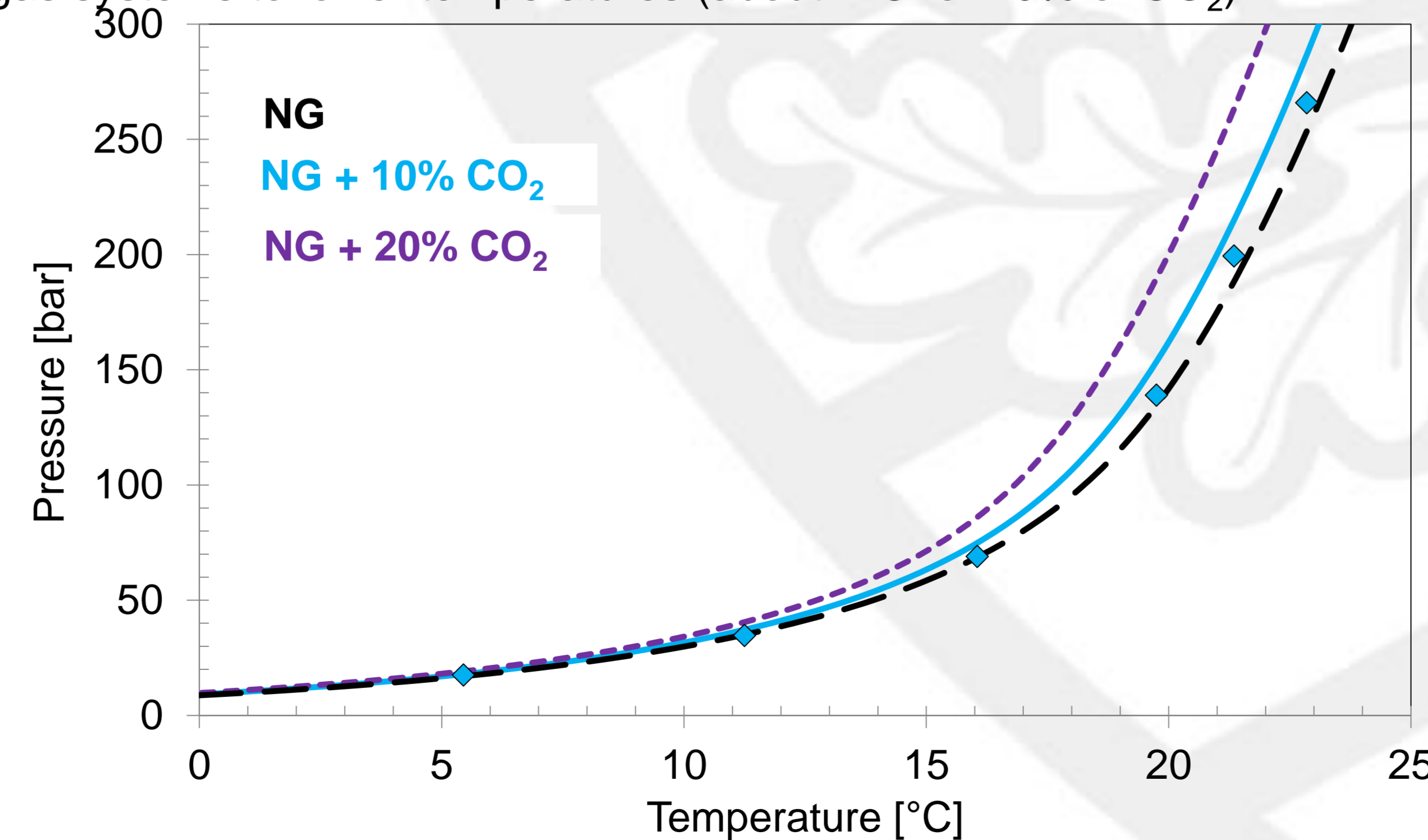
Schematic illustration of the autoclave cell used for hydrate equilibrium studies

Composition of the natural gas

Compounds	%mol
Nitrogen	7.00
Methane	84.13
Ethane	4.68
Propane	2.33
n-Butane	0.93
n-Propane	0.93

Effect of the presence of carbon dioxide on the hydrate dissociation curve

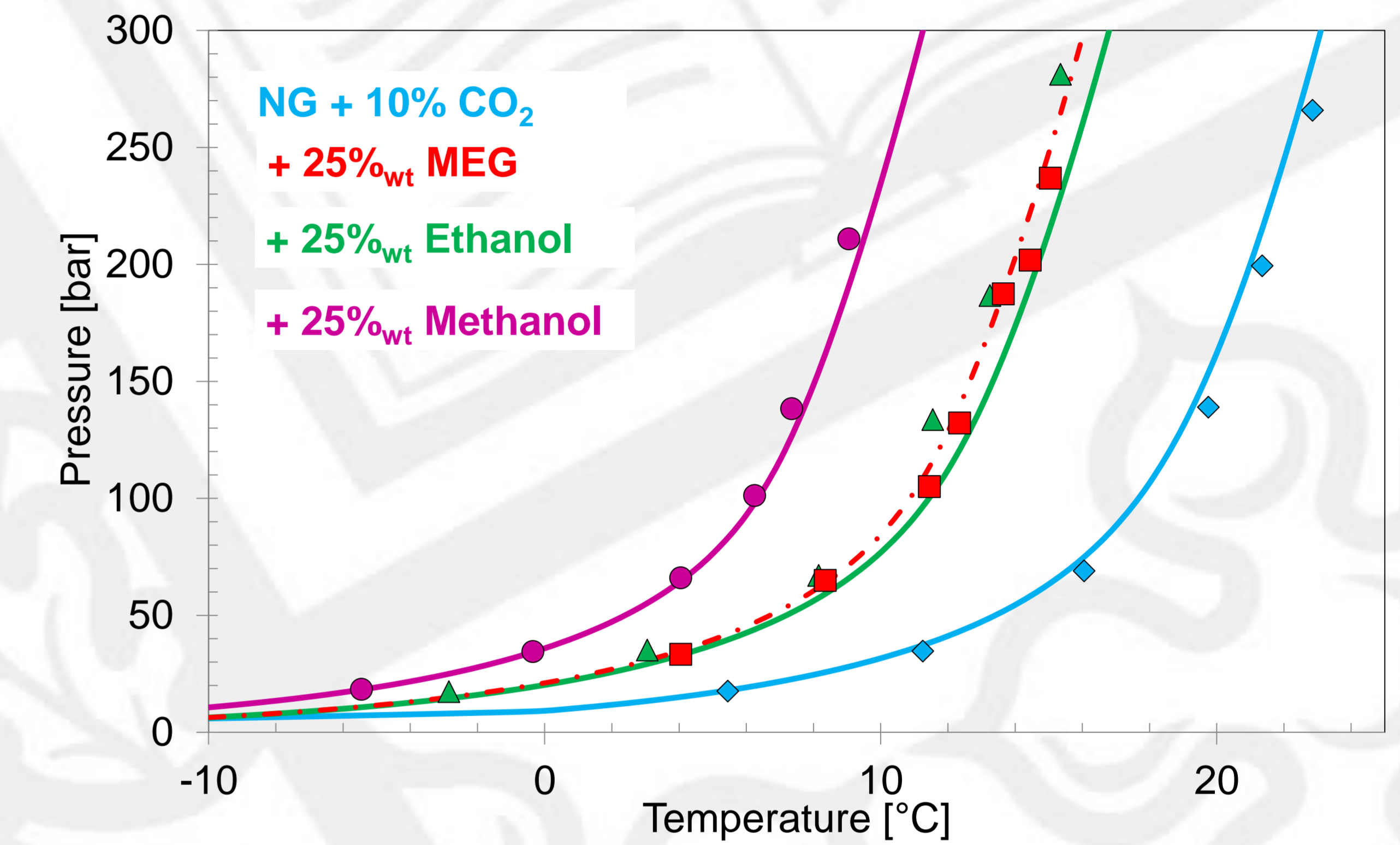
The presence of CO₂ slightly shifts the hydrate stability curve of the natural gas systems to lower temperatures (about 1°C for 10% of CO₂).



Comparison of the hydrate dissociation curves in the presence of 25 %wt of thermodynamic inhibitors

The system presented is the natural gas with 10% of CO₂. While **ethanol and (MEG)** have a similar effect, i.e. a decrease of **8°C** for a same pressure, **methanol** is the most performant inhibitor in this case, with a shift of **13 °C**.

The GC-PR-CPA model predicts accurately the hydrate dissociation curve for the system in pure water and with 25%wt of methanol. There a slight discrepancies for systems with ethanol. Glycols have not been added to the model yet.



Comparison of the hydrate dissociation curves in the presence of 25 %wt and 50 %wt of thermodynamic inhibitors

The system presented is the natural gas with 10% of CO₂. Double the quantity of thermodynamic inhibitors decreases the temperature of hydrate formation of about:

- ❖ **10°C for ethanol and MEG**
- ❖ **17°C for methanol**

