Microfluidic approach for the determination of complex mixture critical point

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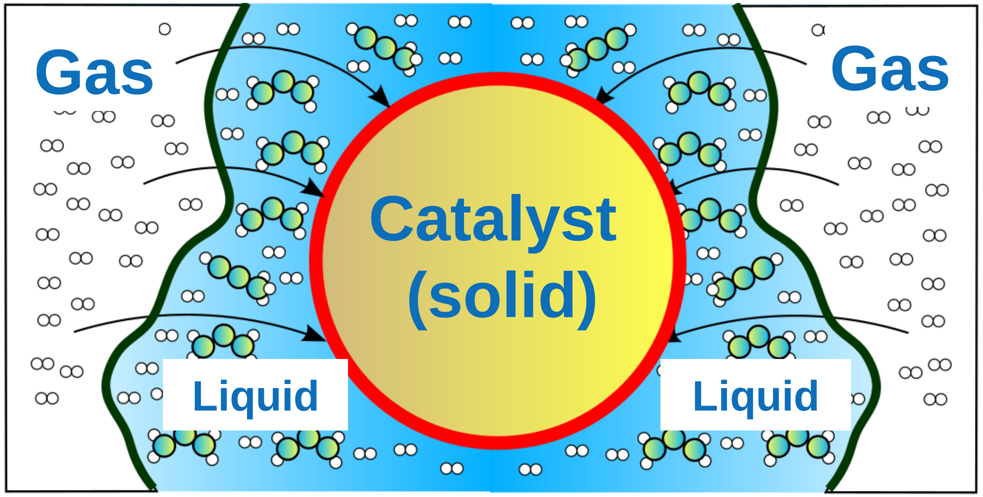
Outline

- Context
- Set-up & methodology
- Results
- Conclusion & perspectives

Context

Problem: **<u>fast</u>** reactions in G/L/S systems



Consequence: mass transfer masks the intrinsic reaction kinetics

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Different performance depending on the scale studied

Particularly at pilot scale ➔ Problem to predict industrial catalyst performance

➔Use SC conditions to investigate mass transfer problem

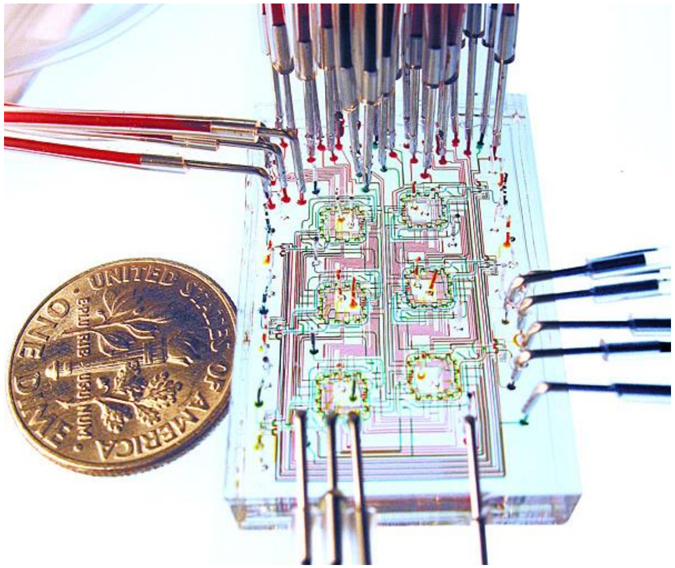
Context

What are the P and T to achieve supercritical conditions in our reactor?

➔ Determination of phase diagrams industrial feed mixture + H_2+ solvent (to limit SC temperature) using high pressure and high temperature microfluidic device

Microfluidics definition:

Microfluidics is the science that deals with the flow of liquids in channels of **micrometer size**.

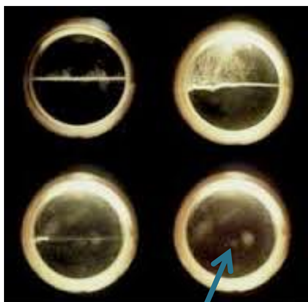


Stanford microfluidic bioreactors by professor Stephen Quake

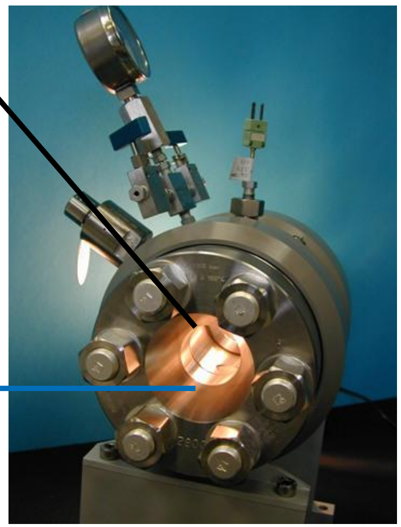
Experimental determination of critical points

Set-ups typically found in literature

High-pressure optical cell; sound velocity methods; …



Critical transition



High-pressure optical cell

↑↑ points required

Innovation

Microfluidic approach

Phase behavior inside a channel

+
- High precision
- Visualization

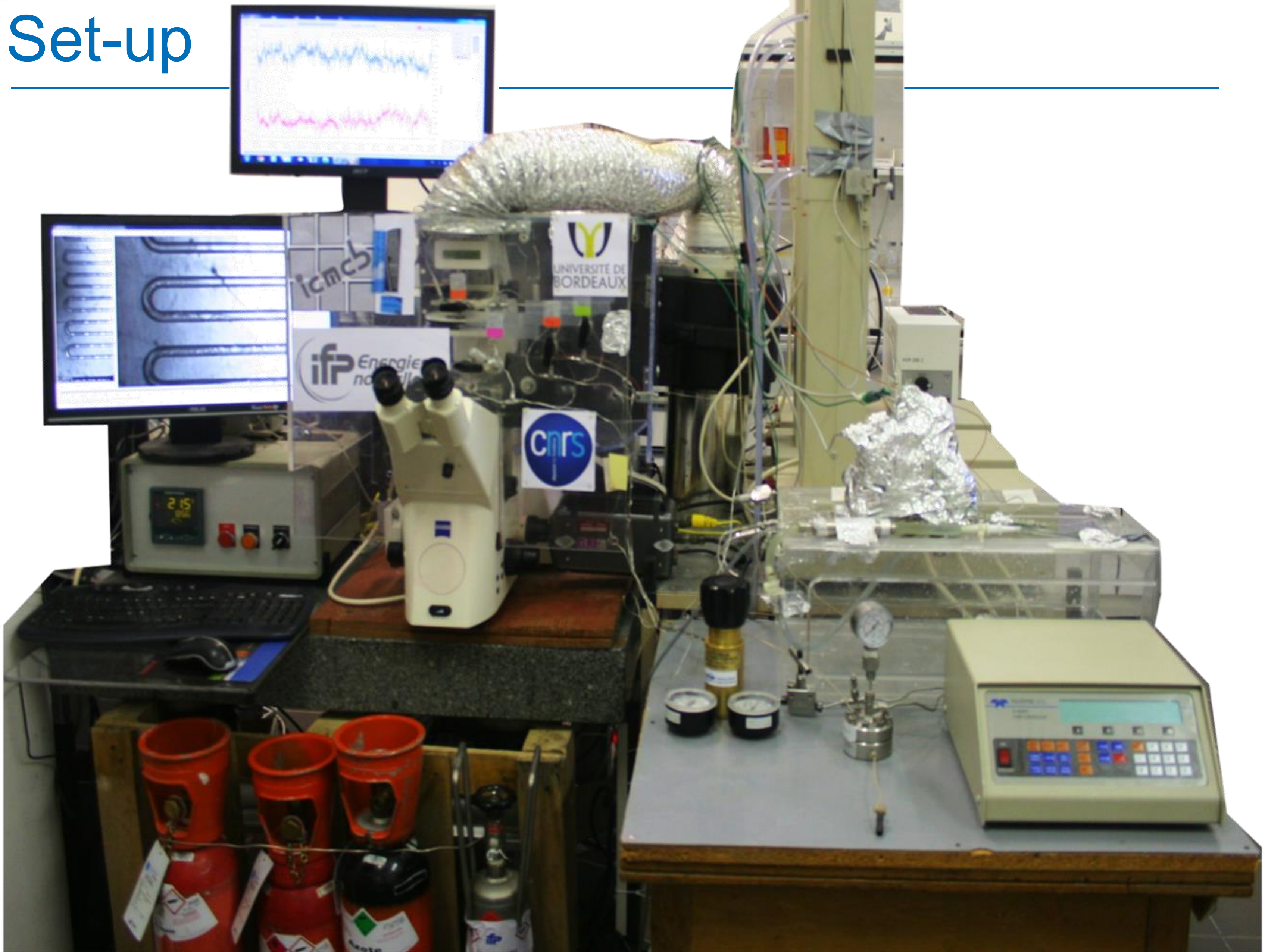
-
- Experimental duration of each tests (↑↑ **time to reach equilibrium:** mass and heat transfer)

+
- Visualization
- Fast screening of pressure and temperature (↓↓ **time to reach equilibrium:** mass and heat transfer)
- Continuous and small

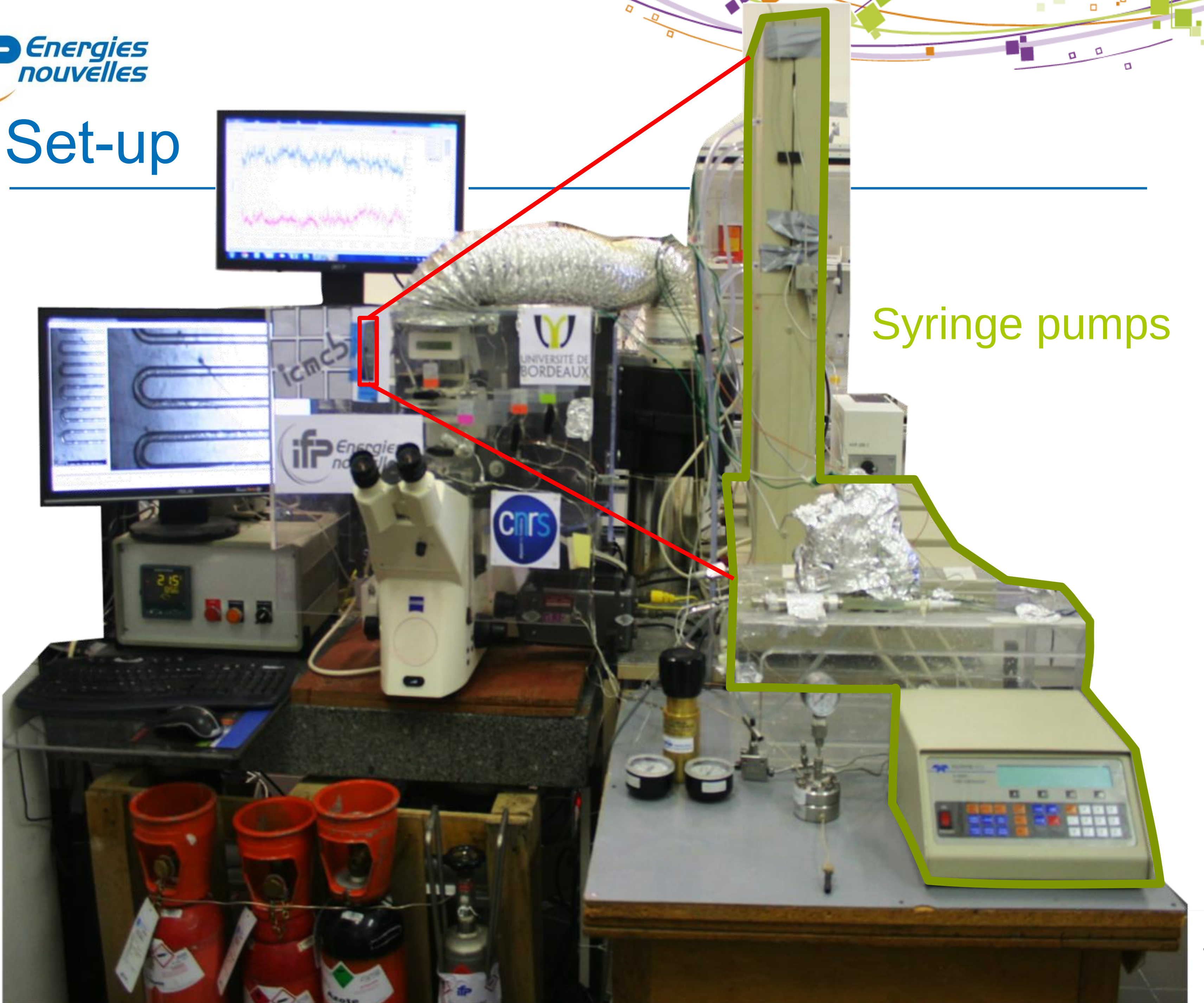
?
- Accuracy need to be verified

[1] N. Juntarachat, P. D. Beltran Moreno, S. Bello, R. Privat, and J.-N. Jaubert, J. Supercrit. Fluids, Aug. 2012.
[2] A. Kordikowski and D. Robertson, J. Phys. Chem., 1997.
[3] S. Marre, Y. Roig, and C. Aymonier, J. Supercrit. Fluids, Jun. 2012.

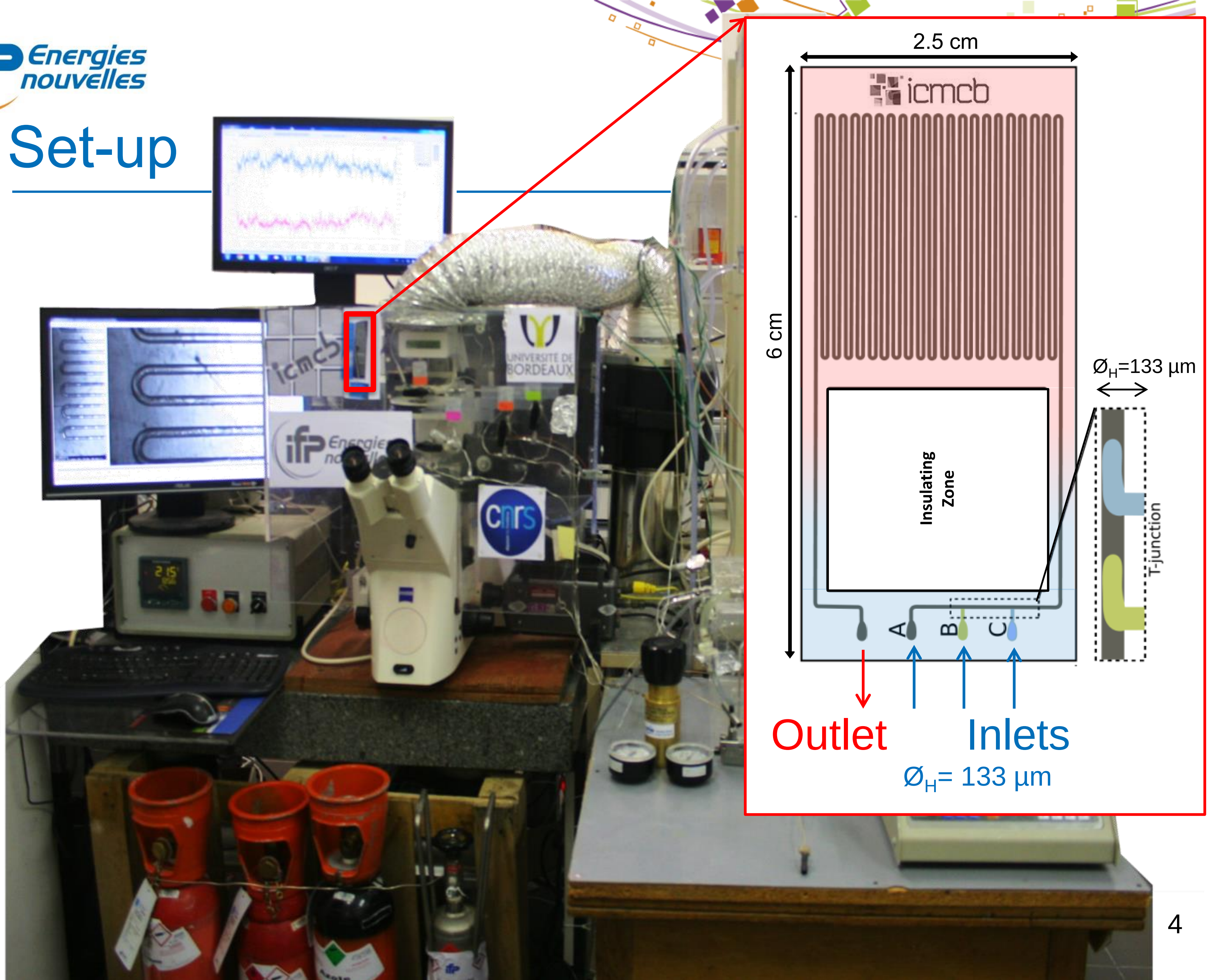
Set-up



Set-up



Set-up


2.5 cm
6 cm
icmcb
Insulating Zone
A
B
C
Ø$_H$=133 µm
T-junction
Outlet
Inlets
Ø$_H$= 133 µm
UNIVERSITÉ DE BORDEAUX
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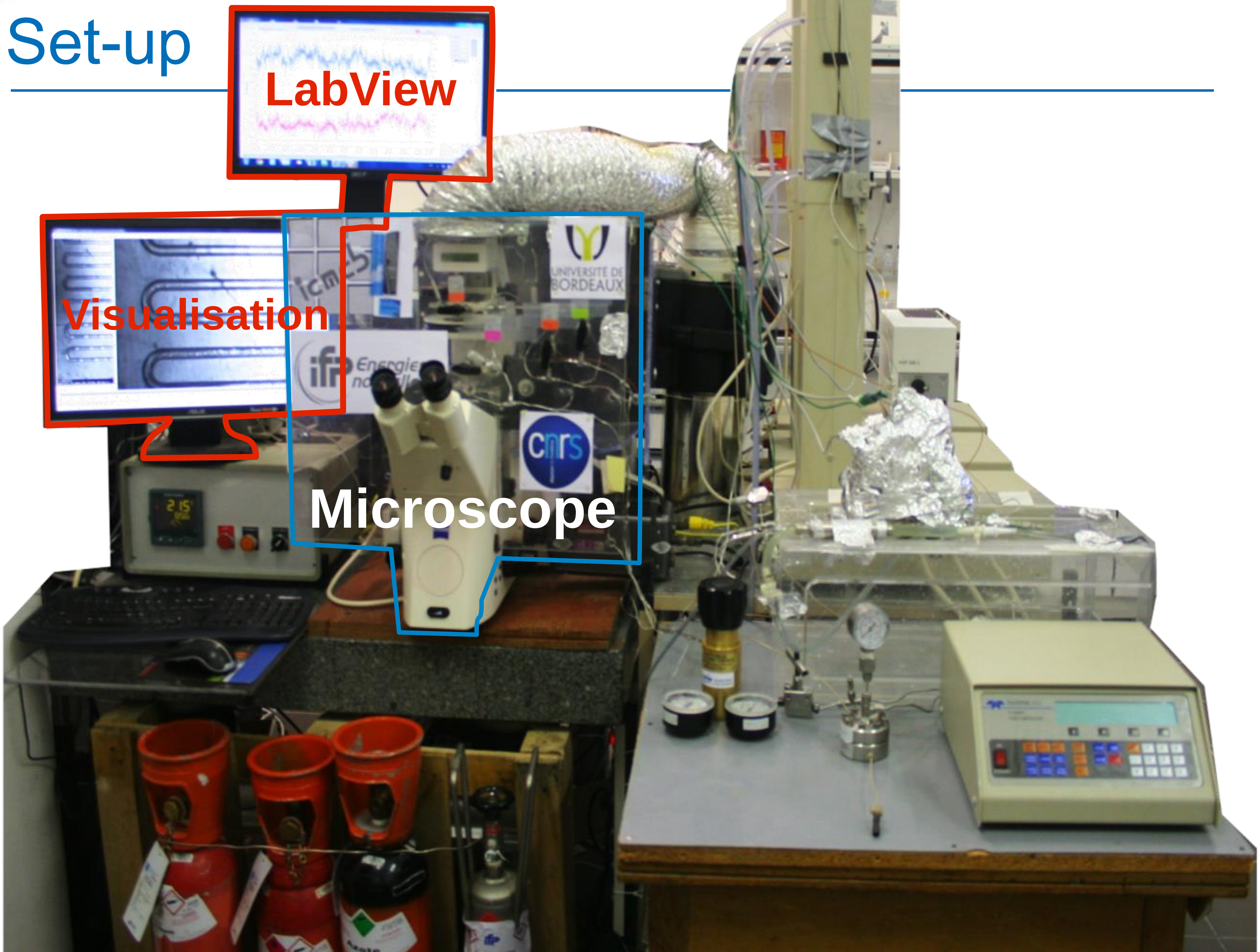
Set-up


LabView
Visualisation
Microscope
UNIVERSITÉ DE BORDEAUX
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Set-up

Fluids used:

Industrial feed

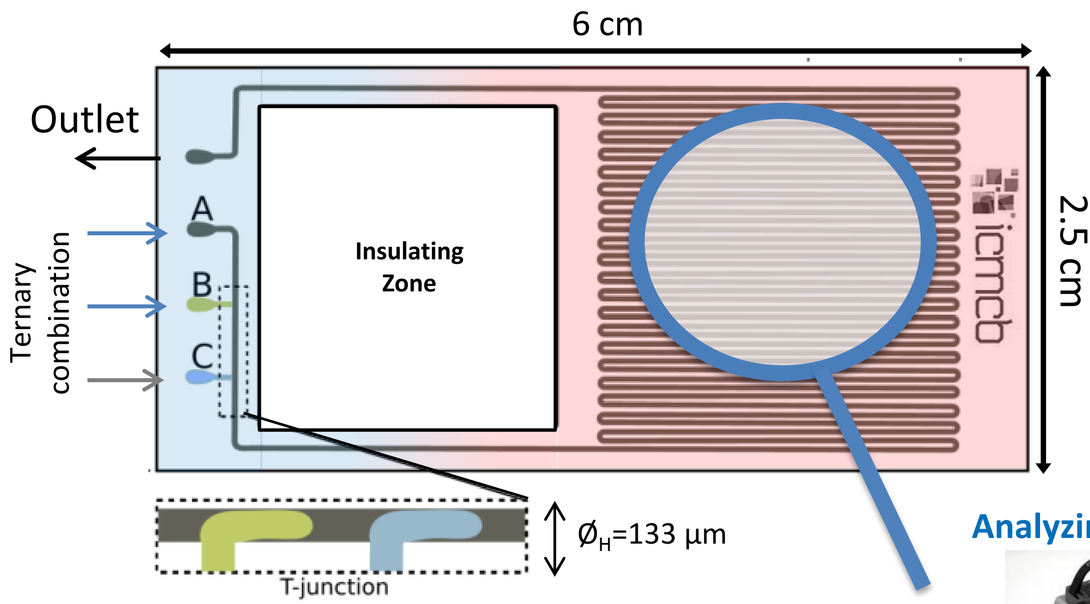
H_2

Solvent

(CH_4 or Ethane or CO_2)

↓

Chosen using thermodynamic model

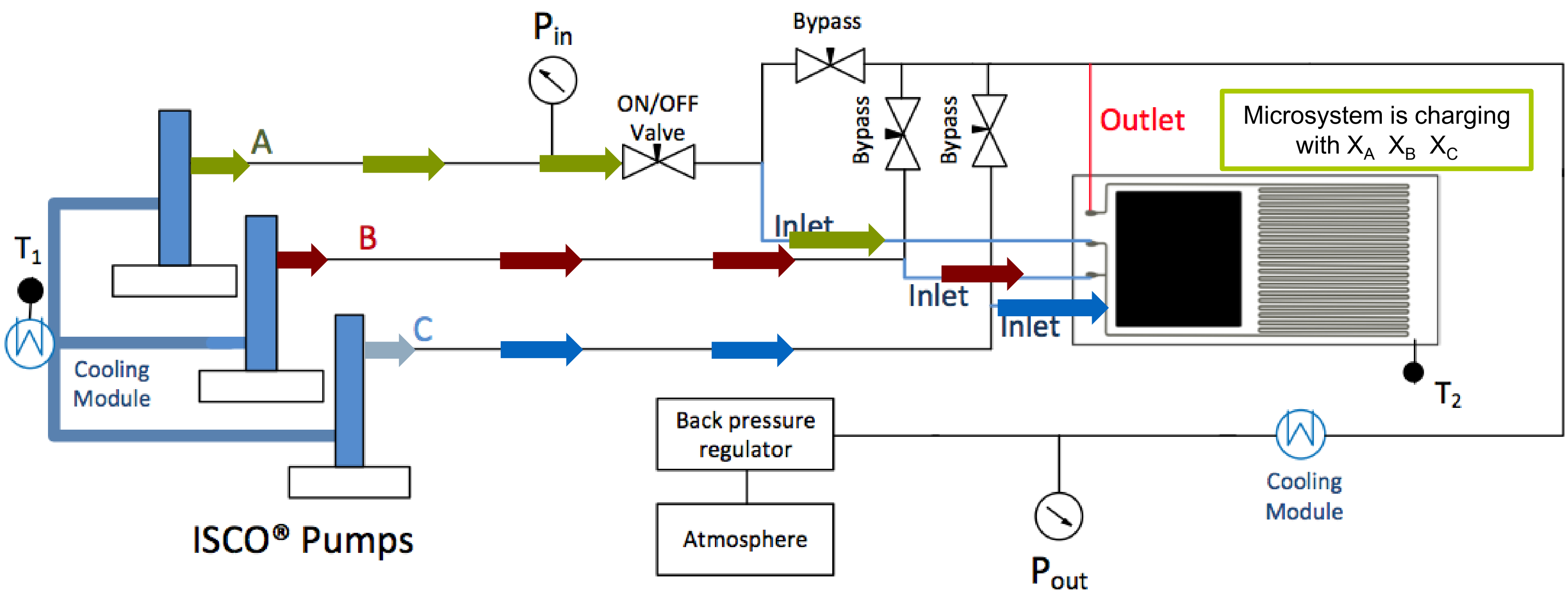


Analyzing zone

Methodology: Dynamic stopflow (**B. Pinho, et al. , Lab Chip (2014)**)

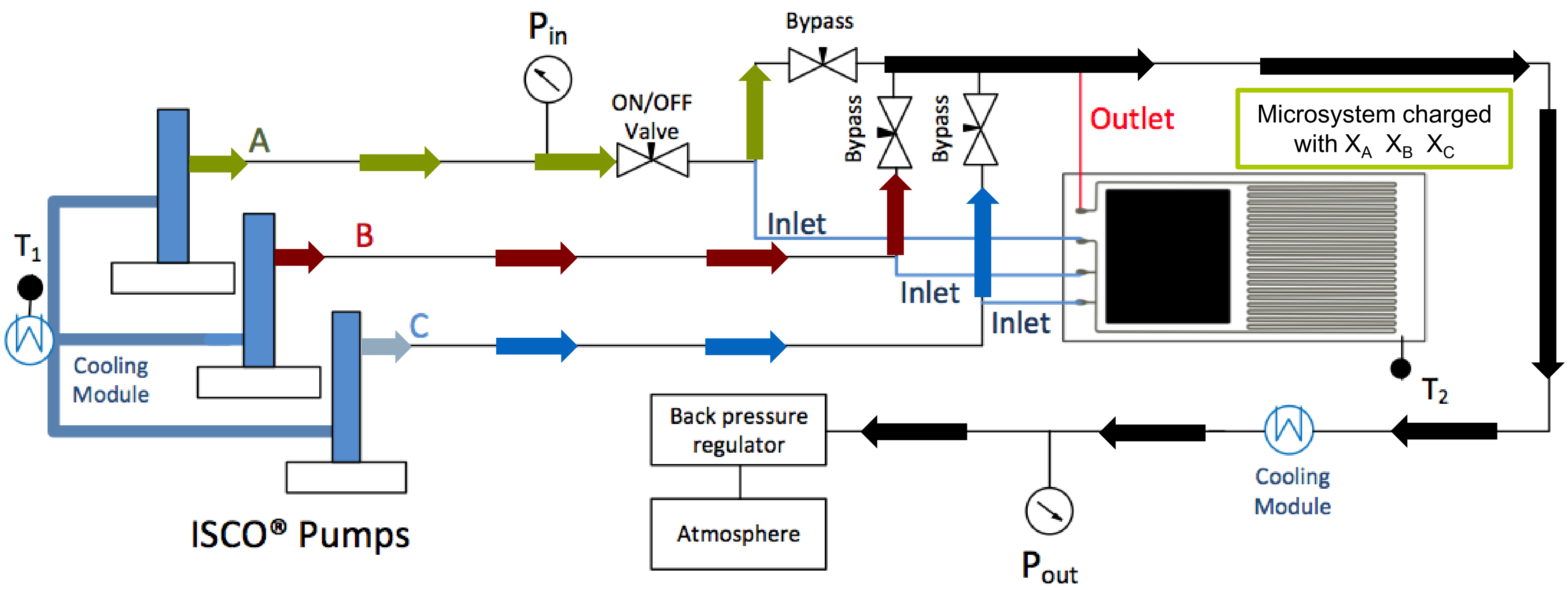
Advantage: **safe, easy and fast acquisition of the experimental data**

Methodology : dynamic stop-flow



Why it was necessary to develop this set-up?

Methodology : dynamic stop-flow



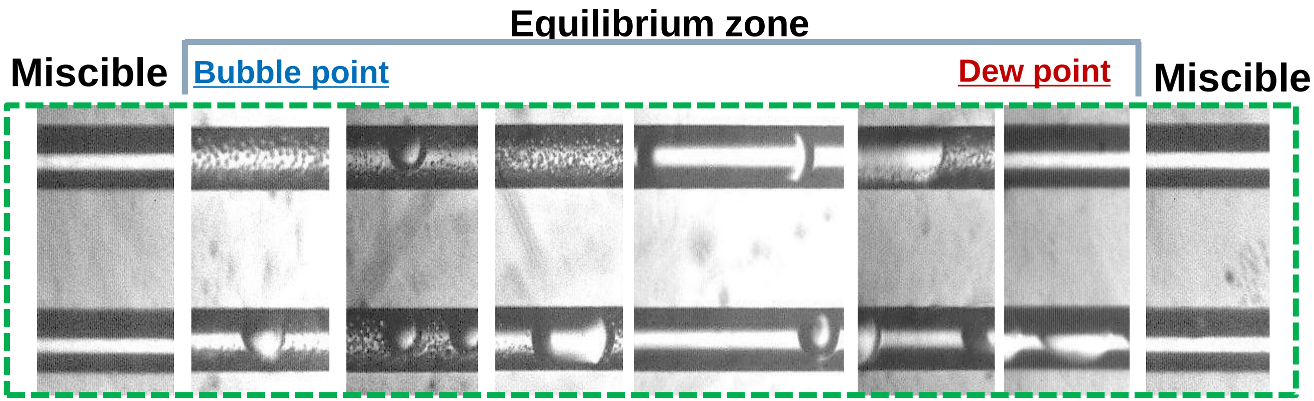
Why it was necessary to develop this set-up?

Continuous system: ΔP inside the µsystem
Close system: unknown pressure inside µsystem when temperature change

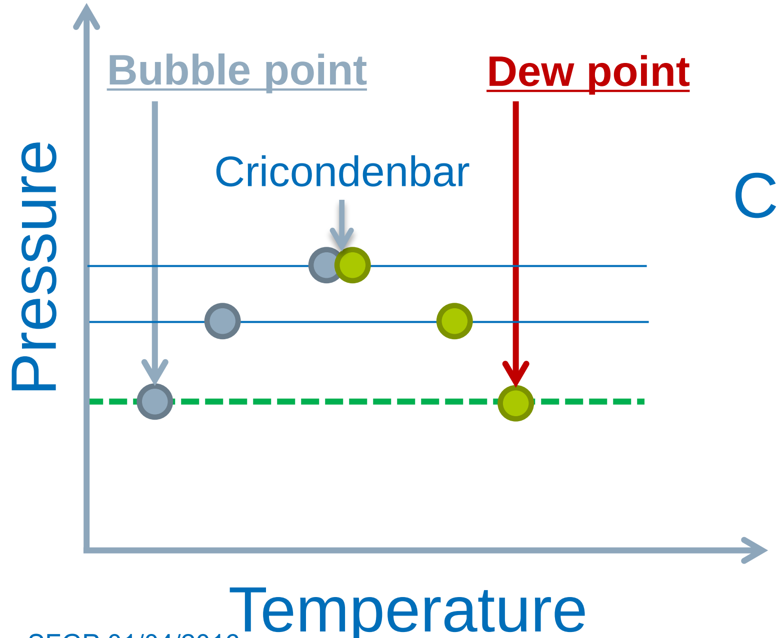
Advantages of the new approach:

ΔT ➔ without changing the P
or
ΔP ➔ without changing the T

Binary system



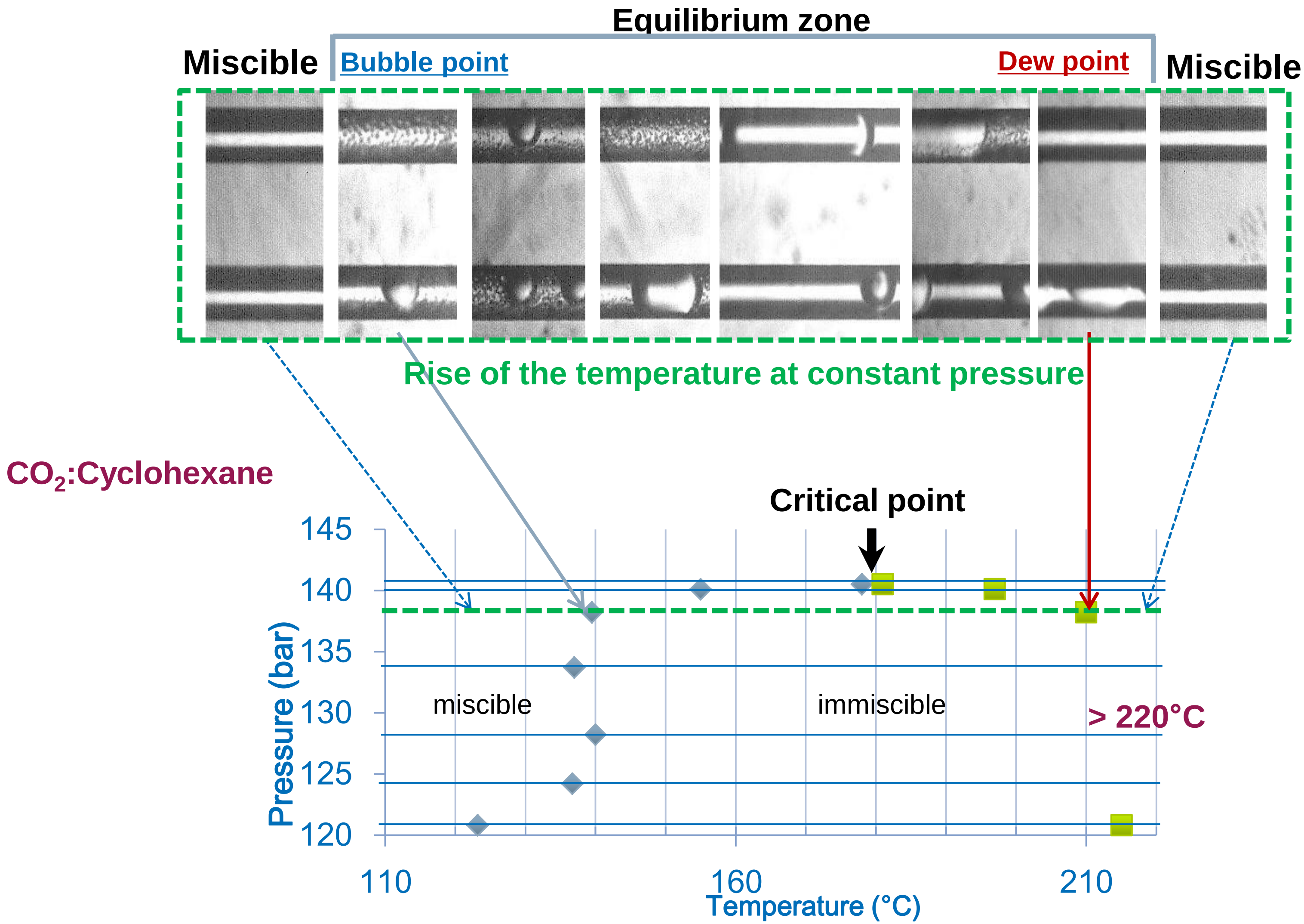
Rise of the temperature at constant pressure



Critical point condition

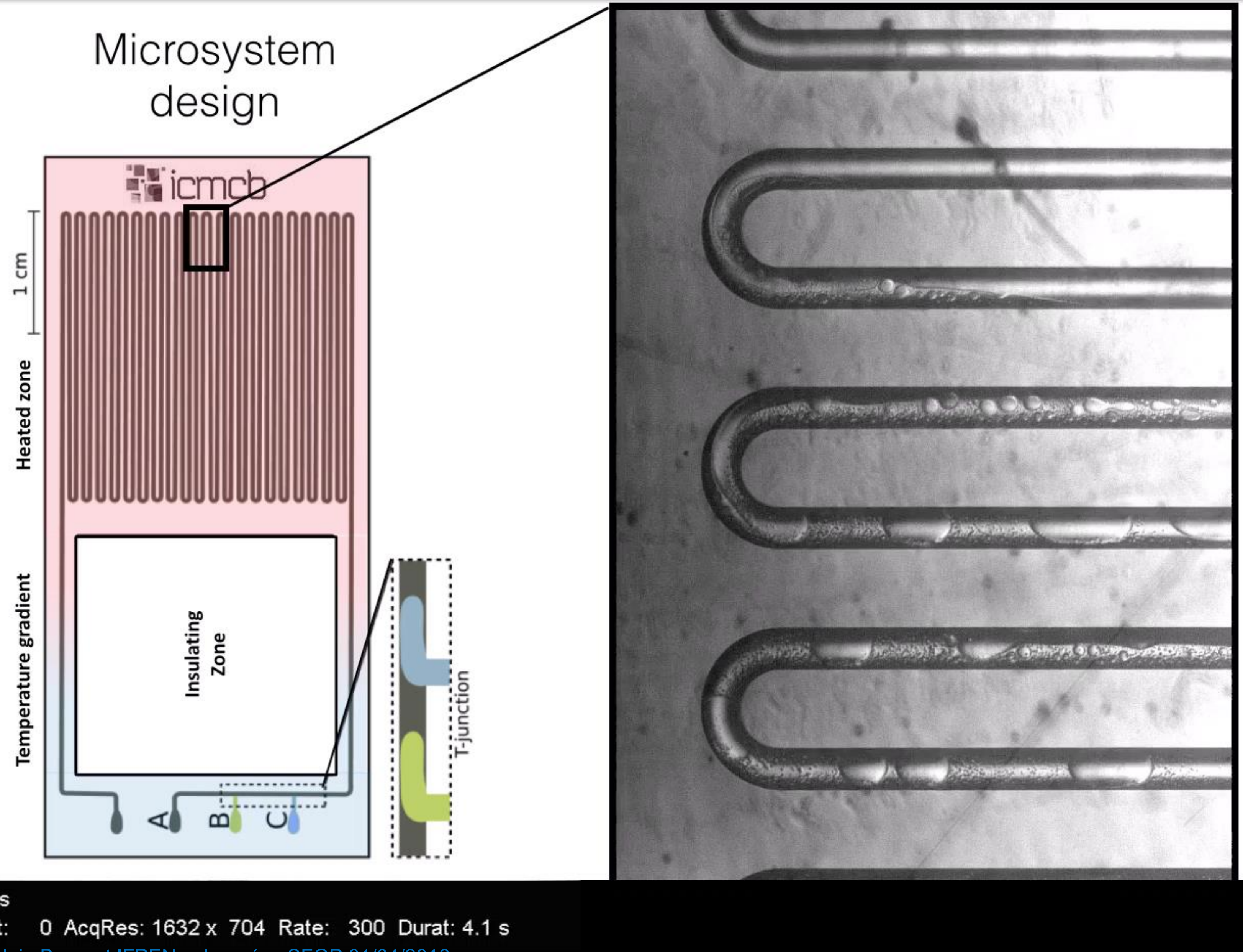
$$\left.\frac{d^2P}{dT^2}\right|_V = 0$$

Binary system



Bubble point

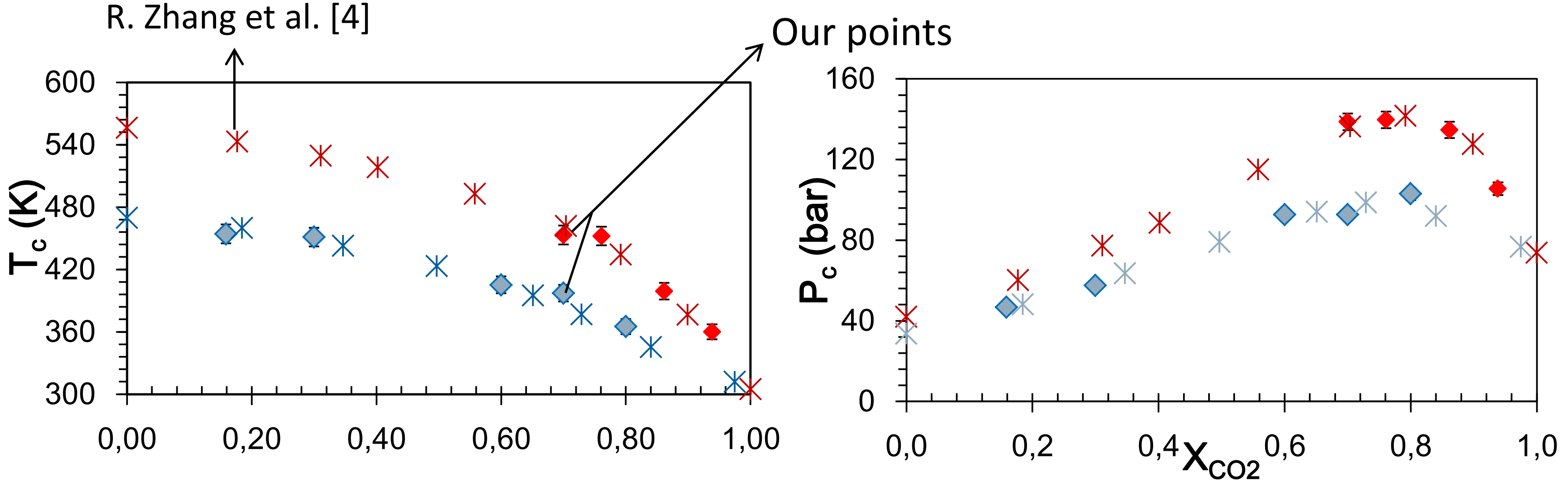
300 fps



Comparison with the literature

Validation case

Binary system:
CO_2 + Cyclohexane (red)
CO_2 + Pentane (blue)



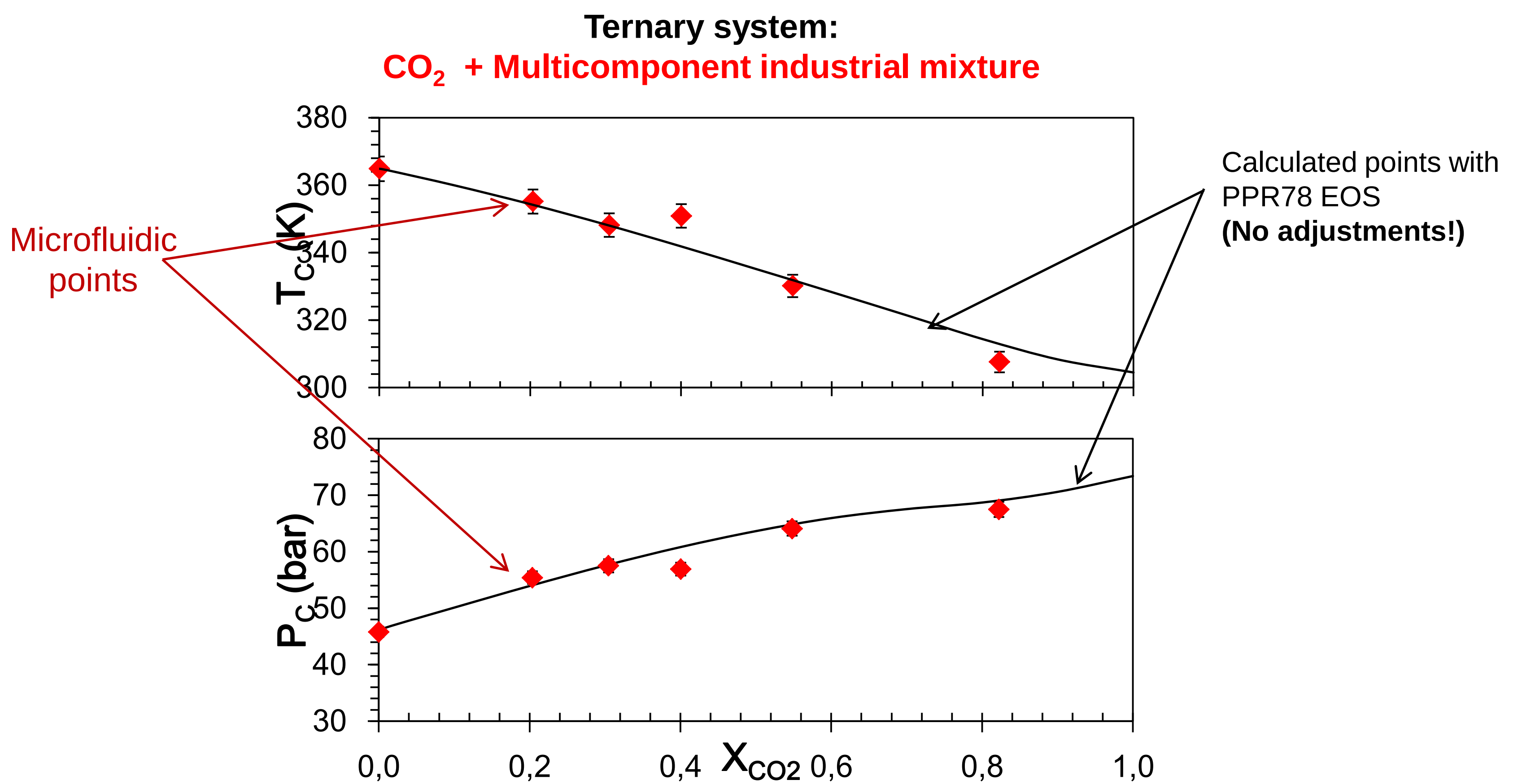
Conclusion : Validation of the experimental system (ARD 3%)
Good agreement between experiments / literature

Time of analysis: 1 day (around 5 x faster than the classical method*)

[4] R. Zhang, Z. Qin, G. Wang, and M. Dong, J. Chem. Eng. Data,, Jul. 2005.

*Ref: 1 critical point per day

Example of results with industrial feed

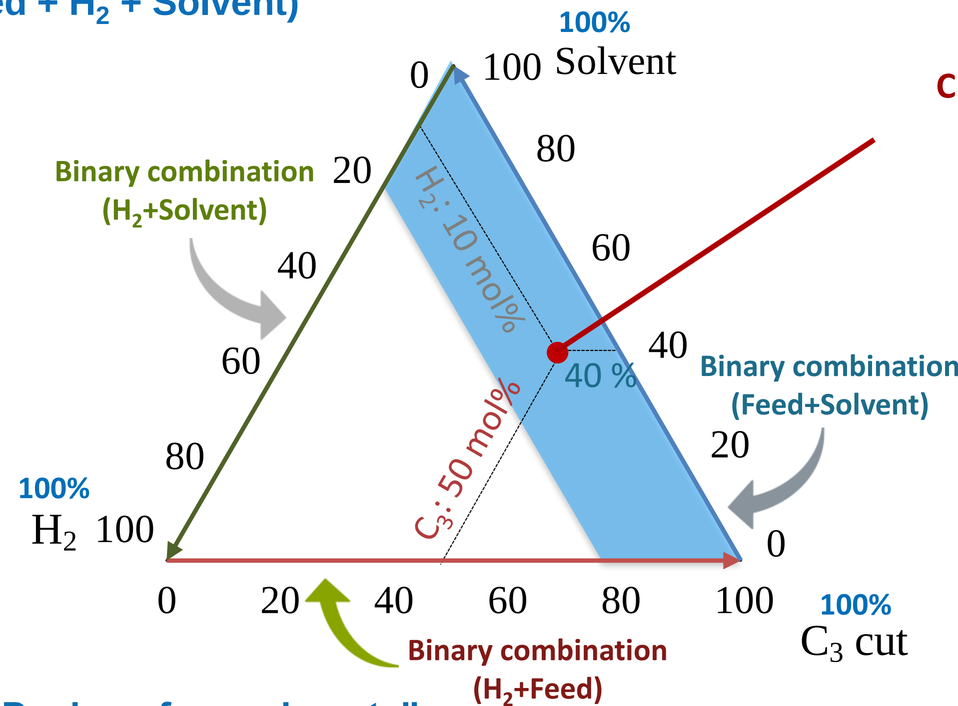


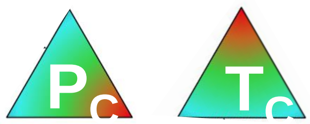
Conclusion : Validation of the experimental system
Good agreement between experiments / model

Application to the industrial mixture

Ternary combination → ternary diagram (best way to represent)

(Industrial feed + H_2 + Solvent)





"Design of experiments"

Elevated number of points → To reduce the number of experimental points → Optimal interpolation with thermodynamic model (PPR78)

Application to the industrial mixture

Microsystem applied to

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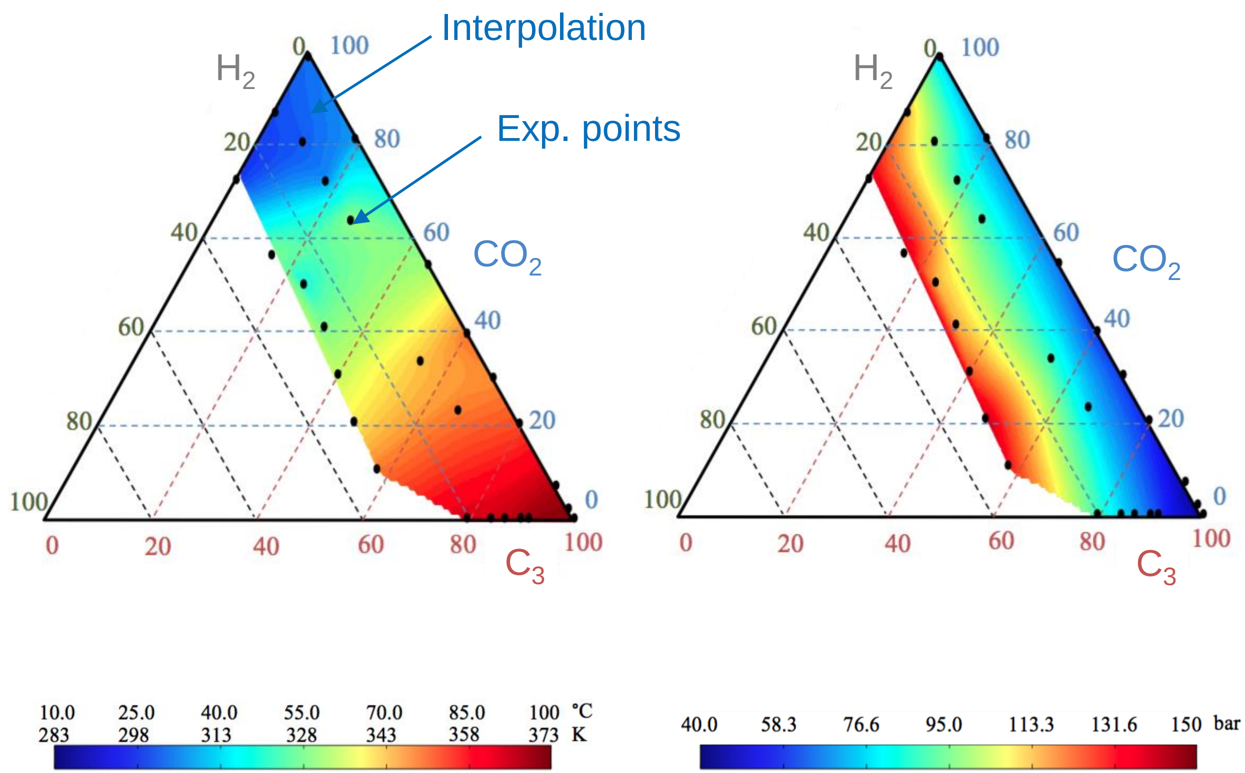
$C_3+H_2+CO_2$

C_3+H_2+Methane

C_3+H_2+Ethane

Critical temperature **Critical pressure**



Access to operating conditions to have supercritical medium for all the solvents

Conclusions & perspectives

- **Development and validation of experimental method**
  - New approach (fast, economical and repeatable) (around 5 x faster than classical method*)
- **Application:**
  - Experiments with Solvents + H_2 + industrial mixture
  - Possibility to analyze multicomponent mixtures

➔ **New PhD Thesis on October 2016 for other thermodynamic data with similar devices**

*Ref: 1 critical point per day

Thank you for you attention

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