High pressure and high temperature microfluidic approach for the determination of complex mixtures critical point

Bruno S. PINHO [a,b], Stéphane GIRARDON [a], Frédéric BAZER-BACHI [a], Ghislain BERGEOT [a],
Samuel MARRE [b], Cyril AYMONIER[b]*
[a] IFPEN, Rond-Point de l'Echangeur de Solaize, 69390 Solaize, France.
[b] CNRS, Univ. Bordeaux, ICMCB, F-33600, Pessac, FRANCE. Fax: +0033 5 40 00 27 61;
Tel: +0033 5 40 00 26 72; E-mail: aymonier@icmcb-bordeaux.cnrs.fr.

ABSTRACT

The advantages of supercritical fluids are now well known and are used in many processes.
One of their main advantages stand in their adjustable properties by small changes of temperature and pressure to fit the process needs. However, the limitation of applying supercritical fluids to conventional processes is the lack of experimental critical point data for multicomponent mixtures. Conventionally, critical point data can be obtained in High-Pressure Optical Cells (HPOCs) using isochoric or dynamic methods. Although it is a very precise technique, it is still time-consuming.

In this work, recent experimental developments are presented to detect supercritical transitions. The critical point is detected based on high-pressure / high temperature microsystems. The microfluidic approach for thermodynamic studies is much faster than conventional methods and, in addition, it seems to ensure a better control over the operating conditions. One of the great advantages of microfluidics is the ability to create custom microsystems, giving the possibility to control the mixing process.

The presented system approach allows a faster screening of the critical point in relation to the conventional methods, because the heat/mass transfer problems are greatly reduced.

INTRODUCTION

Getting to know whether a complex fluid mixture will be multiphasic, monophasic, subcritical or supercritical depends on the operating parameters and the reaction profile is a crucial data required by chemical engineers to build up their process, in particular when considering high pressures high temperatures systems. In relation to phase behaviors, the industry starts being interested in supercritical fluids [1-5], when pressure and temperature are above the critical point (P_c, T_c) because of their properties: liquid-like densities and gas-like viscosities and diffusivities [6]. Moreover, those properties can be continuously adjusted by small changes (temperature and pressure) to fit the process needs.

In isochoric systems like High-Pressure Optical Cells (HPOC), the pressure is directly controlled by temperature raise or decrease [7]. Although this approach provides very precise and reliable data, it lacks flexibility when targeting fast screening of the phase behavior. To overcome this limitation, a new approach was developed based on the use of high pressure / high temperature microsystems

To validate this technology towards phase behavior studies, the present work focuses on the critical point determination of multicomponent mixtures. To achieve this goal, the microsystem was designed to use binary/ternary mixing channels and *in situ* microfluidic state-of-the-art characterization techniques.

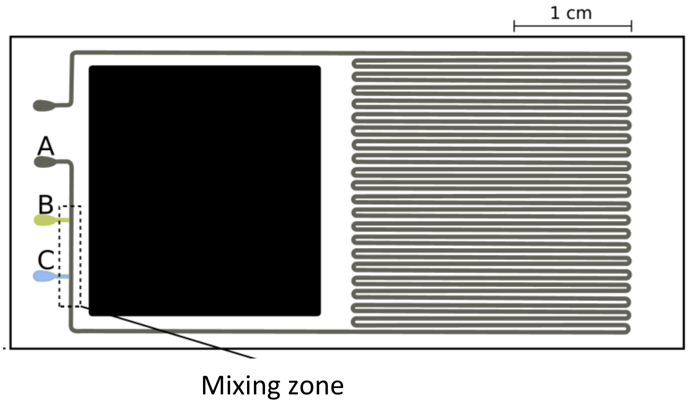
This proceeding focuses on the validation of the method to conduct on-chip multicomponent phase behavior studies at high pressures and temperatures.

MATERIALS AND METHODS

Methodology

In order to construct a multi-component P-T diagram, our approach is based on the optical on-chip detection of bubble and dew points. Initially, a fluid mixture with a particular composition is introduced at equilibrium in the microsystem, displaying liquid-fluid immiscibility, *i.e.*, droplets/bubbles are formed inside the microchannel and can be easily observed. Based on this point, the temperature was subjected to variations at isobaric conditions to find the bubble and the dew point. This means that the mixture turns to a fully miscible mixture by crossing the immiscibility / miscibility line in the P/T diagram. The mixtures critical locus curves can then be obtained through pressure-temperature (P-T) diagrams, the critical point being located at:

$$\left.\frac{d^2P}{dT^2}\right|_V = 0 \tag{1}$$



Experimental apparatus

Figure 1: Scheme of the microsystem developed to study phase diagrams.

A silicon / Pyrex microreactor was fabricated using standard lithography/dry etching techniques [8]. Microsystem channels have perfect rectangular shape: 200 µm and 100 µm of width and depths, respectively, for a total length of 1 m. To guarantee the mixture quality and fluid temperature, the microsystem has three different zones [8]: inlets/outlet zone, mixing zone, and analysis zone, see Fig. 1.

Flowrates are controlled by three high-pressure piston pumps (ISCO® 100DM), while a back pressure regulator (Equilibar® ULF) placed downstream is used to maintain a constant pressure in the microsystem. Temperatures are controlled within a ±0.1K interval by a EuroTherm® 3200. The microdevice is heated with an electrical resistance to compensate for convection heat losses. Two pressure transducers are placed upstream and downstream the

microsystem, respectively. The analyses were conducted within a temperature range from 300 to 500 K and a pressure range from 60 to 150 bars.
To construct these thermodynamic diagrams, movies were recorded with a Phantom® V9.1 at different capturing velocities, depending in the moment of analysis wanted.

RESULTS

Two benchmark binary mixtures were considered: cyclohexane+CO_2 and pentane+CO_2 (type *I-a* from the Scott and van Konynenburg classification system[9]), for which literature data are available, allowing estimating the overall set-up deviation. Fig. 2 shows the evolution of the critical pressure and temperature, which was experimentally obtained and compared with literature.

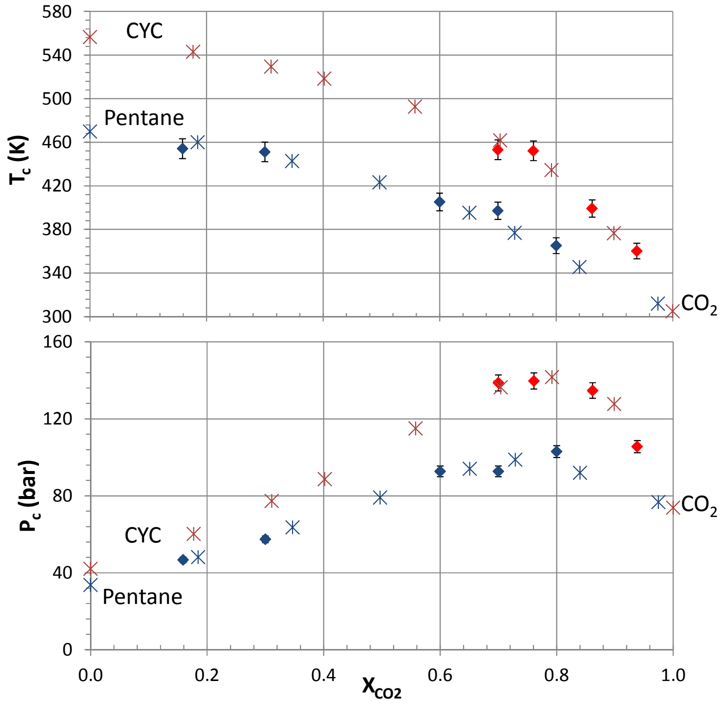


Figure 2: Critical points for the binaries cyclohexane (CYC)+CO2 and pentane+CO_2. ✳On-chip experimental results; ♦ Literature data (cyclohexane+CO_2: Zhang et al. 2005 ; pentane+CO_2: Cheng *et al.* 1989).

Literature, experimental and numerical results are very close to each other with a relative deviation of 2% and a maximum relative deviation of 5%. A part of the deviations can be due to composition variations in the system inlet.

CONCLUSION

A microfluidic-based approach was presented to determine actually the P-T phase diagrams of multicomponent mixtures. This method couples an on-chip optical detection of both bubbles and dew points.
We have demonstrated that this strategy can provide accurate data for multicomponent mixtures. Our results were compared to literature data. Additionally, this microfluidic approach can work very efficiently, taking advantage of (i) the fast heat and mass transfer and (ii) the easy control of all the set-up operating parameters.

Although the presented method was only used to investigate P-T diagrams, it is also possible to envision building PVT diagrams, taking into account the void fraction, as previously reported [12].

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