REACTION CALORIMETRY IN SUPERCRITICAL FLUIDS - A novel tool -

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A new reaction calorimeter was developed with Mettler-Toledo GmbH in order to investigate reactions under supercritical conditions. The first measurements realized with this new equipment: a reaction calorimeter RC1e with a 1.2 liter autoclave are presented. The intrinsic behavior of pure supercritical carbon dioxide is examined: constant volume heat capacity is compared to theoretical values obtained by Wagner and Span's equation of state in the range of 35 to 80 °C and densities from 500 to 800 kg/m^3. The influence of scCO$_2$ heat capacity on heat transfer coefficient is discussed based on a complete Wilson plot study realized with a double-stage turbine stirrer type for various rotation speeds from 100 to 2500 rpm. The flow behavior is in transient regime, neither turbulent nor laminar indicating that both density and viscosity will play a role. The heat transfer analysis indicates that in contrast to classical liquids, in supercritical CO$_2$, the lower the temperature (above the critical point) the better the internal heat transfer coefficient.

An endoscope has been used to follow the liquid-gas CO$_2$ transition at equilibrium to supercritical phase at reactor scale. The digital camera system coupled with an endoscope allows observing inside the reactor through a sapphire window placed on the reactor cover. Inhomogeneities are appearing at the liter scale indicating that agitation should play a role even if the apparent viscosity is low.

INTRODUCTION

A substance in supercritical fluids domain (SCFs domain) shows very specific properties that lie between those of a gas and a liquid. This particularity emphasize the great interest in supercritical fluids, due to the fact that by varying SCFs pressure or temperature, properties such as product solubility, as example, could be tuned to accelerate the separation as density has been changed from gas to liquid one [1]. At pressures and temperatures near the critical point, spectacular changes in specific properties could occur which are fundamental in order to understand supercritical fluids behavior. The most widely used SCFs is supercritical carbon dioxide (scCO$_2$), which has the advantage to be non-toxic, non-flammable and environmentally "friendly". It could be suitable for organic solvent replacement in chemical processes, especially extraction processes, due to its high diffusion rates [2, 3].

Industrial applications of supercritical fluids are scarce and only few reactive processes have been effectively developed. Thus SCFs are at first stage of understanding before any spread-off industrial application. Future is aware of the need to replace organic liquids, for environmental reasons, or to benefit from new productive routes [4]. A financial

balance has to be made to evaluate the process viability, keeping in mind that infrastructure and energy costs for gas compression is a very strong limitation. An example of an economical study is given by Hâncu and Beckmann [5] with the system anthraquinone /anthrahydroquinone in sub and supercritical CO_2 and pilot-scale development for extraction purposes by Ganado et al. [6]. It appears that only continuous flow processes with SCFs could be valuable trying to decompress less as possible the fluids before recycling in order to decrease energy consumption [7].

Reaction calorimetry is a common tool to investigate chemical reaction kinetics, to determine required data for chemical processes safety and to access fundamental information about phases change and mixing behavior [8]. To our knowledge, very few published literature deals with calorimetry applied to supercritical phase and these results are one of the firsts using and developing a reaction calorimeter in supercritical field.

EXPERIMENTAL AND METHODS

A new supercritical reaction calorimeter system composed of a high-pressure metallic reactor (HP350) with a total volume of 1.2 l coupled with Mettler-Toledo RC1e reaction calorimeter is presented in figure 1. The maximum operating pressure and temperature are respectively 350 bar and 300 °C. The reactor is equipped with a magnetic drive, a two-stage pitch blade turbine, a 25 W calibration heater, a PT100 temperature and pressure sensor.
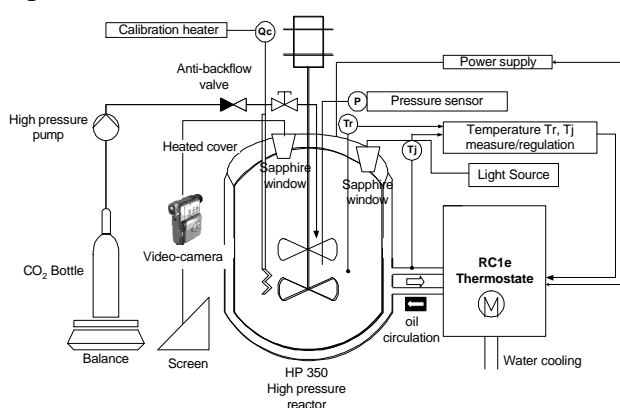
Process and control variables are monitored and controlled using the WinRC-NT software. Carbon dioxide bottle is equipped with a dip tube allowing pumping liquid CO_2. The bottle is mounted on a balance with an extended precision of $\pm$ 0.1 g over the range of 0-12.8 kg. Additionally, two sapphire windows are on the cover, in order to have a visual access of what is happening in the reactor: an endoscope from Fiberoptik AG equipped with a miniature video-camera is fixed over the window.
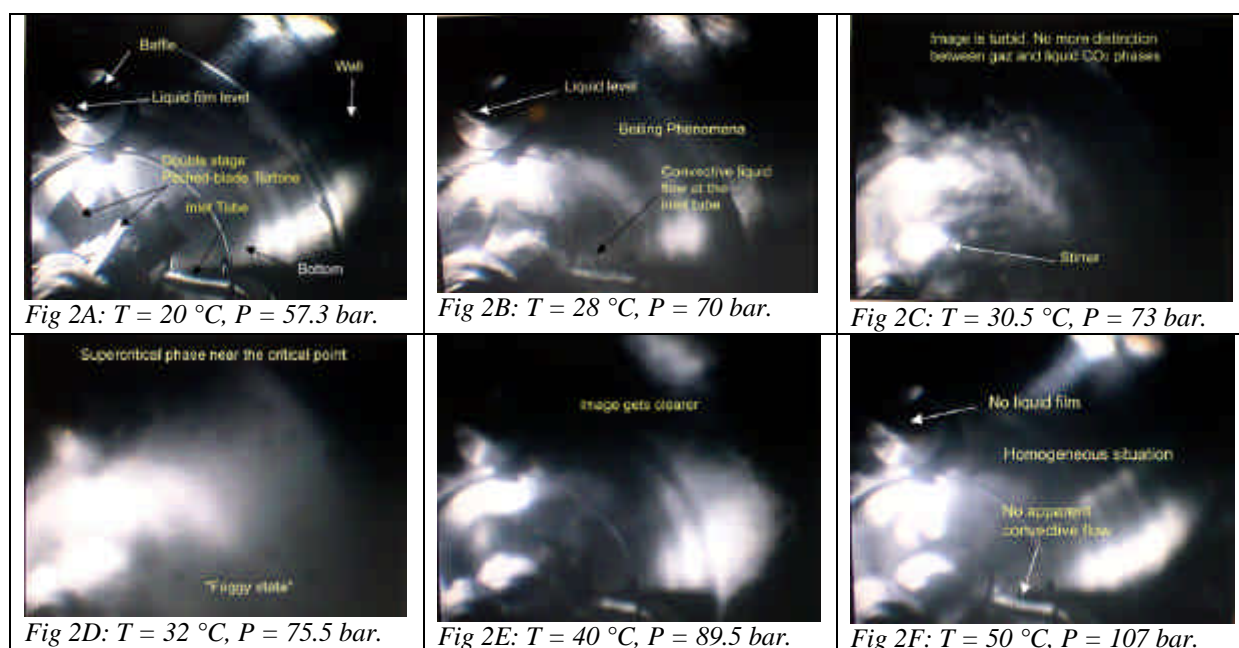
Figure 1: Calorimeter schematic view

Supercritical fluids take up all the allowable volume of the system and are not at equilibrium with other phases. A small change in temperature results in pressure change as the system is isochoric. In that situation, constant volume heat capacity c_v is the right quantity being measured through a temperature ramp. c_p will be the heat capacity measured as soon as more than one phase are present. The evaluation of the scCO$_2$ c_v has been realized using a 3°C in 10 minutes ramp and two calibrations, one for the initial temperature and the second for the upper temperature (eq. 1). The total heat capacity (J/K) of the inserts, C_{insert}, is known (standard equipment or calibrated one) and should be deducted to the total heat capacity of the reaction mass. On the other hand, the contribution of the flange, C_{flange}, to the heat flow model is more complicated and could be obtained by calibration.

$$c_v = \frac{[\Delta(T_j - T_R)/(dT_R/dt)] \cdot \overline{UA} - C_{insert} - C_{Flange}}{m_r}$$

(1)

RESULTS AND DISCUSSIONS

The digital camera system coupled with an endoscope allows observing inside the reactor through a sapphire window in the reactor cover. The macroscopic media behavior in the autoclave could be observed and analyzed by real time image acquisition. Phase transition of $scCO_2$ is presented in figures 2A-F at 200 rpm and 470 kg/m^3 $scCO_2$ density, being intentionally very close to the critical density (466 kg/m^3) in order to get the most impressive observations. The first image is clear and allows seeing the liquid level. This situation evolves as soon as temperature increase and boiling phenomena occurs. The small bubbles in figure 2B allow seeing convective flow by the trace behind the inlet tube. At 30.5 °C (figure 2C) boiling is maximum and results in a "foggy" state as soon as the critical temperature is over passed (figure 2D). It was quite impossible at this scale to observe the well known critical opalescence. For higher temperature (figure 2E and 2F) the image returns clearer.

Fig 2A: T = 20 °C, P = 57.3 bar. *Fig 2B: T = 28 °C, P = 70 bar.* *Fig 2C: T = 30.5 °C, P = 73 bar.*

Fig 2D: T = 32 °C, P = 75.5 bar. *Fig 2E: T = 40 °C, P = 89.5 bar.* *Fig 2F: T = 50 °C, P = 107 bar.*

Figures 2A-F: Images of the reactor inside for CO_2 phase transition from liquid-gas equilibrium to supercritical phase.

Having a direct look from the reactor top has the advantage to see what is happening inside (for example during a reaction), depending on rotation speed and reaction parameters. Moreover it is more difficult, compared to any reactor side view where phase levels are more visible, to assess multiple phase determination.

A first aspect is the calorimetric signal quality. For this purposes, c_v values have been measured and compared to calculated ones issued from Span and Wagner's equation of state [9] in order to evaluate the accuracy of the system's heat flow model (figure 3). Theoretical c_p and c_v values for $scCO_2$ and liquid-vapor CO_2 at equilibrium are compared with experimental c_v values obtained through the T_j-T_R signal integration. A good agreement between experimental and calculated values is observed with a deviation inferior to 10%. This indicates that calorimetric evaluations are correct and allows performing reaction calorimetry in reliable conditions.
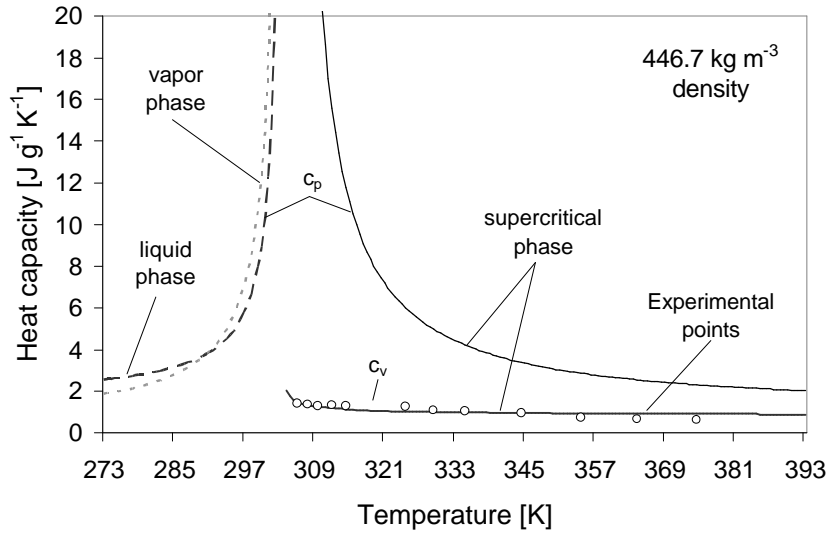
Figure 3 : Theoretical values of c_p and c_v and experimental points of c_v.

The second aspect is the evaluation of heat transfer phenomena in SCFs. Wilson plot analysis combines two expressions [10]. The first, for global heat transfer coefficient, could be expressed as the sum of three resistances: one for the internal film h_r, one through the jacket wall and one for the external oil coolant film, the two last being combined in a global resistance expression $1/\varphi$ independent of the internal media (equation 2). The second being the Nusselt correlation using Reynolds and Prandtl numbers (equation 3).

$$Nu = C \cdot Re^a \cdot Pr^b \left(\frac{h}{h_w} \right)^c = \frac{h_r \cdot d_c}{l} = C \cdot \left(\frac{n \cdot d_a^2 \cdot r}{h} \right)^a \cdot \left(\frac{c_p \cdot h}{l} \right)^b \left(\frac{h}{h_w} \right)^c \quad (2)$$

$$\frac{1}{U} = \frac{1}{h_r} + \frac{e}{l_w} + \frac{1}{h_{oil}} = \frac{1}{C' \cdot N^{2/3}} + \frac{1}{j} \quad (3)$$
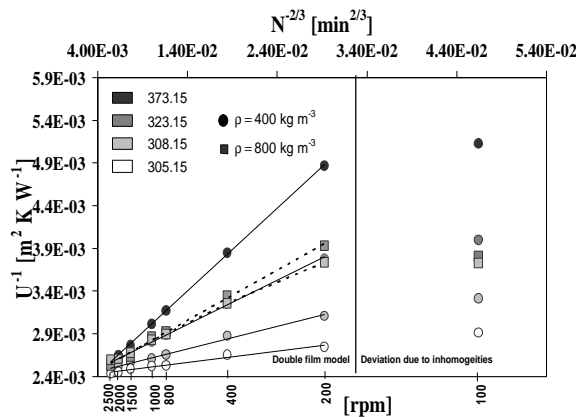

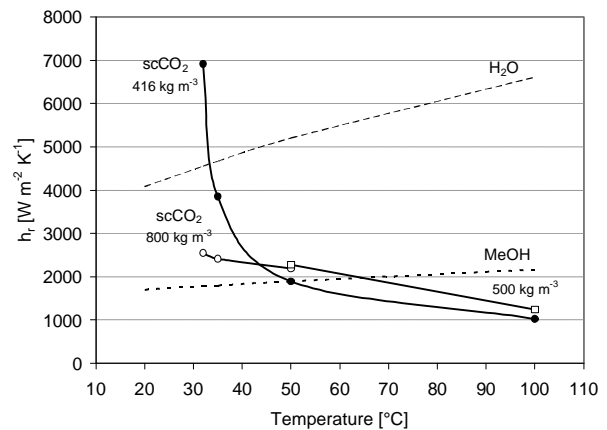**Figure 4**: Wilson plots for the double-stage turbine, eight rotation speeds and two scCO₂ densities.

Figure 5: Internal heat transfer coefficient h_r with turbine at 1000 rpm for scCO₂, water and methanol.

The Reynolds number exponent in the Nusselt expression is usually 2/3 for a stirred tank reactor equipped with a turbine in liquid media [11]. The linear plot in figure 4 confirmed that power 2/3 is still valid with supercritical carbon dioxide and that global heat transfer coefficient completely follows the Wilson plot regression, except for 100 rpm. This allows concluding that 100 rpm are not sufficient with this kind of turbine to homogenize the media in terms of temperatures and densities.

Another fundamental conclusion extrapolated from the Wilson plots analysis is that the internal heat transfer coefficient behavior is inverse to the one observed for classical liquid systems. In contrast to classical liquids, in supercritical CO_2, the lower the temperature (above the critical point) the better the internal heat transfer coefficient as presented in figure 5. The internal heat transfer coefficient is improving asymptotically close to the critical point for $scCO_2$. This tendency could be explained by the evolution of the thermodynamical and transport properties of $scCO_2$ around the critical point. In fact it is known that c_p and λ being in the numerator of equation 2 have a strong divergence around the critical point as plotted in a previous work by Lavanchy et al. [8] for the c_p (see also figure 3) and by Wakeham et al. [12] for λ. c_p has an asymptotical behavior and could rise up to 2 order of magnitude for it's classical supercritical value. Viscosity appearing at the denominator is also submitted to some excess behavior around the critical point, but contrary to heat conductivity, μ has a very short range of densities where critical enhancement is significant and moreover at temperature very close to the critical one (less than 1 °C) [13].

CONCLUSIONS

This new supercritical calorimeter system allows addressing the evaluation of calorimetric measurements under supercritical conditions as they are not trivial. On one hand the complex phenomena of heat transfer with SCF should be carefully taken into account in order to proceed with correct chemical reactions evaluation. Even constant volume heat capacity measurement is not a trivial matter and needs a well defined heat transfer model. On the other hand, Wilson plot study has allowed understanding the fundamental behavior of the internal film coefficient which does not follow the same tendency as classical liquids with respect to temperature. The coupling with video-camera recording has shown to be a necessary tool to optically follow the CO_2 phase transition leading to valuable information on equilibrium and multiple components mixing, especially during a reaction. This information added to the calorimetric one represents a huge potential for reactions investigation in supercritical media.

Some preliminary results in supercritical reaction calorimetry, using the esterification reaction of acetic anhydride with methanol in ethylacetate (classical liquid phase) compared to same reaction in supercritical conditions indicate that $scCO_2$ leads to higher reaction rate at same operating conditions (temperature, concentrations, rpm) [14].

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