

# HEAT TRANSFER AND HYDRODYNAMICS IN SUPERCRITICAL CARBON DIOXIDE

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A new tool, composed of a high pressure reactor (HP350) coupled with a Mettler-Toledo RC1e reaction calorimeter, is developed for the investigation of chemical reactions, under supercritical conditions. The reactor (V=1.3 liter) can be pressurized up to 350 bars and heated up to 300 °C. Results presented in this paper reflect a complete Wilson plot analysis with pure supercritical CO<sub>2</sub> and two types of stirrer: a double-stage turbine and a three-stage Ekato MIG<sup>®</sup>. They reveal that in contrast to classical liquids, the lower the temperature (above the critical point) the better the internal heat transfer coefficient. The Nusselt correlation equation has been successfully applied in order to confirm that heat conductivity and heat capacity evolution around the critical point of scCO<sub>2</sub> are responsible for that specific behaviour. The corresponding constant value (C) for the turbine and the MIG<sup>®</sup> has been found to be  $0.53 \pm 0.03$  and  $0.27 \pm 0.03$  respectively.

## INTRODUCTION

Reaction calorimetry is a useful tool to investigate chemical reaction kinetics, to determine required data for chemical processes safety and to access fundamental information about phases change and mixing behaviour. The fundamental study of the behaviour of the supercritical phase is still under intensive research and will need further investigations. Literature has proved to be very poor in the domain of calorimetry linked to supercritical phases and even more, to our knowledge, this work act as a pioneer using and developing a reaction calorimeter in supercritical field [1-3].

One of the main advantages of this reaction calorimeter is that it allows to study the effect of mixing, heat conduction and heat transfer at a reasonable scale (1.3 litre) where these phenomena could no longer be neglected in contrast to small-scale batch or tubular cells calorimeter (1-10 cm<sup>3</sup>). Moreover, this reactor size is an opportunity to add in-line probes as, for example, FTIR or ultrasonic. Therefore, it give access to fundamental phase and concentration evolution throughout the system, as it has been proved that even a small portion of a solute could alter the complete phase diagram of a supercritical mixture [4]. The coupling of reaction calorimetry and in-line sensors could be very efficient and promising in order to understand fundamental aspects of supercritical fluids involved in reactions.

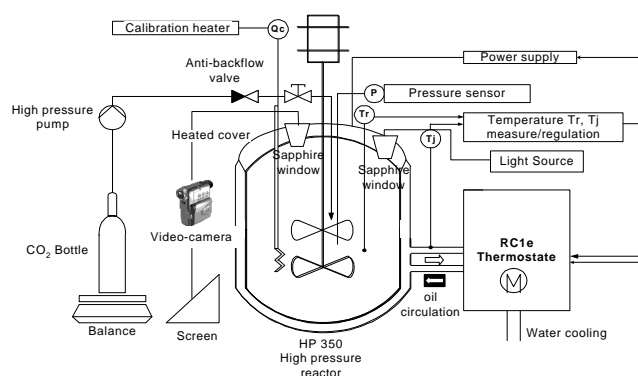
This paper concentrates on the mixing and hydrodynamics aspects in supercritical carbon dioxide as these important fields are not yet understood or even known for a stirred tank reactor at the litre scale, in addition to recent work, by Piro et al.[5], concerning continuous flow systems.

## I - MATERIALS AND METHODS

The reaction calorimeter has been developed for supercritical conditions, in collaboration with Mettler-Toledo GmbH, using a high-pressure stainless steel autoclave HP350 (Premex, Switzerland), depicted in Figure 1. The double jacketed reactor has a total volume of 1.3 liters ( $V_r$ ). The thermostat unit (RC1e) controls the reaction temperature by pumping silicon oil at high flow rate through this double jacket. A technical scheme of the installation is given in Figure 2. Process and control variables are monitored and controlled using the WinRC-NT<sup>®</sup> software. Carbon dioxide is supplied by a bottle equipped with a dip tube allowing to pump liquid CO<sub>2</sub>. The bottle is mounted on a balance with an extended precision of  $\pm 0.1$  g over the range of 0-12.8 kg. The pressure inside the bottle is 49.5 bar and the CO<sub>2</sub> purity is more than 99.9 % (CO<sub>2</sub> 30 quality).



**Figure 1:** Picture of the autoclave.



**Figure 2:** Technical scheme of the RC1e unit and additional equipment.

The maximum operating pressure and temperature are 350 bar and 300 °C. The reactor is equipped with a magnetic drive, a 25 W calibration heater, a PT100 temperature sensor and a pressure sensor. The stirrers used are a three-stage Ekato MIG<sup>®</sup> (MIG) and a two-stage turbine (turbine) depicted in Figure 3a and b respectively.



Three-stage Ekato MIG<sup>®</sup>



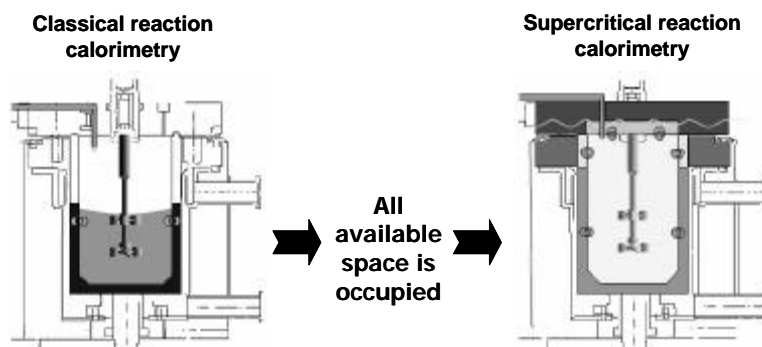
Two-stage Turbine

**Figure 3a and 3b:** Pictures of the two stirrers used.

The calorimeter is able to work in three different operating modes: *adiabatic*, where the jacket temperature ( $T_j$ ) is adjusted in such a manner that there is no heat transfer through the reactor wall; *isoperibolic*, where the jacket temperature is kept constant and the reaction temperature ( $T_r$ ) follows the reaction profile; and *isothermal*, where the desired reaction temperature is set to a constant value and  $T_j$  is changed automatically to maintain  $T_r$  at the

specified value. All the experiments presented in this paper are performed using the isothermal mode.

The “supercritical reaction calorimetry” has first to overcome some technical problems mainly due to the fact that the supercritical phase occupies all available space as illustrated in Figure 4. Thus, not only the jacket area has to be perfectly controlled but also the cover and the other parts have to be separately temperature-controlled in order to apply the heat balance equations without any additional heat transfer interferences. In our case, all the reactor parts in contact with the reacting media are adjusted to  $T_r$  in order to neglect the heat accumulation term.



**Figure 4:** Difference between classical liquid and supercritical reaction calorimetry.

The typical Wilson experiments procedure is the following: The reactor is filled two times with about 50 g of  $\text{CO}_2$  and emptied through the purging valve, then continuously purged by  $\text{CO}_2$  flowing. The valve is then closed and the reactor is filled up to a desired mass using the pump. The valve is then closed again and 10 minutes stabilization time is systematically applied before noting the total injected  $\text{CO}_2$  mass. Eight stirrer speeds between 100-2000 rpm have been tested with the turbine and the MIG for four isotherms: 32, 35, 50, 100 °C and different densities ranging from 270 to 750  $\text{kg/m}^3$ .

The global energy balance for the system could be found in previous papers [2-3]. In the case of pure isothermal mode with the calibration heater as the only heat production source, the global heat transfer coefficient can be measured using equation 1.

$$UA = \frac{\int_{t_1}^{t_2} (Q_c - Q_b) dt}{\int_{t_1}^{t_2} (T_r - T_j) dt} \quad (1)$$

Where  $U$  is the global heat transfer coefficient, [ $\text{W/m}^2 \cdot \text{K}$ ].  $A$  is the total heat transfer area between the jacket and the media, [ $\text{m}^2$ ].  $Q_c$  is the heat produced by the calibration heater (25W), [W].  $Q_b$  is the baseline signal, [W].  $T_r$  is the inner media temperature, [K] and  $T_j$  the coolant temperature, [K].

Wilson plot analysis combines two expressions [6]. The first expression concerns the global heat transfer resistance  $1/U$  being expressed as the sum of three resistances: one from the internal film  $h_r$ , one for the jacket wall and one from the external oil coolant film  $h_{oil}$ . The last two are combined in a global resistance expression  $1/\phi$  being independent of the internal media (eq 2). The second expression is the dimensionless “Nusselt correlation” relating Nusselt number ( $Nu$ ) to Reynolds ( $Re$ ) and Prandtl ( $Pr$ ) numbers (eq 3).

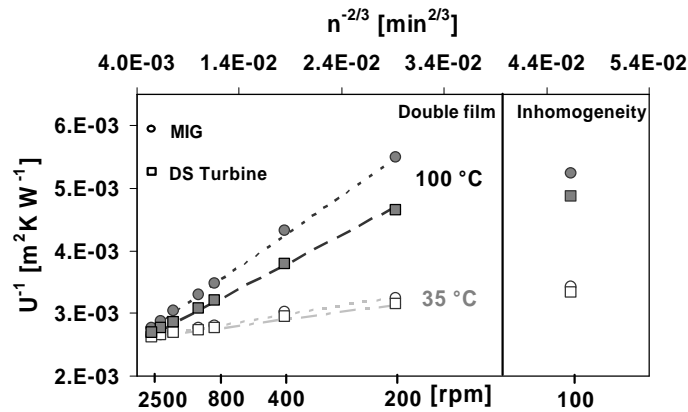
$$\frac{1}{U} = \frac{1}{h_r} + \frac{e}{\lambda_w} + \frac{1}{h_{oil}} = \frac{1}{C' \times N^{2/3}} + \frac{1}{j} \quad (2)$$

$$Nu = C \times Re^a \times Pr^b \frac{\mu_w^{0.14}}{\mu} = \frac{h_r \times d_R}{\lambda} = C \times \frac{N \times d_S^2 \times \rho}{\mu} \times \frac{c_p \times m \times \mu_w^{0.14}}{l} \quad (3)$$

Where  $h_r$  is the internal heat transfer coefficient, [W/(m<sup>2</sup>·K)].  $e$  is the thickness of the metallic wall, [m].  $\lambda_w$  is the heat conductivity of the metallic wall, [W/(m·K)].  $h_{oil}$  is the coolant part heat transfer coefficient, [W/(m<sup>2</sup>·K)].  $d_R$  is the reactor internal diameter, [m].  $\lambda$  is the bulk heat conductivity, [W/(m·K)].  $\mu$  is the bulk dynamic viscosity, [kg/(m·s)].  $N$  is the rotation speed of the stirrer, [s<sup>-1</sup>].  $d_S$  is the stirrer characteristic diameter, [m].  $\rho$  is the bulk density, [kg/m<sup>3</sup>].  $c_p$  is the bulk constant pressure heat capacity, [J/(kg·K)].  $C$  and  $C'$  are constants. The exponent  $a$  for the Reynolds number in the Nusselt expression is usually 2/3 for a stirred tank reactor equipped with a turbine in liquid media [7]. Exponent  $b$  for the Prandtl number is 1/3. The viscosity ratio, which exponent  $c$  is usually 0.14, is neglected since the maximum temperature difference between the bulk  $\mu$  and the wall  $\mu_w$  is less than 1 °C in the isothermal mode. This allows the isolation of  $h_r$  and its substitution in the resistance expression as all other properties are constant at isothermal conditions.

## RESULTS AND DISCUSSION

An example of the Wilson plot comparison obtained for the turbine and the MIG at a scCO<sub>2</sub> density of 470 kg/m<sup>3</sup> is given in figure 5.

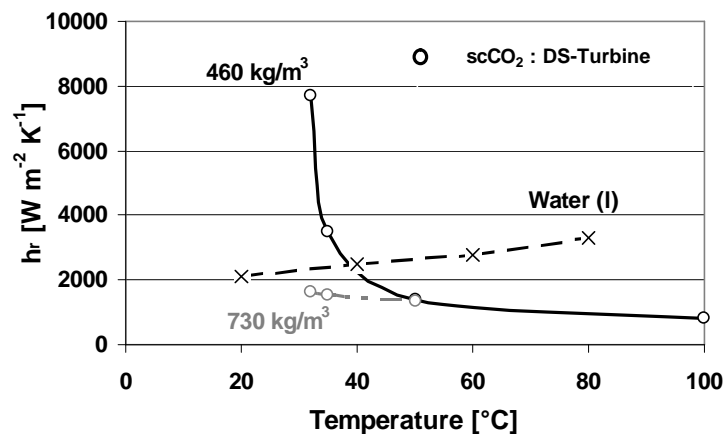


**Figure 5:** Wilson plot comparison between the MIG and the turbine for a scCO<sub>2</sub> density of 470kg/m<sup>3</sup> and two temperatures.

The linear trend confirms that power 2/3 is still valid with supercritical carbon dioxide for the two stirrer types. This linear behaviour clearly indicates that the global heat transfer coefficient completely follows the Wilson plot regression at all temperatures and scCO<sub>2</sub> densities, except for 100 rpm stirrer speed, where the system is inhomogeneous due to insufficient stirring. Moreover, the fact that the regression line of the turbine is below the one for the MIG reveals that the turbine is more efficient, with respect to heat transfer, than the MIG at the given temperatures.

The slope of the Wilson plot regression lines allow to calculate the internal film coefficient. The intercept with the  $U$  axis (meaning an infinite rotation speed) determines the

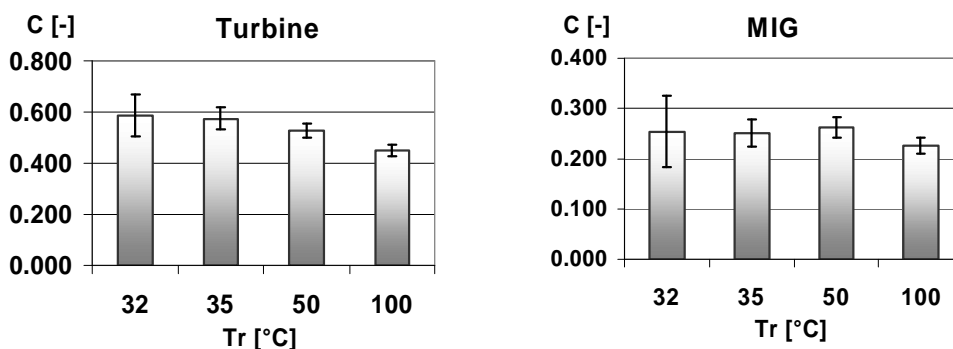
global heat transfer coefficient of the external part  $\phi$  taken from equation 2. It comes out that the regression lines cross before the U axis, indicating that the external film behaviour is exactly the opposite of the internal film with respect to temperature. This tendency clearly shows the accuracy of the experiments, as it demonstrate that independently on the media, the external heat transfer coefficient part, which includes conduction through the vessel wall and transfer through the stagnant coolant film, is improving with temperature. This effect is mainly due the decrease of the coolant viscosity with temperature. The experimental behaviour of  $h_r$  is presented in Figure 6 which compares experimental  $h_r$  for a classical liquid (water) and  $scCO_2$  at 400 rpm with the turbine.



**Figure 6:** Experimental internal heat transfer coefficient for two  $scCO_2$  densities and liquid water.

The internal heat transfer coefficient is improving asymptotically close to the critical point for  $scCO_2$ . This tendency is drastically opposite from the one of water where  $h_r$  is improving quite linearly with the temperature. To understand why this particular behavior occurs with  $scCO_2$ , we should have a look back to the equation 3. The correlation of the Nusselt number relates the internal film coefficient with the Reynolds number at a power  $2/3$  and to the Prandtl number at a power  $1/3$ . The quantities  $c_p$ ,  $\lambda$  and  $\mu$  in equation 3 are those of interest, the other parameters remaining constant with temperature. The combination of the diverging behavior of  $\lambda$  and  $c_p$  explains the one of the internal heat transfer coefficient  $h_r$  as this last is proportional to  $\lambda^{2/3}$  and  $c_p^{1/3}$  and is thus, submitted to the same asymptotic divergence in the vicinity of the critical point.  $h_r$  is also inversely proportional to viscosity  $\mu$  at a power  $1/3$ . Viscosity shows also some divergence around the critical point, but in contrary to heat conductivity,  $\mu$  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).

Theoretical values for  $c_p$ ,  $\lambda$  and  $\mu$  (obtained from NIST) and experimental  $h_r$  have been used to calculate the constant C of the Nusselt correlation equation (eq. 3). An example of the results for the two stirrers and a  $scCO_2$  density of 540 kg/m<sup>3</sup> is presented in figure 7. The global constant C values for each stirrer and all experiments are  $0.53 \pm 0.03$  for the turbine and  $0.27 \pm 0.03$  for the MIG. C values are well known to be depending on the system and agitator types as well as the reaction media. These results indicate that supercritical fluids cannot be considered as classical liquids and that parameters values available in literature for conventional liquid media could not be used directly for supercritical phases.



**Figure 7:** C values for the turbine and the MIG at scCO<sub>2</sub> density of 540 kg/m<sup>3</sup>.

## CONCLUSION

This new supercritical calorimeter system allows the evaluation of calorimetric measurements under supercritical conditions which is definitely not trivial. However, the complex phenomena of heat transfer with SCFs should be carefully taken into account in order to proceed with correct chemical reactions evaluation.

Some preliminary results in the “supercritical reaction calorimetry” field have been presented: The Wilson plot study allowed the understanding of the fundamental behaviour of the internal film coefficient, which does not follow the same tendency as for classical liquids with respect to temperature, due to the very specific properties of scCO<sub>2</sub> near its critical point. On the other hand, the linear trends of the Wilson plot regressions confirm the 2/3 value of the power of the Reynolds number in the Nusselt expression which equation was used to calculate the constant C for our system.

## ACKNOWLEDGEMENT

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