Supercritical Reaction Calorimetry: A Novel Route to Supercritical Fluid Reaction Monitoring

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Supercritical fluids have been intensively investigated during the past decade as alternative, environmentally benign reaction solvents, in order to eliminate the use of toxic and flammable organic solvents and the generation of large volumes of aqueous waste. The most common among them is carbon dioxide, due to its easily attainable critical temperature (31.1°C) and pressure (7.38MPa) [1]. A new analytical technique is derived from the merge of classical heat flow reaction calorimetry and the supercritical fluid technology, namely the supercritical reaction calorimetry [2].

The experimental set-up used is shown in picture 1 and consists of a bench scale autoclave (approx. 1.3liter), coupled with a Mettler-Toledo RC1*e* calorimeter. The whole system is fully computer controlled and able to operate up to 300°C and 35MPa. The inserts of the reactor consist of a magnetically driven stirrer, a calibration heater, temperature and pressure sensors, and an ultrasound probe (Picture2). Moreover, the cover of the reactor has a sapphire window which permits optical observation of the reaction conditions. This equipment allows us to combine calorimetric measurements with optical observations and speed of sound information, in order to monitor reactions with supercritical fluids in more detail.

Picture 1. The reactor-calorimeter system

Picture 2. The inserts of the reactor (ultrasound probe, stirrer, heater, temperature sensor)

The primary challenge in supercritical reaction calorimetry is that the reaction medium occupies not only a part of the reactor as in classical calorimetry, but all the available volume. For that both the reactor cover and the reactor flange, that come into contact with the medium and contribute to the heat transfer, had been modified in order to be thermally controlled.

In reaction calorimetry the major assumptions that permit the expression of the following main heat flow equation are the temperature and the composition homogeneity in the reactor. Thus the fact that the heat accumulation in the reactor equals the inflow minus the outflow of heat is mathematically interpreted as [3]:

$$\sum\left(\rho_i V_i c_{p,i} + m_{ins} c_{p,ins}\right)\frac{dT_r}{dt} = \left(\dot{Q}_r - \dot{Q}_{dos} + \dot{Q}_{mix} + \dot{Q}_{stir} + \dot{Q}_{calib}\right) - \left(\dot{Q}_{flow} + \dot{Q}_{loss}\right) \tag{1}$$

The term that we will focus on in our analysis is the heat flow from the reaction medium to the reactor ($\dot{Q}_{flow}$). In classical calorimetry this term is calculated using the following equation.

$$\dot{Q}_{flow} = UA(T_j - T_r) \tag{2}$$

On the other hand in our case of supercritical fluid calorimetry we have to take into consideration the heat transfer contribution of the two additional reactor parts, namely the reactor cover and the reactor flange. Hence, this term becomes more complicated and can be expressed by means of the following equation.

$$\dot{Q}_{flow} = UA(T_j - T_r) + U_{cover} A_{cover}(T_{cover} - T_r) + U_{flange} A_{flange}(T_{flange} - T_r) \tag{3}$$

To validate such a development, the calibration heater was used to simulate an exothermic reaction by introducing a known amount of heat, and the response of the system was monitored. The results are shown in Figure 1, where $\dot{Q}_{calib}$ is the heat introduced by the calibration heater. Ideally, the reactor response signal should be exactly the same as the heat introduced. However, the reactor's initial delay of response (inertia) and the heat losses to the surroundings are responsible for the deviation and overshoot of the curve. When the accumulation term $\dot{Q}_{acc}$ is introduced, the response oscillates around the calibration heat curve showing a better behavior, yet without significantly improving the time needed to coincide. Finally, it can be clearly seen that when all the terms are taken into consideration ($\dot{Q}_{flow} + \dot{Q}_{acc} + \dot{Q}_{cover} + \dot{Q}_{flange}$) in the heat flow equation, the response of the reactor although it oscillates due to the accumulation term, coincides with the calibration heat introduced, in almost half the time. Consequently the hypothetical reaction is better monitored with the modified heat balance equation.

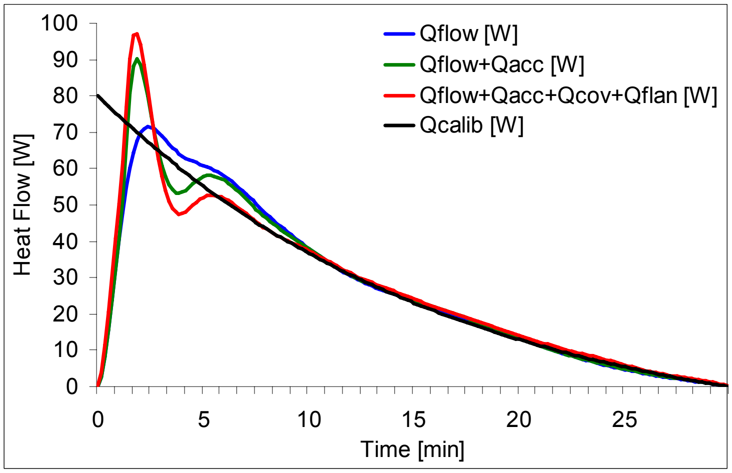

Figure 1. Correction of the system's response by introducing the two new terms in the heat flow equation.

After the investigation of a hypothetical reaction, we proceeded with the performance of a model reaction in the reactor. For that purpose we have chosen the esterification of acetic anhydride with methanol. The reaction was performed in both classical organic solvent (THF) and supercritical carbon dioxide ($scCO_2$). Results are presented in Figure 2.

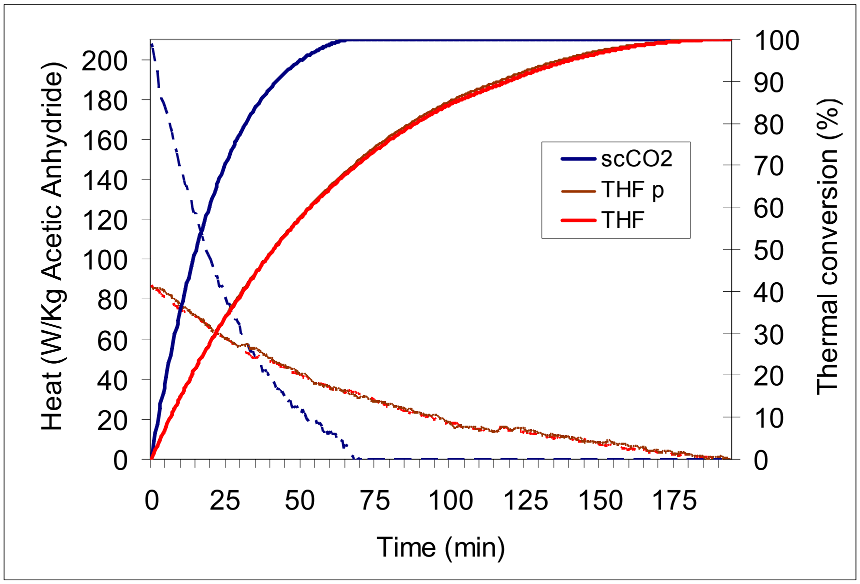

Figure 2. Reaction acceleration with supercritical fluids as reaction media.

As a first step the reaction was performed in the organic solvent at atmospheric pressure. The reaction was considered complete when the difference between the reactor temperature and the jacket temperature was stabilized, meaning that no more heat was dissipated through the reactor walls due to the exothermic reaction. The thermal conversion presented is the ratio of the accumulative heat released at any point of time over the total heat of the reaction.

Secondly the reaction was carried out using supercritical carbon dioxide as solvent. The initial mixture of methanol and $scCO_2$ was selected so that the initial mixture was a homogeneous supercritical one [4]. The resulting initial pressure of the reaction was 120 bar. Figure 2 shows that the reaction occurred much faster than in the classical solvent, and reached 100% thermal conversion in almost one third of the time. However an important difference between these two reactions is the pressure. Therefore a third experiment had to be performed to investigate the role of the pressure in the acceleration of the reaction.

In this third reaction THF was used again but the mixture was pressurized in the reactor using an inert gas (N_2) at the same pressure of 120 bar. The superposition of the curves of the first and the third experiment reveal that the pressure has actually no influence at all on the reaction rate. Therefore the observed acceleration in $scCO_2$ has to be attributed to the intrinsic properties of the supercritical solvent.

Indeed as it can be seen in Figure 3 two significant intrinsic properties of $scCO_2$ that play an important role are the density and the viscosity. Both properties exhibit much lower values than the respective ones of a liquid phase, facilitating in this way the movement of the molecules and thus accelerating the reaction.

This last remark brings us to another part of our investigation, which is the overall heat transfer coefficient between the reaction medium and the jacket's cooling liquid. In non-dimensional analysis the Nusselt correlation relates the three important numbers, i.e.

the Nusselt, Prandtl and Reynolds numbers, and describes the heat transfer through convection.

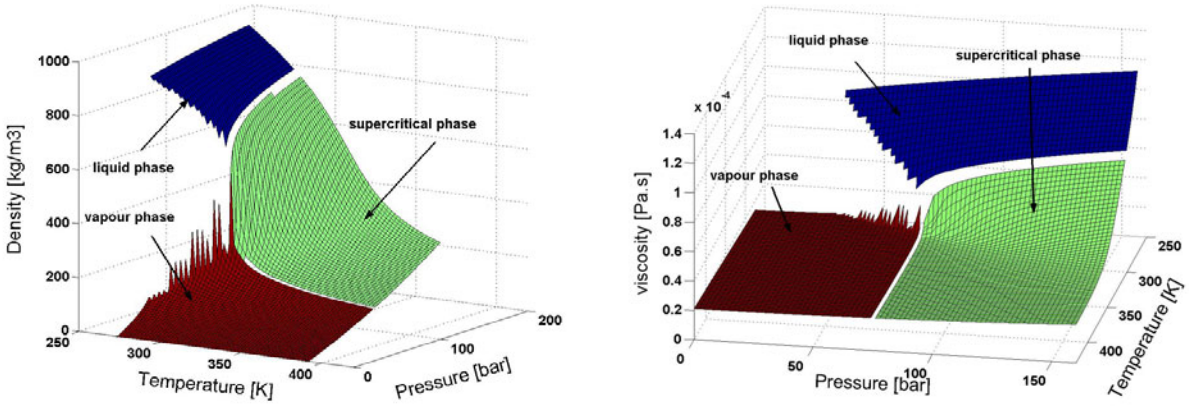

Figure 3. Density and viscosity of $scCO_2$ as predicted by the Span and Wagner EOS

By substitution of the analytical expressions for these numbers we can finally derive an equation that relates the overall transfer coefficient (U) with the stirring speed. Analytical derivation can be found elsewhere [5].

$$\frac{1}{U} = C'\frac{1}{N^a} + \frac{1}{\varphi} \tag{4}$$

This study is focused on the application of this correlation in the case of supercritical fluids. For that purpose, several Wilson plots have been produced, where the resulting overall heat transfer coefficient was calculated, using the calorimeter, for pure $scCO_2$, at different temperatures, different stirring speeds and for different CO_2 densities. Selected results are presented in Figure 4 and they clearly demonstrate the linear trend of the 1/U values with respect to $N^{-2/3}$, with the exception for 100rpm, where the reaction content appears not to be homogeneous and the linearity does not apply. This proves that the exponent of 2/3, for classical liquids in stirred tank reactors, can be also used in the case of supercritical carbon dioxide. Furthermore, the constant C' can be calculated from the slope of the regression lines. For carbon dioxide we have found this constant to be 0.53.

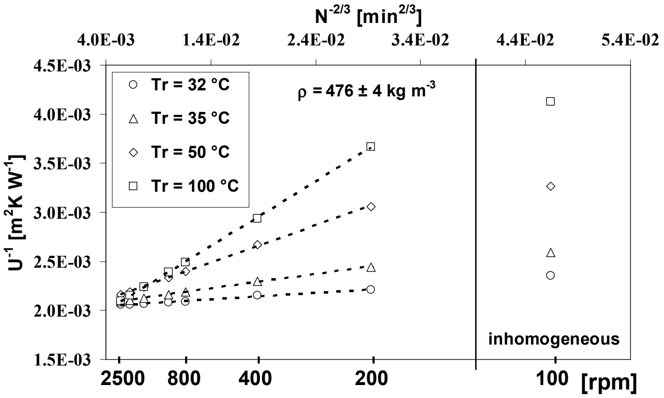

Figure 4. Selected Wilson plot in pure scCO2. The vertical line schematically delimits the region where the system is no longer homogeneous, due to the low rotation speed

Furthermore the y-interception of the regression lines gives us the second right-hand side term of equation 4, which is the contribution of the reactor's characteristics in the overall heat transfer coefficient. Having found that, we can reverse the calculations and find the film heat transfer coefficient for pure $scCO_2$ through the following equation.

$$\frac{1}{h_r} = \frac{1}{U} - \frac{1}{\varphi} \tag{5}$$

Results of these calculations are presented in Figure 5, where it is shown that $scCO_2$ demonstrates a decrease of h_r with increasing temperature. Such behavior is completely opposite to that of classic liquids, such as water.

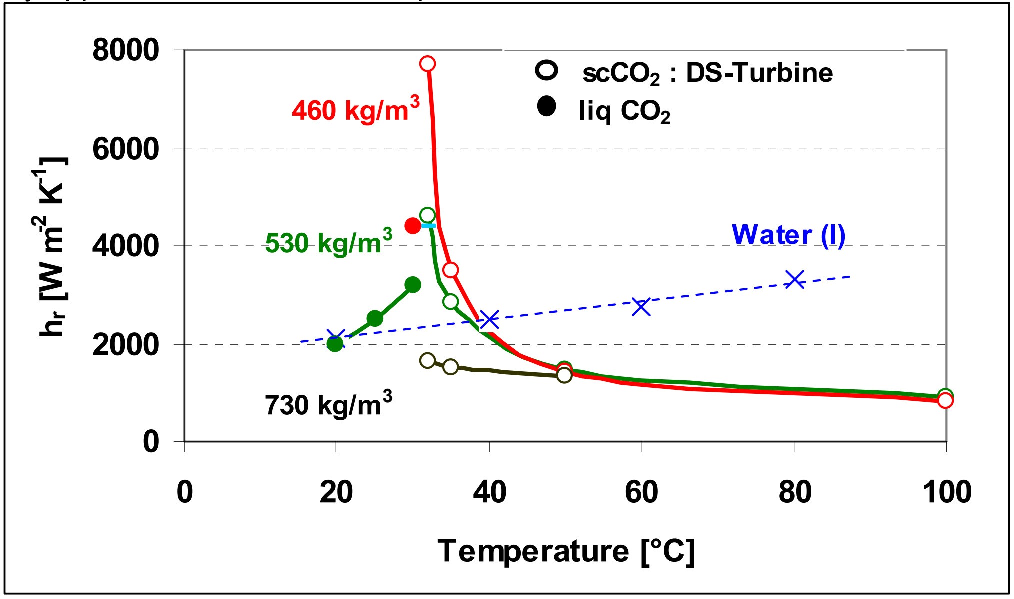

Figure 5. Variation of the film heat transfer coefficient for pure $scCO_2$ with temperature, in comparison with water

Another important observation with regards to the heat production and dissipation capability during the reaction when using SCFs is that when an exothermic reaction is performed at a higher temperature, acceleration occurs and the released heat is higher as well. For classic organic solvents, with increasing temperature also the internal heat transfer coefficient (h_r) increases, which results in the increase of the overall heat transfer coefficient (U). Hence, the reaction system remains relatively safe, as more heat can be removed in a situation where more heat is produced. However, when using SCFs, the internal heat transfer coefficient decreases with increasing the temperature. Thus, there is a distinct limit of the heat that can be dissipated. As a result a compromise has to be made between a high reaction temperature, where the reaction will be faster, but less safe, and a low reaction temperature, where the reaction will be slower but within the safety limits in terms of heat removal.

References

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