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Particularities of Calorimetry with Supercritical Fluids

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During the past years there is an increasing interest for the development of environmentally benign chemical processes. For that purpose, supercritical fluids are investigated as alternative 'green' solvents in numerous chemical reactions. The most widely used is the carbon dioxide because it has an accessible critical point (73.8 bar, 31.1 °C), it is less expensive with respect to other organic solvents and is non-toxic and non-flammable.

Reaction calorimetry is an efficient tool used to obtain kinetic, thermodynamic and safety data. This information is crucial to promote supercritical fluid processes applied to chemical reactions. 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.

When heat flow calorimetry is applied to reactions using SCF as reaction media, the particular heat transfer behavior of these fluids has to be considered. Especially in the vicinity of the critical point, the physical and the thermodynamical properties of SCF exhibit drastic changes as two distinct phases, namely the gas and the liquid phase, merge to create the supercritical one. Heat transfer efficiency in SCF has been shown to decrease with increasing the temperature, whereas classical liquids show exactly the opposite behavior. This effect, explainable by applying the appropriate thermodynamic behavior, has a direct impact on the overall heat transfer coefficient and consequently on the heat dissipation in the media.

This effect of decreasing heat transfer capability is coupled with the fact that in reactions using SCFs as solvent a certain acceleration is observed due to their particular transport properties. The esterification of acetic anhydride with methanol has been chosen as a model reaction to investigate this acceleration and interesting results are derived.

Finally, the reaction mixture in supercritical conditions does not occupy only part of the reactor volume, but all the available volume, considering that it is in the supercritical state. Therefore, it comes into contact with the reactor cover and the reactor flange. Thus, both the cover and the flange temperature have to be controlled in the same way the reactor jacket temperature is. This effect is interpreted in the heat flow balance, by introducing two additional terms, with respect to classical calorimetry, namely, the reactor cover heat flow term ($\dot{Q}_{flow,cover}$) and the reactor flange heat flow term ($\dot{Q}_{flow,flange}$).