

Precise Heat Capacity Determination of Organic Heat Transfer Fluids

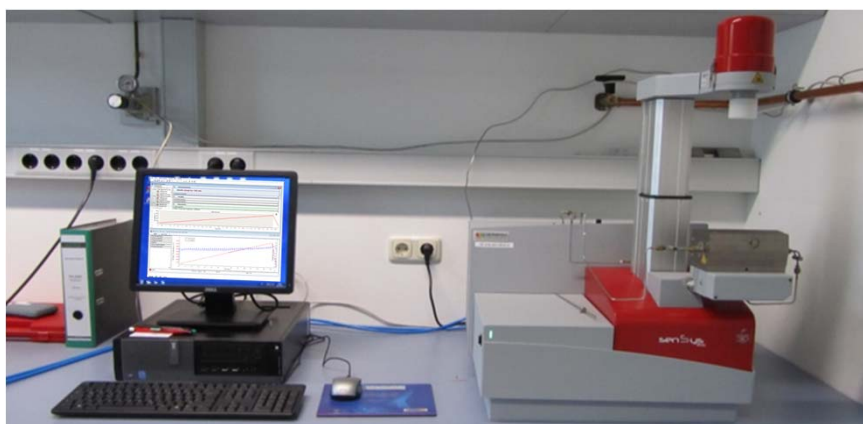


Fig. 1: Differential Scanning Calorimetry with Calvet-Detector for precise heat capacity determination of HTFs

Background

Organic heat transfer fluids (HTF) are typically used for the thermal control of manufacturing or processing operations in a range of 140 – 400 °C. The heat transfer systems can be often designed for almost no or low excess pressures due to the low vapor pressures of organic HTFs. Organic heat carriers are also used in the energy technology since they allow the transfer of heat up to 400 °C with relatively low demands on the apparatus technology.

The most common HTF in solar thermal parabolic trough power plants is an eutectic mixture of diphenyl oxide (DPO) and biphenyl (BP). HTFs based on silicone oil (e.g. Syltherm 800) are also applied but so far only in test facilities.

For the layout of HTF systems the essential HTF characteristics must be known in the operating temperature range according to DIN 51522. For solar thermal power plants the heat capacity is particularly important as it affects the costs.

Heat capacity measurement

Differential Scanning Calorimetry (DSC) is most commonly used for the heat capacity determination. The measurements are performed according to ASTM E 1269 (a relative measurement against sapphire) and represented as specific heat capacity in the technical data sheets in the form of compensatory functions. Since no measured values are reported in the data sheets, the uncertainty of the data and the temperature range that is actually covered by measurements remain unclear.

Hence, an independent verification of these data in the entire operating temperature range of new or used heat transfer samples is of interest.

In order to perform measurements above ~300 °C the crucibles have to be made of steel to withstand the pressure of the sample. These crucibles exhibit relatively high masses and the heat flow which is detected by the DSC is mainly caused by the relatively high heat capacity of the crucibles. A sensitive instrument is necessary to differentiate the sample signal and the use of a spatial Calvet detector becomes essential. The latter provides a very high sensitivity for the heat flow measurements (1% uncertainty).

Analysis results

A Calvet DSC (Sensys evo, Setaram) was thermally calibrated by means of numerous references (In, Sn, Bi, Pb, and CsCl, Ag₂SO₄).

Since the Calvet detector was absolutely calibrated calorically (by Joule effect), the heat capacity was determined by an absolute measurement (step-method) instead according to ASTM E 1269.

The accuracy of the caloric and thermal calibration was confirmed with the measurement of single-crystal sapphire.

Dowtherm A as an example of the eutectic mixture of DPO/BP and Syltherm 800 as an example of a commercially available polydimethyl siloxane (silicone oil) were used (see figure 2 and 3, reference data in red). The heat transfer fluids were investigated in mint condition with varying filling levels of the crucibles.

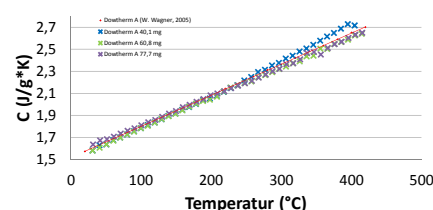


Fig 2: Heat capacity measurements of Dowtherm A

In the case of the eutectic mixture a low sample quantity results in larger heat capacities at high temperatures.

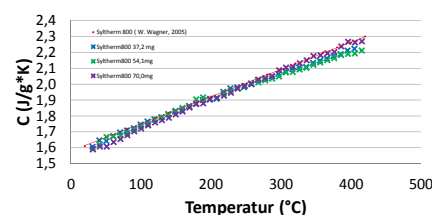


Fig 3: Heat capacity measurements of Syltherm 800

Smaller values were found at high temperatures by measuring low sample quantities of Syltherm 800. At the same time at low temperatures, the values slightly increase. The reproducibility of these data was confirmed by multiple measurements.

The applied evaluation method interprets the heat flow into the sample as being solely caused by the heat capacity during the heating of the sample. Actually, the HTFs are not only heated up and the impact of evaporation processes on the heat flow has to be taken into account. In addition, the density of the samples decreases considerably with temperature. Hence, at the same time the gas volume decreases continuously while the sample expands. Thus in the DSC measurement of volatile HTFs, enthalpies of vaporization and condensation or volatilization and absorption of dissolved light boilers will be detected. In particular for low filling levels of the crucibles, these processes can affect significant enthalpy contributions. In order to achieve more reliable heat capacity data, a set of samples with maximal filling of the crucibles should be measured over the temperature range of interest.

The authors would like to thank the Federal Ministry for Economic Affairs and energy for funding the project SI-HTF (0325453C).

Supported by:

