1 Aim

The aim of the experiments carried out within this study is to show the accuracy of the Syrris Atlas Calorimetry system with respect to low temperature calorimetry applications.

2 Method

350ml of Methanol was cooled to -10°C whilst being overhead stirred in an Atlas Potassium jacketed vessel system.

To this cold, stirred mixture was added 100ml of Methanol via an Atlas Syringe pump, this Methanol was added at room temperature (21°C).

The temperature was maintained isothermally at -10°C during the Calorimetry experiments.

The experiment was carried out under Power Compensation Calorimetry (PCC) control.

3 Theoretical Calculations

The Overall Enthalpy 'Q' can be expressed as the addition of the three enthalpies as below:

$$Q = \Delta H_R + \Delta H_{add} + \Delta H_X$$

Enthalpy of Reaction and Enthalpy of Solvation are = 0KJ in this case as we are adding Methanol to Methanol.

So, therefore: $Q = \Delta H_{add} = Cp \cdot M_X \cdot (T_f - T_i)$

Q being the overall enthalpy measured by the software.

Key

- Q= Overall Enthalpy
- ΔH = change in energy of the system
- T_f = Circulator fluid temperature
- T_i = Internal temperature
- Cp = Specific Heat Capacity at a constant pressure.

The Theoretical calculation is therefore:

- M is 80g [100ml x 0.8 (density of MeOH)]
- Cp is 2.5j/g/K at -10°C
- Temp difference: 31°C

Therefore Enthalpy of addition should be 6.2KJ. (Theoretical value)

4 Results

4.1 Power Compensation Calorimetry

The reactor temperature is shown in Figure 1: Reactor and Circulator temperature, and is shown to be isothermally held at -10°C, with the circulator temperature maintaining -17°C.

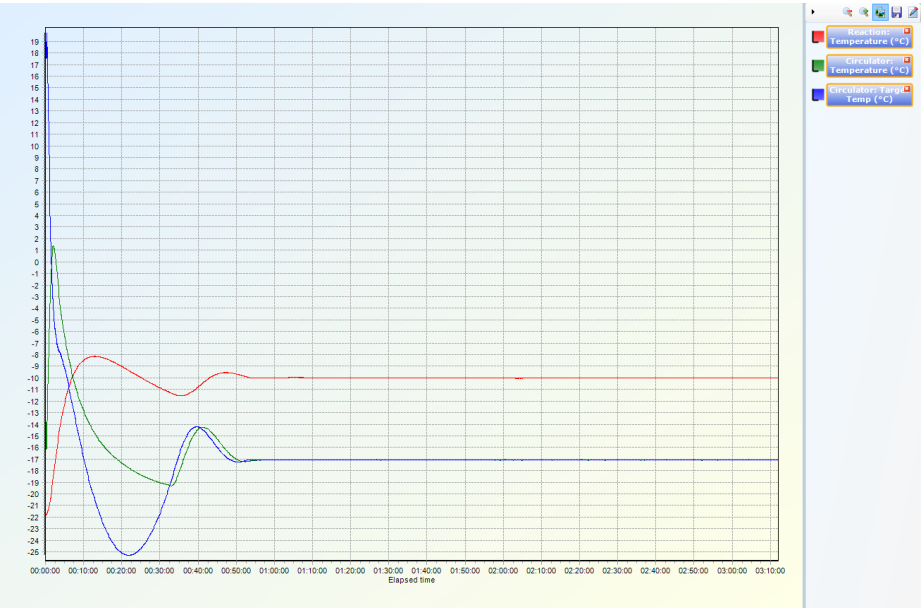

Figure 1: Reactor and Circulator temperature

The dosing from the Atlas Syringe pump of 100ml of room temperature Methanol is shown in Figure 2: Atlas Pump Volumetric Dosing below.

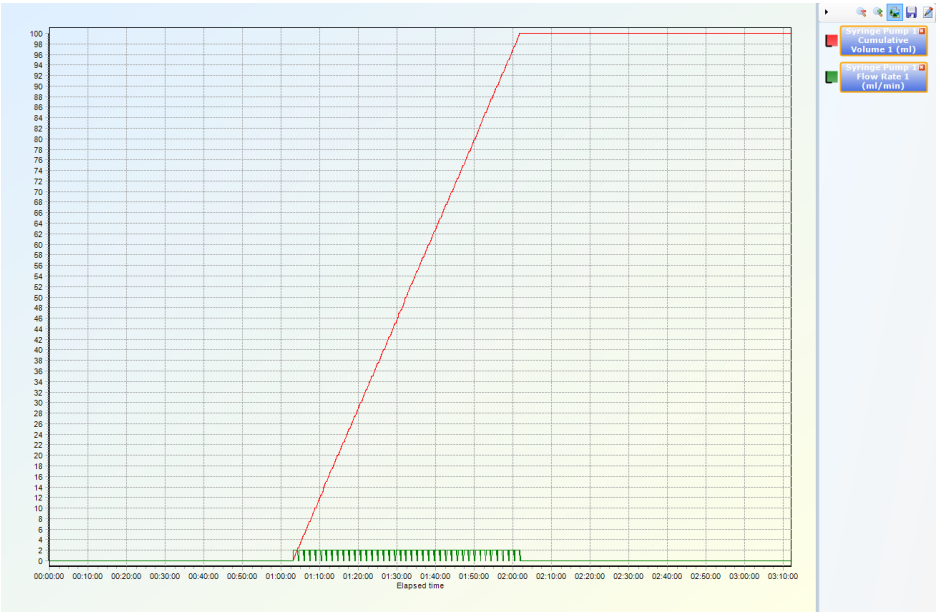

Figure 2: Atlas Pump Volumetric Dosing

The overall enthalpies of the addition reaction are shown in Figure 3: Overall Enthalpy, shown below.

This graph shows that the enthalpy of addition for this reaction is 6.3KJ.

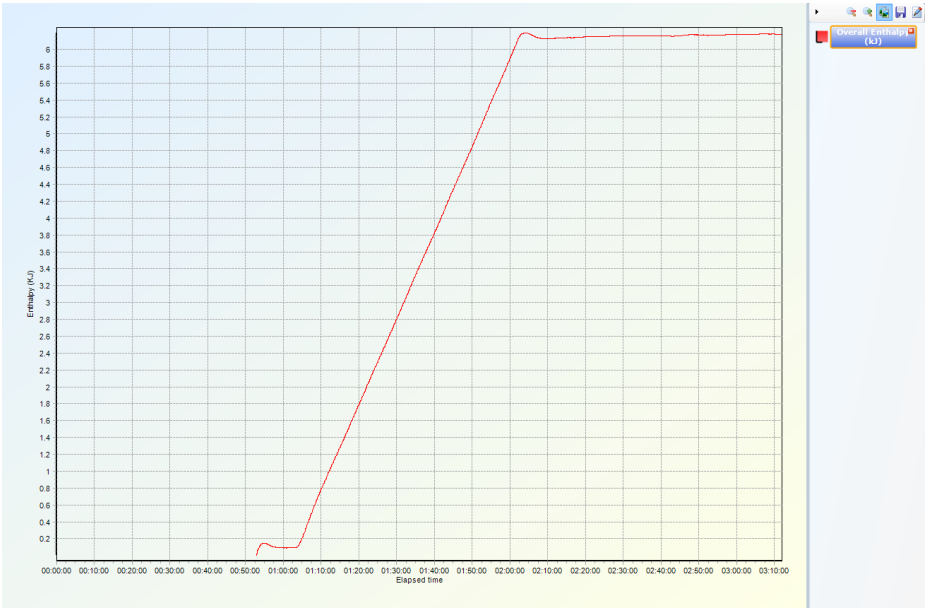

Figure 3: Overall Enthalpy

It is also shown, in Figure 4: Enthalpy and Temperature Comparison below, that during the addition and calorimetry experiment the temperature of the reaction did not deviate from the isothermal -10°C by more than 0.1°C.

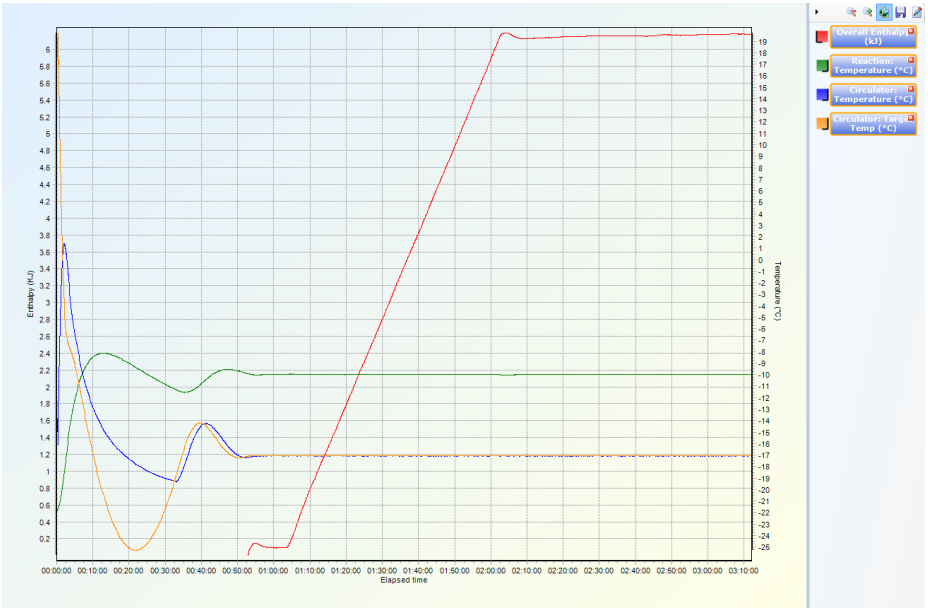

Figure 4: Enthalpy and Temperature Comparison

It is also shown that the increase in enthalpy is directly related to the dosing strategy, see Figure 5: Enthalpy and Dosing Comparison, below

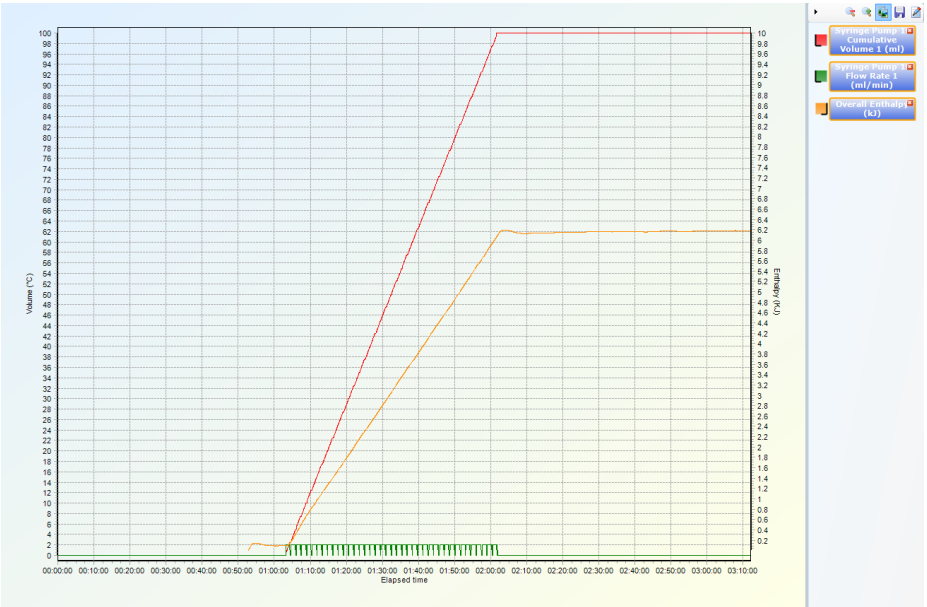

Figure 5: Enthalpy and Dosing Comparison

5 Conclusions

These results show that Power Compensation Calorimetry can be carried out at sub-ambient conditions with very accurate results on the Atlas system.

These results show that the overall reaction enthalpy for the addition of 100ml of room temperature Methanol to 350ml of Methanol at -10°C has been measured to be 6.3KJ.

The experimentally obtained value of 6.3KJ is only a 1.6% deviation from the theoretical value of 6.2KJ.

These results show that low energy reactions, with enthalpies lower than 7KJ, can be measured accurately with the Atlas Calorimetry software.

It is also shown, that the internal reaction temperature (Ti) can be maintained within 0.5°C even with reactions taking place at very low, sub-zero temperatures.

6 Acknowledgements

The author would like to thank Marc Ujma of YMC Europe for obtaining the data used within this application note.