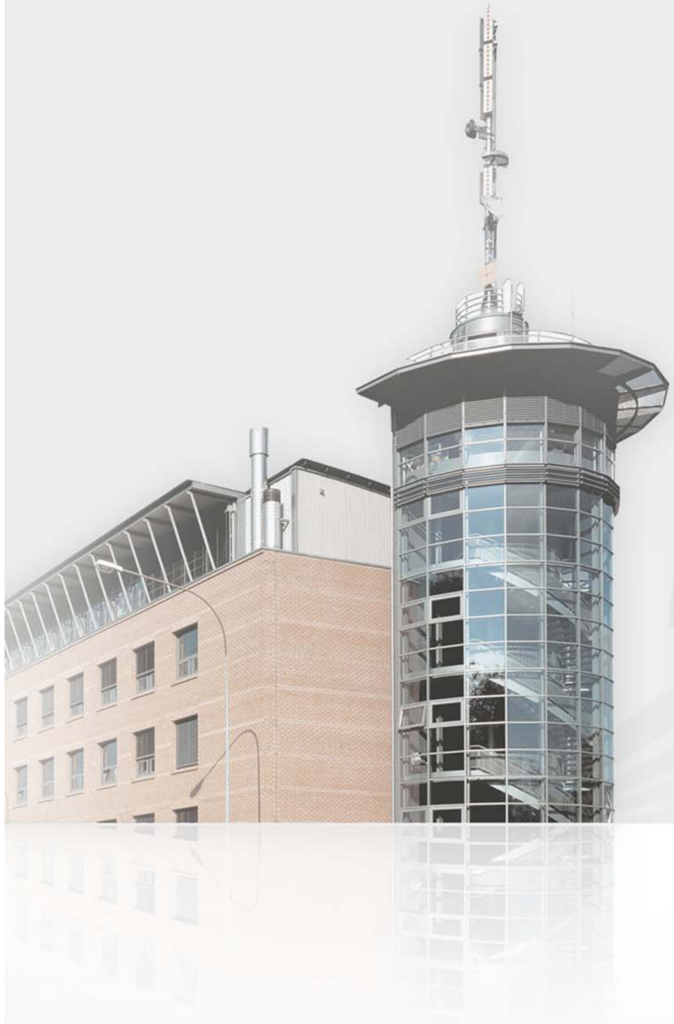

Haute école d'ingénierie et d'architecture Fribourg
Hochschule für Technik und Architektur Freiburg

Custom-made ml-scale Reaction Calorimeter for thermal safety screening purposes

ChemTech
Institute of Chemical Technology

Hes·so // FRIBOURG FREIBURG
Haute Ecole Spécialisée de Suisse occidentale
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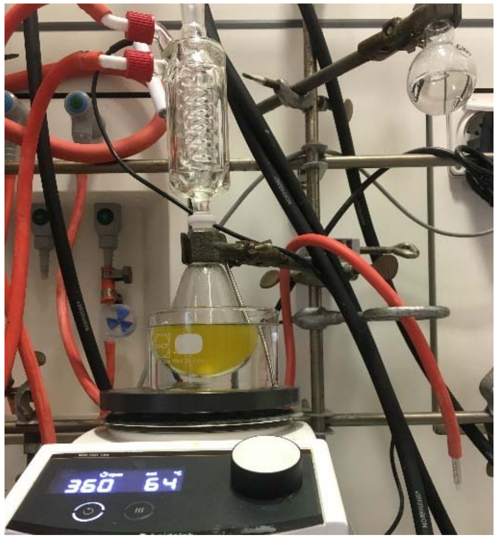
University of Applied Sciences and Arts Western Switzerland

ChemTech | 24/11/2020 | **Caitlin Blum** & Thomas Ferrari & Lara Amini & Michal Dabros & Pierre Brodard & Roger Marti

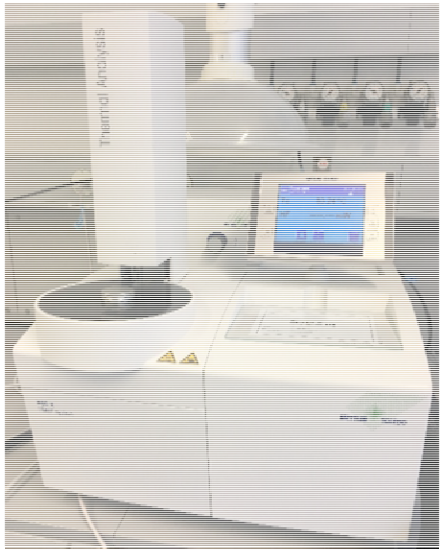
Introduction

- Thermal safety of reactions and substances
  - Important to know how a substance reacts to avoid incidents when doing the reaction at a larger scale



Introduction

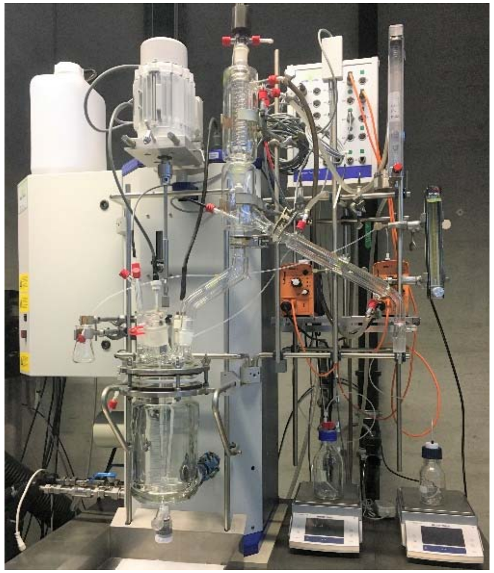
- Calorimeters for thermal safety analysis of substances
    - DSC
    - C80 Calvet Calorimeter



Very small volumes → possible to test reaction up to the runaway with limited risks

Introduction

- Calorimeters for thermal safety analysis of reactions
  - EasyMax 50-100ml
  - RC1 500-2000ml



Larger volumes → can't afford to go up to the runaway

Introduction

- Calorimeters for thermal safety analysis of reactions
  - Nanocalorimetric platform[1] nl-µl scale
  - THT Micro reaction calorimeter µl scale

New instruments with small volumes

[1] ***RSC Adv.***, 2015,**5**, 97133-97142

Our Goal

- Build a custom-made ml-scale calorimeter that meets a need for an on-going project

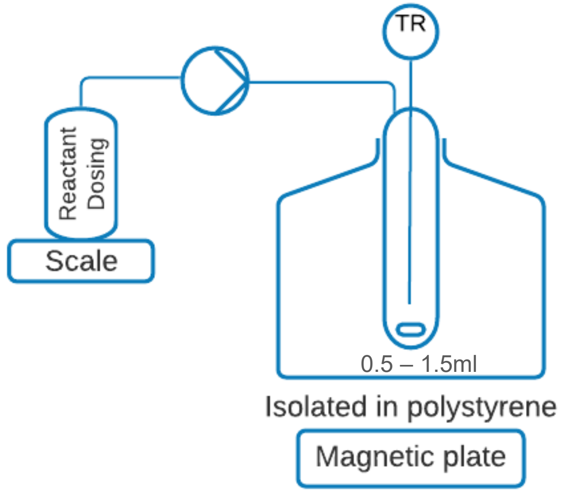
→ Quick set-up and easy to use

→ Adaptable set-up for research purposes

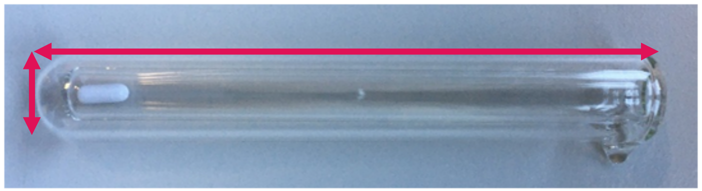
→ Tests on small volumes

→ Safe screening of highly exothermic reactions

First Set-up Idea



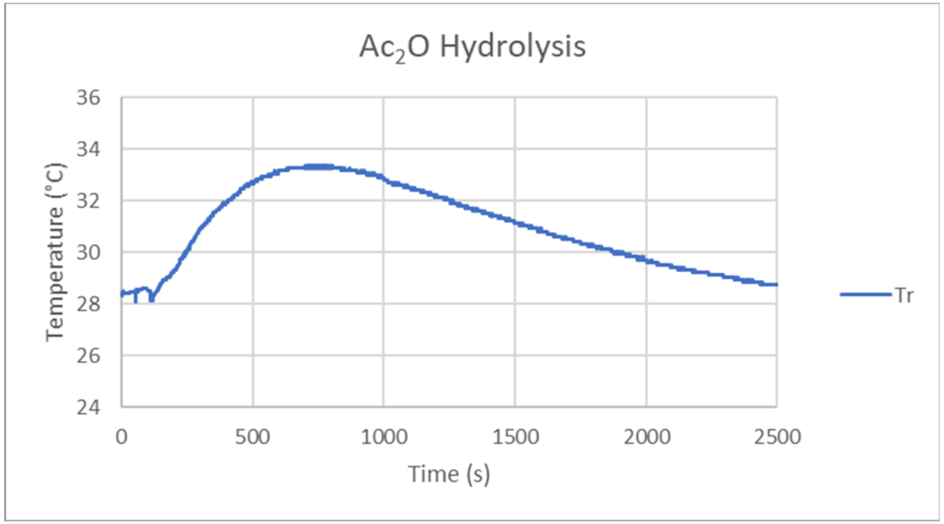
- Custom-made double jacketed test tube with magnetic stirrer

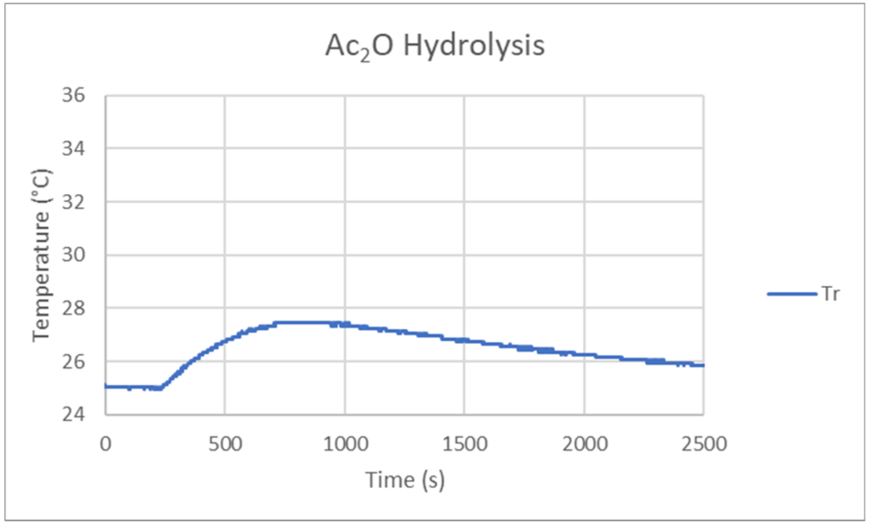


90x10mm

First result on known reaction

- Acetic anhydride hydrolysis:





	Experimental Value		Literature Value
Ac_2O Hydrolysis	ΔT_{ad} (°C)	ΔrH (kJ/mol)	ΔrH (kJ/mol)
Experiment – left	25°C	-58.7 kJ/mol	-58.6 ± 0.4 kJ/mol[2]
Experiment – right	14°C	-29.6 kJ/mol	

[2] Acetic anhydrid, NIST, https://webbook.nist.gov/cgi/cbook.cgi?ID=108-24- 7&Units=SI, 14.07.2020

Challenges encountered

- Precision of heat loss calculation
  - From the reactor
  - From dosing the reactant

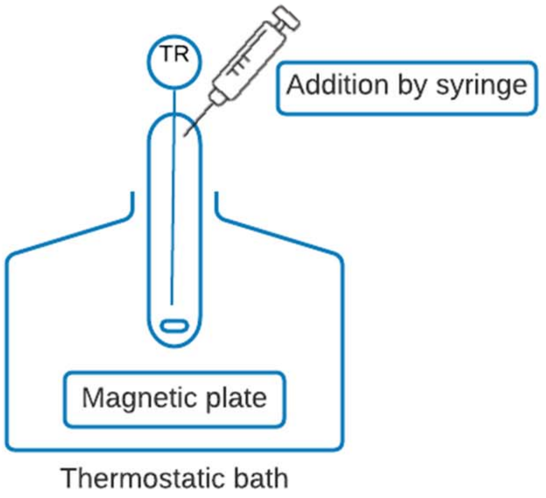
- Precision of the dosing mass

New set-ups tested

- Dosing by syringe instead of pump
- Other isolating material
- In thermostatic water bath

Current Design

New calorimeter set up in thermostatic bath



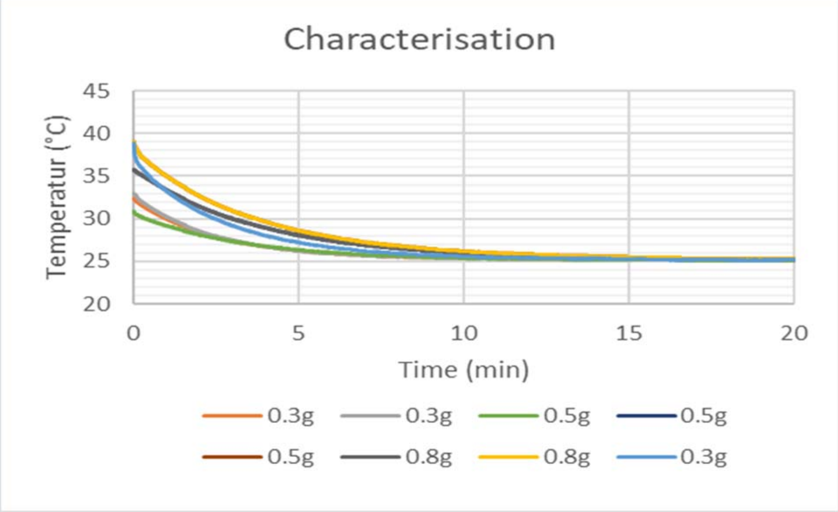
System specifications:
- Reactor volume: 2.2 mL (working volume 0.5 – 1.5 mL)
- Temperature probe: Thermocouple Type K
- Temperature recording via LabView
- Magnetic stirrer: 100 – 1600 rpm
- Addition by syringe

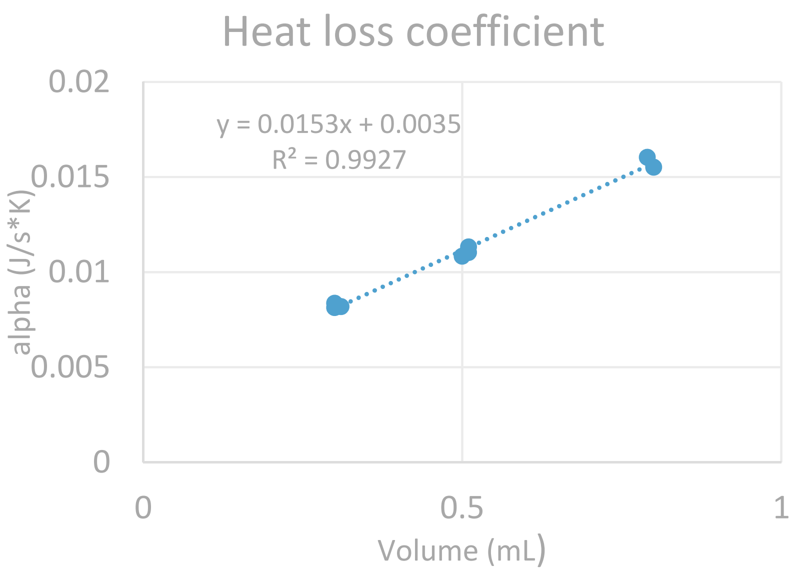
Calorimeter Characterisation

Dewar Calorimeter Characterisation:

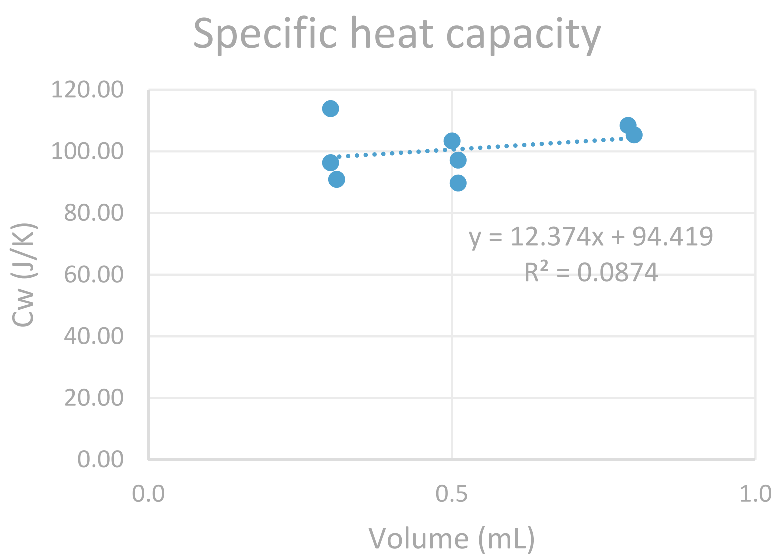
1.) α [W/K] : heat loss coefficient
2.) Cw [J/K]: specific heat capacity of the calorimeter

Method for the experiments:
Three different volumes of hot water (35-45°C) were introduced in the reactor and then wait until temperature is stable (around RT)





α for 0.5mL: **0.0111 W/K**



Cw for 0.5mL: **100.6 W/K**

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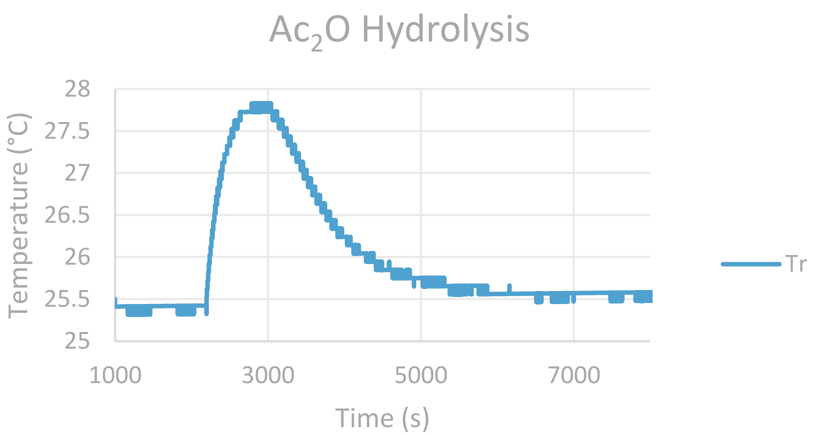
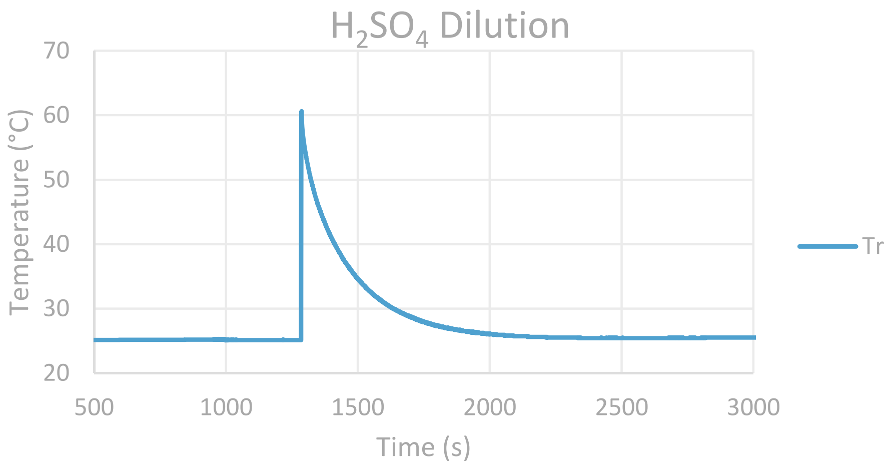
Calorimeter Validation

Validation by $\Delta_r H$ and ΔT_{ad} determination of Ac_2O hydrolysis & H_2SO_4 dilution:





Example mass balance Ac_2O Hydrolysis:

$$\underbrace{\cancel{IN} - OUT}{} + RXN = ACC$$

$$-Qloss - Qdos + Qrxn = Qacc$$

$$-27 - 0.44 + Qrxn = 6.8$$

$$Qrxn = 34.5\,J$$

$$\Delta rH = \frac{Qrxn}{n(Ac2O)} = 58.7\ \text{J/mol}$$

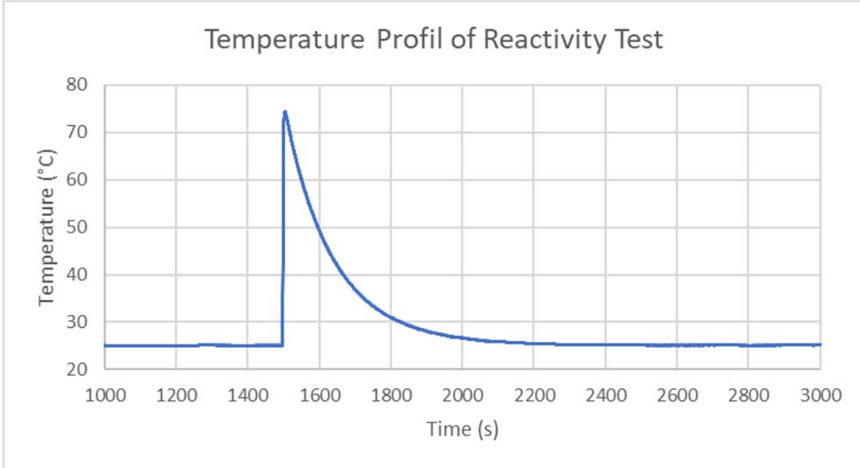
$$\Delta Tad = \frac{Qrxn}{cpr} = 25°\text{C}$$

	Experimental Value		Literature Value
	ΔT_{ad} (°C)	ΔrH (kJ/mol)	ΔrH (kJ/mol)
Ac_2O hydrolysis	29°C	-56.1 ± 5.7 kJ/mol	-58.6 ± 0.4 kJ/mol[2]
H_2SO_4 dilution	44°C	-56.8 ± 10.5 kJ/mol	-61.8 ± 0.5 kJ/mol[3]

Both experiments were repeated in triplicate

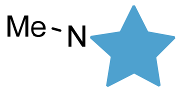
[2] Acetic anhydrid, NIST, https://webbook.nist.gov/cgi/cbook.cgi?ID=108-24- 7&Units=SI, 14.07.2020
[3] Value found from previous experiments on EasyMax/RC1

Our application



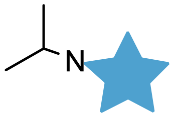
- Reaction screening
- Measure high exotherms with limited risks
- Observe effect of different substituents on the reaction enthalpy

Reactivity results



Model compound

ΔT_{ad}	57.7 ± 4.6°C
ΔrH	894.5 ± 73.6 kJ/kg



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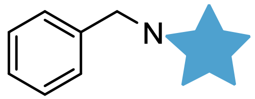
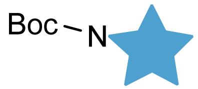
ΔT_{ad}	64.4 ± 2.9 °C
ΔrH	763.6 ± 33.9 kJ/kg



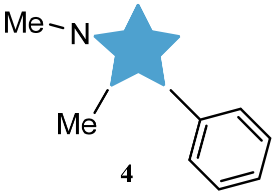
2*

ΔT_{ad}	71.0 ± 10.5 °C
ΔrH	756.2 ± 115.4 kJ/kg

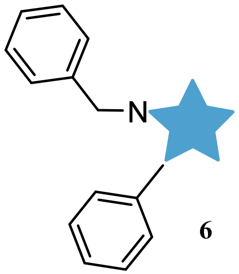


3*

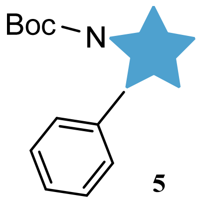
ΔT_{ad}	40.2 ± 2.1 °C
ΔrH	676.4 ± 37.4 kJ/kg



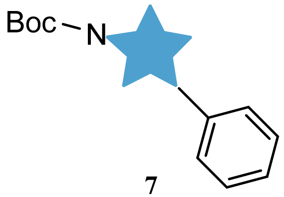
ΔT_{ad}	44.4 ± 2.3 °C
ΔrH	471.9 ± 25.1 kJ/kg



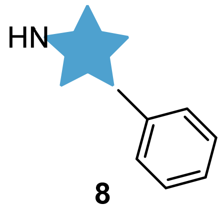
ΔT_{ad}	42.4 ± 2.4 °C
ΔrH	451.1 ± 26.1 kJ/kg



ΔT_{ad}	33.50 ± 2.4°C
ΔrH	456.6 ± 31.2 kJ/kg



ΔT_{ad}	8.4 ± 1.5 °C
ΔrH	88.9 ± 16.0 kJ/kg



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ΔT_{ad}	4.3 ± 1.4°C
ΔrH	49.5 ± 18.2 kJ/kg

* Solid formed during reaction which could have an influence on the measured temperature

Conclusion & Perspectives

- ✓ Works well for our application
- ✓ Easy and cheap set-up

Next Steps

- ➢ Tests with the higher limit of working volume of the calorimeter
- ➢ Thermostat the syringe containing the [illegible]nt
- ➢ MS at exit of reactor

Acknowledgements

- Collaboration with Novartis

- Thanks to everyone who has worked or is still working on the project !

Thank you for your attention !

Any questions