

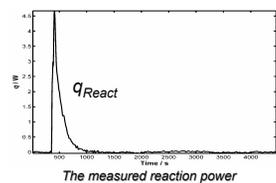
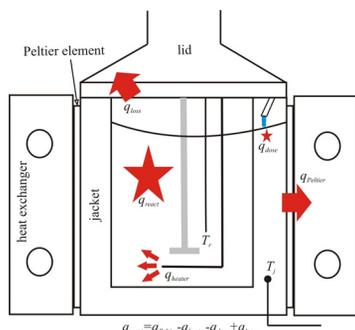
# Measurement and modeling of semi-batch reactions using small-scale reaction calorimetry, spectroscopy and gas consumption/production

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The rapid and complete characterisation of chemical reaction mechanisms is of the utmost importance in terms of chemical understanding, safety and efficiency. A family of new small volume semi-batch reactors (25-45mL), the combined reaction calorimeters (CRCs), have been developed for this purpose. With these reactors it is possible to make calibration free calorimetry measurements, *in-situ* UV-vis and IR measurements and gas production/consumption measurements. Additionally, any other probe type of appropriate dimensions can be used. The reactors have been and are being used for the characterisation of a number of reaction systems, with the hydrogenation of nitrobenzene and ethyl-4-nitrobenzoate given as an examples below. We are also working on the problem of how to fit a single chemical model simultaneously to the different types of analytical signals. To this end a multiobjective function genetic algorithm has been developed which allows the user to see the trade-off between the different objective functions for the optimised set of model parameters.

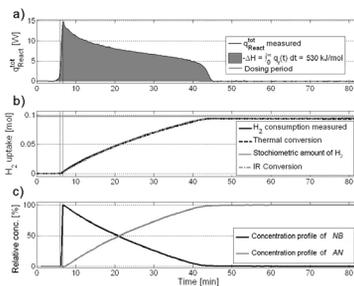
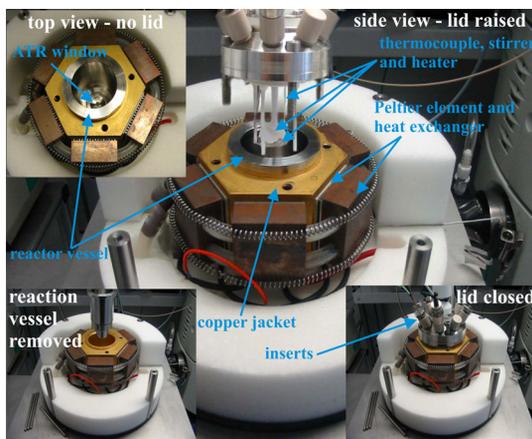
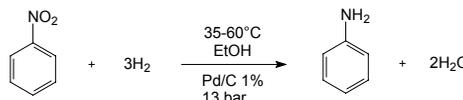
## Calorimetry Principle

Combining power compensation and heat-flow principles in a single device means **calibration free calorimetry**<sup>1</sup>.



## Hydrogenation Reactions

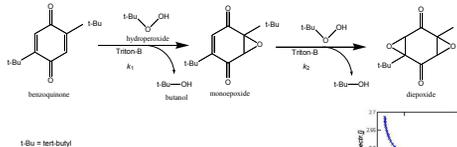
Because the reactor is **pressure-proof** multiphase reactions involving gas consumption or production can be studied. This example shows the hydrogenation of nitrobenzene at 50°C, using a Pd/C 1% dispersed solid catalyst and a H<sub>2</sub> pressure of 13 bar<sup>2</sup>.



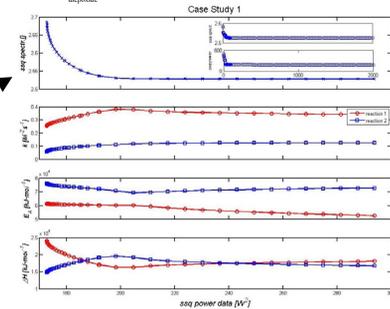
For the hydrogenation of ethyl-4-nitrobenzoate the **simultaneous measurement of calorimetry, spectroscopy and gas consumption** allows the formation of an **intermediate to be detected and quantified**.

## Modeling

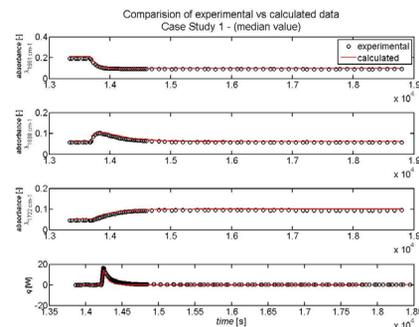
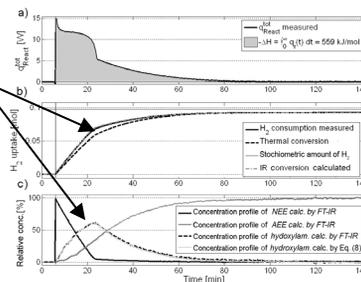
The goal here is the **fitting of chemical models to all the *in-situ* measurements simultaneously** for rapid and complete reaction characterisation. We use local optimization methods (e.g. Newton-Gauss) and a **multiobjective function genetic algorithm (MOGA)** in which Pareto optimality is used for selection step within the genetic algorithm. The application of the MOGA to spectroscopic and calorimetric measurements of the epoxidation of 2,5-di-tert-butyl-1,4-benzoquinone is shown below<sup>3</sup>.



Pareto optimal curve showing the trade-off between the spectroscopic and calorimetric objective functions.



The presence of an intermediate is suggested by the difference between thermal conversion and gas consumption and confirmed by the IR spectra and off-line HPLC.



<sup>1</sup> Visentin, F.; Gianoli, S. I.; Zogg, A.; Kut, O. M.; Hungerbühler, K. *Org. Process Res. Dev.* **2004**, *8*, 725-737.  
<sup>2</sup> Visentin, F.; Puxty, G.; Kut, O. M.; Hungerbühler, K. *Ind. Eng. Chem. Res.* **2006**, In Press.  
<sup>3</sup> Gianoli, S.; Puxty, G.; Fisher, U.; Maeder, M.; Hungerbühler, K. *Chemom. Intell. Lab. Sys.* **2006**, Accepted.

