Real-Time Kinetic Hard-Modelling for the Optimisation of Reaction Conditions and the Detection of Process Upset in Semi-Batch Reactors

Julien Billeter[1], Yorck-Michael Neuhold[1],
Graeme Puxty[2], Konrad Hungerbühler[1]

Contact: julien.billeter@chem.ethz.ch

[1]ETH Zürich, Institute for Chemical and Bioengineering,
Safety and Environmental Technology Group, Zürich, Switzerland.
[2]CSIRO Energy Technology, PO Box 330, Newcastle NSW 2300, Australia

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Safety and Environmental Technology Group

CSIRO

Motivation

- **Loss of productivity:** Fluctuations in reaction processes are partly due to variations in the concentration of initial reactants (sub-optimal operating conditions).

  Another source of fluctuations comes from impurities present in the initial reactants causing unexpected side reactions.

- **Loss of time:** Initial concentrations are often determined by offline analysis (e.g. HPLC, spectroscopy) and can result in delaying the batch start.

Trends in favour of online Kinetic Hard-Modelling (KHM)

- **Improving knowledge:** Fine chemical industries try to improve manufacturing by elucidating the underlying kinetic model (rate law) of processes whose patents have expired.

- **Multivariate on-line sensors:** Recent progress in Process Analytical Technology (PAT) allows now the monitoring of processes in real time using multivariate probes.

KHM in Research phase

- Kinetic hard-modelling compares a measured signal with a modelled one obtained from a 1st principle hard model (rate law). The residuals are used as driving force for the least-square optimisation of the kinetic parameters.

Hard model = *function* (kinetic parameters, IC, CV, NCV)

IC	**I**nitial **C**onditions	e.g. initial concentrations
CV	**C**ontrol **V**ariables	e.g. dosing rate, temperature
NCV	**N**on-**C**ontrolled **V**ariables	e.g. concentration of the dosing agent

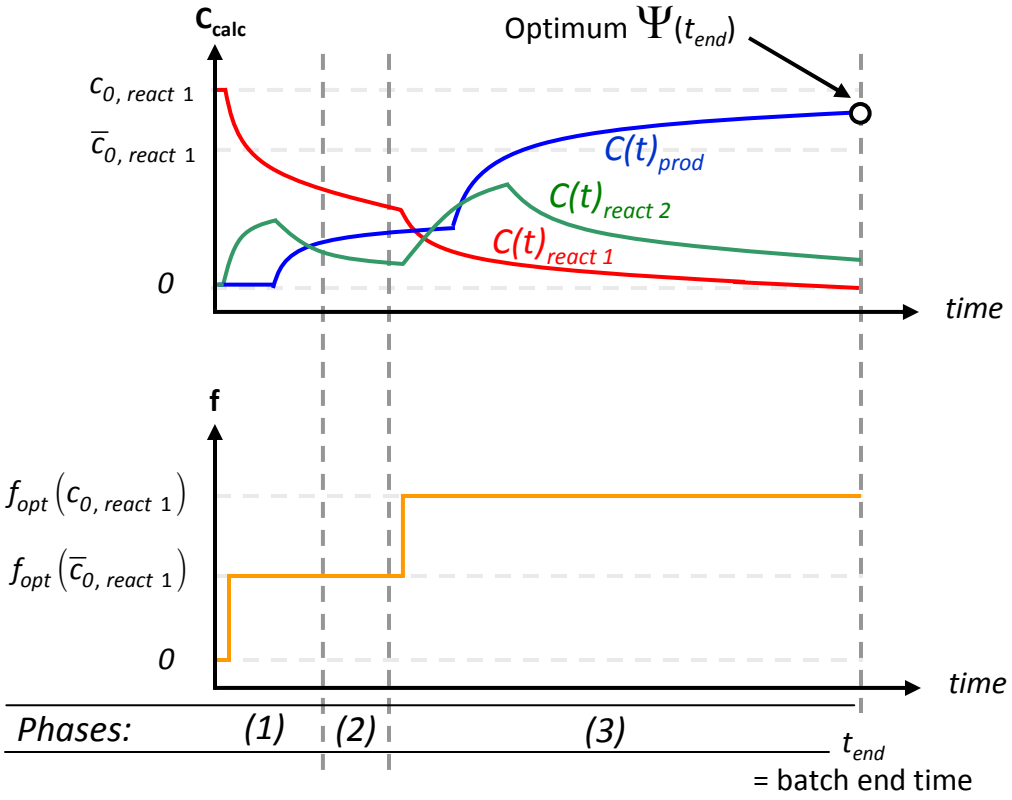
- Our kinetic hard-modelling approach is a calibration free method in the sense that the calibration (the absorptivity spectra) is nested into the non-linear optimisation and linearly fitted at each iteration.

Online KHM in Production phase

- In production phase, differences between batches result from different IC and/or NCV that can be optimised in a non-linear way, setting the kinetic parameters to the values found during the research phase.

- Subsequently, Control Variables (e.g. dosing flow rate) can be optimised and/or the process can be monitored for detection of possible faults.

Concept of online KHM



$\bar{c}_{0,\,react\ 1}$ = mean initial concentration,

$f_{opt}\left(\bar{c}_{0,\,react\ 1}\right)$ = optimum dosing rate for $\bar{c}_{0,\,react\ 1}$

Phase 1: OPTIMISATION OF THE IC/NCV AND PROCESS UPSET DETECTION

Optimisation of **IC/NCV** (e.g. $c_{0,\,react\ 1}$ and $c_{dos,\,react\ 2}$) with kinetic parameters fixed.
Possible Process Fault is detected.

Phase 2: OPTIMISATION OF THE CV

Extrapolation to a future time and optimisation of future **CV** under constraints to maximise Ψ (= Yield, Selectivity or Conversion).

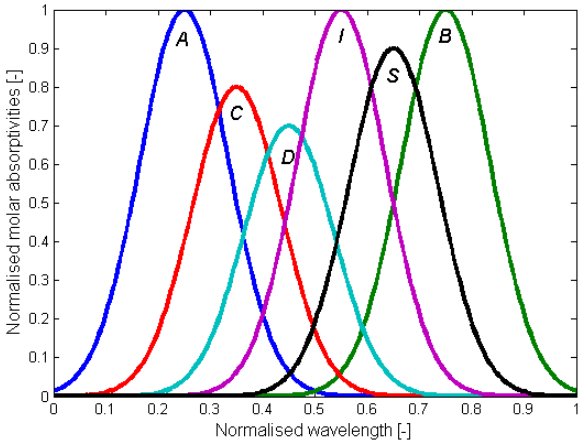
$$\max_{f(t)} \Psi\left(t_{end}\right)$$
$$s.c.\ \ V\left(t_{end}\right) \le V_{max}$$
$$f_{min} \le f\left(t\right) \le f_{max}$$

Phase 3: OBSERVATION PHASE

Process running under optimal **CV**.

Kinetic model

Absorptivity spectra



Heat released

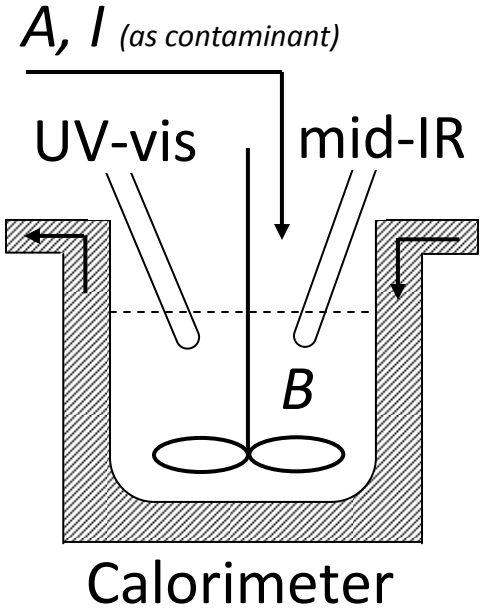
modelled:

$\Delta H_{r1} = -10.0 \text{ kJmol}^{-1}$

$\Delta H_{r2} = -5.0 \text{ kJmol}^{-1}$

unmodelled:

$\Delta H_{r3} = -10.0 \text{ kJmol}^{-1}$



modelled:

$A + B \xrightarrow{k_1 = 0.0656} C$

$A + C \xrightarrow{k_2 = 0.0383} D$

unmodelled:

$B + I \xrightarrow{k_3 = 0.0468} S$

A : dosed
C : wanted product
D : side product
I : contaminant in *A*

Base Case simulation
Mean IC / NCV
No process fault

$$\text{IC}: \overline{c}_0 = \begin{matrix} A & B & C & D & I & S \\ \end{matrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

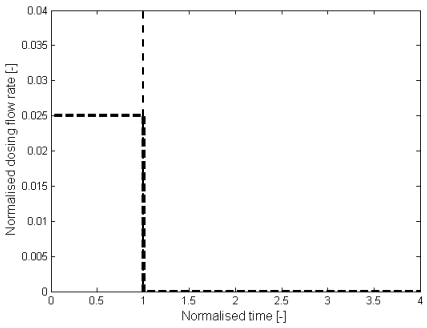
$$\text{NCV}: \overline{c}_{dos} = \begin{matrix} A & B & C & D & I & S \\ \end{matrix} \begin{bmatrix} 2 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$f_{opt}\left(\overline{c}_0, \overline{c}_{dos}\right) = 0.025$$

Base case

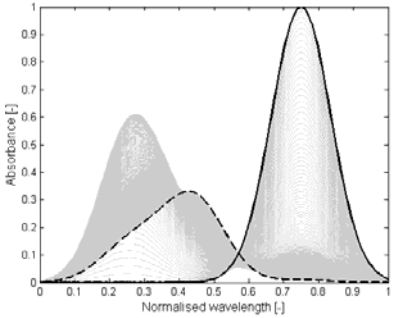
$$\begin{matrix} & A & B & C & D & I & S \end{matrix}$$
$$\text{IC}: \bar{c}_0 = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$
$$\begin{matrix} & A & B & C & D & I & S \end{matrix}$$
$$\text{NCV}: \bar{c}_{dos} = \begin{bmatrix} 2 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Dosing rate (a CV)



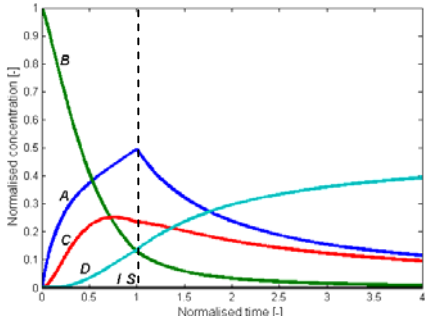
$f_{opt}\left(\bar{c}_0, \bar{c}_{dos}\right) = 0.025 \ \left(f_{\max} = 1\right)$

Spectroscopy



Added noise: 10^{-4}

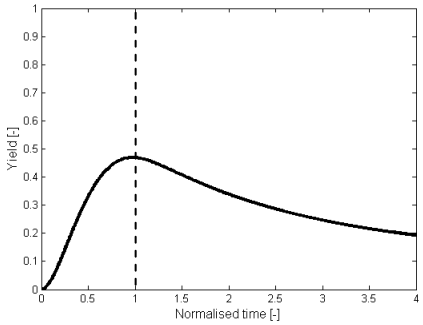
Concentration profiles



$V_0 = 0.3, \ V_{end} = 0.6 \ \left(V_{\max} = 1\right)$

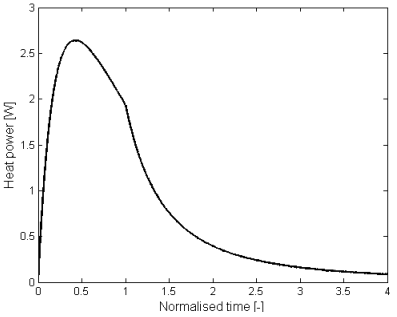
Time normalised to normal batch duration
(1: one normal batch duration)

Ψ = Yield



$\Psi\left(t_{end}\right) = \text{Yield}_{C/A,\,opt}\left(\bar{c}_0, \bar{c}_{dos}\right) = 46.98\%$

Calorimetry



Added noise: 10^{-3}

Optimisation of the **I**nitial **C**onditions (**IC**) and **N**on-**C**ontrolled **V**ariables (**NCV**)

and subsequent optimisation of the **C**ontrol **V**ariables (**CV**)

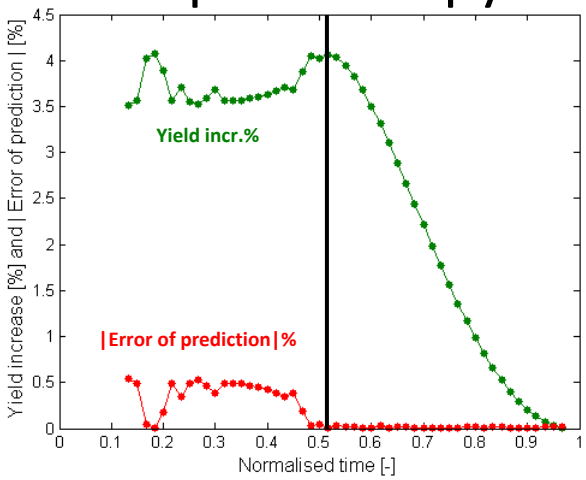
$$\text{IC}: \overline{c}_0 - 15\% = \begin{bmatrix} A & B & C & D & I & S \\ 0 & 0.85 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\text{NCV}: \overline{c}_{dos} + 15\% = \begin{bmatrix} A & B & C & D & I & S \\ 2.30 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

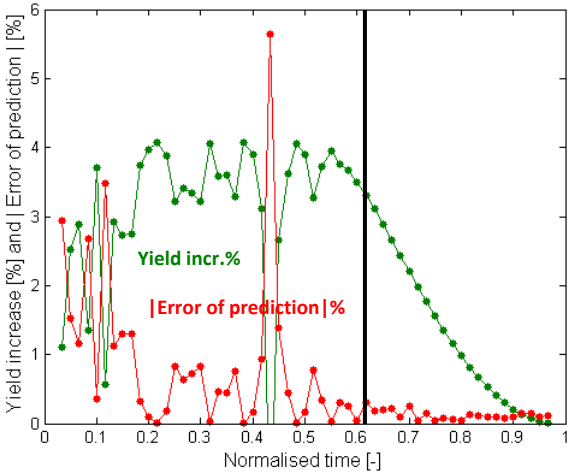
$$f_{opt}\left(\overline{c}_0 - 15\%, \overline{c}_{dos} + 15\%\right) = ?$$

Optimisation of the Control Variables (CV)

Spectroscopy



Calorimetry



	UV-vis	Calorimetry
Time of calculation	0.516	0.616
σ_p/p	≤0.20%	≤1.70%
Calculated dosing rate	0	0
Yield increase	+4.05%	+3.30%
Maximum Yield increase	+4.08%	+4.08%

Extrapolation time = 0.0167

CV optimisation and comparison with offline analysis

IC	*NCV*	Signal	Yield increase	Error of prediction	Time criterion for online KHM to be more efficient than offline analysis
0% (base case)	0% (base case)	Spectroscopy	0.09%	+0.00%	always
		Calorimetry	0.09%	+0.00%	always
		Offline	0.09%	-	-
-15%	+15%	Spectroscopy	4.05%	+0.02%	0.02%
		Calorimetry	3.30%	+0.30%	0.75%
		Offline	4.08%	-	-
-30%	+30%	Spectroscopy	11.06%	+0.15%	3.30%
		Calorimetry	8.47%	+0.45%	5.76%
		Offline	14.72%	-	-

Optimisation of the CV

- For this particular mechanism and these pure component spectra, spectroscopy can be used to optimise online the CV.
- Due to its univariate nature, **calorimetry** produces a low improvement in yield when used in online KHM.
- For **extreme variations in the IC/NCV**, online KHM is only better than offline analysis if the time required for the offline analysis largely delays the batch start.
- For this particular mechanism, the concentration of the dosing agent has the most impact on the yield.

Process **F**ault **D**etection (**PFD**)
or Process Upset Detection

$$\text{IC}: \overline{c}_0 = \begin{bmatrix} \overset{A}{0} & \overset{B}{1} & \overset{C}{0} & \overset{D}{0} & \overset{I}{0} & \overset{S}{0} \end{bmatrix}$$

$$\text{NCV}: \overline{c}_{dos} + I = \begin{bmatrix} \overset{A}{2} & \overset{B}{0} & \overset{C}{0} & \overset{D}{0} & \overset{I}{c_{dos,I}} & \overset{S}{0} \end{bmatrix}$$

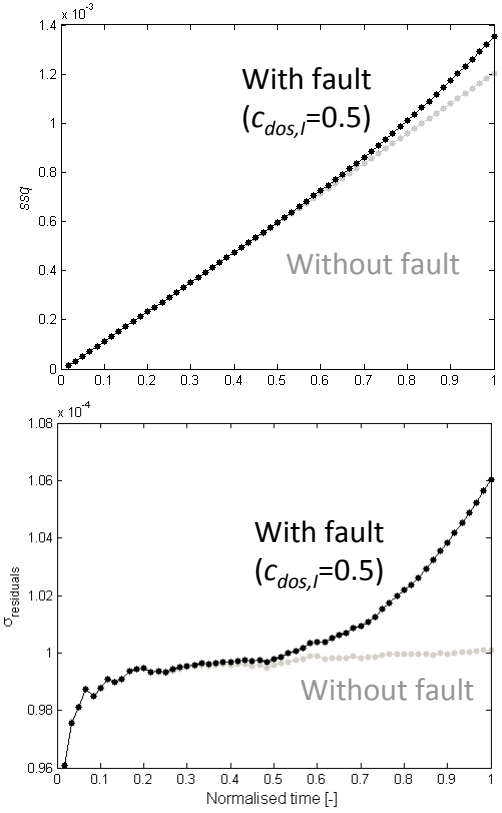
$$f_{opt}\left(\overline{c}_0, \overline{c}_{dos}\right) = 0.025$$

SSQ and Standard deviation of the residuals as Process Fault indicators

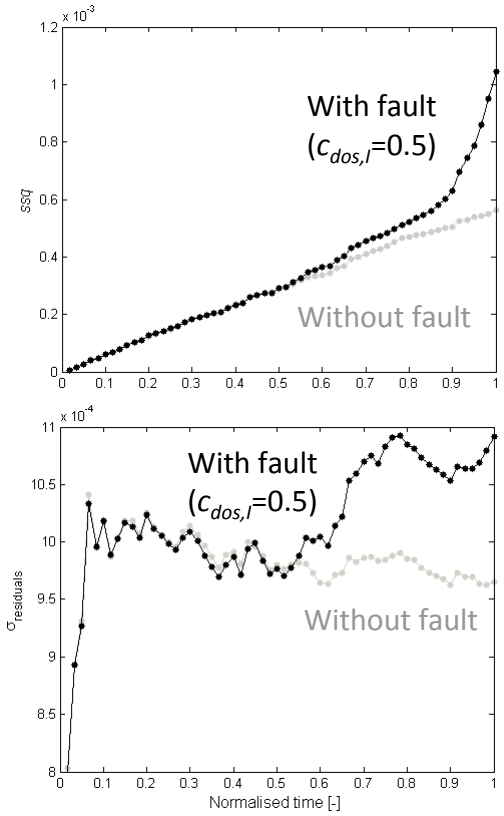
ssq

$\sigma_{residuals}$

Spectroscopy



Calorimetry

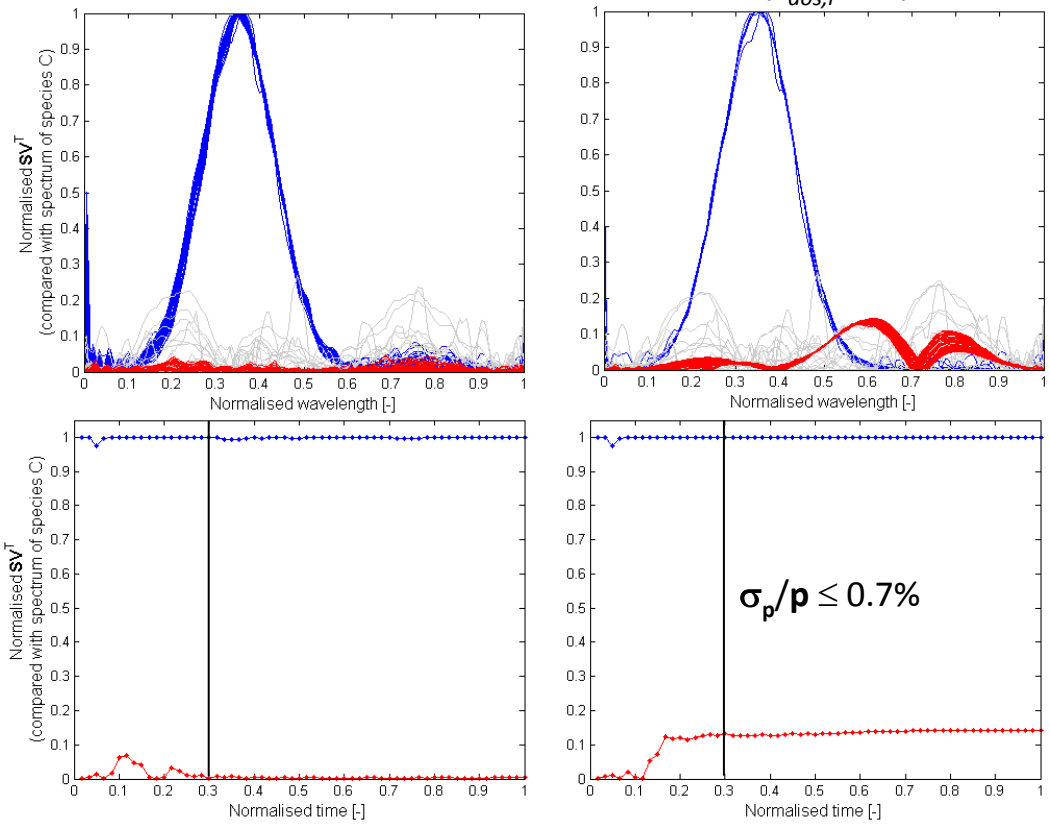


Known absorptivity spectra (in eigen-space) as Process Fault indicators

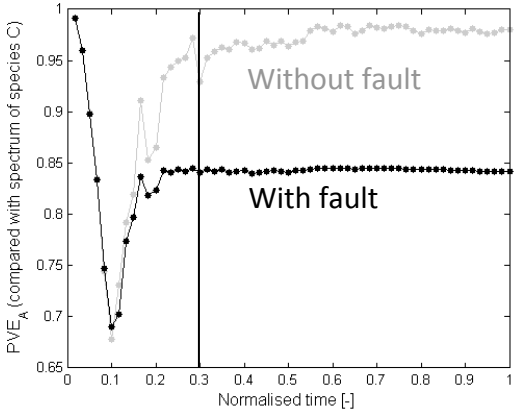
$\mathbf{SV}^T$ (benchmark: spectrum of *C*)

Without fault

With fault ($c_{dos,I}$=0.1)

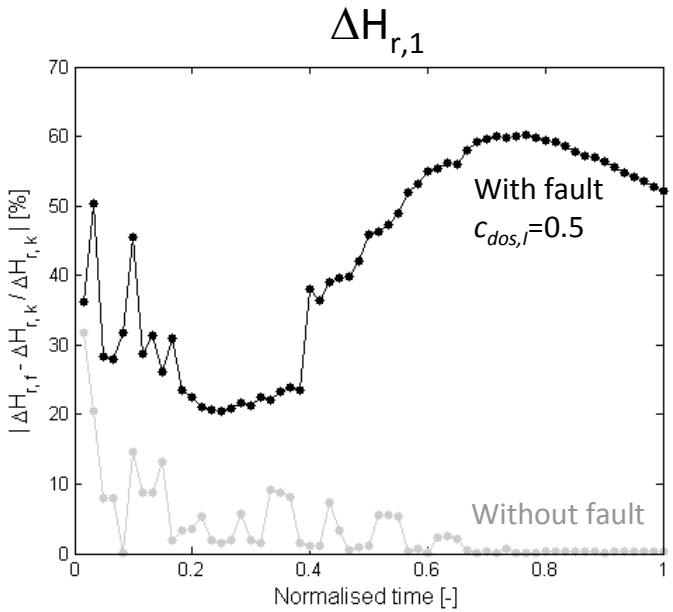


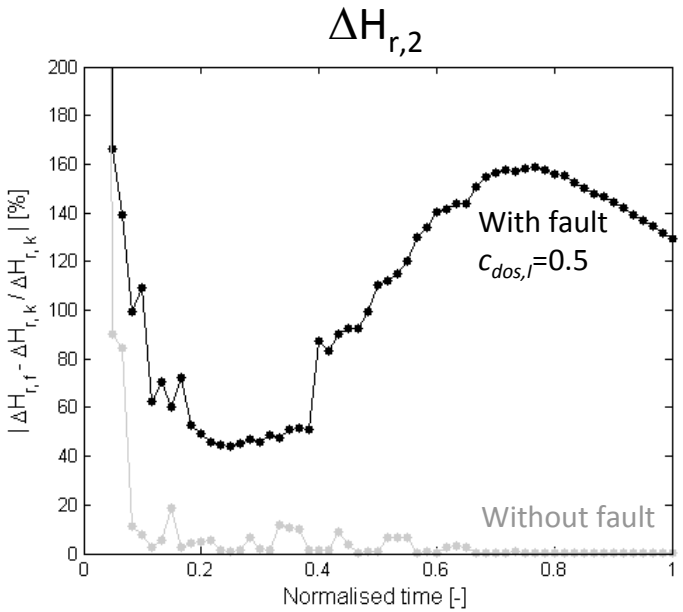
PVE_A



Spectrum selected for PFD	PVE_A at t_{end}	
	With fault	Without fault
Spectrum of *A*	85.51%	98.68%
Spectrum of *B*	98.50%	99.47%
Spectrum of *C*	78.33%	97.57%
Spectrum of *D*	69.82%	96.62%

Known reaction enthalpies as Process Fault indicator





Process Fault Detection

- Spectroscopy and calorimetry can be used to detect Process Faults
- The best process fault indicators are generally the ones based on a priori information, i.e. the absorptivity spectra and the reaction enthalpies

Conclusion

- The capabilities of online KHM have been demonstrated by:
  - Optimisation of the Initial Conditions (IC) and Non-Controlled Variables (NCV)
  - Subsequent optimisation of the Control Variables (CV)
  - And constant Detection of possible Process Faults (PFD)
- Next, online KHM will be applied on experimental data for a simple chemical system.

Thank you for your attention