On-line concentration estimation during chemical reactions using adaptive heat/ mass balances

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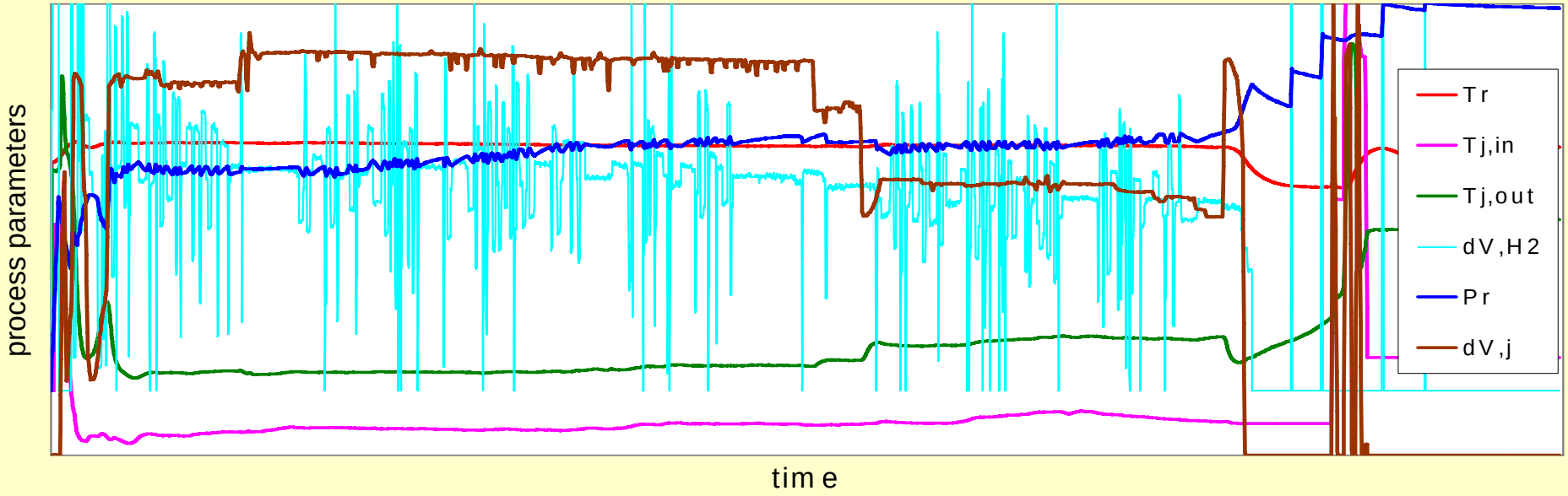
Fraunhofer Institute Umsicht, Oberhausen/ Germany

Motivation

- Unsteady-state conditions in discontinuous batch reactors

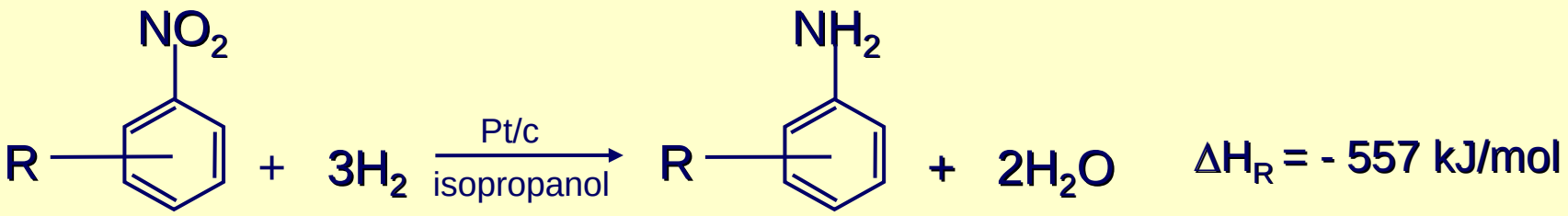


- Operators have difficulties to distinguish between allowable and undesired process deviations
- Reasons:
  - Process parameters (T, p, dV/dt) are usually used to control and monitor complex chemical reactions
  - Concentrations describing the state of a reacting system are measured, if at all, off-line or only at the end of reaction

Objectives

- Development of an on-line process monitoring system to estimate the current concentration of chemical species (educts, products, intermediates)
- Prototype development for a multiphase hydrogenation process
- Test process: Catalytic hydrogenation of a special aromatic nitro compound

Simplified reaction equation:



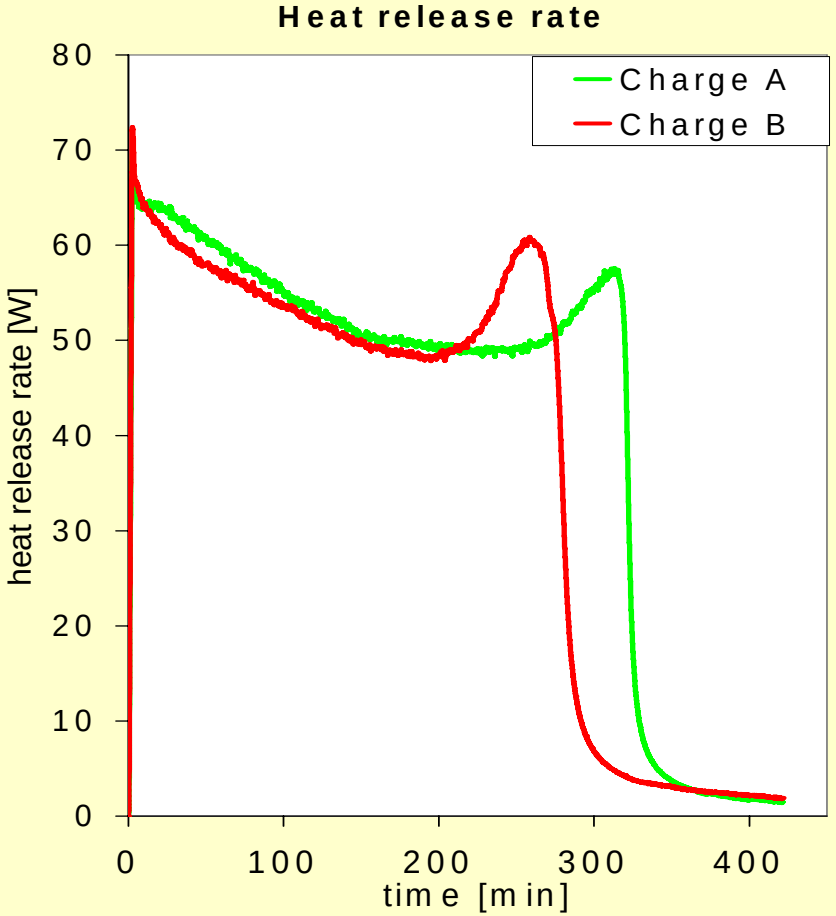
SNBE (reactant) SABE (product)

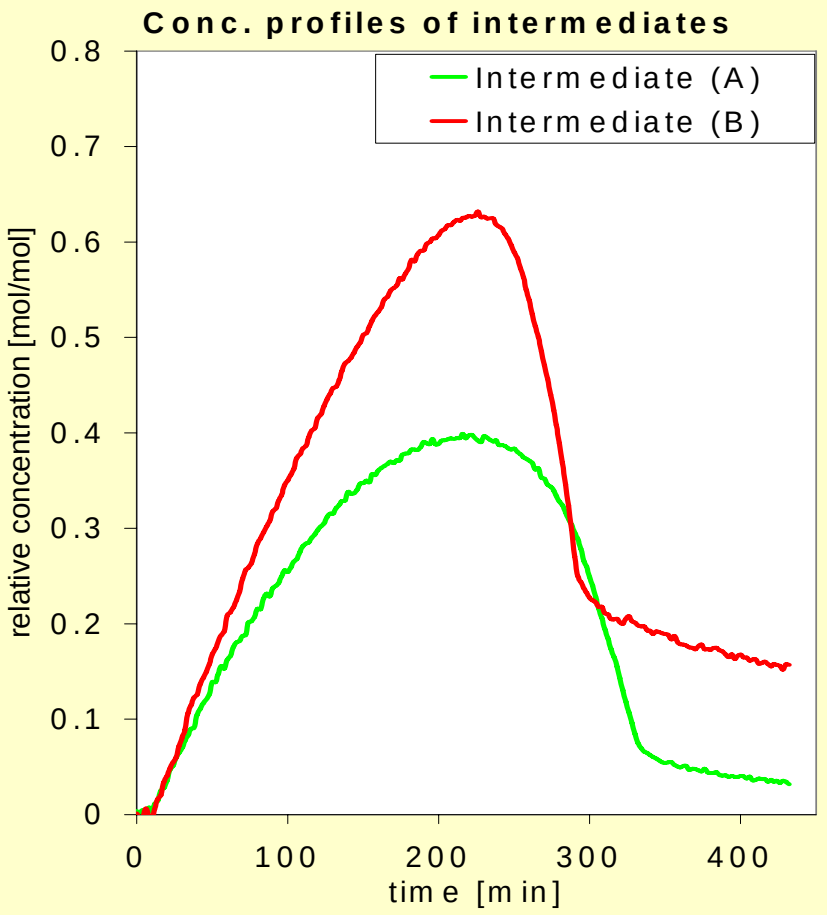
Detailed reaction mechanism:

- Complex network of consecutive and side reactions (Haber reduction scheme)
- Accumulations of intermediates influence: - process safety
  - product quality and rate of yield

Laboratory Investigations – RC1 / FTIR

Hydrogenations of different educt charges in the reaction calorimeter RC1 under process conditions (isothermal/ isobaric)

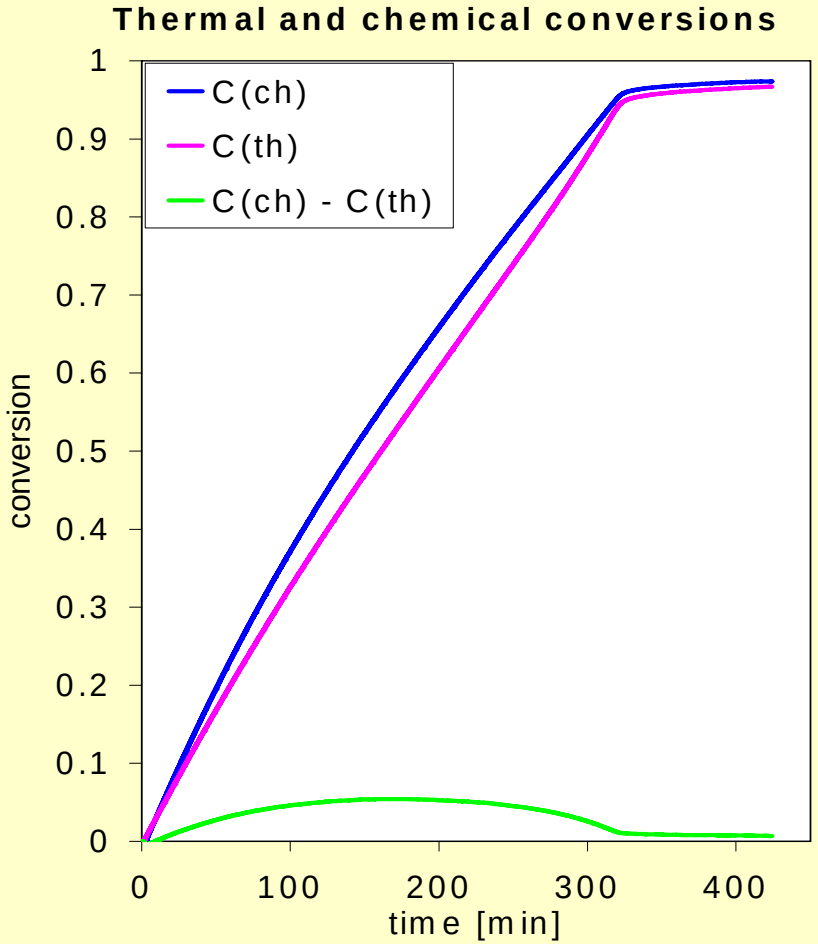


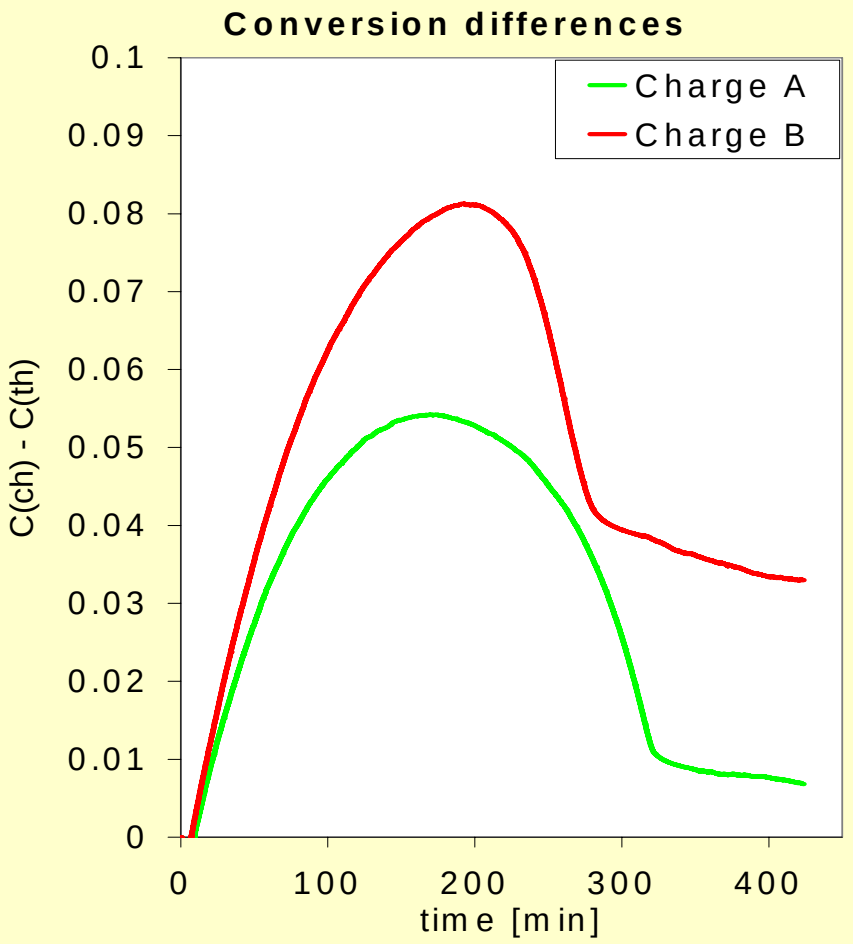


Different product qualities are caused by different intermediate accumulations

Laboratory Investigations – Conversion Profiles

Hydrogenations of different educt charges in the reaction calorimeter RC1

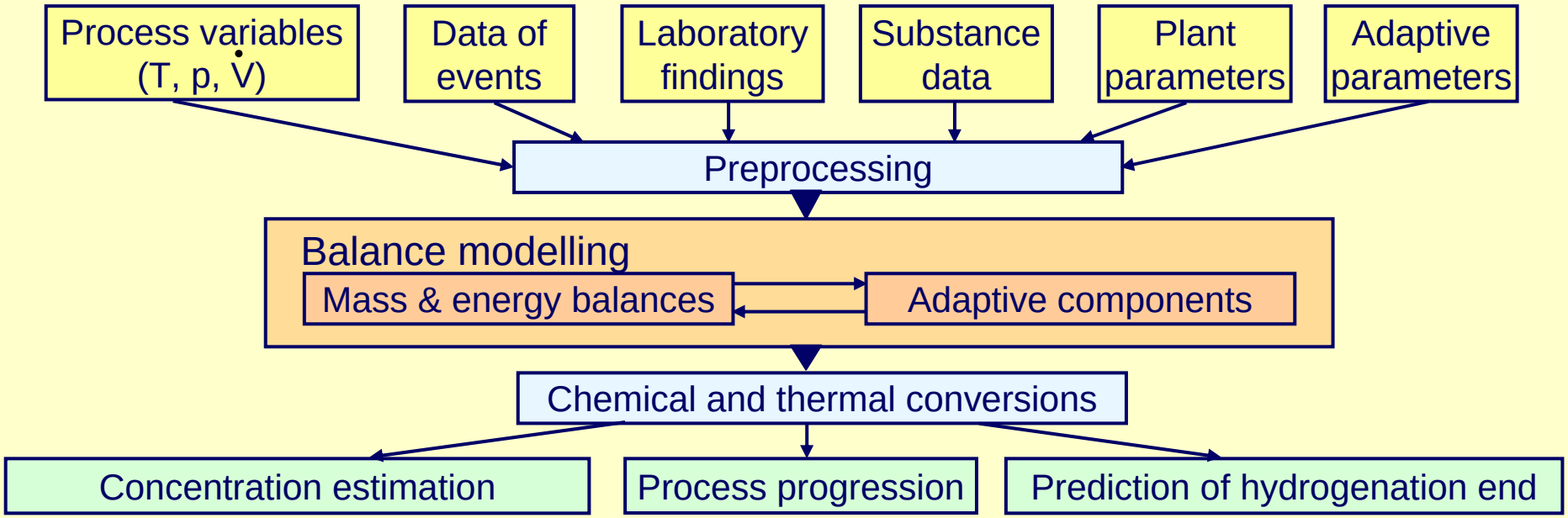




Conversion differences go approximate proportionally to the intermediate concentration profiles

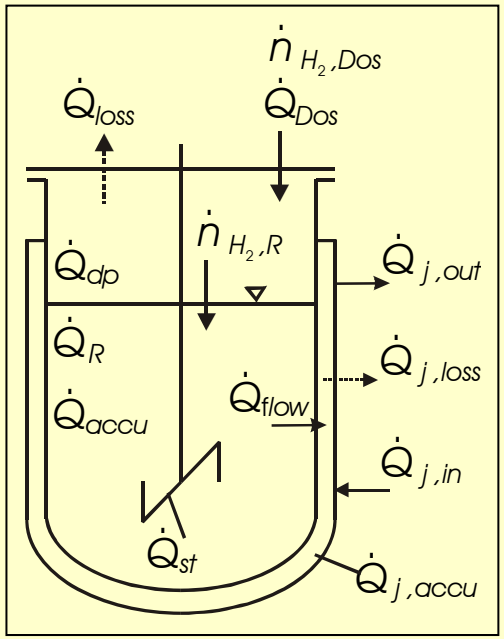
Working principle of mass & energy balance approach

- Consideration of balance terms whose modelling is very difficult (heat losses, heat bridges, systematic measuring errors) by adaptive components



- $C_{th}(t)$ and $C_{ch}(t)$ are used for calculating the concentration profiles, process progression and for prediction of hydrogenation end (on-line mode)
- Adaptation is done by using complete data sets from at least one normal batch course in the chemical target reactor (off-line mode)

Energy- and mass-balancing (simplified)



Balances

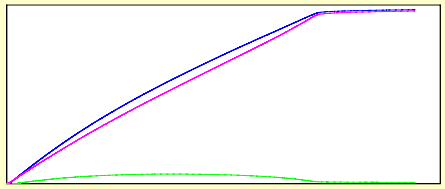
$$\dot{Q}_R = \Delta\dot{Q}_j + \dot{Q}_{accu} - \dot{Q}_{st} - \dot{Q}_{dp} - \dot{Q}_{Dos} + \dot{Q}_{j,accu} + \dot{Q}_{corr}$$

$$\Delta\dot{Q}_j = \rho_{j,in}\dot{V}_j\left(c_{p,j,out}T_{j,out} - c_{p,j,in}T_{j,in}\right)\cdot\alpha_1 \qquad \dot{Q}_{corr} = \alpha_2\left(\bar{T}_j - T_{Amb}\right) + \alpha_3\left(T_R - T_{Amb}\right)$$

$$\dot{n}_{H_2,R} = \frac{\dot{V}_{N,H_2}}{v_M}\cdot\alpha_4 - \left(\frac{dp_R}{dt}\frac{V_{Gas}}{R\cdot T_R} + \frac{dV_{Gas}}{dt}\frac{p_R}{R\cdot T_R} - \frac{dT_R}{dt}\frac{p_R\,V_{Gas}}{R\cdot (T_R)^2}\right)$$

$$C_{th}(t) = \frac{\int_{t_{start}}^{t_{act}} \dot{Q}_R(t)dt}{(-\Delta H_R)}\cdot\frac{M_{SNBE}}{m_{SNBE}}$$

$$C_{ch}(t) = \frac{\int_{t_{start}}^{t_{act}} \dot{n}_{H_2,R}dt}{n_{H_2,stoich}}$$



Adaptive parameters α

- Consideration of difficult to model terms
- Software supported adaption to the target plant

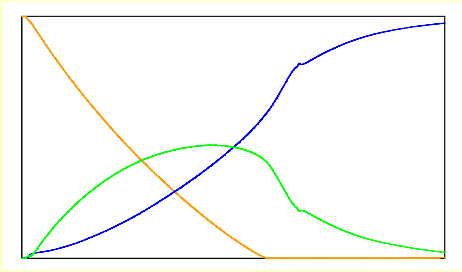
Concentration profiles

$$SNBE \xrightarrow{\Delta H_{R_1}} intermediate\ (IM) \xrightarrow{\Delta H_{R_2}} SABE.$$

$$C_{th}(t) = H_{V,1}\left[1 - \varepsilon_{SNBE}(t)\right] + H_{V,2}\,\varepsilon_{SABE}(t)$$

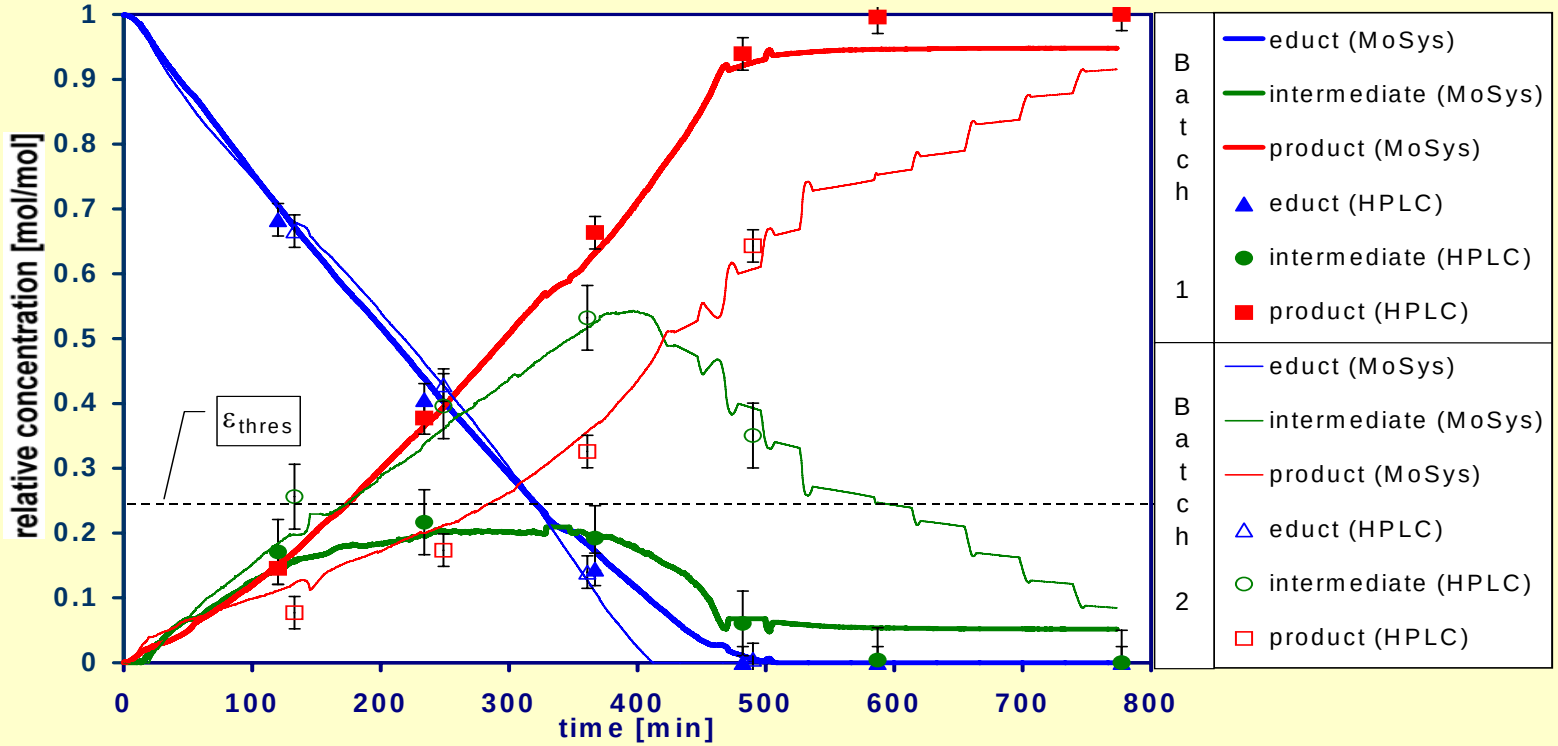
$$C_{ch}(t) = n_{V,1}\left[1 - \varepsilon_{SNBE}(t)\right] + n_{V,2}\,\varepsilon_{SABE}(t)$$

$$\varepsilon_{SNBE}(t) + \varepsilon_{SABE}(t) + \varepsilon_{IM}(t) = 1$$



Results: MoSys-concentrations compared to HPLC

- On-line MoSys was tested at 4 m³-STR during two campaigns (15 and 10 batches)
- To validate concentration estimations, samples were taken during hydrogenation and analysed by off-line HPLC

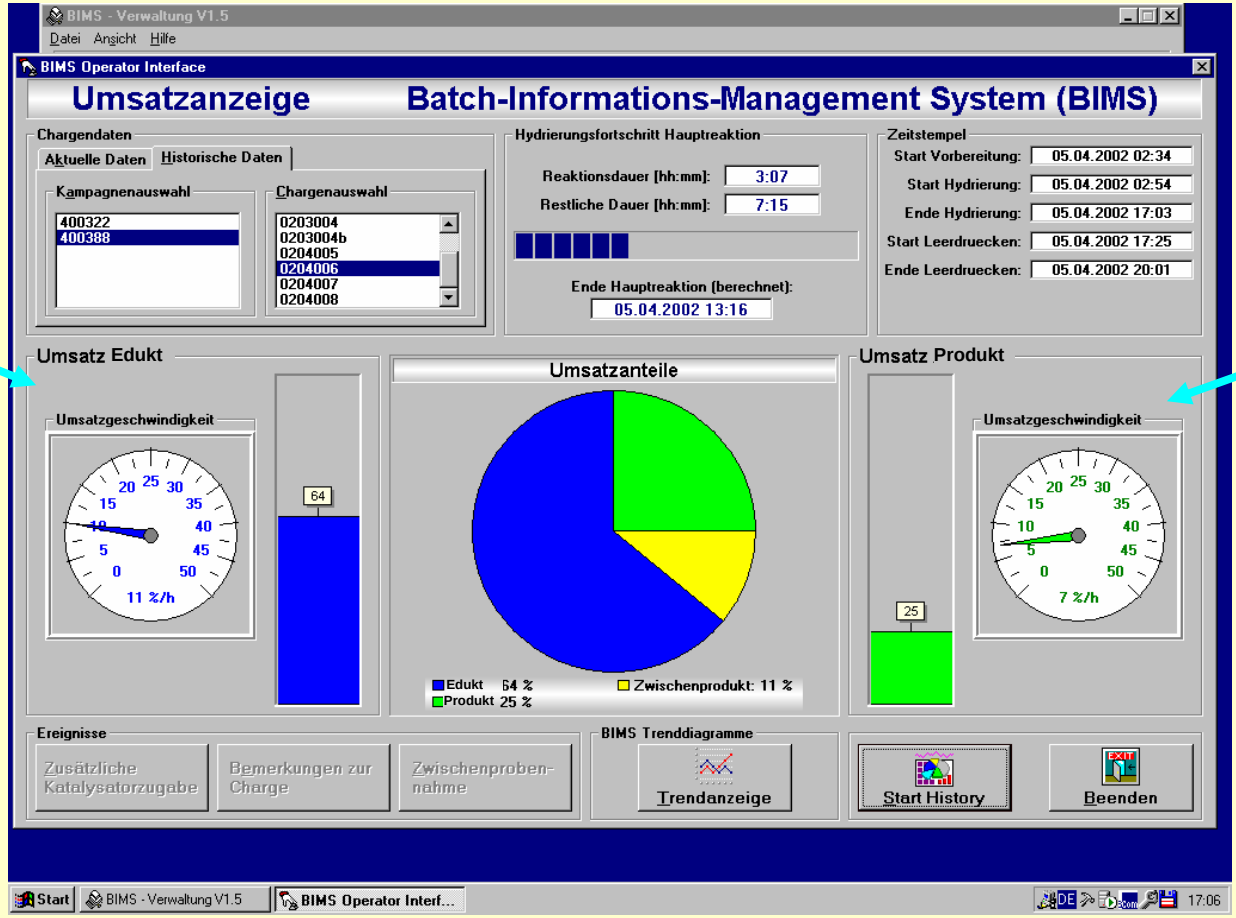


- MoSys-concentration profiles of two batches in comparison to HPLC analyses
- Intermediate accumulation (batch 2) oversteps defined allowable threshold ($\varepsilon_{thres} = 0.25$)

☞ **Alerting (pop-up window)**

Results: On-line display of chemical conversion rates

- Most important information on hydrogenation course in graphical form
  - diagrams for chemical conversion rates and for conversion proportions



Educt

Product

- By clicking the button “Trendanzeige”, additional information on profiles of MoSys-results are depicted as trend graphs.

Concluding Remarks

- Adaptive energy & mass balance approach is suitable to estimate concentration courses of educts, products and intermediates without any expensive on-line chemical process analysis.

- Accuracy of the estimations sufficient to identify undesired process states at an early stage

Absolute measuring inaccuracies: (RMSE-values)	Educt	2.5 Mol%
	Product	3.1 Mol%
	Intermediate	4.6 Mol%

- By using MoSys, the demand for traceability (e.g. batch with bad product quality) of complex batch processes could be fulfilled.

- Archived data allow to optimise chemical batch processes (e.g. yield, quality)

- Preconditions:
  - precise plant instrumentation and computer controlled data logging
  - knowledge of substance data, plant parameters, process parameters