

# Online NMR Spectroscopy for Process Monitoring in Intensified Continuous Production Plants

Svetlana Guhl<sup>1</sup>, Simon Kern<sup>1</sup>, Klas Meyer<sup>1</sup>, Lukas Wander<sup>1,2</sup>, Patrick Gräßer<sup>1,2</sup>, Michael Maiwald<sup>1</sup>

<sup>1</sup>Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstätter-Str. 11, D-12489 Berlin, Germany

<sup>2</sup>Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, D-12489 Berlin, Germany

## Motivation

- Continuous processing
  - Standardized modular equipment
  - Numbering-up on demand
  - Fast response to market change
- More efficient and flexible  
low to medium scale  
production of specialty  
chemicals

Intensified production concepts require for adaptive sensor and process control technology

- Compact module (850 x 570 x 570 mm)
- Commercial laboratory spectrometer
- ATEX certified safety concept
- Full automated control and spectra evaluation included
- Adaptive communication standards:



## Concept of Online NMR Analyzer

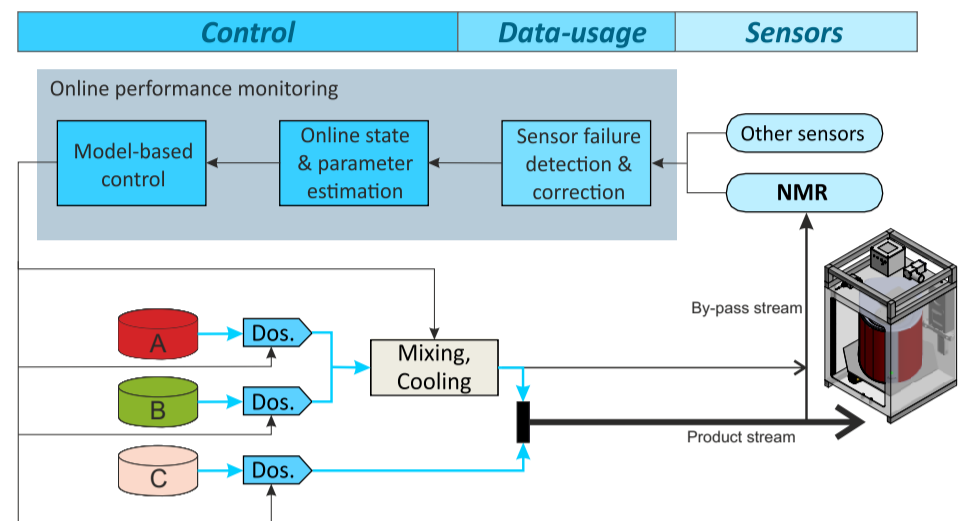
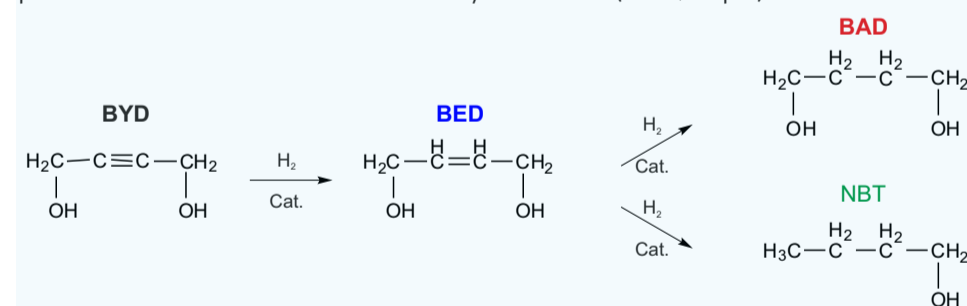


Fig. 1: Concept for process control within a continuous chemical production plant based on an Online-NMR Analyzer

- Integration of compact NMR Analyser to technically relevant processes
- Validation of data evaluation models based of batch and continuous reactions

## Example 1: Batch Hydrogenation Reaction Model and Laboratory Experiment Results

Technically relevant example of the catalytic hydrogenation of 2-butyne-1,4-diol, which represents an important step in the production of the solvent tetrahydrofuran (THF, Eq. 1):



Eq. 1: Reaction scheme, BYD: 2-Butyne-1,4-diol, BED: 2-Butene-1,4-diol, BAD: Butane-1,4-diol, NBT: n-Butanol

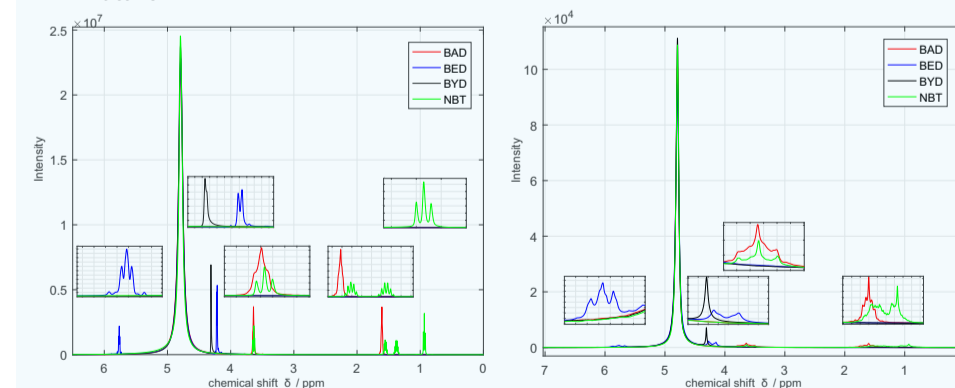


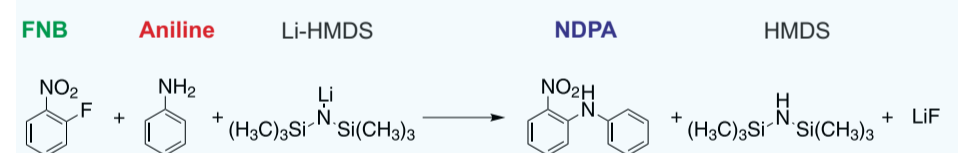
Fig. 2: High-Field NMR spectra (500 MHz, left) and Low-Field NMR spectra (43 MHz, right) of pure component of the hydrogenation

## Conclusions + Outlook

- Good agreement between LF- and HF-NMR method
- Low-Field NMR is suitable for monitoring the model reaction
- Low-Field NMR is promising for the monitoring of the hydrogenation reactions
- ATEX proof housing is currently in construction and certification
- Implementation in plant environment planned for April 2017

## Example 2: Continuous Lithiation Reaction

In the studied model reaction two aromatic substances (Eq. 2) are coupled initiated by a lithiation step:



Eq. 2: Reaction scheme, FNB: 1-Fluoro-2-nitrobenzene, Li-HMDS: Lithium bis(trimethylsilyl)amide, NDPA: 2-Nitrodiphenylamine, HMDS: Bis(trimethylsilyl)amine

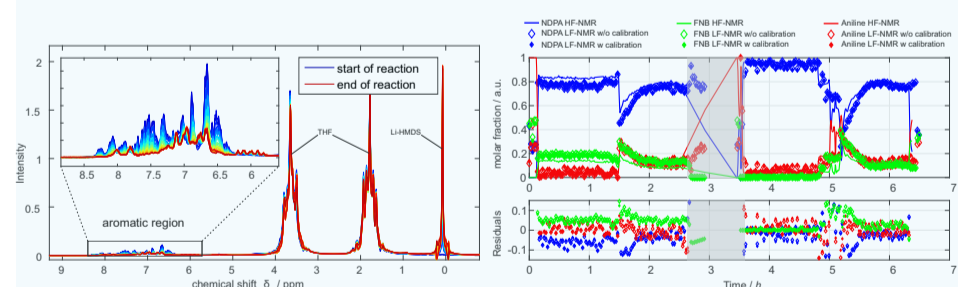


Fig. 3: Low-Field NMR spectra (43 MHz, left) and trend of molar fractions from LF-NMR model during study showing 6.5 hours of continuous operation at different setpoints compared to High-Field NMR reference data (right)

- Reaction was investigated under various process conditions
- Mixture composition was adjusted by variation of feed rates leading to either a lack or excess of a certain component
- Data evaluation with calibrated and calibration-free models
- 500 MHz online NMR (HF-NMR) as a reference
- Dynamic process operation in laboratory scale (Fig. 3)