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Title D2.2 Report on the selection of the analytical methods for the REI calculation for chemical plants based on renewable feedstock

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PU	Public	PU
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Abstract :

Analytical tools for the determination of crucial process parameters for a chemical plant based on renewable feedstock have been assessed. Required process information for the REI calculation has been deduced from definitions in WP 1. The most relevant measurement quantities for optimised process operation have been deduced qualitatively from the existing offline process analytics: a) residual substrate in the reactive step, b) excess reactant after purification, c) optical quality in the post-processing step.

Due to the challenges of handling offline samples and achieving representative measurements, an early implementation of online sensors into the production plant was strongly favoured and has already been achieved. A first 6-week campaign served as a benchmark for the potential of the selected online analysers.

The results have been assessed in close consultations with the plant operators, especially with regard to the expected operational benefit. Spectroscopy turned out to be appropriate for the post-processing step. For the excess reactant monitoring spectroscopy is a promising method with the need of further evaluation. The expected benefit from a spectroscopic monitoring of the reactive step was too low to suggest further evaluation of the method.

Authors (organisations): Clemens Minnich, Sonja Hardy (S-PACT)

Reviewed by: Sebastian Engell (TUDO)

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Renewable feedstock, Batch and continuous production, Automation, Inline spectroscopy, PLS.

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V2	2015-03-20	Update	Nadine Melchert (BASF)
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Table of Content

1. DESCRIPTION OF THE WORKFLOW	5
1.1. Layout of the decision process	5
1.2. Interaction with other MORE activities	6
2. DECISION ON SUITABLE ANALYTICAL METHODS	7
2.1. Overview of analytical tasks	7
2.1.1. Measurement 1: Residual substrate in reactive step (batch)	7
2.1.2. Measurement 2: Excess reactant in purification step (continuous)	7
2.1.3. Measurement 3: Post-processing step (continuous)	7
2.2. Measurement campaign under real-life conditions	8
2.2.1. Measurement 1 (reaction)	8
2.2.2. Measurement 2 (purification)	9
2.2.3. Measurement 3 (post-processing)	9
2.3. Assessment	10
3. DECISIONS AND OPEN ISSUES	11

List of Figures

Figure 1: Schematic layout of decision process for analytical method selection	5
Figure 2: Predicted substrate concentration profiles for different batches (lines) of a special product, compared with offline analysis (markers)	8
Figure 3: Batch trajectories for one of the major products.	9
Figure 4: Recovery plot of a calibrated PLS model for the purification measurement.	9
Figure 5: Time profile of optical quality predicted from online measurement (line) compared with reference analytics from external sampling (markers)	10

1. Description of the Workflow

Typically, the elaboration of a process analytical solution to a given process is characterised by many process-specific criteria. The individualisation e.g. of the analyser interface to the process is dominated by operation parameters like flow-rate or temperature of the by-pass stream, rather than by bottom-up specifications like idealised geometries for the selected technique. Nevertheless, in order to work out a procedure with a realistic potential for generalisation and transferability, an abstraction of the required design steps was attempted.

Since the BASF Case Study provides a setting which is typical to processes with significant batch elements that require moderate flexibility due to variations in feedstock (e.g. renewables), a focus was on exploring the transferability of methods across different product specifications.

1.1. Layout of the decision process

The decision process for suitable analytical methods requires a type of “top-down” approach, starting at the selection of the desired optimisation parameter. In case of MORE, the decision has been to select the resource efficiency indicators (REIs) as targets for the subsequent process analysis. A possible way towards a systematic selection of the analytical technology to achieve the real-time optimisation is suggested in Figure 1.

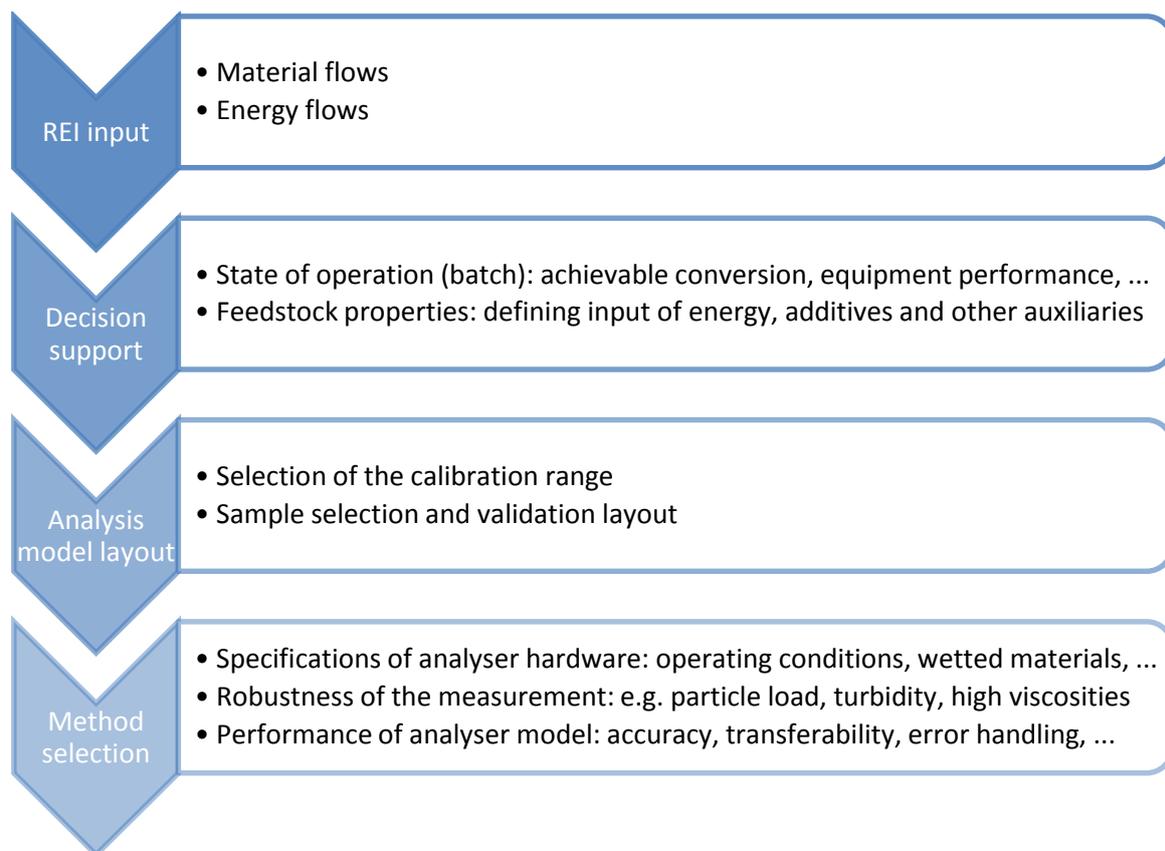


Figure 1: Schematic layout of decision process for analytical method selection.

1.2. Interaction with other MORE activities

A concept for the REIs is defined in WP 1. The selection of the target REI for the given process – focussed on environmental issues, stressing commercial aspects etc. – is a management decision as well as influenced by technical issues. Accordingly, the REIs should be designed in such a way that process data requirements should be easily deducible. This includes:

- ✓ the selection of relevant input process parameters
- ✓ the required precision/accuracy
- ✓ the required time resolution

Typically, the REIs are not calculated directly from primary sensor information, but use an auxiliary calculation from a process or plant model in order to reduce the influence of sensor performance (noise etc.). Data reconciliation (Task 2.3) is therefore adapted to the requirements of REI calculation.

The analytical equipment selected in WP 2 has to be integrated into the deployment platform developed in WP 4 or connected to the available process control systems by standard interfaces. Hence, a decision criterion for analytical hardware must be the availability of communication interfaces like OPC or bus systems. In the WP 5 demonstration activities the long-term applicability and stability of all involved sensing techniques for REI computations need to be proven.

2. Decision on suitable analytical methods

For the three most important process parameters that were chosen due to their influence on the REIs, matching analytical methods had to be found and evaluated. These three process parameters are the residual substrate in the reactive step, excess reactant after purification and the optical quality in the post-processing step, each parameter having to be measured at a different location and under different operating conditions.

2.1. Overview of analytical tasks

2.1.1. Measurement 1: Residual substrate in reactive step (batch)

The reaction takes place between a solid substrate and a liquid reactant. The medium turns from a dispersion into a homogeneous solution at high conversion. The process is performed in batch mode, with periodic sampling for offline analysis.

The current purification procedure and offline analysis is well-trusted, but laborious, time-consuming, and unfit for automation. Hence, an inline measurement is of high interest. From preliminary lab tests, spectroscopy is expected to meet the requirements of the analysis.

The main interest in the analytical results is in **optimizing (reducing) the batch time, leading to the reduction of cost and energy consumption** in this process step. The main challenge for the new analytical approach is the compatibility with varying solid content and the low analyte concentration in the crucial process phase.

2.1.2. Measurement 2: Excess reactant in purification step (continuous)

The raw product mixture is treated thermally in order to remove excess reactant. This purification step is performed in continuous mode..

The current offline analysis is well-established, but slow and unfit for automation. Sampling frequency is very limited, so that a good time-resolution of the inline analysis is crucial. Spectroscopy has proven in advance to be capable of detecting the excess reactant in principle.

The main interest in the analysis output is in **minimising the thermal stress on the product**, thus inhibiting deterioration of the product and reducing post-processing efforts as well as **minimising the energy cost of the thermal treatment**. The main challenge lies in the comparatively harsh process conditions and in the low reactant concentration expected in the process stream.

2.1.3. Measurement 3: Post-processing step (continuous)

The final product is treated with various additives in order to meet the specifications. Closely related to the performance of the purification step described above is the specified optical quality, which is a major criterion for the economic assessment of the product. Post-processing is performed in continuous mode, with periodic sampling for offline analysis.

The current process analysis is conducted offline by means of a laboratory test. The procedure is performed manually and the test only allows a limited number of discrete values. An inline spectroscopic measurement is expected to meet the need for better time and optical quality resolution.

The main interest lies in the **general applicability** of the method to the entire range of products processed in the plant, which may become a major challenge. Other challenges may be the process stream properties like temperature-dependent turbidity and degassing.

2.2. Measurement campaign under real-life conditions

After initial lab studies on representative sample material, a process installation of spectroscopic analysers for Measurements 1-3 (reaction, purification and post-processing) was prepared and operated for a total of 6 weeks.

During this period, different products based on slightly different feedstock were processed and other process conditions like temperature, material flows etc. were actively varied where possible.

2.2.1. Measurement 1 (reaction)

The sampling point of the main reactor was equipped with an immersion probe connected to a process analyser. Routine offline analysis was conducted in parallel in order to provide an appropriate data base for subsequent method calibration.

The following observations have been made:

- Fluorescence is increasing with increasing conversion, i.e. it is most problematic in the most interesting phase of the reaction.
- Turbidity in the initial phase of the reaction is not causing problems.
- There is a lack of systematic correlation between spectra and substrate content measured offline for the most relevant products.
- Only for a special product with very different physical properties, a useful calibration could be set up (Figure 2). A transfer of this method to the other products cannot be expected.

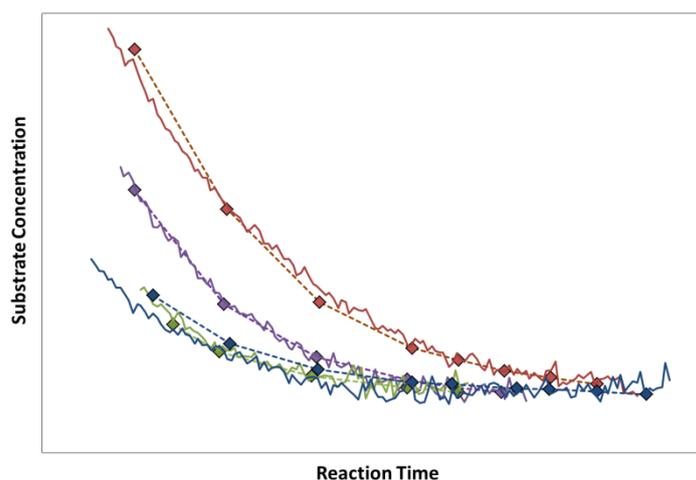


Figure 2: Predicted substrate concentration profiles for different batches (lines) of a special product, compared with offline analysis (markers).

- For the main products, trajectories can be calculated from a simple univariate analysis of a characteristic section of the pre-treated spectra. These may serve as a semi-quantitative measure of the reaction progress.

Typical trajectories of different batches calculated for one of the major products show good accordance (Figure 3).

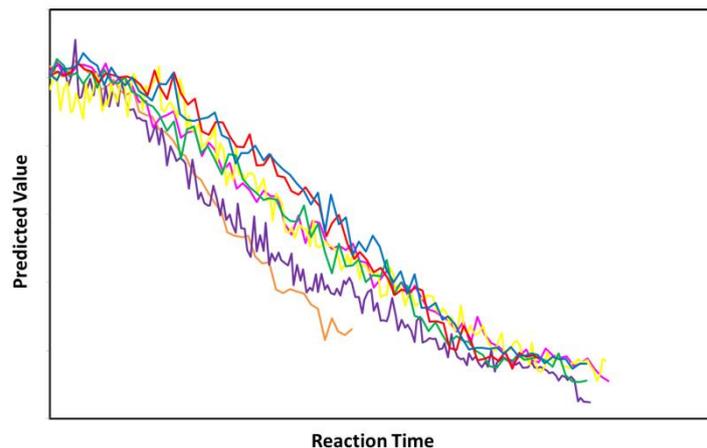


Figure 3: Batch trajectories for one of the major products.

2.2.2. Measurement 2 (purification)

The sampling point of the process line after the purification unit was equipped with an immersion probe connected to a process analyser. Routine offline analysis was conducted in parallel in order to provide an appropriate data base for the subsequent calibration of the method.

The following observations have been made:

- Even under the harsh process conditions, the spectroscopic equipment delivers spectra reproducibly.
- Background fluorescence is significant, but not detrimental for the spectral range selected for the analysis.
- For yet unidentified reasons, several production phases, including the one with the most pronounced variations in process parameters, did not deliver representative spectra. Hence, the available data for calibration purposes is limited.
- A good correlation can be established for one major product for excess reactant concentrations close to desired specifications and below (Figure 4).

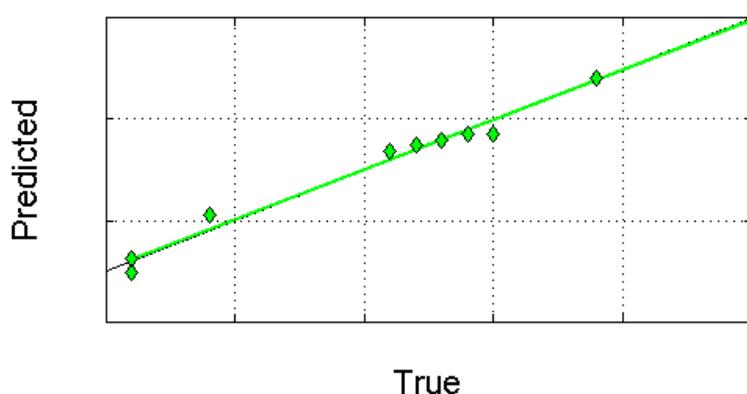


Figure 4: Recovery plot of a calibrated PLS model for the purification measurement.

2.2.3. Measurement 3 (post-processing)

The process line of the post-processing unit was equipped with a transflexion probe connected to a process spectrometer. Routine offline analysis was conducted in parallel in order to provide an appropriate data base for subsequent method calibration.

The following observations have been made:

- The expected influence of turbulences, degassing etc. was of only minor relevance and could be compensated by data pretreatment.
- Else than expected, probe fouling was not an issue during the 6 weeks campaign.
- Separate calibrations for two major products had to be based on comparably small data sets, which did not appear useful.
- A multi-product approach covered the most relevant low range of the optical quality scale reasonably and delivered good results for the online analysis of the optical quality (example in Figure 5).

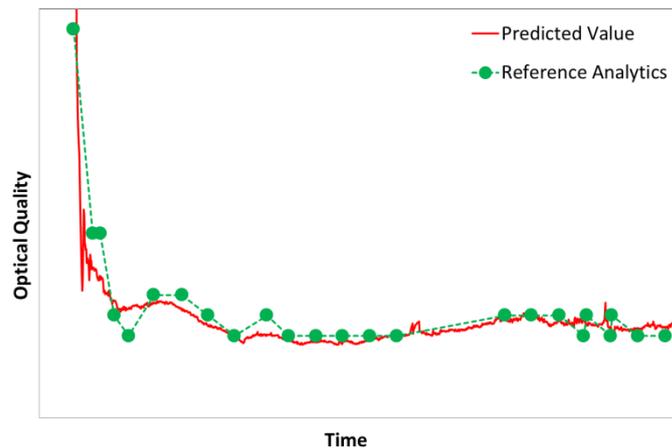


Figure 5: Time profile of optical quality predicted from online measurement (line) compared with reference analytics from external sampling (markers).

2.3. Assessment

The results of the measurement campaign were discussed with the plant operation team, leading to the following assessment of the methods:

1. The expected benefits of spectroscopy in the reaction step are too insignificant to justify a change of technology:
 - a. Semi-quantitative (uncalibrated) monitoring possible.
 - b. No improvement in precision expected.
 - c. No significant benefit from improved time resolution due to strong point-to-point fluctuations in predicted profiles.
 - d. The identification of the optimum time for batch termination is not facilitated.
2. The application of spectroscopy for the purification step bears significant potential:
 - a. Highly improved time resolution.
 - b. Good accordance with reference analysis for one major product, hence trustable analysis.
 - c. Correlation with process parameter changes is well indicated, but not sufficiently validated due to steady-state operation in the most reliable measurement period.
3. Spectroscopy represents a sound alternative to the current offline analysis:
 - a. Can be applied to two major products equally.
 - b. Is robust enough to compensate influences from turbidity, degassing etc.
 - c. Needs further validation if it is to be applied to samples with lower optical quality.

3. Decisions and open issues

The assessment of the methods led to the following decisions:

1. Measurement 1 (reaction) will no longer be pursued. To test the room for improvement, some representative reaction samples will be measured with another instrument reducing fluorescence.
2. Measurement 2 (purification) will be further evaluated in a new campaign, so that ideally more process changes and a wider concentration range will be monitored. Some preparatory measurements will be performed in order to compare the potential of another instrument and the transferability of the results to other products.
3. Measurement 3 (post-processing) was already successful enough to justify a change of technology also under economic considerations.