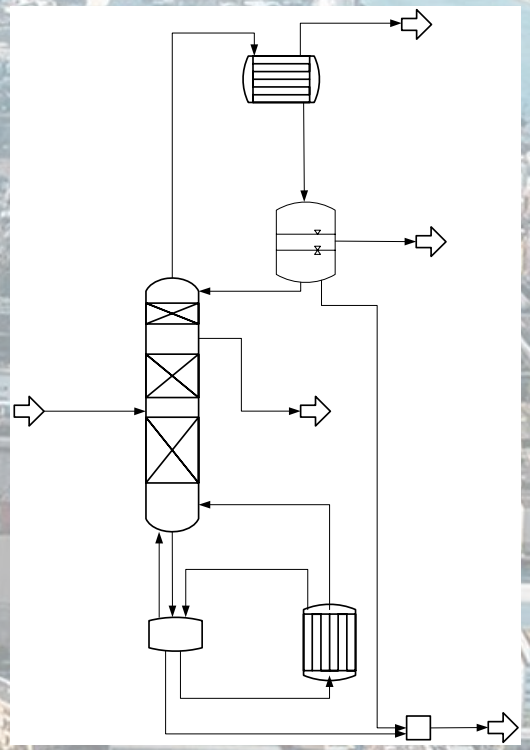
# Model meets Reality

## Distillation Simulation at BASF




Regina Benfer
regina.benfer@basf.com

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# BASF worldwide

**Chemicals**

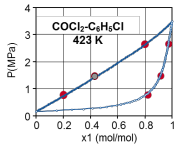
**Performance Products**

**Functional Materials & Solutions**

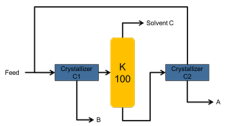
**Agricultural Solutions**

**Oil & Gas**

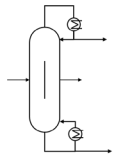
# Topics




- Physical property data in simulation

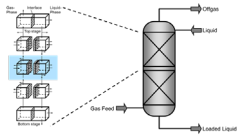



- Conceptual design of conventional or hybrid separations



- Modeling of special distillation systems (like divided wall columns, reactive distillation, dynamic systems)


- Parameter adaptation for plant snapshots and miniplant experiments




- Modeling of mass- and heat-transfer in distillation and absorption.



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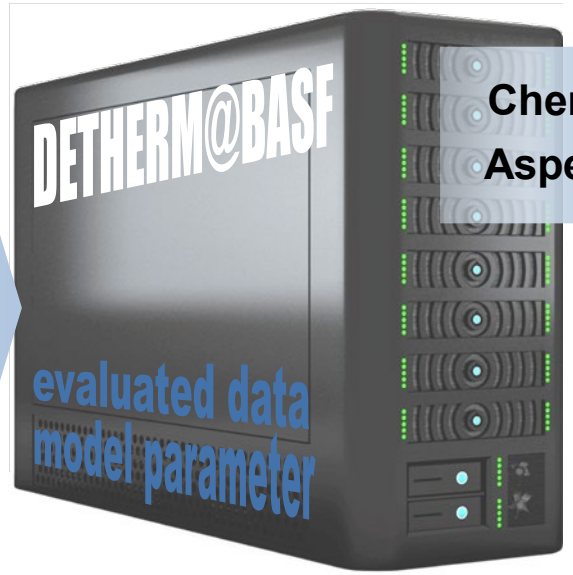
# Physical Property Data
# BASF Database Structure

Courtesy: M. Heilig, BASF SE

Continuously updated experimental data

- BASF data
- Commercial databases

  e.g. DIPPR,DDB




**Chemasim**
**AspenPlus**

**Process Simulation**

**CAPEOPEN / DLL interface to simulation tools**

**Thermodynamic Modules e.g. Multi-flash** (Infochem)

**DPP Data Preparation Package** (Dechema)

## Further Data Sources

→ Databases and Monographs (e.g. DDB, TDE-NIST, TRC, IUPAC)

→ References Database (variety of properties)



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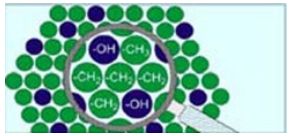
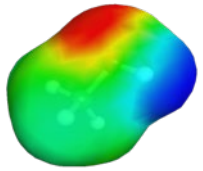
# Physical Property Data Models in Use

- **NRTL / PSRK**:
  - Mainly used for daily work, binary NRTL parameter sets from DETHERM@BASF
- **Group contribution methods:**
  - Estimation of pure component data



- **Cosmo-RS/QSPR/Simularity**:
  - Estimation of mixture phase equilibria
  - Screening of additives

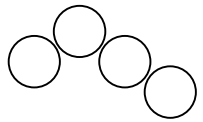


- **PC-SAFT (EOS)**:
  - For enhanced applications, e.g. entrainer selection for azeotropic or extractive distillation

$$A^{res} = A^{hard\ chain} + A^{dispersion} + A^{association} + A^{multipole}$$

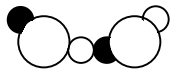
pure component

binary interaction



$m,\sigma$

$u,\ k_{ij}$



$\kappa,\varepsilon,(l_{ij})$


$\mu,\alpha,Q$

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# Physical Property Data
# Example Solvent Screening

**Das NMP-Verfahren zur Gewinnung von Butadien aus $C_4$-Crackschnitten***

DR.-ING. B. HAUSDORFER, DR. U. WAGNER UND DR. H. M. WEITZ
Badische Anilin- & Soda-Fabrik AG, Ludwigshafen a. Rh.

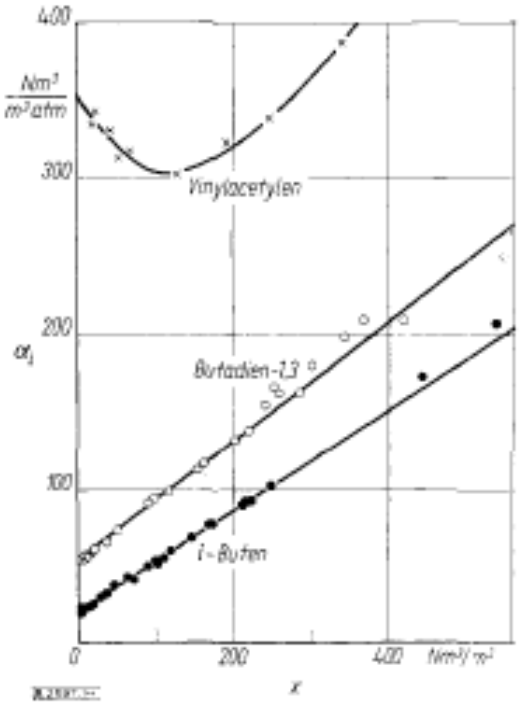
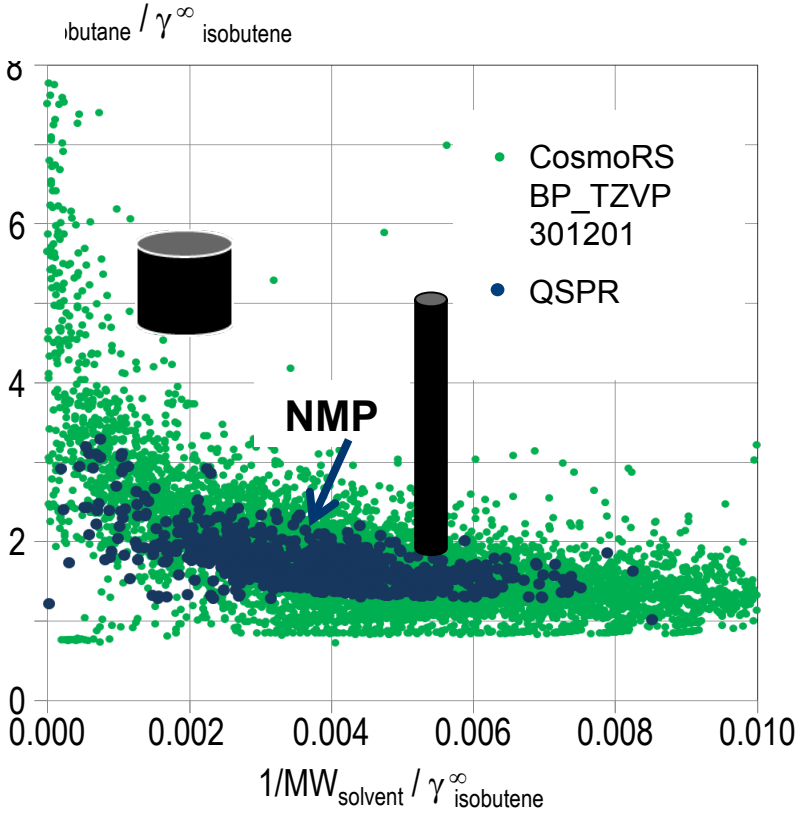
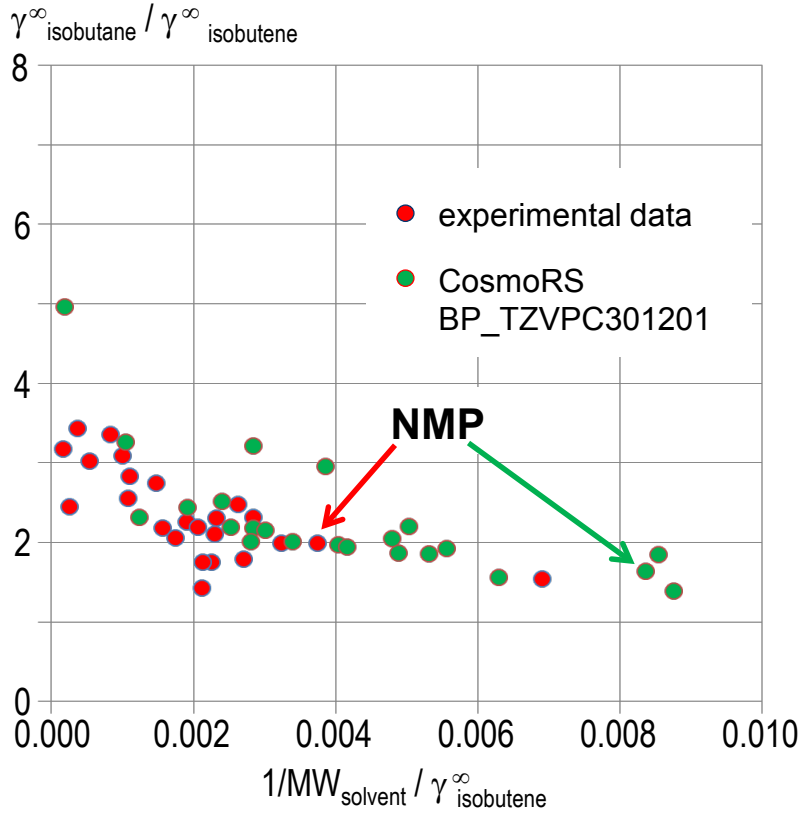



Abb. 1. Löslichkeit einiger $C_4$-Kohlenwasserstoffe in NMP bei 20 °C. Bunsenscher Löslichkeitskoeffizient $\alpha_i$ als Funktion der Beladung x.

Chemie-Ing.-Techn. 40. Jahrg. 1968 / Heft 23

## C4 steam cracking raw material – alkane reduction by extractive distillation



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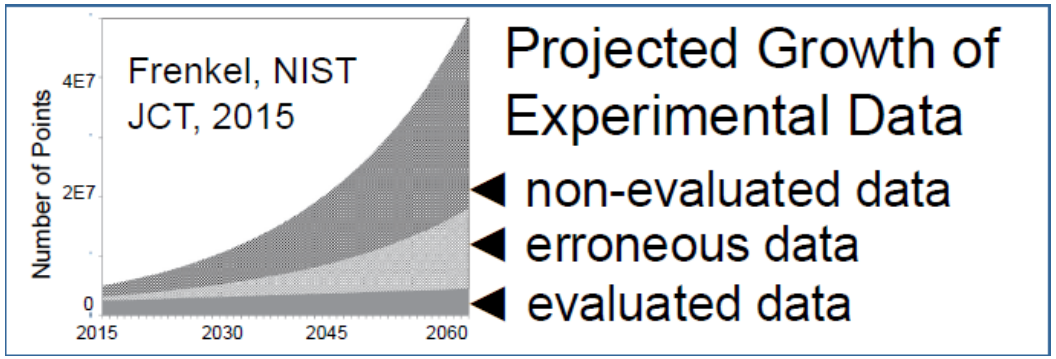
# Physical Property Data – Challenges and Perspectives

- Exponential increase in available experimental data –> **Evaluation** necessary!



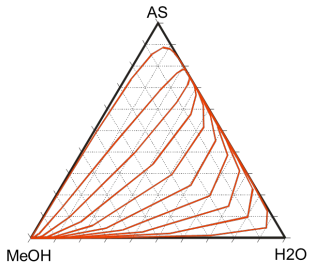

M. Frenkel / J. Chem. Thermodynamics 84 (2015) 18–40

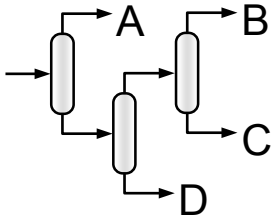
- Development and improvement of **EOS-Models** for simulation applications
  Limitation: Parmeterization, numerical effort in simulation
  Extension to group contribution approach:
  Evaluation of predictive capability of SAFT-$\gamma$-Mie in collaboration with Imperial College London

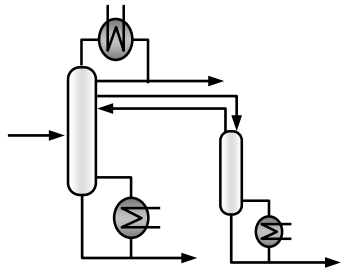
- Extended utilisation of molecular methods to get intermolecular interaction information.

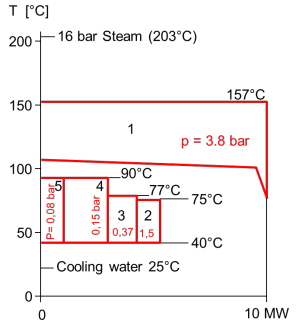
# Conceptual Design of Conventional or Hybrid Separations
# Conventional Procedure

- Typical workflow for distillation systems consist of
  - Physical properties analysis
  - Choice of separation sequence (by heuristics or shortcut)
  - Design of equipment (considering more complex network)
  - Design of heat integration (e.g. Pinch-analysis)






- For multiproduct systems and hybrid separations the complexity of options increases

# Conceptual Design of Conventional or Hybrid Separations Tools and Developments

- Use of **molecular simulation methods**
  - ➢ E.g. Design of additives for azeotropic or extractive distillation
- **Short-Cut Software CoDeSC**:
  Feasibility of simple and hybrid reaction and separations.

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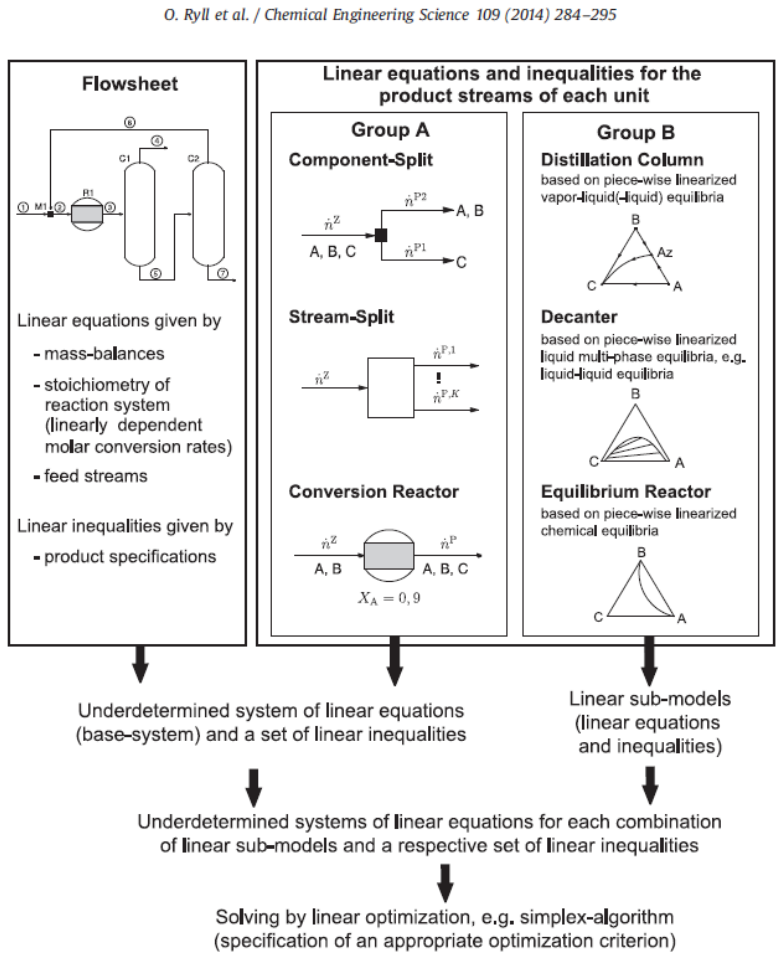
Fraunhofer ITWM

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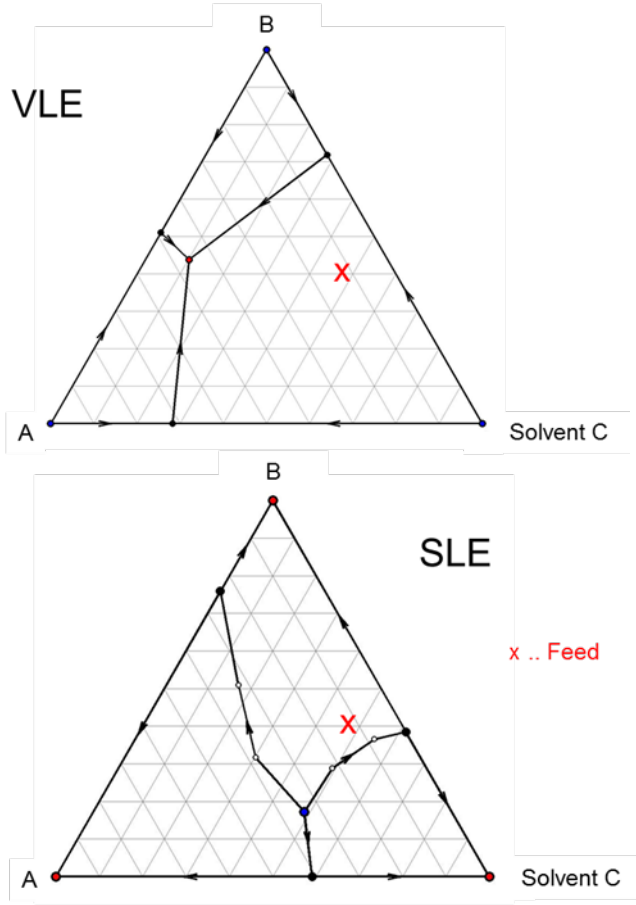
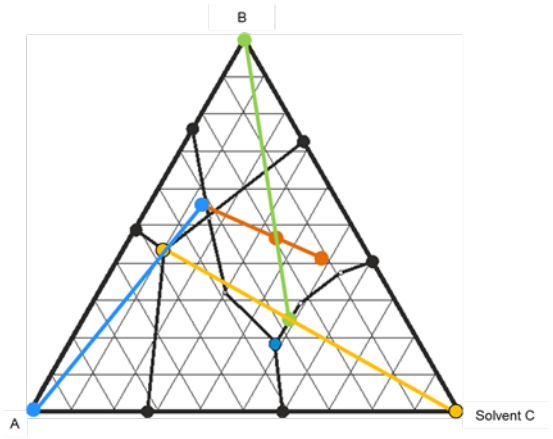
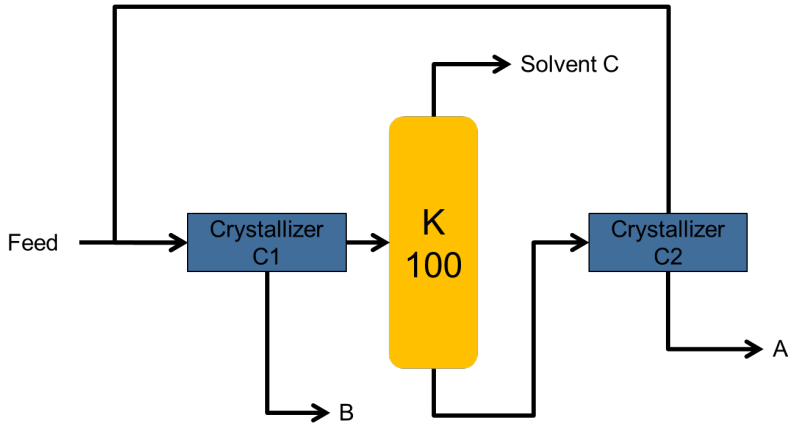
# Conceptual Design of Conventional or Hybrid Separations
# Example CoDeSC: Hybrid Distillation-Crystallization Process




Assumption: Ideal split in each unit



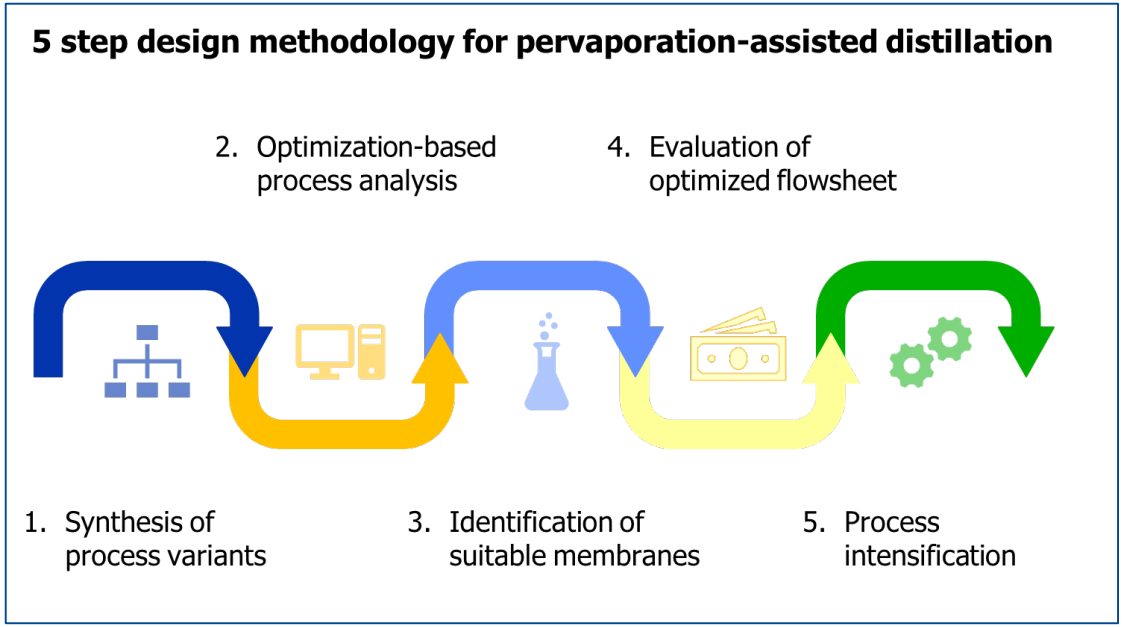

Courtesy: S. Deublein, BASF SE




| Stream | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $\dot{N}$[mol/s] | 10.000 | 14.947 | 10.752 | 4.195 | 4.705 | 6.047 | 4.947 | 1.100 |
| $\dot{n}_A$[mol/s] | 1.100 | 2.787 | 2.787 | 0.000 | 0.000 | 2.787 | 1.687 | 1.100 |
| $\dot{n}_B$[mol/s] | 4.200 | 6.850 | 2.697 | 4.153 | 0.047 | 2.650 | 2.650 | 0.000 |
| $\dot{n}_C$[mol/s] | 4.700 | 5.309 | 5.267 | 0.042 | 4.658 | 0.609 | 0.609 | 0.000 |
| $x_A$[mol/mol] | 0.110 | 0.186 | 0.259 | 0.000 | 0.000 | 0.461 | 0.341 | 1.000 |
| $x_B$[mol/mol] | 0.420 | 0.458 | 0.251 | 0.990 | 0.010 | 0.438 | 0.536 | 0.000 |
| $x_C$[mol/mol] | 0.470 | 0.355 | 0.490 | 0.010 | 0.990 | 0.101 | 0.123 | 0.000 |

# Conceptual Design of Conventional or Hybrid Separations Tools and Developments

- Use of **molecular simulation methods**
  - ➢ E.g. Design of additives for azeotropic or extractive distillation
- **Short-Cut Software CoDeSC**:
  Feasibility of simple and hybrid reaction and separations
- **Systematic design approach for hybrid processes combining distillation and membrane separation:**
  Ongoing transfer project from SFB Transregio 63




fvt laboratory of fluid separations



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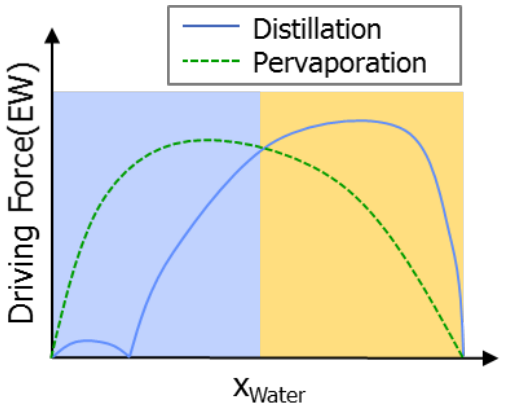
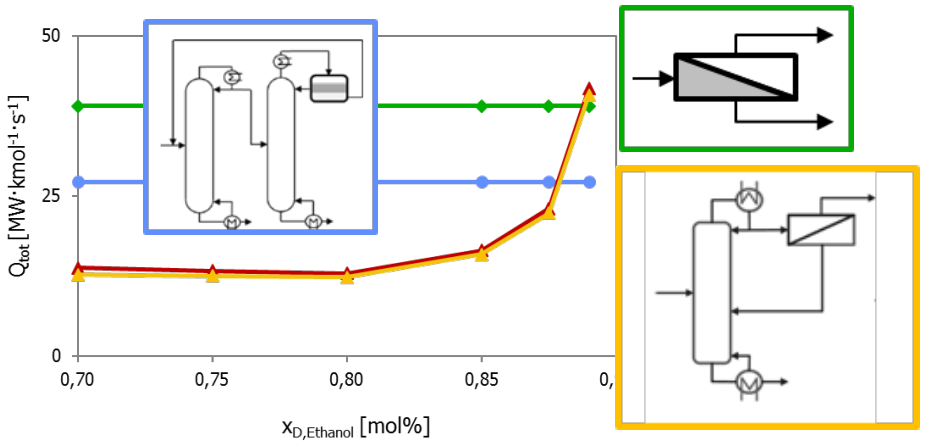
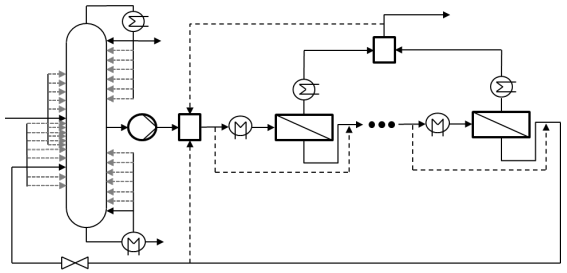
# Conceptual Design of Conventional or Hybrid Separations
# Example: EtOH-Water Separation by Distillation & Pervaporation

1. Synthesis of process variants
2. Optimization-based process analysis
3. Identification of suitable membranes
4. Evaluation of optimized flowsheet
5. Process intensification



Scharzec et al. Chem. Ing. Tech. 2017, 89, No 11 1534 – 1549
Skiborowski et al., Ind. Eng. Chem. Res., 2014, 53, 15698-15717

fvt laboratory of fluid separations



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# Conceptual Design of Conventional or Hybrid Separations Challenges

- Tools for systematical (reaction)/separation development are scarcely used.
  Reasons:
  - For distillation system the build up of a simple rigorous simulation is quickly done.
  - Property data for distillation may be available, but for other unit operations they are rare.
  - At the beginning of a process development side-components, which are tricky to eliminate, are often not known.
  - Frequently boundary conditions like time-to-market, research capabilities and costs, catalyst-life-time, available raw materials and utilities... determine the selection of pathways.

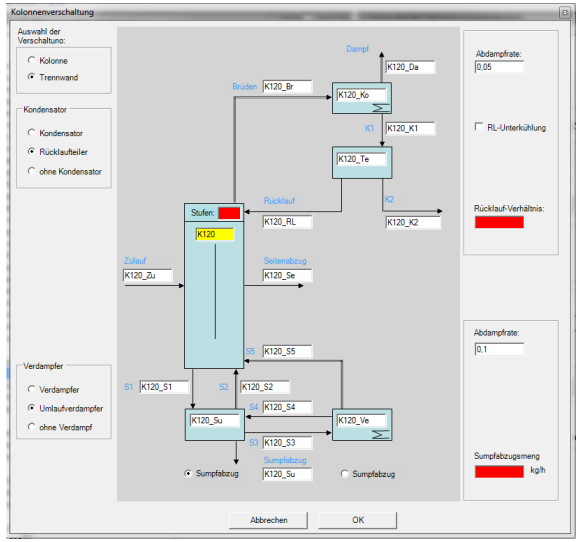
# Modeling of Special Distillation Systems
# Reactive Distillation

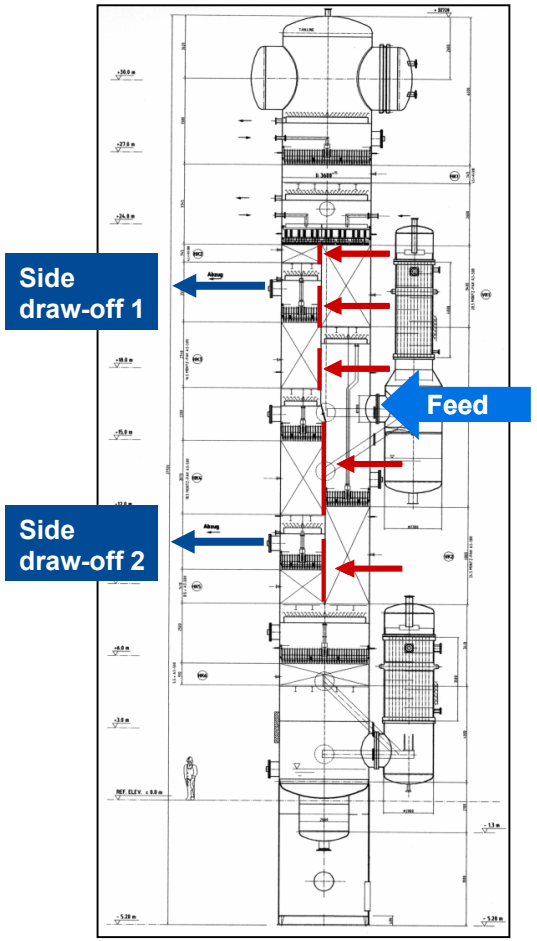
- BASF builds on more than 20 years of intensive investigations on reactive distillation, having joined different cooperations with universities, chemical companies and equipment suppliers.
- This resulted in
  - multiple apparatus- and process-patents and publications
  - Knowhow and availability of special equipment for miniplant design
  - Knowhow on simulation and scale-up for homogeneous and heterogeneous catalyzed reactive distillation
  - Application of different detail levels of simulations: EQ-reaction, defined conversion, kinetics, mass transfer
- Main challenges: description of reaction system (kinetic investigations)

Miller, Ch. Et al. Chem.Ing.Tech. (2004) 76 No 6, 730-733
Kaibel, G. et al. Chem.Ing.Tech. (2005) 77 No 11, 1749-1758
von Harbou, E. et al. AIChE J (2013), 59 No 5, 1533-1543

# Modeling of Special Distillation Systems
# Divided Wall Columns

- More than 30 years ago BASF had implemented the first divided wall column, meanwhile there may be around 100 columns.
- Simulation in CHEMASIM (equation oriented) with special DWC module:



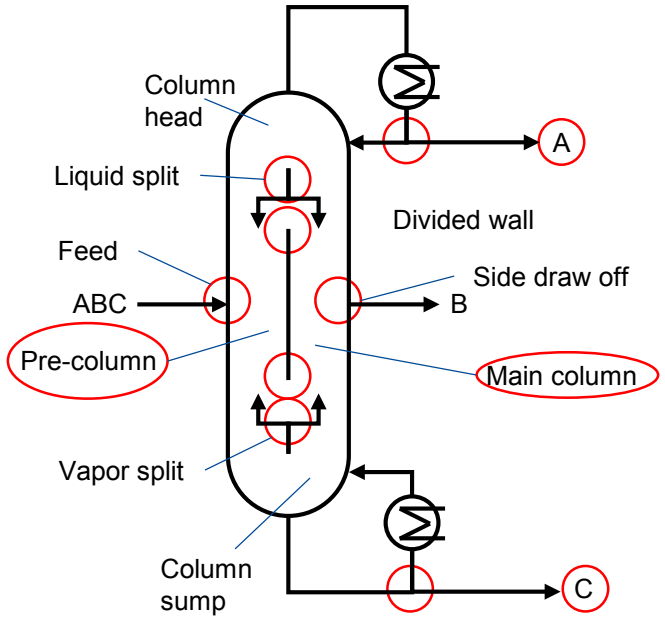





Kaibel, G. Chem.Eng.Technol. 10 (1987) 92-98
Asprion, N.; Kaibel, G. Chem.Eng.Proc. 49 (2010) 139-146

# Modeling of Special Distillation Systems
# Divided Wall Columns

- More than 30 years ago BASF had implemented the first divided wall column, meanwhile there may be around 100 columns.
- Simulation in CHEMASIM (equation oriented) with special DWC module.
- Different optimization methods available:
  - Sequential 1-criterion optimization (S-SCO)
  - Parallel 1-criterion optimization (P-SCO)
  - Multi criteria optimization (MCO)
- Well established!




Benfer, R. PN JT Fluidverfahrenstechnik 2016, Garmisch-Partenkirchen

# Modeling of Special Distillation Systems
# Dynamic Simulation of Distillation

- Ten years ago rigorous dynamic simulation was a rarity and took long time to be implemented in conventional flowsheet simulation.
- Meantime the software has much improved -> lower hurdle, but still consuming higher runtime.
- In CHEMADIS (BASF‘s dynamic inhouse simulator) all functions of steady-state simulation are available, but only some of them are constantly used.
- Need in dynamic simulation seems to increase with extension of simulation life cycle.

➢ Expertise in dynamic simulation has to be built up.

# Parameter Adaptation for Plant Snapshots and Miniplant Experiments
# Ideal MSO Workflow

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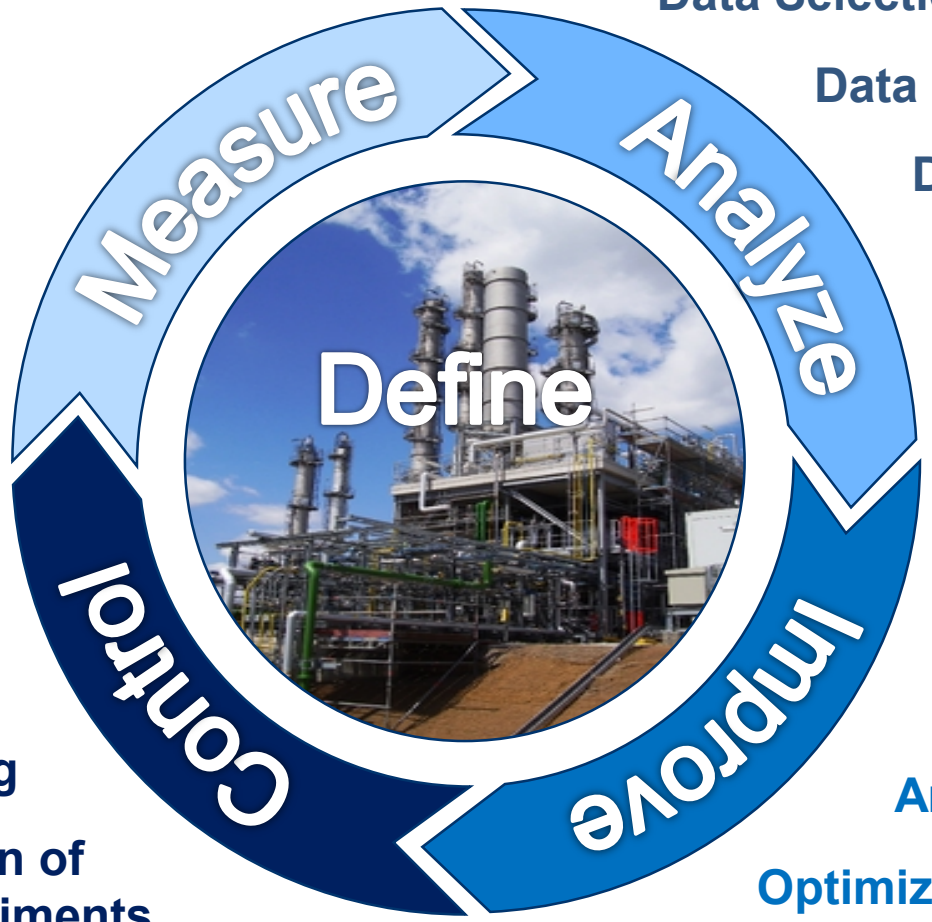
Technische Universität Kaiserslautern



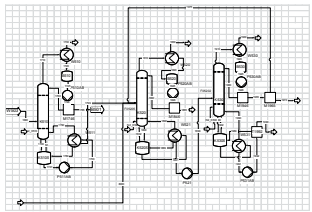

Data Selection

Data Reconciliation

Data Mining

Model Validation

Model

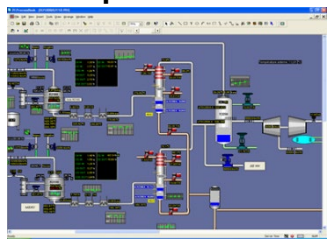


Model Adjustment

Sensitivity Analysis

Optimization

Operation



Online Optimization

Robust Planning

Design of Experiments



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# Parameter Adaptation for Plant Snapshots and Miniplant Experiments
# Ideal MSO Workflow

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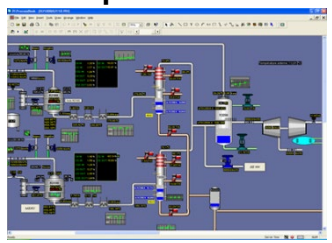
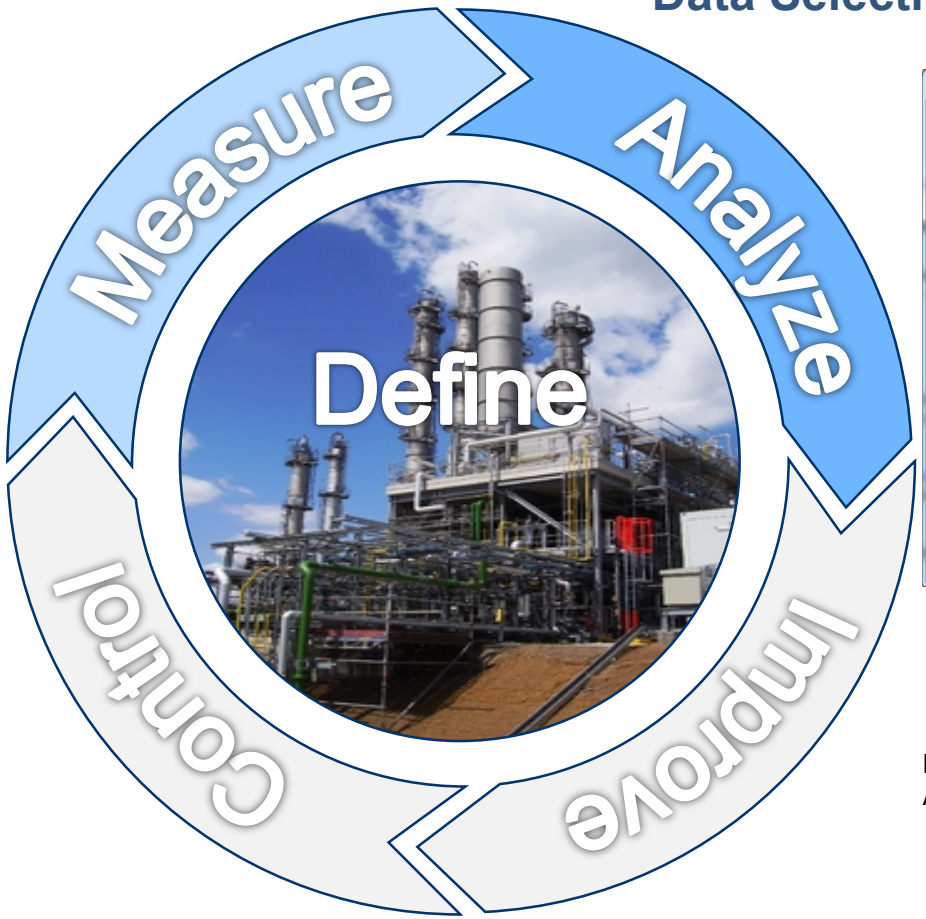
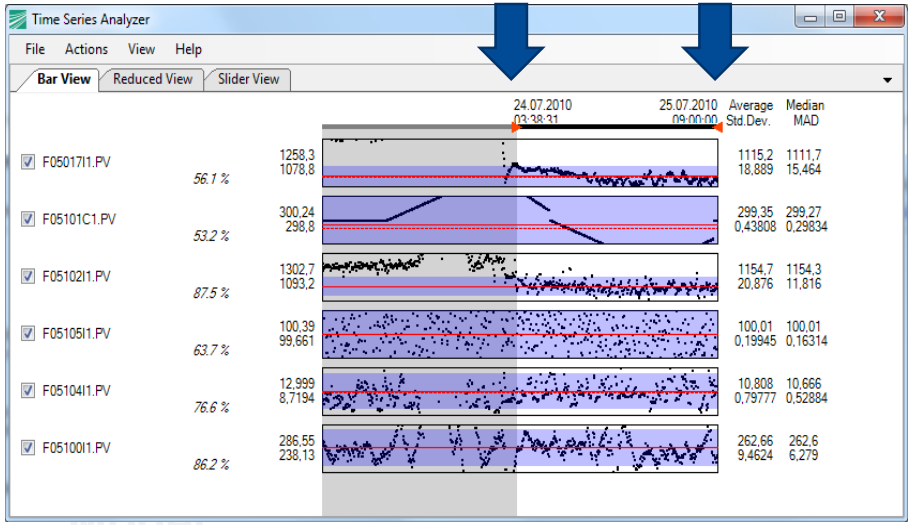
Operation






Data Selection




Model Adjustment


Bortz, M. et al.; Ind. Eng. Chem. Res. 2017, 56, 12672-12681
Asprion, N. et al.; Chem. Ing. Tech. 2015, 87, No. 12, 1810-1825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# Parameter Adaptation for Plant Snapshots and Miniplant Experiments
# Ideal MSO Workflow

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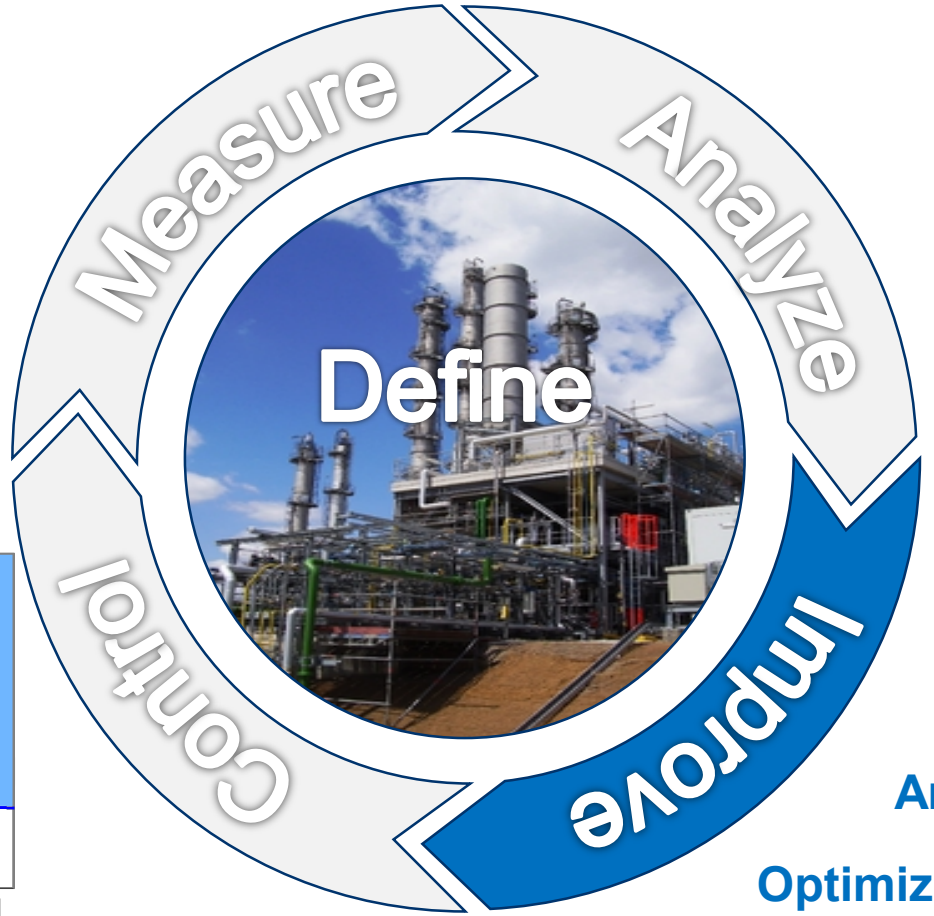
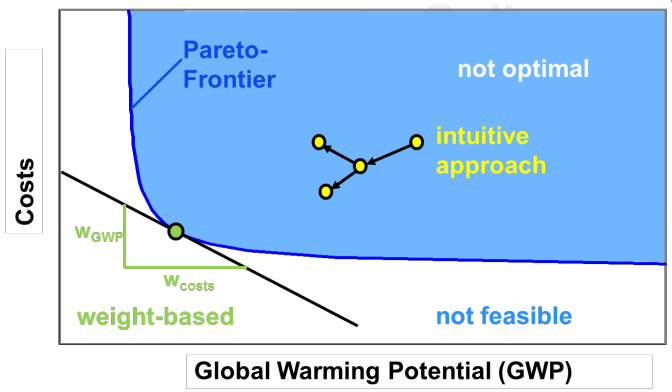



**Properties accessible for variation**

- Process parameters (T, p, m, x, … )
- Physical properties (activity coefficients, vapor pressures, enthalpies, …)
- Reaction parameters (equilibrium and kinetic constants)
- Evaluation properties (costs, life cycle indicators, etc.)

Sensitivities estimated from scenarios (variation of uncertain parameters)




**Sensitivity Analysis**

**Optimization**

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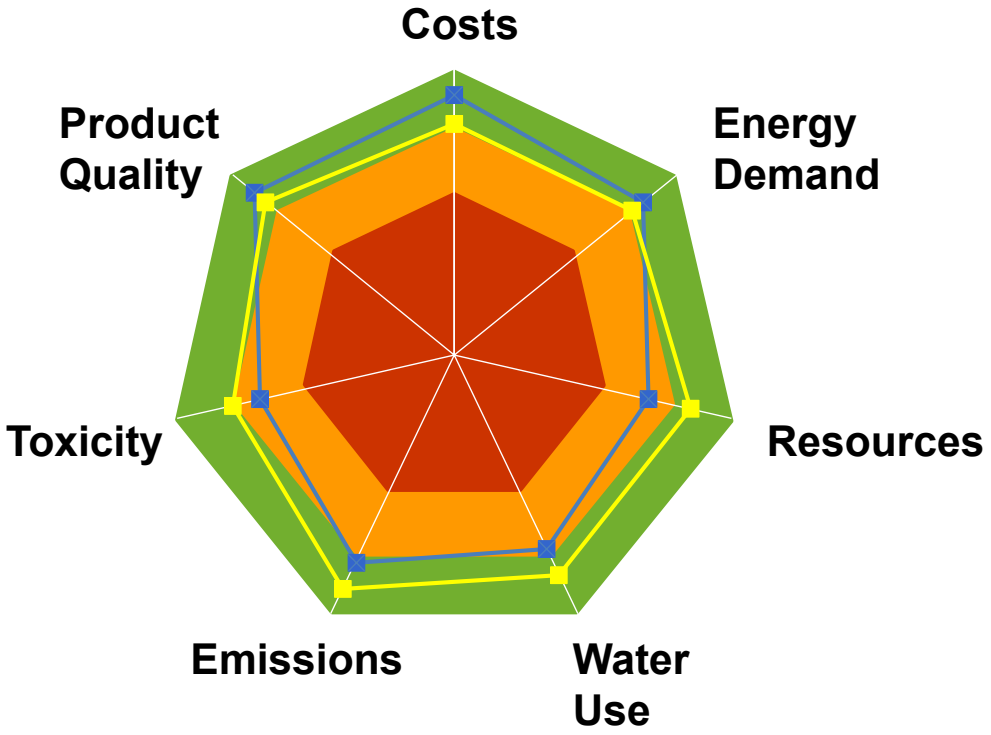
# Sustainable Process Design – a Multicriteria Optimization Problem


Courtesy N. Asprion, BASF SE

**Parameters:**

- Feed stocks
- Utilities
- Process Configurations
- Equipment
- Operating Conditions
- Site
- …



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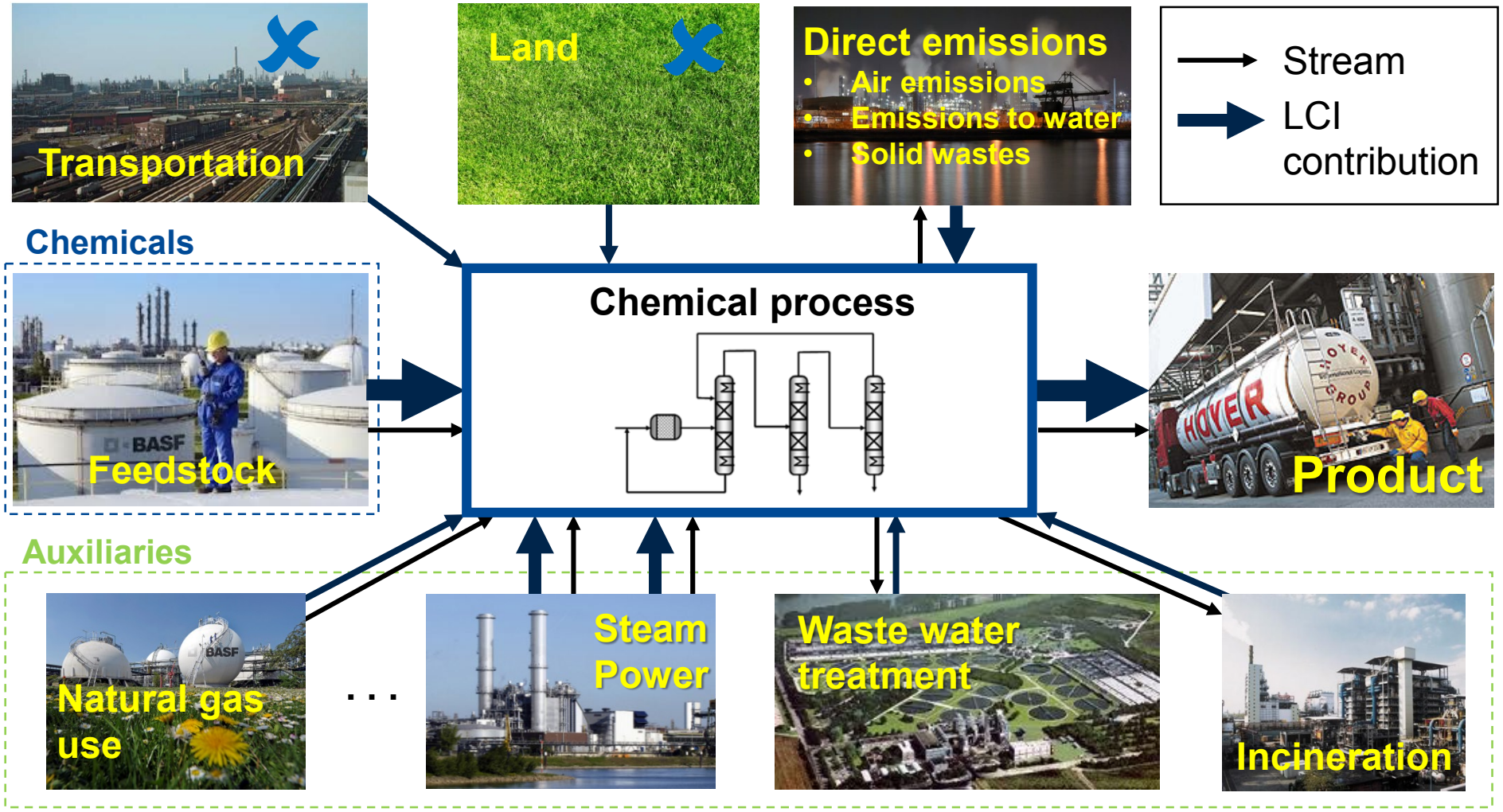
# Life Cycle Analysis in Simulation

## Mapping of LCIs to Streams and Account for Direct Emissions




Not available from simulation



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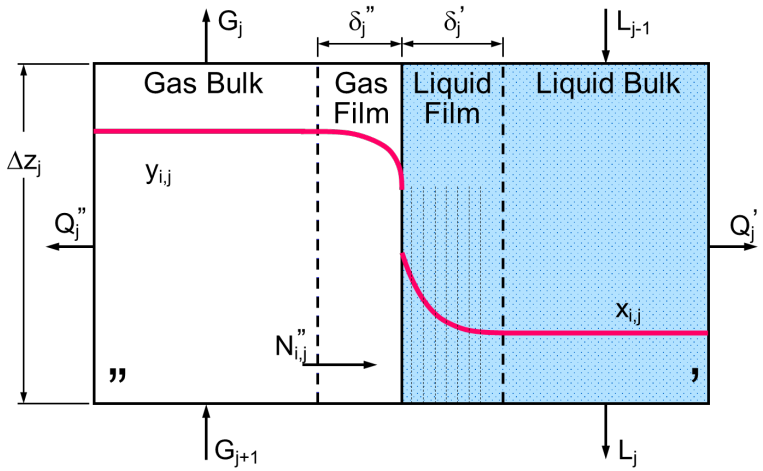
# Mass Transfer in Distillation and Absorption
# BASF‘s Rate-based Simulator


- BASF‘s business with gas treatment solutions has started the concepts for mass transfer simulation already more than 15 years ago.
- Driven by the absorption team a rate-based rigorous simulation tool was developed, fully integrated in our in-house flowsheet simulator CHEMASIM (equation oriented), covering
  - Kinetic and equilibrium reactions
  - Connection to our physical property library, especially also containing electrolyte-thermodynamics
  - Implementation of routines for the calculation of transport properties

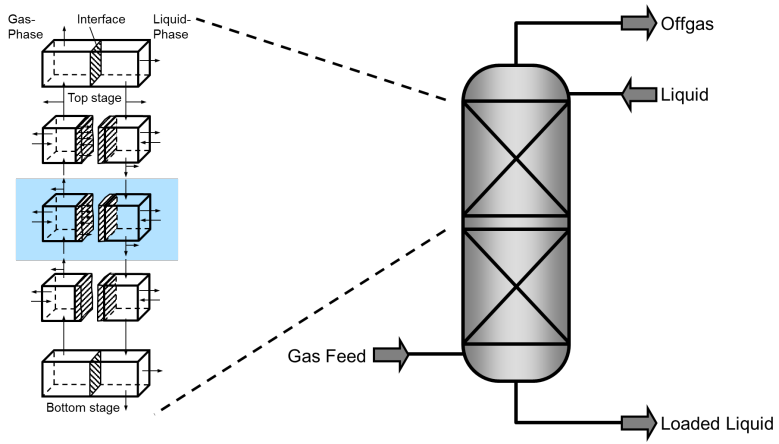
# Mass Transfer in Distillation and Absorption
# BASF‘s Rate-based Simulator

## Two-Film-Model in Segment j




- Radial film segmentation
- Chemical reactions in bulk and film
- Different transfer models available
  - → Maxwell-Stefan
  - → Fick-Law

## Axial Segmentation of Apparatus



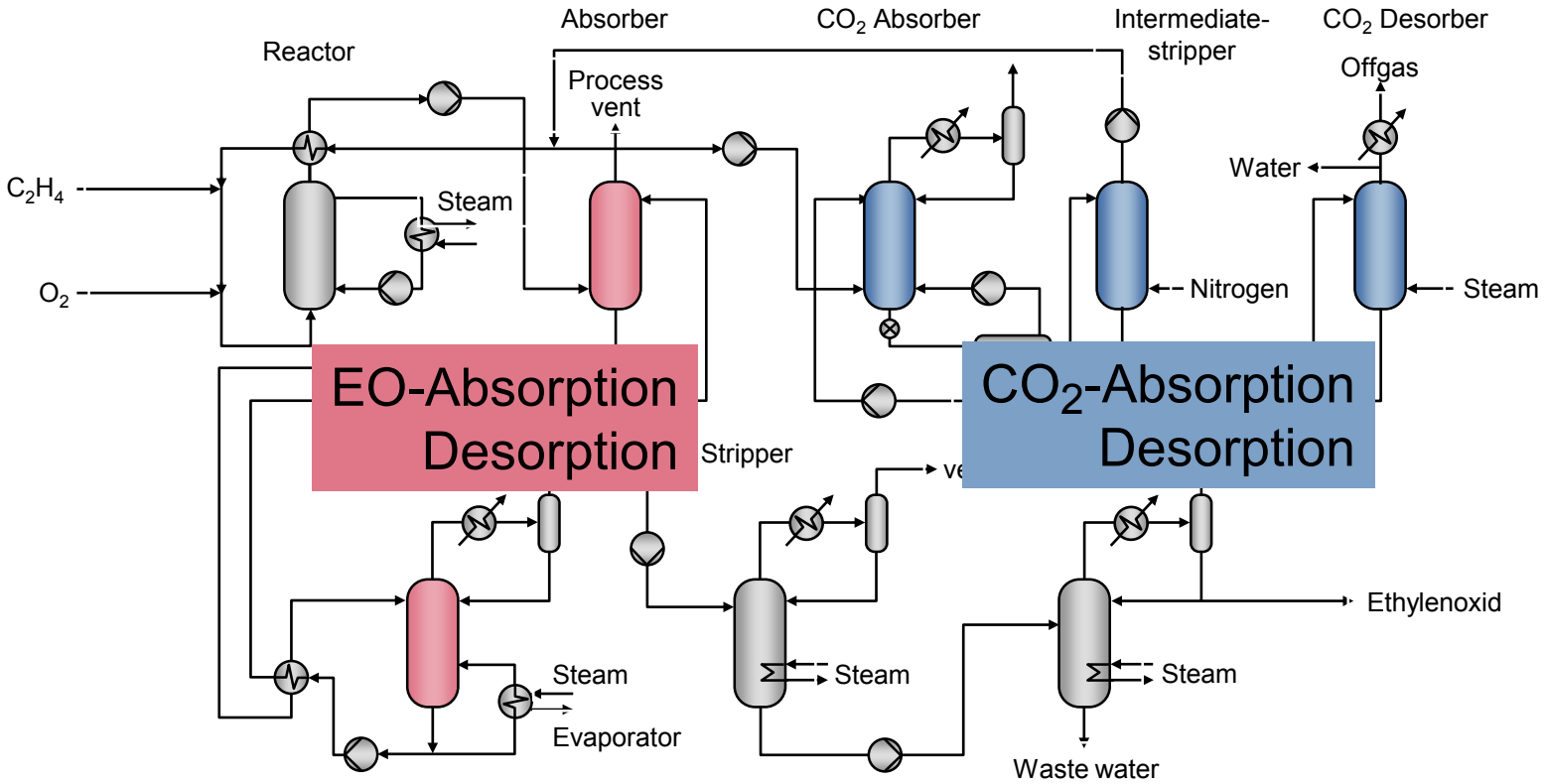

- Axial non-equilibrium segments
- Internals + mass transfer equipment
  - → Mass transfer correlation
  - → Fluiddynamics

# Mass Transfer in Absorption
# Example: EO Production Process

Courtesy R. Thiele, BASF SE

**Main reactions:**

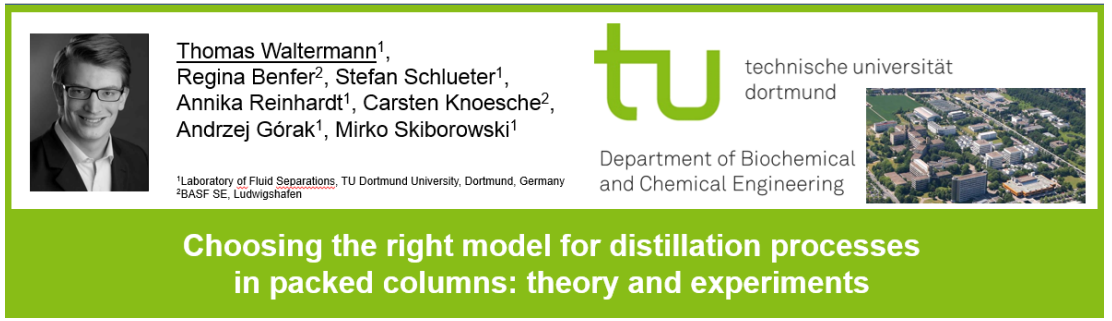
1) $C_2H_4 + 1/2\ O_2 \rightarrow C_2H_4O$
2) $C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$




Kirk, Othmer, *Encyclopedia of Chemical Technology, 4th ed. 1991-1998*

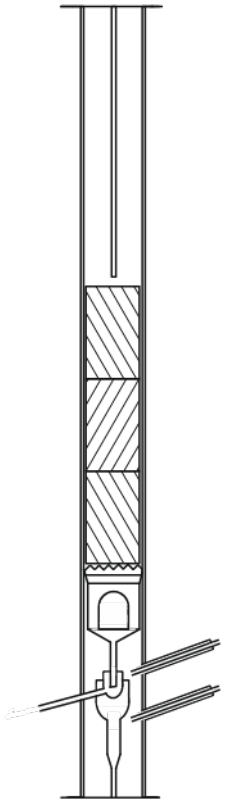
# Mass Transfer in Distillation

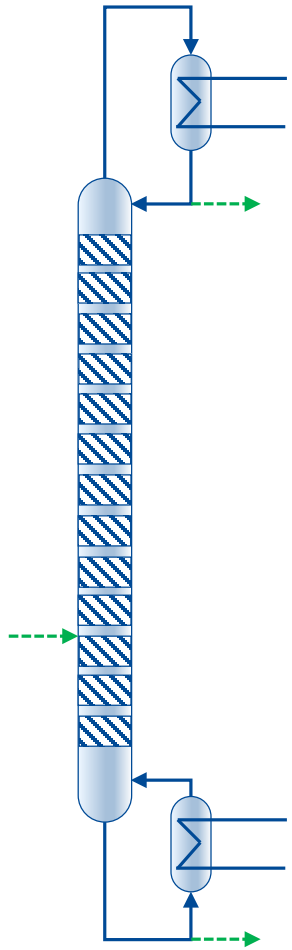
- In contrast to absorption we use rigorous equilibrium stage simulation in distillation. Advantages:
  - Much faster
  - Better in convergence
  - Less physical property data necessary
  - HETP-values are more published than parameters for mass transfer correlations
- In some cases we fail in process description.
  - In which cases should rate-based simulation be used for distillation?
- Poster 36



# Mass Transfer in Distillation
# Experimental Investigations at BASF

- Laboratory equipment:
  - Column D = 50 mm, H = 10 m;
    2.56 m packing Montz A3-500 (≅ Sulzer BX),
    segmented in parts of 240 mmm height
  - 15 resp. 16 sample positions along the height
- Operation conditions:
  - Continuous operation or infinite reflux
  - F-Factor: 0.6 – 2 $\sqrt{\mathrm{Pa}}$ at 950 mbar
  - **Measurement of concentration and temperature profiles**
  - Wide-boiling mixtures



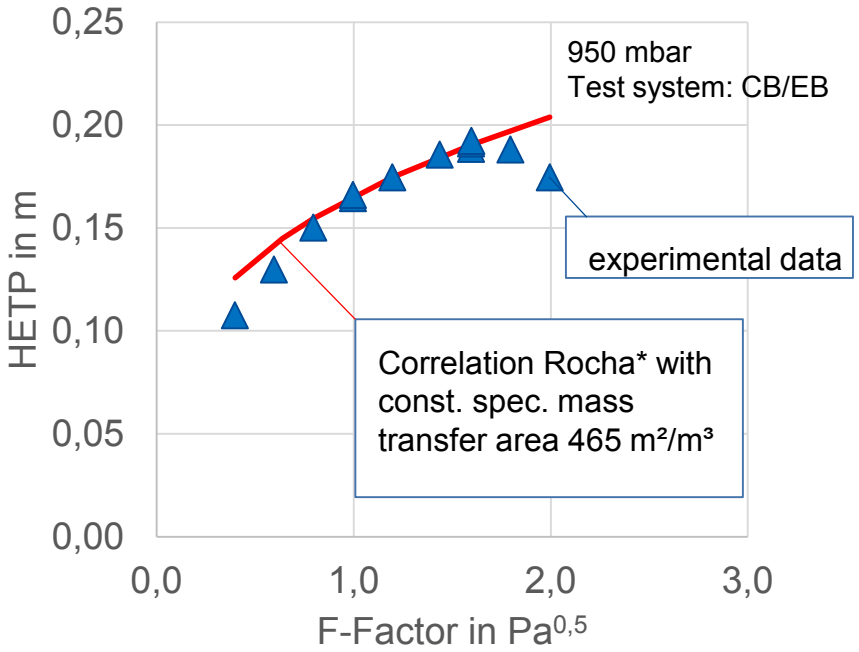


# Mass Transfer in Distillation
# Models used

- **EQ-model:**
  Choose number of theor. trays from HETP value according to the mean F-factor.

- **RB-model:**
  - Stefan-Maxwell diffusion
  - Segment height 3.33 mm
  - Chosen mass transfer correlation:

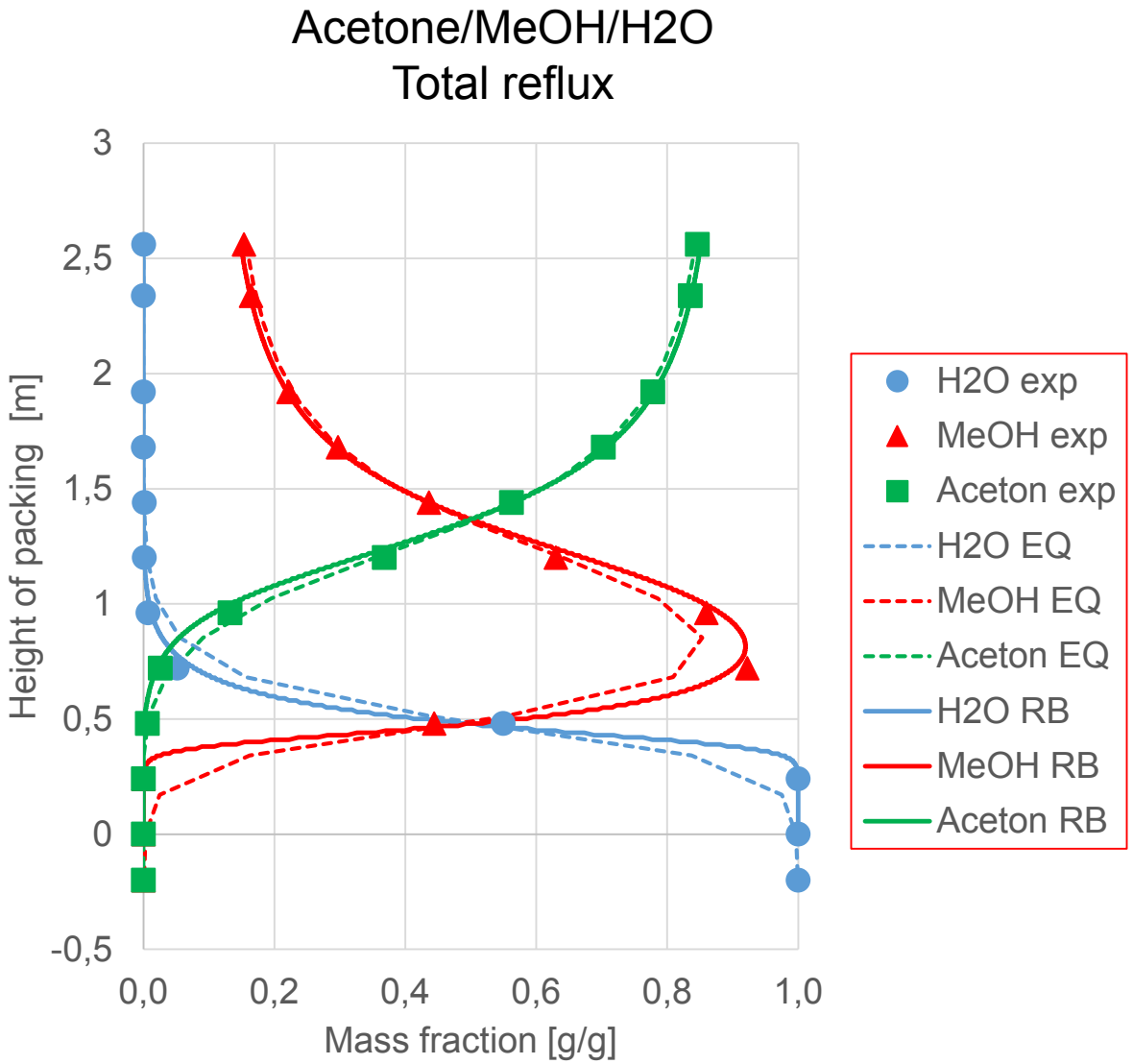
    *Rocha et al.** for gauze wire packing with const. specific transfer area (465 m²/m³)




* Rocha et al., Ind. Eng. Chem. Res. 1996, 35, 1660 - 1667

# Mass Transfer in Distillation
# Examplary Results

- EQ-model and RB-model give similar values for sump and distillate composition (fixed by mass balance for this system).
- Differences can be visible for ternary composition points and inflection points.
- RB-modeling gave better predicition of experimental results, but in some cases the differences were only minor.



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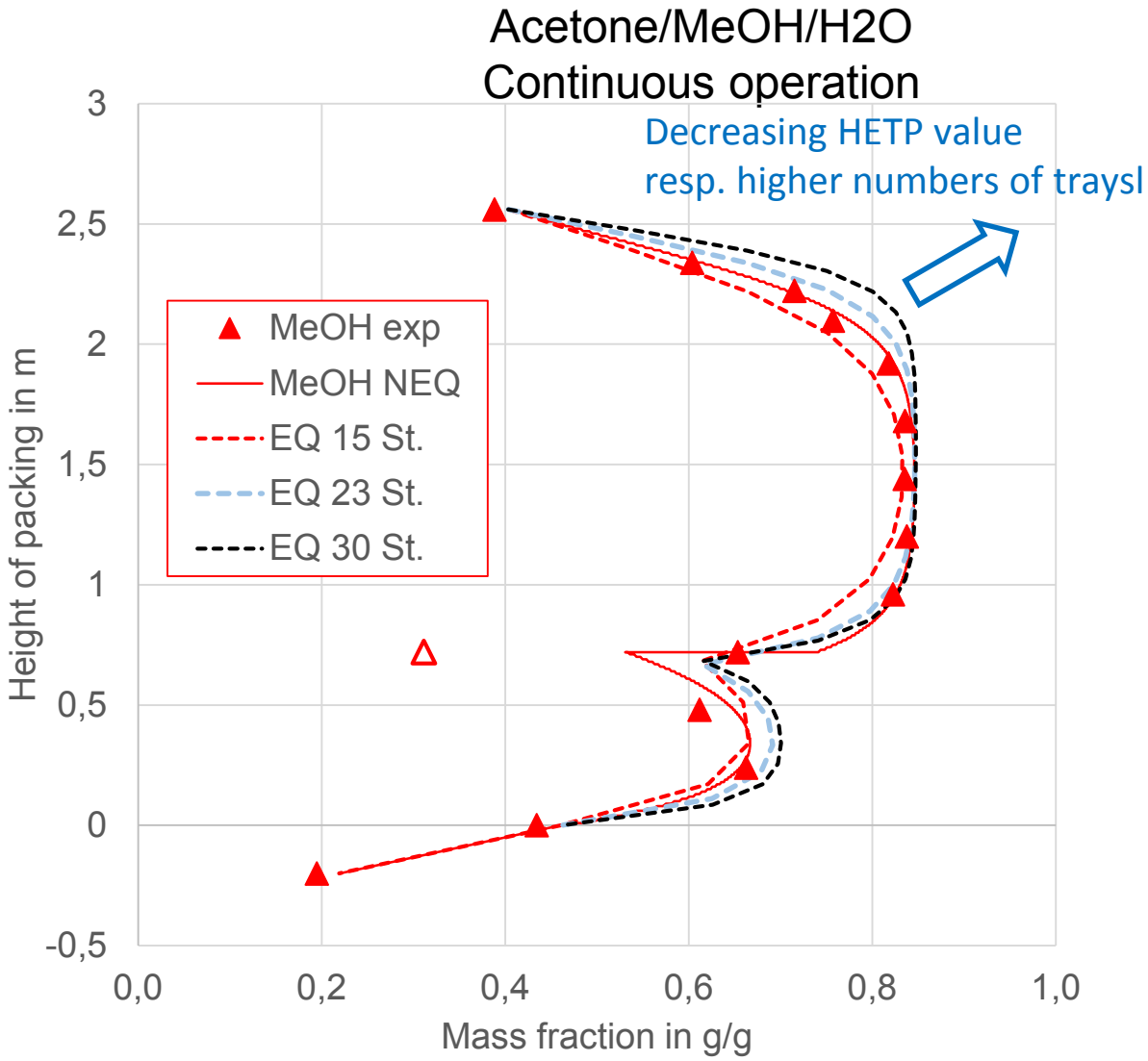
# Mass Transfer in Distillation
# Examplary Results

- Adjustment of HETP value can improve the fit of EQ-modeling piecewise.
- Adjustment of HETP must be done according to material system composition profile
- RB-modeling gave better predicition of experimental results – no parameter adjustment according to loading range or material system are necessary.



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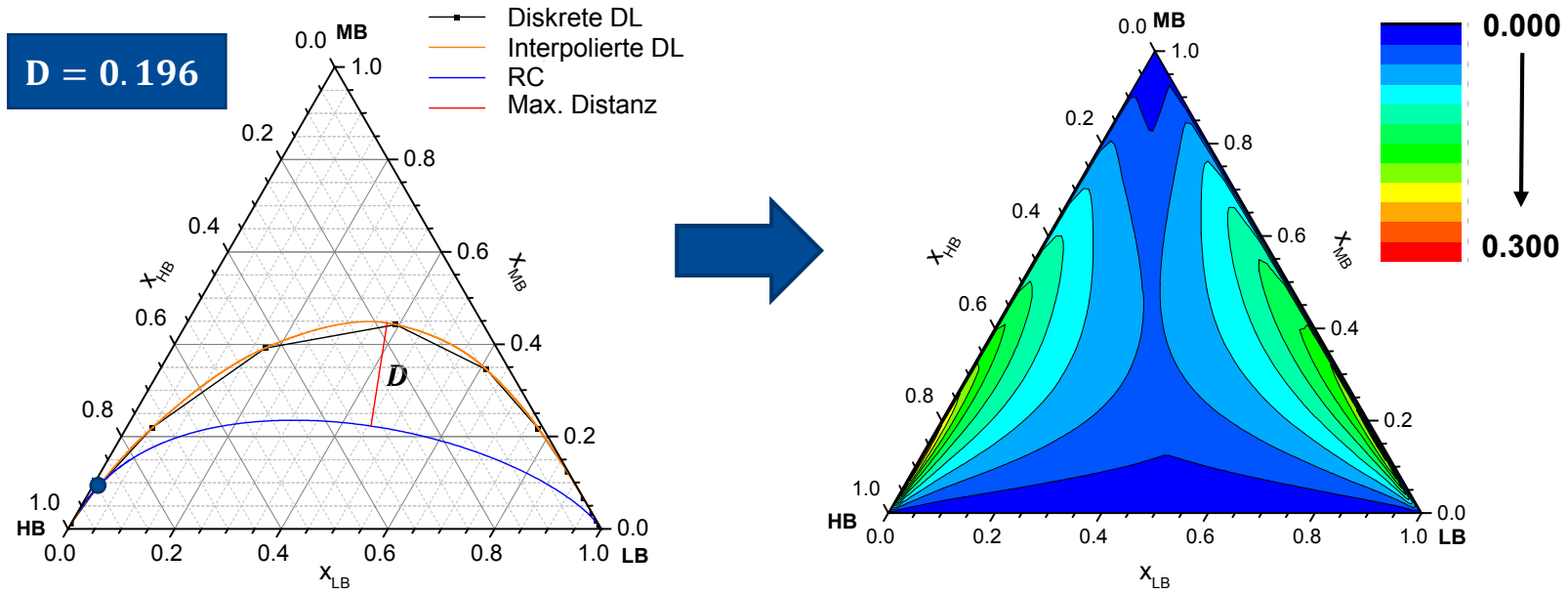
# Mass Transfer in Distillation
# Theoretical investigations

- Simplified calculation of the maximum differences between EQ-model and RB-model and visualisation in ternary plot

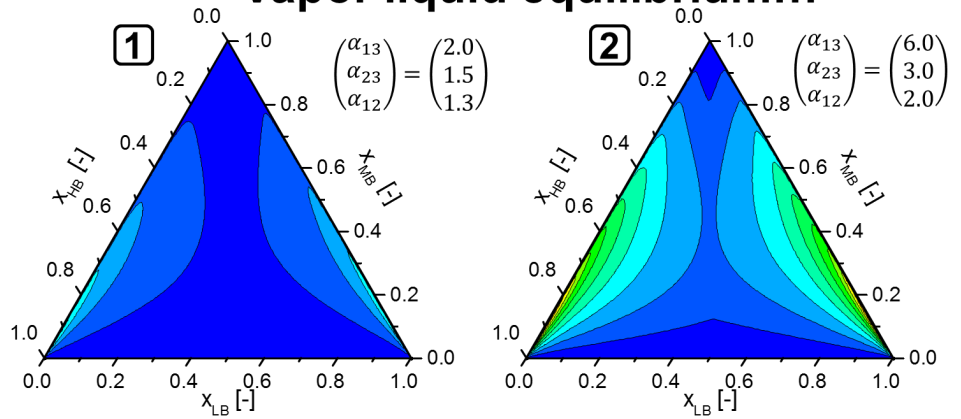


# Mass Transfer in Distillation
# Theoretical investigations

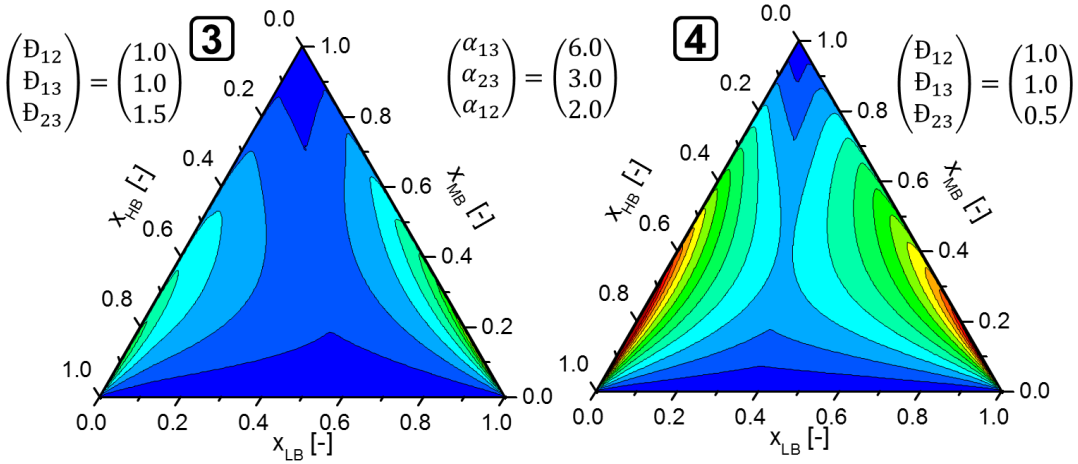
fvt laboratory of fluid separations

- Results show impact of the following parameters on model discrimination:
  - Relative volatility
  - Diffusion coefficient
  - Trace component concentration
- Workflow for best choice of model is in preparation

**Vapor liquid equilibrium…**




**… & component specific mass transfer**

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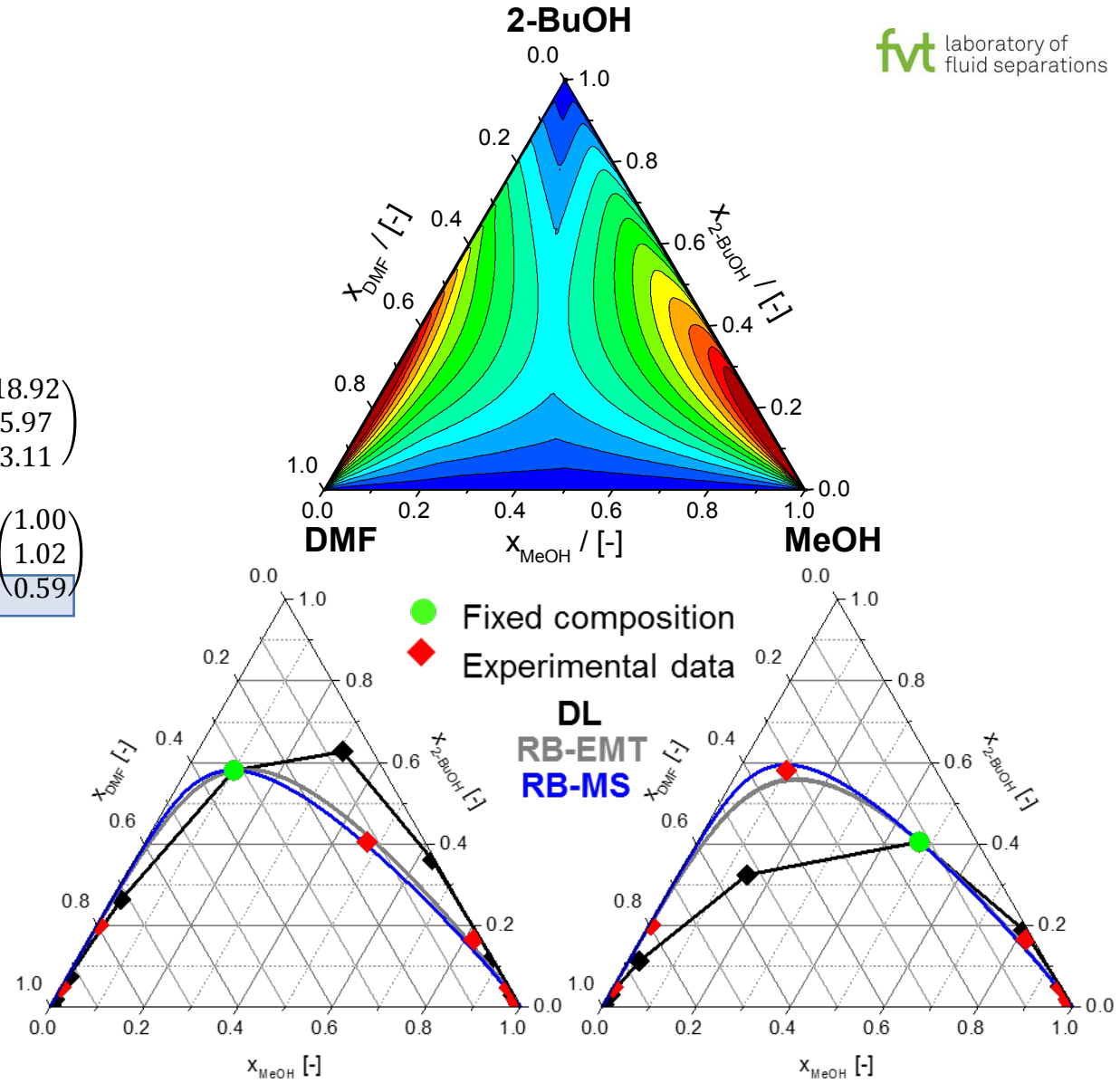
# Mass Transfer in Distillation Example

- System DMF/2-BuOH/MeOH
  - Wide-boiling
  - Strong differences in diffusion coefficients
- Comparison of experimental data from BASF experiments and calculated data from different models in composition trajectories

$$\begin{pmatrix}\bar{\alpha}_{13}\\ \bar{\alpha}_{23}\\ \bar{\alpha}_{12}\end{pmatrix} = \begin{pmatrix}18.92\\ 5.97\\ 3.11\end{pmatrix}$$

$$\begin{pmatrix}\bar{D}_{12}\\ \bar{D}_{13}\\ \bar{D}_{23}\end{pmatrix} = \begin{pmatrix}1.00\\ 1.02\\ 0.59\end{pmatrix}$$




This work was performed in the knowledge transfer project ‘‘Hybrid separation processes: Modeling and design of membrane-assisted distillation processes’’, which is part of the Collaborative Research Centre on ‘‘Integrated Chemical Processes in Liquid Multiphase Systems’’.
Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

# Conclusion

- Continous rigorous process simulation is „Standard“ in distillation and absorption applications
- Although being the most developed separation unit, there is still much improvement in the description by simulation
- Trends:
  - Physical property modeling tends to more sophisticated models
  - Flowsheet simulators get universal in application:
    Coupling of simulation – apparatus design – cost-, material- and energy-flow analysis – automatisation – real time optimization
  - Creation of Apps for quick information of selected applications
  - Increasing use of instationary simulation
  - Rate-based modeling will increase

# Challenges und Perspectives

- Technical understanding is necessary for applying simulations and vice versa.
- Tools and applications have to be used on a regular base, otherwise they won‘t get alive.
- The extensive increase of data needs more emphasized standardization and documentation.
- Experiments will still be necessary!
  -> But they can be done more focussed (DoE) and with better technical support (MSO Workflow).
- The extended life cycle of models needs a continuous maintenance by experts.

**Process simulation is challenging & exciting!**

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