**Thursday, 2 June 2016**

10h30  **Registration**

11h00 – 11h30  **Welcome and Opening + Introduction**  
Matthias Kraume

<table>
<thead>
<tr>
<th><strong>SESSION 1</strong></th>
<th><strong>CHAIR: Andrzej Góra</strong></th>
</tr>
</thead>
</table>
| **1.1** 11h30 – 12h15 | James H. Clark  
Towards an intelligent approach to solvent substitution |
| **1.2** 12h15 – 13h00 | Dmitry Yu. Murzin  
Unified kinetic analysis of solvent effects in complex catalytic reactions |
| **1.3** 13h00 – 13h30 | Gabriele Sadowski  
Thermodynamic modeling of reaction equilibria and reaction kinetics |

13h30 – 14h30  **LUNCH BREAK (60 MIN)**

<table>
<thead>
<tr>
<th><strong>SESSION 2: ROUND TABLE DISCUSSION</strong></th>
<th><strong>MODERATION: Andrzej Góra</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>14h30 – 15h15</td>
<td>“Tunable Solvents For Green Processing”</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>SESSION 3</strong></th>
<th><strong>CHAIR: Dominique Thévenin</strong></th>
</tr>
</thead>
</table>
| **3.1** 15h15 – 16h00 | Rodney O. Fox  
Recent advances in CFD modeling of multiphase reactors |

16h00 – 16h30  **COFFEE BREAK (30 MIN)**

<table>
<thead>
<tr>
<th><strong>SESSION 3</strong></th>
<th><strong>CHAIR: Dominique Thévenin</strong></th>
</tr>
</thead>
</table>
| **3.2** 16h30 – 17h15 | Michael Schlüter  
Improvement of empirical models for multiphase flows by detailed experimental analysis |
| **3.3** 17h15 – 18h00 | Dieter Bothe  
Modeling and simulation of mass-transfer across clean/contaminated fluid interfaces |

<table>
<thead>
<tr>
<th><strong>SESSION 4: Poster</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>18h00 – 19h00</td>
</tr>
</tbody>
</table>
### SOCIAL EVENTS:

- **19h00 – 20h00**: **Tour „Germany’s Oxford“**
  - **Meeting Point**: Harnack-Haus, Ihnestr. 16
- **20h30**: **Dinner**
  - **Location**: Harnack-Haus

### Friday, 3 June 2016

#### SESSION 5

**Chair: Arno Behr**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>09h00</td>
<td>Reinhard Schomäcker</td>
<td>Multi-phase systems for tandem reactions</td>
</tr>
<tr>
<td>09h30</td>
<td>Peter Wasserscheid</td>
<td>Ionic Liquid Thin Film Materials for Catalysis and Separation Technologies</td>
</tr>
<tr>
<td>10h15</td>
<td>Walter Leitner</td>
<td>Continuous-flow organometallic catalysis using advanced fluids</td>
</tr>
</tbody>
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11h00 – 11h30 **COFFEE BREAK (30 MIN)**

#### SESSION 6

**Chair: Matthias Kraume**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>11h30</td>
<td>Bala Subramaniam</td>
<td>Processes intensification with pressure-tunable media</td>
</tr>
<tr>
<td>12h15</td>
<td>Jason P. Hallett</td>
<td>Tuning ionic liquids for low cost: applications in lignocellulose deconstruction</td>
</tr>
<tr>
<td>13h00</td>
<td>Kai Sundmacher</td>
<td>Integrated solvent selection and process design for the efficient recovery of homogeneous catalysts in hydroformylation processes</td>
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</table>

13h30 – 14h15 **LUNCH BREAK (45 MIN)**

#### SESSION 7

**Chair: Kai Sundmacher**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>14h15</td>
<td>Irina Smimova</td>
<td>Implementation of surfactants in continuous (reactive) separation processes</td>
</tr>
<tr>
<td>15h00</td>
<td>Philip G. Jessop</td>
<td>CO₂-switchable solvents for facilitated separations</td>
</tr>
</tbody>
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15h45 – 16h15 **Final Discussion**

16h15 **Closing**
**Abstracts:**

**Integrated reactor–separator system for recycling of homogeneous catalysts** -
- J. DREIMANN$^{1,2}$, M. SKIBOROWSKI$^2$, A. J. VORHOLT$^1$, A. GÓRAK$^2$, AND A. BEHR$^1$

$^1$ Laboratory of technical chemistry, BCI, TU Dortmund, Emil-Figge-Straße 66, 44227 Dortmund
$^2$ Laboratory of fluid separations, BCI, TU Dortmund, Emil-Figge-Straße 70, 44227 Dortmund

Homogeneous transition metal catalysts allow highly selective conversion of reactants at mild reaction conditions. Thermomorphic solvent systems and organic solvent nanofiltration are two techniques to tackle the crucial challenge of catalyst recovery. We have developed a suitable combination of reaction and separation to reach high selectivity and yield on one hand and prevent catalyst loss on the other. Only the combination of suitable solvents, reaction conditions and separation methods guarantee a successful performance of the whole catalytic system.

**Hydroformylation of fatty compounds in aqueous thermomorphic solvent systems** -
- T. GAIDE, J. DREIMANN, A. BEHR, AND A. J. VORHOLT

Technical University Dortmund

Herein we describe the application of aqueous thermomorphic solvent systems (TMS) in the homogeneously catalyzed hydroformylation of methyl 10-undecenoate as model compound for fatty acid derivatives. The catalyst consists of Rh(CO)$_2$acac/Sulfoxantphos. With this catalyst in a water/1-butanol TMS high turnover frequencies (1500 h$^{-1}$) and high regioselectivities ($l/b=89/11$) such as low catalyst leaching values into the product phase are achieved. The catalyst was successfully recycled in a continuously operated miniplant.

**Solvent effects on the hydroformylation of long chain olefins** -
- M. GERLACH$^1$, M. LEMBERG$^2$, G. SADOWSKI$^2$, A. SEIDEL-MORGENSTERN$^{1,3}$, AND C. HAMEL$^{1,4}$

$^1$ Otto von Guericke University, Institute of Process Engineering, Magdeburg/DE
$^2$ Technical University Dortmund, Laboratory of Thermodynamics, Dortmund/DE
$^3$ Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg/DE
$^4$ Anhalt University of Applied Sciences, Processing Engineering, Köthen/DE

The solvent effect on the rhodium-catalyzed hydroformylation of 1-dodecene in a thermomorphic solvent system consisting of N,N-dimethylformamide (DMF), decane and 1-dodecene was studied experimentally. Kinetic experiments revealed a
significant solvent influence of DMF. The dominant isomerization in the reaction network of the hydroformylation seems to be inhibited by the polar solvent DMF which enables the development of dosing strategies to control the temporal and local reaction rates, respectively.

**Prediction of liquid-liquid and solid-liquid phase equilibria of branched molecules** -  
T. Goetsch¹, P. Zimmermann², R. van den Bongard², S. Enders², and T. Zeiner¹

¹ Laboratory of Fluid Separations, TU Dortmund, Emil-Figge-Straße 70, 44227 Dortmund, Germany  
² Institute of Technical Thermodynamics and Refrigeration Engineering, Karlsruhe Institute of Technology, Engler-Bunte-Ring 21, 76131 Karlsruhe, Germany

During the hydroesterification of long-chain unsaturated esters of fatty acids linear and branched diesters are produced. In general, these isomers can be separated by solvent crystallization. The challenge is the appearance of a superposition of a liquid-liquid equilibrium and a solid-liquid equilibrium which can affect the product properties. The aim of this contribution is the experimental and theoretical investigation of the mentioned superposition.

**Iterative set-point optimization of multiphase homogeneously catalyzed processes** -  
R. Hernández and S. Engell

Process Dynamics and Operations Group, Technische Universität Dortmund, Emil-Figge-Straße 70, 44221 Dortmund, Germany

We consider the optimization of the operating point of chemical processes, specifically of multiphase processes. Due to different uncertainties, the optimal operating point that is calculated based upon a process model can differ from the actual plant optimum and constraints may be violated. Iterative set-point optimization uses measurements from the process to modify the optimization problem such that the true plant optimum is realized. We demonstrate the applicability of iterative set-point optimization to two different homogeneously catalyzed processes multiphase processes.
Influence of drop size distribution and droplet interaction on phase separation processes in liquid multiphase systems -  L. HÖHL, S. RÖHL, J. SCHULZ, AND M. KRAUME
TU Berlin, Chair of Chemical & Process Engineering, Ackerstraße 76, 13355 Berlin, Germany

In liquid multiphase systems, fastest phase separation can be achieved under three phase conditions. The occurrence of a third liquid phase leads to various types of droplet interaction (e.g. droplets attached to each other or multiple emulsions). Besides the drop size distribution, the droplet interaction is an important factor influencing the mechanism and duration of the phase separation process.

Hydroformylation in microemulsion systems - Long term mini-plant operation and model validation -  M. ILLNER1, T. POGRZEBA2, E. ESCHE1, R. SCHOMÄCKER2, AND J.-U. REPKE1
1 Fachgebiet Dynamik und Betrieb technischer Anlagen, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin
2 Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin

One approach to enable the hydroformylation of long chained olefins is the application of a microemulsion system. To prove the feasibility of this concept, we present operation data for the conversion of 1-dodecene in a surfactant containing system. For a 200 hours mini-plant operation a product yield of 40% at stable phase separation conditions are highlighted. The obtained reaction data is then used to validate a kinetic model derived and estimated from lab scale experiments.

Towards integrated process synthesis, reactor optimization and solvent selection exemplified for the hydroformylation of 1-dodecene in a thermomorphic solvent systems -  N. M. KAISER, K. MCBRIDE, AND K. SUNDMACHER
Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany

The profitability of a homogeneously catalyzed chemical process depends strongly on the efficiency of the catalyst system and its recovery rate. During process synthesis is it important to optimize the reaction conditions, i.e. reactor characteristics and control strategy, and to design a solvent system that minimizes the catalyst loss while having a nonnegative effect on the reaction. For these reasons, new concepts based on elementary process functions and the COSMORS theory are developed and applied to the hydroformylation of 1-dodecene in a thermomorphic solvent system.
The reaction mechanism of Rh-catalysed hydroformylation of long-chain olefins -

E. Kohls, K. Elbassyouni, and M. Stein

Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany

The intermediates in the catalytic cycle of conversion of dodecene into tridecane were elucidated using quantum chemical calculations. Spectral assignment of infrared spectroscopic data was possible by applying scaling factors from a carefully chosen training set of Rh(I) carbonyl complexes. The influence of the solvent mixture (DMF/decane) on the thermodynamics and kinetics was examined. This is critical for a reliable process modelling and optimization.

Prediction of solvent effects on reaction kinetics –

M. Lemberg, and G. Sadowski

Technical University Dortmund, Laboratory of Thermodynamics, Dortmund, Germany

This work focuses on the solvent influence on the kinetics of the esterification of acetic acid with ethanol. The reaction was on the one hand performed in neat reaction mixtures at different reactant ratios and on the other hand in the solvents acetonitrile, tetrahydrofuran, and dimethylformamide. The progress of the reaction was observed by in situ Raman spectroscopy.

Whereas acetonitrile promotes the esterification kinetics, it is slowed down in DMF. Describing the reaction-rate law in terms of reactant activities (obtained from PC-SAFT) allowed for considering the different interactions between the components in the different reaction mixtures. Based on kinetic data of the solvent-free reaction mixture and accounting for the reactant thermodynamic activities in the different solvents, the reaction kinetics in all investigated solvents could be predicted in almost quantitative agreement with the experiments.

Global Optimization of Integrated Liquid Multiphase Systems –

N. Mertens¹, C. Kunde², D. Michaels³, and A. Kienle²,³

¹ Department of Mathematics, TU Dortmund University, Dortmund, Germany
² Institute for Automation Engineering, Otto von Guericke University, Magdeburg, Germany
³ Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany

This contribution deals with deterministic global optimization of MINLPs for the design of hydroformylation processes in thermomorphic solvent systems. New methods for branch-and-bound based approaches are developed to reduce the often extensive computational effort. Enhanced relaxation strategies, problem-specific MINLP-modeling and systematic reduction of the search space are presented for
multicomponent distillation, multistage separation networks and closed-loop reactor-separator networks.

Optimization-based design of chemical processes using surrogate models -

C. NENTWICH, AND S. ENGELL

Process Dynamics and Operations Group, Technische Universität Dortmund, Emil-Figge-Straße 70, 44227 Dortmund/ Germany

We consider the optimization-based design of chemical processes, in particular multiphase processes. The reliability of a process design is highly dependent on the quality of the process models, in particular on the accuracy of the thermodynamic predictions and of the kinetic models. For an accurate prediction of phase equilibria of mixtures, advanced thermodynamic models as e.g. PC-SAFT are available. But these models are complex and must be solved iteratively, therefore to use them directly in the optimization leads to large models and long computation times. In this work it is proposed to use surrogate models which approximate the results of the thermodynamic calculations to make the use of advanced thermodynamic models within algorithmic design approaches possible.

Polymer Particles as Phase Transfer Agents and Catalyst Carriers in Multiphasic Reactions –

D. PERAL1, B. BIBOUCHE1, H. YU1, J. MARDOUKH1, R. SCHOMÄCKER1, AND D. VOGT2

1 Technische Universität Berlin, Berlin, Germany
2 University of Edinburgh, Edinburgh, United Kingdom

Multiphasic reaction-systems with homogeneous catalysts are attractive for industrial applications, however phase transfer agents are needed for some substrates to achieve feasible systems. Water soluble polymer particles have been synthesized and successfully been used for multiphasic hydroformylation and epoxidation reactions. The synthesis and characterization of particles with different properties have been investigated.

Mass transfer and interfacial phenomena in Pickering emulsions with silica nanoparticles -

M. PETZOLD1, L. HOHL1, S. RÖHL1, D. STEHL2, R. VON KLITZING2, AND M. KRAUME1

1 FG Verfahrenstechnik TU Berlin, Ackerstraße 76, 13355 Berlin

The mass transfer between the phases of dispersed liquid/liquid systems is majorly influenced by the interface. Silica nanoparticles can be used as emulsifiers in those systems to increase the surface area. They adsorb at the interface without lowering
the interfacial tension and decrease the drop size distribution through inhibition of coalescence. Despite the increasing surface area the mass transfer is reduced due to the additional transport resistance by the nanoparticles at the interface.

**Catalytic upgrading of long-chain olefins in surfactant modified multiphase systems** -


Technische Universität Berlin, Department of Chemistry, Str. des 17. Juni 124, D-10623 Berlin

We investigate the application of microemulsion systems as smart solvent systems for homogeneous catalysis. Based on the kind of catalysis, microemulsion systems allow for the reuse of dissolved catalysts or even for a better solubilisation of hydrophobic reactants. To prove their applicability we investigate the hydroformylation and the hydroxycarbonylation of long-chain olefins in these systems.

**Membrane filtration of w/o Pickering emulsions** -

T. Skale, L. Hohl, D. Stehl, R. von Knitting, M. Kraume, and A. Drews

1 HTW Berlin, Process Engineering in Life Science Engineering, Wilhelminenhofstr. 75A, 12459 Berlin/ Germany
2 TU Berlin, Process and Chemical Engineering, Fraunhoferstr. 33-36, 10587 Berlin/ Germany
3 TU Berlin, Applied Physical Chemistry, Straße des 17. Juni 124, 10623 Berlin/ Germany

Pickering emulsions (PE) are studied as a possible reaction system for the rhodium catalyzed hydroformylation of 1-dodecene. To retain the catalyst in a continuous process and to withdraw the product, membrane filtration is investigated. Filtration experiments in a dead end stirred cell showed that the filtration of PE is possible. The PE could be concentrated from an initial aqueous phase fraction of 22 vol% to over 80 vol%.
Particle stabilized emulsions, so-called Pickering emulsions, are very stable against coalescence. Therefore they are promising candidates for a successful separation of the catalyst after catalytic reactions. The focus of this contribution is on emulsions stabilized either with modified silica particles or Halloysites which are tuned to obtain high product yield, selectivity and separation of the catalyst.

For the optimization of the reactor design, different geometries, e.g. a stirred tank and a helically coiled tube, were investigated using optical laser measurement techniques as Particle Image Velocimetry (PIV) and Laser Induced Fluorescence (LIF). These techniques are able to show the flow structures in the reactor geometries, the mixing behavior and the mass transfer. The experimental data is used to verify corresponding CFD-simulations (Computational Fluid Dynamics).