



DEAN'S LETTER

On behalf of Texas A&M University at Qatar, it is my pleasure to welcome you to the Qatar Fertilizer Company–Texas A&M at Qatar Conference 2015.

Texas A&M at Qatar is pleased to host the eighth meeting of this annual conference — the seventh presented in collaboration with Qatar Fertilizer Company (QAFCO).

This event illustrates the importance of industry and academic partnerships in the developing new knowledge and creating scientific solutions that directly impact the world around us.

The focus of the conference this year is on sustainable chemical processes. Sustainability is a top priority worldwide for governments, industry and academia. Developing new chemical processes that use less-harmful solvents, are more energy efficient and generate little or no waste or byproducts is a major driving force for research in chemistry and in chemical engineering. The keynote lecture and all invited talks will provide different aspects of this theme, from fundamental, experimental and computational studies all the way to new process development with immediate industrial applications.

QAFCO has been a steadfast and dynamic partner to Texas A&M at Qatar in these collaborations and I thank QAFCO for its unwavering belief in the strength of our academic and research programs, our faculty, and our current and former students.

Thank you for sharing your expertise with the professionals participating in this influential gathering of industry practitioners and scholars.

Best wishes for a very productive conference and thank you to QAFCO for their partnership in this influential meeting of international experts.

Best regards,

Dr. Mark H. Weichold
Dean and CEO, Texas A&M
University at Qatar





CHAIR AND CO-CHAIR'S LETTER

On behalf of the Science and Chemical Engineering programs at Texas A&M University at Qatar, we are pleased to welcome you to the annual QAFCO–Texas A&M at Qatar Conference 2015.

We are very proud of our partnership with QAFCO, which has generously supported us in hosting the first conference series in Qatar since 2007. This series has attracted an impressive list of world renowned scientists over the years (65 invited speakers from 15 countries). In addition, the list of speakers in previous years included two Nobel laureates, Dr. Robert H. Grubbs and Dr. Ei-Chi Negishi.

The theme for this year's edition is sustainable chemical processes. We are glad to have Prof. Peter Wasserscheid, head of the Institute of Chemical Reaction Engineering at Friedrich-Alexander University in Erlangen, Germany, and founding director of the Helmholtz Institute on Renewable Energy Production, as keynote speaker of the 2015 edition of the conference. In addition, we have 15 distinguished invited speakers from the U.S., Europe and Middle East.

We hope this conference will be an outlet for the exchange of scientific knowledge, sharing ideas, discussing future collaborations and building new projects. Your presence at this conference affirms our pursuits of cutting-edge chemistry and chemical engineering research in Qatar and the region. We wish you a very productive time at this event.

Best regards,

Hassan S. Bazzi

Chair, QAFCO–Texas A&M at Qatar Conference 2015
Assistant Dean for Research and Graduate Studies

Ioannis Economou

Co-chair, QAFCO–Texas A&M at Qatar Conference 2015
Professor, Chemical Engineering Program







SCHEDULE OF EVENTS

8 – 8:45 a.m.	REGISTRATION AND LIGHT BREAKFAST	
8:50 – 8:55 a.m.	DR. HASSAN S. BAZZI Professor and Assistant Dean for Research and Graduate Studies	
8:55 – 9 a.m.	DR. EYAD MASAD Professor and Executive Associate Dean	
9 – 9:05 a.m.	MR. KHALIFA AL-SOWAIDI Vice Chairman and CEO, Qatar Fertiliser Company	
9:05 – 10:10 a.m.	KEYNOTE LECTURE (LH 238)	
	CHAIR: IOANNIS ECONOMOU	
9:05 – 10:10 a.m.	Prof. Peter Wasserscheid, University of Erlangen-Nuremberg, Germany <i>"Reaction Engineering Challenges Related to Hydrogen Storage in Liquid Organic Hydrogen Carriers (LOHCs)"</i>	
10:10 – 10:30 a.m.	COFFEE BREAK	
SESSIONS I	CHEMISTRY	CHEMICAL ENGINEERING
	CHAIR: DR. HASSAN S. BAZZI LH 143	CHAIR: DR. AHMED ABDEL-WAHAB, LH 144
10:30 – 11 a.m.	Prof. C. Oliver Kappe University of Graz, Austria <i>"Process Intensification Utilizing High-Temperature/Pressure Flow Chemistry"</i>	Prof. Athanassios Z. Panagiotopoulos Princeton University, USA <i>"Simulations of Thermodynamic and Transport Properties for Aqueous Mixtures"</i>
11 – 11:30 a.m.	Prof. David E. Bergbreiter Texas A&M University, USA <i>"Polyolefin Oligomers as Recyclable Solvents"</i>	Prof. Cor J. Peters Petroleum Institute, Abu Dhabi, UAE <i>"Ionic Liquids versus Deep Eutectic Solvents in Gas Treatment"</i>
11:30 a.m. – noon	Prof. Steve Howdle University of Nottingham, UK <i>"Polymer Synthesis and Supercritical Carbon Dioxide"</i>	Prof. Alberto Striolo University College London, UK <i>"The Role of Interfacial Water on Oil and Gas Production, Water Purification, and Hydrates Formation"</i>



SCHEDULE OF EVENTS

Noon – 1:30 p.m.	LUNCH	
SESSIONS II	CHEMISTRY	CHEMICAL ENGINEERING
	CHAIR: DR. ASHFAQ BENGALI LH 143	CHAIR: DR. IOANNIS ECONOMOU, LH 144
1:30 – 2 p.m.	Prof. Johannes Lercher Technische Universität München, Germany <i>"New Insight into Hydrocarbon Formation Routes in the Methanol to Olefin Process"</i>	Prof. Efstratios N. Pistikopoulos Texas A&M University, USA <i>"Multiparametric Model-based Optimization & Control"</i>
2 – 2:30 p.m.	Prof. Tobin J. Marks Northwestern University, USA <i>"Thermodynamic Strategies for New Catalytic Process Design. Biofeedstock Processing via Tandem C-O Hydrogenolysis"</i>	Prof. Marianthi Ierapetritou Rutgers University, USA <i>"A General Framework of Process Design and Evaluation of Renewable Production of Chemicals from Biomass Feedstocks"</i>
2:30 – 3 p.m.	COFFEE BREAK	
SESSIONS III	CHEMISTRY	CHEMICAL ENGINEERING
	CHAIR: DR. ED. BROTHERS LH 143	CHAIR: DR. NIMIR ELBASHIR LH 144
3 – 3:30 p.m.	Prof. D. Michael Heinekey University of Washington, USA <i>"Versatile Homogeneous Catalysts for Biomass Utilization: Iridium Pincer Complexes"</i>	Prof. Mert Atilhan Qatar University, Qatar <i>"CO₂ Capture via Ionic Liquid Blends and Deep Eutectic Solvents"</i>
3:30 – 4 p.m.	Prof. John A. Gladysz Texas A&M University, USA <i>"Werner Complexes: A New Class of Chiral Hydrogen Bond Donor Catalysts for Enantioselective Organic Reactions"</i>	Prof. Joao Coutinho University of Aveiro, Portugal <i>"Extractions, Separations and Purifications with Aqueous Solutions of Ionic Liquids"</i>
4 – 4:30 p.m. (LH 144)	Prof. Patrick Linke Texas A&M University at Qatar, Qatar <i>"Design and Optimization of Sustainable Processing Systems"</i>	



REACTION ENGINEERING CHALLENGES RELATED TO HYDROGEN STORAGE IN LIQUID ORGANIC HYDROGEN CARRIERS (LOHCS)

Peter Wasserscheid

Lehrstuhl für Chemische Reaktionstechnik

Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

ABSTRACT

Hydrogen is often considered a very capable future energy vector. It can be produced from renewable wind or solar power via water electrolysis and has a wide range of potential applications in all important fields of energy supply. The gravimetric storage density of hydrogen is excellent. One kilogram H_2 carries 33,3 kWh (LHV) of energy. However, being the chemical element with the lowest density, the volumetric storage density of hydrogen is only 3 Wh/liter at ambient pressure. In existing technical applications hydrogen is therefore either stored as gas under very high pressures (up to 700 bar, called "compressed gaseous hydrogen" or CGH_2) or in its liquid state at 253 °C (called "liquid hydrogen" or LH_2).

A very attractive way to store and release hydrogen is in form of liquid organic hydrogen carrier (LOHC) systems. Aromatic molecules, such as N-ethylcarbazole (NEC) [1] or dibenzyltoluenes can be reversibly hydrogenated and dehydrogenated in order to store and transport hydrogen in form of diesel-like liquids. The presentation introduces shortly the LOHC concept for energy storage and future hydrogen logistics. Afterwards it concentrates on material and process aspects of LOHC hydrogenation and dehydrogenation catalysis covering the full range from studies on the molecular level (XPS-, IR-studies) to demonstrator units. Challenges and optimization

potentials will be discussed; novel options (LOHC transfer hydrogenation, hydrogen purification through LOHC hydrogenation/dehydrogenation) will be presented.

BIOGRAPHY

Dr. Peter Wasserscheid is head of the Institute of Chemical Reaction Engineering at the Friedrich-Alexander-University Erlangen-Nuremberg (FAU), co-coordinator of the Erlangen Excellence Cluster "Engineering of Advanced Materials" (EAM), coordinator of the EAM Advanced Catalytic Materials research area, and founding director of the Helmholtz-Institute on Renewable Energy Production Erlangen-Nürnberg. Wasserscheid studied chemistry at the RWTH Aachen and finished his Ph.D. in 1998 at the Institute of Technical Chemistry. After a six-month industrial postdoc with BP Chemicals in Sunbury (UK) he returned to the RWTH Aachen where he completed his "habilitation," entitled "Ionic Liquids — a New Solvent Concept for Catalysis" in December 2002. In the meantime, he became co-founder of Solvent Innovation GmbH, the first company specialized on ionic liquid manufacturing and application. (In 2007 the company was taken over by Merck KGaA.) In 2003, Wasserscheid took up his current position at the FAU. Since March 2014, he has acted as director of the IEK 11 at Forschungszentrum Jülich





and is founding director of the Helmholtz-Institute Erlangen-Nuremberg on Renewable Energies.

Wasserscheid's research group numbers more than 35 students and postdoctoral researchers. He has already mentored and graduated more than 40 Ph.D. students and postdocs in his professorial career. All of his former doctoral students and postdocs have been offered attractive positions in leading chemical companies or academic institutions.

Wasserscheid has more than 250 publications with more than 13,000 citations (h-index = 54, ISI Web of Science) in peer-reviewed scientific journals and 62 patents or patent applications. He is co-editor and co-author of the monograph "Ionic Liquids in Synthesis" that is widely accepted as the standard introduction to ionic liquid chemistry. In 2013 he co-published the Wiley-VCH textbook *Chemical Technology*.

Wasserscheid's research efforts have earned him a number of awards, including the Max-Buchner-award of DECHEMA (2001), the Innovation Award of the German Economy in 2003, the Leibniz Award of the Deutsche Forschungsgemeinschaft in 2006 and an Advanced Investigator Grant

of the European Research Council in 2010.

The key research interests of the Wasserscheid research group center on reaction engineering aspects of multiphase catalytic processes with a particular focus on homogeneous catalysis and heterogeneous catalysis involving ionic liquid reaction media. For various reaction types the group has successfully demonstrated greatly enhanced performance of ionic liquid-based catalyst systems vs. conventional systems. It has also pioneered the so-called supported ionic liquid phase (SILP) technology and the solid catalyst with ionic liquid layer (SCILL) technologies. Both technologies build on supported thin films of liquid salt in macroscopically heterogeneous catalysts and are practiced on commercial pilot plants scale. In its ERC Advanced Grant project, "SMS-H₂-cat," the Wasserscheid group focuses on the engineering of supported molten salt catalysts for dehydrogenation reactions and hydrogen production technologies. In its recent research efforts concerning chemical energy storage, the group has developed a certain focus on liquid organic hydrogen carrier (LOHC) systems and develops this technology for stationary and mobile applications.





PROCESS INTENSIFICATION UTILIZING HIGH-TEMPERATURE/ PRESSURE FLOW CHEMISTRY

C. Oliver Kappe

Institute of Chemistry
University of Graz, Austria

ABSTRACT

The use of micro- and mesofluidic reactors has opened up new horizons for synthetic organic chemistry and the chemical manufacturing industry. Traditionally, most synthetic transformations performed in microreactors have involved ambient or even low-temperature conditions in order to safely conduct highly exothermic reactions. More recently, processes at elevated temperature conditions in pressurized microreaction devices (and related continuous flow reactors) have been reported, although the number of publications describing synthetically valuable transformations in a genuine high-temperature and high-pressure (>200°C/>50 bar) flow regime is rather limited. Process intensification philosophies, such as the exploration of novel process windows at exceptionally high temperatures and pressures are made possible with this technology and result in a majority of reactions being completed within only a few minutes of residence time.

This high-temperature microreactor approach can also be used to overcome the scale-up limitations inherent to high-speed microwave batch processing in sealed vessels. Vice versa, microwave reactors can be used for rapid method development, since the reaction time at a certain temperature obtained in a microwave reactor can be directly translated to a residence time in a flow reactor.

In this lecture the execution of a number of synthetically valuable organic transformations in a high-temperature/high-pressure continuous flow format will be described, including monophasic and multiphasic (liquid/liquid, gas/liquid) processing conditions. Chemistry examples include the formation of heterocycles, homogeneous, heterogeneous and flow nanocatalysis, and several reduction and oxidation processes that can safely be conducted in a continuous flow environment.

BIOGRAPHY

Dr. C. Oliver Kappe received his undergraduate and graduate education at the University of Graz with Professor Gert Kollenz. After periods of postdoctoral research work with Professor Curt Wentrup at the University of Queensland and with Professor Albert Padwa at Emory University, he moved back to the University of Graz in 1996 to start his independent academic career. In 1999 he became associate professor and in 2011 was appointed professor for Technology of Organic Synthesis at the University of Graz. His current research interests involve continuous flow chemistry, API manufacturing, and process intensification technologies. Since 2011 he has been editor-in-chief of the *Journal of Flow Chemistry*.



POLYOLEFIN OLIGOMERS AS RECYCLABLE SOLVENTS

David E. Bergbreiter

Department of Chemistry
Texas A&M University, USA

ABSTRACT

The work that will be discussed describes systems where polyolefin oligomers serve as recyclable nontoxic, nonvolatile hydrocarbon solvents. Spectroscopic studies including studies using dye labeled polyolefins as probes show that these solvents can be both recycled as part of multisolvent systems, that they serve as phase anchors for homogeneous catalysts, and that they serve as anti-leaching agents for polyolefin-bound catalysts. Such solvents are readily available polyolefins produced on scale that are low viscosity oils at room temperature or form low-viscosity melts at temperatures <100 °C. In their applications, they replace low molecular weight toxic hydrocarbon solvents. For example, a polyethylene or polypropylene oligomer can replace hexane or heptane in mixed solvent systems that have thermomorphic or latent biphasic properties, such solvent replacements serve as a recyclable nonvolatile alternative to heptane for recycling homogeneous catalysts. In other cases, such solvents can be used as cosolvents in batch type homogeneous reactions where a catalyst that is phase selectively soluble in heptane is used under pseudobiphasic conditions. Examples of reactions under thermomorphic, latent biphasic, or pseudobiphasic conditions include ring closing metathesis, cross coupling chemistry, photoredox catalysis, allylic substitution chemistry, and cyclopropa-

nation and O-H insertion chemistry, and polymerization chemistry. Detailed studies of a variety of solvent mixtures using polyisobutylene bound dyes and poly(alpha olefins) will be described showing how the extent of phase separation of a dye in the recyclable hydrocarbon oligomer solvent phase can vary depending on the molecular weight of the oligomer solvent and the nature of the polar cosolvent.

BIOGRAPHY

Dave Bergbreiter has been a professor at Texas A&M since 1974. In that time, he and his students have worked on physical organic, surface, polymer and catalysis chemistry. In the past 15 years, a major effort in his group in conjunction with the Bazzi group at Texas A&M University at Qatar has been to develop new ways to facilitate reactions with polymers. This has included developing smart catalysts and thermomorphic separation technology that autonomously controls reaction rates or simplifies catalyst/product separation. He has been recognized with every major teaching award at Texas A&M University and has the lifetime distinction of Presidential Professor for Teaching Excellence. He is currently the Eppright Professor of Undergraduate Teaching Excellence.





POLYMER SYNTHESIS AND SUPERCRITICAL CARBON DIOXIDE

Steve Howdle

School of Chemistry
University of Nottingham, UK

ABSTRACT

Supercritical fluids have a unique combination of gas-like and liquid-like properties. This lecture will describe the background and how we exploit these properties to synthesise new polymers and new materials that could not easily be made using conventional solvents. One of the major attractions is that carbon dioxide is freely available, inexpensive and provides an environmentally acceptable and cleaner alternative to the use of conventional organic solvents, particularly for medical and pharmaceutical applications.

We have utilized controlled/living radical (RAFT) routes and dispersion polymerization to create microparticles formed of block co-polymers. These microparticles show expected and also unusual morphologies on the nanoscale that arise from phase separation of the block copolymers.

Additionally we will describe approaches to the preparation and synthesis of new renewably sourced materials that could be of value in a wide range of everyday applications. In particular, we highlight the utilization of enzyme-mediated polymerization where scCO_2 could bring significant advantages.

BIOGRAPHY

Dr. Steve Howdle's research focuses on sustainable chemistry and in particular on the utilization of supercritical carbon dioxide for polymer synthesis, polymer processing and preparation of novel polymeric materials for tissue engineering and drug delivery. He has published 315 peer-reviewed papers in this field and these have received more than 7,000 citations. He has an h-index > 45 and is also an inventor on 11 patent families.

He holds a professorship in the School of Chemistry at the University of Nottingham and previously held a Royal Society University Research Fellowship (1991-1999). He has received the Jerwood-Salters' Environment Award for Green Chemistry (2001); RSC Corday-Morgan Medal and Award (2001); Royal Society-Wolfson Research Merit Award (2003); RSC Interdisciplinary Award (2005); DECHEMA-Award of the Max Buchner Research Foundation (2006); RSC/SCI Macro Group UK Medal (2008); and the Hanson Medal of the IChemE (2009).

He has commercialized his research through a spin out company *Critical Pharmaceuticals* (www.criticalpharmaceuticals.com) focused on using supercritical fluids to prepare drug delivery devices for delicate protein based biopharmaceuticals.



SIMULATIONS OF THERMODYNAMIC AND TRANSPORT PROPERTIES FOR AQUEOUS MIXTURES

Athanasios Z. Panagiotopoulos

Department of Chemical and Biological Engineering
Princeton University, USA

ABSTRACT

The development of accurate force fields and simulation methods for prediction of thermodynamic and transport properties of water and aqueous solutions are important for the design of desalination, oil recovery and carbon sequestration applications. This talk will focus on recent efforts in the speaker's group to model properties of water-electrolyte-CO₂ systems over a broad range of temperatures and pressures. Properties of interest include activity and osmotic coefficients of electrolyte solutions, the phase behavior at elevated pressures, and the diffusivity and viscosity of CO₂-rich and H₂O-rich phases at geological storage reservoir conditions. For fixed-point-charge models of water, we find that the H₂O-CO₂ phase behavior is represented most accurately when using the exponential-6 functional form with optimized cross-interactions, while the transport properties are generally modeled accurately with the Lennard-Jones (LJ) form of many common models using conventional Lorentz-Berthelot

combining rules. By contrast, for the H₂O-NaCl system, the phase behavior and activity coefficients are only moderately well represented by the LJ-based common potential, while the exponential-6 models are totally inadequate. For future model development, polarizable water models (e.g., the Baranyai-Kiss model) are promising for achieving higher accuracy and transferability than it is possible with fixed-point-charge models.

BIOGRAPHY

Dr. Athanasios Z. Panagiotopoulos received an undergraduate degree from the National Technical University of Athens (Greece) and a Ph.D. from the Massachusetts Institute of Technology (USA), both in chemical engineering. He is currently the Susan Dod Brown Professor of Chemical and Biological Engineering at Princeton University. He is a member of the U.S. National Academy of Engineering and the American Academy of Arts and Sciences.





IONIC LIQUIDS VERSUS DEEP EUTECTIC SOLVENTS IN GAS TREATMENT

Cor J. Peters

Chemical Engineering Department
The Petroleum Institute, Abu Dhabi, U.A.E.
Department of Chemical Engineering and Chemistry
Eindhoven University of Technology, The Netherlands

ABSTRACT

The removal of CO_2 from natural gas or the capturing of CO_2 from flue gas produced by post-combustion industries became a big challenge due to the large volumes of CO_2 and often the low CO_2 concentration in the source gases. Most of the commercial absorption processes for CO_2 use different types of alkanolamine solvents, e.g. monoethanolamine (MEA), diethanolamine (DEA) or N-methyldiethanolamine (MDEA). Despite their good performance as solvents for chemical absorption, amine technologies show several important drawbacks in terms of operational cost, solvent regeneration and the susceptibility of amines to undergo thermal or oxidative degradation. Moreover, the emissions of amines and its degradation products may cause serious damage to the environment and human health as well. For this reason, the search for alternative solvents for CO_2 capturing became a prominent research activity in solvent design.

Ionic liquids (ILs) attracted particular attention over the past decade because they can be designed by choosing the proper cation-anion combination to pursuit the best performance as solvents for a certain application. Together with their, in general, extremely low volatility, the so-called "task specific ionic liquids" show promising

advantages for CO_2 capture compared to the conventional solvents. However, the "green" character of ILs can be questioned because most of them are produced from fossil resources and their synthesis cannot be considered as being "green." Moreover, the high production and purification cost do not make ILs technology competitive with traditional solvents.

To overcome some of the limitations of ILs, deep eutectic solvents (DES) were recognized as potential alternatives. These low-transition temperature mixtures (LTTMs) consist of at least one hydrogen bond donor and one hydrogen bond acceptor counterpart, resulting in the formation of a liquid mixture showing an unusual low freezing point. Due to the high hydrogen bonding interaction, some of the promising characteristics of ILs as solvents are shared by DESs. They often possess an extremely low volatility, and their properties can be adjusted by selecting the nature and ratio of the hydrogen bonding pairs. They can also be designed to show a wide liquid range, water compatibility, nonflammability, non-toxicity, biocompatibility or biodegradability. Finally, they can be easily prepared from readily available starting materials and becoming a competitive solvent in terms of cost.





BIOGRAPHY

Dr. Cor Peters holds a B.Sc. in mathematics and received his Ph.D. in chemical engineering from Delft University of Technology, The Netherlands. Currently, he is a distinguished professor in the Department of Chemical Engineering at the Petroleum Institute in Abu Dhabi. At the same institute, he was the department chair and simultaneously the first director of the Gas Research Center. He is also a visiting professor at Eindhoven University of Technology (The Netherlands), the Univer-

sity of Maryland (USA), Colorado School of Mines (USA) and the Universiti Teknologi PETRONAS (Malaysia). Peters is the author of more than 250 refereed journal papers, among them in *Science* and *Chemical Reviews*. His research interests include applied and statistical thermodynamics, phase equilibria and thermodynamics of complex fluids, interfacial phenomena, gas processing, hydrogen storage, ionic liquids, deep eutectic solvents, desalination and gas hydrates.





THE ROLE OF INTERFACIAL WATER ON OIL AND GAS PRODUCTION, WATER PURIFICATION AND HYDRATES FORMATION

Alberto Striolo

Department of Chemical Engineering
University College London, UK

ABSTRACT

The molecular structure of interfacial water, and in particular of the electric double layer, is known to determine the outcome of a number of physical processes, including the dissolution of minerals, corrosion and perhaps even the biological activity of enzymes. Our research group has employed massive molecular simulation studies to quantify how interfaces, in particular wet ones, determine the outcome of processes of vast societal importance. In this presentation we will explore how water adsorption within clays can affect the transport of natural gas through shale formations, how water and CO₂ affect the mobility of hydrocarbons through silicates, how designing appropriately carbon-based electrodes could lead to new processes for water desalination, and finally how hydrates particles assemble within hydrocarbon systems. We will discuss how experimental information, obtained via appropriate collaborations, could be used to validate our predictions and perhaps lead to advancements in all the processes just discussed.

BIOGRAPHY

Dr. Alberto Striolo is professor of molecular thermodynamics in the Department of Chemical Engineering at University College London. He holds B.S. and Ph.D. degrees from the Università degli Studi di Padova (Italy) both in chemical engineering. In 2013, he was named the Lloyd and Joyce Austin Presidential Associate Professor at the University of Oklahoma. He received the Regents' Award for Superior Research and Creative Activity from the University of Oklahoma and the HP Outstanding Junior Faculty Award from the American Chemical Society. He has been co-author of more than 100 papers on interfacial aqueous systems, energy storage and Pickering emulsions.





NEW INSIGHT INTO HYDROCARBON FORMATION ROUTES IN THE METHANOL-TO-OLEFIN PROCESS

Johannes Lercher

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Institute for Integrated Catalysis Pacific Northwest National Laboratory, USA

ABSTRACT

The methanol-to-olefin process has emerged as one of the leading catalytic processes to generate light alkenes. At steady-state the catalysis is characterized by two catalytic cycles, one which is based on homologization of olefins by methanol and one on alkylation of aromatic structures and ring contraction and cracking. While these Brønsted acid catalyzed reaction pathways are important for the bulk of steady-state reactions, they are hardly important for the early stages of the reaction and the stability of the catalysts. The lecture will address the principal features of the reactions responsible for catalyst deactivation, which are characterized by oxygen-containing intermediates and their relation to the overall catalytic chemistry. Routes to unravel that chemistry by combining detailed kinetic studies with characterization of the catalysts will be presented. Molecular level strategies to enhance catalyst stability and options to direct selectivity will be discussed.

BIOGRAPHY

Johannes A. Lercher studied chemistry at TU Wien, receiving his Ph.D. in 1981 at the same institution. After a visiting lecture-

ship at Yale University, he joined TU Wien as lecturer, later associate professor. In 1993 he was appointed professor in the Department of Chemical Technology at the University Twente, the Netherlands, and in 1998 in the Department of Chemistry of TU München, Germany. Since 2011 he has been director of the Institute for Integrated Catalysis at the Pacific Northwest National Laboratory in the United States. He is external member of the Austrian Academy of Sciences and member of the Academia Europaea, as well as honorary professor at several institutions in China. He is the author of more than 480 papers and 17 patents and is currently editor-in-chief of the *Journal of Catalysis*. Recent awards include the Kozo Tanabe Award for Acid-Base Catalysis, the Burwell Lectureship of the North American Catalysis Society and the Francois Gault Lectureship of the Federation of European Catalysis Societies. His interests are related to catalysis in zeolites as well as on nanostructured oxides and sulfides, focusing on bifunctional and concerted catalysis, as well as understanding the influence of the steric and chemical environment on the properties of active centers in a catalytic site.





THERMODYNAMIC STRATEGIES FOR NEW CATALYTIC PROCESS DESIGN, BIOFEEDSTOCK PROCESSING VIA TANDEM C-O HYDROGENOLYSIS

Tobin J. Marks

Department of Chemistry
Northwestern University, USA

ABSTRACT

This lecture focuses on thermodynamics/mechanism-based strategies for converting abundant biofeedstocks into useful chemicals. New approaches to the hydrogenolysis of C-O bonds are discussed with the ultimate goal being the processing of diverse biomass feedstocks. It is shown that selective hydrogenolysis of cyclic and linear etheric C-O bonds is effected by a tandem catalytic system consisting of recyclable metal triflate Lewis acids and supported palladium nanoparticles or related catalysts in either "green" ionic liquid solvents or in the neat substrates. In this tandem process, the metal homogeneous triflates catalyze the endothermic retro-hydroalkoxylation of the ether, with the supported palladium catalyst subsequently catalyzing the hydrogenation of the resulting intermediate alkenols, to afford saturated alkanols with high overall activity and selectivity. Kinetic and DFT computational studies show that the turnover-limiting step in these reactions is the retro-hydroalkoxylation, followed by rapid alkenol hydrogenation. Furthermore, the metal triflate catalytic activity scales approximately with the DFT-computed charge density on the triflate metal ion. With the most active of these catalysts, ethereal substrates are rapidly converted, via the alkenol,

to the corresponding saturated hydrocarbons. In similar tandem processes, it is shown that esters and triglycerides are also rapidly and selectively converted to alcohols and, ultimately, to saturated hydrocarbons. The kinetics and mechanism of these ester hydrogenolysis processes, as deduced by experimental results and DFT computation, are compared and contrasted with those of the corresponding ethers.

BIOGRAPHY

Tobin Marks is the V.N. Ipatieff Professor of Catalytic Chemistry and professor of Materials Science and Engineering at Northwestern University. He received a B.S. from the University of Maryland (1966) and a Ph.D. from MIT (1971). Among his recognitions, he received the 2006 U.S. National Medal of Science, the 2008 Principe de Asturias Prize, the 2009 the MRS Von Hippel Award, the 2011 Dreyfus Prize in the Chemical Sciences, and the 2012 NAS Award in Chemical Sciences. He is a member of the U.S., German and Indian National Academies of Sciences, a member of the U.S. National Academy of Engineering, and a fellow of the Royal Society of Chemistry and of the American Academy of Arts and Sciences.





MULTIPARAMETRIC MODEL-BASED OPTIMIZATION AND CONTROL

Efstratios N. Pistikopoulos

Artie McFerrin Department of Chemical Engineering
Texas A&M University, USA
Department of Chemical Engineering
Imperial College London, UK

ABSTRACT

Model-based multiparametric programming provides a complete map of solutions of an optimization problem as a function of unknown but bounded parameters in the mode in a computationally efficient manner without exhaustively enumerating the entire parameter space. In a model-based predictive control (MPC) framework, multiparametric programming can be used to obtain the governing control laws — the optimal control variables as an explicit function of the state variables. The main advantage of this approach is that it reduces repetitive online control and optimization to simple function evaluations, which can be implemented on simple computational hardware, such as a microchip, thereby opening avenues for many applications in chemical, energy, automotive and biomedical equipment, devices and systems.

In this presentation, we will first provide a historical progress report of the key developments in multiparametric programming and control. We will then describe PAROC, a prototype software system that allows for the representation, modeling and solution of integrated design, scheduling and control problems. Its main features include a high-fidelity dynamic model representation, also involving global sensitivity analysis, parameter estimation and mixed integer dynamic optimization capabilities; a suite/toolbox of model approxima-

tion methods; a host of multiparametric programming solvers for mixed continuous/integer problems; a state-space modeling representation capability for scheduling and control problems; and an advanced control toolkit for multiparametric/explicit MPC and moving horizon reactive scheduling problems. Algorithms that enable the integration capabilities of the systems for design, scheduling and control are presented along with applications in sustainable energy systems, smart manufacturing and personalized healthcare engineering.

BIOGRAPHY

Dr. Efstratios N. Pistikopoulos has been a professor of chemical engineering at Imperial College London (UK), where he was a director of its Center for Process Systems Engineering. He holds a Ph.D. from Carnegie Mellon University and was with Shell Chemicals in Amsterdam before joining Imperial College London in 1991. He has been author or coauthor of more than 350 major research publications, 10 books and two patents in the areas of modeling, control and optimization of process, energy and systems engineering applications. Pistikopoulos is a fellow of the Institution of Chemical Engineers; editor of *Computers & Chemical Engineering*; co-editor of *Process Systems Engineering* and the book series





Computer Aided Chemical Engineering; on the editorial boards of *Industrial & Engineering Chemistry Research* (2011-2013), the *Journal of Global Optimization* and the *Journal of Computational Management Science*. Pistikopoulos has been a co-founder/non-executive director of Process Systems Enterprise (PSE) Ltd. and a founder/director of Parametric Optimization Solutions (ParOS) Ltd. In 2007, Pistikopoulos was a co-recipient of the prestigious MacRobert Award from the Royal Academy of Engineering; in 2008, he received an Advanced Investigator Award from the European Research Council; in 2009, he delivered the Bayer Lecture in Process Systems

Engineering at Carnegie Mellon University, USA; in 2014, gave the 21st Professor Roger Sargent Lecture at Imperial College London; and in 2014, received the Doctor Honoris Causa from the University Politehnica of Bucharest. In 2012, he received the Computing in Chemical Engineering Award of the Computing and Systems Technology (CAST) Division of the American Institute of Chemical Engineers and in 2013, he was elected fellow of the Royal Academy of Engineering in the UK. He joined the Artie McFerrin Department of Chemical Engineering at Texas A&M in early 2015 having accepted an endowed chair there.





A GENERAL FRAMEWORK OF PROCESS DESIGN AND EVALUATION OF RENEWABLE PRODUCTION OF CHEMICALS FROM BIOMASS FEEDSTOCKS

Marianthi Ierapetritou

Department of Chemical and Biochemical Engineering
Rutgers, The State University of New Jersey, USA

ABSTRACT

Depleting resource and increasing environmental concerns of petroleum sources have motivated the development of biorefinery ideas in order to efficiently integrate different biomass feedstocks to produce fuels, power and chemicals. There is an increased interest during the past few years for the development of bio-based chemicals in which the main challenge is the selection of chemical platforms. Some of the top value-added chemical platforms that have been suggested include ethanol, furfural, glycerol and derivatives, levulinic acid and hydroxymethylfurfural. Two important chemical platforms from second-generation lignocellulosic biomass have been selected in our work. Those are the renewable production routes to manufacture p-xylene and 2,5-furandicarboxylic acid (FDCA), as well as the production of phthalic anhydride. The acceptance of bioproducts in the market place is easier if they can successfully compete with petroleum-based products not only in terms of economics

but also in terms of process sustainability.

A general framework has been proposed to evaluate the renewable conversion process based on the experimental discoveries, that implements process design, simulation, heat integration and life cycle assessment (LCA). The framework includes 1) the techno-economic analysis to design the product manufacturing and determine the economics of production; 2) the heat integration with process flowsheets to minimize the energy consumption; 3) LCA to evaluate the environmental impacts of the bio-based production and 4) multicriterion process optimization and synthesis. A detailed case study will be presented to illustrate the main ideas of the framework and proved its effectiveness to achieve towards better sustainable process. The presentation will cover the detailed process flowsheet, the results of techno-economic analysis and LCA on the overall process, and black-box optimization on the flowsheet modeling.



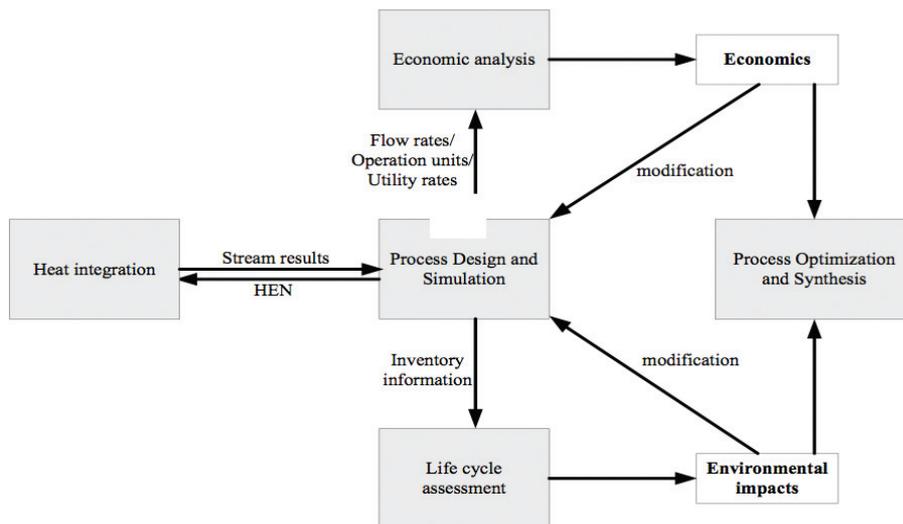


Figure 1

The general framework to design and evaluate the renewable biobased chemical productions

BIOGRAPHY

Dr. Marianthi Ierapetritou is a professor and chair in the Department of Chemical and Biochemical Engineering at Rutgers University in Piscataway, N.J. Ierapetritou's research focuses on process operations; design and synthesis of flexible manufacturing systems, concentrating on pharmaceutical; modeling of reactive flow processes; and metabolic engineering. Her research is supported by several federal (NIH, NSF, ONR, NASA) and industrial (Pfizer, Exxon-Mobil, BOC, Honeywell, Cardinal Health) grants. Among her accomplishments

are the Outstanding Faculty Award, the Rutgers Board of Trustees Research Fellowship for Scholarly Excellence, and the prestigious NSF CAREER award. She has nearly 180 publications and has been an invited speaker to numerous national and international conferences. Ierapetritou obtained her B.S. from The National Technical University in Athens (Greece) and her Ph.D. from Imperial College London (UK) in 1995, and completed her postdoctoral research at Princeton University before joining Rutgers University in 1998.





VERSATILE HOMOGENEOUS CATALYSTS FOR BIOMASS UTILIZATION: IRIIDIUM PINCER COMPLEXES

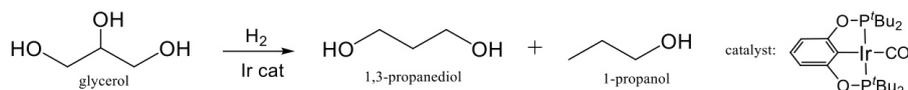
D. Michael Heinekey

Department of Chemistry
University of Washington, USA

ABSTRACT

Biomass derived materials are promising feedstocks for renewable production of chemicals. Catalytic processes for efficient utilization of these materials must allow for selective reaction of highly functionalized

molecules. We have developed an iridium pincer-based catalyst system for the hydrogenolysis of glycerol to 1,3-propanediol and 1-propanol.



The mechanism of this reaction has been studied and catalyst variants have been explored.

Similar catalysts have been employed in an aldehyde oxidation reaction:



The development of effective catalysts for this reaction will be described.

BIOGRAPHY

A native of Canada, Heinekey received a B.Sc. from the University of Victoria in 1977 and a Ph.D. from the University of Alberta in 1982. He was a Natural Sciences and Engineering Research Council of Canada postdoctoral fellow at the Univer-

sity of California, Berkeley, before joining the chemistry department at Yale University (1984-1992) where he was first an assistant professor and later associate professor. He joined the University of Washington faculty in 1992.





WERNER COMPLEXES: A NEW CLASS OF CHIRAL HYDROGEN BOND DONOR CATALYSTS FOR ENANTIOSELECTIVE ORGANIC REACTIONS

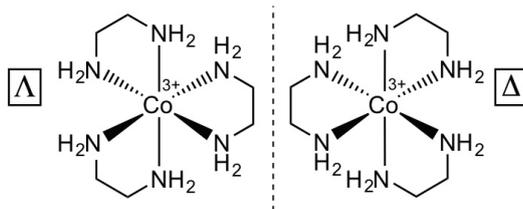
John A. Gladysz

Department of Chemistry
Texas A&M University, USA

ABSTRACT

Salts of the chiral tris(ethylenediamine)-substituted octahedral trication $[\text{Co}(\text{en})_3]^{3+}$ and related species have played important historical roles in the development of inorganic chemistry and stereochemistry. As Werner described in 1912, the two enantiomers,

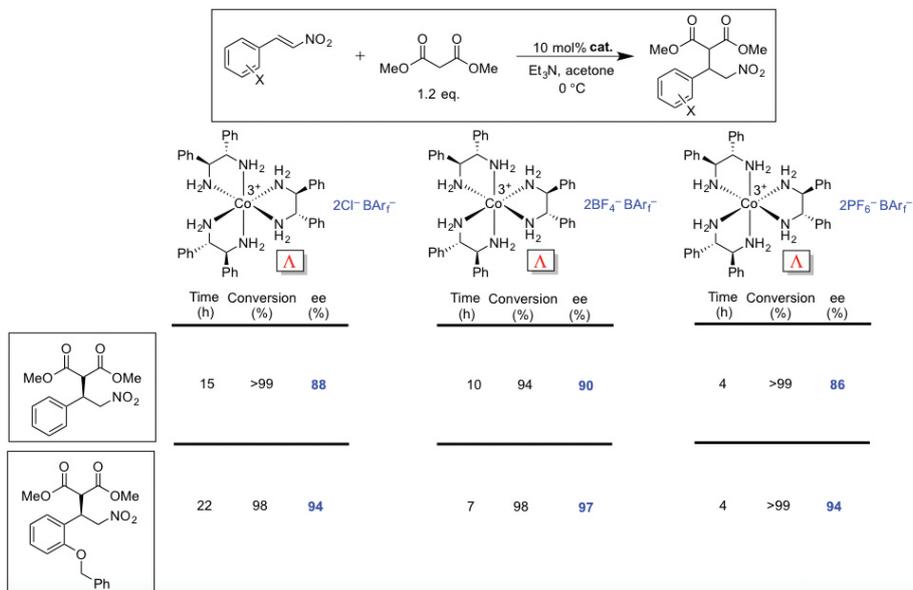
commonly designated Λ and Δ , can be separated by crystallization of the diastereomeric tartrate salts. However, despite the low cost and ready availability of the building blocks, there have been no applications in enantioselective organic synthesis.



We have found that $[\text{Co}(\text{en})_3]^{3+}$ and related cations can be rendered soluble in organic solvents by using lipophilic anions such as "BAr_f⁻".⁴ Suitably functionalized derivatives act as highly enantioselective catalysts for a variety of carbon-carbon bond forming reac-

tions. The mechanisms involve outer sphere activation of the electrophile by hydrogen bonding to the NH moieties. Other types of metal-containing chiral hydrogen bond donors are also effective, including a chelate of the CpRuL fragment.





BIOGRAPHY

John A. Gladysz obtained his B.S. degree from the University of Michigan (1971) and his Ph.D. from Stanford University (1974) with E.E. van Tamelen. He subsequently held appointments at the University of California, Los Angeles (assistant professor, 1974-1982), the University of Utah (associate professor and professor, 1982-1998) and the University of Erlangen-Nuremberg in Germany (professor ordinarius, 1998-2007). He then assumed the Dow Chair in Chemical Invention at Texas A&M University, where he is Distinguished Professor of Chemistry.

Gladysz has been a fellow of the Alfred P. Sloan Foundation (1980-1984) and a Camille and Henry Dreyfus Teacher-Scholar Grant recipient (1980-1985). He received an Arthur C. Cope Scholar Award in 1988, the University of Utah Distinguished Research Award in 1992, the ACS Award in Organometallic Chemistry in 1994, a von

Humboldt Foundation Research Award for Senior Scientists in 1995, the International Fluorous Technologies Award in 2007, the Texas A&M Distinguished Achievement Award in Research in 2013, and the Royal Society of Chemistry Award in Organometallic Chemistry in 2013. He was elected a fellow of the American Chemical Society in the inaugural year (2009) and became a fellow of the Royal Society of Chemistry in 2013.

From June 1984 to July 2010, he was associate editor of *Chemical Reviews*. He then was editor-in-chief of *Organometallics* until January 2015.

Gladysz has been author of more than 490 papers, book chapters, patents and editorials, and his research spans a wide range of problems in the general areas of synthetic and mechanistic organometallic chemistry and catalysis.





CO₂ CAPTURE VIA IONIC LIQUID BLENDS AND DEEP EUTECTIC SOLVENTS

Mert Atilhan

Department of Chemical Engineering
Qatar University, Qatar

ABSTRACT

Ionic Liquids (ILs) have emerged as a new generation solvents due to their potentials applications in diverse areas, such as biocatalytic processes, extraction solvents, functional materials design or electrochemistry. ILs are low-melting salts composed by an organic cation and an inorganic/organic anion. Many ILs present attractive physico-chemical properties such as high thermal and chemical stability, high ionic conductivity, nonflammability or being good solvents for a wide range of organic compounds. Nevertheless, the main advantage of ILs is the possibility of fine-tuning their properties through the correct combination of both ions (task-specific compounds). Although serious drawbacks — such as high viscosity, poor biodegradability, toxicity or high cost — have been shown in the literature for some ILs, these are not general characteristics for all the ILs because it would be possible to fulfill most of the technological and environmental requirements for ILs if suitable and judicious anion-cation combinations were developed using the plethora of possible molecules leading to ILs.

On the other hand, a suitable recent approach trying to overcome the above-mentioned reported IL-related issues are based on the development of deep

eutectic solvents (DES), which are emerging as a new alternative to ILs. DESs can be described as a salt and a second compound leading to a low melting mixture. The formation of DESs, with melting point close to room temperature, is due to the development of a network of intermolecular hydrogen bonds. DESs have a freezing point significantly lower than that of either individual component, which is related with a charge delocalization process. In addition to the advantages described for ILs, DESs are cheaper to produce, less toxic and often biodegradable.

In this communication, we report a systematic approach on the ionic liquids of a specific ammonium family and its 1:1 molar mixing ratio blends for their physical properties and more importantly their CO₂ capture performances before and after the blend. Corrosion data is also collected for benchmarking analysis in comparison with the classical amine-based CO₂ capture process. On the other hand, we also report two DES obtained by using choline-based ionic liquid and its mixture with phenylacetic acid and levulinic acid with 1:1 molar mixing ratio. CO₂ sorption process explained through *in situ* FTIR investigation as well.





BIOGRAPHY

Dr. Mert Atilhan received B.S. in chemical engineering from Ege University (Turkey), and M.S. and Ph.D. degrees in chemical engineering from Texas A&M University (USA). He is an associate professor at Qatar University and adjunct professor in the Chemical Engineering Program at Texas A&M University at Qatar. He has more than 15 years of experience in applied thermodynamics energy and environmental-related topics. His research activities are mainly focused on very high-accuracy property measurements, including PVT-density-viscosity, equation of state development for pure and mixture gases, VLE systems, natural gas hydrate equilibrium and inhibition, ionic liquid

properties and their application in various engineering applications, development of high-stability and high-capacity novel CO₂ capture sorbents at both pre- and post-combustion conditions, and gas mixture separations including olefin/paraffin and CO₂/CH₄/N₂ separation through various membranes. Atilhan has been author on 68 refereed publications and has secured more than \$8 million in research funding through various funding agencies in Qatar, USA and the European Union since 2007. He received The Best Researcher of the Year Award at Qatar University in 2008 and 2011.





EXTRACTIONS, SEPARATIONS AND PURIFICATIONS WITH AQUEOUS SOLUTIONS OF IONIC LIQUIDS

João A.P. Coutinho

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University of Aveiro, Portugal

ABSTRACT

Ionic liquids (ILs) have many drawbacks in their use as solvents in separation processes but many of these can be overcome by their use in aqueous solution, where many of the IL's most relevant characteristics are kept. Aqueous solutions of ILs are thus emerging as promising media for application in extraction and separation processes for a broad range of compounds, and among these ionic liquid based aqueous biphasic systems (IL-ABS) are one of the most promising approaches. Initially based on ionic liquids + salt systems, they have meanwhile been prepared with a wide range of inorganic and organic salts, amino acids, sugars and polymers extending the range of potential systems available. The molecular mechanisms responsible for the phase formation have been identified and range from simple salting out to much more complex competitive interactions observed in polymer containing systems. Being based on a wide variety of hydrophilic ionic liquids they provide a much broader range of phase polarities for enhanced and selective extraction and lower phase viscosities than conventional polymer-based ABS allowing for a faster mass transfer and easier fluid handling.

In our research group we have been studying the mechanism of IL aqueous solutions extraction and IL-ABS formation with both salts and polymers, and the effect of the ionic liquid cation and anion

on the solvation of target compounds. We will present an overview of the work developed and the successes achieved in the purification of biomolecules, as well as recent results addressing the use of ILs as hydrotropes, the characterization of pH-reversible and thermoreversible IL-ABS, and a discussion on the potential of these systems for extraction and fractionation of complex mixtures. Some challenges on the future developments of this area, including its scale up, will be discussed.

BIOGRAPHY

Dr. João A. P. Coutinho is a professor in the chemistry department of the University of Aveiro, Portugal, where he is the director of the Sustainability and Health Research Line at CICECO Laboratory. He studied thermodynamics and petroleum technology at Technical University of Denmark where he got his Ph.D. in chemical engineering in 1995. Since 1997 he leads a multidisciplinary research team that focuses on a range of different subjects from the petroleum production in nonconventional reservoirs, to the production and formulation of biofuels, and the development of novel separation processes for the biorefinery. Currently he strives to apply ionic liquids to these processes and is trying to better understand their physico-chemical behavior for that purpose.





DESIGN AND OPTIMIZATION OF SUSTAINABLE PROCESSING SYSTEMS

Patrick Linke

Chemical Engineering Program
Texas A&M University at Qatar, Qatar

ABSTRACT

The basic materials industries together with the utility sector provide the foundation for strong economies in many parts of the world. On the downside, the industries are associated with significant environmental footprints and constantly challenged to improve on the sustainability of their operations. Production processes are often co-located in industrial parks or cities, resulting in spatially concentrated, stationary environmental footprints. Process systems engineering approaches can provide invaluable insights and guide design-decision making towards systematic footprint reduction and enhanced sustainability of the basic materials industries. Optimal design approaches will be presented and discussed that can inform decision making within different boundaries, from industrial park wide design decision down to decisions at the level of individual processes. The presentation will place particular emphasis on reducing water, energy and GHG footprints at the level of the industrial city through process integration and highlight possible synergies across the water-energy nexus. At the level of individual processes, approaches to optimal conceptual process

design and integrated molecular design will be presented and discussed. Examples of relevance to Qatar will be shared to illustrate the approaches and their usefulness to explore scenarios during design and policy decision making.

BIOGRAPHY

Professor Linke is a professor and Chemical Engineering Program chair at Texas A&M University at Qatar in Education City, Doha. He is also the co-founder and managing director of the Qatar Sustainable Water and Energy Utilization Initiative, a center of excellence for research and capacity building. Linke's research activities focus on the development of systems engineering approaches for the design of sustainable processes, integrated systems and associated infrastructures with an application focus on the sustainable utilization of water, energy and other natural resources. Linke regularly serves on multiple national and international committees and advisory boards. He received his Ph.D. in process integration from the University of Manchester Institute of Science and Technology in the UK.



