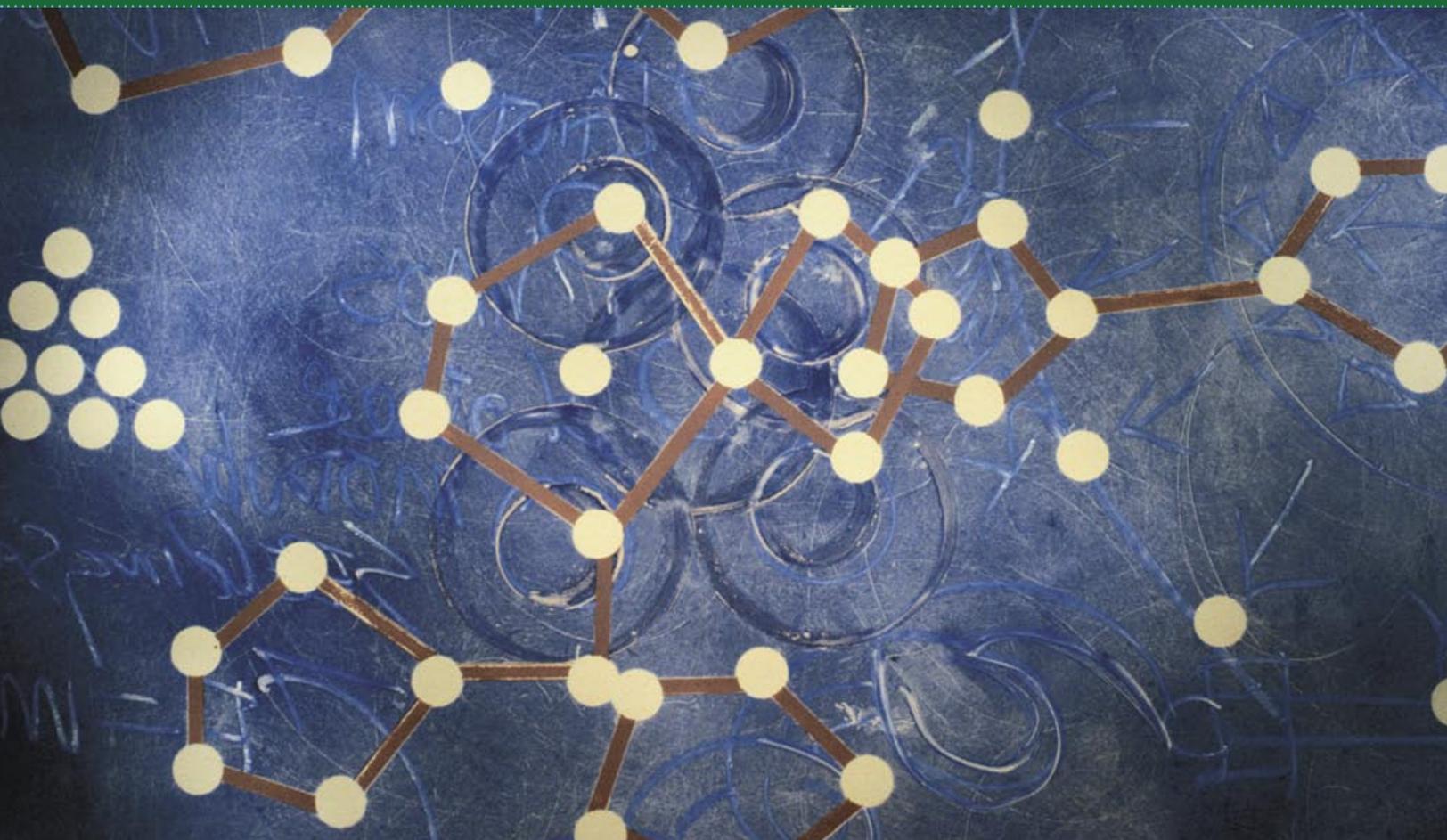


10th Annual Green Chemistry & Engineering Conference



› **Designing for a Sustainable Future**

June 26–30, 2006

CAPITAL HILTON ■ WASHINGTON, DC



www.GreenChem2006.org

IN APPRECIATION OF YOUR ATTENDANCE AT THE

10th Annual Green Chemistry & Engineering Conference

We have calculated and off-set the carbon emissions of all participants
through a collaboration with Global ReLeaf resulting in

The planting of 1500 trees.



10th Annual Green Chemistry & Engineering Conference



› **Designing for a Sustainable Future**

June 26–30, 2006

CAPITAL HILTON ■ WASHINGTON, DC



www.GreenChem2006.org

Welcome from the Organizing Committee

ON BEHALF OF THE ORGANIZING COMMITTEE, we welcome you to the 10th Annual Green Chemistry & Engineering Conference. This conference is driven by a belief in one simple but powerful idea: as chemists and engineers, we have it in our power to design a sustainable future. From energy to agriculture, materials to medicine, our ability to create at the most fundamental level gives us the power to change whole sectors of the world economy.



Will our innovations be sustainable?

The answer lies in the decisions we make every day as we design the newest molecules, materials, products, processes, and systems. This conference is meant to inform those decisions. Formal and informal events throughout the week will expose each of us to the latest advances in green chemistry and engineering from across the spectrum of the chemical enterprise. It will be an exciting time to teach, learn, collaborate, inspire, and be inspired.

- › *The conference begins on Monday morning with student workshops in Green Chemistry & Engineering. Educating the innovators of tomorrow must always remain a crucial part of our collective mission.*
- › *On Monday evening we will celebrate the best innovators of today with the 2006 Presidential Green Chemistry Challenge Awards Ceremony.*
- › *The technical program kicks off Tuesday morning and will feature keynote addresses, plenary talks, and technical presentations from leading experts representing a wide range of progress in green chemistry and green engineering.*

Interaction and collaboration generate new knowledge, and it is in this spirit of shared innovation that we convene the 10th Annual Green Chemistry & Engineering Conference. Thank you for joining us. We hope it will be your designs that help to define our sustainable future.

KEYNOTE SPEAKERS



Dan E. Arvizu, Ph.D.
Director,
National Renewable Energy Laboratory (NREL)



George M. Gray, Ph.D.
Assistant Administrator,
Office of Research and Development
U.S. Environmental Protection Agency



Stuart L. Hart, Ph.D.
Samuel C. Johnson Chair in Sustainable Global Enterprise
Cornell University

BANQUET SPEAKER



Henry Red Cloud
Descendant, Chief Red Cloud
President, Lakota Solar Enterprises



GreenChem2006

Conference Sponsors



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A division of the American Chemical Society

CHEMICAL ABSTRACTS SERVICE

ACS GCI
Pharmaceutical
Roundtable

Lilly



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Organizing Committee

MEMBERS

Paul Anastas, Chair

Green Chemistry Institute
American Chemical Society

Ellyn Beary

National Institute of Standards
and Technology

Berkeley Cue, Jr.

ACS GCI Pharmaceutical Roundtable

Rich Engler

U.S. Environmental Protection Agency

Peter Kelly

American Chemical Society

Larry Koskan

Global Green Products, LLC

Steve Lingle

U.S. Environmental Protection Agency

Julie Manley

ACS GCI Pharmaceutical Roundtable

Bob Marianelli

Consultant

Tina Masciangioli

National Research Council

Raul Miranda

U.S. Department of Energy

Nhan Nguyen

U.S. Environmental Protection Agency

Doug Raber

GreenPoint Science

Robin Rogers

The University of Alabama

Glenn Schrader

National Science Foundation

Darlene Schuster

American Institute of Chemical Engineers

Jim Solyst

Navigant Consulting

Julie Zimmerman

U.S. Environmental Protection Agency

Dorothy Zolandz

National Research Council

CONFERENCE ADMINISTRATORS

Kathryn Parent

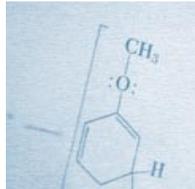
James Rea

Michelle Stevenson

Nancy Todd

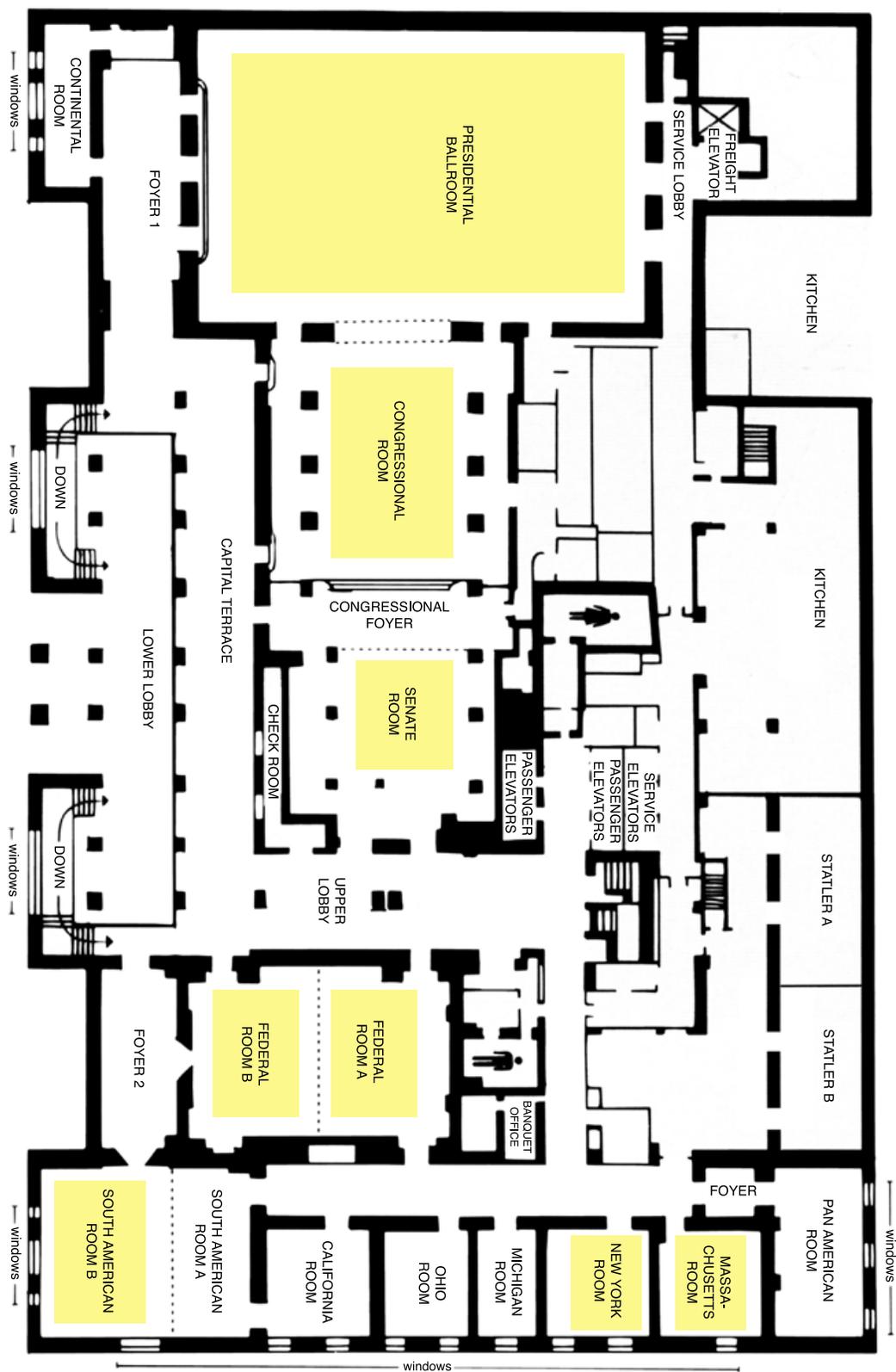
Jennifer Young

Schedule at a Glance

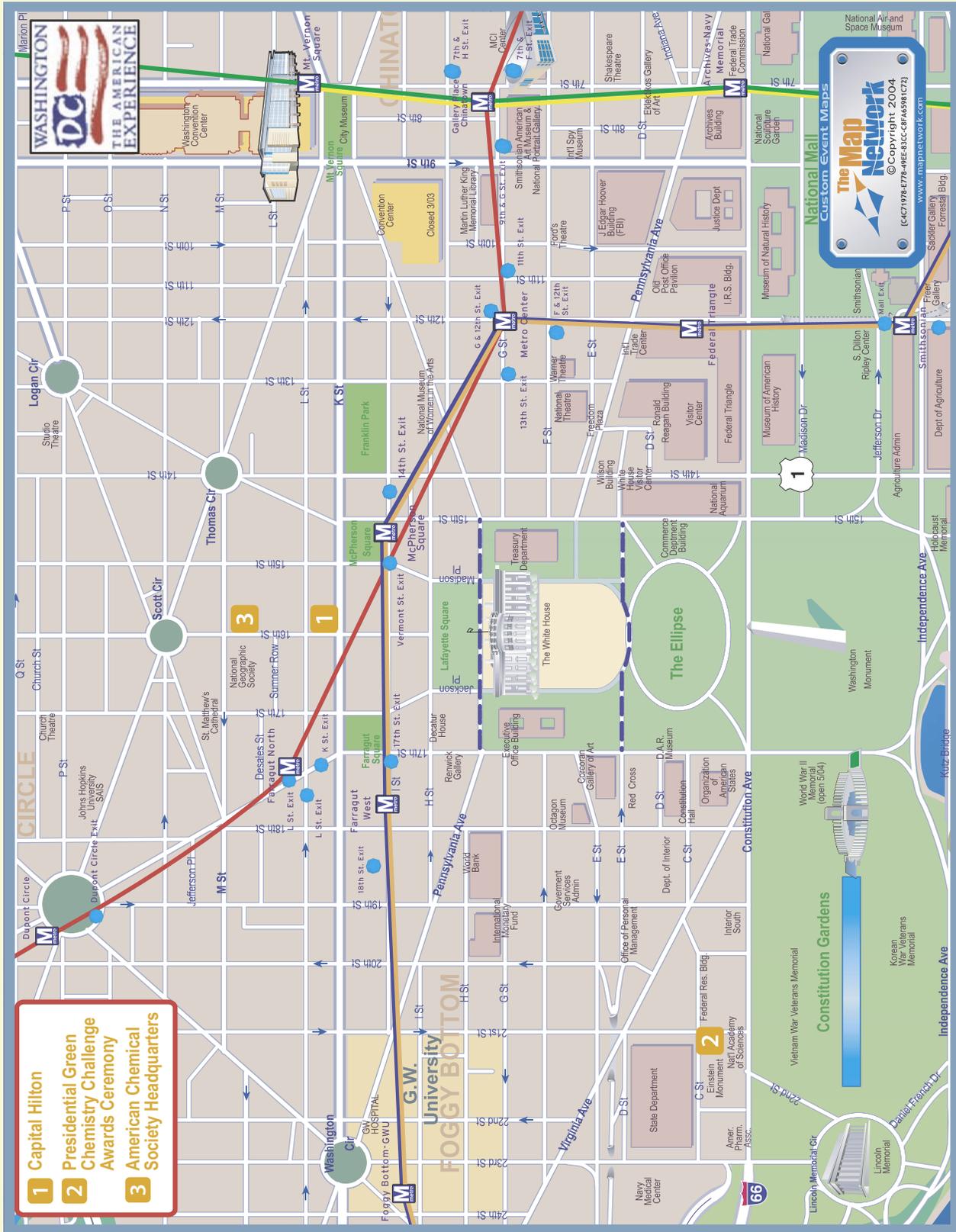
		Morning	
Monday, June 26	STUDENT WORKSHOP: Green Chemistry and Engineering Education		
Tuesday, June 27	OPENING SESSION: Presidential Green Chemistry Challenge Award Winners  KEYNOTE: George M. Gray, Ph.D. Assistant Administrator, Office of Research and Development U.S. Environmental Protection Agency	TECHNICAL SESSIONS: <ul style="list-style-type: none"> ■ Green Chemistry Awards I ■ Renewable Feedstocks ■ Alternative Synthesis I ■ Benign Solvents I ■ Stocking the Green Chemistry Toolbox 	
Wednesday, June 28	 KEYNOTE: Stuart L. Hart, Ph.D. Samuel C. Johnson Chair in Sustainable Global Enterprise Cornell University	TECHNICAL SESSIONS: <ul style="list-style-type: none"> ■ Future Energy ■ Water Technologies I ■ Bio-based Materials I ■ Alternative Processes I ■ Benign First Time Manufacturing ■ Small Business Panel 	
Thursday, June 29	 KEYNOTE: Dan E. Arvizu, Ph.D. Director, National Renewable Energy Laboratory (NREL)	TECHNICAL SESSIONS: <ul style="list-style-type: none"> ■ Energy Efficient Technologies I ■ Agriculture I ■ Green Nanotechnology ■ Alternative Synthesis II ■ Industrial Applications II PANEL DISCUSSION: Federal Programs for R&D That Can Enhance Green Chemistry & Engineering	
Friday, June 30	WORKSHOP: Train the Trainers <div style="display: flex; justify-content: space-around; align-items: center;">    </div>		

Afternoon		Evening	
STUDENT WORKSHOP (Continued): Green Chemistry and Engineering Education		Presidential Green Chemistry Challenge Awards Ceremony Conference participants are cordially invited to attend this ceremony, which will be held at 5:30 PM at the National Academies, 2100 C Street, NW, Washington, DC. See map on page 7. Please wear business attire.	
TECHNICAL SESSIONS: <ul style="list-style-type: none"> ■ Green Chemistry Awards II ■ Design for Biodegradation ■ Benign Solvents II ■ Engineering for Sustainability ■ Green Metrics Symposium ■ Information Resources & Assessment ■ Industrial Applications I 		Poster Session and Reception Pharmaceutical Industry Reception <i>(by invitation only)</i> 	
TECHNICAL SESSIONS: <ul style="list-style-type: none"> ■ Sustainable Energy Systems ■ Water Technologies II ■ Bio-based Materials II ■ Alternative Processes II ■ Designing Safer Chemicals & Toxicity Reduction I ■ Greener Processing & Innovative Technology ■ Forum: Research Needs to Drive Innovation 		BANQUET  BANQUET SPEAKER: Henry Red Cloud Descendant, Chief Red Cloud President, Lakota Solar Enterprises	
TECHNICAL SESSIONS: <ul style="list-style-type: none"> ■ Energy Efficient Technologies II ■ Agriculture II ■ Designing Safer Chemicals & Toxicity Reduction II ■ Alternative Synthesis III CLOSING SESSION: Designing for a Sustainable Future: What Role Will Green Chemistry & Engineering Play?			
GENERAL DAILY SCHEDULE		TECHNICAL SESSIONS KEY	
7:00 AM – 8:00 AM	Registration; Continental Breakfast	Centered around the theme of design, the program features green chemistry and green engineering innovations in five core tracks:	■ Energy
8:00 AM – 9:00 AM	Keynote Address		■ Agriculture & Foods
9:30 AM – 12:00 PM	Technical Sessions		■ Resources & Renewables
12:00 PM – 1:30 PM	Lunch <i>(on your own)</i>		■ Toxics & Materials
1:30 PM – 5:00 PM	Technical Sessions		■ Health & Medicine
5:00 PM – 7:00 PM	Posters/Receptions/Social Events		

Capital Hilton Floorplan—Second Floor



Washington Area Map



Monday, 26 June 2006

Green Chemistry & Engineering Student Workshop

Monday Morning

7:30 AM – 8:30 AM

Statler Rooms A & B

Breakfast (for participants only)

8:00 AM – 4:00 PM

Upper Lobby

Registration

8:30 AM – 12:00 PM

South American Room B

Student Workshop

8:30 AM – 9:45 AM

Introduction and Background

Paul Anastas

9:45 AM – 10:30 AM

Solvents

Philip Jessop

10:30 AM – 10:45 AM

Break

10:45 AM – 11:30 PM

**Materials from
Renewable Resources**

Richard Wool

11:30 AM – 12:00 PM

Polymers

Jennifer Young

12:00 PM – 12:30 PM

Group Discussion

12:30 PM – 2:00 PM

Statler Rooms A & B

Networking Lunch

(for participants only)

Monday Afternoon

2:00 PM – 5:00 PM

South American Room B

2:00 PM – 3:00 PM

Catalysis

Terry Collins

3:00 PM – 3:45 PM

Engineering

Julie Zimmerman

3:45 PM – 4:00 PM

Break

4:00 PM – 4:30 PM

Closing Session

5:30 PM

*National Academy of Sciences —
Auditorium*

**2006 Presidential Green
Chemistry Challenge
Awards Ceremony**



Conference participants are cordially invited to attend this ceremony, which will be held at 5:30 PM at the National Academies, 2100 C Street, NW, Washington, DC. See map on page 7. Please wear business attire.

Technical Program

Tuesday Morning

7:00 AM – 5:00 PM

Upper Lobby

Registration

7:00 AM – 8:00 AM

Upper Lobby

Continental Breakfast

8:00 AM – 9:00 AM

Opening Session: Winners of the 2006 Presidential Green Chemistry Challenge Awards

Session Chairs: Paul Anastas, ACS Green Chemistry Institute, and Steve Lingle, U.S. Environmental Protection Agency

9:00 AM – 10:00 AM

Presidential Ballroom



Keynote Address: Innovation: The Future of Environmental Protection

George M. Gray, Ph.D.

Assistant Administrator, Office of Research
& Development, U.S. Environmental Protection Agency

10:00 AM – 10:30 AM

Upper Lobby

Tea and Coffee Break

Technical Sessions

GENERAL GREEN CHEMISTRY & GREEN ENGINEERING SYMPOSIA

10:30 AM – 12:10 PM

Federal Room A

Green Chemistry Awards I

Session Chair: Rich Engler, U.S. Environmental Protection Agency

- 10:30** Introductory Remarks
- 10:50** 1 Bio-based propylene glycol and monomers from natural glycerin. **Galen J. Suppes**, University of Missouri-Columbia
- 11:30** 2 Environmentally safe washout solvents and cold reclaim systems™ in the flexographic printing industry. **Connie M. Hendrickson** and David C. Bradford, Arkon Consultants & Nupro Technologies

RESOURCES & RENEWABLES

10:30 AM – 11:50 AM

Senate Room

Renewable Feedstocks

Session Chair: Peter Kelly, American Chemical Society

- 10:30** 3 Aqueous phase catalytic hydrogenation and C-H activation of organic acids using Ru/C. **Jennifer E. Farrugia**, James E. Jackson and Dennis J. Miller
- 10:50** 4 Ethanol as a renewable feedstock for commodity chemicals: Acetic acid as an example. **Betina Jørgensen**, Jeppe Rasmussen, Anders Riisager, Kresten Egeblad and Claus Hviid Christensen
- 11:10** 5 Continuous esterification of bio-based organic acids: Formation of triethyl citrate. **Navinchandra Asthana**, Aspi Kolah, Dennis Miller and Carl Lira
- 11:30** 6 Alternative feedstocks for the chemical industry. **Joanna McFarlane** and Sharon M. Robinson

TOXICS & MATERIALS

10:30 AM – 12:10 PM

New York Room

Alternative Synthesis I

Session Chair: Ferdinando Bruno, U.S. Army RDECOM Natick Soldier Center

- 10:30** 7 Plenary: Base and acidic catalysis in dimethyl carbonate chemistry. **Pietro Tundo**, Ca' Foscari University
- 11:10** 8 Biocatalysis for material science. **Ferdinando F. Bruno**, Subhalakshmi Nagarajan, Ramaswamy Nagarajan, Donna McIntosh, Susan J. Braunhu, Jayant Kumar and Lynne A. Samuelson
- 11:30** 9 Synthesis of cyclic carbonates from fatty materials using supercritical carbon dioxide. **Kenneth M. Doll** and Sevim Erhan
- 11:50** 10 Green chemoselective and highly stereodivergent solutions to affect the dihydroxylation of allylic amines. **Marcus J.C. Long** and S.G. Davies



Technical Program, *Continued*

10:30 AM – 12:10 PM

Federal Room B

Benign Solvents I

Session Chair: István Horváth, Eötvös University

- 10:30** 11 Plenary: Switchable solvents and surfactants. **Philip G. Jessop**¹, Charles A. Eckert², and Charles L. Liotta² (1) Queen's University, (2) Georgia Institute of Technology
- 11:10** 12 Atom transfer radical polymerization (ATRP) in aqueous dispersed media. **Ke Min** and Krzysztof Matyjaszewski
- 11:30** 13 Biocatalysis of uranium in presence of ionic liquids. **Sanjay V. Malhotra**, Chengdong Zhang and A.J. Francis
- 11:50** 14 Controlling the reactivity of chlorophosphines with ionic liquids. **Marie Migaud**

HEALTH & MEDICINE

10:30 AM – 12:10 PM

South American Room B

Stocking the Green Chemistry Toolbox

Session Chair: Ann Lee-Jeffs, Johnson & Johnson

Sponsored & Organized by the GCI Pharmaceutical Roundtable

- 10:30** 15 Plenary: Sustainability Indexes: Holistic approach to measure corporate economic performance. **Rodrigo Amandi**, SAM Sustainable Asset Management Group
- 11:10** 16 Sustainability and life cycle principles in practice: Implementing FLASC™ (Fast Life cycle Assessment of Synthetic Chemistry) and early results. **David J. C. Constable**, Concepción Jiménez-González and Richard K. Henderson
- 11:30** 17 Selection and reduction of organic solvents in the pharmaceutical industry. Erin Frey, **C. Stewart Slater**, Mariano J. Savelski and Robert P. Hesketh
- 11:50** 18 UDCaT-5: Novel and efficient solid acid catalyst for green Claisen rearrangement of allyl phenyl ethers. **Ganapati D. Yadav** and Sharad V. Lande

12:10 PM – 1:30 PM

Lunch Break (*on your own*)

Tuesday Afternoon

Technical Sessions

Tuesday Afternoon Break sponsored by the Chemical Abstracts Service

GENERAL GREEN CHEMISTRY & GREEN ENGINEERING SYMPOSIA

1:30 PM – 5:40 PM

Federal Room A

Green Chemistry Awards II

Session Chair: Rich Engler, U.S. Environmental Protection Agency

- 1:30** 19 The asymmetric catalytic hydrogenation of unprotected enamines enables a highly efficient, green synthesis of sitagliptin, the active ingredient in Januvia™. Merck & Co., Inc.
- 2:10** 20 The new commercial "green-by-design" biocatalytic process for the key chiral intermediate for atorvastatin enabled by the directed evolution of three biocatalysts. **John Grate**, Codexis, Inc.
- 2:50** 21 SC Johnson's patented Greenlist™ process used to reformulate consumer products. **David Long and John Weeks**, S.C. Johnson & Sons, Inc.

RESOURCES & RENEWABLES

1:30 PM – 5:40 PM

Massachusetts Room

Design for Biodegradation

Session Chair: Lyn Beary, National Institute of Standards and Technology

- 1:30** 22 Plenary: Designing biodegradable chemicals. **Bob Boethling**, David DiFiore and Elizabeth Sommer. U.S. Environmental Protection Agency
- 2:10** 23 Biodegradation experiments in the marine environment. **Jo Ann Ratto**, Robert Stote, Jean Herbert, Christopher Thellen and Carl Wirsén
- 2:30** 24 Electron beam modification of starch with lignins and lignin model compounds: Evidence of grafting reactions. **Xavier Coqueret**
- 2:50** 25 Towards 'Advanced Green Composites'. **Anil N. Netravali**
- 3:10** 26 Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. **Piyush S. Lathi** and Bo Mattiasson

TOXICS & MATERIALS

1:30 PM – 5:40 PM

Federal Room B

Benign Solvents II

Session Chair: Philip Jessop, Queen's University

- 1:30** 27 Plenary: γ -Valerolactone: A sustainable liquid for energy and carbon based chemicals. **István T. Horváth**, Eötvös University
- 2:10** 28 Unleashing cellulose potential: BASF ionic liquids. **Calvin J. Emanuel** and Matthias Maase
- 2:30** 29 Chemical engineering in multiphase CO_2 -expanded liquid systems: Study of the Pictet-Spengler reaction. **Rocco P. Ciccolini**, Joshua R. Dunetz, Morgan Froling, Scott M. Paap, Andrew J. Allen, Rick L. Danheiser and Jefferson W. Tester,
- 2:50** 30 Ionic liquids: Benign solvents for supported liquid catalyst systems. **Anders Riisager**, Rasmus Fehrmann, Marco Haumann and Peter Wasserscheid
- 3:10** 31 Rapid optimization of supercritical hydrogenation flow systems. **Richard A. Bourne**
- 3:30** Break
- 4:00** 32 Direct synthesis of hydrogen peroxide from oxygen and hydrogen in carbon dioxide. **Qunlai Chen** and Eric Beckman
- 4:20** 33 Reduction of total VOC emissions in flexographic washout solvents. **Connie M. Hendrickson** and David C. Bradford
- 4:40** 34 Continuous acid-catalyzed reactions in supercritical CO_2 . **Peter N. Gooden**
- 5:00** 35 Formamide as a green solvent. **Mikhail M. Bobylev** and Lioudmila I. Bobyleva
- 5:20** 36 Identification, design and synthesis of oxygenated hydrocarbon-based CO_2 -soluble polymers for chemical, pharmaceutical, biomedical and petroleum engineering applications. **Lei Hong**, Yang Wang, Robert Enick, Eric Beckman and Karl Johnson



HEALTH & MEDICINE

1:30 PM – 3:30 PM

South American Room B

Engineering for Sustainability

Session Chair: Berkeley W. Cue, Jr., Private Consultant

Sponsored & Organized by the GCI Pharmaceutical Roundtable

- 1:30** 37 Plenary: Increasing chemical efficiency: Incorporating advances in synthetic design into continuous processes. **Steven J. Broadwater** and D. Tyler McQuade, Cornell University
- 2:10** 38 Green chemistry and biotransformations in API manufacturing processes. Junhua Tao and **Kim F. Albizzati**
- 2:30** 39 Lipase catalyzed microwave-assisted resolution of naproxen methyl ester. **Ganapati D. Yadav**, Shrikant B. Dhoot and Ashwini D. Sajgure
- 2:50** 40 Integrated environmentally benign product design, process design and optimal control: A case study in the pharmaceutical industry. **Saadet Ulas** and Urmila Diwekar
- 3:10** 41 Preparative SFC at the kilogram scale to support pharmaceutical development. **Derek W. Henderson**, Jinchu Liu, William R. Leonard and Christopher J. Welch
- 3:30** Break

4:00 PM – 5:00 PM

South American Room B

Green Metrics Symposium

Moderator: David J.C. Constable, GlaxoSmithKline

Sponsored & Organized by the GCI Pharmaceutical Roundtable

This session will review metrics currently being used by major corporations to assess the "greenness" of synthetic chemical processes. A mass intensity metric will be proposed as a means to objectively benchmark while driving process innovation in the pharmaceutical industry. Although the metric is being proposed by the pharmaceutical industry, we intend to engage in an open discussion about its broader use and adoption.

- 4:00** 51 Application of metrics in driving green chemistry initiatives at GSK. **David J.C. Constable**, Richard K. Henderson and Concepción Jiménez-González
- 4:07** 52 Measuring green chemistry implementation: Building EHS performance into products. **John M. Kindervater** and Stephen A. Leeper
- 4:14** 53 Merck's API mass intensity metric. **Beth Berglund**, John Leazer, Ephraim Bassan and Mary Buzbyc
- 4:21** 54 Defining a mass intensity metric for the pharmaceutical industry. **GCI Pharmaceutical Roundtable**, ACS Green Chemistry Institute
- 4:28** Discussion

Technical Program, *Continued*

GENERAL GREEN CHEMISTRY & GREEN ENGINEERING SYMPOSIA

1:30 PM – 5:40 PM

New York Room

Information Resources & Assessment

Session Chair: Denny Hjeresen, Los Alamos National Laboratory

- 1:30 42 Plenary: Emerging chemical issues. **N.I. McClelland¹** and M.A. Taubitz², (1) N.I. McClelland LLC, (2) American National Standards Institute (ANSI)
- 2:10 43 Green chemistry resource exchange. **Jennifer L. Young**, James C. Rea and Paul T. Anastas
- 2:30 44 Challenge of classifying “green” chemicals and products. **George R. Thompson**
- 2:50 45 Building CleanGredients: Using a multi-stakeholder process to design an information resource for green cleaning product formulation. **Tarek Rached** and Lauren Heine
- 3:10 46 Evaluating the environmental implications of agricultural feedstocks for biobased production. **Amy E. Landis**, Shelie A. Miller and Thomas L. Theis
- 3:30 Break
- 4:00 47 Plenary: Green chemistry principles applied to an ISO 14001 environmental management system. **Denny Hjeresen**, Los Alamos National Laboratory
- 4:40 48 Green chemistry through hands-on experience for undergrad students. **Bhanumati Soundararajan**
- 5:00 49 Putting the fizz into chemistry: Taking green chemistry to the public. **Samantha L.Y. Tang**, Martyn Poliakoff, Steve Howdle and Mike George
- 5:20 50 Chemistry Literacy Network: Environmental chemistry education, research and action. **Sheryl Dee Mebane**

4:00 PM – 5:40 PM

Federal Room A

Industrial Applications I

Session Chair: Karen O'Brien, ACS Green Chemistry Institute

- 4:00 55 Advances in green product design. **Neville Hargreaves**
- 4:20 56 Improving IAQ in commercial buildings through alternative green solutions: TractionBack[®] and 180 Walls[®]. **Joseph R. Royer** and Bill Gregory
- 4:40 57 Invention and commercialization of environmentally smart thermosetting binders. Barry Weinstein, **Griffin Gappert** and **Derek Bristol**
- 5:00 58 Breakthrough synthetic-based drilling fluid system (SBF) improves environmental and technical performance. **John A. Hall** and Charles Mowrey
- 5:20 59 Decolorable toner e-blue. **Sano Kenji**, Satoshi Takayama, Takeshi Gotanda and Yumiko Sekiguchi

4:00 PM – 6:00 PM

Massachusetts Room

Chemical Abstracts Service Demonstrations

Tuesday Evening

GENERAL POSTER SESSION & RECEPTION

6:00 PM – 9:30 PM

Congressional and Senate Rooms

Odd numbered poster presenters should be stationed at their posters 6:00 PM – 7:30 PM. Even numbered poster presenters should be stationed at their posters 7:30 PM – 9:00 PM.

ENERGY

- 60 Simulation study of soot oxidation in NO₂. Ruiqiang Liu, Xinhong Chen, C. Purushothama, **J.O. Chae** and Valentin Puchkov
- 61 Generation of electricity and no excess sludge from wastewater by an activated sludge process integrated with a microbial fuel cell. **Toshihide Kakizono**, Sunao Mihara and Naomichi Nishio
- 62 Towards the development of a chitosan membrane for enzyme immobilization. **Tamara Klotzbach**, Michelle Watt and Shelley D. Minter
- 63 Tide Coldwater: Energy conservation through residential laundering innovation and commercialization. **Darius Sabaliunas**

AGRICULTURE & FOODS

- 64 Stoller's Root Feed enhances crop root growth, crop productivity and stress tolerance. **Albert Liptay**, Jerry H. Stoller and Ron A. Salzman
- 65 Alternatives to azinphos methyl in apples. **Benjamin Newton**
- 66 Organic farming: A need for sustainable agriculture. **Pramila Maini**
- 67 Fungal diseases of sweet potatoes (*Ipomoea batatas*). **Mojeed Oladapo Oyewale**
- 68 Agriculture waste utilization in Madhya Pradesh: A case study. **Monika Vishwakarma**

RESOURCES & RENEWABLES

- 69 Synthesis of monofunctionalized cyclodextrin polymers for the removal of organic pollutants from water. **Bhekia B. Mamba**, Rui W.M. Krause, Tshepo J. Malefetse and Edward N. Nxumalo
- 70 Bio-gas plant slurry and its application. **Neena V. Arora**
- 71 TiO₂-photocatalyzed As(III) oxidation in a fixed-bed, flow-through reactor. **Megan A. Ferguson** and Janet G. Hering

- 72 Novel enzymatic synthesis and properties of aliphatic polythioester. **Makoto Kato**, Kazunobu Toshima and Shuichi Matsumura
- 74 Visible light photocatalysis with platinized titanium dioxide for water treatment. **Wenbing Li** and Tingying Zeng
- 75 Thermal properties of poly(L-lactic acid) ionomers synthesized from chemical recycling. **Andrew J. Ro**, Robert A. Weiss and Samuel J. Huang
- 76 Scope and principles of green chemistry and engineering. **Anil K. Sharma**
- 78 Synthesis of some new bispyrrolidine derivatives for biological interest. **Amal Sabet Yanni**

TOXICS & MATERIALS

- 79 Production of recombinant human gelatin in transgenic rice cell cultures. **Corey N. Dodge**, Karen A. McDonald, Julio Baez and Mysore Sudarshana
- 80 Protein-transition metal ion networks. **Justin Barone**, Kirsten Dangaran and Sylvia Chin
- 81 Analyzing the “greenness” of analytical methods. **Rajender K. Brahma**, Jennifer L. Young, Paul T. Anastas and Larry Keith
- 82 Polyaspartic acid as a cleaning agent for calcite and barite deposits. Christine S. Grant and **Jonathan Braxton**
- 83 New family of iron-centered tetra-amido macrocyclic ligand complexes. **William C. Ellis**, Colin P. Horwitz and Terrence J. Collins
- 84 Mechanochemistry for the reduction of solvent waste. **Dennis A. Fulmer**
- 85 Extraction of metal ions using surface-modified silica gel: A greener analytical method. **Bhagwan S. Garg** and R.K. Sharma
- 86 Magnesium hydroxide from mineral source as benign flame retardant for paper and polymers. **Iara F. Gimenez**, Charlene R.S. Matos, Francys K.V. Moreira and Ledjane S. Barreto
- 87 Natural biosensor-based assay for the efficient screening of complex mixtures. **Gerald T. Gourdin**, Sheryl M. Verbitski, Larissa M. Ikenouye and James D. McChesney
- 89 New amino acid-based surfactants for carbon dioxide. **Hakwon Kim**, Younja Kwon, Yeonju Kim, Daeil Bae, Hongdoo Kim and Kwangheon Park
- 90 Facile “green” synthesis, characterization and catalytic function of β -D glucose-stabilized Au nanocrystals. **Juncheng Liu**, Gaowu Qin, Yutaka Ikushima and Christopher B. Roberts
- 91 Surge of green: A proposed sustainable approach to conductive polymers. **Bethany A. Masten** and Edward J. Brush
- 92 Toxicity of selected room-temperature ionic liquids to industrial wastewater treatment bacteria. Maria A. Azimova and **Samuel A. Morton III**
- 93 Green chemistry approach for the removal of heavy metal ions from industrial waste land. R.K. Sharma, **Parul Pant**, Shuchi Dhingra and Alok Adholeya
- 94 Transient and steady-state kinetic studies of Fe^{III}-TAML[®] activators of H₂O₂ and organic peroxides. **Delia-Laura Popescu**, Alexander D. Ryabov and Terrence J. Collins
- 95 Design and synthesis of intercalated polyolefin/graft oligomer/organo-silicate nanocomposite architectures by green reactive extrusion *in situ* processing. **Zakir M.O. Rzayev** and Aziz Yilmazbayhan
- 96 Imidazolium carboxylates as precursors to novel N-Heterocyclic carbene complexes of Rh, Ir, Ru, Pt and Pd. **Adelina M. Voutchkova**, and Robert H. Crabtree
- 97 Hydrogen peroxide oxidations catalyzed by an iron complex of the new tetra-amide macrocycle (TAML[®]), H₂B[†]. **Hayden J. Smith**, L. James Wright, Trevor Stuthridge, Terry Collins and Colin Horwitz
- 98 Evaluating the sustainability of green chemistries. **Raymond L. Smith** and Michael A. Gonzalez
- 99 Combined determination of mercury and other heavy metals in biological objects. **Leonid I. Toropov**
- 100 Key green chemistry research areas: Perspective from pharmaceutical manufacturers. **GCI Pharmaceutical Roundtable**



Technical Program, *Continued*

INFORMATION RESOURCES AND ASSESSMENT

- 101 Green Chemistry Institute Sabbatical/Fellow Program: Valuable research experiences and collaborations with the GCI. **Edward J. Brush**
- 102 Greener scheme for qualitative analysis of cations without H₂S and sulfur compounds in the presence of interfering anions. **Sushmita Chowdhuri** and Indu Tucker Sidhwani
- 103 Green agents for organic reduction reactions: Low cost, eco-friendly experiments. **Sunita Dhingra** and Renu Aggarwal
- 104 Green science and technology: Spreading the message to non-scientists. **Thomas Marrero** and Stanley Manahan
- 105 Study of ligand substitution reactions in various cobalt (III) complexes. **Indu Tucker Sidhwani** and Sushmita Chowdhuri
- 106 Web-based course modules to incorporate green engineering concepts into the chemical engineering curriculum. **C. Stewart Slater**, Robert Hesketh, Mariano Savelski, Ann Marie Flynn, Jim Henry and Martin Abraham
- 107 Research twinning at the University of Nottingham. **Samantha L.Y. Tang**
- 108 Pharmaceuticals in the environment: Development of an active pharmaceutical ingredient (API) waste treatment software tool. **Andrew S. Wells**, Paul Bainbridge and Neil Adlington

Wednesday Morning

7:00 AM – 5:00 PM

Upper Lobby

Registration

7:00 AM – 8:00 AM

Upper Lobby

Continental Breakfast

8:00 AM – 9:00 AM

Presidential Ballroom



Keynote Address: Green Chemistry and Sustainable Value

Stuart L. Hart, Ph.D.

Samuel C. Johnson Chair in Sustainable Global Enterprise, Cornell University

9:00 AM – 9:30 AM

Upper Lobby

Tea and Coffee Break

Technical Sessions

ENERGY

9:30 AM – 12:10 PM

Federal Room A

Future Energy

Session Chair: Robert Marianelli, Consultant

- 9:30 109 Plenary: Devil is in the details — or is it? Designing clean energy technologies and pathways. **Stephen R. Connors**, Massachusetts Institute of Technology
- 10:10 110 Development of carbon dioxide removal bioreactor using *Methanococcus jannaschii*. **Jong Hee Jang**, Daisuke Kakei, Megumi Nishikawa, Makoto Takada, Satoshi Nakai and Masaaki Hosomi,
- 10:30 111 Eco-efficient solutions for a sustainable future. **Charlene A. Wall**
- 10:50 Break
- 11:10 112 Effects of iron-based catalysts on hydro-liquefaction of wood biomass in supercritical ethanol. **Charles Xu** and Timothy Etcheverry
- 11:30 113 Wise energy investment decisions: not just [KJ out/KJ in]. **Lise Laurin**

RESOURCES & RENEWABLES

9:30 AM – 12:10 PM

Federal Room B

Bio-based Materials I

Session Chair: Joseph Fortunak, Howard University

- 9:30 114 Plenary: Bio-based polymers and composites manufacturing plant. **Richard P. Wool**, University of Delaware
- 10:10 115 Bio-based polyurethane foams from soyoil polyols. **Laetitia M. Bonnaille**, A. Campanella, Richard P. Wool and Raghavan Jayaraman
- 10:30 116 Development of a low-k material from renewable resources. **Mingjiang Zhan**, Chang K. Hong and Richard P. Wool
- 10:50 Break
- 11:10 117 Carbonization of chicken feathers for use in biocomposites. **Melissa E.N. Miller** and Richard P. Wool
- 11:30 118 Carbon nanotube composites from soy-based resins. **Ian M. McAninch** and Richard P. Wool
- 11:50 119 Progress in the development of a general biomass-based chemistry. **Rawle I. Hollingsworth**

9:30 AM – 12:10 PM

Senate Room

Water Technologies I

Session Chair: Terry Collins, Carnegie Mellon University

- 9:30** 120 Plenary: Integrated water management: An environmentally sensible approach to industrial water treatment. **Manian Ramesh**, Nalco Company
- 10:10** 121 Nanoparticulate iron oxide for removing arsenic from drinking water and effluent. **Robert Trozenski**, Kim O'Connor, Andreas Schlegel, Hendrik Kathrein, Ulrike Pitzer, Karl-Heinz vanBonn, Udo Holtman, Jürgen Kischkewitz, Paul Malsch and Linda Huntley
- 10:30** 122 Closing the loop on waste: biodiesel and bioreactor waste products as feedstocks. **Kendra Zamzow**, T.K. Tsukamoto and G.C. Miller
- 10:50** Break
- 11:10** 123 Water treatment by combination of iron nanoparticles and cyclodextrin polymers. **Rui W.M. Krause**, Bhekie B. Mamba and Ketulo Salipira
- 11:30** 124 Removal of natural organic matter and odor causing compounds from water using nanoporous polymers. **Bhekie B. Mamba**, Rui W.M. Krause, Tshupo J. Malefetsa and Sabelo D. Mhlanga

TOXICS & MATERIALS

9:30 AM – 12:10 PM

New York Room

Alternative Processes I

Session Chair: Doug Raber, GreenPoint Science

- 9:30** 125 Plenary: Green electronics: challenges and opportunities. **Jeff Omelchuck**, Green Electronics Council
- 10:10** 126 Green HAZOP analysis: A novel green engineering guidance tool for design, assessment and implementation of processes. **Juan García Serna**, Jose Luis Martínez Gonzalez and María José Cocero Alonso
- 10:30** 127 Remarkably improved route to the manufacture of superacid catalysts. **Zoe A.C. Schnepf**, Mark A. Harmer and Christopher Junk
- 10:50** Break
- 11:10** 128 Enzymatic degumming of vegetable oils. **Chris L.G. Dayton**
- 11:30** 129 Chemical recycling of polymer matrix composites (PMCs) with supercritical fluids: Recovery of carbon fibers from epoxy resins composites. **Raul Piñero Hernanz**, Christopher Dodds, Jason Hyde, Juan García Serna, Edward Lester and Martyn Poliakov
- 11:50** 130 Homologous recombination of a mutated fungal xylanase into *Thermomyces lanuginosus* and expression in yeast. **Nokuthula P. Mchunu**

HEALTH & MEDICINE

9:30 AM – 12:10 PM

South American Room B

Benign First Time Manufacturing

Session Chair: Julie B. Manley, ACS Green Chemistry Institute
Sponsored & Organized by the GCI Pharmaceutical Roundtable

- 9:30** 131 Plenary: PAT and Green Chemistry. **D. Christopher Watts**, U.S. Food and Drug Administration
- 10:10** 132 Green chemistry: Meeting Schering-Plough's global challenges within chemical and physical sciences. **Ingrid Mergelsberg**
- 10:30** 133 The status of Green Chemistry at Merck & Co., Inc. **John Leazer**, David Hughes, Mary Buzby, Dave Mathre and Skip Volante
- 10:50** Break
- 11:10** 134 Designing a green manufacturing process for a novel active pharmaceutical ingredient (API): Reducing environmental impact and adding value to the business. **Laurence J. Harris**
- 11:30** 135 Aqueous mediated EDC peptide forming reactions. **David Mitchell**, Radhe Vaid, John Pu, Sathish Boini, Christopher Doecke and Kenneth Moder
- 11:50** 136 *Please see Amendments to the Conference Program.*

GENERAL GREEN CHEMISTRY & GREEN ENGINEERING SYMPOSIA

9:30 AM – 12:10 PM

Massachusetts Room

Small Business Panel

Moderator: Larry Koskan, Global Green Products

- 9:30 – 10:10** **Matthew Patsky**, Winslow Green Fund. A well written business plan is the key to success in raising capital. We will discuss the essential elements in the development of the plan and how to sell your concept.
- 10:10 – 10:50** **James Barber**, Metabolix. The company was formed from an unusual and unorthodox concept. Bringing key research and management people together was one key in the success story.
- 11:10 – 11:30** **Mark Hockwalt**, Innovium. The St. Louis company was a merger of two ideas relating raw materials and finished products. This process led to identifying a marketing potential and the development of products for that market.
- 11:30 – 11:50** **Richard Sapienza**, METSS. The success of this company was primarily due to its ability to apply for and receive SBIR grants. We will detail the essence of applying for these loans and grants.
- 11:50 – 12:10** **William Hayday**, Rynex Holdings. The development of several patents was a key ingredient in the establishment of the business. Partnering with the EPA to add credibility to the technology was an important step.

Technical Program, *Continued*

12:10 PM – 1:30 PM

Lunch Break *(on your own)*

Wednesday Afternoon

Technical Sessions

ENERGY

1:30 PM – 5:40 PM

Federal Room A

Sustainable Energy Systems

Session Chair: Darlene Schuster, American Institute of Chemical Engineers

- 1:30 137 Plenary: Metrics for energy systems: Sustainable energy strategies. **Calvin B. Cobb**, Calvin Cobb & Co.
- 2:10 138 Non-covalent forces in dendrimer-structured dye-sensitized solar cells. **Timothy E. Cain**, Roger A. Boggs and John C. Warner
- 2:30 139 Solar thermal for industry: Why the time is now. **Judy Kosovich**, Carlo La Porta and Albert Nunez Cem
- 2:50 140 BP Alternative Energy, Growing Low Carbon Power. **Lee Edwards**
- 3:10 141 Technology developments towards greener automotive fuels. **Frits Dautzenberg**
- 3:30 Break
- 4:00 142 Mobility aspects of used oil re-refining. **A.E. Alkhalidi**
- 4:20 143 Optimal flowsheet synthesis for biorefinery systems. **Demetris Josephides** and Urmila Diweka
- 4:40 144 New biomass catalytic reforming processing for SOFC power generation. **Savvas Vasileiadis**

RESOURCES & RENEWABLES

1:30 PM – 5:40 PM

Federal Room B

Bio-based Materials II

Session Chair: Richard Wool, University of Delaware

- 1:30 145 Valuable products from Nigerian elephant sawgrass. **Joseph Fortunak**, Frank Ohwoavworhua, Olobayo Kunle and Robin D. Rogers
- 1:50 146 Green monomers and polymers for functional and reactive polyesters and nylons. **Lon J. Mathias**, Allison M. Sikes, Kaitian Xu, Carl Bennett and Eylem Tarkin-Tas
- 2:10 147 Corn (sugars)-based polymer chemistries. **Michael Jaffe**, George Collins, Anthony East and Yi Zhang
- 2:30 148 Exopolymer as a raw material. **Joan Combie**
- 2:50 149 Chemical investigation of *Anthemis tigreensis* for bioactive sesquiterpene lactones. **Nigist Asfaw**, Sinedu Dejene and Senait Dagne

- 3:10 150 Effects of a star-branched polyol and poly(vinyl alcohol) on the electrospinning behavior of wheat protein. **Dara L. Woerdeman** and Suresh Shenoy
- 3:30 Break
- 4:00 151 Eco-friendly bioplastics from renewable feedstocks: Microbial conversion and downstream recovery. **Jian Yu**
- 4:20 152 Acacia and Tamarix as green corrosion inhibitors of galvanized steel. **Ahmed A. Taha**
- 4:40 153 Ecofriendly decolorization of wastewater using seed galactomannans from renewable resources. **Rashmi Sanghi**, Ishan Desai, Binayak Adhikary and P.A. Parikh
- 5:00 155 LCA of bio-based products: A comparison of starch and polyethylene foams. **Chisa K. Brookes**, Bruce Dale, Seungdo Kim and Ramani Narayan

1:30 PM – 5:40 PM

Senate Room

Water Technologies II

Session Chair: Manian Ramesh, Nalco

- 1:30 156 Oxidative degradation of nitrophenols and nitroanilines in aquatic environment. **Arani Chanda**, George J. Diabes, Alexander D. Ryabov, Sushik K. Khetan and Terrence J. Collins
- 1:50 157 Deactivation of surrogates of microbial pathogens: Toward green water disinfection. **Deboshri Banerjee**, Sushik K. Khetan, Yong-Li Qian, Philip Dulac, Mark Krotec and Terrence J. Collins
- 2:10 158 Oxidative degradation of Lipitor® and Zolof® with the Fe-TAML® catalyst and hydrogen peroxide. **Yan Xiang**, Melanie Vrabel, Evan Beach, Colin Horwitz, Sushil Khetan and Terrence Collins
- 2:30 159 Decolorization of pulp mill bleach plant effluent by hydrogen peroxide activated by an Fe-TAML® catalyst. **Evan S. Beach**, Colin P. Horwitz, Jonathan Spatz, William C. Ellis, Charles S. Merris Jr. and Terrence J. Collins
- 2:50 160 Green approach to remediation of waste streams containing dyes. **Ryan Malecky**, Evan Beach, Colin P. Horwitz and Terrence J. Collins
- 3:10 Break
- 4:00 161 Multi-electron transfer and carbene formation at heme functionalized nanocrystalline TiO₂: Reductive dechlorination of DDT and CCl₄. **Jonathan R. Stromberg**, Rachelle Ann Pinlac, Joshua Wnuk and Gerald J. Meyer
- 4:20 162 Chicago water use: Steps to sustainability. **Yi Meng** and Paul R. Anderson
- 4:40 163 Current issues on water use and reuse in chemical processes. **Daniel Sujo**, Robert P. Hesketh, Mariano J. Savelski and C. Stewart Slater
- 5:00 164 Sustainable environmental management for mercury in water: Part I, Industrial sustainability. **Yogendra N. Shastri** and Urmila Diwekar

- 5:20** 165 Sustainable environmental management for mercury in water: Part II, Ecological sustainability. **Yogendra N. Shastri** and Urmila Diwekar

TOXICS & MATERIALS

1:30 PM – 5:40 PM

New York Room

Alternative Processes II

Session Chair: Doug Raber, GreenPoint Science

- 1:30** 166 Chemical synthesis in flow reactors: A Greener alternative. **Paul Watts** and Charlotte Wiles
- 1:50** 167 Beneficiation and utilization of coal combustion fly ash: A major success in reducing solid waste and increasing supplies of construction materials while reducing of greenhouse gas emissions. **Stephen Gasiorowski** and James D. Bittner
- 2:10** 168 Microwave assisted synthesis of novel spirocyclic quaternary ammonium salts and their conversion into N-heterocycles of biological importance. **Subhash C. Jain**, Archana Gupta and Rajeev Sakhuja
- 2:30** 169 Selective oxidation of alcohols alternative catalytic processes. **Endalkachew Sahle-Demessie**
- 2:50** 170 Chemical recycling of polycarbonate by supercritical alcohol-CO₂ assisted process: A green-efficient route for CD-DVD's wastes recycling. **Raul Piñero Hernanz**, Juan García Serna and María José Cocero Alonso
- 3:10** 171 Identifying greener analytical methods. **Jennifer L. Young**, Rajender K. Brahman, Paul T. Anastas and Larry Keith

1:30 PM – 5:40 PM

Massachusetts Room

Designing Safer Chemical & Toxicity Reduction I

Session Chairs: Pete Myers, Environmental Health Sciences, and Eric Beckman, University of Pittsburgh

- 1:30** 172 Plenary: Approaches to Designing Innovative Sustainable Products. **Eric Beckman**, University of Pittsburgh
- 2:10** 173 Chromate-replacing corrosion inhibitors and primers for aluminum alloys. **Zhangzhang Yin**, Anuj Seth and William van Ooij
- 2:30** 174 Zinc-clad lead: A safer alternative for ammunition. **Philip G. Malone**, Charles A. Weiss, Jr. and Joe G. Tom
- 2:50** 175 Picaridin: A safe, effective, environmentally friendly insect repellent that people will use. **Frank Lueckgen**, Hans Essensbreis, Thomas Gernot and Paul Malsch
- 3:10** 176 Properties and performance of flexible Noryl*resin for wire coating. **James J. Xu**, Weiguang Yao and Mukund Parthasarathy
- 3:30** Break

- 4:00** 177 Plenary: New design signals for green chemistry from the environmental health sciences. **John Peterson Myers**, Environmental Health Sciences
- 4:40** 178 Massachusetts model for evaluating alternative chemicals. **Pamela A. Civie**
- 5:00** 179 Enzyme-based technology for decontamination of toxic organophosphorus compounds. **Joseph J. DeFrank**, Vipin K Rastogi, Tu-chen Cheng and Christopher S. Penet

HEALTH & MEDICINE

1:30 PM – 5:40 PM

South American Room B

Greener Processing & Innovative Technology

Session Chair: Benjamin A. Anderson, Eli Lilly and Company
Sponsored & Organized by the GCI Pharmaceutical Roundtable

- 1:30** 180 Green oxidations in organic synthesis: Learning from nature? **Andrew S. Wells**, Neil Adlington and Tove Åqvist
- 2:10** 181 Environmental considerations in pharmaceutical process development. **Douglas Kjell**
- 2:50** 182 Chemical process research and development for atorvastatin lactone. **Jade D. Nelson**

4:00 PM – 5:40 PM

South American Room B

Forum: Research Needs to Drive Innovation

Moderator: Peter J. Dunn, Pfizer, Inc.

Sponsored & Organized by the GCI Pharmaceutical Roundtable

Session Overview: The results of two surveys on green chemistry research challenges in the pharmaceutical industry will be presented. These surveys will establish a foundation for a broader discussion on green chemistry and engineering research needs for industrial application

- 4:00** 183 Plenary: Analysis of the reactions used for the preparation of drug candidate molecules. John S. Carey¹, David Laffan², Colin Thomson³, and **Michael T. Williams⁴**, (1) GlaxoSmithKline Pharmaceuticals, (2) AstraZeneca PR&D, (3) AstraZeneca R&D, (4) Pfizer, Inc.
- 4:40** 184 Key green chemistry research areas: A perspective from pharmaceutical manufacturers. **Peter J. Dunn**, GCI Pharmaceutical Roundtable
- 4:50** Discussion

5:40 PM – 6:00 PM

Break

Technical Program, *Continued*

6:00 PM – 7:00 PM

Congressional Room

Reception

7:00 PM

Presidential Ballroom



Banquet

Guest speaker: **Henry Red Cloud**
Descendant, Chief Red Cloud
President, Lakota Solar Enterprises

Thursday Morning

7:00 AM – 5:00 PM

Upper Lobby

Registration

7:00 AM – 8:00 AM

Upper Lobby

Continental Breakfast

8:00 AM – 9:00 AM

Presidential Ballroom



Keynote Address: Renewable Energy: Achieving the Goal of 30% Transportation Fuels from Biomass by 2030

Dan E. Arvizu, Ph.D.
Director,
National Renewable Energy Laboratory (NREL)

9:00 AM – 9:30 AM

Upper Lobby

Tea and Coffee Break

Technical Sessions

ENERGY

9:30 AM – 12:10 PM

Federal Room A

Energy Efficient Technologies I

Session Chair: Ray Stolts, National Renewable Energy Laboratory

- 9:30** 185 Plenary: Enhancing the Soy Biorefinery. **George A. Kraus**, Iowa State University
- 10:10** 186 Light to electrical energy conversion with thin film goethite (α -FeOOH) nanocrystals. **James Gardner** and Gerald Meyer
- 10:30** 187 PVC hydrocracking with recovering of a large amount of H_2 : Characterization of the catalysts and the products after each step of the process. **Thierry Giornelli**, Franck Dumeignil and Atsushi Ishihara

10:50 Break

11:10 188 Energy from waste in Kenya: Waste and energy demand inventories. **Joseph Keriko**

11:30 233 Novel lignocellulose fractionation by cellulose- and organic solvents. **Y.-H. Percival Zhang**

AGRICULTURE & FOODS

9:30 AM – 12:10 PM

Senate Room

Agriculture I

Session Chair: Larry Koskan, Global Green Products

- 9:30** 189 Plenary: Efficient Agriculture for the Environment. **Dean Kleckner**, Truth About Trade and Technology
- 10:10** 190 Green composites using poly(lactic acid) and agricultural co-products. **Victoria Finkenstadt**, LinShu Liu, C.K. Liu, Steven C. Cermak, Roque Evangelista, Milagros Hojilla-Evangelista and J.L. Willett
- 10:30** 191 Pesticide environmental stewardship program. **John Steiner**
- 10:50** Break
- 11:10** 192 Nitamin steady delivery fertilizers for improved nitrogen efficiency in crops. **John S. Kruse**, Stacey L. Wertz, James M. Wargo and Kurt D. Gabrielson,
- 11:30** 193 Anaerobic digested slurry: An input for sustainable agriculture. **Neena V. Arora**

TOXICS & MATERIALS

9:30 AM – 12:10 PM

Federal Room B

Alternative Synthesis II

Session Chair: Ferdinando Bruno, U.S. Army RDECOM Natick Soldier Center

Sponsored by the GCI Pharmaceutical Roundtable

- 9:30** 194 Plenary: Towards "green" atom transfer radical polymerization (ATRP): Strategies to significantly reduce the amount of copper-based catalyst. **Nicolay V. Tsarevsky**, Krzysztof Matyjaszewski, Ke Min and Wojciech Jakubowski, Carnegie Mellon University
- 10:10** 195 Oxidation of benzyl alcohol to benzoic acid with H_2O_2 catalyzed by dectungstates. **Huaming Li**, Wenshuai Zhu, Huoming Shu, Meiling He, Zhijun Luo and Junxinag Guo
- 10:30** 196 Bromine-free TEMPO-based catalyst system for the oxidation of alcohols. **Robert L. Augustine**, Setrak K. Tanielyan, Kenneth Furlong and Handley Jackson
- 10:50** Break

- 11:10** 197 Towards a more environmentally benign synthesis of a doped perovskite, barium titanate. **Anne E. Marteel-Parrish**, Danielle Harlan and Jonathan Martin
- 11:30** 198 Simplified green chemistry approaches to organic synthesis in solid media: Activated fly ash, an industrial waste (pollutant) as an efficient and novel catalyst for some selected organic reactions in 'dry media'. **Mannathusamy Gopalakrishnan**, Purusothaman Sureshkumar, Jayaraman Thanusu, Vijayakumar Kanagarajan and Ramalingam Govindaraju
- 11:50** 199 DNA photolyase for the enzymatic crosslink reversal of bioinspired thymine containing photopolymers. **Justin R. Whitfield**, Laura R. Ingalls and John C. Warner

9:30 AM – 12:10 PM

South American Room B

Green Nanotechnology

Session Chair: Nhan Nguyen, U.S. Environmental Protection Agency

- 9:30** 200 Plenary: Green nanoscience. **James E. Hutchison**, University of Oregon
- 10:10** 201 Production of polymer nanocomposites using renewable polymers with solid-state shear pulverization. **Amanda Walker** and John M. Torkelson
- 10:30** 202 Benign process for silver nanoparticles' synthesis and processing in neat carbon dioxide solvent using fluorine-free compounds. **Madhu Anand**, Philip W. Bell and Christopher B. Roberts
- 10:50** Break
- 11:10** 203 Development of supported nanoparticulate metal complexes using compressed carbon dioxide. **Chad A. Johnson**, Sarika Sharma, Andrew S. Borovik and Bala Subramaniam
- 11:30** 204 Synthesis and extraction of β -D glucose stabilized Au nanoparticles processed into low defect, wide area thin films and ordered arrays using CO₂-expanded liquids. **Juncheng Liu Sr.**, Madhu Anand and Christopher B. Roberts
- 11:50** 205 Photocatalytic activity of TiO₂ foam and TiO₂/RuO₂/SiO₂ nanoparticles for water purification. **Alex Omo Ibhadon**, Gilian Greenway and Yue Yue

GENERAL GREEN CHEMISTRY & GREEN ENGINEERING SYMPOSIA

9:30 AM – 12:10 PM

New York Room

Industrial Applications II

Session Chair: Terry Collins, Carnegie Mellon University

- 9:30** 206 Closing the loop with "Benign by Design" bio-based fabrics and backings. **Bill Foley**

- 9:50** 207 Catalytic hydrogenation of 2,5-piperazinedione to piperazine. **Andrea S. Molengraft**, James E. Jackson and Dennis J. Miller
- 10:10** 208 Development of Nike brand footwear outsole rubber as environmentally preferred material. **Andy F. Chen**, John Yu, Marcos Predovic, Tom Wilson, Kim Ames, Juliet Bautista and Jeff Bailey-Darland
- 10:30** 209 Non-chemical microbiological control for industrial cooling water systems. **Joanne Kuchinski**, Andrew Ledlie and Winston Go
- 10:50** Break
- 11:10** 210 Degradation of estradiol and ethinylestradiol with an Fe-TAML[®] oxidant activator and hydrogen peroxide. **Nancy W. Shappell**, Kyoung Ro, Melanie Vrabel, Peter Madsen, Colin Horowitz, Patrick G. Hunt and Terrence J. Collins
- 11:30** 211 New approaches to sustainability: The power of abduction. **Judy K. Kosovich**, James S. Turner and Emanuel Dash
- 11:50** 212 Engineering analysis in environmentally benign microwave-assisted chemo-enzymatic epoxidation of styrene over immobilized lipase. **Ganapati D. Yadav** and Indrakant V. Borkar

9:30 AM – 12:10 PM

Massachusetts Room

Panel: Federal Programs for R&D That Can Enhance Green Chemistry & Engineering

Session Chair: Bob Marianelli, Consultant

Representatives from federal programs for R&D will discuss those programs and then respond to questions from conference participants.

- 9:30** Department of the Army
- 9:45** NSF Directorate for Mathematical & Physical Sciences, Division of Chemistry
- 10:00** EPA Office of Science Coordination and Policy
- 10:15** DOE Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division
- 10:30** NIST, Chemical Science and Technology Laboratory
- 10:45** Break
- 11:10** White House Office of Science and Technology Policy, Division of Science
- 11:25** U.S. House Committee on Science
- 11:40** Discussion

12:10 PM – 1:30 PM

Lunch Break (on your own)

Technical Program, *Continued*

Thursday Afternoon

ENERGY

1:30 PM – 3:30 PM

Federal Room A

Energy Efficient Technologies II

Session Chair: Darlene Schuster, American Institute of Chemical Engineers

- 1:30 213 Plenary: Toward efficient catalytic routes to hydrogen from bioresources. **Claus Hviid Christensen**, Technical University of Denmark
- 2:10 214 Novel nanocomposite oxygen carriers for chemical looping combustion. Tengfei Liu, Thomas Simonyi, Tom Sanders, Ranjani Siriwardane and **Goetz Vesper**
- 2:30 215 Multi-scale modeling of H₂ storage in clathrates. **Prasad Yedlapalli**, Sangyong Lee and Jae W. Lee
- 2:50 216 Coal refining: A near-term green energy process. **E. Gerald Meyer**

AGRICULTURE & FOODS

1:30 PM – 3:30 PM

Senate Room

Agriculture II

Session Chair: Larry Koskan, Global Green Products

- 1:30 218 Plenary: Presporulating entomopathogenic fungi attract, infect and control termites and ants. **Paul E. Stamets**, Fungi Perfecti
- 2:10 219 New asymmetric hydroxylation technology for the commercial manufacture of indoxacarb. **Albert L. Casalnuovo**
- 2:30 220 ARS biopolymers research — yesterday, today, and tomorrow. **Robert L. Fireovid**
- 2:50 221 Development of domestic crops to produce industrially useful products. **Maureen C. Whalen**, Colleen McMahan, Grace Chen, Jiann-Tsyh Lin, and Thomas McKeon

TOXICS & MATERIALS

1:30 PM – 3:30 PM

Federal Room B

Alternative Synthesis III

Session Chair: Ferdinando Bruno, U.S. Army RDECOM Natick Soldier Center

Sponsored by the GCI Pharmaceutical Roundtable

- 1:30 222 Green isoparaffin alkylation process. **James P. Nehlsen**, Mitrajit Mukherjee, G. Dan Suciu, Sankaran Sundaresan, Richard V Porcelli and John Dixon
- 1:50 223 Improved regioselectivity in the nitration of toluene: The key to cleaner manufacture of 2,4,6-trinitrotoluene (TNT). Ross W Millar, **Anthony W. Arber**, Javid Hamid and Robert M. Endsor

- 2:10 224 Green synthesis of adipic acid with hydrogen peroxide catalyzed by oxo-peroxo tungsten complexes. **Huaming Li**, Wenshua Zhu, Xiaoying He, Jianming Pan, Huoming Shuang and Junxiang Guo
- 2:30 225 Gas-phase catalytic oxidations using titania nanocatalysts. **Alex Ibhaddon**, Polycarpos Falaras, Dimitris Tsoukleris and Ioannis Arabatzis
- 2:50 226 Core-bound polymer nano micelles based on hydrogen bonding and photocrosslinking of thymine. **Kei Saito**, Laura R. Ingalls and John C. Warner
- 3:10 227 Entropic control in meta-stable noncovalent derivatives. **Benjamin Bowers**, Ankan Dahl, Roger Boggs and John C. Warner

1:30 PM – 3:30 PM

South American Room B

Designing Safer Chemical & Toxicity Reduction II

Session Chair: Pamela Civie, Toxics Use Reduction Institute

- 1:30 228 Plenary: Tinkering with toxicity: Avoiding environmental problems by understanding toxicant metabolism. **David Epel**, Hopkins Marine Station of Stanford University
- 2:10 229 Alternative synthesis for surfactants: Thermally cleavable surfactants. **Reagan Charney**, Colin Thomas, Ross Weikel, Pamela Pollet, Charles Eckert, Charles Liotta and Philip Jessop
- 2:30 230 Environmentally-benign, effective and economical totally-organic wood preservative systems. **Tor P. Schultz** and Darrel D. Nicholas
- 2:50 231 Use of Postsaver to minimize forestry land depletion and mitigate pesticide chemicals migration into soil. **C.R. McIntyre**, Mike H. Freeman and John Makuvek
- 3:10 232 Efficient molecular simulations for environmentally benign products and processes. **Saadet Ulas** and Urmila Diwekar

3:30 PM – 4:00 PM

Tea and Coffee Break

Upper Lobby

4:00 PM – 5:00 PM

Senate Room

Closing Session: Designing for a Sustainable Future: What Role Will Green Chemistry Play?

Session Chair: Paul Anastas, ACS Green Chemistry Institute



Friday, 30 June 2006

Train the Trainers Workshop

Friday Morning

8:00 AM – 12:00 PM

South American Room B

Workshop

7:00 AM – 8:00 AM

Statler Rooms A & B

Breakfast (for participants only)

8:00 AM – 9:00 AM

Introduction, Background & Philosophy

Paul Anastas

9:00 AM – 10:00 AM

Tools and Discussion for Training Faculty

Jim Hutchinson

10:00 AM – 10:30 AM

Break

10:30 AM – 11:30 AM

Teaching and Training Young Students & the Public

John Warner

11:30 AM – 12:00 PM

Group Discussion

12:00 PM – 1:00 PM

Statler Rooms A & B

Lunch Break (for participants only)

Friday Afternoon

1:00 PM – 6:30 PM

South American Room B

1:00 PM – 2:00 PM

Tools for Teaching & Training Industry

Eric Beckman

2:00 PM – 2:30 PM

Group Discussion

2:30 PM – 3:00 PM

Break

3:00 PM – 4:00 PM

Tools for Teaching and Training Government & Funders

Paul Anastas

4:00 PM – 4:30 PM

Tools & Methods for Communicating with the Public

Amy Kostant

4:30 PM – 5:00 PM

Group Discussion

5:00 PM – 5:30 PM

Sample Presentation 1

5:30 PM – 6:00 PM

Q & A Discussion

6:00 PM – 6:30 PM

Closing Session



Abstracts

Green Chemistry Awards I

1. Bio-based propylene glycol and monomers from natural glycerin.

Galen J. Suppes, University of Missouri-Columbia

The U.S. biodiesel industry is expected to introduce one billion pounds of additional glycerin into a market that is currently only 600 million pounds. The economics of biodiesel depend strongly on using its glycerin byproduct: a high-value use for glycerin could reduce the cost of biodiesel by as much as 40¢/lb. Professor Suppes and his team have developed an improved process for converting natural glycerin to propylene glycol. Approximately 2.4 billion lb/yr of propylene glycol are currently made each year, almost exclusively from petroleum-based propylene oxide.

Professor Suppes's process can use the crude glycerin produced by biodiesel facilities as a coproduct. His patent-pending process uses a copper chromite catalyst and reactive distillation to produce either acetol or propylene glycol in high yields. Simply put, his process (1) uses a current waste steam; (2) replaces a popular petroleum-based chemical with a bio-based one; (3) costs less; (4) has actual yields that approach 100% carbon economy; (5) produces near-zero greenhouse gases; and (6) paves the way for displacing ethylene glycol, one of the most widely distributed toxic chemicals in our society.

Pilot plant tests will be completed by the end of January 2006; the first commercial facility (50 million lb/yr) is expected to begin production by June of 2006. The advantages range from assisting the growth of the burgeoning biodiesel industry to removing toxic ethylene glycol from our homes and streets.

2. Environmentally safe washout solvents and cold reclaim systems™ in the flexographic printing industry.

Connie M. Hendrickson¹ and David C. Bradford², (1)Arkon Consultants, Irving, TX, (2) Nupro Technologies, Winston-Salem, NC

Flexographic printing plates are developed by immersing a light-exposed polymer plate in a solvent that can remove the unpolymerized material while leaving the polymerized material intact. The developing solvent, referred to as the washout solvent, is typically a mixture of chloro- or aromatic hydrocarbons. Xylene is historically the most commonly used solvent base. Most traditional washout solvents are considered hazardous air pollutants subject to stringent reporting requirements and give rise to worker safety issues and recycling and disposal problems. The methyl esters, terpene derivatives and highly substituted cyclics described herein offer significant improvement over traditional solvents, including higher flash points and lower toxicities, thus minimizing workplace hazards, worker safety issues and regulatory reporting. All are designed to be used with the centrifugation and filtration recovery system for recycling of dirty (used) washout solvent. In contrast to traditional vacuum distillation, this combination of filtration and centrifugation yields lowered exposures, decreased maintenance and reduced waste. The methyl esters and terpene derivatives are biodegradable and can be manufactured from vegetable sources, making them renewable resources.

Renewable feedstocks

3. Aqueous phase catalytic hydrogenation and C-H activation of organic acids using Ru/C

Jennifer E. Farrugia, James E. Jackson and Dennis J. Miller, Michigan State University, East Lansing, MI

Many industrially important chemicals are currently produced using petroleum and natural gas as feedstocks. These fossil fuel resources are finite and nonrenewable. Organic acids compose a major class of renewable-resource feedstock chemicals. Aqueous-phase catalytic hydrogenation of organic carboxylic acids as a route to alcohols has been investigated as a possible pathway to novel, high-valued products. The Jackson/Miller group has probed the Ru/C-catalyzed aqueous-phase hydrogenation pathway of several organic acids; namely, lactic acid (hydrogenation to propylene glycol) and amino acids (stereoretentive amino alcohol synthesis) as well as sugar alcohol processing to high-valued polyols. The effects of vicinal substituents on organic acids' reactivity and selectivity toward hydrogenation over 5% Ru/C in water were studied by comparing reduction rates over a wide range of carboxylic acids with electron-withdrawing, hydrogen-bonding or sterically demanding vicinal substituents. Protonated alanine and lactic acid undergo aqueous-phase hydrogenation over a Ru/C catalyst ca. 10 and 2-3 times as fast as their unsubstituted analogue, propanoic acid. Reaction rate data at three different temperatures for the methylated glycine series indicate that the reactivity decreases ca. 1/3 with each additional methyl added. To evaluate the extent of C-H activation versus hydrogenation in the methylated glycine series, ¹H NMR was used to monitor H/D exchange at the *alpha* carbon. At 100°C, the rate of H/D exchange is ca. 15x that of the hydrogenation of protonated glycine. The results suggest organic acid hydrogenation with 5% Ru/C is a relatively "clean" reaction with carbon balances greater than 90%.

4. Ethanol as a renewable feedstock for commodity chemicals: Acetic acid as an example

Betina Jørgensen, Jeppe Rass-Hansen, Anders Riisager, Kresten Egeblad and Claus Hviid Christensen, Technical University of Denmark, Kgs. Lyngby, Denmark

Gold has always been a fascinating element among chemists and, recently, it has been found to be catalytically active in several reactions. To date gold catalysis has mainly been focusing on CO oxidation¹ but, lately, several reports concerned with selective oxidation of alcohols have also emerged². Presently, acetic acid is mainly produced from petrochemical sources, but due to the diminishing amount of fossil fuels it is important to investigate new routes. One possibility is to use renewable feedstocks such as bioethanol. The production of bioethanol is growing and it could be economically feasible to convert the ethanol into acetic acid. Today, bioethanol is mainly used as a fuel or fuel additive, but it has also attracted interest as a source for hydrogen³. However, it appears much more feasible to use ethanol as a feedstock for chemical production from both an economical and green perspective. In addition, the demand for acetic acid is increasing, which further indicates that it is time to find alternative routes to the fossil fuel-based methods. In our studies we have investigated the aqueous-phase oxidation of ethanol to acetic acid by air. The catalytic experiments have been conducted in stirred, pressurized autoclaves, where both temperature and pressure dependences have been examined. The results showed ethanol conversions above 90% and yields of acetic acid around 80%. Importantly, the activities of the catalysts seem apparently independent of pH, in contrast to present catalysts based on Pt and Pd.

5. Continuous esterification of bio-based organic acids: Formation of triethyl citrate

Navinchandra Asthana, Aspi Kolah, Dennis Miller and Carl Lira, Michigan State University, East Lansing, MI

Organic acids and alcohols, produced by fermentation of carbohydrate feedstocks, constitute an important class of biorenewable platform chemicals that can be further converted to useful products. Tri-ethyl citrate is currently gaining a lot of attention because it is a non-toxic, biocompatible plasticizer that can be used in place of petroleum-based phthalate compounds. The potential application of tri-ethyl citrate is currently limited by the lack of large-scale, efficient and economic production facilities. Though there is a dearth of published literature on synthesis of tri-ethyl citrate from citric acid and ethanol, relatively little information on the kinetics and thermodynamics of its formation is available. We present here a continuous process for the formation of triethyl citrate using cationic exchange resins as catalysts in a reactive distillation column and batch reactor. Vapor-liquid equilibrium studies for important binary mixtures have also been conducted. In a standard batch reaction, equilibrium was achieved after 16 hours; 99% of the citric acid was converted to a mixture of monoethyl, diethyl and triethyl citrate, with a batch triethyl citrate selectivity of 64%. Kinetic parameters that include both ion-exchanged catalyzed reactions and self-catalyzed reactions were generated by non-linear regression of batch experimental data in MATLAB. Chemical and physical parameters thus obtained were inserted into AspenPlus process simulation software to model citric acid esterification in our semi-pilot reactive distillation column (5 cm diameter x 4 m height) and various column performance parameters (liquid holdup, catalyst efficiency) were determined by comparing pilot-scale column results with model predictions.

6. Alternative feedstocks for the chemical industry

Joanna McFarlane and Sharon M. Robinson, Oak Ridge National Laboratory, Oak Ridge, TN

The current high prices for petroleum have spurred the chemical industry to take a long-term look at alternative feedstocks in the production of commodity chemicals. Oak Ridge National Laboratory and chemical industry representatives undertook a review of the use of non-petroleum-based feedstocks in the manufacture of the largest volume organic chemicals. The team identified both the near term opportunities for feed substitution into existing chemical plants and longer term application of new technologies, new products and new equipment. The feedstocks that were considered in this analysis included those derived through unconventional processing technologies, such as coal gasification and coal liquefaction, unconventional reserves such as stranded natural gas and heavy oil from tar sands or oil shale and novel resources such as biomass. The feedstocks were evaluated as to readiness for implementation and feasibility for production of the highest volume commodity chemicals produced in the U.S. Technical barriers for implementation were identified and suggestions have been made on a path forward both in terms of research requirements and policy decisions.

Abstracts, Continued

Alternative Synthesis I

7. Base and acidic catalysis in dimethyl carbonate chemistry

Pietro Tundo, Ca' Foscari University

Dimethylcarbonate (DMC) is a versatile compound which represents an attractive eco-friendly alternative to both methyl halides (or dimethyl sulfate) and phosgene for methylation and carbonylation processes, respectively. In fact, the reactivity of DMC is tunable: at $T \leq 90^\circ\text{C}$, methoxycarbonylations take place, while at higher reaction temperatures, methylation reactions are observed with a variety of nucleophiles. In the particular case of substrates susceptible to multiple alkylations (e.g. CH_2 -active compounds and primary amines), DMC allows unprecedented selectivity towards mono-*C*- and mono-*N*-methylation reactions.

The high selectivity in methylation reactions is due to the ambident electrophilic character of DMC which reacts on its hard centre (the carbonyl group) with harder nucleophiles and on its soft one (the methyl group) with softer nucleophiles, according to the Hard-Soft Acid and Base (HSAB) theory. Recently achieved selectivity with nucleophiles on N, O, S and C will be reported.

Nowadays produced by a clean process, DMC possesses properties of nontoxicity and biodegradability which makes it a true *green reagent* to use in syntheses that prevent pollution at the source. Moreover, DMC-mediated methylations are catalytic reactions which use safe solids (alkaline carbonates or zeolites), thereby avoiding the formation of undesirable inorganic salts as by-products.

The reactivity of other carbonates is reported as well: higher homologues of DMC (*i.e.* diethyl- and dibenzyl-carbonate), are excellent mono-*C*- and mono-*N*-alkylating agents, while asymmetrical methyl alkyl carbonates (ROCO_2Me with $R \geq \text{C}_3$) undergo methylation processes with a chemoselectivity up to 99%.

8. Biocatalysis for material science

Ferdinando F. Bruno¹, Subhalakshmi Nagarajan², Ramaswamy Nagarajan², Donna McIntosh², Susan J. Brauhu², Jayant Kumar² and Lynne A. Samuelson¹, (1)U.S. Army RDECOM Natick Soldier Center, Natick, MA, (2)University of Massachusetts Lowell, Lowell, MA

A novel biomimetic route for the synthesis of conducting homopolymers and copolymers from aniline, phenol, pyrrole and 3,4-ethylenedioxythiophene in the presence of a polyelectrolyte, such as polystyrene sulfonate (SPS) is presented. A poly(ethylene glycol)-modified hematin (PEG-Hematin) and the enzyme horseradish peroxidase (HRP) were used to catalyze the copolymerization of different monomers. UV-vis, FTIR, XPS, TGA and electrical conductivity studies for all complexes indicated the presence of a stable and electrically conductive form of these polymers. Furthermore, the presence of a polyelectrolyte, such as SPS, in this complex provides an unique combination of properties such as processability and water-solubility. Additionally catechins, the active compounds found in green tea, were polymerized and found to show very interesting anti-carcinogenic properties. Here we report an unique enzymatic approach for the synthesis of water-soluble poly(catechins) with enhanced stability and anti-cancer activity. Various stereoisomers of catechin [(+), (-), (±)] and (-)-epicatechin have been biocatalytically polymerized using HRP in ethanol/buffer mixtures. This one-pot biocatalytic polymerization is carried out in ambient conditions yielding water-soluble poly(catechins). These synthesized poly(catechins) were tested *in vitro* for the anti-tumorigenic activity on commercially available normal and cancerous human breast cell lines. The poly(catechins) exhibit greater growth inhibitory effects than the monomers and have higher specificity towards highly metastatic cells as opposed to normal cells thus achieving a high therapeutic ratio. The synthesis, characterization and the growth inhibitory effects of these novel water-soluble poly(catechins) will also be presented.

9. Synthesis of cyclic carbonates from fatty materials using supercritical carbon dioxide

Kenneth M. Doll and Sevim Erhan, NCAUR-USDA, Peoria, IL

We have demonstrated the synthesis of the cyclic carbonates of from the oleochemical-based, methyl oleate, methyl linoleate and methyl linolenate using a simple two-step synthesis. First, we perform an environmentally friendly epoxidation reaction using hydrogen peroxide and formic acid. Next, the epoxidized materials; epoxidized methyl oleate (EMO), epoxidized methyl linoleate (EMLO) and epoxidized methyl linolenate (EMLEN), are reacted with supercritical carbon dioxide directly using a small amount of ring opening catalyst. We have also demonstrated similar carbonate syntheses starting from commercially available epoxidized soybean oil (ESO) and epoxidized 2-ethyl-hexyl soyate (VF). The use of supercritical carbon dioxide allows the synthesis to be performed at a significantly reduced reaction time, compared to literature syntheses of the carbonated soybean oil. Our synthesis also avoids the use of environmentally unfriendly phosgene and, because the carbon dioxide is used directly, our reaction is highly atom efficient. The compounds that we have synthesized may be useful as lubrication fluids and are valuable building blocks in the synthesis of isocyanate-free polyurethanes.

10. Green chemoselective and highly stereodivergent solutions to affect the dihydroxylation of allylic amines

Marcus J. C. Long and S.G. Davies, Oxford University, Oxford, United Kingdom

Both allylic amines and their stoichiometric salts undergo chemoselective *N*-oxidation by most oxidants, but it was found that treating an allylic amine with five equivalents trichloroacetic acid [(TCA)OH] and 1.1 equivalents *m*CPBA gave in one clean, mechanistically-understood step, without purification, for allylic tertiary-amines, amino *anti*-diols, and for allylic secondary-amines, hydroxy oxazolidin-2-ones, which were converted to the *syn*-2,3-diol or 1,3-diamino alcohol epimers *via* activation of the free hydroxy group, then $\text{S}_{\text{N}}2$ displacement. Dihydroxylation of 1 gave 2 as a single diastereoisomer (Figure 2). Changing the protic protecting agent, coupled with further manipulation gave all stereoisomers 3-5. Generality was shown by application of this methodology to the 5-membered ring analogue 6 to give 7-10. Novel manipulation of *syn*-epoxides 11 and 12 enabled synthesis of *anti*-epoxides 13 and 14 and allylic alcohols 15 and 16, allowing the synthesis of conduramine analogue 17 in 60% overall yield. 7 and 8-membered analogues furnished the *anti*-directed oxidation products in >90% d.e. and >80% yield.

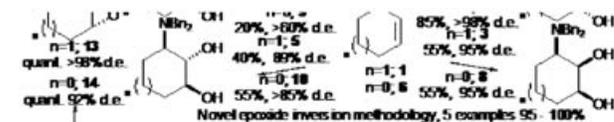


Figure 2. Stereoselective and stereodivergent oxidations.

Further investigations centered upon stereodivergent manipulations of allylic amines yielding: differentially-protected cyclic 1,3-diamino-2-alcohols (2 diastereoisomers >90% d.e., >50% overall yield); medically important cyclic and bicyclic *N*-phenyl morpholinones (2 diastereoisomers >90% d.e., >40% overall yield); acyclic amino epoxides, formed by epoxidation under A(1,3) strain control (5 examples >65% yield, >90% d.e.); different stereoisomers of enantiopure pyrrolidene diols, including a total synthesis of anisomycin and analogues with α -Rhamnosidase activity; and the synthesis of β and γ -amino acid derivatives.

Benign Solvents I

11. Switchable solvents and surfactants

Philip G. Jessop¹, Charles A. Eckert² and Charles L. Liotta³,⁽¹⁾Chemistry Department, Queen's University, Kingston, Canada, ⁽²⁾School of Chemical & Biomolecular Engineering, Institute of Technology, Specialty Separations Center, Georgia Institute of Technology, Atlanta, ⁽³⁾School of Chemistry & Biochemistry, Specialty Separations Center, Georgia Institute of Technology, Atlanta

Imagine a solvent that would change itself into a different solvent, upon command!

A switchable solvent is a solvent that can be reversibly converted from one form to another, where the two forms differ in one or more physical properties. For example, the solvent might be fairly polar in one form but much less polar in the other. Solvent switchability is desirable for processes in which consecutive operations (a reaction followed by a separation, reaction followed by another reaction, or an extraction followed by a precipitation) require a change in solvent; the solvent that allows the first step to perform optimally is not the same as the solvent that allows the second step to perform optimally. For example, if a polar solvent is needed for a particular extraction, but a much less polar solvent would make it much easier to subsequently separate the product from the solvent, then the ability to switch the solvent from polar to relatively nonpolar would be advantageous.

We have identified several strategies for creating switchable solvents. These strategies will be presented, with discussion of the relative advantages and disadvantages of each. If time permits, the extension of the chemistry to the development of switchable surfactants will be described.

12. Atom transfer radical polymerization (ATRP) in aqueous dispersed media

Ke Min and Krzysztof Matyjaszewski, Carnegie Mellon University, Pittsburgh, PA

In this study, atom transfer radical polymerization (ATRP) has been extended to economically viable and environmentally benign aqueous dispersed media, which have found extensive application in industry and are applicable to a diverse choice of hydrophobic monomers. In order to conduct ATRP in aqueous dispersed media the crucial issue was to carefully select an appropriate initiation system. For instance, Simultaneous Reverse and Normal Initiation (SR&NI) and Activators Generated by Electron Transfer (AGET) ATRP are appropriate for aqueous ATRP in dispersed media, since the catalyst precursor is added to the reaction in its higher stable oxidation state. Especially, AGET ATRP can be carried out in the presence of a limited amount of air, thereby reducing inadvertent volatile organic compound emissions. Furthermore, recently an important extension of the AGET technique, Activators ReGenerated by Electron Transfer (ARGET), has been employed in ATRP and the catalyst concentration has been dramatically decreased to only a few parts per million by using environmentally benign reducing agents. Many SR&NI and AGET mini-emulsion ATRPs have been successfully carried out forming homopolymers, block copolymers, gradient copolymers, star copolymers, polymer brushes and polymer composites. An extension of AGET ATRP allowed the first successful microemulsion ATRP to be conducted, resulting in production of a translucent microlatex with narrow particle size distribution. This led to development of the first successful *ab initio* emulsion ATRP performed using a "two-stage" emulsion approach, where a microemulsion ATRP was initiated before addition of the second monomer.

13. Biocatalysis of uranium in presence of ionic liquids

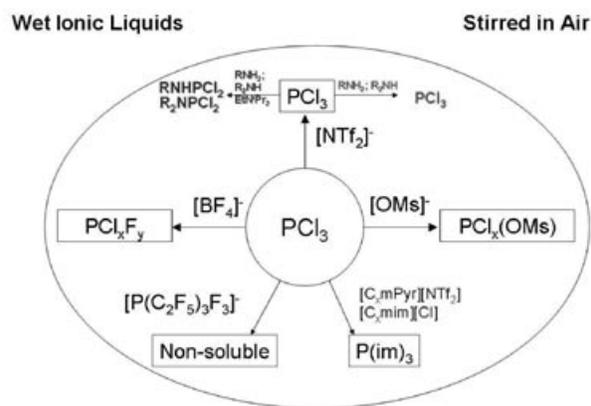
Sanjay V. Malhotra¹, Chengdong Zhang¹ and A.J. Francis²,
⁽¹⁾New Jersey Institute of Technology, Newark, NJ,
⁽²⁾Brookhaven National Laboratory, Upton, NY

Ionic liquids (ILs) as a replacement for organic solvents in liquid-liquid extraction of heavy metal ions are receiving much attention. Although the extractions of metals by hydrophobic ILs from aqueous solution have been reported, little is known of the effects of hydrophilic ILs which are widely used in biocatalysis. We investigated the interactions of uranium with hydrophilic ILs BMIMPF₆, EtPyBF₄ and EtPyCF₃COO⁻. Complexation of ILs with uranium was determined by change in pH, potentiometric titration and UV-vis absorbance. LC-MS and extended x-ray absorption spectroscopic (EXAFS) analyses showed the formation of a monodentate complex of U with BMIMPF₆, EtPyBF₄ and a bidentate complex with EtPyCF₃COO⁻. Bioreduction of U(VI) to U(IV) by an anaerobic bacterium *Clostridium* sp. was affected by the ILs. The rate of reduction of U(VI) to U(IV) in the presence of BMIMPF₆ and EtPyBF₄ was similar to the reduction of uranyl nitrate. However, there were differences in the rate of precipitation of reduced uranium from solution; without ILs > BMIMPF₆ > EtPyBF₄. The precipitation of bioreduced U(IV) from solution appears to be related to the nature of the complex formation with the IL. The U(VI) complexed with EtPyCF₃COO⁻ was not reduced by the bacterium. These results suggest the potential application of ILs in conjunction with microbiological action to separate and recover redox sensitive actinides from solution.

14. Controlling the reactivity of chlorophosphines with ionic liquids

Marie Migaud, Queen's University Belfast, Belfast, United Kingdom

We have recently established that triflamide-based ionic liquids offered unprecedented properties with regard to modulating the stability and reactivity of chlorophosphines (PCl₃ and POCl₃) in air at room temperature in "wet" ILs. Here, we wish to report on our observations and present a rationale which could account for such unanticipated phenomena.



methylimidazolium (C_mmim)⁺ and methylpyrrolidinium (C_mmPyr)⁺ based ILs

Abstracts, *Continued*

Stocking the Green Chemistry Toolbox

Sponsored & Organized by the GCI Pharmaceutical Roundtable

15. Sustainability Indexes: Holistic approach to measure corporate economic performance

Rodrigo Amandi, SAM Sustainable Asset Management Group, Zurich, Switzerland

Launched in 1999, the Dow Jones Sustainability Indexes are the first global indexes tracking the financial performance of the leading sustainability-driven companies worldwide. Based on the cooperation of Dow Jones Indexes, STOXX Limited and the Sustainable Asset Management Group (SAM), they provide asset managers with reliable and objective benchmarks to manage sustainability portfolios. The indexes are based on SAM's corporate sustainability assessment, which identifies global sustainability leaders on the basis of economic, environmental and social criteria. Increasingly investors are diversifying their portfolios by investing in companies that set industry-wide best practices with regard to sustainability. Two factors drive this development; first, the concept of corporate sustainability is attractive to investors because it aims to increase long-term shareholder value. Since corporate sustainability performance can now be financially quantified, they now have an "investable" corporate sustainability concept. Second, sustainability leaders are increasingly expected to show superior performance and favorable risk/return profiles. A growing number of investors is convinced that sustainability is a catalyst for enlightened and disciplined management and, thus, a crucial success factor. The identification of sustainability leaders for the Dow Jones Sustainability Indexes is based on the Corporate Sustainability Assessment of SAM Research. Thus, a defined set of criteria and weightings is used to assess the opportunities and risks deriving from economic, environmental and social developments for the eligible companies. A major source of information is the SAM questionnaire which is completed by companies participating in the annual review. Further sources include company and third-party documents as well as personal contacts between the analysts and companies. Based on SAM Research's corporate sustainability assessment, companies are ranked within their industry group and selected for the Dow Jones Sustainability Indexes, if they are among the sustainability leaders in their field.

16. Sustainability and life cycle principles in practice: Implementing FLASC™ (Fast Life cycle Assessment of Synthetic Chemistry) and early results

David J. C. Constable¹, Concepción Jiménez-González², and Richard K. Henderson³, (1)GlaxoSmithKline, Philadelphia, PA (2)GlaxoSmithKline, Research Triangle Park, NC (3)GlaxoSmithKline, Ware, Hertfordshire, England

One approach to assessing progress towards more sustainable practices in the pharmaceutical industry is to determine and benchmark the degree of "greenness" of synthetic chemical processes for manufacturing active pharmaceutical ingredients (APIs). Having a simple, easy to calculate metric is particularly important at an early stage in R&D development, when route and processes are being selected and detailed environmental data are not available. FLASC™ (Fast Life Cycle Assessment of Synthetic Chemistry) is a web-based tool and methodology developed by and for GlaxoSmithKline in order to respond to those needs. FLASC™ was developed from a detailed assessment of the

cradle-to-gate life cycle environmental impacts associated with the manufacture of materials used in a typical pharmaceutical process. FLASC™ provides a quick, streamlined assessment of life cycle impacts of synthetic routes on development, as well as benchmarking information and some guidance. This presentation will describe GlaxoSmithKline's tools and recent experiences in routinely assessing the streamlined life cycle impacts of its development routes.

17. Selection and reduction of organic solvents in the pharmaceutical industry

Erin Frey, C. Stewart Slater, Mariano J. Savelski and Robert P. Hesketh, Rowan University, Glassboro, NJ

The pharmaceutical industry is one of the largest users of organic solvents per amount of finished product. The average mass intensity in the pharmaceutical industry is also very high compared to other chemical processing industries. This is due to the need for high purity products, multiple synthesis steps and batch processing. Through an EPA funded grant, Rowan University, in collaboration with the pharmaceutical industry, has been working to develop methods to quantify and ultimately decrease the amount of solvents used in pharmaceutical manufacture. Through an unique academic-industrial partnership program, "engineering clinics", a student team has worked with Bristol-Myers Squibb to gain an insight into the issues related to pharmaceutical processing. A spreadsheet-based method, solvent selection table has been developed to show environmental impacts of solvents commonly used in the pharmaceutical industry based on 18 environmental parameters. The table also allows for a quick comparison of the "greenness" of two alternate processes using different solvents. Based on the mass of the solvents and the given environmental parameters, the table can quantify which solvent(s) and resulting process is more environmentally benign. In addition to solvent metrics, an examination of solvent processing was undertaken with the goal to recover or reduce the amount of solvents used. Pervaporation was studied as a replacement to extractive distillation for dehydration of azeotropic organic solvent/water process streams. Pervaporation has the potential to effectively dehydrate the stream without the addition of more solvents and at reduced energy costs.

18. UDCaT-5: Novel and efficient solid acid catalyst for green Claisen rearrangement of allyl phenyl ethers

Ganapati D. Yadav and Sharad V. Lande, University of Mumbai Institute of Chemical Technology, Mumbai, India

The Claisen rearrangement reaction has become one of the most powerful tools for carbon-carbon bond formation in organic synthesis. They have widespread synthetic application due to the simplicity of the protocol and the high degree of stereoselectivity and functional group reorganization. The Claisen rearrangement of allyl phenyl ethers provides a convenient access to o-allyl phenols, which are precursors to a variety of natural products including chromones and coumarones. Different solid acid catalysts such as heteropolyacids supported on clay, hexagonal mesoporous silica, sulfated zirconia and UDCaT-5 have been tested. Among these, UDCaT-5, a novel solid superacid, is found to be a superior catalyst. The kinetic interpretation has been made by studying the important process parameters using UDCaT-5 for the Claisen rearrangement of several compounds. A complete theoretical and experimental analysis is also presented. The reactions are 100% atom economical and conducted under mild conditions. The catalyst UDCaT-5 is reusable.

Green Chemistry Awards II

19. The asymmetric catalytic hydrogenation of unprotected enamines enables a highly efficient, green synthesis of sitagliptin, the active ingredient in Januvia™.

Merck & Co., Inc.

Sitagliptin, a chiral β -amino acid derivative, is the active ingredient in Januvia™, a new treatment for type II diabetes. Merck used a first-generation synthesis of sitagliptin to prepare over 100 kilograms for clinical trials. With modifications, this synthesis would have been a viable manufacturing process, but it required eight steps including a number of aqueous work-ups and was not atom-economical.

While developing a highly efficient second-generation synthesis for sitagliptin, Merck researchers discovered a completely unprecedented transformation: the asymmetric catalytic hydrogenation of unprotected enamines. In collaboration with Solvias, a company with expertise in this area, Merck scientists discovered that hydrogenation of unprotected enamines using rhodium salts of a ferrocenyl-based ligand as the catalyst gives β -amino acid derivatives of high optical purity and yield. This new method provides a general synthesis of β -amino acids, a class of molecules well known for interesting biological properties. Merck scientists and engineers applied this new method in a completely novel way, using it in the final synthetic step to maximize the efficiency of the route. The new synthesis has only three steps and increases the overall yield by nearly 50 percent.

This strategy is broadly applicable to other pharmaceutical syntheses; Merck has used it to make several exploratory drug candidates. Implementing the new route on a manufacturing scale has reduced the amount of waste by over 80 percent and completely eliminated aqueous waste streams. This second-generation synthesis will create 220 kilograms less waste for each kilogram of sitagliptin manufactured; over the lifetime of the drug, Merck expects to eliminate 150,000 metric tons or more of waste, including nearly 50,000 metric tons of aqueous waste. Merck filed for regulatory approval of Januvia™ in December 2005.

20. The new commercial “green-by-design” biocatalytic process for the key chiral intermediate for atorvastatin enabled by the directed evolution of three biocatalysts

John Grate, Codexis, Inc.

Codexis has developed a method to produce biocatalysts through “directed evolution” and applied that method to a major pharmaceutical ingredient. Codexis designed, enabled, and developed an innovative green process for commercial production of ethyl (*R*)-4-cyano-3-hydroxybutyrate (hydroxynitrile; HN), the key chiral intermediate in the synthesis of atorvastatin (Lipitor®). Previous commercial processes involved a resolution step with 50% maximum yield or syntheses from chiral precursors; they also required HBr to generate a bromohydrin for cyanation. All previous commercial HN processes ultimately substituted cyanide for halide under heated alkaline conditions, forming extensive byproducts. Purification required high-vacuum fractional distillation, which decreased the yield even further.

The nominated technology is an alternative process using readily available feedstocks and two particularly clean biocatalytic reactions under neutral conditions. Codexis developed each of three enzymes

using directed evolution technologies to provide the activity, selectivity, and stability required for a practical and economic process. In the first step, two enzymes catalyze an enantioselective reduction. In the second step, a third enzyme catalyzes the novel biocatalytic cyanation under neutral conditions. Compared to other biocatalysts, the evolved enzymes have improved the productivity of the first step (reduction) by approximately 100-fold and that of the second step (cyanation) by approximately 4000-fold. The evolved biocatalysts produce HN of such purity that fractional distillation of the product is no longer needed. Pfizer is now using the Codexis process to manufacture HN for atorvastatin calcium.

21. SC Johnson’s patented Greenlist™ process used to reformulate consumer products

David Long and John Weeks, S.C. Johnson & Son, Inc.

SC Johnson formulates and manufactures a wide variety of consumer products. To evaluate the environmental and health effects of their formula ingredients, they developed the Greenlist™ classification system. SC Johnson uses Greenlist™ to choose the most sustainable and effective ingredients. In recent years, SC Johnson has used Greenlist™ to reformulate multiple products to make them safer and more environmentally responsible.

Greenlist™ is based on four to seven specific criteria for chemicals within 17 functional categories that cover more than 90% of the raw materials SC Johnson currently uses. SC Johnson selected criteria to be meaningful and discriminating within each functional category. These criteria include biodegradability, aquatic toxicity, human toxicity, European Union Classification, source/supply, vapor pressure, octanol/water coefficient, and others, as appropriate. The Greenlist™ process assigns an environmental classification (EC) score to each raw material by averaging its scores for the criteria in its category. SC Johnson lowers the EC score for chemicals with other significant concerns including persistence, bioaccumulation, and toxicity (PBT); endocrine disruption; carcinogenicity; and reproductive toxicity. EC scores range from Best (3) to SC Johnson Restricted Use Material (0).

SC Johnson’s Greenlist™ EC average in fiscal year 2000-2001, the baseline year, was 1.12. Their goal for fiscal 2007-2008 was an average EC of 1.40. Yet, the company reached this goal three years early with an average EC of 1.41 in fiscal 2004-2005 covering almost 1.4 billion pounds of raw materials.

SC Johnson used Greenlist™ to remove a particular volatile organic compound (VOC) from Windex®. They developed a novel new formula containing amphoteric and anionic surfactants, a solvent system with lower VOCs, and a polymer for superior wetting. Their formula cleans 30 percent better and eliminates over 1.8 million pounds of VOCs per year.

Abstracts, *Continued*

Design for Biodegradation

22. Designing biodegradable chemicals.

Bob Boethling, David DiFiore and Elizabeth Sommer, U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington, DC.

Under the Pollution Prevention Act of 1990 it is the policy of the United States that pollution should be prevented or reduced at the source whenever possible. One way to accomplish this is to design safer chemicals. Chemicals that persist in the environment remain available to exert toxic effects and may bioaccumulate. Since microbial degradation is the major loss mechanism for most organic chemicals in soil, water and sewage treatment, biodegradability should be viewed as integral to product design. It is essential to extend the "benign by design" concept broadly because i) we cannot know in advance all possible toxic effects of released chemicals; ii) production and release may increase significantly if a chemical is successful in the marketplace, potentially with unforeseen consequences; iii) new uses may develop over time, leading to greater emissions and/or different routes of exposure. The relationship between molecular structure and biodegradability is understood well enough to be useful in chemical design. A variety of predictive models are also available and reliable enough to assist. It is shown by means of examples drawn from high-volume chemicals in current use how enhanced biodegradability has-or might have—avoided unnecessary environmental damage. Other examples are taken from EPA's Design for the Environment program and show how voluntary partnerships can promote product substitution through knowledge transfer. Further, the examples illustrate how currently available models may be used to make predictions about relative biodegradability in advance of commercialization.

23. Biodegradation experiments in the marine environment

Jo Ann Ratto¹, Robert Stote¹, Jean Herbert¹, Christopher Thellen¹ and Carl Wirsen², (1)U.S. Army Natick Soldier Center, Natick, MA, (2)Woods Hole Oceanographic Institution, Woods Hole, MA

The U.S. Army and Navy are working together to determine what biodegradable polymers could potentially be used by the U.S. Navy for packaging items on board ships. A laboratory respirometry test, ASTM-6691-01, "Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium" is performed on different biobased/biodegradable samples to determine at what level they biodegrade. Respirometry data on percent biodegradation vs. time for a variety of test samples and positive/negative controls will be presented. The ASTM method consists of using a consortium of cultured marine microorganisms for the inoculum; however, a modification to the standard method was also performed using natural seawater with its indigenous microflora and the data is compared.

24. Electron beam modification of starch with lignins and lignin model compounds: Evidence of grafting reactions

Xavier Coqueret, Universite de Reims Champagne Ardenne, Reims, France

Starch can be used alone and in combination with other compounds to make biodegradable articles from renewable resources. Lignins and their derivatives are good candidates for limiting the water sensitivity of starch-based materials, but they exhibit poor compatibility in blends with polysaccharides. Electron beam (EB) processing is proposed as an efficient method for inducing covalent linkages between the two constituents. Compared to unirradiated starting materials, the surface and bulk properties of EB-irradiated starch-lignin blends submitted to EB irradiation showed an interesting reduction of hydrophilicity. The reactivity under EB of model blends was examined by several analytical methods. Maldi-ToF mass spectrometry allowed us to propose reasonable free radical mechanisms that account for the grafting of various benzyl and cinnamyl alcohols onto maltodextrines. Radiation induced grafting of lignin models onto starch was shown to impede long-term retrogradation, with limited loss of mechanical properties.

25. Towards 'Advanced Green Composites'

Anil N. Netravali, Cornell University, Ithaca, NY

Environment-friendly, sustainable, 'green' composites fabricated using plant-based fibers and resins are increasingly being developed for various applications as replacements for non-degradable composites derived from petroleum-based fibers and resins. Green composites developed to date have moderate mechanical properties. As a result, their applications are limited to packaging, casings, paneling, furniture and secondary structural applications in automotive or housing. However, recently there have been many developments that allow significant improvements in the mechanical properties of these composites. With significant improvements these composites may be used in primary structural applications. Yet at the end of their life they can be easily disposed of or composted without harming the environment. This paper will discuss some of the recent developments in cellulosic fibers and soy protein-based resins that allow possibilities of fabricating such high strength 'Advanced Green Composites'. Mechanical properties of such composites fabricated using high strength cellulose fibers and modified soy protein-based resin will be discussed.

26. Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil

Piyush S. Lathi and Bo Mattiasson, Lund University, Lund, Sweden

A novel process for the production of biodegradable lubricant-based stocks from epoxidized vegetable oil with a lower pour point *via* cationic ion exchange resins as a catalyst was developed. It involves two steps: first, ring opening reactions by alcoholysis followed by esterification of resulting hydroxy group which was generated in the first step. The ring opening reaction of epoxidized soybean oil with different alcohols such as *n*-butanol, *iso*-amyl alcohol and 2-ethylhexanol was carried out in the presence of Amberlyst 15 (Dry) as catalyst; identity of products were confirmed by IR and NMR. Pour points of the products were observed in the range of -5 to -15 °C. The hydroxy group of the ring opening product of *n*-butanol was further reacted with acetic anhydride in the presence of catalyst Amberlyst 15 (Dry), which was previously used to carry out ring opening reaction by alcoholysis and identity of the resulting product was confirmed by IR. Pour point of the resulting product was observed -5 °C.

Benign Solvents II

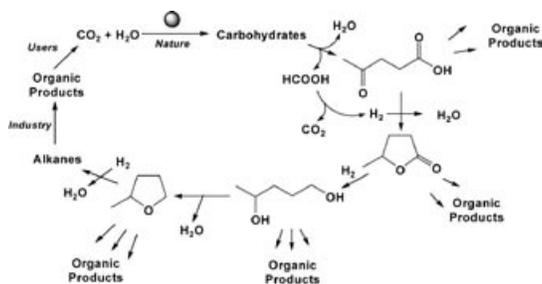
27. γ -Valerolactone: A sustainable liquid for energy and carbon based chemicals

István T. Horváth, Institute of Chemistry, Eötvös University, Budapest, Hungary

We propose that γ -valerolactone exhibits the most important characteristics of an *ideal sustainable liquid* including the possibility to use it for the production of *both* energy or carbon-based consumer products, renewable, easy and safe to store and move globally in large quantities, has low melting, high boiling and open cup flash points, a definitive but acceptable smell for easy recognition of leaks and spills, low toxicity, and high solubility in water to assist biodegradation.

	Methanol	Ethanol	MTBE	γ -Valerolactone	2-Me-THF
MW (g/mol)	32.04	46.07	88.15	100.12	86.13
Carbon (w%)	37.5	52.2	66.1	60	69.7
Hydrogen (w%)	12.6	13.1	13.7	8	11.6
Oxygen (w%)	49.9	34.7	18.2	32	18.7
Boiling Point (°C)	65	78	55	207-208	78
Melting Point (°C)	-98	-114	-109	-31	-136
Density (°C)	0.79	0.8	0.74	1.05	0.86
Open Cup Flash Point (°C)	16.1	14	-33	96	-11
LD ₅₀ , oral for rat (mg/kg)	5628	7060	4800	8800	N/A

We have been investigating the selective conversion of carbohydrates to various C₅-oxygenates including levulinic acid, γ -valerolactone, and 2-methyl-THF. The dehydration of carbohydrates to levulinic and formic acids is a particularly attractive approach. Since formic acid can be converted either directly or via the water-gas shift reaction to carbon dioxide and hydrogen, the latter can be used for the hydrogenation of levulinic acid to γ -valerolactone, making the process hydrogen-independent and readily useable even at remote parts of the world. It is also important to recognize that the use of a single chemical entity, such as γ -valerolactone, as a sustainable liquid instead of a mixture of compounds could significantly simplify its worldwide monitoring and regulation.



28. Unleashing cellulose potential: BASF ionic liquids

Calvin J. Emanuel¹ and Matthias Maese² (1) BASF Corporation, Florham Park, NJ, (2) BASF AG, Ludwigshafen, Germany

Ionic liquids have gained significant interest over the past years. They are unique new materials that offer novel solutions to the chemical industry as well as to its customers. Being developed by the chemical scientific community as well as by the chemical industry, the first published applications have naturally been related to chemical processes. BASF is the first company that dedicatedly used them on the large scale to improve a chemical process. However, BASF is strongly convinced that ionic liquids can offer a similar or even greater potential outside the classical chemical applications. Ionic liquids can offer solutions

for various kinds of industries such as machinery, automotive, energy, textile, paper, electronics, etc. It is BASF's aim to foster a broader use of these new innovative materials in industrial applications. BASF has set up a research partnership with the University of Alabama to study the dissolution and processing of cellulose by means of ionic liquids. Under this partnership the company has licensed the exclusive use of various intellectual property rights. Present globally at a volume of some 700 billion tons, cellulose is the Earth's most widespread natural organic chemical and, thus, is highly important as a biorenewable resource. But even out of the 40 billion tons of cellulose that nature renews every year, only 0.1 billion tons are used as feedstock for further processing. BASF is in the process of evaluating a variety of ideas that might improve the use of cellulose. The lecture will highlight recent advances at BASF.

29. Chemical engineering in multiphase

CO₂-expanded liquid systems:

Study of the Pictet-Spengler reaction

Rocco P. Ciccolini, Joshua R. Dunetz, Morgan Froling, Scott M. Paap, Andrew J. Allen, Rick L. Danheiser and Jefferson W. Tester, Massachusetts Institute of Technology, Cambridge, MA

For more than 12 years, the MIT Departments of Chemistry and Chemical Engineering have engaged in a collaborative effort to study various synthetic transformations in environmentally-friendly media. Recently, our collaboration has grown to include members of Cambridge University who have similar strengths in the field of Green Chemistry. We are currently exploring the synthesis of pharmaceutically-attractive nitrogen heterocycles and are developing strategies for effecting C-N bond-forming reactions in scCO₂ and multiphase CO₂-based media. To do so, it is essential to apply fundamental chemical engineering principles. Specifically, we are engaged in studies concerning reaction engineering, mass-transport and thermodynamics. Herein we report the results of our study on the Pictet-Spengler cyclization in multiphase scCO₂/CO₂-expanded liquid media and the development of a successful strategy for effecting this important reaction in scCO₂ that should be applicable to other C-N bond-forming processes as well.

30. Ionic liquids: Benign solvents for supported liquid catalyst systems

Anders Riisager¹, Rasmus Fehrmann¹, Marco Haumann² and Peter Wasserscheid², (1) Technical University of Denmark, Kgs. Lyngby, Denmark, (2) Universität Erlangen-Nürnberg, Erlangen, Germany

Ionic liquid (ILs) have recently attracted an increased interest for catalysis and separation technology in the form of supported ionic liquid phase (SILP) systems. SILP catalyst systems can be obtained directly by confining an IL on a solid material or by invoking, e.g., metals catalysts as complexes or particles. By use of well-defined, homogeneous metal complexes a rational catalyst design through ligand selection and/or catalyst-ionic liquid interactions can facilitate improved catalyst performance resulting in, e.g., improved catalyst selectivity. Similar heterogeneous metal catalysts confined on SILP materials can benefit from an enhanced stabilization provided by the ILs, thereby effectively preventing particle aggregation and a resulting catalyst deactivation. Importantly, the non-volatility of ILs and their characteristic of being liquid over a large temperature range ensure that the catalyst phase remains fluid on the support at typical reaction temperatures; this makes SILP catalysts highly suitable for continuous processes using preferred, gas-solid fixed-bed reactor technology. In addition, a high degree of dispersion of the IL catalyst phase on the support surface, corresponding to a diffusion layer of only a few molecules of thickness, generates a very large interfacial reaction area. This circumvents diffusion problems

Abstracts, *Continued*

which regularly are found for reactions involving bulk ILs and enables a very efficient IL catalyst phase material use. Thus, the SILP concept allows preservation of high catalyst performance in a technologically simplified and benign manner. In this presentation the progress of SILP catalysis are surveyed and new applications involving homogeneous, complex-based and heterogeneous nanoparticle SILP catalysts are introduced.

31. Rapid optimization of supercritical hydrogenation flow systems

Richard A. Bourne, University of Nottingham, Nottingham, United Kingdom

Hydrogenation of organic substrates in supercritical carbon dioxide ($scCO_2$) has been shown to provide numerous advantages over more traditional methods using organic solvents. This is primarily due to the complete miscibility of H_2 gas in $scCO_2$. During hydrogenation reactions using $scCO_2$, the liquid phase is either expanded by the supercritical solvent or forms a single phase mixture. Both of these situations result in the concentration of H_2 at the catalyst surface being greatly enhanced. This leads to an increased rate of reaction and allows for hydrogenation reactions to be performed effectively in a flow system with short reactor residence times. A new automated hydrogenation flow apparatus is described which enables the use of automated online gas-liquid chromatographic analysis combined with an integrated means of safely controlling the addition of H_2 . A selection of results from the automated hydrogenation flow reactor is presented, including the hydrogenation of isophorone to 3,3,5-trimethylcyclohexanone. These results demonstrate the effectiveness of the automated hydrogenation system for performing continuous flow hydrogenation reactions in $scCO_2$. Rapid optimization of the system is achieved by utilization of multivariate statistical analysis. The work presented shows the potential for multivariate analysis to model and optimize the flow reactor system, thereby reducing waste and minimizing the optimization timescale.

32. Direct synthesis of hydrogen peroxide from oxygen and hydrogen in carbon dioxide

Qunlai Chen and Eric Beckman, University of Pittsburgh, Pittsburgh, PA

Hydrogen peroxide is currently produced by the anthraquinone auto-oxidation (AO) process. This AO process is far from green in view of 12 principles of green chemistry. Direct synthesis of H_2O_2 from O_2 and H_2 is an attractive green technology to replace the current AO process since it is the most atomic effective method by which H_2O_2 can be generated. Most researchers used methanol or the mixture of methanol and water as the solvent in order to obtain high H_2O_2 yield. However, methanol is a flammable and volatile solvent; it can also be oxidized by H_2O_2 to generate aldehyde and other by-products. CO_2 can be used as an environmentally benign solvent to replace methanol since it is non-flammable, cannot be oxidized and is miscible with O_2 and H_2 above $31^\circ C$. In this study, a novel method was developed to measure the amount of in situ generated H_2O_2 in CO_2 by reacting it immediately with a selected indicator. Our experimental results showed that H_2O_2 can be effectively synthesized from O_2 and H_2 over precious metal-loaded titanium silicate (TS-1) in CO_2 .

33. Reduction of total VOC emissions in flexographic washout solvents

Connie M. Hendrickson¹ and David C. Bradford², (1)Arkon Consultants, Irving, TX, (2)Nupro Technologies, Winston-Salem, NC

Flexographic printing plates are developed by immersing a light-exposed polymer plate in a solvent which removes the unpolymerized material while leaving the polymerized material intact. The developing solvent, called the washout solvent, is typically a mixture of organic solvents classified as Volatile Organic Compounds or VOCs. The primary solvent removes unpolymerized material, the cosolvent removes the protective "skin" from the plate, and the balance is a diluent to minimize costs.

After treatment in the plate processor, the developed plate is then dried in a high temperature oven and sometimes run through a finishing machine, readying it for use in printing. Assuming that two washout solvents are each 100% VOCs, the emissions from dryer and finisher will be the same regardless of the actual compositions of the washout solvents. However, loss from the plate processor constitutes the bulk of the emissions. Consideration of physical characteristics of solvent and cosolvent can minimize loss from the processor and drastically reduce annual emissions for users.

34. Continuous acid-catalyzed reactions in supercritical CO_2

Peter N. Gooden, University of Nottingham, Nottingham, United Kingdom

Volatile organic solvents account for a significant proportion of total hazardous chemical emissions. A major facet of green chemistry is the investigation of alternative solvent systems such as supercritical carbon dioxide ($scCO_2$). $scCO_2$ is an attractive alternative as it is inexpensive, non-toxic and its critical parameters are easily accessible. The work presented here examines the feasibility of performing acid-catalyzed reactions in $scCO_2$ as a more sustainable method of fine chemical production. Acid-catalysis is a fundamental tool in synthetic chemistry. Environmental concerns over the widespread use of mineral acids such as hydrogen fluoride have led to the increased use of heterogeneous solid acid catalysts in industrial processes. These are attractive because they produce very little waste and reduce equipment corrosion. Continuous flow $scCO_2$ technology is ideally suited to incorporating commercially available solid acid catalysts into a heterogeneous fixed-bed reactor. A selection of results is presented including the continuous desymmetrization of 1,6-hexanediol in $scCO_2$ by etherification with methanol. This reaction has been optimized to afford synthetically useful, unsymmetrical, value-added products from inexpensive, symmetrical substrates. The etherification of 1,6-hexanediol in $scCO_2$ is remarkable as the selectivity towards the etherified products can be tuned by varying the reaction pressure. This effect has been attributed to a combination of factors involving the phase behavior of the reaction mixture and the residence time of the reactor. This concept has also been successfully applied to the continuous selective etherification and esterification of other commercially viable substrates.

35. Formamide as a green solvent

Mikhail M. Bobylev and Lioudmila I. Bobyleva, Minot State University, Minot, ND

Formamide is a solvent that is not commonly used in chemical reactions. The main reason for this is its high polarity, close to that of water. As a result of this formamide, just like water, does not dissolve low to moderately polar substances, *i.e.*, the majority of organic compounds. However, this seeming disadvantage is increasingly looking like a tremendous advantage from the viewpoint of green chemistry. Water is specifically attracting attention as an almost perfect solvent for green processes. Our investigation of the Leuckart reaction for the synthesis of formamide fungicides shows that formamide has a potential as a green solvent, too. Similar to water, at temperatures close to 200°C formamide begins to dissolve regular organic compounds and can be used as a solvent for organic reactions. At 200°C these reactions run exceptionally fast. When cooled to room temperature, the organic products become practically insoluble and could be easily separated. Unlike many organic solvents, and similar to water, formamide does not deteriorate at high temperatures. As a result, the formamide filtrate could be repeatedly used as the solvent in the same reaction. And unlike water, formamide produces much lower pressure at 200°C, which allows its practical use with the commonly available equipment. The specific data for the Leuckart reaction as applied to the synthesis of formamide fungicides and other formamides will be presented.

36. Identification, design and synthesis of oxygenated hydrocarbon-based CO₂-soluble polymers for chemical, pharmaceutical, biomedical and petroleum engineering applications

Lei Hong, Yang Wang, Robert Enick, Eric Beckman and Karl Johnson, University of Pittsburgh, Pittsburgh, PA

Supercritical carbon dioxide (*scCO*₂) has attracted much interest recently as an alternative solvent for material synthesis and processing. Researchers have promoted CO₂ as a sustainable and “green” solvent because it is non-toxic, non-flammable and naturally abundant. Unfortunately, CO₂ is a feeble solvent. One technical barrier to the use of *scCO*₂ is the limited availability of inexpensive CO₂-soluble surfactants, ligands and phase transfer agents because the majority of systems reported so far have been highly fluorine-substituted and the associated costs may prohibit commercial scale use for many applications. In addition, fluorinated materials often have poor environmental degradability. The research objective is to develop inexpensive, oxygenated hydrocarbon-based polymers which have significant solubility in CO₂ under moderate conditions (<100 °C, <40 MPa). The novel environmentally benign, highly CO₂ soluble polymers will be used as the construction blocks for surfactants, copolymers and dispersants, which would significantly enhance the *scCO*₂ applications in chemical, pharmaceutical and petroleum engineering industries. Molecular modeling to be introduced in designing CO₂-philic polymers for the first time. Poly(3-acetoxy oxetane), poly(vinyl methoxy methyl ether), poly(vinyl 1-methoxyethyl ether) and cellulose triacetate oligomers were prepared and their solubility in CO₂ was identified.

Engineering for Sustainability

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37. Increasing chemical efficiency: Incorporating advances in synthetic design into continuous processes

Steven J. Broadwater and D. Tyler McQuade, Cornell University, Ithaca, NY

Our group is focused on increasing synthetic efficiency of chemical transformations. In addition, we are pursuing safer and more sustainable approaches to produce value-added molecules. The approach we are taking is a merger of advances in synthetic chemistry with innovations in microreactor technology. One method we attempt to employ is reaction telescoping, which allows for multiple reaction steps to be carried out in the same reaction vessel and, therefore, reduces resources spent on product purification. We also envision the use of tandem catalysis as a method to achieve multi-step, one-pot reactions. To this end, we have explored novel methods of catalyst immobilization and site-isolation with the goal of preventing catalyst fouling and enabling recoverability and recyclability. In addition, we have begun exploring the replacement of hazardous reagents with user-friendly molecular surrogates. All of these approaches are initially being employed to improve processes that are applicable to structural classes of molecules, as opposed to single molecules. This will allow the benefits of synthetic advances to be realized in multiple syntheses. In recent years, substantial progress has been made in the field of microreactors and the obvious benefits of this technology have been demonstrated. We are interested in integrating our approach to synthetic chemistry with this exciting field in order to maximize our synthetic impact. We are currently in the process of transitioning batch reactions into continuous processes using microreactors and packed bed reactors with the goal of developing processes that can be carried out with increased efficiency and sustainability.

38. Green chemistry and biotransformations in API manufacturing processes

Junhua Tao and **Kim F. Albizzati**, BioVerdant, Inc., San Diego, CA

The use of enzymes in organic synthesis has a lengthy and storied history that reaches into the 1960s. However, only recently have advances in genomics and proteomics allowed the tuning and enhancement of enzyme reactivity and selectivity such that important practical applications are possible. The key to the successful development of biocatalytic processes at industrial scale is the synergistic integration of modern chemical process development and biotechnology at the retrosynthetic strategy level. Further, enzymatic catalysis of chemical reactions allows truly green processes to be developed involving the use of renewable resources under aqueous conditions at ambient temperatures and pressures. The talk will focus on some specific uses of enzymes in drug manufacturing which have led to unprecedented efficiencies and the development of truly green processes for drug manufacturing.

Abstracts, *Continued*

39. Lipase catalyzed microwave-assisted resolution of naproxen methyl ester

Ganapati D. Yadav, Shrikant B. Dhoot and Ashwini D. Sajgure, University of Mumbai Institute of Chemical Technology, Mumbai, India

(S)-2-(6-Methoxy-naphthalen-2-yl)propanoic acid [(S)-naproxen] is a powerful anti-inflammatory agent whose asymmetric synthesis continues to be a challenging undertaking. Naproxen is one of the best known NSAIDs and the S-isomer is 28 times more active compared to the R-isomer. The bioreversible derivatives (prodrugs) of naproxen have been investigated to reduce their GI side effect and other possible systemic side effects due to high plasma peak levels after oral administration. The ester group of NSAIDs is promising for reducing or abolishing the GI toxicity due to the localized effect replaces the carboxyl group of NSAIDs. The present study deals with the effect of microwave irradiation on the enantioselectivity in resolution of the methyl ester of naproxen via lipase (Novozyme 435) catalysis. Effect of various parameters like different solvents, speed of agitation, catalyst loading, buffer pH, temperature and mole ratio has been studied.

40. Integrated environmentally benign product design, process design and optimal control: A case study in the pharmaceutical industry

Saadet Ulas and Urmila Diwekar, Vishwamitra Research Institute & University of Illinois at Chicago, Westmont, IL

In pharmaceutical manufacturing, solvents are frequently used for various processes operated in batches. As a result, complex mixtures of waste solvents are generated which need to be disposed of in an environmentally friendly manner. Due to the thermodynamic complexities associated with these mixtures, they cannot be easily separated by conventional methods such as distillation and a mass separating agent or an entrainer is needed to perform the task. This paper presents an integrated framework for waste solvent recycling in the pharmaceutical industry and the wide applicability and advantages of this framework are shown in a case study provided by Tyco Healthcare, MO, where a mixture of acetonitrile and water is generated as a result of the peptide drug purification process. The first step of this framework is product design, where the environmentally benign and efficient mass separating agent/entrainer is selected by using a computer-aided molecular design (CAMD) approach. The next step is process synthesis and design where the optimal batch column configuration for separation is selected according to performance indices. The final step is optimal control, where the optimal operating profile for the batch column is obtained, so as to maximize the product yield. The uncertainties in mathematical models are taken into consideration in every stage of this framework. For dynamic uncertainties, a new approach based on Ito processes is used, which originate from finance literature and real options theory. Integrating product design, process design and optimal control allows us to reach the best performance and minimize environmental impacts of waste solvents.

41. Preparative SFC at the kilogram scale to support pharmaceutical development

Derek W. Henderson, Jinchu Liu, William R. Leonard, Christopher J. Welch, Merck Research Laboratories, Merck & Co., P. O. Box 2000, Rahway, NJ

Preparative chromatography is increasingly used to access kilogram quantities of developmental compounds to support preclinical pharmaceutical development. Typically these separations have been performed using HPLC and often require large volumes of organic solvents. Supercritical fluid chromatography (SFC) has many chromatographic advantages over HPLC and has long been our preferred method for chiral chromatographic analysis or small scale (<20 g) purifications. In addition, SFC employs carbon dioxide as the principal mobile phase which replaces the petrochemical-derived hydrocarbon solvents commonly used in HPLC. We have recently acquired two different preparative SFC instruments which we have utilized for preparation of pharmaceutical intermediates at the kilogram scale. We present here several case studies illustrating the considerable advantages of using SFC for kilogram-scale preparative chromatography including solvent savings of up to 95% compared to HPLC. These case studies clearly demonstrate the green chemistry advantage of SFC in which recycled carbon dioxide replaces green-house producing, flammable, and toxic petrochemical-derived hydrocarbon solvents while providing superior chromatography and productivity.

Information Resources & Assessment

42. Emerging chemical issues

N.I. McClelland¹ and M.A. Taubitz², (1)N.I. McClelland LLC and Company Member Forum (CMF), American National Standards Institute (ANSI), Ann Arbor, MI, (2)American National Standards Institute (ANSI)

Emerging chemical issues is a subject of continuing and ubiquitous interest and concern. Chemistry IS "the central science." It affects our lives in everything we are, everything we do and all that we have. It is a root cause of successful global commerce for virtually all U.S. manufacturers and their supply chains. Green chemistry continues to be a model for chemical issues with impacts on human health and safety and environmental quality and it has been called "the third leg of the stool" for achievement in business and industry. Through an impressive public-private partnership, green chemistry has been not only an axiom for growth opportunity, but an "imperative for continued success." The mix of science-based policy and economically feasible technology that has supported the green chemistry initiative is required to assure the continuum of progress for U.S./global business and industry with green chemistry and with other chemical issues. It follows, then, that other emerging chemical issues are a matter of great concern. To be competitive in world markets requires the assurances of early, informed and active technical/professional input to regulatory mandates which frequently emerge outside of the United States. Directives from Europe and the United Nations in which there has been no U.S. scientific input during their development have brought both confusion and staggering costs to our segmented industrial community...e.g., WEEE (Waste Electrical and Electronic Equipment Directive), RoHS (Restriction of Hazardous Substances Directive) and REACH (Registration, Evaluation and Authorization of Chemicals). This paper describes a current activity in which NIST and private sector representatives, including diverse U.S. industry members of the CMF of ANSI, the American Chemical Society

(ACS) and related trade, professional, scientific and voluntary standards organizations are collaborating to develop and implement a process to address the challenge—and opportunity—of successfully proactively integrating our science and public policy expertise into initiatives that drive innovations in areas of health, safety and the environment. Voluntary, consensus standards methodologies are being followed. A conference with global significance, to be hosted by NIST at its Gaithersburg facilities in the fall, 2006, will be announced.

43. Green chemistry resource exchange

Jennifer L. Young, James C. Rea and Paul T. Anastas, Green Chemistry Institute, Washington, DC

The ACS Green Chemistry Institute has developed the Green Chemistry Resource Exchange as part of a cooperative agreement with the U.S. EPA Design for the Environment program. As it grows, this web-based database will become a comprehensive collection of green chemistry technologies and information. The entries in the database are text searchable and searchable by specific keywords (industry sectors, chemicals/materials and green chemistry keywords). The resource exchange was developed to provide value to a broad audience, including chemists and non-chemists, business leaders, technology experts, students and the general public. The initial set of database entries is composed of the 52 winning technologies from the first ten years of the Presidential Green Chemistry Challenge Awards (1996-2005). The Green Chemistry Resource Exchange is an ever-growing database with many features and capabilities. By registering on the site, users can receive notifications when new entries meeting their fields of interest are added to the database. In addition, registrants can submit entries to the database through the “contribute” feature. New entries can include resources such as websites, journal articles, books, news articles, audio or video clips and presentations/lectures.

44. Challenge of classifying “green” chemicals and products

George R. Thompson, Chemical Compliance Systems, Inc., Lake Hopatcong, NJ

The definition of “green” chemicals and products has slowly evolved over the past 13 years. In 1993, Executive Order (E.O.) 12873 included a generic stipulation that “... ‘environmentally preferable’ means products or services that have a lesser or reduced effect on human health and the environment.” In 1995, EPA published their generic “Environmentally Preferable Products [EPPs] – Proposed Guidelines.” E.O. 13101 defined “biobased” products for the first time in 1998. In 2004, the federal Joint Group on Environmental Attributes changed the terminology from EPPs to “green” products and the Department of Defense (DoD) established their Green Procurement Program (GPP). The current DoD “green” attributes include only a single factor related to human health. Little consideration has been given to the pros and cons of defining “greenness” at points within, or across, the entire life cycle. Additionally, many new, alternative products and processes are considered “green” in the absence of data, simply because they are new or because they offer economic advantages. Definition of a broad spectrum of chemical hazard criteria (that predict specific effects on human health and the environment) provides an objective basis for quantitatively calculating and comparing the “greenness” of products—regardless of the industry. The Web-based “Green” Products Compliance Analytical System (GP-CAS) provides a current basis to significantly and objectively expand the definition of “green” chemicals and products, while also offering flexibility and scalability to incorporate future considerations (e.g., biobased factors).

45. Building CleanGredients: Using a multi-stakeholder process to design an information resource for green cleaning product formulation

Tarek Rached¹ and Lauren Heine², (1)University of Virginia, Charlottesville, VA, (2)GreenBlue Institute, Charlottesville, VA

Over the past 18 months, a new information resource to support green cleaning product formulation was developed using a multi-stakeholder process that engaged experts from the industrial and institutional cleaning product industry, EPA’s Design for the Environment program and non-governmental organizations. The information resource, called CleanGredients, facilitates a completely new approach to formulating environmentally preferable products by allowing cleaning product formulators to consider their ingredients’ key human and environmental health profiles alongside their performance properties during the design process. We describe the process developed for gathering, verifying and distributing human and environmental health and safety (HEHS) information on chemical ingredients used in the industrial and institutional cleaning product sector and the efficiencies made possible by using CleanGredients in the formulation process. This HEHS information strikes a balance in presenting hazard data that supports both risk assessment and decision making based on inherent hazard criteria. This innovative approach is receiving broad support and appears to offer greater utility than information resources with more extensive value judgments embedded in attributes, criteria and cutoffs. Other elements of the program, including the approach to identifying ingredients with favorable hazard profiles are also described.

46. Evaluating the environmental implications of agricultural feedstocks for biobased production

Amy E. Landis, Shelie A. Miller and Thomas L. Theis, Institute for Environmental Science and Policy, Chicago, IL

Bio-based production life cycle assessments (LCAs) have thus far focused largely on energy (fossil fuel) usage and greenhouse gas emissions during the agriculture and production stages. Tradeoffs above and beyond these two popular impact categories have been neglected. Increased demand on the agricultural sector will have implications on other nutrient cycles, such as nitrogen and phosphorus, which are the primary contributors to hypoxia and eutrophication in the U.S. A life cycle inventory (LCI) module capable of capturing the Corn Belt’s variable conditions in the form of probability distributions will be presented, while the tradeoffs manifested in the agricultural phase of biobased production will be discussed in an impact assessment. The GREET tool (Greenhouse Gases, Regulated Emissions and Energy Use in Transportation) developed at Argonne National Labs was employed to create the LCI while Monte Carlo Analysis was used to capture the variability and uncertainty in the agricultural system.

Abstracts, *Continued*

47. Green chemistry principles applied to an ISO 14001 environmental management system

Denny Hjeresen, Los Alamos National Laboratory, Los Alamos, NM

Los Alamos National Laboratory (LANL) has implemented an Environmental Management System (EMS) designed to both meet ISO 14001 requirements and employ green chemistry principles to drive improvements in environmental performance. The ISO structure drives continual improvement through pollution prevention while upstream process changes in facilities yield actual performance results. Green chemistry offers a powerful set of practical tools that can function well within the ISO 14001 structure. The LANL EMS is driven on prevention principles and asked all 31 operating Divisions within the Laboratory and major subcontractors to identify upstream opportunities for less hazardous chemical synthesis, designing safer processes (especially in nuclear chemistry), using safer solvents, efficient building and facility design, designing inherently safer processes as well as energy and fuel conservation projects. The Divisions responded with nearly 600 separate process improvements in FY06. The presentation will feature examples ranging from machine shop improvements to advanced new methods of DNA sequencing chemistry. The application of upstream design principles in national security and nuclear research are especially important when dealing with extremely hazardous chemicals and radioactive materials. This upstream focus serves as a new adjunct to the traditional waste management, recycling, reuse and energy issues typically addressed in ISO 14001 programs. The LANL lesson offers an opportunity to expand green chemistry applications to organizations wishing to expand the impact of their ISO 14001 EMS.

48. Green chemistry through hands-on experience for undergrad students

Bhanumati Soundararajan, Gargi College, Delhi University, New Delhi, India

The present paper focuses on sensitizing the student community about the paradigms of green chemistry through hands-on-experience. Students need to be inducted into the science and ethics of this discipline to make chemistry environment savvy and to transform chemistry from TOXIC to a BENIGN subject. Merely appending the principles of green chemistry with known examples to the curriculum is not the right solution. An *ad hoc* Laboratory Survey after a day's lab sessions pointed towards the end wastes besides the student results. Broadly there are glass, paper and chemical wastes which pose practical problems. These have been looked into with discretion. Glass wastes are selectively reused and recycled. Measuring cylinders are fabricated from broken burettes and boiling tubes. Burettes with broken tips are reused with I.V. set regulator attachments. Gas generators are devised from broken viscometers. Filter paper use is minimized by button/nail filtration. Nails are fabricated by students from empty ball pen refills and broken glass rods. Using the green chemistry metrics, hazard and toxicity is reduced at the source. Twin burette and micro-scale titrations, altered synthetic pathways, benign chemical substitutes, less energy intensive and resource consuming preparations are being performed simultaneously with the conventional textbook recipes for students to evaluate by "Judge yourself" dictum. Drain disposal of chemical effuse is made safer by pretreatment. The emphasis is invariably towards the in-process options rather than end-of-pipe solutions. In essence, revamping of practical procedures is perceived as a possible solution for rendering the labs a greener luster.

49. Putting the fizz into chemistry: Taking green chemistry to the public

Samantha L. Y. Tang, Martyn Poliakoff, Steve Howdle and Mike George, University of Nottingham, Nottingham, United Kingdom

Leading researchers are keen to communicate the importance of their research to the general public but never have the time to do it. Our research group at The University of Nottingham has devised a cost-effective way of overcoming this problem and spreading the message of green chemistry. Our solution is the UK's first Public Awareness Scientist (PASc), a full-time post-doctoral researcher with a background in chemistry. The PASc has a unique role in that she is based in an active research group but her principal aim is to facilitate the communication of the group's green chemistry and engineering by the researchers themselves. This presentation will focus on three recently established projects, all with the principal aim of involving researchers within and outside of the Clean Technology Group in schools science outreach. First is the development of an informative slideshow and hands-on experiment for 4th/5th grade school children.

The second has a "Research Twin", a postgraduate student, regularly visiting an 8th grade class to describe their green chemistry research and inform them of university life. The third project is modeled on Café Scientifique, with the set up of a regular discussion forum for teenagers where they listen to invited speakers talk about the research that takes place in their local university.

The time and labor saved by the PASc's organization has meant that some researchers with no prior experience of schools outreach have taken the opportunity to communicate science in the classroom and have found they enjoy it!



50. Chemistry Literacy Network: Environmental chemistry education, research and action

Sheryl Dee Mebane, University of California at Berkeley, Berkeley, CA

The Chemistry Literacy Network synthesizes research contributions enhancing environmental chemistry education, environmental and green chemistry research and organizational theory to design and pilot classroom and extracurricular environmental and green chemistry education programs that increase student understanding, inform environmental justice actions of community groups and provide access to knowledge for underserved communities. In this presentation, the observations and analyses, using qualitative and quantitative research methods, of successful programs teaching green or environmental chemistry in informal and formal educational settings will be presented. Also reported are preliminary observation data, perhaps addressing the experienced curricula for chemistry students of all ages and various ethnicities in formal and informal educational settings. The stages of development of an environmental chemistry curriculum with potential impact in underrepresented minority and environmental justice communities are noted. In addition, the best methods of supporting sustainable links between the community and academic groups comprising the network are noted along with the emerging concept of chemistry literacy (knowledge of chemistry that empowers students to think critically about chemistry-related topics inside and outside of the classroom) applied to positive social action.

Green Metrics Symposium

Sponsored & Organized by the GCI Pharmaceutical Roundtable

51. Application of metrics in driving green chemistry initiatives at GSK

David J. C. Constable¹, Richard K. Henderson², and Concepción Jiménez-González³ (1)GlaxoSmithKline, Philadelphia, PA, (2)GlaxoSmithKline, Ware, Hertfordshire, England, (3)GlaxoSmithKline, Research Triangle Park, NC

GSK has been collecting a variety of metrics on its synthetic chemical routes and processes for several years. This presentation will focus on a brief description of those metrics considered to be the most useful in driving towards greener processes. Analysis and examples will be presented.

52. Measuring green chemistry implementation: Building EHS performance into products

John M. Kindervater¹ and Stephen A. Leeper², (1)Eli Lilly and Company, Indianapolis, IN, (2)Eli Lilly and Company, Lafayette, IN

Developing chemical processes for pharmaceutical manufacturing involves optimizing many criteria. With a goal to deliver cost effective, robust and safe processes, Lilly process research and development uses a variety of metrics to track progress and capture successes. Metrics and methods used at Lilly to assess potential safety and environmental burden, applied from early synthetic route choices to bulk process development, will be briefly discussed.

53. Merck's API mass intensity metric

Beth Berglund, John Leazer, Ephraim Bassan and Mary Buzby, Merck & Co., Inc., Whitehouse Station, NJ

The presentation will summarize Merck's API mass intensity metric.

54. Defining a mass intensity metric for the pharmaceutical industry

GCI Pharmaceutical Roundtable, ACS Green Chemistry Institute, Washington, DC

The GCI Pharmaceutical Roundtable is a collaboration between the Green Chemistry Institute and pharmaceutical companies to catalyze the integration of green chemistry and green engineering into the global pharmaceutical industry. Recognizing the variability among the green metrics used in the industry, the Roundtable has defined a mass intensity metric to improve the ability to effectively benchmark while continuing to drive innovation. The metric will be summarized and provide a starting point for more discussion about green metrics.

Industrial Applications I

55. Advances in green product design

Neville Hargreaves, Crystal Faraday, Rugby, United Kingdom

The European chemical industry has been very successful in reducing its environmental impact. In ten years, CO₂ emissions per unit of production fell by 44%. Programs have not only helped the industry to meet the requirements of regulators and society at large, they have also been profitable. However, the focus has almost all been on processes to make existing products. This is only a small part of the lifecycle — for many products, there is far more impact in distribution, use or disposal than in manufacture. For many industries the issue of environmental impact of products through their lifecycle is real, live and of immense importance right now. Legislation on toxic materials in electronic equipment has driven a shift to lead-free solder. Energy labeling of consumer durables focuses attention on designing more efficient products. Regulations on recycling of electronic equipment cause manufacturers to reconsider every material they use. At the UK centre for green chemical technology innovation, CRYSTAL has been taking lessons from green product design in other sectors and applying them to the chemistry-using industries. We have developed a process to identify opportunities for new environmental product benefits that meet market needs and will be commercially viable. It is integrated with a company's existing development processes, but encourages a different perspective on the value chain and product features. The presentation will include many examples of green product design, a practical approach to doing it and the strong links to life cycle assessment and sustainability metrics.

56. Improving IAQ in commercial buildings through alternative green solutions: TractionBack® and 180 Walls®

Joseph R. Royer¹ and Bill Gregory², (1)Milliken & Company, Spartanburg, SC, (2)Milliken Contract, LaGrange, GA

With a single pioneering green chemistry, Milliken & Company addressed one of the top five environmental health risks related to floor and wall coverings—indoor air quality (IAQ). To improve IAQ, research focused on eliminating on-site applied adhesives. The resulting adhesive-free installation system addresses the mechanisms to reduce effects of the three major classes of IAQ pollutants on building occupants in unique ways for each product. Bio-based TractionBack™ applies to the overall chemistry for the application and the patented high-friction coating used to keep carpet securely in place without the use of wet adhesives, floor sealers or primers during repeated installations. Modular carpet with TractionBack will not move laterally on the floor, but lifts vertically to access underfloor wiring, replace damaged tiles or change carpet to reconfigure the space. The ground-breaking technology offers multiple cost, time and environmental advantages. Through life cycle assessments, Milliken replaced selected petroleum-based components of the initial formulation with bio-based surrogates to further reduce its environmental impact. The second equally revolutionary product is a patent pending pressure sensitive wall covering, 180 Walls™, which hangs without paste using a proprietary water-based acrylic, experiences no wet movement, shrinkage or corner peel and can be removed years later without wall damage. Milliken introduced PVC-free carpet tile backings in 1986. Today 180 Walls™ provides an alternative to PVC-based vinyl wall coverings. Milliken remains dedicated to developing products and practices that rely on green chemistry to out-perform traditional non-sustainable solutions.

Abstracts, *Continued*

57. Invention and commercialization of environmentally smart thermosetting binders

Barry Weinstein¹, **Griffin Gappert**¹ and **Derek Bristol**², (1)Rohm and Haas Company, Spring House, PA, (2) Johns Manville, Littleton, CO

Thermosetting binders are used to impart shape, rigidity and communicative properties to nonwoven fibrous materials such as fiberglass insulation, ceiling tiles, air filters and particleboard. The most common thermosetting resins are century-old formaldehyde-based resin systems, including phenol-formaldehyde (PF), urea-formaldehyde (UF) and melamine-formaldehyde (MF). Aquaset™ technology offers an effective alternative and practical solution to many of the health, safety and environmental issues associated with use of formaldehyde-based resins. Aquaset technology is a complete redesign of existing thermoset binders, consisting of a simple but elegant combination of a polyol, polyacid and a hypophosphite catalyst to yield a rigid polyester network with water as the primary by-product. This chemical approach-by-design focuses on waste prevention rather than “end-of-pipe” clean-up. Rohm and Haas Company and Johns Manville collaboratively refined an Aquaset binder and adapted this water-based technology for the manufacture of fiberglass insulation. Since converting its entire line of building insulation products in 2002, Johns Manville has eliminated nearly 110 tons of formaldehyde emissions each year. In addition, phenol, methanol and ammonia emissions—common in the manufacture of formaldehyde-based resins—have been significantly reduced, if not completely eliminated. The development and implementation of environmentally smart Aquaset technology will be described.

58. Breakthrough synthetic-based drilling fluid system (SBF) improves environmental and technical performance

John A. Hall and Charles Mowrey, Halliburton, Houston, TX

The ACCOLADE® synthetic-based drilling fluid system was created to exceed EPA environmental criteria and is an entirely new, unique formulation. Results from system use show that ACCOLADE® meets or exceeds all applicable regulations governing discharge of cuttings generated with synthetic-based fluids (SBF) offshore Gulf of Mexico (GOM). Downhole mud losses normally associated with tripping, running casing, cementing and breaking circulation are reduced when compared to wells using traditional SBFs. The unique formulation of the ACCOLADE system results in less material required at the rig for fluid maintenance. This cutback translates into potentially fewer crane lifts, reduced transportation expense and less exposure of workers to potentially hazardous operations. Results show that the ACCOLADE synthetic-based drilling fluid meets or exceeds applicable environmental requirements and traditional performance standards because it contains no commercial clay or lignite additives. Rheological and fluid loss properties are controlled through the emulsion characteristics of the fluid. The base oil is an ester-internal olefin (IO) blend. The vegetable ester component of the base fluid makes the ACCOLADE system more biodegradable than conventional SBFs. The ACCOLADE system is characterized by desirable rheological properties over a range of temperatures from 40°F to 350°F, properties that provide unprecedented control over viscosity and equivalent circulating density (ECD). The fluid's gel strengths develop quickly but are fragile.

59. Decolorable toner e-blue

Sano Kenji, Satoshi Takayama, Takeshi Gotanda and Yumiko Sekiguchi, Toshiba Corporation, Kawasaki, Japan

The decolorable ink and toner e-blue consists of resin, dye colored by developer and eraser-reagent. The leuco dye is originally colorless dye usually used in thermal paper. In the decolorable toner and ink, colored leuco dye is used as well as the usual pigment of imaging material. The difference is the presence of eraser-reagent that traps developer in an erasing process. We can use decolorable toner e-blue as an ordinary toner and ballpoint pen of the decolorable ink for our office-work. After the use of the printed and hand-written manuscript, we can erase it in large volume like 500 sheets of paper at once by the heat eraser. Then, we can use the paper again and again. Our experiment shows that the paper consumption can be reduced by at least 60%. This means that we can save more than one half of wood resources, as compared to the usual toner. After the repeated use of the same paper with e-blue, handling damages the paper and the paper must be recycled in paper reclaiming plant. In addition to the office system, e-blue™ contributes to the reduction of resources like energy, detergent and water for the de-inking process, 60–70% resources in the plant. E-blue loses its color in alkali solution at the first process of the paper reclaiming plant. Therefore, e-blue can simplify the paper reclaiming plant. The technology, which we have achieved in toner, can be applicable to general ink for newspaper and other image forming materials.

Energy Posters

ORGANIZER: Green Chemistry Institute American Chemical Society, Washington, DC

60. Simulation study of soot oxidation in NO₂

Ruiqiang Liu, Xinhong Chen, C. Purushothama, **J.O. Chae** and Valentin Puchkov, Inha University, Incheon, South Korea

Based on the reaction mechanism of the continuous regeneration trap (CRT®) for diesel emissions control, an engineering simulation model of the soot oxidation by NO₂ in porous media was developed. In a comparatively low temperature range from 200 to 450 °C the heterogeneous reaction between diesel soot and NO₂ can be described in the kinetic regime. The kinetic model suggested and experimentally proved in the literatures were selected such as the reaction model based on simple carbon mass-based pseudo-first-order rate equations, the shrinking core model of carbon surface in Langmuir-Hinshelwood formalisms and the distributive model of porous media for the calculation of initial concentration of soot absorbed in the pores was also involved. This simulation model can predict the oxidation rate of soot in porous media in the form of carbon mass conversion and its dependence on temperature and parameters of the porous and the residence time of oxidant in porous media. The simulation results show that the soot removal rate of 45.2% can be achieved after about 2.5 hours at 600 K. By adding more detailed submodels to this simulation program, it may be modified to get a reasonable approach to the engineering application in the regeneration system of diesel particulate filter.

61. Generation of electricity and no excess sludge from wastewater by an activated sludge process integrated with a microbial fuel cell

Toshihide Kakizono, Sunao Mihara and Naomichi Nishio, Hiroshima University, Higashi-Hiroshima, Japan

Industrial and domestic wastewaters are treated by the activated sludge method, where a large volume of excess sludge should be formed as the inevitable by-product. With integrating the microbial fuel cell system to the water treatment system, it seems likely that less sludge could be generated because sludge can acquire less chemical energy from organic wastes due to the electricity generation. Thus, we have constructed a sludge-based microbial fuel cell fed with artificial wastewater to examine how excess sludge generation can be repressed after wastewater treatment. The microbial fuel cell consists of two identical reactors (650 ml) separated by a proton exchange membrane (non-halogenated carbon-based mono-cation exchange membrane, NeoSepta®, ASTOM Corporation); anode chamber contains sludge, artificial wastewater (glucose, peptone, K-phosphate), electron mediators (methylene blue, ubiquinone or menadione), phosphate buffer (10 mM, pH 7.0) and cathode chamber contains K ferricyanate and the buffer. Carbon paper (3x5 cm) was employed as the electrodes. To study the effect of electron mediators on electricity production, menadione seemed best among several dyes and quinones. The current density was maintained at 0.44 W/m²-anode during batch-wise water treatment. With the addition of menadione, moreover, sludge concentration was found nearly 50% less than that of the initial sludge concentration after completing wastewater treatment, whereas no mediator condition as the control generated 10% more sludge concentration. Thus, it was demonstrated that with integrating microbial fuel cell to part of the current treatment system, zero emission of excess sludge seems feasible.

62. Towards the development of a chitosan membrane for enzyme immobilization

Tamara Klotzbach, Michelle Watt and Shelley D. Minteer, Saint Louis University, St. Louis, MO

Previous research has examined the use of hydrophobically modified Nafion® to modify electrodes for the application to biofuel cells. Biofuel cells are of interest as biodegradable energy sources because they employ biocatalysts such as enzymes instead of heavy metals to catalyze an electrochemical reaction. This research details the first use of hydrophobically modified chitosan to modify electrode surfaces. Chitosan was modified by reacting it with a saturated alkyl aldehyde, allowing the polymer to form micelles. The modified chitosan was resuspended in a 1% by weight mixture in t-amyl alcohol, chloroform or 50% aqueous acetic acid. Nafion® was modified by mixture casting Nafion® with alkyl trimethyl ammonium bromide salts and resuspended as a 5% by weight mixture in ethanol. It was shown that by hydrophobically modifying chitosan and Nafion®, the polymers form micelles and the transport properties of redox species to the electrode surface are altered as a function of size and charge. Micellar polymers are also known to provide a stable environment for the immobilization of enzymes. Fluorescence microscopic assays and cyclic voltammetry were used to determine the optimal modified polymer for effective enzyme immobilization. Enzyme immobilization was carried out with aldehyde, formate and glucose dehydrogenases. Results show that enzymes can be successfully immobilized and will retain their activity in modified chitosan and Nafion® polymers.

63. Tide Coldwater: Energy conservation through residential laundering innovation and commercialization

Darius Sabaliunas, The Procter & Gamble Company, Cincinnati, OH

A break-through chemical innovation in environmentally-friendly cleaning technology has recently been commercialized in the U.S. to provide superior cleaning and significant energy savings under low temperature washing conditions. Tide Coldwater® has been used by over 6 million U.S. households since its introduction in North America in January, 2005. Tide Coldwater® uses more hydrophobic surfactant systems based on proprietary technologies that in combination with unique bleach activator, builder/chelant, soil suspension, enzyme and brightener systems deliver superior cleaning performance in cold water. Tide Coldwater® has been shown to provide superior cleaning under coldwater conditions relative to detergents formulated for warm- and hot-water conditions. Without sacrificing performance in stain removal or whitening, consumers can realize significantly reduced home energy costs (up to \$63 per year) and, at the same time, reduce greenhouse gas emissions from fossil-fueled power plants. Through a peer-reviewed residential energy use model, Tide Coldwater® has been estimated to reduce the fraction of residential energy used to heat water by up to 26–36%, with associated reductions in carbon dioxide emissions of up to 1,259 pounds per household per year. The potential roll-up benefits of this innovation are significant — if everyone switched to cold water, the potential energy savings in the U.S. would be 70–90 billion kWh per year, representing up to 3% of the nation's energy consumption. When converted into carbon dioxide equivalents, these savings amount to 26–34 million tons of CO₂ per year, representing over 8% of the CO₂ reduction target for the U.S. set in the Kyoto protocol.

Agriculture & Foods Posters

64. Stoller's Root Feed enhances crop root growth, crop productivity and stress tolerance

Albert Liptay, Jerry H. Stoller and Ron A. Salzman, Stoller Enterprises Inc, Houston, TX

Stoller's Root Feed is a proprietary crop health product that was formulated to improve crop productivity and crop quality. Root Feed-treated crops give higher numbers of fruit or seed and therefore make more efficient use of fertilizer and thus decrease nutrient pollution of the environment. Root Feed has been used on a number of different crops such as vegetables, fruit trees, nut trees and various other tropical crops. Stoller's Root Feed is applied to the roots of the crop plant which are the "control center", *i.e.*, the "brains" of the plant. Root Feed is delivered directly to the roots with drip irrigation, the most efficient and water-saving way of irrigating crops, for maximum crop management and performance. Crops treated with Root Feed are better developed, appear healthier and serendipitously were found to be more tolerant to virus, fungal, bacterial and insect infestation. Moreover Root Feed suppressed nematodes for more effective crop production and quality. Root Feed-treated crops have better quality and better shelf life. Root Feed gives crop plants more abiotic and biotic stress tolerance in addition to improving yield and crop quality.

Abstracts, Continued

65. Alternatives to azinphos methyl in apples

Benjamin Newton, The Evergreen State College, Olympia, WA

Each year more than 100,000 migrant and seasonal farm workers plant, nurture, harvest and pack apples, potatoes and other crops in Washington State. Their work supports one of the region's agricultural industries and supplies food for people in Washington State and beyond. Workers and their families pay an unacceptable price for the important work they do. Workers who regularly handle neurotoxic pesticides, such as azinphos methyl (guthion), are acutely exposed on a daily basis. Azinphos methyl has been banned for use on many crops. It continues to be used on apples and other small crops in Washington State due to an exception from beneficial use by the Environmental Protection Agency (EPA). Currently the registration of azinphos methyl is under review after a four year interim period. The major concern for human health is the inhibition of acetylcholinesterase. The inhibition of acetylcholinesterase results in continual stimulation of electrical impulses. There are many symptoms associated with this inhibition. The major sites affected include the central nervous system, skeletal muscles, cardiovascular system, respiratory tract and gastrointestinal tract. Although some of these symptoms are reversible over time, they result in symptoms that cause many problems in performing simple everyday tasks. Alternatives to the use of azinphos methyl are currently available and need to be implemented immediately. A complete phase out of azinphos methyl is the aim of this presentation for a healthier agricultural community and food products.

66. Organic farming: A need for sustainable agriculture

Pramila Maini, Institute For Excellence In Higher Education, Bhopal, India

To meet our increasing demand for food we have been resorting to intensive cultivation practices with the use of fertilizers, pesticides, fungicides and other inputs. Use of these inputs has polluted our soil, water and environment and has caused slow degradation of soil health thereby resulting in decreasing yield. Therefore, there is a need to sustain the production and improve the soil health by organic farming. Organic farming aims at cultivating the land and raising crops in such a way as to keep the soil alive and in good health. For organic farming the following methods should be given priority: 1. Organic matter recycling. 2. Biofertilizer as a source of nutrition. 3. Intercropping and mixed cropping. 4. Crop rotation. 5. Integrated pest management. 6. Integrated nutrient management. 7. Water management. Organic farming will check soil degradation, underground water pollution, high occurrence of hazardous chemicals in food, sustain production and improve soil health without affecting crop production.

67. Fungal diseases of sweet potatoes

(*Ipomoea batatas*)

Mojeed Oladapo Oyewale, The Osun State Polytechnic, Iree, Osogbo, NY, Nigeria

Economics losses during production and storage of sweet potatoes (*Ipomoea batatas*) L. Lam are classified into tuber and foliar diseases. These tuber diseases include mortierella rots, rhizopus rots, mucor rots, greymold rots, slimy rots and dirty rots usually associated with post-harvest losses while the foliar diseases include cercospora leaf spot, septoria leaf spot and powdery mildew which are associated with preharvest losses. The principal fungi associated with post-harvest diseases includes *Mortierella ramanniana*, *Rhizopus stolonifer*, *Mucor pusillus*, *Botrytis cinerea*, *Erysiphe polygoni* and *Aspergillus flavus*, while *Cercospora ipomoea*, *Septoria batatas* and *Erysiphe polygoni* are responsible for preharvest losses. Environmental factors such as temperatures have a significant influence on the rate of deterioration; it was concluded that increase in incubation temperatures enhances rotting by the various fungal isolates. *Mucor pusillus* exhibits a linear measurement of 3.6 cm at 30 °C, while *Rhizopus stolonifer* and

Botrytis cinerea produced a linear measurement of 2.9 cm and 4.2 cm at 35 °C while storage of inoculated tubers at freezing temperatures reduces tuber deterioration. Aflatoxins were produced by *Aspergillus flavus* growing on infected dried leaves of sweet potatoes; these mycotoxins were detected to be *Aspergilliacids*, which are soluble in dilute acids, bases, alcohols, acetone, benzene and chloroform, but insoluble in water. Spectral analysis revealed the biodegradation of carbohydrates, proteins and lipids into simpler forms during the growth of various fungi on sweet potatoes, producing carbon IV oxides as end products.

68. Agriculture waste utilization in Madhya Pradesh: A case study

Monika Vishwakarma, NRI Institute of Information, Science & Technology, Bhopal (Affiliated to RG TU, Bhopal), Bhopal, India

In a developing country like India, the whole economy is based on agriculture. Besides this, due to the population explosion, it has become necessary to increase productivity of crops in order to feed one billion people. With the advent in technology, several other problems are posed among which utilization of agrowaste is a teething problem. A lot of toxic components like pesticides and insecticides are coming out with organic waste. A study has been done in Bhopal, state capital of Madhya Pradesh, India, and surrounding areas. Steps were taken to study the conversion of all forms of vegetable and animal wastes into organic matter suitable for the needs of the growing crop and to simplify the process by which the Indian cultivator could prepare an adequate supply of this material from the by-products of their own crop. Besides this, a treatment for washings is also suggested in order to reduce the toxic effects of chemicals used on crops.

Resources & Renewables Posters

69. Synthesis of monofunctionalized cyclodextrin polymers for the removal of organic pollutants from water

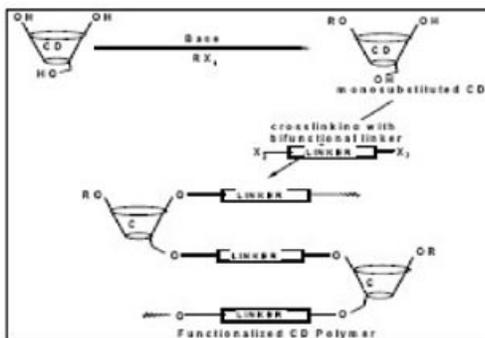
Bhekia B. Mamba, Rui W.M. Krause, Tshepo J. Malefetshe and Edward N. Nxumalo, University of Johannesburg, Doornfontein, South Africa

Cyclodextrins (CDs), basically starch derivatives, are biosynthetic cyclic oligomers consisting of anhydrous glucopyranosyl units linked together through α -1,4-glycosidic linkages¹. They behave as molecular hosts capable of interacting with a range of guest molecules in a noncovalent manner within their cylindrical hydrophobic cavities². These interactions are a basis for the inclusion of various organic species; however, the high solubility of cyclodextrins limits their application in the removal of organic pollutants from water. To make them insoluble, we have converted them into highly crosslinked polymers by polymerizing them with suitable difunctional linkers³. Several monosubstituted CD polymers or "nanosponges" (which are insoluble in water), with an enhanced ability to quench organic contaminants from water to acceptable levels, have been synthesized and successfully characterized. The process entails functionalizing the primary hydroxyls of the parent CD compound followed by crosslinking with a suitable linker to give the desired nanoporous polymer as shown in Scheme 1. It was anticipated that by monofunctionalizing the polymers, there would also be an increase in the surface area of the produced polymers. The polymers obtained have demonstrated great capabilities in removing phenolic compounds from an aqueous medium. The degree of absorption was quantified and measured using UV-visible spectrophotometer and GC-MS analysis.

1. Bender, M.L. and Komiya, M. *Cyclodextrin Chemistry*. Springer Verlag: New York, 1978.

2. Wenz, G. and Thomas, H. *Carbohydrate Research*, 322 1999, 153.

3. Li, D.Q. and Ma, M. *Chemtech*, 5 1999, 31.



Scheme 1: A general synthetic pathway for a monofunctionalized CD polymer

70. Bio-gas plant slurry and its application

Neena V. Arora, Sri Sathya Sai College For Women, Bhopal, India

The slurry coming out of the bio-gas plant is rich in nitrogen, phosphorus, potassium and several trace elements. It also contains vitamins and amino-acids. An experiment was conducted in which animal feed was prepared with the incorporation of bio-gas plant spent slurry to feed 15 lactating cows for two months. After an adoption period, daily milk production was recorded for 30 days. Quality of milk was estimated by estimating milk protein and fat content. The study reveals that production and quality of milk can be improved by 15% by the incorporation of 25% bio-gas plant spent slurry in animal feed.

71. TiO₂-photocatalyzed As(III) oxidation in a fixed-bed, flow-through reactor

Megan A. Ferguson and Janet G. Hering, California Institute of Technology, Pasadena, CA

The new U.S. drinking water standard for arsenic (As) requires thousands of water suppliers to implement treatment technologies for As removal. Although a variety of such technologies is available, most require pre-oxidation of As(III) to As(V) for efficient performance. Previous batch studies with illuminated TiO₂ slurries have demonstrated that TiO₂-photocatalyzed As(III) oxidation occurs rapidly. This study examined reaction efficiency in a flow-through, fixed-bed reactor that provides a better model for treatment in practice. Glass beads were coated with mixed P25/sol gel TiO₂ and employed in an upflow reactor irradiated from above. The reactor residence time, influent As(III) concentration, number of TiO₂ coatings on the beads, solution matrix and light source were varied to characterize this reaction and determine its feasibility for water treatment. Repeated usage of the same beads in multiple experiments or extended use was found to affect effluent As(V) concentrations but not the steady-state effluent As(III) concentration, which suggests that As(III) oxidation at the TiO₂ surface undergoes dynamic sorption equilibration. Catalyst poisoning was not observed either from As(V) or from competitively adsorbing anions, although the higher steady-state effluent As(III) concentrations in synthetic groundwater compared to 5 mM NaNO₃ indicated that competitive sorbates in the matrix partially hinder the reaction. Limitations to the efficiency of As(III) oxidation in the fixed-bed reactor were attributable to constraints of the reactor geometry, which could be easily overcome by improved design. The fixed-bed TiO₂ reactor offers an environmentally benign method for As(III) oxidation.

72. Novel enzymatic synthesis and properties of aliphatic polythioester

Makoto Kato, Kazunobu Toshima and Shuichi Matsumura, Keio University, Yokohama-shi, Japan

Polymers containing thioester linkages in their backbone, "polythioesters" have recently attracted attention as novel polymers due to their interesting characteristics, such as poor solubility against organic solvents and higher heat stability when compared to polyoxyesters. However, no commercial production of the polythioesters has yet been established due to the complex preparation method. In this report, a novel synthesis of polythioester using an enzyme was studied. The enzyme-catalyzed polymerization may become one of the environmentally benign methods that meets the green chemistry requirements, since no hazardous substances will be used or generated. It is also an attractive method since polythioesters with relatively various molecular structures can be prepared when compared to the fermentation method. Polythioesters were synthesized by the direct polycondensation of 1,6-hexanedithiol and diacid diesters with a variety of methylene lengths using lipase CA as a catalyst. The obtained polythioesters showed a higher melting temperature (T_m) and crystallization temperature (T_c) compared to those of the corresponding polyoxyesters. The polythioesters were degraded by lipase CA in diluted condition using *n*-nonane to obtain cyclic thiolactone oligomers. These cyclic oligomers were readily polymerized by lipase CA into the corresponding polythioesters having a higher molecular weight of about 120,000. These results suggested that chemical recycling of polythioester using lipase CA can be established. The biodegradability of polythioesters was also studied. Several polythioester-assimilating microbes were isolated from culture broth containing polythioester as a sole carbon source. It can be expected that the novel polythioesters show biodegradability.

73. Abstract Withdrawn

74. Visible light photocatalysis with platinumized titanium dioxide for water treatment

Wenbing Li and Tingying Zeng, Western Kentucky University, Bowling Green, KY

Titanium dioxide samples containing varying concentrations of platinum were synthesized using titanium tetrachloride as the starting material by a modified sol-gel method. Photocatalytic activities were established for water treatment under visible light. XRD reveals that platinum clusters segregate on the surface of titanium dioxide with increasing platinum contents. The presence of platinum in the titanium dioxide samples was found to improve the performance of the photocatalyst. The effect may be attributed to a spillover mechanism that supplies oxygen to the titanium dioxide surface.

Abstracts, Continued

75. Thermal properties of poly(L-lactic acid) ionomers synthesized from chemical recycling

Andrew J. Ro, Robert A. Weiss and Samuel J. Huang, University of Connecticut, Storrs Mansfield, CT

A carboxylic acid-terminated poly(L-lactic acid) (PLLA) was synthesized by processes of chemical recycling and esterification with itaconic anhydride. Functionalization was confirmed by FT-IR and ¹H-NMR studies. The telechelic polymers were used to make sodium, calcium and yttrium ionomers. The ionomers exhibited higher thermal degradation temperatures than the neat telechelic PLLA. Differential scanning calorimetry (DSC) studies showed an increase in glass transition temperature (T_g) upon ionomerization of the telechelic PLLA. A lower crystallization temperature (T_c) and degree of crystallinity (X_c) were observed for the sodium and yttrium ionomers and higher T_c and X_c values were observed for the calcium ionomer. The varying crystallization behavior is due to the coordination of the telechelic polymer to the metal.

76. Scope and principles of green chemistry and engineering

Anil K. Sharma, Mississippi Valley State University, Itta Bena, MS

Chemistry and engineering are used in all walks of life. They are used in the production of all man-made materials from medicines to cleaning products. When some chemicals are made, more wasteful products are produced than useful. This results in money being lost through finding ways to get rid of or treat the waste. The waste could enter bodies of water or the air causing serious damage to organisms. Chemical substances were not looked at as a threat until 1960. In later years several command and control laws were instituted. These laws deal with correcting the problem after it has occurred. Green chemistry and engineering's purpose is to prevent the pollution problem before it starts. Green chemistry and engineering is defined as "the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products." There are twelve principles of green chemistry and engineering and they are: prevention, atom economy, less hazardous chemical synthesis, designing safer chemicals, safer solvents and auxiliaries, design for energy efficiency, use of renewable feed stocks, reduce derivatives, catalysis, design for degradation, real time analysis for pollution prevention and inherently safer chemistry and engineering for accident prevention. These twelve principles give the whole scope of green chemistry and engineering. Today green chemistry and engineering is being explored constantly. The world could be a cleaner and much safer place if green chemistry and engineering techniques were put into play for all actions everywhere.

77. Abstract Withdrawn

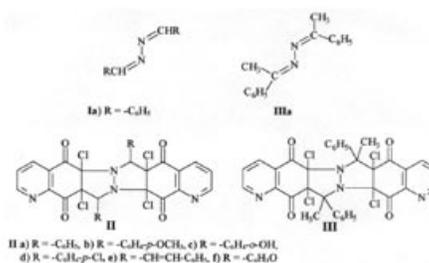
78. Synthesis of some new bispyrrolidine derivatives for biological interest

Amal Sabet Yanni, Assiut University, Assiut, 71516, Egypt

Representatives of this system belong to a class of biological active compounds and, at the same time, are excellent starting materials for developing a new type of biological active compounds. Interaction of two molecules of 6,7-dichloroquinoline-5,8-quinone with one molecule of benzalazine (Ia) in benzene afforded the adduct (IIa) through crisscross reaction 1,2,3,4. The reaction was extended with other arylidenazines (Ib-f), such as anisalazine, *p*-chlorobenzalazine, *o*-hydroxybenzalazine, cinnamalazine and/or furfuralazine afforded (IIb-f). On using acetophenonazine (IIIa) in the above reaction, the adduct III was obtained. The structure of these compounds has been ascertained by elemental and spectral analysis. The processes for obtaining the title compounds reduce the use and generation of hazardous substances.

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3. Amal Sabet Yanni, 16th International Conference on Physical Organic Chemistry, San Diego, CA, August 4-9 (2002).
4. Amal Sabet Yanni, Polymer Networks 2004 Conference, August 15-19, Bethesda, Maryland, USA.



Toxics & Materials Posters

79. Production of recombinant human gelatin in transgenic rice cell cultures

Corey N. Dodge¹, Karen A. McDonald¹, Julio Baez² and Mysore Sudarshana¹, (1)University of California, Davis, Davis, CA, (2)Fibrogen Inc, South San Francisco, CA

Bovine-derived gelatin is used extensively in the manufacturing of pharmaceutical capsules; however, the intrinsic variability and safety concerns have prompted the development of recombinant production technologies. Transgenic plants can provide an attractive technology for the production of low cost/high volume industrial proteins such as gelatin. We are developing plant cell culture as a complementary technology to transgenic plants for the fast evaluation of plant-derived industrial recombinant proteins. Stably transformed rice cell lines were generated containing a plant codon optimized gene coding for a fragment of human $\alpha(1)$ -I collagen (100 kDa rGelatin) and a rice α -amylase secretion signal peptide under the control of a constitutive maize ubiquitin promoter. Transgenic rice cell cultures were scaled up for production in a 3L bioreactor culture. The maximum extracellular gelatin concentration, as measured by ELISA, was 170 μ g/L at 11 days, corresponding to 0.5% of the total extracellular protein. The rGelatin was positively identified by immunoblot following SDS PAGE. Future work will focus on improving bioreactor productivity, improving product quality and introducing human-like proline hydroxylation of rGelatin through metabolic engineering of the rice cell host.

80. Protein-transition metal ion networks

Justin Barone¹, Kirsten Danganan² and Sylvia Chin¹, (1)U.S. Department of Agriculture, Beltsville, MD, (2)U.S. Department of Agriculture, Wyndmoor, PA

Proteins obtained from agricultural sources were blended with divalent metal ions. Feather keratin, egg albumin and wheat gluten had low, medium and high levels of aspartic and glutamic acid, respectively, and FT-IR showed that the divalent transition metal ions Mn^{+2} , Cu^{+2} and Zn^{+2} were tightly bound to the proteins at least at the secondary acid sites. Birefringence experiments performed concurrently with tensile experiments showed refractive index changes indicative of network formation. This resulted in a 3–4 times increase in stiffness. Increasing concentrations of ions resulted in increased stiffness. Binding divalent Ca^{+2} ions did not result in the same increase. Addition of Zn^{+2} to egg albumin resulted in a 34% decrease in water permeability but no change in oxygen permeability.

81. Analyzing the “greenness” of analytical methods

Rajender K. Brahma¹, Jennifer L. Young¹, Paul T. Anastas¹ and Larry Keith², (1)Green Chemistry Institute, Washington, DC, (2)Instant Reference Sources, Inc., Monroe, GA

Selecting appropriate analytical methods for analyzing environmental samples is critical and can be complex. Many methods are themselves not benign to the environment, using hazardous chemical reagents and requiring significant amount of solvents, which may be volatile, toxic or contribute to global warming. The American Chemical Society's Green Chemistry Institute (GCI) is actively involved in identifying and promoting analytical methods that minimize pollution. GCI is working to accomplish this objective using the National Environmental Methods Index (NEMI; www.nemi.gov). NEMI is a database of over 800 methods for environmental testing. GCI is extracting specific data on chemical use and waste generation from all of the full analytical methods currently in NEMI. After applying “greenness” rating rules to this data, the “greenness” rating information is put back into NEMI. As a result, when multiple methods in NEMI are evaluated, the methods' performance criteria and “greenness” ratings can be easily identified and compared.

82. Polyaspartic acid as a cleaning agent for calcite and barite deposits

Christine S. Grant and **Jonathan Braxton**, North Carolina State University, Raleigh, NC

Due to low solubility at high temperatures, mineral salts such as $BaSO_4$, $CaPO_4$ and $CaSO_4$ form deposits which cause cleaning problems in a number of areas. The scaling and fouling of process machinery and piping reduce the overall production efficiency in the dairy and oil production industries. Organic agents have been used as replacements for both hydrochloric/sulfuric acids and more toxic inorganics in the dissolution of both calcite and calcium containing minerals. Chelating agents have arisen as an environmentally friendly alternative to other organic cleaners such as phosphates and polyacrylates. Sodium polyaspartate has been found to enhance the removal of HAP/DCPD deposits from stainless steel during turbulent flow under alkaline conditions. Research by our group demonstrated the environmentally benign polymer polyaspartic acid (PASP) as a possible cleaning agent for calcium-based deposits. The results of calcium mineral experiments can be extended to barium compounds. This study seeks to determine the mechanism of PASP attack on $BaSO_4$ and the optimum operating conditions to increase the dissolution of scaling minerals in industrial processes. Controlled mass transfer rotating disk and batch dissolution experiments provide both kinetic rate and chemical information. The function of polymer concentration, pH and polymer molecular weight

on the dissolution of naturally occurring barite is investigated. Atomic absorption (AA) spectroscopy determines mineral dissolution rates through evaluation of the bulk liquid. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) provide insight into morphological changes of polished surfaces due to interfacial interactions of PASP with $BaSO_4$.

83. New family of iron-centered tetra-amido macrocyclic ligand complexes

William C. Ellis, Colin P. Horwitz and Terrence J. Collins, Carnegie Mellon University, Pittsburgh, PA

Modern society depends on oxidation chemistry for commodity chemicals and industrial processes. Due to its necessity and production volume, oxidation chemistry should be a priority for the application of green chemistry on a large scale. The Institute for Green Oxidation Chemistry has developed and studied one family of iron-centered tetra-amido macrocyclic ligand complexes (Fe-TAMLs[®]), which activates hydrogen peroxide in aqueous conditions. A correlation between Fe-TAML[®] reactivity and ligand electron donor capacity at the amide nitrogen has been established. Using this trend as a design guideline, a new family of Fe-TAML complexes has been synthesized in the hope of attaining high reactivity without the use of halogen substituents to better adhere to the principles of green design. This new family uses phenyl groups to bridge an oxalamide and a malonamide. Rationale, synthesis and characterization will be presented here as well as development of the reactivity trend within this new family of macrocyclic ligands.

84. Mechanochemistry for the reduction of solvent waste

Dennis A. Fulmer, University of Cincinnati, Cincinnati, OH

In an era of increasing concern about environmental pollution due to chemical processes, scientists have determined a need for addressing this issue. Our research objectives are to determine the viability of solid state reactions that are currently carried out in the presence of environmentally harmful solvents. High speed vibrational milling (HSVM) is a method which has proven to be successful in various solid state reactions, such as the Wittig reaction. HSVM is expected to be a process which pioneers the further development of solid state chemistry. Currently being explored is the increased reactivity of carbonyls in the solid state, thus allowing the use of a milder reducing agent such as sodium borohydride. Also being investigated is the change in isomeric ratio of products in the Wittig reaction due to the HSVM process.

85. Extraction of metal ions using surface-modified silica gel: A greener analytical method

Bhagwan S. Garg and R.K. Sharma, University of Delhi, Delhi, India

Accurate analysis of metal ion samples especially at trace levels is one of the most difficult and complicated analytical tasks. Also, the direct analytical methods for metal determination such as AAS, ICP-AES, neutron activation analysis, etc. suffer from serious matrix interferences and contamination problems. To obtain reliable data, the best course is to separate the analytes of interest from the matrix constituents and determine them in an isolated state. Separation of metal ions is usually carried out by liquid-liquid extraction. This method is environmental unfriendly and also uneconomical because it is time consuming, involves several steps and employs large amounts of toxic solvents so the renewal of this method is highly desirable. We have developed a simple, rapid, accurate, precise, reliable and green analytical method for the extraction of metal ions using surface modified silica gel chelating resins^{1,2}. Use of carcinogenic organic solvents and other

Abstracts, Continued

reagents is avoided, and, thus, it is a green analytical method and also highly economic as the resin can be regenerated and reused¹.

1. R.K. Sharma, Sachin Mittal and M. Koel. Analysis of trace amounts of metal ions using silica-based chelating resins: A green analytical method. *Critical Reviews in Analytical Chemistry*, 33, 2003, 183-197.

2. R.K. Sharma. Designing, synthesis and application of chelating polymer for separation and determination of trace and toxic metal ions: A green analytical method. *Pure Appl. Chem.*, 73, 2001, 181-186.

86. Magnesium hydroxide from mineral source as benign flame retardant for paper and polymers

Iara F. Gimenez, Charlene R. S. Matos, Francys K. V. Moreira and Ledjane S. Barreto, UFS, São Cristóvão, Brazil

In this work morphologically controlled Mg(OH)₂ was precipitated under hydrothermal conditions from carnallite (KCl·MgCl₂·6H₂O), an abundant mineral from Sergipe State (Brazil). Most of the flame retardants already in use are based on halogenated compounds, which are potentially harmful both to living beings and to the environment. In this context Mg(OH)₂ has been proposed as a good candidate for replacement of conventional flame retardants since it is non-toxic and its thermal decomposition yields only water and MgO. It has been described that Mg(OH)₂ amounts higher than 60% are necessary in order to provide a satisfactory retardant effect. In the present work we studied the effect of Mg(OH)₂ in two different composites. First Mg(OH)₂ was mixed with commercial PMMA (poly(methylmethacrylate)) by sonication in acetone solution in the proportions 5%, 10%, 30% and 70%, followed by solvent evaporation. The composite with paper was prepared by mixing Mg(OH)₂ with cellulose pulp extracted from coconut shell wastes in a proper mixer in proportions of 10%, 30% and 70%, followed by sheet formation and drying under vacuum. The composites were characterized by scanning electron microscopy and thermal analysis (TGA and DSC) for the study of decomposition kinetics. From thermal analysis it was observed that in both composites the presence of Mg(OH)₂ increases the initial decomposition temperature by up to 80 °C even when present in small proportions without changing the decomposition mechanisms, indicating that an intimate dispersion of submicrometric Mg(OH)₂ particles enables the reduction of the retardant amount.

87. Natural biosensor-based assay for the efficient screening of complex mixtures

Gerald T. Gourdin, Sheryl M. Verbitski, Larissa M. Ikenouye and James D. McChesney, ChromaDex Analytics, Boulder, CO

The bioluminescence assay is a unique biosensor method that directly couples natural bioluminescence to thin-layer chromatography (TLC). This rapid assay can be used to support material identity, detect toxins and chemical adulterations, identify potential bioactive compounds and monitor manufacturing processes. TLC has traditionally been used as a reliable and economical analytical technique for the simultaneous separation of multiple samples using a minimum of harsh chemicals or solvents. A developed TLC plate is then coated with the non-pathogenic, bioluminescent marine bacteria *Vibrio fischeri*. Compounds that interfere with the metabolic process of the bacteria inhibit bioluminescence and are, therefore, detected as contrasting dark spots on the luminescent background of the TLC plate. Activity is measured by a reduction in light emission of the bacteria producing a toxicity pattern characteristic of each analyzed sample that can be viewed and quantitated directly on the TLC plate. Results occur within minutes and can be documented photographically (CCD camera, x-ray, Polaroid or 35 mm film). This technology has been developed into a kit system that provides an effective means of pre-screening a variety of complex mixtures in order to minimize the use of environmentally costly conventional methods.

88. Abstract Withdrawn

89. New amino acid-based surfactants for carbon dioxide

Hakwon Kim, Younja Kwon, Yeonju Kim, Daeil Bae, Hongdoo Kim and Kwangheon Park, Kyung Hee University, Yongin, South Korea

The vast potential of carbon dioxide (CO₂) as an environmentally benign, clean, abundant and tunable solvent has been realized on a variety of fronts, including cleaning protocols in microelectronics and garment care industries, coatings and polymer production and processing. To take advantages of CO₂ benefits, however, it is often necessary to confront an important limitation, namely its low capacity for solubilizing many materials, including water and water-only-soluble material. Here, we report our recent finding on relatively non-toxic amino acid derivatives (for example, glycine, proline and aspartic acid derivatives, etc.) as a CO₂-soluble surfactant that enables significant water uptake within a continuous CO₂ phase, through the formation of W/C microemulsions without the aid of a co-surfactant. Most of our newly synthesized surfactants proved soluble at mild condition (cloud points at 40 °C occurred at below 150 bar). Also, it was observed that addition of water to some CO₂-soluble amino acid surfactants allowed for the formation of a clear, single-phase solution. We have been undertaking an analysis of the existing data to account for the relationship between structure and property and have tried to apply this surfactant to metal extraction, decoupling and synthesis of nanoparticle in scCO₂.

90. Facile "green" synthesis, characterization and catalytic function of β-D glucose-stabilized Au nanocrystals

Juncheng Liu¹, Gaowu Qin², Yutaka Ikushima² and Christopher B. Roberts¹, (1)Auburn University, Auburn, AL, (2)National Institute of Advanced Industrial Science and Technology, Sendai, Japan

Integration of "green chemistry" principles into nanotechnology is one of the key issues in nanoscience research today. Utilization of cheap and nontoxic chemicals, environmentally benign solvents and renewable materials are some of the pivotal issues in the nanomaterials science field considering "green" synthetic strategy and industrial scale manufacture. It is well known that the reaction medium, reducing agent (RA) and capping agent (CA) are three key factors for the synthesis and stabilization of the metal nanoparticles; these factors should be considered comprehensively from economic and "green" chemistry perspectives. Most of the synthetic procedures reported rely heavily on organic solvents (mainly due to the hydrophobicity of the CA used), thus inevitably resulting in a serious environmental issue while addressing industrial production. Herein, we present a facile, economically viable and "green" approach for the synthesis and stabilization of relatively monodisperse Au nanocrystals with an average diameter of 8.2 nm (σ=2.3 nm) using nontoxic and renewable biochemical β-D glucose and simply adjusting pH environment in aqueous medium. The β-D glucose acts both as CA and RA for the synthesis and stabilization of the Au nanocrystals in the system. The UV-vis spectroscopy, FT-IR spectroscopy, TEM, electron diffraction and X-ray diffraction techniques were employed to systematically characterize the Au nanocrystals synthesized. Additionally, it is shown that these β-D glucose-stabilized Au nanocrystals function as an effective catalyst for the reduction of 4-nitrophenol in the presence of NaBH₄ (otherwise unfeasible if only the strong reducing agent NaBH₄ is employed), which was reflected by the catalytic reaction kinetics.

91. Surge of green: A proposed sustainable approach to conductive polymers

Bethany A. Masten and Edward J. Brush, Bridgewater State College, Bridgewater, MA

Polymers capable of carrying an electric current are already in use by the electronics industry and are theorized to have widespread applications, such as electronic newsprint. Currently, the most abundant commercial conductive plastic is polyaniline. This material is synthesized from aniline, a non-renewable feedstock obtained from our valuable and dwindling petroleum resources. Aniline is also problematic in that it is a hazardous chemical material with documented health risks. End-of-life disposal problems are also relevant to polyaniline, which is not easily reclaimed. Before the commercial production and use of this class of conductive plastics becomes more widespread, it is critical that an environmentally sound alternative be found. The goal of this project is to apply green and sustainable chemistry (GSC) principles to investigate a new and unique class of potential conductive polymers based on the naturally-occurring and renewable group of chemicals known as indoles. I will employ GSC methods involving hydrogen peroxide and enzyme catalysts to make indole-based polymers and employ molecular templates to direct the synthesis of linear chains, therefore improving their conductivity. New templates derived from renewable resources will also be evaluated, including DNA and other polyanionic species. Polymer products will be characterized with UV-vis and IR spectroscopy and conductivity using a four-point probe. This project is funded through a Shea Scholar Award, the Adrian Tinsley Program for Undergraduate Research and the Bridgewater State College Foundation.

92. Toxicity of selected room-temperature ionic liquids to industrial wastewater treatment bacteria

Maria A. Azimova and **Samuel A. Morton III**, Lafayette College, Easton, PA

Ionic liquids are negligibly-volatile, thermally stable organic compounds with a wide array of potential applications in industrial processes. Many of the useful properties of ionic liquids, such as high polarity, varying degrees of solubility in organic compounds, significant electrical conductivity, thermal stability and negligible vapor pressure, support their use as replacement solvents and/or catalysts for many synthetic reactions. Due to the potential wide-spread use of the ionic liquids, the question of their environmental impact has been a pressing matter for several years. It is, therefore, important to assess the effects of ionic liquids on the common wastewater treatment bacteria. The reason for this is two-fold: (1) based on this information, disposal techniques for ionic liquids can be developed and (2) the impacts of an ionic liquid release from a process upset can be designed into normal wastewater treatment systems. Toxicity data was obtained for a selection of common room-temperature ionic liquids and correlated to the octanol-water partition coefficients present in the literature as well as evaluated experimentally. The work presented in this paper shows that ionic liquids have been observed to exhibit levels of toxicity consistent with common organic solvents. The understanding of the potential toxicity of these ionic liquids can be used to drive development of effective treatment and/or mitigation strategies that will allow for their industrial use while maintaining the integrity of industrial wastewater treatment systems.

93. Green chemistry approach for the removal of heavy metal ions from industrial waste land

R. K. Sharma¹, **Parul Pant**¹, Shuchi Dhingra¹ and Alok Adholeya², (1)University of Delhi, Delhi-110007, India, (2)The Energy and Resources Institute, New Delhi –110003, India

Contamination of the ecosystem with a diverse range of metal wastes due to various human activities has been a concern over the years. Major sources of heavy metals in the environment include metallurgical plant waste, metal fabrication, paints and pigments, as well as the manufacture of batteries. The major problem is the removal of these contaminants in an eco-friendly way. This problem can be overcome by either physically removing them or by immobilizing them. Biomining of the contaminated sites appears to be the best suited technique for the purpose. Biomining involves the usage of metal hyper-accumulator plants, which have the capability to accumulate and tolerate high concentrations of metal ions. With such loads of metal accumulated in plants, extraction of these metal ions for their reuse in pure and commercial forms also poses a great challenge. In our laboratory we have been designing chelating resins, which work on the methodology of removal of metal ions by using chelating resins¹. Presently, our group is working on a collaborative project "Bio-extraction of Chromium from plants and microbes and formulation development of useful microbes as bio-package for cleaning and reclamation: Field demonstration of bio-package on Tannery effluent affected sites" funded by the Department of Biotechnology, Government of India. The entire work is not just eco-friendly but also there is valuable addition due to the extraction of metal ions from the plants.

[1] R.K.Sharma, Sachin Mittal and Mikhel Koel; *Critical Reviews in Analytical Chemistry*, 33(3):183-197, (2003).

94. Transient and steady-state kinetic studies of Fe^{III}-TAML[®] activators of H₂O₂ and organic peroxides

Delia-Laura Popescu, Alexander D. Ryabov and Terrence J. Collins, Carnegie Mellon University, Pittsburgh, PA

Fe^{III}-TAML activators are homogeneous oxidation catalysts derived from TetraAmido Macrocycle Ligands. These activators have tremendous potential for developing environmentally friendly technologies for many industrial areas, such as pulp and paper, textile, laundry, water cleaning and homeland defense. Therefore, it is of great importance to understand the reactivity characteristics of these activators, to evaluate the conditions under which the catalysts display the highest activity and examine how structural modification affects the reactivity towards different oxidizing agents. The transient and steady-state kinetics of the reaction between Fe^{III}-TAML activators and oxidizing agents (H₂O₂, ^tBuOOH, cumyl hydroperoxide, benzoyl peroxide) were investigated in aqueous media. Transient kinetic measurements were carried out under the pseudo-first-order conditions at 420 nm and 780 nm, pH 6.0-13.8 and 17-45 °C. The observed pseudo-first order rate constants (k_{obs} , s⁻¹) were found to depend linearly on peroxide concentration. The slopes were used to calculate the second-order rate constant k_i . The values of k_i are strongly pH-dependent; bell-shaped pH-profiles have maxima at pH 10.5-12.5 depending on the nature of buffer, Fe^{III}-TAML activator and oxidizing agent. These results were validated under steady-state conditions following the Fe^{III}-TAML-catalyzed bleaching of the Orange II dye at 485 nm.

Abstracts, Continued

95. Design and synthesis of intercalated polyolefin/graft oligomer/organo-silicate nanocomposite architectures by green reactive extrusion

in situ processing

Zakir M. O. Rzayev and Aziz Yilmazbayhan, Hacettepe University, Ankara, Turkey

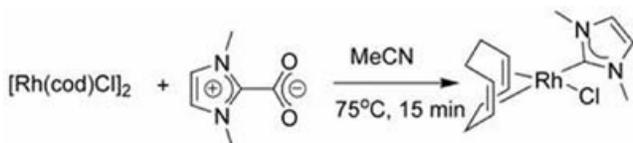
One of the most promising composite systems is nanocomposites based on organic polymers, including maleic anhydride (MA) grafted polyolefins (POs) and inorganic clay minerals, especially the montmorillonite (MMT) type clays, consisting of silicate layers in the form of interlayer galleries. Alkyl(C₆₋₂₀)amine surface-modified silicates (organo-MMT) are used to enable the formation of nanocomposite structures and to provide the effective compatibilization of polymeric matrices, intercalation and exfoliation of polymer chains in nano-interlayer galleries. These MA grafted POs and surface-modified clays are compatible with various thermoplastics and available commercially in several variations. Therefore, process monitoring during the preparation of poly(PO-g-MA)s and nanocomposite materials is of increasing importance. However, MA and its isostructural analogues, used for the chemical modification of POs, especially propylene homo- (PP) and copolymers, are hazardous monomers that partially undergo sublimation and/or migration under the reactive extrusion conditions. To prevent these environmentally unfriendly processes, we have developed an alternative method including (a) plasma surface modification of POs with MA and its homo- and copolymers and (b) preparation of nanocomposite materials by using oligo(PO-g-MA)s synthesized by chemical modification of powder non-stabilized POs in melt by reactive extrusion under the controlled thermal oxidative degradation conditions. The effect of extrusion parameters on MFI, structure and morphology of the grafted POs and PO/oligo(PP-g-MA)/organo-MMT nanocomposites were studied in detail. The formation of nano-structural architectures through strong H-bonding and amidization/imidization *in situ* reactions between anhydride units of exfoliated PP-chain and alkylamine was confirmed by FTIR, XRD, thermal (DSC, TGA and DTA) and TEM analyses.

96. Imidazolium carboxylates as precursors to novel N-Heterocyclic carbene complexes of Rh, Ir, Ru, Pt and Pd.

Adelina M. Voutchkova, and Robert H. Crabtree, Chemistry Department, Yale University, New Haven, CT

N-Heterocyclic carbene (NHC) metal complexes, an important class of catalysts, are usually prepared from the corresponding imidazolium salt. We report that N,N'-disubstituted imidazolium carboxylates (1), ionic liquids usually derived from an alkyl imidazole and dimethyl carbonate, are efficient precursors to N-heterocyclic carbene complexes of Rh(I), Ir(I), Ru(II), Pt(II) and Pd(II), (Scheme 1), allowing mild access to novel NHC complexes such as [Pd(NHC)₃OAc]OAc, [Pt(NHC)₃Cl]Cl and [Ru(NHC)₃Cl(MeCN)₂]Cl (NHC = 1,3-dimethyl imidazol-2-ylidene). In contrast to most current synthetic methods, this process avoids the use of strong bases or stoichiometric silver and releases only carbon dioxide. Optimized synthetic methods for N,N'-disubstituted imidazolium carboxylates are reported. Additives such as acetate are found to facilitate formation of bis-NHC complexes of some metal precursors. Mechanistic studies of the NHC transfer are in progress.

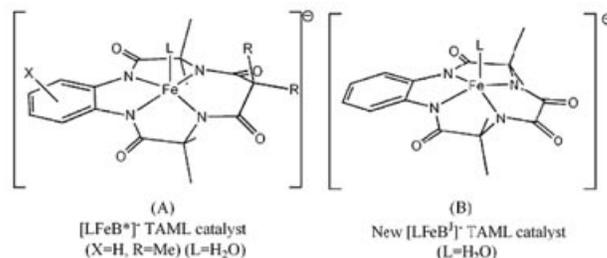
Scheme 1



97. Hydrogen peroxide oxidations catalyzed by an iron complex of the new tetra-amide macrocycle (TAML[®]), H₄B^J

Hayden J. Smith¹, L. James Wright¹, Trevor Stuthridge², Terry Collins³ and Colin Horwitz³, (1)University of Auckland, Auckland, New Zealand, (2)Scion Research, Rotorua, New Zealand, (3)Carnegie Mellon University, Pittsburgh, PA

Many TAML ligands based on the structure shown in (A) below have been synthesized. If the dimethyl malonic acid chloride that is used in the synthesis of the H₄B* ligand is replaced with oxalyl chloride, the new TAML ligand, H₄B^J is obtained. This can be easily metallated with FeCl₃ in the presence of either of the bases NaH or n-BuLi. The macrocyclic ring in H₄B^J is smaller than that in H₄B* and the deprotonated oxalamide nitrogens in [LFeB^J]⁻ are weaker σ-donors toward the iron atom than the corresponding deprotonated malonamide donors in [LFeB*]⁻. These differences have a significant impact on H₂O₂ oxidations catalyzed by [LFeB^J]⁻. For example, catalytic oxidation of the dye Orange II at high pH by H₂O₂ proceeds more slowly in the presence of [LFeB^J]⁻ than in the presence of [LFeB*]⁻; but [LFeB^J]⁻ has a much longer life at lower pHs than [LFeB*]⁻. Details of these and other significant differences in the performance of these two oxidation catalysts will be presented.



98. Evaluating the sustainability of green chemistries

Raymond L. Smith and Michael A. Gonzalez, U.S. Environmental Protection Agency, Cincinnati, OH

The U.S. EPA's National Risk Management Research Laboratory is developing a methodology for the evaluation of reaction chemistries. This methodology, called GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluator), evaluates new chemistries and technologies to determine their current or potential sustainability. Sustainability is defined as showing improvement in four areas, called the four Es: efficiency, environment, energy and economics. Ongoing work has defined sets of indicators for each of the four Es, in terms of economic potentials, environmental impacts, efficiencies and energy use. Recently, research has been performed to consider an example for the one-step oxidation of cyclohexane to adipic acid and a direct comparison to a traditional two-step process. Results are calculated for the four Es showing where efficiency, environmental, energy use, and economic improvements exist and where further development needs to be addressed. It is expected that this type of analysis will help chemists and engineers involved at the beginning stages of development to devise greener and more sustainable processes/products.

99. Combined determination of mercury and other heavy metals in biological objects

Leonid I. Toropov, Perm State University, Perm, Russia

Extraction-spectral determination of mercury and 11 other heavy metals was researched: Cd, Ni, Mn, Co, Zn, V, Cr, Tl, Sb, Pb, Cu. Extraction was done using sulfur-containing reagent diantipyrilthiourea (DATU). Ammonia, chloride and iodide systems were tested. Influence of concentration DATU, ammonia and the hydrochloric and sulfuric acids on extent of extraction of elements was investigated. It was found that from iodide solutions 9 elements (except for Co, V and Tl) were quantitatively extracted. The technique of determination of mercury and other heavy metals in biological samples was developed. The problem of accumulation of mercury in fish and fish products that is caused by the high extent of bioaccumulation of mercury from an aqueous medium, and also high toxicity of methylated forms of mercury which in a fish can attain 90%. Various samples from a fish (bream) were taken: skin, bones, scales, muscles and liver. The greatest quantity of mercury and other heavy metals were found in bones, liver and scales of the fish.

100. Key green chemistry research areas: Perspective from pharmaceutical manufacturers

GCI Pharmaceutical Roundtable, ACS Green Chemistry Institute, Washington, DC

In 2005, the ACS Green Chemistry Institute (GCI) and global pharmaceutical corporations developed the GCI Pharmaceutical Roundtable (Roundtable) to encourage innovation while catalyzing the integration of green chemistry and green engineering in the global pharmaceutical industry. The Roundtable has been developing a list of key research areas with the goal of influencing the research agenda so that environmentally friendly solutions are brought to major green chemistry problems. This poster covers the process of how the member companies pulled together and prioritized a list of key green chemistry research areas.

Information Resources and Assessment Posters

101. Green Chemistry Institute Sabbatical/Fellow Program: Valuable research experiences and collaborations with the GCI

Edward J. Brush, Bridgewater State College, Bridgewater, MA

The Green Chemistry Institute provides supplemental support for professionals seeking a sabbatical or fellowship in green chemistry and/or green engineering through its Sabbatical/Fellow Program. This program provides up to \$50,000 in sabbatical matching support to professionals in academia, industry and government. The project proposal must focus on an area of research analysis and/or development of an area relevant to green chemistry and engineering that is of mutual benefit to the sabbatical fellow and the Green Chemistry Institute. This poster will focus on my experiences as a GCI Sabbatical Fellow: (1) conducting research investigations on greener alternatives for the synthesis of oxindoles and conducting polymers while working in the lab of Dr. John Warner at UMASS Lowell, (2) developing educational outreach projects through collaborations with the GCI and (3) other "activities to benefit green chemistry." I will also discuss how to contact a sabbatical host, develop a research plan, the application process and cost-sharing requirements.

102. Greener scheme for qualitative analysis of cations without H₂S and sulfur compounds in the presence of interfering anions

Sushmita Chowdhuri and Indu Tucker Sidhwani, Gargi College, University of Delhi, New Delhi, India

Throughout the world and particularly in India and south Asian countries, qualitative analysis is an important experiment at the undergraduate level. Cations are separated into groups using H₂S. Keeping in view the toxicity of H₂S and the difficulties encountered with it, a green scheme has been developed for detection of cations. This scheme utilizes HCl, Na₂SO₄, NaOH and ammonia solution as group reagents. The separation is sharp and, in most cases, a very rigid control of pH is not needed. Using selective reagent spot tests and conventional tests have been used. Cations of one group are detected in the same solution by use of specific reagents and masking agents. Interfering anions, borate, fluoride, oxalate and phosphate which are part of the undergraduate curriculum are removed by using a single reagent which quantitatively precipitates them. Analysis is fast. The results have been encouraging and students were more comfortable with this scheme and it brings green chemistry to the grass roots level.

103. Green agents for organic reduction reactions: Low cost, eco-friendly experiments

Sunita Dhingra¹ and Renu Aggarwal², (1)Miranda House, University of Delhi, New Delhi, India, (2)Gargi College, University of Delhi, New Delhi, India

In our endeavour to develop new experiments for the undergraduate students using natural products for various chemical reactions in the laboratory, we in the present work have used the extract of *Emblia officinalis* as a reducing agent. The reducing nature of the extract is demonstrated by use of chemicals like potassium permanganate, bromine and iodine solution, Fehling's, Barfoed and Tollen's reagents, etc. where the reaction is easily seen by color changes. We will present a large number of such reactions with many other natural extracts. We have successfully used the extracts for reduction of some organic compounds. The results of all these will be presented. These experiments are simple, do not require any hazardous chemicals and, hence, serve as perfect examples of green chemistry. No expensive equipment or chemicals are needed and so these can be carried out in any chemical laboratory, at the same time indicating the innumerable applications of natural products.

104. Green science and technology: Spreading the message to non-scientists

Thomas Marrero and Stanley Manahan, University of Missouri, Columbia, MO

Professionals in disciplines other than chemistry and engineering need to have knowledge of the key issues of sustainability and green science and technology. This paper discusses the teaching of these topics in courses that have been taken by non-technical students at the University of Missouri. Green chemistry has been addressed at a very fundamental level using material from a book on this subject (*Green Chemistry and the Ten Commandments of Sustainability*, S. E. Manahan, 2006). More broadly, green science and technology (*Green Science and Technology*, S. E. Manahan, 2006) can be taught from the viewpoint of five spheres of the environment. In addition to the four traditional environmental spheres — hydrosphere, atmosphere, geosphere, biosphere — it is essential to discuss a fifth environmental sphere, the anthrosphere, consisting of the things that humans make and do. Emphasis is placed upon the interrelationships among these environmental spheres and how proper management of the anthrosphere, including input from disciplines other than science and engineering, is crucial to sustainability.

Abstracts, *Continued*

105. Study of ligand substitution reactions in various cobalt (III) complexes

Indu Tucker Sidhwani and Sushmita Chowdhuri, Gargi College, University of Delhi, New Delhi, India

In most Indian universities coordination chemistry is taught in great detail in theory but there are hardly any practical experiments conducted in undergraduate classes. Practical study in this field is limited to preparation of a few complexes *e.g.*, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$, $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ and $[\text{Ni}(\text{dmg})_2]$ but no further study is done. The study of ligand substitution reactions of transition metal complexes is a significant component of the undergraduate course in inorganic chemistry. They are often accompanied by color changes and studied by UV-visible spectroscopy. A green synthesis of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ has been reported in the literature. We have used this as a starting material for preparation of a series of complexes with various ligands and studied their substitution reactions particularly aquation by spectrophotometry and NMR. The end product has also been identified by magnetic and spectroscopic studies. This is an useful undergraduate experiment as it offers a method of correlation of theoretical principles with practical study.

106. Web-based course modules to incorporate green engineering concepts into the chemical engineering curriculum

C. Stewart Slater¹, Robert Hesketh¹, Mariano Savelski¹, Ann Marie Flynn², Jim Henry³ and Martin Abraham⁴, (1)Rowan University, Glassboro, NJ, (2)Manhattan College, Riverdale, NY, (3)University of Tennessee at Chattanooga, Chattanooga, TN, (4)University of Toledo, Toledo, OH

A "green" approach to the chemical engineering curriculum is an important consideration for advancing engineering education and workforce development. Using green engineering principles at the start of the design process can lead to processes and products of a sustainable future. This paper describes the activities on an educational project sponsored by the EPA to integrate green engineering principles into the chemical engineering curriculum. This project has engaged faculty from engineering schools across the country to develop web-based instructional modules to allow for the seamless integration for green engineering principles such as risk concepts, green chemistry, mass and energy integration and life-cycle assessment into chemical engineering courses. The modules consist of solved examples, homework assignments and case studies. This educational project's goal is to integrate green engineering concepts horizontally and vertically into the curriculum by taking existing courses and integrating topics as appropriate through examples, problems and case studies. Faculty have contributed to chemical engineering core courses from material and energy balances to plant design. In addition, modules for multidisciplinary offerings such as freshman-level introduction to engineering and upper-level system dynamics and control have been developed. This paper will review some of the innovative modules, show examples of course materials, and review some of the approaches to using them in the chemical engineering curriculum.

107. Research twinning at the University of Nottingham

Samantha L. Y. Tang, University of Nottingham, Nottingham, United Kingdom

These posters were designed by children at two Nottinghamshire schools as part of an activity called Research Twinning. In this project a PhD student visits a class at a local school every month, using this time to talk about their research. The aim of this project is to show young students what happens at a university, and to encourage them to take an interest in science. Adrian Chapman and Peter Clark have each taught their classes about oxidation reactions and photochemical reactions and pharmaceutical drug synthesis, respectively. In addition, green chemistry and the importance of scientific research have also been discussed. As part of these lessons, students have learned about how scientists communicate their work. The students were asked to design their own poster based on Adrian's or Pete's work. The winning posters are on display here. For further information about this or other science awareness projects at The University of Nottingham, please contact Dr. Samantha Tang.

108. Pharmaceuticals in the environment: Development of an active pharmaceutical ingredient (API) waste treatment software tool

Andrew S. Wells¹, Paul Bainbridge² and Neil Adlington², (1)AstraZeneca, Loughborough, United Kingdom, (2)AstraZeneca, Macclesfield, United Kingdom

Advances in the sensitivity of analytical techniques have allowed the detection of xenobiotic substances in surface waters at parts per billion levels or even lower. Among those found are certain active pharmaceutical ingredients (APIs). The presence of these molecules at very low levels has raised questions over the long-term environmental fate and effect of APIs. AstraZeneca (AZ) is very active in this debate and is committed to further the understanding of this important topic. As part of excellence in product stewardship, AZ seeks to minimize the amounts of any API being released into the environment *via* our manufacturing facilities. This presentation demonstrates a new software tool developed as a collaboration between AstraZeneca process chemists, engineers and environmental scientists. The site of production, scale of operation and dilution factors are identified followed by a detailed composition of the aqueous waste stream *e.g.*, API, solvents, inorganics, metals, etc. The tool asks a series of key questions concerning content and if the waste is suitable for certain direct treatments. The tool then matches the effluent characteristics to twelve remedial technologies ranging from direct biological treatment through to physical absorption/chemical reaction to incineration. The remedies recommended by the tool have indicative operational costs and environmental scores. The most suitable potential technologies can then be validated in the laboratory. The key goals of the tool are to alert chemists/engineers to potential issues early in the development process and to quickly provide the best available technology to treat the effluent with minimal environmental impact.

Future Energy

ORGANIZER: Green Chemistry Institute American Chemical Society, Washington, DC

109. Devil is in the details — or is it? Designing clean energy technologies and pathways

Stephen R. Connors, Massachusetts Institute of Technology, Cambridge, MA

Whether solar, wind or biofuels or the efficient use of energy, tomorrow's clean energy options will be most successful when they embrace the details of renewable resource and other dynamics and put that information to productive use. These dynamics occur all along the value chain, encompassing technology development, deployment and use. MIT, as part of the Alliance for Global Sustainability, has been working on these challenges for the last ten years. In 2005 the AGS initiated its Energy Pathways Program focused on how alternative portfolios of energy technologies can transform regional energy infrastructures to ensure clean, reliable and affordable energy services and deliver those insights to decision makers. This talk will focus on the challenges of pathways energy research, drawing from AGS and MIT research activities from Mexico, China, Europe and the USA. How big a role can hydrogen and biofuels play? How compatible are strategies to reduce greenhouse gas emissions and increase energy security? How radical a change in how we source and utilize energy might be required over the coming decades?

Mr. Connors is director of the AGS Energy Flagship Program and at the MIT Laboratory for Energy and the Environment heads the lab's Analysis Group for Regional Energy Alternatives.

110. Development of carbon dioxide removal bioreactor using *Methanococcus jannaschii*

Jong Hee Jang, Daisuke Kakei, Megumi Nishikawa, Makoto Takada, Satoshi Nakai and Masaaki Hosomi, Tokyo University of Agriculture and Technology, Tokyo, Japan

Recently carbon dioxide (CO₂) emissions as the main global greenhouse gas have reported to be approximately 1,300 million-ton per year in Japan and, therefore, reduction of the CO₂ released to the atmosphere has been researched in diverse fields. We focused on biological treatment of CO₂ by *Methanococcus jannaschii*, as one of thermophilic methanogens using CO₂ and H₂ as carbon and energy sources, to construct a closed carbon cycle system applicable to steam power station as one of the main points of CO₂ release. In this system, CO₂ is converted to a new energy source CH₄ by *M. jannaschii* with H₂ obtained by water electrolysis using cheap night electricity. Note that simultaneously produced O₂ should benefit by selling. Thus, the system with a CO₂ removal bioreactor using *M. jannaschii* is expected to work economically. In order to achieve more than 90% removal efficiency of CO₂, characterization of CO₂ removal by *M. jannaschii* was carried out in the mineral medium at 75°C on batch and continuous culture systems. Temperature, existence of oxygen and nutrient addition were examined as influencing factors for CO₂ removal efficiency of the bioreactor. Also, carbon and nitrogen mass balances were determined by analyses of gas, cells and the culture medium in the reactor during the growth of *M. jannaschii*. Furthermore, packing materials and gas pressure were respectively examined to keep the bacterial density and the removal activity high.

111. Eco-efficient solutions for a sustainable future

Charlene A. Wall, BASF Corporation, Florham Park, NJ

Eco-efficiency analysis (EEA) is a life-cycle analysis method developed and utilized by BASF since 1996. To date, almost 300 studies have been conducted globally on products and processes ranging from automotive applications, chemical and biological processing, human and animal nutrition products to construction technologies and many more. EEA is based upon the ISO 14040 life-cycle analysis standards, with the additional enhancement of a standardized weighting and assessment scheme which allows relative comparisons of technologies. The methodology enables practical business decision-making utilizing complex life-cycle assessment data and results and presents a comparison of the relative life-cycle environmental and economic impacts of products and processes. The results are used for strategic business decisions, product portfolio and technology optimization, promotion of eco-efficient technologies and, externally, to assist other organizations, including governmental groups. This presentation will introduce the audience to BASF's eco-efficiency analysis and its role in sustainable development and present case studies of how EEA is used to promote and optimize green chemistry and engineering. Specifically, case studies will address the use of EEA to support energy efficient and durable construction technologies, which can greatly contribute to reducing the environmental footprint and energy dependence of our society, while providing economic benefits.

112. Effects of iron-based catalysts on hydro-liquefaction of wood biomass in supercritical ethanol

Charles Xu and Timothy Etcheverry, Lakehead University, Thunder Bay, ON, Canada

Hydro-liquefaction of a wood biomass (Jack Pine sawdust) in sub-/supercritical solution of ethanol without and with iron-based catalysts (5 wt% FeS or FeSO₄) has been investigated with a stainless steel micro-reactor (10 mL) at temperatures of 473–623 K for a residence time of 20–60 min. In the experiments, the initial pressure of hydrogen in the reactor varied from 2 to 10 MPa. Without catalyst, the liquid yields are between 17% and 44%, depending on temperature, reaction time and initial hydrogen pressure. With catalysts, the liquid yields significantly increase while the yields of solid and gaseous products decrease. For example, the liquid yield of 63% was obtained with FeSO₄ at 623 K and 5 MPa for 40 min. The effects of the iron-based catalysts on elemental compositions (determined by a CHN analyzer) and chemical compositions (analyzed by GC-MS) of the liquid products will also be discussed.

113. Wise energy investment decisions: not just [KJ out/KJ in]

Lise Laurin, EarthShift, Eliot, ME

While it is widely recognized that the energy systems of the 1990s are not the wisest solution for the future, particularly as India and China increase their energy usage, there are a wide variety of opinions on what energy systems make sense for the future. Hydrogen fuel cells, bio-based ethanol, clean coal, solar and wind energy all have proponents and detractors, both with valid viewpoints.

For chemists, an energy system will only make sense if the energy out is greater than the energy (or fossil-based fertilizer) required to make the fuel. For business people, the energy must be profitable. For environmentalists, the energy system must have fewer environmental impacts than the system it replaces. But there are demands of community, national security, and usability that must be addressed if any new system is going to be more successful than prior systems.

We'll use a case study of a biodiesel facility in Vermont to look at some of

Abstracts, Continued

these issues from a variety of perspectives. We'll use these perspectives to look at some other decisions, bringing up additional questions that must be addressed if we are to live in an energy-secure world.

Bio-based Materials I

114. Bio-based polymers and composites manufacturing plant

Richard P. Wool, University of Delaware, Newark, DE

The first soyoil-based resin manufacturing facility which makes new green materials is described. Recent advances in genetic engineering, composite science and natural fiber development offer significant opportunities for new, improved green materials from renewable resources that are optionally recyclable and biodegradable, thereby enhancing global sustainability. A wide range of new high-performance, low-cost materials can be made using plant oils, natural fibers, lignin, nanoclays and chicken feathers. By selecting the fatty acid distribution function of plant oils *via* computer simulation and the molecular connectivity, we can control chemical functionalization and molecular architecture to produce linear, branched or cross-linked polymers. The resulting thermal and mechanical properties are described by percolation processes. These green materials can be used as pressure-sensitive adhesives, foams, coatings, elastomers, rubbers, composite resins, carbon nanotubes dispersants and nanoclay exfoliants. This work describes the chemical pathways and design rules that were used to modify plant oils and allow them to react with each other and various co-monomers to form materials with useful properties. When bio-based resins derived from natural oils are combined with natural fibers (plant and poultry), glass fibers, carbon nanotubes, nanoclays and lignin, new low-cost composites are produced that are economical in many high-volume applications. These high performance composites are used in hurricane resistant housing, agricultural equipment, automotive sheet molding compounds, civil and rail infrastructures, marine applications, electronic materials and sports equipment. In addition soft materials such as pressure sensitive adhesives (PSA), foams, coatings and elastomers are biocompatible and can be used for tissue scaffolds and wound healing.

115. Bio-based polyurethane foams from soyoil polyols

Laetitia M. Bonnaille¹, A. Campanella², Richard P. Wool¹ and Raghavan Jayaraman³, (1)University of Delaware, Newark, DE, (2)Instituto de Desarrollo Tecnológico para la Industria Química, Santa Fe, Argentina, (3)University of Manitoba, Winnipeg, Canada

The focus of this work was to synthesize bio-based flexible polyurethane (PU) from plant oils. Different monomers from modified soybean oil were used for this purpose: soybean oil monoglyceride, hydroxylated soybean oil prepared from two different routes and soybean oil methanol polyol. They were mixed in different proportions with an industrial polyol (1:0 to 1:3), a di-isocyanate and with two catalysts: N,N-dimethylbenzylamine and *tert*-butylperoxy-2-ethylhexanoate. All the PU produced using N,N-dimethylbenzylamine formed foams within 7 to 9 minutes. If an industrial polyol was added, the foam cured at room temperature after a few minutes. Stress-strain curves and density of the PU foams were measured and compared with the same parameters of an industrial PU. The best PU based on soybean oil that could be used in the sporting shoes industry was obtained from soybean oil monoglyceride; its foam presents small, uniform closed-cells and its apparent density closely resembled that of the industrial PU. The other soybean oil polyols produced open-cell foams that can be used in various applications, such as automotive interiors and office furniture. The new PU foams are compared with our previous biocompatible foams made with 100% soyoil and a CO₂ blowing agent.

116. Development of a low-k material from renewable resources

Mingjiang Zhan, Chang K. Hong and Richard P. Wool, University of Delaware, Newark, DE

The development of low dielectric constant (low-k) materials is considered to be one of the most important topics in modern high-speed microelectronics. Some of the biggest drawbacks to use the current low-k materials are cost and non-sustainability. A new bio-based composite was developed from soybean oil and keratin fibers which is suitable for electronic applications. The composite is attractive from both economic and environmental perspectives and can be a substitute for petroleum-based composite materials. The natural product components can increase the biodegradability and are more environmentally friendly than current low-k materials. Keratin fibers are hollow, light and tough materials which innately contain a significant volume of air and are compatible with several modified soybean resins. Due to the retained air, the dielectric constant can be as low as 2.0–2.7, depending on the keratin fiber fraction. The k values are lower than conventional semiconductor insulators, such as silicon dioxide, polyimides and other dielectric materials. In addition to lowering the dielectric constant, the addition of keratin fibers significantly improved mechanical properties, such as fracture toughness, flexural properties and storage modulus. By optimization of the resin structure and fiber selection, it is possible that the thermal and mechanical stability will be improved considerably.

117. Carbonization of chicken feathers for use in biocomposites

Melissa E. N. Miller and Richard P. Wool, University of Delaware, Newark, DE

Synthetic and fossil fuel-based resources are increasing in scarcity and, thus, becoming more expensive. The push for green engineering is not only more environmentally friendly, but also more practical from a business standpoint. The ability to use renewable materials is an innovative challenge faced by those in the green chemistry/engineering field. Chicken feathers, a huge agricultural waste, offer an inexpensive alternative feedstock for synthesizing carbon fiber with biodegradable prospects. The feathers, containing approximately 97% keratin, are currently used in animal feed; although this usage is decreasing with scares of diseases such as Bovine Spongiform Encephalopathy, commonly called "Mad Cow Disease." Through the use of pyrolysis, chicken feather fibers (CFF) have been synthesized by exposure to N₂ first at 225 °C for 26 hours followed by 450 °C for two hours. This cycle allows for crosslinking to maintain the hollow fiber structure, while still abstracting much of the carbon (80wt% loss). The addition of CFF to an epoxidized soybean oil (AESO) resin results in a biocomposite with a 51% increased modulus, corresponding to 13.5–66.1 GPa. With continued research, the goals are to increase the stiffness of the composite to 100 GPa, while increasing the strength to the range of 5-10 GPa. Characterization of the feathers will be performed using Xray diffraction, comparing the peaks and Miller Indices to that of polyacrylonitrile (PAN)-based fibers. The hollow structure of the chicken feathers resembles that of graphitic carbon nanotubes and the potential for hydrogen storage and its application will be further analyzed.

118. Carbon nanotube composites from soy-based resins

Ian M. McAninch and Richard P. Wool, University of Delaware, Newark, DE

Carbon nanotubes (CNTs) with their impressive mechanical properties are ideal reinforcement material. Acrylated epoxidized soy oil (AESO), a bio-based resin, has been previously shown to have favorable interactions with carbon nanotubes. CNTs mixed into AESO, both with and without styrene as a co-monomer, using mechanical shear mixing resulted in composites with modest mechanical property improvements. By itself, methyl methacrylate (MMA) appears to be a better dispersing agent for CNTs than styrene, so MMA was used as an alternative co-monomer. CNTs were dispersed *via* sonication in MMA, which was then mixed with AESO. CNTs were also mechanically mixed with a MMA/AESO resin. The resulting composites showed little dependence on the mixing method. Overall, the greatest improvements in mechanical properties, as measured by dynamic mechanical analysis, were seen when the resin's viscosity was kept high, either by having no co-monomer or by curing at a lower temperature. All samples showed increased properties in the rubbery modulus, with increases ranging from 20-70%. The dispersion of CNTs in the composites was investigated using SEM and optical microscopy. Some micron-sized aggregates were seen in all samples though the fewest were seen in the AESO-only composites, the ones with the highest bio-based content. The most were seen in the AESO/styrene composites.

119. Progress in the development of a general biomass-based chemistry

Rawle I. Hollingsworth, Michigan State University, East Lansing, MI

We have been developing ways of transforming carbohydrates into general chemical intermediates and have recently developed an integrated scheme for the high yield recovery and separation of xylose and arabinose from plant processing residue. Progress has been made in the transformation of a variety of carbohydrate-derived intermediates to a variety of materials and pharmaceutically important substances that are in active use in industry. Biomass sources used in this work include corn and sugar beets. The work we will describe will involve transformations of refined products such as starch and maltodextrins as well as unrefined materials such as sugar beet pulp. Several elements of the processes are in commercial production in the multi-ton scale for the pharmaceutical sector. End products from our biomass conversion activities include polymers, thin films, drug delivery vehicles, drug intermediates and drug discovery libraries for a variety of diseases including cancer, microbial infections, diabetes and neurological disorders. A review of the key chemistries underlying the biomass transformations we employ, a report on successes thus far and a vision for the future will be presented. We will also address the business development and commercialization aspects of our programs and briefly introduce our efforts in educating the stakeholders across the board.

Water Technologies I

120. Integrated water management: An environmentally sensible approach to industrial water treatment

Manian Ramesh, Nalco Company, Naperville, IL

Industrial evolution during this first decade of 21st century, especially in the developing countries, has outpaced such an evolution occurred during the past 100 years. Readily useable water, with its limited availability, continues to become a precious resource. Programs related to water conditioning, prior to its use in industrial applications and its treatment, after its utilization are gradually transforming to incorporate environmental sensibility. Automation, Water/Energy balance and green chemistry principles are being incorporated by the Industry in their quest to reduce the Total Cost of Operation. The lecture will focus on recent advances in such water treatment approaches and the industry trends.

121. Nanoparticulate iron oxide for removing arsenic from drinking water and effluent

Robert Trozenski¹, Kim O'Connor¹, Andreas Schlegel², Hendrik Kathrein², Ulrike Pitzer², Karl-Heinz vanBonn², Udo Holtman², Jürgen Kischkewitz², Paul Malsch¹ and Linda Huntley¹, (1)LANXESS Corporation, Pittsburgh, PA, (2)LANXESS Deutschland GmbH, 47812 Krefeld, Germany

In many regions of North America, Europe, South America and Asia, very high concentrations of arsenic sometimes occur in groundwater as both arsenite and arsenate compounds. These arsenic compounds are readily absorbed by living organisms and are highly toxic. Numerous medical studies also confirm their carcinogenic action, *i.e.*, people drinking arsenic-polluted water over an extended period may develop pathological skin changes (hyperkeratoses) and various types of tumors as a result of chronic arsenic poisoning. In 1992, the World Health Organization (WHO) recommended a worldwide, maximum, safe level of arsenic in drinking water of 10 µg/l. This level has been in force in Germany since 1996 and in other countries of the European Union since 2003. The United States Environmental Protection Agency (U.S. EPA) mandated that the U.S. must comply with the 10 µg/l standard by January 23, 2006. It is estimated that this will protect an additional 13 million Americans. Adsorption technology is among the simplest approaches for treating metals in water. Conventional adsorbents such as activated carbon or activated alumina have a limited capacity for arsenic. To improve upon removal efficiencies economically, LANXESS Deutschland GmbH developed the adsorption medium Bayoxide[®] E33 from iron oxide. It is a nanoparticulate iron oxide hydroxide in the -FeOOH form which has a very high specific surface area and a high adsorption capacity. At the same time, the granules are stable to the water flow. When Bayoxide[®] E33 is examined under an electron microscope, discrete needle-shaped nanoparticles of the -FeOOH form can be seen. Their unique structure allows for the crystallites to agglomerate forming macroscopic, stable granules and at the same time forming a pore-rich surface area. The form currently commercially available is a granular material with a particle size of between 0.5 and 2 mm. Recently a pellet variant with a very narrow particle size distribution has also been introduced. LANXESS, in cooperation with the global water technology company Severn Trent Services, applies this adsorber medium in a continuous fixed-bed process that removes the arsenic rapidly and selectively.

Abstracts, Continued

122. Closing the loop on waste: biodiesel and bioreactor waste products as feedstocks

Kendra Zamzow, T. K. Tsukamoto and G.C. Miller, University of Nevada, Reno, Reno, NV

Part of designing for a sustainable future includes the reduction of waste products, and in particular finding ways to use waste products from one industry as feedstock for another. A project in the Sierra Nevada began as a watershed remediation design using a semi-passive bioreactor to treat acidic mine water effluent in a remote mountain location. This reactor has now operated successfully for several years. Our recent research seeks to use this operating bioreactor as part of a closed loop of waste products. A large agricultural firm near the mine site makes biodiesel to fuel its farm vehicles. The waste from this process consists primarily of glycerol and potassium hydroxide, and has excellent potential as a carbon source for the mine-water bioreactor bacteria. In exchange, the sludge generated as waste in the bioreactor process has potential to be used by the agriculture firm as a soil amendment. In this way, waste from the farm is used in the reactor, and waste from the reactor may be used by the farm. Lab experiments have shown that biodiesel waste is a successful carbon source for sulfate-reducing bacteria, and these results will be presented, along with analytical results of reactor sludge and the overall concept of cycling the wastes.

123. Water treatment by combination of iron nanoparticles and cyclodextrin polymers

Rui W.M. Krause, Bhekie B. Mamba and Ketulo Salipira, University of Johannesburg, Doornfontein, South Africa

Cyclodextrins (CDs) are biosynthetic cyclic oligomers consisting of anhydrous glucopyranosyl units linked together through α -1,4-glycosidic linkages. We have polymerized CDs containing modified carbon nanotubes to form highly crosslinked polymers. We have further filled the nanotubes with iron nanoparticles, which are known to catalyze the dehydrohalogenation of chlorinated organic species. Several such CD polymers or "nanosponges" with an enhanced ability to quench organic contaminants, particularly chlorinated organics, from water to acceptable levels, have been synthesized and successfully characterized. This work will illustrate the synthesis and application of these polymers to the remediation of water polluted with various quantities of organic species.

124. Removal of natural organic matter and odor causing compounds from water using nanoporous polymers

Bhekie B. Mamba, Rui W.M. Krause, Tshelo J. Malefetse and Sabelo D. Mhlanga, University of Johannesburg, Doornfontein, South Africa

Organic compounds such as geosmin and 2-methylisoborneol (2-MIB) are often found in varying concentrations in natural waters especially after a rainy season¹. Their presence produces aesthetically undesirable odor and bad taste in water. Natural organic matter, on the other hand, promotes the formation of potentially harmful disinfection by-products (DBPs) such as trihalomethanes, haloacetic acids, halo ketones and other toxic chlorinated organic compounds^{1,2}. To date, the removal of such organic species to parts per billion levels (ppb) remains a challenge not only to local governments and industry but also to human health. A completely new class of nanoporous polymers called cyclodextrin (CD) polymers has recently been developed^{3,4}. We have investigated the ability of these CD polymers to remove NOM, geosmin and 2-MIB at very low concentrations. Water samples spiked with these

pollutants of known concentration were preconcentrated by solid phase extraction (SPE) and quantified using GC/MS. Quantification of humic substances was done by total organic carbon (TOC) measurement and UV absorbance. Quantitative analysis shows that the CD polymers are much more effective than granular activated charcoal (GAC) at removing the organic contaminants at $\mu\text{g/L}$ and ng/L levels.

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Alternative Processes I

125. Green electronics: challenges and opportunities

Jeff Omelchuck, Green Electronics Council, Portland, Oregon

The WEEE and RoHS initiatives in Europe, similar pending legislation in China, other countries and several US states, and recent videos on the improper disposal of e-waste in China and Africa have focused the public's attention on the environmental impacts associated with the end-of-life disposal of electronics. What do LCAs tell us about the life-cycle impacts of electronic products? Where should we focus our efforts, and what are some of the leading initiatives? This presentation will reflect a balanced perspective on the environmental impacts of electronic products and the role chemists and engineers can play to accelerate movement toward sustainable electronics.

126. Green HAZOP analysis: A novel green engineering guidance tool for design, assessment and implementation of processes

Juan García Serna¹, Jose Luis Martínez Gonzalez² and María José Cocero Alonso¹, (1)University of Valladolid, Valladolid, Spain, (2)REPSOL-YPF, Ciudad Real, Spain

Qualitative environmental and green impact assessment is part of the detailed sustainability analysis of chemical processes from a green engineering, green chemistry and cradle-to-cradle viewpoint. Green HAZOP is one of the first concise and systematic green engineering guidance tools especially designed by engineers for the process industry. This methodology is aimed at discovering how deviations from the green design intent can occur during the different phases of a project realization in equipment, actions or materials and whether the consequences of these deviations can result in a non-green or non-sustainable process. Thus, Green HAZOP is a powerful tool for tackling non-green problems by the identification and subsequent elimination of their causes not just by mitigating their consequences. This innovative approach will allow engineers and companies to reach the highest design standards for the millennia. This tool is based on already existing tools for safety (*i.e.*, Hazardous and Operability Analysis) which simplifies enormously its implementation in the industry. To illustrate the use and application of this tool a comprehensive industrial example about Bhopal's pesticide plant and the dramatic accident will be presented. This striking example shows how green engineering is applied using this tool and, more importantly, how chemical processes can be transformed into environmentally-friendly and safety-enhanced processes by the correct application of the principles. Fundamental methodology of Green HAZOP and an example of application (Bhopal's pesticide plant) will be thoroughly presented in this paper.

127. Remarkably improved route to the manufacture of superacid catalysts

Zoe A. C. Schnepf¹, Mark A. Harmer² and Christopher Junk², (1)University of Bristol, Bristol, BS81TS, United Kingdom, (2)Dupont Central Research and Development, Wilmington, DE

The future of green chemistry depends, to a large extent, on the continued development and use of efficient catalysts. As tools for selectivity, waste reduction and energy minimization, these materials offer the invaluable combination of sustainability and economic advantage across many sectors of the chemical industry. One area of considerable interest is the field of superacid catalysis and, in particular, the development of safer and more cost-effective acid catalysts. There has been little interest as yet, however, in the sustainability and safety of superacid manufacture. Here, we will present the results of significant improvements to the production of the liquid superacid catalyst tetrafluoroethanesulfonic acid (TFESA). Our results demonstrate remarkably improved efficiency, reduced starting materials, considerable waste reduction and elimination of an unwanted by-product.

128. Enzymatic degumming of vegetable oils

Chris L. G. Dayton, Bunge, Oil Center of Excellence, Bradley, IL

Typical production of refined, bleached and deodorized vegetable oil, particularly soy oil, involves the removal of the naturally occurring gums, also called lecithin and phospholipid, by the use of phosphoric acid and caustic in succession such that the final aqueous-oil mixture can be centrifuged, removing the aqueous phase along with the gum. The new process uses relatively small amounts of citric acid and caustic along with a phospholipase (Lecitase® Ultra) with about 2% water. The aqueous mixture containing lyso-lecithin, of value to the animal feed industry, is readily removed by centrifugation. The free fatty acids are then removed in the deodorization step and can be used as a valuable co-product, or further processed into other products, such as biodiesel fuel. Enzymatic degumming of vegetable oil reduces phosphorous content of the oil, a measure of residual gums, to below 5 parts per million. The process generates less waste, both water and soapstock and increases oil yield, reducing environmental impact versus traditional processing. The average annual production of soy oil in the United States is approximately 9.5 million metric tons. Lifecycle analysis shows that if all of this oil was refined using the enzymatic process, the reduction in carbon dioxide (CO₂) emissions would be equivalent to the average population environmental affects of over 200 million people and the energy savings of over 2 million barrels of refined gasoline a year.

129. Chemical recycling of polymer matrix composites (PMCs) with supercritical fluids: Recovery of carbon fibers from epoxy resins composites

Raul Piñero Hernanz¹, Christopher Dodds², Jason Hyde³, Juan García Serna¹, Edward Lester² and Martyn Poliakoff², (1)University of Valladolid, Valladolid, Spain, (2)University of Nottingham, Nottingham, United Kingdom, (3)University of Southampton, Southampton, United Kingdom

A novel process for the chemical recycling of carbon fiber reinforced composites using supercritical fluids as reactive-extraction media will be presented in this paper. Polymer composites and carbon fiber reinforced materials, in particular, have received great attention during the last years in the aerospace, automotive and construction sectors due to the excellent combination of properties that they exhibit, e.g., strength, durability, low weight and corrosion resistance. Currently, carbon fiber consumption stands at around 3,000 tons/year and is increasing at

10% per year in Europe. In addition, around 40% of long carbon fiber, pre-impregnated material is wasted as offcuts during fabrication which, along with the high added value of the fibers, represent an important potential for recycling. A novel clean high-efficient process for clean undamaged carbon fibers' recovery has been developed within this work. This innovative process allows for the integral recovering of the composite material obtaining both the fibers and different compounds from the resins. Experiments were performed in batch mode, using water, propanol and ethanol as reagent-solvents at temperatures between 300 and 400°C and pressures up to 30 MPa. The produced fibers are totally resin free. Mechanical properties of the recovered fibers and the virgin untreated fibers are comparable and meet the standards. A range of resin decomposition products are obtained. These compounds may be potentially reused as chemical feedstock for resin manufacturing. Economics, sustainability and green engineering aspects of the process will be discussed during the presentation.

130. Homologous recombination of a mutated fungal xylanase into *Thermomyces lanuginosus* and expression in yeast

Nokuthula P. Mchunu, Durban Institute of Technology, Durban, South Africa

The success of applying xylanase enzymes in the pulp and paper industry depends on having an enzyme with suitable characteristics for this industrial process which include stability at alkaline pH, high temperature and high levels of expression. In order to achieve this goal, a xylanase gene D2 (xynA) from a thermophilic fungus *Thermomyces lanuginosus* which was previously created by random mutagenesis, was further engineered using directed evolution to make the gene more pH stable. The 1003 bp xylanase gene was mutated using error-prone PCR. The PCR products and the vector plasmid (pBSK) were restricted, ligated and transformed into *E. coli*. Positive clones were selected on their ability to produce a zone of clearing on the plate containing 0.37% RBB-xylan-LB plates supplemented with ampicillin. Clones that were further screened for alkaline xylanase variants at alkaline pH by growing the mutants on plates containing 0.1 % xylan at pH 9 and 12. After screening, selected mutants displaying activity at these pHs were further analyzed for pH and temperature stability. NC38 was retained at 43% at pH 9 and 38% at pH 10, of its activity after 90 minutes at 60°C respectively. Because expression in bacteria was very low the enhanced gene was then transformed into *Pichia pastoris* and *Thermomyces lanuginosus* which was the original producer of this xylanase.

Benign First Time Manufacturing

Sponsored & Organized by the GCI Pharmaceutical Roundtable

131. PAT and Green Chemistry

D. Christopher Watts, U.S. Food and Drug Administration, Silver Spring, MD

In September 2004, the FDA issued guidance for industry on Process Analytical Technology (PAT), outlining a scientific, risk-based framework intended to support innovation and efficiency in pharmaceutical development, manufacturing, and quality assurance. Efficiency in these systems, which is critical to an effective health care system, can be realized through effective use of the most current pharmaceutical science and engineering principles. This presentation will focus on the advantages of implementing such systems, specifically those related to green chemistry.

Abstracts, *Continued*

132. Green chemistry: Meeting Schering-Plough's global challenges within chemical and physical sciences

Ingrid Mergelsberg, Schering-Plough, Union, NJ

Outline of the challenges to integrate green chemistry early within the chemical development of drug substances. Discussion of two typical examples where the waste generation has been significantly improved during the development of the synthetic route by selecting suitable reagents and reaction conditions.

133. The status of Green Chemistry at Merck & Co. Inc.

John Leazer, David Hughes, Mary Buzby, Dave Mathre and Skip Volante, Merck & Co. Inc., Rahway, NJ

Sponsorship at the highest levels in the research and manufacturing divisions for Green Chemistry has resulted in unprecedented advances in Green Chemistry at Merck & Co. A collaborative Green Chemistry effort was set up between the divisions in 2004 and has resulted in numerous awards and technological advances, all within the Green Chemistry arena. A discussion of Merck's approach and philosophy to Green Chemistry will be discussed.

134. Designing a green manufacturing process for a novel active pharmaceutical ingredient (API): Reducing environmental impact and adding value to the business

Laurence J. Harris, Pfizer Global Research & Development, Sandwich, United Kingdom

The commercial synthesis of APIs is challenging when viewed from a green chemistry perspective. They are often linear multi-step syntheses where impurities can result from poorly selective or inefficient chemical transformations. Purging of these impurities to acceptable limits often results in additional process steps and waste generation. Often the synthetic route is clearly sub-optimal and alternative routes of synthesis can offer attractive green chemistry benefits. Nevertheless, an overhaul of an existing route can also deliver significant green chemistry results. In our development work towards a novel sulfonamide API we applied the principles of green chemistry and enhanced every step of the synthesis to reduce the potential negative impact on the environment. The work described in the presentation provides an excellent case study of how focused process development efforts can optimize the environmental performance of API manufacturing. Our improved process is of benefit to the business by dramatically reducing waste, saving energy, utilizing safer reagents and solvents and avoiding the use (and purchase) of unnecessary reagents while still ensuring control of the API purity. Green chemistry metrics will be presented as a measure of the reduced environmental burden of our commercial API manufacturing process. Of particular note are the complete removal of dichloromethane and solid waste from every chemical step of the synthesis and E-factor and total organic solvent use reductions of >70%. The use of on-line technology (Lasentech FBRM and IR) at both laboratory and large pilot plant scale will also be described.

135. Aqueous mediated EDC peptide forming reactions

David Mitchell, Radhe Vaid, John Pu, Sathish Boini, Christopher Doecke and Kenneth Moder, Eli Lilly and Company, Indianapolis, IN

The formation of peptides or amides *via* condensations of an amine and carboxylic is among the most common reactions in organic chemistry. Aqueous mediated reactions are gaining importance due to the negative impact of organic waste on the environment (green chemistry). In the early development of a drug candidate, two peptide forming transformations involved standard reaction conditions in methylene chloride. We report an alternative condition involving an aqueous base process that circumvents the traditional organic solvent conditions using N-(3-dimethylaminopropyl)-N-ethylcarbodiimide (EDC) as a coupling agent.

136. Please see Amendments to the Conference Program.

Sustainable Energy Systems

137. Metrics for energy systems: Sustainable energy strategies

Calvin B. Cobb, Calvin Cobb & Co., Cypress, TX

Future energy developments must be sustainable if the world is to advance its energy supply and demand systems. Changing historical energy supplies like crude oil and natural gas will require large investments in new technology to achieve economical breakthroughs. As these technologies are brought forward the environment for project development will be significantly different in the future as considerations range far beyond just project economics. The sustainability view of project economics and financial performance will be linked with environmental performance and societal performance. AIChE's Institute for Sustainability is developing a Sustainability Index that will measure corporate performance in sustainable development. Components of this index measure technology-based performance in key areas: 1. Energy/Green House Gases a. Considerations along the Supply Chain 2. Products and raw materials a. Hazardous materials quality; risk. b. Life cycle of product 3. Eco-efficiency of manufacturing (process) of products 4. Environmental Performance 5. Safety and Health issues 6. R&D and Innovation slated toward Sustainable Development 7. Transparency of measurements and metrics (cross cutting factor) 8. Robustness

138. Non-covalent forces in dendrimer-structured dye-sensitized solar cells

Timothy E. Cain, Roger A. Boggs and John C. Warner, University of Massachusetts Lowell, Lowell, MA

In the past several years we have been exploring technologies that allow the processing and coating of titanium dioxide semiconductors on various substrates at ambient temperature and conditions. We have also been developing a fundamental understanding of the role of molecular recognition and self assembly in noncovalent derivatization. We are currently exploring a combination of these efforts in the pursuit of low cost, environmentally benign solar energy devices. It has been shown that covalently linked dendritic light-harvesting complexes can absorb a large spectrum of solar energy and enable efficient energy transfer between chromophores in the dendrimer. Energy can be directed to a central core which can then emit a photon or an electron. These characteristics of dendritic molecules make them very attractive

as panchromatic sensitizers for use in dye-sensitized titanium dioxide-based solar cells. Our research is attempting to construct similar dendritic systems based not on traditional covalent synthesis, but on noncovalent self-assembly through the use of geometrically aligned hydrogen bond conjugates. It is our expectation that these self-assembled noncovalent systems will display "self-repairing" behavior which will provide significantly enhanced stability as well as allow for a more benign construction. This presentation will describe preliminary syntheses and characterization of self-assembled bilayer systems on titanium dioxide surfaces. Other green chemistry implications will be discussed.

139. Solar thermal for industry: Why the time is now

Judy Kosovich, Carlo La Porta and Albert Nunez Cem, Capital Sun Group, Cabin John, MD

The industrial sector uses more than 35% of the primary energy in the United States and, of this, 70% is for heat. Commercial usage is similar. Solar heating of fluids, most commonly air and water, is a proven technology. It is more efficient than solar electricity (photovoltaics, "PV") per unit area of collector (>4x) and per dollar invested (>3x). Yet it is harder to sell solar thermal to these large users, largely because of historically low natural gas prices. Another reason is that federal and state laws favor PV in various ways, including subsidies and renewable portfolio standards. The Energy Policy Act of 2005 provides 30% federal tax credits for both solar thermal and PV installed in 2006 and 2007. This law also provides incentives for producing biofuels, particularly ethanol. We will discuss our strategy for introducing solar thermal to the ethanol production industry to improve its energy balance and reduce its reliance on fossil fuels. Other incentives include the sale of carbon credits, the use of "off-sets" in meeting Clean Air Act requirements, and the use of supplemental environmental projects as an alternative to non-compliance penalties. Solar thermal applications with 4-year paybacks will be presented.

140. BP Alternative Energy, Growing Low Carbon Power.

Lee Edwards, BP Solar, Frederick, MD 21703

BP's Alternative Energy business was launched in November, 2005 to meet the world's growing demand for secure, cleaner, low-carbon power. The portfolio of technologies BP Alternative Energy is actively pursuing includes Solar, Wind, Hydrogen for stationary, and high efficiency combined cycle gas turbine generation. The rationale and business strategy will be presented along with further details of specific programs now underway. The Alternative Energy story is based on business objectives to meet growing requirements for material alternative sources of power while providing returns to shareholders.

141. Technology developments towards greener automotive fuels

Frits Dautzenberg, Serenix LLC, San Diego, CA

This paper reviews and discusses three important trends. 1. As oil consumption starts to become limited by oil production not too long from now, refineries are being challenged to make greener gasoline and diesel. For gasoline, one needs better alkylation technology, while very low S diesel is high on the list of environmentally concerned end users. 2. In the meantime, exploitation of heavy crude oil reserves is becoming a high priority. Apart from classical C-rejection technologies, H₂-addition approaches are being introduced. Current cutting edge developments as well as near-term technologies in an advanced stage of development will be critically analyzed. 3. As the world's appetite

for energy and transportation fuels forces many countries to import crude oil at increasing costs, there is growing need for automotive fuels based on renewable biomass. It will be shown that ethanol as a gasoline component and bio-diesel offers promising alternatives. The emerging technologies to do this are being implemented and this trend can lead to substantial savings and less CO₂ emissions.

142. Mobility aspects of used oil re-refining

A.E. Alkhalidi, FluidPhase Technologies, Inc., Pittsburgh, PA

FluidPhase technological advantages: Compact size, can be located on military unit or navy ship easily; less costly to built; Low operating costs; Mobile and modular systems for maximum dependability; On site remediation of hazards, low transport cost; Depends on fast active mixing process (patented); Versatility, one system can process many types of materials; Relatively low temperature operation (100C-110C); Profitable at low capacity (1 gal/min); Made from off the shelf components; Generated residues can be sold as an asphalt; The process employs a closed loop system and No EPA license required regarding hazardous gas release. Competing technologies disadvantages: Large size; Very expensive; High operating costs; Fixed structures; High transportation costs of hazard waste material; Depends on passive and slow mixing process; One system for one type of hazard material; High temperature operation 400-500C); Profitable only at large capacity (20 gal/min); Made from special made components; The generated residues removal is costly; Open loop system and EPA license is required due to release of VOC.

143. Optimal flowsheet synthesis for biorefinery systems

Demetris Josephides¹ and Urmila Diwekar², (1)University of Illinois at Chicago and Vishwamitra Research Institute, Westmont, IL, (2)Vishwamitra Research Institute, Westmont, IL

The U.S. Department of Energy (DOE) Biomass Program promotes the development of technologies for converting biomass into ethanol to provide an alternative to petroleum-based transportation fuels. This will have impact on air quality due to cleaner combustion and reduce the greenhouse gas emissions. Furthermore there will be less dependence on crude oil from foreign countries and this technology will expand the market opportunity in the agricultural field. To be economically viable, ethanol production costs must be below market values for ethanol. DOE has chosen a target ethanol selling price of \$1.07 per gallon as a goal for 2010. In order to reach this target, this work analyzes a process flowsheet for bioethanol production in ASPEN. The flowsheet includes process stages such as prehydrolysis, saccharification and co-fermentation, product recovery and purification. This task will analyze system-level models for performance and cost and develop a methodology to handle both discrete decisions like crop selection, energy option selection and process synthesis options and continuous decisions such as the process parameters. Environmental objectives as well as low-cost options are a part of decision making. Furthermore, uncertainties inherent in process model, objectives and data also need to be addressed, resulting in additional complexities to this integrated approach. Therefore, efficient multi-objective optimization algorithms and uncertainty analysis methods for discrete and continuous optimization problems will be used to tackle this problem. The analysis is expected to give insights toward the reduction of the final cost of the bioethanol per gallon as set by the DOE.

Abstracts, Continued

144. New biomass catalytic reforming processing for SOFC power generation

Savvas Vasileiadis, Zivatech Institute, Princeton, ME

Use of biomass resources for fuel cell power generation *via* catalytic reforming is a new process which was recently reported. Utilization of improved catalytic reactors and reaction systems for hydrogen production and delivery in fuel cells from biomass is of high importance for the optimized operation of the FC. Low temperature fuel cells (*i.e.*, operating below 200°C) such as PEMFCs work only with pure hydrogen, therefore requiring a definite separation step after the reactor. High temperature fuel cells on the other hand (*i.e.*, operating above 450°C) such as MCFCs and SOFCs work well on output mixtures from reformers and gas shift reactors including mixtures of hydrogen and carbon oxides coming from biomass processing. Achieving high enough conversions in the preceding reactors/catalytic processors is, therefore, a condition for direct utilization of the hydrogen rich gas in consecutive high temperature FCs. The hydrogen rich mixture is utilized as fuel in the anode to produce electricity *via* electrochemical oxidation reactions. Conversion processes of carbon dioxide mixtures into chemicals and fuels for elimination of greenhouse gas emissions and their related negative environmental side-effects are also discussed. Both PFRs and tubular inorganic membranes and other types of separative reactors were utilized to study the reactions kinetically and from comparative conversion and yields point of view. These catalytic processors can be used well for the above biomass conversion processes for fuel cells (primarily for SOFCs) *via* the new described method. The current problems are focused on improving catalysts, fuel cells and electrode materials issues and the feedstocks specification.

Bio-based Materials II

145. Valuable products from Nigerian elephant sawgrass

Joseph Fortunak¹, Frank Ohwoavworhua², Olobayo Kunle² and Robin D. Rogers³, (1)Howard University, Washington, DC, (2)Nigerian Institute of Pharmaceutical R&D, Abuja F.C.T., Nigeria, (3)University of Alabama, Tuscaloosa, AL

Cellulose is one of the most common types of biomass in green plants. Microcrystalline cellulose(MCC) is a high "value-added" material obtained by the processing of *alpha*-cellulase. The Nigerian market for cellulose is approximately 13,000 metric tons/year, with approximately 40% of this being MCC. This presentation describes processes for (a) the production of MCC from renewable grassy materials and (b) the production of ethanol from the same process streams. The keys to reliable, efficient production of MCC are to: 1. understand the variability of materials entered into the process, 2. set appropriate limits for raw materials and processing conditions and 3. use analytical technologies that provide meaningful measurements to assess and control process outcomes.

146. Green monomers and polymers for functional and reactive polyesters and nylons

Lon J. Mathias, Allison M Sikes, Kaitian Xu, Carl Bennett and Eylem Tarkin-Tas, The University of Southern Mississippi, Hattiesburg, MS

We have been involved for several years in the development of novel monomers and polymers based on raw materials from renewable sources. Two exploratory materials have been incorporated into a variety of chain and step growth polymer systems based on an 18-carbon diacid and beta-hydroxypropionic acid. Both of these are available through fermentation processes. The former is obtained from terminal methyl oxidation of oleic acid and leads to both an intermediate possessing a cis-alkene group and the saturated C18 diacid. The unsaturated diacid allows pre- and post-polymerization modification of the monomer and polymer, respectively, while the saturated diacid generates high-hydrocarbon polymeric systems with a range of potential applications. These include low moisture nylons and polyesters as well as high performance materials for space shielding applications. We have synthesized dozens of new polyamides and polyesters containing either the unsaturated or saturated diacid and examined their properties and performance in detail. In an unrelated project, a commercial fermentation process opens up the inexpensive availability of the beta-hydroxypropionic acid which can be incorporated into a variety of homo- and copolyesters that have outstanding properties and good biodegradability. We have examined also the acrylate-terminal oligomers and polymers of the AB polyester for use in biomaterials. Overall, these two projects both offer bio-based materials with significantly enhanced chemical and physical properties that offer improvements in a large number of applications ranging from coatings and thermoplastic resins to biomaterials and packaging materials that are biodegradable.

147. Corn (sugars)-based polymer chemistries

Michael Jaffe, George Collins, Anthony East and Yi Zhang, New Jersey Institute of Technology, Newark, NJ

Sugars may be viewed as a chemical feedstock to produce new monomers, polymers and additives for the commercial polymer industry. Interest is focused on compounds such as isosorbide and itaconic acid that offer molecular geometry and chemical functionality compatible with many existing commercial polymers. Applications ranging from the creation of new polymer backbones for use as thermoplastics or thermosets to the identification of low molar mass compounds that can act as plasticizers, stabilizers or compatibilizers are under investigation. Of special interest is the impact of chirality and controlled stereochemistry in the design and performance of new, cost-effective structures with commercial potential. As petroleum becomes more expensive and the assurance of long-range, cost-effective supply questionable, creation of alternative chemistries from renewable resources such a corn (glucose) becomes more attractive.

148. Exopolymer as a raw material

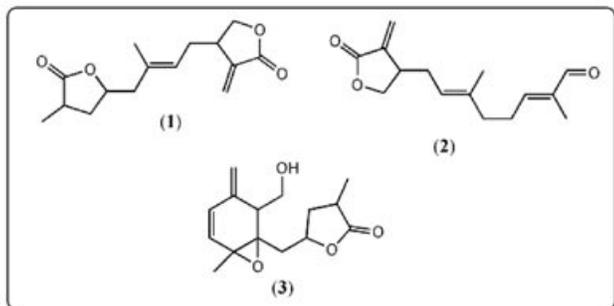
Joan Combie, Montana Polysaccharides Corp., Rock Hill, SC

Carbon is the chemical industry backbone. Most carbon comes from petroleum, but carbon from sugar is just as useful for many applications, less toxic and renewable. Levan, a polymer of fructose, is being developed as a raw material to replace petrochemicals in several industries. This polysaccharide has an extremely low intrinsic viscosity (using less energy to handle), does not swell in water, is heat and acid stable, is not cytotoxic and causes no skin or eye irritation. As a raw material, levan can serve as an alternative for chemicals with a poor eco-profile. Levan is a strong adhesive, forms oxygen barrier films, can be derivatized to make powerful surfactants, can be extruded into plastics and can replace petrochemicals in certain personal care products. Cost is a critical factor in determining commercial success of a raw material. Levan is made by the fermentation of sugar, currently selling for 17 cents/kg. Levan is an exopolymer. Unlike products from corn, soy and waste biomass, requiring significant amounts of energy and solvents for separation from cells, levan is naturally exported from producing microorganisms. Either sugar beets or sugar cane can be the source. Sugar beets are grown on marginal lands while sugar cane is an excellent CO₂ sink. The by-product, glucose, is a basic feedstock for numerous chemicals, providing additional revenue.

149. Chemical investigation of *Anthemis tigreensis* for bioactive sesquiterpene lactones

Nigist Asfaw¹, Sinedu Dejene² and Senait Dagne¹, (1)Addis Ababa University, Addis Ababa, Ethiopia, (2)Jimma University, Jimma, Ethiopia

Sesquiterpene lactones possess anti-leukaemic, cytotoxic and antimicrobial activities. A structural feature of all these compounds, which appears to be associated with much of the biological activity, is the α,β -unsaturated γ -lactone. Sesquiterpene lactones are common in plant species of the family *Asteraceae*. *Anthemis* species in the family *Asteraceae* are important in traditional medicine. *Anthemis nobilis* (chamomile) has been known as an antispasmodic and sedative in folk treatment of digestive and rheumatic disorders. *A. cotula* shows antimicrobial activity. There are 210 species in the genus *Anthemis* distributed in southern Europe, southwest Asia and north Africa. In Ethiopia the genus is represented by one species, namely *Anthemis tigreensis*. *A. tigreensis* is important in traditional medicine and used to treat wet eczema in Ethiopia. In this preliminary work, three sesquiterpene lactones, Antheindurolid A (1), 8-(tetrahydro-3'-methylene-2'-oxofuran-4'-yl)-2,6-dimethylocta-2,6-dienal (2) and sesquiterpene lactone (3) were isolated and characterized from *A. tigreensis*. UV, IR, 1D- and 2D-NMR spectroscopic techniques were used for characterization of the compounds. To the best of our knowledge, the sesquiterpene lactone (2) was reported for the first time.



150. Effects of a star-branched polyol and poly(vinyl alcohol) on the electrospinning behavior of wheat protein

Dara L. Woerdeman¹ and Suresh Shenoy², (1)Drexel University, Philadelphia, PA, (2)Case Western Reserve University, Cleveland, OH

The present work investigates the electrospinning behavior of a natural polymer, wheat gluten, in combination with two different hydrophilic additives: a star-branched polyol, ethoxylated trimethylolpropane, and a synthetic biodegradable polymer, poly(vinyl alcohol). The fiber-forming capability of each blend or mixture is analyzed to assess the nature of the molecular interactions in solution; addition of the star-branched polyol to the system causes a notable decrease in the required number of molecular entanglements or junctions in the gluten protein, while the addition of poly(vinyl alcohol) leads to a significant improvement in the mechanical properties of the electrospun fibrous mats. An order of magnitude increase in the tensile strength of the electrospun fibrous mats is observed at 13% (w/w) loading, followed by a rapid increase in the measured toughness at 26% (w/w) loading. Dough rheology reveals the effects of the star-branched polyol on the gluten protein system in a higher concentration regime, namely, when the hydrated gluten proteins are in the form of a viscoelastic dough. Experimental evidence suggests that a small fraction of the protein-water interactions are replaced by favorable polyol-protein interactions in this concentrated viscoelastic regime.

151. Eco-friendly bioplastics from renewable feedstocks: Microbial conversion and downstream recovery

Jian Yu, University of Hawaii, Honolulu, HI

Polyhydroxyalkanoates (PHAs) are produced *via* microbial biosynthesis from sugars and organic acids derived from grain, organic wastes and lignocellulosic biomass. The bioplastics can be molded like petroleum-derived plastics and are CO₂-neutral in the cycle of microbial production and biodegradation. A novel process is designed and demonstrated at bench-top scale to produce PHAs from organic wastes. The bioprocess includes acidogenic digestion of organic solids and biosynthesis of PHAs on the fermentative organic acids. The two-step biological conversions by specific microbial species are integrated in a membrane bioreactor, which reduces the consumption of acid and base used for process control. The produced PHA biopolymers are rigid thermoplastics like polystyrene. From the major hydrolytic products of lignocellulosic biomass including glucose, levulinic and acetic acids, ductile PHA polyester is formed, which exhibits the same failure elongation (400-500%) of polyethylene. The PHA biopolymers, accounting for 40-70% of cell mass, are stored in the cells as micro-granules. Recovery and purification of the biopolyesters from cell residues pose a challenge to green production of the bioplastics. Based on selective dissolution of non-PHA cell mass by protons in aqueous solution and crystallization kinetics of PHA biopolymers, a simple processing is designed and demonstrated to recover PHAs to a high purity (>97 wt%) with a high yield (> 95 wt%). The average molecular weight of biopolyesters is controlled with process severity. Compared with conventional chemical treatment or solvent extraction, this new technology substantially reduces the cost of and potential pollutants from downstream PHA recovery and purification.

Abstracts, Continued

152. Acacia and Tamarix as green corrosion inhibitors of galvanized steel

Ahmed A. Taha, University of Bahrain, Sakheer, Bahrain

Activity of a galvanized steel alloy was measured in pure distilled water and tap water against the passivating effect of *A. arabica* and *T. arabica* aqueous near neutral extracts at 25°C using the potential polarization method over a 33-day period. The two green chemical sources Acacia and Tamarix showed good to moderate inhibition in comparison to the non-green chemical inhibitor K_2CrO_4 . The two plant extracts, which tested positive for tannins, gave intensities of corrosion inhibition of the same order as gallic acid. The anodic character of the inhibitors was recognized by the shift of corrosion potential towards more positive values. The nontoxicity of these organic plant constituents, their anti-microbial properties and their sustainable sources of production present them as having a wide scope of applications as green corrosion inhibitors and anti-scalants in boiler and potable water systems.

153. Ecofriendly decolorization of wastewater using seed galactomannans from renewable resources

Rashmi Sanghi¹, Ishan Desai², Binayak Adhikary² and P. A. Parikh², (1)302 Southern Laboratories, Facility for Ecological and Analytical Testing, Indian Institute of Technology, Kanpur, India, (2)Sardar Vallabhbhai National Institute of Technology, Surat, India

Stringent environmental norms regarding disposal of textile effluents have led to the investigation of environmentally friendly treatment technologies. Flocculation is an essential phenomenon in domestic/ industrial wastewater treatment where aluminium and iron salts are the chemicals most commonly used coagulants. With aluminium salts, there is always the concern about residuals in the treated water and Alzheimer's disease and, while iron salts are a cheaper option, the cost of any imported chemicals can be a serious problem for developing countries. Thus, in recent years, there has been considerable interest in the development of natural coagulants which can be workable alternatives to conventional coagulants like polyaluminium chloride (PAC) as they are biodegradable, safe to human health, are cost effective when compared to imported chemicals, easy to handle, inert to pH changes and have versatile tailorability. The present investigations have been carried out for the possible exploitation of *Ipomoea Dasysperma* (ID) seeds as a potential source of commercial gum to coagulate dyes and is of interest in replacing the synthetic coagulants for which there are serious health concerns. The use of galactomannans derived from plants in this system presents a novel sustainable method of textile effluent treatment. Optimization of different parameters namely pH, coagulant dose, dye concentration, time and temperature of the bioflocculant ID on synthetic solution of Direct Orange Dye was performed and was found not only to be very effective and comparable to PAC (75% decolorization) but could also perform without any alteration of solution pH.

154. Abstract Withdrawn

155. LCA of bio-based products: A comparison of starch and polyethylene foams

Chisa K. Brookes, Bruce Dale, Seungdo Kim and Ramani Narayan, Michigan State University, East Lansing, MI

Recent U.S. government initiatives to support biomass R&D suggest the importance of having viable alternatives to foreign oil be economically and environmentally attractive. This paper explores the environmental value of bio-based starch and petrochemical-based polyethylene (PE) foam via a comparative LCA. The methodology used follows that outlined in the ISO 14040 and the ASTM D7075 standards. Data and models are gathered directly or from collaborations between Argonne, Cargill Dow, U.S. EPA, NIST, and more. Eight impact categories are covered, each normalized to the associated U.S. normalization value. Starch dominates one of the seven impact categories—the eutrophication potential—and only by 19%. The total energy required for producing 17,000 ft³ of PE and starch foam is 1.13E6 MJ and 1.02E5 MJ, respectively. Rising energy prices may disclose starch to be economically attractive as the energy required to process starch is an order of magnitude less than that of polyethylene.

Water Technologies II

156. Oxidative degradation of nitrophenols and nitroanilines in aquatic environment

Arani Chanda, George J. Diabes, Alexander D. Ryabov, Sushik K. Khetan and Terrence J. Collins, Carnegie Mellon University, Pittsburgh, PA

Nitroaromatic compounds are recalcitrant and toxic to aquatic life forms. Several have been classified as priority pollutants by the U.S. EPA. They are primarily anthropogenic pollutants that mostly originate from the wastewater discharges of dyes, pesticides, explosives and other chemical industries. Developing processes for their safe removal has been a field of active research. The presentation will be focused on an efficient, rapid, environmentally friendly and easy-to-use catalytic oxidation process for the total degradation of substituted nitrophenols and nitroanilines using Fe-TAML[®] (Tetra-Amido-Macrocyclic-Ligand)-activated hydrogen peroxide under ambient conditions at pH 8. Analysis of the degradation mixtures indicated partial mineralization accompanied by the formation of small aliphatic acids such as oxalic, formic, and maleic acids as well as nitrate and nitrite ions. Comparative rates of oxidation for different nitrophenols will also be presented. Aquatic toxicity tests of the degradation mixtures have shown no measurable toxicity. The present method is effective over a broad pH range and has an advantage over some of the Fenton chemistry-based methods, which require high iron concentrations and work only at acidic pH.

157. Deactivation of surrogates of microbial pathogens: Toward green water disinfection

Deboshri Banerjee¹, Sushik K. Khetan¹, Yong-Li Qian¹, Philip Dulac², Mark Krotec² and Terrence J. Collins¹, (1)Carnegie Mellon University, Pittsburgh, PA, (2)Central Catholic High School, Pittsburgh, PA

Chlorine disinfection of drinking water results in by-products that pose health and environmental concerns. The development of a non-toxic, practical, inexpensive, environmentally benign and chlorine-free disinfection process would eliminate such concerns. At a minimum, such a system must efficiently deactivate all pathogenic microorganisms in drinking water, e.g., *Cryptosporidium*, *Giardia*, total coliforms including *Escherichia coli* and harmful viruses. Fe-TAML[®] (Tetra Amido Macrocyclic

Ligand) activators of peroxides destroy surrogates of many of these microbial pathogens. A >7-log kill (10^7 -fold decrease) of spores of *Bacillus atrophaeus* (ATCC 9372, formerly known as *B. subtilis* var. *niger*), often considered as a microbial indicator for *Cryptosporidium parvum* and *B. anthracis*, was achieved with an Fe-TAML[®]/peroxide system within 15 minutes. A high deactivation rate was also observed for the *E. coli* strain DH5alpha. Studies are currently underway to analyze the efficiency of the Fe-TAML[®]/peroxide system towards the deactivation of T2 phage viruses. An overview on these disinfection results will be presented.

158. Oxidative degradation of Lipitor[®] and Zolof[®] with the Fe-TAML[®] catalyst and hydrogen peroxide

Yan Xiang¹, Melanie Vrabel², Evan Beach², Colin Horwitz², Sushil Khetan² and Terrence Collins², (1)Beihang University, Beijing, China, (2)Carnegie Mellon University, Pittsburgh, PA

Pharmaceuticals and personal care products are emerging aquatic contaminants because of environmental persistence. We are seeking safe and effective processes for destroying these residuals. Hydrogen peroxide in the presence of an Fe-TAML[®] catalyst (TAML is tetraamido macrocyclic ligand) efficiently and rapidly oxidizes the major pharmaceuticals, Lipitor[®] and Zolof[®]. Lipitor was degraded within 1 h at concentrations as high as 0.1 mM with 1 μ M Fe-TAML[®] and 8.3 mM H₂O₂ (1:100:8300); at least 26 products have been observed by HPLC. Zolof[®] degrades more easily to produce fewer products. For both drugs, small acids including formic, maleic and acetic acid were formed as the major partial mineralization products. Optimal pHs and catalyst/peroxide/substrate ratios have been identified. Microtox[®] tests (at starting concentration of Lipitor or Zolof[®] of 25 μ M) indicate the breakdown products are nontoxic to this simple assay. The results suggest a possible role for Fe-TAML[®] catalysts and H₂O₂ for pharmaceutical wastewater treatment.

159. Decolorization of pulp mill bleach plant effluent by hydrogen peroxide activated by an Fe-TAML[®] catalyst

Evan S. Beach¹, Colin P. Horwitz¹, Jonathan Spatz¹, William C. Ellis¹, Charles S. Merris Jr.² and Terrence J. Collins¹, (1)Carnegie Mellon University, Pittsburgh, PA, (2)Glatfelter, Spring Grove, PA

Two field trials in United States pulp mills have shown that an Fe-TAML[®] catalyst is effective for both in-process and post-process ("end-of-pipe") treatment of colored wastewater, compared to hydrogen peroxide (H₂O₂) alone. In the presence of pulp fiber in a caustic extraction stage tower, Fe-TAML[®]/H₂O₂ removed >30% color without affecting pulp quality. In a sewer system carrying caustic extraction filtrate, Fe-TAML[®]/H₂O₂ removed approximately 50% color. Fe-TAML[®] technology is competitive with other technologies for pulp mill wastewater treatment, offering several key advantages: the catalyst is non-toxic, used in very small amounts, does not generate sludge and can work with as little as five minutes contact time; also implementation is easy, with simple delivery mechanisms and minimal capital cost. The details of the trial design and results will be presented.

160. Green approach to remediation of waste streams containing dyes

Ryan Malecky, Evan Beach, Colin P. Horwitz and Terrence J. Collins, Carnegie Mellon University, Pittsburgh, PA

Tartrazine (FD&C Yellow #5) is a widely used dye in food, textile and paper industries. Its utility stems from its bright color, high molar absorptivity and stability. These traits create a problem when it ends up in waste streams as tartrazine is known to be particularly resistant to biodegradation. Oxidation processes have been investigated as potentially effective remediation strategies for tartrazine and many other dyes. Hydrogen peroxide in the presence of an Fe-TAML[®] (TAML[®] — tetraamido macrocyclic ligand) catalyst provides a particularly effective means for oxidizing tartrazine. The use of hydrogen peroxide as an oxidizing agent avoids hazards associated with oxidants such as hypochlorite and chlorine. The Fe-TAML[®] catalyst/hydrogen peroxide system can effectively oxidize tartrazine over a wide concentration range of dyes, 10 μ M (5 ppm) to 0.04M (20 ppt). The reaction occurs at room temperature over a wide pH range. Oxidation of tartrazine produces a mixture of small acids (HPLC) as well as aromatic and aliphatic compounds (¹H NMR and ESI-MS). When sodium hypochlorite is used instead of Fe-TAML[®]/H₂O₂ the reaction produces different products including chlorinated organics. Because the Fe-TAML[®]/H₂O₂ combination is capable of oxidizing dyes in low and high concentrations without using hazardous reagents, it has the potential to be used in the remediation of industrial dye baths in a green manner.

161. Multi-electron transfer and carbene formation at heme functionalized nanocrystalline TiO₂: Reductive dechlorination of DDT and CCl₄

Jonathan R. Stromberg, Rachele Ann Pinlac, Joshua Wnuk and Gerald J. Meyer, Johns Hopkins University, Baltimore, MD

There exists some evidence that molecular catalysts anchored to nanocrystalline semiconductors can undergo multi-electron transfer (MET) reactions with organohalide pollutants. This is important as MET processes avoid high-energy free radical intermediates and can yield desired reaction products under mild, environmentally relevant conditions. In this presentation, we will describe the first direct evidence for MET reactivity at these interfaces. Well-defined molecular catalysts (hemes) anchored to nanocrystalline TiO₂ particles dispersed in mesoporous thin films were found to trap, store and reduce organohalide pollutants. Each nanoparticle was found to store > 500 reducing equivalents upon illumination and are abbreviated heme/TiO₂(e⁻). Reactions of heme/TiO₂(e⁻) with DDT and CCl₄ were found to form carbenes through two-electron transfer reactions. Significantly, the carbene product was stable on the anatase nanocrystallites and could be removed from the contaminated solution. Ongoing studies designed to determine a rate law for the reactions as well as elucidate the mechanisms will also be discussed.

162. Chicago water use: Steps to sustainability

Yi Meng and Paul R. Anderson, Illinois Institute of Technology, Chicago, IL

Water use practices in the Chicago metropolitan area are inefficient. The region has had problems meeting the current water diversion limit from Lake Michigan and it is likely there will be problems meeting the future water demand. The purpose of this project is to explore the potential for reusing municipal wastewater in the Chicago metropolitan area. We examined policy, health risk, technology and economic issues to find incentives and barriers to treated wastewater reuse. By integrating treated wastewater reuse to the traditional water resource management model, the multi-objective decision support system based on this model can reach sustainable urban water use. All the efforts will lay the foundation for a water reuse ordinance in the Chicago metropolitan area.

Abstracts, *Continued*

163. Current issues on water use and reuse in chemical processes

Daniel Sujo, Robert P. Hesketh, Mariano J. Savelski and C. Stewart Slater, Rowan University, Glassboro, NJ

This paper reviews the state of the art in water allocation and wastewater reuse alternatives in manufacturing processes. Water is one of the most highly used solvents in industry. For decades, industry had only been concerned with the end-of-pipe wastewater treatment, so it could be disposed in compliance with environmental regulations. In the past ten years, water use and reuse have become the focus of study for several researchers, the main reason being the scarcity of water in many parts of the world and the dramatic increase in environmental legislation. This paper discusses the tools and methodologies used in designing and retrofitting water networks as well as the different solution alternatives for different industrial applications. It also discusses the highlights of solving water reuse problems graphically or through mathematical programming methods, whether for a single contaminant or multiple contaminants. In addition, cost constraints are addressed. Finally, the paper presents new challenges in this area such as plant operability, data uncertainty and process reliability.

164. Sustainable environmental management for mercury in water: Part I, Industrial sustainability

Yogendra N. Shastri¹ and Urmila Diwekar², (1)University of Illinois, Chicago, Chicago, IL, (2)Vishwamitra Research Institute, Westmont, IL

Mercury is recognized internationally as an important pollutant, since mercury and its compounds are persistent, bioaccumulative and toxic, posing human and ecosystem risks. Mercury can cycle in the environment in all media as part of both natural and anthropogenic activities. Consequently, control of mercury pollution at various stages of this cycle is important. Industries, being an important source of mercury to the atmosphere, are strictly regulated, resulting in heavy financial burden on them. Hence, optimizing the selection and design of the waste treatment technology is important for economic viability. Pollutant trading is another option to achieve simultaneous economic and ecological sustainability. Trading also provides an option to the regulators to achieve better environmental goals. This work proposes an optimization-based approach to assist decision making related to technology selection, design and pollutant trading for mercury generating plants. When considered simultaneously, such decisions can be complicated and often beyond heuristics. The optimization model allows the authorities to evaluate various regulatory options to achieve optimality. The analysis proposes to include health care costs in decision making to account for the harmful effects of mercury. The analysis is further extended to include various sources of uncertainty, making it robust. The optimization model is implemented on a watershed level mercury pollution reduction case study. The results, while indicating significant cost reductions due to trading, also emphasize the importance of accounting for the health care costs. Pollutant trading is, therefore, perceived as an attractive option for sustainable management of toxic chemicals.

165. Sustainable environmental management for mercury in water: Part II, Ecological sustainability

Yogendra N. Shastri¹ and Urmila Diwekar², (1)University of Illinois, Chicago, Chicago, IL, (2)Vishwamitra Research Institute, Westmont, IL

Mercury is recognized internationally as an important pollutant and has become a major concern to the environmentalists. Although mercury can cycle in the environment in all media as part of both natural and anthropogenic activities, it is most dangerous in water due to its bioaccumulative nature. Once introduced into the water body, either through direct discharge or dry and wet deposition, it bioaccumulates along the aquatic food chain, finally affecting humans through contaminated fish consumption. Since methyl mercury is the primary form of mercury that bioaccumulates, mercury methylation is a key step in this process. Although the reaction mechanism is still not clear, controlling water pH can control mercury methylation and, hence, the bioaccumulation. In this work, we look at the option of time-dependent liming to control water pH. There are multiple sources of uncertainty in this process. Various uncertainty representation techniques from real options theory are used to model these uncertainties. Stochastic optimal control theory is being used to derive the time-dependent liming strategy. While executing liming operations, it is essential to obviate any adverse effects on the lake biota. We are proposing to use Fisher information-based measures to quantify food web sustainability, resulting in a multi-objective problem. In the overall scheme of managing the mercury pollution problem, this work constitutes the management at the ecosystem level.

Alternative Processes II

166. Chemical synthesis in flow reactors: A greener alternative

Paul Watts and Charlotte Wiles, University of Hull, Hull, United Kingdom

The importance of minimizing the impact that chemical processing has on the environment is growing with an increased appreciation of the need to reduce pollution and the depletion of our finite environmental resources. Optimal use of material, energy and consequent waste management can be recognized as important factors for environmental protection. In this presentation it will be illustrated that within flow reactors, products are generally produced in higher yield, higher purity and where relevant higher selectivity without using excess reagents. Clearly each of these factors may be regarded as being environmentally attractive. Furthermore, the use of solid supported reagents adds even greater diversity to the range of reactions that may be achieved within such systems. The presentation will discuss how flow reactors may be fabricated for use with supported reagents. It will be demonstrated that the dimensions of packed reactors may be increased in size while maintaining the classic advantages associated with miniaturization. In such examples analytically pure products may be manufactured without formal purification, the consequence being a significant reduction in solvent requirements. It will also be highlighted that the technique is suitable for the multi-step synthesis of fine chemical involving in situ reagent generation. Furthermore, the possibility of preparing the chemicals in the required volume at point of use negates the need to store and transport hazardous materials by using the numbering up approach.

167. Beneficiation and utilization of coal combustion fly ash: A major success in reducing solid waste and increasing supplies of construction materials while reducing of greenhouse gas emissions

Stephen Gasiorowski and James D. Bittner, Separation Technologies, LLC, Needham, MA

Over 70 million tons of fly ash from coal fired electric utility boilers are generated in the United States each year, the majority of which is disposed in landfills. Separation Technologies LLC (ST) has developed and implemented innovative, patented processes to reduce unburned carbon and detrimental ammonia levels in coal fly ash for use in concrete production while creating useful fuel for utility boilers. This beneficiated fly ash is used as a partial replacement of ordinary Portland cement (OPC) in the production of concrete. Manufacturing of OPC normally produces approximately one ton of carbon dioxide per ton of OPC. Utilization of fly ash as a cement substitute is, thus, a means to substantially reduce greenhouse gas emissions from the construction product industry while simultaneously avoiding landfill disposal of the ash. ST's technology is operating commercially at eight large coal-fired electric power plants in the United States, Canada and the United Kingdom to beneficiate coal ash into raw materials for concrete production as well as recovering unburned carbon in the ash for its fuel value. Cumulatively, ST has produced 4 million tons of concrete-grade fly ash with a corresponding reduction in solid waste disposal and greenhouse gas (CO₂) emissions.

168. Microwave assisted synthesis of novel spirocyclic quaternary ammonium salts and their conversion into N-heterocycles of biological importance

Subhash C. Jain, Archana Gupta and Rajeev Sakhuja, University of Delhi, Delhi, India

1-Azaphenothiazine are known to possess marked pharmaceutical properties such as antihypertensive, antitussive and CNS depressant. Prothiopyridyl, an aminoalkylated 1-azaphenothiazine is an effective CNS depressant and its potency is reported to enhance by introducing lipophilic side chain. In an effort to increase its potency, N-alkylation of 1-azaphenothiazine, using various N-(bromoalkyl)phthalimide was carried out, for the first time, using microwave irradiation, under solvent free conditions. To our surprise, we obtained a novel class of bioactive spirocyclic quaternary ammonium salts, known as azoniaspiro compounds, in addition to the desired N-alkylated product. These azoniaspiro compounds were then hydrolysed under controlled conditions to obtain various N-heterocycles such as aziridines, azetidines, pyrrolidine and piperidine derivatives. The yield of these N-heterocycles was improved by further studying the catalytic activity of substituted 1-azaphenothiazines, required for cyclization. Thus, we reported here a new eco-friendly, efficient and convenient method for the synthesis of spirocyclic quaternary ammonium salts and converted them successfully into N-heterocycles of biological importance. Detailed synthetic methodology and the role of 1-azaphenothiazine as a catalyst will be presented and discussed at the Conference.

169. Selective oxidation of alcohols alternative catalytic processes

Endalkachew Sahle-Demessie, U.S. Environmental Protection Agency, Cincinnati, OH

Oxidation of alcohols to aldehydes, ketones or carboxylic acids is one of the most desirable chemical transformations. Newer methodologies for alcohol oxidation are needed due to the significance of this reaction. Oxidation over metal catalysts using eco-friendly oxidants such as hydrogen peroxide and molecular oxygen are preferred now for environmental and economical benefits. A comparison of different catalytic processes will be presented for the alcohol oxidation such as various metal containing catalysts *viz.*, Fe³⁺/montmorillonite-K10, vanadium phosphorus oxide (VPO) and Pd/MgO using hydrogen peroxide and molecular oxygen as environmentally benign oxidants and ozonation with UV/photocatalysis over TiO₂. Selective oxidations of various primary and secondary alcohols were studied in the liquid phase using Fe³⁺/montmorillonite-K10 catalyst prepared by the ion-exchange method and VPO catalyst was suitable for selective oxidation of secondary alcohols to the corresponding ketones using H₂O₂. Presence of -CH₃ group at the -OH bearing carbon was deleterious to the oxidation. Magnesia-supported Pd catalyst was found to be a highly active heterogeneous catalyst for the selective oxidation of alcohols to the corresponding carbonyl products using molecular oxygen in the presence of trifluoro toluene in which a variety of activated and non-activated alcohols could be effectively oxidized in the absence of any additives. Studies were on the gas phase photochemical reactor using immobilized TiO₂ catalyst at 150–200 °C. A novel corona discharge reactor with immobilized TiO₂ is used for simultaneous ozonation and photocatalytic oxidation of alcohols. Reaction mechanism and catalyst deactivation and high energy costs are the drawbacks of this gas phase processes.

170. Chemical recycling of polycarbonate by supercritical alcohol-CO₂ assisted process: A green-efficient route for CD-DVD's wastes recycling

Raul Piñero Hernanz, Juan García Serna and María José Cocero Alonso, University of Valladolid, Valladolid, Spain

Polycarbonate (PC) is used extensively in the manufacture of CDs and DVDs as well as a large variety of plastic materials in the automotive and electronic sectors. Due to the increasing consumption of polycarbonate-based products and the incipient demand of more clean-efficient processes, it is necessary to develop a suitable process to recycle these waste materials. An efficient alkali-catalyzed depolymerization of PC wastes by alcoholysis in supercritical or near critical conditions will be presented in this paper. The essential monomer, bisphenol A (BPA), and dimethyl carbonate (DMC) as a valuable co-product were obtained. Methanol, ethanol and *iso*-propanol were employed as a clean solvents/reagents and CO₂ as a swelling agent. Alkali and acid catalysts (NaOH, KOH, HCl) were also attempted in order to enhance the kinetics and optimize the process at lower temperatures. A mechanism of reaction has been proposed. Influence of the operation conditions on products yield, selectivity and reaction rate have been studied, including temperature, pressure, alcohol/CO₂ ratio and catalyst concentration. High BPA yields ca. 90%*ww* were achieved with a further crystallization and separation of the final product, resulting BPA pure crystals (99.9 %) DMC was also obtained as a valuable co-product (85–70%*ww* yield) and non desired by-products yield was negligible, especially at high pressure and moderate flow rate and temperature conditions. In addition, continuous kinetics analysis was carried out. Preliminary economic and sustainability studies analyzing the feasibility of scaling-up this process will be presented.

Abstracts, *Continued*

171. Identifying greener analytical methods

Jennifer L. Young¹, Rajender K. Brahman¹, Paul T. Anastas¹ and Larry Keith², (1)Green Chemistry Institute, Washington, DC, (2)Instant Reference Sources, Inc., Monroe, GA

The ACS Green Chemistry Institute (GCI) has initiated a new project to actively define, identify and promote analytical chemistry methods that use fewer harmful solvents, use safer chemicals and prevent waste. GCI has led the efforts to define metrics and rules to rate the “greenness” of analytical methods and is applying these rules to the over 800 methods in the National Environmental Methods Index (NEMI; www.nemi.gov). To accomplish this, GCI is extracting specific data on chemical use and waste generation from all of the full analytical methods currently in NEMI. After applying “greenness” rating rules to this data, the “greenness” rating information is put back into NEMI. As a result, when multiple methods in NEMI are evaluated, the methods’ performance criteria and “greenness” ratings can be easily identified and compared. Other applications and future directions of the project may include the development of a teaching module, evaluation and rating of other types of analytical methods, identification of areas in which greener methods are needed and guidance on how to make an analytical method greener.

Designing Safer Chemicals & Toxicity Reduction I

ORGANIZER: Green Chemistry Institute American Chemical Society, Washington, DC

172. Plenary: Approaches to Designing Innovative Sustainable Products

Eric Beckman, University of Pittsburgh

Green design principles have been applied in ways that have resulted in more sustainable products. Often these improvements have been incremental rather than the type of leap-frog technologies that are going to be needed to address some of the most pressing concerns with regard to energy, food, water, resource depletion, and toxicity. There have been some frameworks which can be used to facilitate innovative designs. Through the combination of approaches to innovation and sustainability, there may be new design frameworks that could be useful in the next generation of products.

173. Chromate-replacing corrosion inhibitors and primers for aluminum alloys

Zhangzhang Yin, Anuj Seth and William van Ooij, University of Cincinnati, Cincinnati, OH

Aerospace aluminum alloys such as AA 7075-T6 are subject to localized corrosion due to the existence of Fe-Cu rich intermetallics. Chromate is currently widely used in aerospace industry as the corrosion inhibitor for those alloys. However, chromate needs to be replaced due to its strong carcinogenicity. In this study, extensive pigment screening has been done to find replacements for chromate. Different categories of inhibitors have been evaluated and the effectivenesses of inhibitors were determined. Phosphates, zinc salts, cerium salts, vanadates and BTA were found to be effective inhibitors for AA7075. Among those inhibitors, zinc phosphate was found to be the overall best pigment in our novel silane-based, one-step primer system (termed superprimer). The performance of our primer is comparable to that of currently used chromate primers in accelerated corrosion tests, while it is completely chromate-free and contains five times less VOC than

current primers. Studies by SEM/EDS showed that the unique structure of the superprimer accounts for the strong anti-corrosion performance of the zinc phosphate pigment, which is not considered by the industry as a strong inhibitor in traditional solvent-based primers. The self-assembled stratified double-layer structure of the superprimer is characterized by a less-penetrable hydrophobic layer on the top and a hydrophilic layer accommodating the inhibitors underneath. The top layer functions as the physical barrier against the corrosion, while the underneath layer function as a fast leaching-out vehicle for the inhibitor. The presence of silane also improves the adhesion and anti-corrosion performance of the primer.

174. Zinc-clad lead: A safer alternative for ammunition

Philip G. Malone, Charles A. Weiss, Jr. and Joe G. Tom, U.S. Army Engineer Research and Development Center, Vicksburg, MS

There are over 10,800 small arms firing ranges in the United States. Over 80,000 tons of lead are deposited on these ranges every year. Containment and recovery of lead on the ranges in a safe and environmentally acceptable manner is a vital step in controlling soil and ground water pollution at these localities. Ranges are periodically “mined” for lead, but the corrosion of the lead fragments in soil results in lead compounds moving into the environment. The zinc-lead composite bullet uses zinc as a sacrificial metal to protect the lead in the bullet. This is similar to the effect that zinc has on iron, where zinc corrodes and the iron is protected. Pure lead bullet slugs leached over 14 ppm lead in a standard acetic acid leaching test. Zinc-plated lead composite slugs containing 14% zinc leached less than 0.2 ppm Pb in the same acetic acid leach test. The lead pellets with only 14% zinc leached lead at levels that were less than 1.4% of that leached by the unprotected lead. A properly constructed lead slug could remain in the soil on the range between “mining” events without producing mobile lead corrosion products. The mixture of lead and zinc in the composite should produce a material with a density of 10.71 as opposed to 11.34 for the pure lead (a decrease in density of only 5.5%). Substituting a lead-zinc composite for lead in bullets is an economical and environmentally-beneficial development.

175. Picaridin: A safe, effective, environmentally friendly insect repellent that people will use

Frank Lueckgen¹, Hans Essenbreis¹, Thomas Gernot² and Paul Malsch¹, (1)LANXESS Corporation, Pittsburgh, PA, (2)LANXESS Deutschland GmbH, Krefeld, Germany

LANXESS Corporation and its parent company, LANXESS Deutschland GmbH, developed, manufacture and market an insect repellent that offers a safe, effective, user-friendly, and environmentally responsible alternative to traditional repellents based on diethyl-*m*-toluamide (DEET), which has been in frequent, wide use as an active ingredient since its discovery in 1954. Picaridin demonstrates broad effectiveness against mosquitoes, ticks, sand flies and horseflies. It is gentle on the skin, is non-sticky and has almost no scent to humans. Picaridin is not damaging to plastics, fibers or coating and sealing compounds. This product is safe for use by the whole family. Thus, Picaridin overcomes cosmetic disadvantages that lead people to decline using insect repellents and accept the risk of bites, infection, disease and death associated with malaria, dengue fever, West Nile Virus and Lyme disease. Malaria, discussed by President Bush in his 2006 State of the Union Address, alone kills about three million persons a year. About 260 persons in the United States died in 2003 after being infected with West Nile Virus. The World Health Organization recommends repellents as protection against malaria due to increasing

resistance of *Plasmodium falciparum* (Welch) to anti-malarial drugs (e.g., chloroquin). Picaridin biodegrades quickly, undergoing a fast, thorough primary biodegradation that yields the more stable metabolite picaridin acid. In tests, neither groundwater nor tap water contained residues of picaridin or picaridin-acid, indicating the complete degradation and removal of the substances by sewage treatment plants and groundwater conditioning systems.

176. Properties and performance of flexible Noryl*resin for wire coating

James J. Xu¹, Weiguang Yao² and Mukund Parthasarathy¹, (1)General Electric Company, Plastics, Selkirk, NY, (2)General Electric Company, Plastics, Moka, Japan

The global annual consumption of polyvinyl chloride (PVC) is reaching one million metric tons worldwide for wire and cable applications. In the automotive industry alone, almost 150,000 metric tons of coated wires are produced yearly, measuring more than 96 million kilometers, enough to circle the Earth to moon 938 times. The PVC life cycle is of human health and environmental concern. PVC releases toxic smoke containing hydrogen chloride and cancer-suspect dioxin during its incineration. Likewise, the vinyl chlorine monomer ("VCM") used to manufacture PVC is a known carcinogen. The release of this material may occur during the manufacturing process. Chlorine-containing materials, such as "VCM", along with other halogen-containing substances contribute significantly to ozone depletion. The industry trend is to eventually eliminate PVC for wire and cable applications. GE Plastics invented innovative non-halogen flexible Noryl*resins, targeted as a replacement to PVC for wire coating. The flexible NORYL*resin production process is a relatively safe process compared to that of halogen-containing PVC. Flexible NORYL*resins are blends of polyarylene ether, polyolefin and specially designed flame retardants that are sufficiently flexible and flame resistant for many wire coating applications. The new technology allows one kilogram of flexible NORYL*resins to contain zero kilograms of halogenated compounds, heavy metal stabilizers or pigments and phthalates. This paper deals with the thermal, electrical, mechanical and flame-retardant properties of the resins and their performance behaviors in coated wire and cable. Flexible Noryl*resins can be used for not only various automotive wires, but also industrial wire and cable applications.

177. New design signals for green chemistry from the environmental health sciences.

John Peterson Myers, Environmental Health Sciences, Charlottesville VA

A new generation of scientific findings in the environmental health sciences are overturning long-held concepts that have guided use of toxicological results in developing public health standards. Much of this stems from new discoveries about the role of contamination in altering gene behavior through impacts on epigenetic mechanisms. These discoveries should also inform design decisions made by green chemists in their development of new materials.

178. Massachusetts model for evaluating alternative chemicals

Pamela A. Civie, Toxics Use Reduction Institute, Lowell, MA

In August 2005 the Commonwealth of Massachusetts requested that the Toxics Use Reduction Institute conduct a scientific study to assess safer alternatives for the following five toxic or hazardous chemicals: lead, formaldehyde, perchloroethylene, hexavalent chromium and di-(2-ethylhexyl)phthalate (DEHP). The Five Chemicals Study is limited to industries and applications where the use of the chemical is most significant and where alternatives exist. Since many criteria are evaluated to assess each substitution, the final report (due to the Legislature July 1, 2006) will not present a prioritized list of alternatives for each application and chemical. Rather, the report will present factual information to help organizations understand the tradeoffs between using each alternative to make better decisions for their particular applications. This presentation will discuss the specific methodology used to conduct this assessment and will present a summary of the preliminary findings.

179. Enzyme-based technology for decontamination of toxic organophosphorus compounds

Joseph J. DeFrank¹, Vipin K. Rastogi¹, Tu-chen Cheng¹ and Christopher S. Penet², (1)U.S. Army Edgewood Chemical & Biological Center, Aberdeen Proving Ground, MD, (2)Genencor International, Inc., Rochester, NY

With an increasing need to respond to real world threats such as a deliberate chemical warfare (CW) agent attack or accidental release of toxic industrial chemicals quickly and efficiently, an enzyme-based technology was developed and patented to neutralize organophosphorus CW agents and pesticides. This technology simplifies and improves the process of decontaminating a class of highly toxic chemicals, including neurotoxic CW agents. Other decontamination methods rely on corrosive or highly reactive chemicals that are more costly, less efficient and generate a substantial amount of residual waste. The enzyme-based technology is non-toxic, non-corrosive, does not generate hazardous waste and is environmentally safe. It can be applied using existing water-based application systems such as fire-fighting foams and sprays or aircraft de-icing solutions. In an incident resulting in the release of highly toxic chemicals, the enzymes quickly hydrolyze/neutralize them before they can contaminate a wider area and pose a greater danger. Since these hydrolysis/neutralization reactions are catalytic (the enzymes are not used up in the reactions), only very small quantities of the enzymes are required. While initially intended for decontaminating equipment, facilities and large areas, the enzymes could potentially be used for spot decontamination of sensitive equipment and in shower systems for decontaminating personnel and casualties.

Abstracts, *Continued*

Greener Processing & Innovative Technology

Sponsored & Organized by the GCI Pharmaceutical Roundtable

180. Green oxidations in organic synthesis: Learning from nature?

Andrew S. Wells¹, Neil Adlington² and Tove Åqvist³ (1)AstraZeneca, Loughborough, United Kingdom, (2)AstraZeneca, Macclesfield, United Kingdom, (3)AstraZeneca, Södertälje, Sweden

The question should be asked, why should the synthetic chemist seek out novel oxidation techniques? For example, aldehydes and acids can be produced *via* oxidation with a wide range of reagents, chromates, manganese, selenium dioxide, hypervalent iodine, halogens, sodium hypochlorite/hydrogen peroxide plus catalyst, Swern-type reagents, metals plus oxygen and many others. However many of these traditional chemical reagents have handling and environmental issues when used on a large scale, selectivity may be poor and some reagents may have very meager atom economy. Hydrogen peroxide and bleach are cheap, readily available with few apparent environmental concerns (not true for bleach) but chemical selectivity and safety issues like reagent accumulation and highly exothermic reactions can make scale-up and production hazardous. So as we strive for a greener and more sustainable economy; there is a growing interest in the application of more environmentally friendly oxidation technologies. To address this demand there is an emergent interest in the use of laccase enzymes in water, sometimes in combination with organic co-catalysts, to oxidize organic substrates using air as the terminal oxidant at or near ambient temperature. This presentation will look at some prospective applications of laccase oxidations in the pharmaceutical industry, both in the synthesis of organic intermediates and as a more sustainable technology for the removal of active pharmaceutical ingredients from aqueous waste streams.

181. Environmental considerations in pharmaceutical process development

Douglas Kjell, Eli Lilly, Indianapolis, IN

Process optimization within the pharmaceutical industry is subject to competitive pressures. In particular the desire to develop green chemistry must be balanced against the stringent requirements for product quality. Even the 12 principles of green chemistry may be in competition. This talk illustrates the competitive pressures and provides examples of how green chemistry principles were applied to pharmaceutical manufacture.

182. Chemical process research and development for atorvastatin lactone

Jade D. Nelson, Pfizer Global Research & Development, Groton, CT
Atorvastatin calcium, the active pharmaceutical ingredient (API) in Lipitor[®], is a selective, competitive inhibitor of HMG CoA reductase, the enzyme responsible for the rate-determining step in cholesterol biosynthesis. Since its 1997 U.S. launch, Lipitor[®] has developed into one of the world's most important medications, contributing to the cardiovascular health of millions of patients. As part of a Pfizer initiative to continually design and develop improved chemical processes for the manufacture of its products, an alternative process to atorvastatin lactone was developed. Key steps include an efficient Paal-Knorr pyrrole synthesis, a medium-temperature acetoacetate dianion condensation, an asymmetric β,δ -diketoester hydrogenation and a highly stereoselective oxy-Michael addition. A detailed account of this alternative approach and an overview of the current API manufacturing process will be presented.



Forum: Research Needs to Drive Innovation

SESSION OVERVIEW: The results of two surveys on green chemistry research challenges in the pharmaceutical industry will be presented. These surveys will establish a foundation for a broader discussion on green chemistry and engineering research needs for industrial application.

183. Analysis of the reactions used for the preparation of drug candidate molecules

John S. Carey¹, David Laffan², Colin Thomson³, and **Michael T. Williams**⁴, (1)GlaxoSmithKline Pharmaceuticals, nr. Leigh, Tonbridge, United Kingdom, (2)AstraZeneca PR&D, Macclesfield, Cheshire, United Kingdom, (3)AstraZeneca R&D Charnwood, Loughborough, Leics, United Kingdom, (4)Pfizer, Inc., Sandwich, Kent, United Kingdom

The purpose of this perspective is to indicate the range of chemistries used in the manufacture of drug candidate molecules and to highlight certain gaps in current technologies. To do this, a survey was carried out of chemical syntheses within the Process Chemistry R&D Departments of GlaxoSmithKline, AstraZeneca and Pfizer.

184. Key green chemistry research areas: A perspective from pharmaceutical manufacturers

Peter J. Dunn, Pfizer, Inc., Sandwich, Kent, United Kingdom and GCI Pharmaceutical Roundtable, ACS Green Chemistry Institute, Washington, DC

In 2005, the ACS Green Chemistry Institute (GCI) and global pharmaceutical corporations developed the GCI Pharmaceutical Roundtable (Roundtable) to encourage innovation while catalyzing the integration of green chemistry and green engineering in the global pharmaceutical industry. The Roundtable has been developing a list of key research areas with the goal of influencing the research agenda so that environmentally friendly solutions are brought to major green chemistry problems. This presentation covers the process of how the member companies pulled together and prioritized a list of key green chemistry research areas.

Energy Efficient Technologies I

ORGANIZER: Green Chemistry Institute American Chemical Society, Washington, DC

185. Enhancing the Soy Biorefinery

George A. Kraus, Iowa State University, Ames, IA

This presentation will describe a joint venture between the ISU Center for Catalysis and West Central Cooperative, a farmer-owned cooperative in Ralston, Iowa. A new set of catalysts that were discovered by scientists from the Center for Catalysis at Iowa State. The new catalysts are heterogeneous and recyclable, eliminating the "wash step" of biodiesel production, which, in turn, significantly lowers the cost of manufacturing biodiesel. Center for Catalysis researchers have also discovered a novel ionic hydrogenation reaction to convert glycerin, the by-product of biodiesel production, into 1,3-propanediol.

186. Light to electrical energy conversion with thin film goethite (α -FeOOH) nanocrystals

James Gardner and Gerald Meyer, Johns Hopkins University, Baltimore, MD

Goethite (α -FeOOH) nanocrystals were synthesized and cast as thin films for use as electrodes and photoelectrodes for the first time. Voltammetry experiments showed that the films were stable to both water reduction and oxidation. In addition, the goethite band gap was estimated from photoelectrochemical measurements and was found to be suitable for water splitting applications. Photon-to-current efficiencies were measured for the goethite thin films in aqueous electrolytes with a Pt counter electrode. Photocurrent action spectra agreed well with the goethite absorbance spectrum and revealed significant sensitivity to visible light. Ongoing experiments to optimize the conversion efficiency through surface functionalization, electrolyte modification and applied potential will also be presented.

187. PVC hydrocracking with recovering of a large amount of H₂: Characterization of the catalysts and the products after each step of the process

Thierry Giornelli¹, Franck Dumeignil² and Atsushi Ishihara¹, (1)Tokyo University of Agriculture and Technology, Koganei, Japan, (2)Universite des Sciences et Technologies de Lille, Villeneuve d'Ascq, France

A million tons of plastics are disposed all over the world every year. PVC is refractory to recycling processes. Different methods for recycling PVC exist (reprocessing, land-filling, incineration). They are used to retreat PVC wastes but they give unacceptable levels of gases' emissions in the presence of oxygen: harmful compounds such as nitrous oxide, SO_x, dioxins and HCl are released. Our work consists in the development of an environmental-friendly hydro-catalytic process for PVC recycling without formation of pollutants, while allowing the recovering of large quantities of hydrogen (clean energy source). It's a three-stepped process: cracking, gasification by steam reforming and HCl trapping (alkali-containing wastes). Our research focused on the PVC cracking. We worked at atmospheric pressure under steam (known to enable a large hydrogen recovering). HCl gas, released during the experiment, was trapped in water (the recovered amount was 97 % \pm 2%). Tars obtained were analyzed by GC-MS. The nature of all the compounds constituting the tars was determined. A small amount of gas was recovered (methane, carbon oxide, carbon dioxide and hydrogen were recovered). Used catalysts were analyzed: 1)The amount of coke on each catalyst after test was quantified by thermal analyses. 2)The porous structure was determined by BET before and after test and after the removal of the coke on the catalysts: catalysts keep their initial properties. 3)The coke composition was determined by chemical analyses. The results are interesting compared to those found in the literature. We plan to regenerate the catalysts with the hydrogen formed.

188. Energy from waste in Kenya: Waste and energy demand inventories

Joseph Keriko, Institute of Energy and Environmental Technology of Jomo Kenyatta University of Agriculture and Technology, Nairobi, Kenya
Kenya is facing environmental problems with haphazard dumping of wastes. It has been observed that waste generation growth is coupling with economical growth that is being witnessed today. This improper waste management is leading to a lot of damage of water resources. Inadequate electrical energy supply is another problem of great concern in our country. Thus, the scope of this project was to develop a system for producing electricity from different kinds of waste: dry wastes which can be combusted to produce steam for electricity generation in steam turbines and wet biodegradable wastes that can be treated by anaerobic digestion to produce organic fertilizer and biogas. This report will give the inventory of waste in the major towns of Kenya and also the current and future energy demand for Kenya.

Abstracts, Continued

Agriculture I

ORGANIZER: Green Chemistry Institute American Chemical Society, Washington, DC

189. Efficient Agriculture for the Environment

Dean Kleckner, Truth About Trade and Technology

Agricultural production is changing. Farmers are becoming more environmentally aware and concerned. Farmers may, indeed, be the premier environmentalists of today. We live out there in the fields and on the farms of America. I was taught by my father, as most of us were, to leave things better than they were when we took over. We do that by using less chemicals and pesticides, by making less trips over the fields, meaning less compaction and using less diesel fuel.

190. Green composites using poly(lactic acid) and agricultural co-products

Victoria Finkenstadt¹, LinShu Liu², C.K. Liu¹, Steven C. Cermak², Roque Evangelista², Milagros Hojilla-Evangelista¹ and J.L. Willett¹, (1)National Center for Agricultural Utilization Research, USDA, Peoria, IL, (2)Eastern Regional Research Center, USDA, Wyndmoor, PA

Poly(lactic acid) is a biodegradable plastic made from renewable resources and has similar mechanical properties to polypropylene. PLA is more expensive than petroleum-based plastics and the use of a low-cost fillers and extenders is desirable. Agricultural co-products (AcP) were collected after initial processing. Cuphea (C) and Lesquerella (L) are oil seed crops. Milkweed (M) is being investigated for industrial uses of its fiber. PLA was melted then AcP (0%, 8%, 15%, 22%, 30% and 45% w/w) was added producing a homogeneous resin which was injection molded. As AcP content increased, tensile strength for all PLA composites decreased as predicted by the Nicolais-Narkis model. PLA-C exhibited increased stiffness. In contrast, the modulus of PLA-M & PLA-L decreased slightly. Unexpectedly, PLA-M showed extensive stress-cracking under tensile stress and exhibited an elongation value 50% to 200% more than the PLA control.

191. Pesticide environmental stewardship program

John Steiner, NaturaLawn of America, Frederick, MD

In 1986, an eco-entrepreneurial business was started to offer consumers an alternative to the traditional chemical lawn care approach. When NaturaLawn of America began, it was labeled a "radical concept and too far ahead of its time". The need to design and/or develop a program and product line that was environmentally friendly yet delivered the necessary results for consumer satisfaction was the initial obstacle NaturaLawn of America had to overcome. While organic products had been around, they were extremely costly to use in a commercial endeavor and the results were very slow and unacceptable to the consumer. NaturaLawn[®] of America designed and developed their own line of fertilizer products and coined the term "organic-based" in 1986 to identify this unique product line. Using a self-designed IPM program based on prevention, monitoring and controlling of pest pressures, NaturaLawn of America has also radically reduced the use of all synthetic pesticides in their programs. Today, NaturaLawn of America now services over 50,000 customers in 23 states, generates over \$20 million in annual revenues, is the 19th largest franchisor headquartered in the State of Maryland and is the 4th largest lawn care service provider in the United States.

192. Nitamin steady delivery fertilizers for improved nitrogen efficiency in crops

John S. Kruse, Stacey L. Wertz, James M. Wargo and Kurt D. Gabrielson, Georgia-Pacific Corporation, Decatur, GA

Approximately 82 million metric tons of nitrogen fertilizer, primarily urea, is applied to cropland annually worldwide. Nitrogen release into the soil from urea hydrolysis and salt-based fertilizers such as ammonium nitrate is often too rapid for complete plant uptake, resulting in excess nitrogen leaching through the soil and contaminating groundwater. Nitamin[®] fertilizers provide an economic solution to this problem by slowing the rate at which nitrogen is available to the plant. By reacting urea with ammonia and formaldehyde under specific conditions to form a safe blend of small urea-formaldehyde polymers and cyclic compounds, the rate at which the nitrogen is released can be controlled, resulting in a more efficient release pattern. The primary Nitamin[®] fertilizer product releases nitrogen for approximately ninety days, which corresponds well to the nitrogen requirements of many crops. This controlled delivery allows the plant to use more of the applied nitrogen, resulting in reduced application rates and reduced leaching. It is this improved "Nitrogen Use Efficiency", coupled with affordability that is the highlight of this technology.

193. Anaerobic digested slurry: An input for sustainable agriculture

Neena V. Arora, Sri Sathya Sai College For Women, Bhopal, India

Crop cultivation requires supplementation of available nutrients to the plant for achieving yield potentialities. The supplementation is generally achieved through application of chemical fertilizer in the soil at different stages of crop life. These chemical fertilizers have hazardous effects. Anaerobic digestion of agro residues and cattle waste produces bio-gas which is used as domestic fuel and the digested slurry can be used as manure for crop production. The effectiveness of the bio-gas plant spent slurry in cultivation of various crops has been studied through extensive field trials. An experiment was conducted to assess the effect of application of nitrogen through chemical fertilizer and bio-gas plant spent slurry in different proportion on production of soybean-wheat rotation. Study reveals that 75% of the recommended dose of nitrogen can be replaced with bio-gas plant spent slurry without significant loss in grain yield. It also improves the soil health by maintaining higher microbial population than use of chemical fertilizer alone.

Alternative Synthesis II

Sponsored by the GCI Pharmaceutical Roundtable

194. Towards "green" atom transfer radical polymerization (ATRP): Strategies to significantly reduce the amount of copper-based catalyst

Nicolay V. Tsarevsky, Krzysztof Matyjaszewski, Ke Min and Wojciech Jakubowski, Carnegie Mellon University, Pittsburgh, PA

Atom transfer radical polymerization (ATRP) is a novel very efficient method for preparation of environmentally friendly well-defined (co)polymers. The resulting benign materials include thermoplastic elastomers (recyclable rubber), self-plasticizing PVC, sealants for self-cleaning windows, dispersants for inks and pigments, various lubricants and additives. ATRP relies on the reversible formation of growing radicals in the presence of transition metal compounds, such as copper complexes with organic ligands. Typical amount of catalysts used in laboratory and also in commercial processes is in the range of ~1,000 ppm. We have recently developed new methods for a dramatic reduction

of the level of copper complexes down to <10 ppm. These processes rely on activators re-generated by electron transfer (ARGET) and initiators for continuous activators regeneration (ICAR). They employ reducing agents that do not initiate new polymer chains and small amounts of radical initiators, respectively. Non-initiating reducing agents include ascorbic acid, sugars, hydrazine or tin(II) compounds. The essence of both processes is a continuous regeneration of Cu^I species by reduction of the Cu^{II} complex formed in the termination process, according to the persistent radical effect. To provide satisfactory control, the catalyst should be stable towards dissociation and protonation. Therefore, the ligands for such catalysts should have high stability constants for both Cu^I and Cu^{II} complexes. The rules for development of highly active catalysts that mediate ATRP at low concentration will be presented. Fundamentals of ARGET and ICAR will be discussed and illustrated by synthesis of various well-defined copolymers.

195. Oxidation of benzyl alcohol to benzoic acid with H₂O₂ catalyzed by dectungstates

Huaming Li¹, Wenshuai Zhu¹, Huoming Shu², Meiling He¹, Zhijun Luo¹ and Junxinag Guo¹, (1)Jiangsu University, Zhenjiang, China, (2)Hainan Normal University, Haikou, China

Six kinds of dectungstates such as (C₅H₅NC₁₆H₃₃)₄W₁₀O₃₂(I), [(CH₃)₄N]₄W₁₀O₃₂(II), [(CH₃)₃NC₁₀H₂₁]₄W₁₀O₃₂(III), [(CH₃)₃NC₁₆H₃₃]₄W₁₀O₃₂(IV), [(CH₃)₃NC₁₈H₃₇]₄W₁₀O₃₂(V) and [C₆H₅CH₂N(C₂H₅)₃]₄W₁₀O₃₂(VI) have been synthesized and characterized by IR, UV-vis, TG-DSC and element analysis. Their catalytic properties in oxidation of benzyl alcohol to benzoic acid were investigated with aqueous 30% hydrogen peroxide. The results show (C₅H₅NC₁₆H₃₃)₄W₁₀O₃₂(I) catalyst exhibits best activity in seven kinds of cations. Moreover, the larger of the single carbon chain of quaternary ammonium dectungstates, the better activity the catalysts exhibit. Benzoic acid can be obtained in 91.4% yield when the mixture of benzyl alcohol, 30(wt.%) H₂O₂ and catalyst I (in mol ratio of 100:300:0.1) was stirred vigorously at 90°C for 10 h. The catalytic system was carried out without organic solvent and halogen conditions in an economically, technically and environmentally satisfying manner. The oxidation procedures meet the needs of contemporary green chemistry and are suitable for practical organic synthesis.

196. Bromine-free TEMPO-based catalyst system for the oxidation of alcohols

Robert L. Augustine¹, Setrak K. Tanielyan¹, Kenneth Furlong² and Handley Jackson², (1)Seton Hall University, South Orange, NJ, (2)The NutraSweet Corporation, Augusta, GA

The selective oxidation of alcohols to the corresponding carbonyl compounds is one of the more important transformations in synthetic organic chemistry. A large number of oxidants have been reported in the literature but most of them are based on the use of transition metal oxides such as those of chromium and manganese are toxic species so their use creates serious problems concerning their handling and disposal, especially in large scale, commercial applications. A common alternative is the oxidation using NaOCl and TEMPO as described by Anelli. This reaction is carried out in a two-phase (CH₂Cl₂/H₂O) system with TEMPO as a catalyst and NaOCl as the oxidant. A co-catalyst, KBr, increases the reaction rate. The oxidation procedure described here is an extension of the Anelli process which does not require any organic solvents and replaces the KBr co-catalyst with the more benign, Na₂B₄O₇ (Borax). In the absence of any organic solvents the reactant alcohol comprises about 38% of the total reaction volume as compared with only about 2.5% when the classic reaction is run in dichloromethane. This has positive cost, environmental and process safety implications.

A further advantage to the use of the solvent-free reaction is the fact that the product can be isolated by phase separation from the aqueous solution, another energy savings since no solvent needs to be removed. This modified process was used for the selective oxidation of a number of primary and secondary alcohols giving the corresponding aldehydes or ketones in very good to excellent yields.

197. Towards a more environmentally benign synthesis of a doped perovskite, barium titanate

Anne E. Marteel-Parrish, Danielle Harlan and Jonathan Martin, Washington College, Chestertown, MD

The most investigated member of the perovskite family, barium titanate, BaTiO₃, is the major raw material for the production of multilayer ceramic capacitors used in decoupling, filtering, timing and other applications. A high dielectric constant at room temperature is an essential property needed for capacitor applications. This can be achieved through doping. The goal of this study is to develop a more environmentally benign method of doping barium titanate. Examples of previous methods of doping consisted of the sol-gel technique, wet chemical synthesis route and the direct precipitation method. The major disadvantages with these doping routes were a poor stoichiometric control resulting in low yields, production of unwanted side-products and the use of necessary post-treatments requiring high temperatures and pressures, special handling, storage, and disposal procedures. The doping strategies presented here are based on the strict thermodynamic control over the barium-to-strontium solubility product ratios in the presence of an excess reagent. These routes involve a solid-state means and reactions using a microwave and a centrifuge. The intermediate product, BaTi(cat)₃·3 H₂O, and both doping sources, strontium oxalate, SrC₂O₄ and strontium carbonate, SrCO₃, are used in this project. X-ray powder diffraction, infrared spectroscopy and inductively coupled plasma-atomic emission spectroscopy are the characterization techniques used to analyze the final products. All three of these processes prove to be environmentally friendly and economical, combining green chemistry with materials science. The synthesis and characterization data are detailed in this presentation.

198. Simplified green chemistry approaches to organic synthesis in solid media: Activated fly ash, an industrial waste (pollutant) as an efficient and novel catalyst for some selected organic reactions in 'dry media'

Mannathusamy Gopalakrishnan, Purusothaman Sureshkumar, Jayaraman Thanusu, Vijayakumar Kanagarajan and Ramalingam Govindaraju, Annamalai University, Chidambaram, India

Activated fly ash, an industrial waste (pollutant) is found to be well suited for catalyzing reactions which are having industrial, pharmacological and therapeutic importance, e.g., Knoevenagel condensation, 'One-Pot' conversions of ketones to amides *via* Beckmann rearrangement, Schiff Bases formation, Biginelli and Hantzsch reactions under solvent-free conditions. Moreover, this catalyst shows a promising future in that it can provide environmentally clean processes for the chemical industry of the next millennium.

Abstracts, *Continued*

199. DNA photolyase for the enzymatic crosslink reversal of bioinspired thymine containing photopolymers

Justin R. Whitfield, Laura R. Ingalls and John C. Warner, University of Massachusetts Lowell, Lowell, MA

We have applied bioinspired thymine containing polymers to a wide variety of applications ranging from controlled drug delivery devices to microelectronic photoresists. These environmentally benign systems function through the photoinduced (2+2)-cyclodimerization of pendant thymine units on preformed water soluble polymers to create crosslinks that render the polymers insoluble. We have discovered that DNA photolyase, an enzyme found in *E. coli* bacteria, functions to reverse this photodimerization [and thus the crosslinking] in our bioinspired polymers. This reversal returns them back to their original state for reuse. Unfortunately, the thermal stability and large-scale availability of this enzyme has made use in any practical applications problematic. The focus of this research has been to determine whether the DNA photolyase found in certain extremophiles might also be capable of such chemistry in our polymer systems. We have developed a method of synthesis of extremophile derived DNA photolyase through cloning, expression and purification. Potential benefits of this enzyme versus the *E. coli* variant include its enhanced thermal stability and widened processing window as well as the ability to prepare large quantities of enzyme in large scale syntheses. The green chemistry implications of the synthesis and use of this enzyme will be discussed.

Green Nanotechnology

ORGANIZER: Green Chemistry Institute American Chemical Society, Washington, DC

200. Green nanoscience

James E. Hutchison, University of Oregon, Eugene, OR

Nanotechnology promises considerable benefit to society and the environment. However, the products of nanotechnology and the manufacturing processes used to produce these products may pose threats to human health, the environment, worker safety and security. The challenge will be to develop nanotechnology to provide maximum benefit, while minimizing the hazards. Green chemistry and engineering principles can be adopted to guide the early stages of product and process development to meet this challenge. Discoveries in nanoscience will provide new opportunities for the development of sustainable technologies. In this presentation, I will discuss how green chemistry principles can guide the responsible development of nanotechnology and how nanoscience can enable the discovery of greener products and processes. Examples of greener materials, processes and applications of nanoscience will be presented, with an emphasis on greener nanomaterials and nanomanufacturing methods.

201. Production of polymer nanocomposites using renewable polymers with solid-state shear pulverization

Amanda Walker and John M. Torkelson, Northwestern University, Evanston, IL

Nanocomposites are an inexpensive and efficient way to produce polymeric materials with new or improved properties. By incorporating a nanofiller such as clay, the thermal barrier and mechanical properties can be altered. The overall effect of the clay is dependent upon many factors, including dispersion. The ideal platelet dispersion, exfoliation, is often difficult to achieve using conventional polymer processing techniques. This suggests using a novel method for nanocomposite production. For this work, solid-state shear pulverization (SSSP) was used to create polymer/clay nanocomposites. This process utilizes a modified twin-screw extruder which is cooled to keep the polymer below the transition temperature. Consequently, all processing occurs in the solid state. This eliminates any thermodynamic limitations associated with blend formation, providing the opportunity for a well dispersed system. In addition, SSSP has the potential to eliminate the need for solvents, organic modifiers and plasticizers necessary in conventional processes. The dispersion, thermal properties, and barrier characteristics of several polymer systems were examined. Nanocomposites were created from thermoplastic starch and poly(caprolactone) with clay. Small angle x-ray scattering demonstrated increasing levels of exfoliation in the thermoplastic starch nanocomposites processed using different experimental conditions. The incorporation of the clay was shown to improve the thermal stability of the polymers when held at a constant temperature near the polymer degradation temperature. For poly(caprolactone), processing *via* SSSP produced changes in the crystallization behavior of the neat polymer. This was demonstrated by differential scanning calorimetry and oxygen permeation. By incorporating small quantities of clay, these effects were increased.

202. Benign process for silver nanoparticles' synthesis and processing in neat carbon dioxide solvent using fluorine-free compounds

Madhu Anand, Philip W. Bell and Christopher B. Roberts, Auburn University, Auburn, AL

Carbon dioxide presents certain advantages in nanoparticles' synthesis and processing due to its tunable solvent properties, vanishingly low-surface tensions and environmentally green characteristics. Unfortunately its advantages are limited by the use of environmentally persistent fluorinated compounds since most current techniques employed to synthesize and disperse nanoparticles in carbon dioxide use fluorinated compounds as metal precursors and/or stabilizing ligands. This paper illustrates a one-step process for synthesis and stabilization of silver nanoparticles in carbon dioxide without using any fluorinated compounds. Silver nanoparticles were formed and stably dispersed through arrested precipitation by reducing non-fluorinated organic metal precursor in the presence of non-fluorinated organic acid as a capping ligand in neat carbon dioxide solvent. Non-fluorinated co-solvents were examined as a means to enhance the dispersibility of the silver nanoparticles. An increase in carbon dioxide solvent density by an increase in pressure also enhances the dispersibility of the particles due to an increase in solvent strength. The dispersibility of the silver nanoparticles diminishes with time until a stable dispersion is achieved due to the precipitation of a fraction of particle sizes too large to be stabilized by the solvent medium, thereby leaving a smaller size fraction of nanoparticles stably dispersed in the CO₂ mixtures. This paper presents the first report of synthesis and stabilization of metallic nanoparticles in carbon dioxide solvent without the use of any fluorinated compounds thereby further enabling the use of CO₂ as a green solvent medium in nanomaterials' synthesis and processing.

203. Development of supported nanoparticulate metal complexes using compressed carbon dioxide

Chad A. Johnson, Sarika Sharma, Andrew S. Borovik and Bala Subramaniam, University of Kansas, Lawrence, KS

The properties of nanomaterials are governed by a variety of factors including size, shape and surface morphology. For example, gold nanoclusters of sizes ranging from 1-10 nm have dramatically different properties than their bulk forms. Few, if any, studies have reported about the characteristics of nanostructured materials composed exclusively of metal complexes because limited preparative methods have hindered production. It is demonstrated in this work that precipitation with compressed antisolvent (PCA) technology could be utilized to create nanoparticles of transition metal complexes. Our findings demonstrate that the molecular structure of the precursor starting material dramatically influences the morphology of the final precipitate. Preliminary results demonstrate that the [Co(salen)] nanoparticles are able to bind nitric oxide in the solid state, while commercial [Co(salen)] shows no binding capacity. The nanoparticles have been supported on solid supports such as alumina, glass, and cellulose for use as heterogeneous catalysts. The core particles (or support) are suspended in $scCO_2$ by fluidization and the solution containing the compound of interest is sprayed into the suspension similar to the PCA process. The $scCO_2$ selectivity dries the solvent forming nanoparticles that are then deposited on the fluidized support. Fluidization velocities utilized and the internal glass column design was based on correlations developed by previous researches. These results will be presented and discussed.

204. Synthesis and extraction of β -D glucose stabilized Au nanoparticles processed into low defect, wide area thin films and ordered arrays using CO_2 -expanded liquids

Juncheng Liu Sr., Madhu Anand and Christopher B. Roberts, Auburn University, Auburn, AL

Herein, we report a straightforward and benign β -D glucose assisted aqueous phase process for the synthesis of Au nanoparticles followed by extraction of the particles into an organic phase *via* ligand exchange. This extraction process results in a Au nanoparticle dispersion with a narrow size distribution in an organic solvent. This organic nanoparticle dispersion was subsequently processed into close packed, wide area thin films and ordered arrays using a precisely controlled CO_2 -expanded liquid particle deposition technique. This strategy has several technical advantages and attributes. First, it provides a facile and effective nanoparticle synthesis/extraction approach to produce relatively monodisperse nanoparticles without the need for elaborate, solvent intensive post-synthesis processing to narrow the particle size distribution. Notably, the process utilizes small amounts of β -D glucose as a "green" alternative to expensive phase transfer catalysts while also allowing complete recycle of the β -D glucose. Second, CO_2 -expanded liquid process was implemented as a means to remove organic solvents thereby avoiding the detrimental dewetting effects and interfacial tensions that exist in conventional solvent evaporation techniques. As a result, low defect and wide area nanoparticle thin films were formed with local order. Finally, the environmentally benign solvents of water and CO_2 were employed along with the "green" capping agent β -D glucose and a small amount of inexpensive dodecanethiol (as opposed to the expensive and environmentally persistent fluorinated compounds required in $scCO_2$ based processes). The highly concentrated Au nanoparticle dispersions in hexane could be achieved upon extraction, hence, providing another "green" virtue of this strategy.

205. Photocatalytic activity of TiO_2 foam and $TiO_2/RuO_2/SiO_2$ nanoparticles for water purification

Alex Omo Ibadon, Gilian Greenway and Yue Yue, University of Hull, Hull, United Kingdom

Silicon and ruthenium dioxide modified high surface area titania dioxide nanoparticles resulting from hydrogen reduction and a mesoporous TiO_2 foam were characterized by XRD, AFM and Raman spectroscopy and examined for their catalytic activity towards the photodegradation of methyl orange (MO), a common water pollutant in the textile industry. The modified materials present enhanced photocatalytic activity and can decompose the MO faster than TiO_2 , TiO_2/RuO_2 . Results showed that doping with RuO_2 only offered a marginal benefit over TiO_2 alone. Doping with SiO_2 resulted in a marked increase in the rate constant and the photodegradation efficiency. These results are consistent with the unique structural, morphological and surface characteristics of the composite titania dioxide/ruthenium dioxide/silicon dioxide materials. The lower the average particle size, roughness and fractal dimensions, the higher the photodegradation percentage and the rate constant. The surface doping effect appears synergetic to the charge separation process and the photocatalytic results are explained on the basis of the mechanism involving efficient separation of electron-hole pairs induced by silicon ions. This enhances the ability of the modified particles to effectively capture protons. Results also show that the modified nanoparticles can be used repeatedly over a long time without loss of efficiency.

Industrial Applications II

206. Closing the loop with "Benign by Design" bio-based fabrics and backings

Bill Foley, Interface Fabrics, Grand Rapids, MI

Interface Fabrics has introduced a sustainable quality textile fabric that utilizes bio-based fibers, environmentally preferable textile finishing dyes and chemicals and a bio-based textile coating. The base material for the bio-based Terratex[®] fabric and the BioBac[™] textile coating is a 100% homo-polymer of polylactate (PLA). The fabric is woven from Ingeo[™] PLA fiber and BioBac[™] is made from NatureWorks[™] PLA resin. PLA Terratex[®] is an alternative to petroleum-derived fibers and BioBac[™] replaces acrylic or synthetic SBR latex coatings. The inherent biodegradability of PLA allows for re-assimilation into plant matter as a biological nutrient, thereby "closing the loop" on raw material utilization. PLA Terratex[®] can be successfully composted in a commercial composting facility without compromising the process or the agronomic quality of the mature compost product, including the eco-toxicity profile. Interface Fabrics has developed a stringent Dye and Chemical Protocol to screen all ingredients used to dye and finish the fabric in order to selectively specify only those ingredients that are not harmful to human health or the environment. The protocol has screened to date 279 different chemical ingredients contained in about 147 products (dyes, finishes and auxiliaries), of which only 30 have been approved for use. To validate the benign nature of the Dye and Chemical Protocol, fabric samples of six colorways were subjected to hazardous waste characterization and synthetic precipitation leaching procedure analyses. A total of 179 chemicals of concern were screened, including VOCs, semi-VOCs, metals, polychlorinated biphenyls, pesticides and carbonyls with no chemicals of concern being detected.

Abstracts, *Continued*

207. Catalytic hydrogenation of 2,5-piperazinedione to piperazine

Andrea S. Molengraaf, James E. Jackson and Dennis J. Miller, Michigan State University, East Lansing, MI

Amide hydrogenation is a process of importance in the chemistry community because its target products serve a wide variety of applications such as pH adjusters, surfactants, detergent additives, metal ion scavengers and support materials or building blocks for pharmaceuticals. Amide hydrogenation and hydrolysis have been found to be competitive processes under aqueous conditions. We aimed to conduct 'green' selective heterogeneous catalytic reductions of amides, under aqueous conditions, at low temperature and pressure. The cyclic anhydride of glycine, 2,5-piperazinedione, was used as a model amide substrate. Optimal conditions for its reduction were achieved using a systematic experimental design, the Box-Benken model. Under the optimized conditions, 2,5-piperazinedione was reduced to 35% piperazine at 24 hours, with 29% selectivity. The secondary hydrolysis products, glycyl glycine, glycine and ethanolamine were formed only in 10% and 1% yield, respectively. The reduction of 2,5-piperazinedione is a model for our ongoing work for the selective reduction of peptide amides to their corresponding polyamido and polyamino alcohol polymers. The development of this 'green' process and the formation of polyamido and polyamino alcohol polymers opens the door to utilization of a new renewables-based feedstock fraction, the proteinaceous component, for economical production of value-added products.

208. Development of Nike brand footwear outsole rubber as environmentally preferred material

Andy F. Chen¹, John Yu¹, Marcos Predovic¹, Tom Wilson², Kim Ames³, Juliet Bautista⁴ and Jeff Bailey-Darland⁵, (1)Nike, Beaverton, OR, (2)Nike, Toulou, Taiwan, (3)Nike, Taichung, 406, Taiwan, (4)Nike, Guangzhou, China, (5)Nike, Busan, South Korea

One of Nike's long-term corporate environmental goals is to eliminate from its products all substances known or suspected to be harmful to human health or the environment. Nike is pursuing the vision of Considered Design, where the goal is to making innovative, performance-quality products that demand less of our natural resources and to strive to incorporate sustainability as a design component from the beginning. With these ultimate goals, Nike Footwear has demonstrated its industry leadership by successfully eliminating many toxic substances from its rubber outsoles. Nike Footwear redesigned two of its rubber formulations using the Cradle to Cradle™ Design Protocol for assessing chemicals against 19 human health and environmental criteria. Using this protocol, Nike identified rubber ingredients to replace and preferred alternatives that would meet performance requirements. Through the use of more benign accelerators, vegetable oils and modified processing, Nike created new environmentally preferred rubber for outsoles. The new formulations contain 96% fewer toxics by weight than the original formulations, provide equal performance, look the same and cost no more than traditional rubber. To Nike's knowledge, these are the most advanced rubber formulations from a sustainability perspective within the footwear industry and will help initiate collaboration with manufacturers in other industries in the design and use of more sustainable materials. Nike is currently pursuing the establishment of a consortium of companies to pool resources in order to jointly research, develop and utilize preferred chemicals, helping improve cost factors, as well as the sustainability of materials that can be collectively used.

209. Non-chemical microbiological control for industrial cooling water systems

Joanne Kuchinski, Andrew Ledlie and Winston Go, Ashland Specialty Chemical, Boonton, NJ

Effective microbiological control is a critical component to maintaining system cleanliness and optimizing operating efficiencies in industrial cooling water systems. Microbiological control is oftentimes difficult to achieve and maintain and is traditionally accomplished through the use of oxidizing and/or non-oxidizing microbiocides. The selection of microbiocides is substantially affected by a combination of factors involving economic, demographic, regulatory and technological issues. Due to a wide range of reasons involving environmental discharge issues, worker safety concerns, storage, troublesome feed equipment and impact on system metallurgy, the selection and/or application of microbiocides are often compromised. As a result, the desire to minimize and even eliminate chemical microbiocides is becoming typical. A novel, non-chemical means of maintaining total system microbiological control has been successfully developed and effectively applied to industrial cooling water systems. The process involves the unique and practical application of ultrasound and provides both planktonic and sessile biological control. This paper describes the treatment process as well as the advantages and benefits achieved by maintaining system cleanliness.

210. Degradation of estradiol and ethinylestradiol with an Fe-TAML® oxidant activator and hydrogen peroxide

Nancy W. Shappell¹, Kyoung Ro², Melanie Vrabel³, Peter Madsen³, Colin Horowitz³, Patrick G. Hunt² and Terrence J. Collins³, (1)USDA-ARS Biosciences Research Laboratory, Fargo, ND, (2)USDA-ARS Coastal Plains Research Center, Florence, SC, (3)Carnegie Mellon University, Pittsburgh, PA

Endocrine disruptors have been found in our surface waters as a result of incomplete wastewater treatment and contamination from animal rearing facilities. Two identified contaminants with estrogenic activity are 17 β -estradiol (E_2 , the most potent natural estrogenic hormone) and 17 α -ethinylestradiol (EE_2 , the synthetic estrogen found in most birth control pills). A peroxide-activating catalyst Fe-TAML® (TAML® is tetraamido macrocyclic ligand) was evaluated for its capacity to degrade these compounds. While EE_2 is resistant to most biological degradation processes, the Fe-TAML® catalyst plus hydrogen peroxide (pH 10) resulted in degradation of $\geq 95\%$ within 5 minutes at room temperature (by HPLC analysis). Similar degradation was observed with E_2 when the Fe-TAML®: E_2 ratio was 1:250, while degradation kinetics were measurable using ratios of 1:1,000. The reaction closely followed first-order decay kinetics. Using LC MS-MS, neither estrogenic metabolite estrone nor estradiol was detected post-reaction. These results indicate a potential use for Fe-TAML® in remediation of municipal and agricultural wastewater containing estrogenic compounds.

211. New approaches to sustainability: The power of abduction

Judy K. Kosovich, James S. Turner and Emanuel Dash, P Street Institute, Washington, DC

Often the barriers to sustainability are due to limited thought. Barriers may manifest as “solutions” that are overly complex or simplistic, have unanticipated consequences or lead to deadlock and conflict. A recent article in Science reported that conscious or traditional “rational” thinking, best for simple situations, led to worse outcomes for complex situations. This article adds to a growing body of evidence that modern people over-rely on deductive and inductive thinking, forms of logic which can be used to test hypotheses and to draw conclusions, but cannot create novel hypotheses. The logic used to create hypotheses, identified by Aristotle as “apagogue,” was further explored in the 19th century by Charles Saunders Peirce, who called it “abduction.” Pierce articulated how logic and math could be used in conjunction with instinct and intuition to develop strategies for change and that randomness is an essential part of abduction. Other aspects of abduction were articulated by Nobel Laureate Kenneth Arrow, who proved that aggregated data could lead to false conclusions. Using abductive logic to solve problems, resulting solutions may seem obvious, even though previously overlooked. The solutions may also be surprising, though their market value may be obvious. The link to sustainability and a sampling of techniques will be presented.

212. Engineering analysis in environmentally benign microwave-assisted chemo-enzymatic epoxidation of styrene over immobilized lipase

Ganapati D. Yadav and Indrakant V. Borkar, University of Mumbai Institute of Chemical Technology, Mumbai, India

The use of microwave radiation in enzymatic synthesis remains limited. Literature on this subject is still poor and controversial. Kinetics and selectivity improvements of enzymatic reactions carried out under a microwave field in organic media have been reported but the effect of radiation on reaction mechanism and enzyme stability in non-conventional media have not yet been investigated. Here we have used *Candida antarctica* lipase B immobilized on polyacrylic resin (Novozym 435) to generate perlauric acid directly from lauric acid and hydrogen peroxide. This perlauric acid formed was then applied for *in situ* as well as *ex situ* epoxidations of styrene. Both the *in situ* and *ex situ* epoxidation of styrene were studied in a systematic way including the effect of various parameters, mechanism, kinetic modeling and deactivation. It was observed that Novozym 435 gets deactivated by temperature, concentration of hydrogen peroxide and perlauric acid. Here for the first time we have studied extensively the effect of microwave irradiation on reaction mechanism, stability and deactivation of *Candida antarctica* lipase B. Under microwave irradiation the deactivation of Novozym 435 was substantially reduced; there was an increase in the frequency factor resulting from enhanced collision of molecules, which can in turn be attributed to the increasing entropy of the system. Kinetic models were proposed for the reaction and deactivation and used to simulate the conversion profiles, which are in good agreement with the experimental profiles. The *in situ* epoxidation of styrene was found to be a better method than the *ex situ* epoxidation.

Energy Efficient Technologies II

213. Toward efficient catalytic routes to hydrogen from bioresources

Claus Hviid Christensen, Technical University of Denmark, Kgs. Lyngby, Denmark

In a few decades, the reserves of oil may have decreased significantly resulting in further increasing oil prices. At the same time, less polluting energy production processes and a lowering of CO₂ emissions are required. A decrease in air pollution from vehicles can be obtained by the introduction of fuel cell-driven automobiles, which in addition are able to utilize the fuel much more efficiently than a combustion engine. Optimally, the hydrogen for the fuel cells should be obtained from a renewable resource. To produce the hydrogen from biomass, strong chemical bonds must be broken and new bonds formed. These reactions are activated and typically catalyzed by solid surfaces. Thus, in most scenarios more efficient hydrogen production methods require more efficient catalysts. It is shown how the emerging molecular-level picture of hydrogen production on catalytic surfaces may soon allow us to design such catalysts on the basis of insight. This is done by using the steam-reforming of ethanol, obtained e.g., by fermentation, as an example. For this reaction, the challenge is to find inexpensive and stable catalyst that can be operated at low temperatures. After steam-reforming, it is also necessary to purify the hydrogen by removing traces of CO that would otherwise poison the fuel cell electrode. This purification could be done by preferential catalytic oxidation or by selective catalytic hydrogenation of CO. Both options are discussed, with emphasis on the selective hydrogenation where a new technical catalyst was recently discovered solely on the basis on computation screening. This novel approach to catalyst discovery and optimization is expected to generally facilitate the development of improved catalysts for hydrogen production.

214. Novel nanocomposite oxygen carriers for chemical looping combustion

Tengfei Liu¹, Thomas Simonyi², Tom Sanders¹, Ranjani Siriwardane³ and **Goetz Vesper¹**, (1)University of Pittsburgh, Pittsburgh, PA, (2)Research Development Solutions, Morgantown, WV, (3)DOE-NETL, Morgantown, WV

Chemical looping combustion (CLC) is an emerging technology for clean energy production from fossil and renewable fuels. In CLC, an oxygen carrier (typically a metal) is first oxidized with air. The hot metal oxide is then reduced in contact with a fuel in a second reactor, thus combusting the fuel. Finally, the reduced metal is transferred back to the oxidizer, closing the materials “loop”. CLC is a ‘green’ combustion technology since it allows for flameless and completely NO_x-free combustion without requiring expensive air separation. Furthermore, CLC produces sequestration-ready CO₂-streams without significant energy penalty. Combined with sequestration, CLC thus enables high efficiency, CO₂ emissions-free combustion of fossil fuels or combustion processes with negative CO₂ footprint from biomass-derived fuels. However, CLC is suffering from insufficient stability of the oxygen carrier (particularly metal sintering) and slow metal re-oxidation kinetics. We report a significant step towards overcoming these hurdles based on novel nanocomposite carriers. Ni- and Fe-based nanocomposites were synthesized, characterized (BET, XRD, EDX, TEM, TGA) and evaluated in comparison with conventional Ni- and Fe-bentonites using a syngas fuel. The metal nanoparticles are embedded in a high-temperature ceramic matrix, resulting in exceptionally stable carriers with highly reproducible oxidation-reduction cycles at reaction conditions. Most significantly, the nanocomposite re-oxidation is accelerated by up to two orders of magnitude in comparison

Abstracts, *Continued*

to conventional carriers. Our experimental results and the great potential of these novel carrier materials for clean energy applications will be discussed in detail in the presentation.

215. Multi-scale modeling of H₂ storage in clathrates

Prasad Yedlapalli¹, Sangyong Lee² and Jae W. Lee¹, (1)The City College of the City University of New York, New York, NY, (2)Texas A&M University-Kingsville, Kingsville, TX

The research and development of new hydrogen storage methods have been driven by the need for a new energy source that will replace the limited amounts of petroleum. The technology of using hydrogen as an environmentally clean and efficient fuel became an active research area. To achieve a secure supply of hydrogen, a safe and economical storage technique needs to be developed. Hydrogen gas hydrates are one such promising medium for hydrogen storage. Gas hydrates are crystalline compounds, also known as clathrates. The H₂ molecules are entrapped in a cage-like structure of hydrogen bonded water molecules. The design of gas hydrate storage systems needs an accurate prediction of dissociation pressures with temperature. The dissociation pressures are generally predicted using van der Waals and Platteeuw theory. It is only applicable to singly occupied cavities. To overcome this limitation, multiple H₂ molecules in one water cavity are handled by assuming that bi-hydrogen and tetra-hydrogen molecules are single-cluster molecules. *Ab initio* calculations are performed for determining binary interaction potential of one H₂ cluster with one water molecule for various inter molecular distances and various spatial cluster configurations using GAMESS. The interaction energies are fit using Exp 6 form that is used to calculate the Langmuir constant. At equilibrium, the chemical potential of the water phase will be equal to that of water in the hydrate phase. The reference chemical potential will be adjusted to get close agreement between the experimental dissociation pressure and the calculated dissociation pressure using a cell distortion model.

216. Coal refining: A near-term green energy process

E. Gerald Meyer, University of Wyoming, Laramie, WY

Coal has the largest reserves of any fossil fuel. In the U.S. coal reserves are 25 times greater than those of oil plus gas. In the world this number is three. While mid- and long-term energy systems are important to develop, so is it necessary to satisfy the nation's current annual energy appetite of 100 quads (quadrillion Btu). Because it is abundant and inexpensive coal is a critically important contributor. Coal is burned to produce power resulting in SO_x and NO_x emissions. Removing these from the stack gas is expensive and inefficient. A precombustion technology, coal refining, removes the sulfur and nitrogen prior to combustion and further recovers them as salable products. This technology is similar to petroleum refining in that the coal is hydrocracked to produce a slate of value-added products. One such is char, a substitute for coal; it is a high heat value, uniform fuel with no sulfur or nitrogen. Other refinery products are syngas, BTX, naphtha and a #4 fuel oil. Some of the coal carbon is sequestered by conversion of the liquid products to plastics, which also reduces the use of petroleum. Chemical engineering processes, environmental effects and plant economics are fully discussed.

217. Abstract Withdrawn

Agriculture II

218. Presporulating entomopathogenic fungi attract, infect and control termites and ants

Paul E. Stamets, Fungi Perfecti, Shelton, WA

The promise of biopesticides made from fungi for controlling termites and ants has failed to overcome a simple fact of nature: insects are repelled by the spores of entomopathogenic fungi. A novel approach of using these fungi, prior to sporulation, has provided a solution to the fungi's inherent repellency. The basis of this new discovery is that the mycelium, prior to sporulation, attracts and causes significant phagostimulation, trail-following behavior and infection deep into the colonies. Two patents have been awarded, with more pending, for techniques and products centered upon the pre-sporulating mycelium of the entomopathogenic fungi *Metarhizium anisopliae* and *Beauveria bassiana* as natural agents to control termites and ants. Fungal cultures can be isolated from naturally infected insects and, through a selection process, can be cultured in the laboratory to create strains that delay spore production for several weeks. The pre-sporulating entomopathogenic mycelia draw select pests to a chosen locus, from where they then spread the infectious fungi throughout the targeted nest and ultimately to the queen. In choice tests, termites prefer the pre-sporulating mycelium of *Metarhizium anisopliae* to wood as food. Current research shows that diverse insect species share specific affinities to these fungi in their pre-sporulating state. Extracts made from these fungi can be optimized, in some cases, by dilution of the originals to 50 ppm. This discovery may reinvigorate research on using fungi for controlling insect pests worldwide, social and non-social. The submitted green mycotechnology is economical, scaleable and utilizes cell culture methods currently in practice.

219. New asymmetric hydroxylation technology for the commercial manufacture of indoxacarb

Albert L. Casalnuovo, DuPont, Newark, DE

Indoxacarb is a major new insecticide marketed worldwide by DuPont Crop Protection. It is the insecticidally active S-form of a racemic pair of which the R-form is not active. In such cases it is undesirable to manufacture and apply racemic mixtures, due both to the environmental burden of the inactive enantiomer itself and, additionally, the waste generated in its production. Recognizing this, scientists at DuPont developed new proprietary technology for the asymmetric synthesis of indoxacarb. The first generation process, an asymmetric hydroxylation catalyzed by cinchonine, afforded a 50% enantiomerically enriched product. This technology was utilized in the first commercial production of indoxacarb in January, 2000. Now a recently developed second generation process based on chiral zirconium-diamine complexes has been demonstrated with the commercial production of the first fully enriched (>98% ee) indoxacarb in September, 2005. At the current indoxacarb production volumes, this represents a further reduction in the total material burden on the environment of hundreds of tons per year.

220. ARS biopolymers research — yesterday, today, and tomorrow.

Robert L. Fireovid, USDA Agricultural Research Service, Beltsville, MD

The Agricultural Research Service (ARS) was created in 1953 as the primary in-house research agency of the USDA. USDA has been conducting research to discover new uses for agricultural commodities and byproducts for over 60 years, primarily at the four ARS Regional Research Centers in Albany, CA, Peoria, IL, New Orleans, LA, and Wyndmoor (near Philadelphia), PA. Many of the products developed by ARS through the years have been biopolymers and composites. Past USDA research generated xanthan gum, starch-based superabsorbents, and soy-based epoxide plasticizers & dimer resins. ARS researchers use physical, chemical, and biological processes to extract and convert agricultural fats and oils, starches, proteins, and cellulose into valuable polymers and composites for industrial and personal applications. Recent accomplishments and projected work and applications will be discussed.

221. Development of domestic crops to produce industrially useful products

Maureen C. Whalen, Colleen McMahan, Grace Chen, Jiann-Tsyh Lin, and Thomas McKeon, USDA ARS Western Regional Research Center, Albany, CA 94710

The United States is dependent on importing two important industrial commodities, natural rubber and castor oil. The goal of our work is to develop domestic sources of natural rubber and castor oil. Development of commercially viable crops that produce these two bioproducts is underway using metabolic engineering strategies. For natural rubber, *cis*-1,4-polyisoprene, we are focusing on two plant species, guayule (*Parthenium argentatum*) and sunflower (*Helianthus annuus*). We are supporting the commercialization of guayule latex, which is hypoallergenic making it useful in the biomedical latex industry. Our strategy to metabolically engineer the isoprenoid pathway to improve the quantity of guayule latex and rubber and the quantity and quality of sunflower latex will be described. We have incorporated biotechnological risk mitigation into our research strategy. In addition, we are working on development of bioproducts and biofuels from the non-rubber components to minimize agricultural waste. The castor plant (*Ricinus communis*) produces seeds with 90% of their fatty acid content being the hydroxy fatty acid ricinoleate. Ricinoleate and its derivatives have many industrial uses as lubricants, coatings, plastics, and fungicides. Our progress in preventing production of toxic and allergenic proteins by castor, and in developing an alternative oilseed to produce castor oil, will be presented.

Alternative Synthesis III

Sponsored by the GCI Pharmaceutical Roundtable

222. Green isoparaffin alkylation process

James P. Nehlsen, Mitrajit Mukherjee, G. Dan Suci, Sankaran Sundaresan, Richard V. Porcelli and John Dixon, Exelus, Inc., Livingston, NJ

Isoparaffin alkylation is an important process in the refining of petroleum. The process converts light isoparaffins and olefins into alkylate, a non-toxic, high-octane blending component of reformulated gasoline whose use nationwide is expected to increase significantly as MTBE is phased out. Unfortunately, all alkylation processes available today use hazardous liquid acid catalysts, either hydrofluoric (HF) or sulfuric acid. HF poses a significant safety hazard due to its aggressive nature and tendency to form stable aerosols upon release. The 50 HF-based alkylation plants in the U.S. endanger 15.6 million people in the surrounding areas. Sulfuric acid is also dangerous and produces unsafe waste streams of organic oligomers dissolved in acid. The use of benign solid acid catalysts offers a viable alternative to these liquid acid-catalyzed processes. However, the commercial use of solid acids has been hindered by rapid catalyst deactivation. Severe coking rapidly deactivates most solid acid catalysts, resulting in short lifetimes under commercially relevant operating conditions. This new process solves these issues by integrating an engineered solid acid with a novel alkylation reactor. The process is designed to be economically competitive with liquid acid technologies by using simple fixed-bed reactors and long cycle times between catalyst regeneration. The long catalyst lifetime is achieved by designing a catalyst with a unique distribution and strength of active sites. The catalyst pore structure is further optimized to provide the ideal reaction conditions at the active sites. The result is a safe, energy efficient and environmentally benign alternative to liquid acid-catalyzed alkylation processes.

223. Improved regioselectivity in the nitration of toluene: The key to cleaner manufacture of 2,4,6-trinitrotoluene (TNT)

Ross W. Millar, **Anthony W. Arber**, Javid Hamid and Robert M. Endors, QinetiQ Ltd., Sevenoaks, United Kingdom

There are concerns over the environmental effects of manufacturing processes currently available to make TNT (trinitrotoluene). The first step (toluene to mononitrotoluenes (MNTs)) is currently carried out by a non-selective process using mixed acid (nitric and sulfuric acids) which results in the formation of ca. 4% of *meta*-nitrotoluene (*m*-NT). In subsequent nitration steps the *m*-NT impurity, which cannot be separated from the main products (*ortho*- and *para*-nitrotoluenes), gives rise to unsymmetrical trinitrotoluene isomers, present in levels of 3.5–4%, which contaminate the TNT rendering it unfit for military use. Present purification methods use a sulfiting process which removes the unsymmetrical trinitrotoluene isomers, but also produces a wastestream called redwater, which is environmentally unfriendly and costly to dispose of. The key to solving this problem lies in the first step and a process has been developed which improves regioselectivity in the nitration of toluene (formation of *m*-NTs is suppressed). Here alternative chemistry is used which reduces the proportion of *m*-NTs to levels of 1.4% or less, whereby dinitrogen pentoxide solution in dichloromethane (DCM) is used as the nitrating agent instead of nitric-sulfuric acid mixture. These lower levels of *meta*-isomers, when carried through to the final product, are predicted to produce TNT of such purity that sulfite treatment will be unnecessary. Furthermore, use of flow reactor technology has added advantages of precise temperature control and reduction of inventory.

Abstracts, Continued

The work, which commenced June 2004, comprises lab-scale synthesis and scale-up studies. Collaboration with a North American explosives manufacturer will constitute a follow-on project.

224. Green synthesis of adipic acid with hydrogen peroxide catalyzed by oxo-peroxo tungsten complexes

Huaming Li¹, Wenshuai Zhu², Xiaoying He², Jianming Pan¹, Huoming Shu¹ and Junxiang Guo¹, (1)Jiangsu University, Zhenjiang, China, (2)China West Normal University, Nanchong, China

Adipic acid (AA) is an important chemical biacid, which is used to produce Nylon 66 and other compounds. The current industrial process of manufacturing AA involves an oxidation of cyclohexanone and cyclohexanol with nitric acid, which inevitably produces a contaminative by-product NO_x. Efforts have been accomplished in clean synthesis with H₂O₂ instead of the traditional method. We synthesized four novel oxo-peroxo tungsten and molybdenum complexes WO(O₂)₂•2QOH(I), WO(O₂)₂•Phen•H₂O(II), MoO(O₂)₂•2QOH(III), MoO(O₂)₂•Phen(IV) (QOH: 8-hydroxyquinoline; Phen: 1,10-phenanthroline monohydrate). Their catalytic properties in oxidation of cyclohexene, cyclohexanol, cyclohexanone and 1,2-cyclohexanediol to AA were investigated with 30(wt.%) H₂O₂. The results show W analogous complexes offered good catalytic activity in synthesis of AA, whereas Mo analogous complexes were far less active. AA can be obtained in 84% yield when the mixture of catalyst I, H₂O₂ and cyclohexene (in mol ratio of 0.9:538:100) was stirred vigorously at 90°C for 20 h.

TABLE 1. CATALYTIC ACTIVITIES OF CATALYSTS

Entry	Substrate	Yield/%			
		I	II	III	IV
1	cyclohexene	84	83	0	0
2	cyclohexanol	44	42	0	0
3	cyclohexanone	47	60	0	0
4	1,2-cyclohexanediol	86	0	41	20

Substrate: 100 mmol; Catalyst I, III: 0.9 mmol, Catalyst II, IV: 1.2 mmol; H₂O₂: 538 mmol. a cyclohexanone: 150 mmol, b H₂O₂: 401 mmol.

The results indicate oxo-peroxo tungsten complexes are effective catalysts under the aqueous-oil biphasic system, which was carried out without organic solvent and halogen conditions in an economically and environmentally satisfying manner. The oxidation procedures meet the needs of contemporary green chemistry and are suitable for practical organic synthesis.

225. Gas-phase catalytic oxidations using titania nanocatalysts

Alex Ibadon¹, Polycarpos Falaras², Dimitris Tsoukleris² and Ioannis Arabatzis², (1)University, Hull, United Kingdom, (2)Institute of Physical Chemistry, Athens, Greece

A direct reaction between a surface modifier, acetyl acetone, a binder molecule, octylphenol ethoxylate (Triton X-100) and TiO₂ powder, results in a paste from which porous nanocrystalline TiO₂ films are made. X-ray diffraction of the titania films indicates a well organized structure of anatase and rutile titania nanoparticles. Analysis by SEM shows that the surface of the films possess a sponge-like structure, with extended roughness and complex characteristics. Atomic force microscopy (AFM), show that the films are made up of high mountains and deep valleys and their height histogram shows a Gaussian-like distribution. The films are made up of a porous network with extended surface area and are ideal for heterogeneous energy conversion processes such as photooxidation reactions. To evaluate the effectiveness of the titania films for gas-phase photocatalytic oxidation, the degradation of benzene, toluene and xylene (BTX) was studied in a packed bed photoreactor which was operated in a batch mode. Photocatalytic oxidation results indicate that conversions of more than 90% were achieved in the reactor that combined low cost manufacture with a simple design. This study demonstrates that the titania films are fully viable as photocatalysis for the removal of VOCs (benzene, toluene and *o*-, *m*-, *p*-xylenes) present in ambient air or water at low concentrations. The immobilization of the catalyst as a film presents the advantage of easier photocatalyst separation and opens up the possibility of developing more efficient photocatalysts in the form of porous and high surface area inorganic oxide matrices.

226. Core-bound polymer nano micelles based on hydrogen bonding and photocrosslinking of thymine

Kei Saito, Laura R. Ingalls and John C. Warner, University of Massachusetts Lowell, Lowell, MA

Core-bound polymer nano micelles can be synthesized with amphiphilic block copolymers. By designing self-assembly mechanisms based on reversible hydrogen bonding and irreversible photocrosslinking, we have been able to control the stability, size and other properties of such micellar systems. A series of thymine functionalized amphiphilic block copolymers of vinylbenzylthymine and vinylphenylsulfonate were synthesized by 2,2-tetramethylpiperidin-1-oxyl (TEMPO)-mediated living radical polymerization. Block copolymer micelles formed in aqueous solution. The micelle characterization and the critical micelle concentration measurement demonstrate that the thymine functionalized amphiphilic block copolymers can form stability enhanced self-assembling micelles based on hydrogen bonding of the attached thymines. The stability can be further controlled by core-photocrosslinking of the attached thymines. This technology provides a novel approach of designing stable and controllable nano micelles based on the principles of green chemistry.

227. Entropic control in meta-stable noncovalent derivatives

Benjamin Bowers, Ankan Dahl, Roger Boggs and John C. Warner, University of Massachusetts Lowell, Lowell, MA

Noncovalent derivitization uses intermolecular forces to form ordered crystalline matrices to tailor various physical properties of target molecules. In certain cases, this technology offers the opportunity to avoid the use of multi-step tradition covalent syntheses, reduces solvent use and, as such, is an example of green chemistry. We seek to understand the contributions of individual forces [hydrogen bonding, pi-stacking and lipophilic interactions] on the overall stability of multi-molecular systems. With this understanding, we attempt to generate "disruptions" in hydrogen bond patterns to create hydrogen bond "defects." These "defects" can then serve to trigger a transition between equilibrium states. We have discovered that ternary systems of hydroquinone, benzoquinone and various bis[N,N-dialkyl]terephthalamides display meta-stable properties in solution. Sonication of these systems destabilizes and causes them to ultimately dissociate at varying rates. This presentation will discuss the effect of various alkyl groups on the terephthalamides and the ratio of individual components on the dynamic behavior of these systems.

Designing Safer Chemicals & Toxicity Reduction II

228. Tinkering with toxicity: Avoiding environmental problems by understanding toxicant metabolism

David Epel, Hopkins Marine Station of Stanford University, Pacific Grove, CA

Global pollution occurs if a chemical is stable, fat-soluble and not transformed by cell metabolism. This paradigm however does not account for global contamination by the perfluorinated chemicals (PFCs) used in stain repellents and non-stick cookware. Our research on efflux transporters explains this phenomenon and suggests smart chemistry strategies to avoid future problems. These transporters act as cellular "bouncers", kicking foreign chemicals out of cells *via* an ATP-dependent mechanism. If a chemical inhibits transporter activity or is not recognized by the transporters it will remain in the cell as a long-term contaminant. This behavior accounts for the accumulation of the major global pollutants; DDT, PCBs, synthetic musks and the PFCs are either not recognized by these transporters or inhibit transporter activity. This work has predictive value since simple screens exist for testing chemicals with these transporters. Tinkering with structure can yield chemicals that do not affect these transporters whilst still retaining desired properties.

229. Alternative synthesis for surfactants: Thermally cleavable surfactants

Reagan Charney¹, Colin Thomas¹, Ross Weikel¹, Pamela Pollet¹, Charles Eckert¹, Charles Liotta¹ and Philip Jessop², (1)Georgia Institute of Technology, Atlanta, GA, (2)Queen's University, Kingston, ON, Canada

Although surfactants are used in minute quantities, they are nonetheless critical to many industries. Unfortunately, their strength is also their weakness because they are difficult to dispose of and result in emulsions that are undesirably stable. Several cleavable surfactants have been designed with a "built-in" group that will allow the surface active character to be switched off. Such abilities will tremendously change the use and disposal of surfactants to the benefit of industries, customers and the environment. We have designed cleavable surfactants that with a "switch" will break into a hydrocarbon molecule and a gas molecule as an alternative to the current commercial surfactants. In addition, these molecules have little or no water solubility or can be easily removed from aqueous stream, reducing water waste. We report the alternative synthesis, characterization and cleavability of novel surfactants containing thermal and photochemical switches. The results demonstrate their potential for chemical processes and beyond.

230. Environmentally-benign, effective and economical totally-organic wood preservative systems

Tor P. Schultz and Darrel D. Nicholas, Mississippi State University, Mississippi State, MS

Lumber for residential applications is treated with copper-rich preservatives. However, starting in 2010 minor use restrictions will be placed on copper-treated lumber. Additional restrictions will undoubtedly occur and disposal of metallic-treated lumber will become more difficult. Thus, a need exists to develop organic preservatives, but no organic system is currently available. Fungi utilize metal-mediated reactions to form the free radicals that degrade wood. Utilizing this basic knowledge, we combined numerous commercial organic biocides with an economical, benign and commercial free-radical scavenger/antioxidant, BHT, and found synergism in short-term laboratory tests. In further studies, we showed that metal chelators are also synergistic when combined with various organic biocides. Results from long-term outdoor exposure tests were even more promising. Further, BHT helps protect a commercial biocide against microbial degradation. Since BHT and/or metal chelators are synergistic when combined with organic biocides and BHT reduces biodegradation of the biocide, less of the relatively expensive organic biocide is necessary to protect wood. BHT is also low cost and safe. Thus, wood treated with an organic biocide/non-biocidal mixture will be safer and possibly more economical, have a reduced environmental impact and be easier to dispose of than metallic-treated lumber. We are currently evaluating an organic metal complexing agent, obtained from a natural source and commercially available, that is very economical and safe and also provides water repellent properties to the lumber. The concept of adding low-cost and benign antioxidants and/or metal chelators can be employed with any organic biocide and, thus, is an universal concept.

Abstracts, *Continued*

231. Use of Postsaver to minimize forestry land depletion and mitigate pesticide chemicals migration into soil

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Postsaver® is a patented invention which can reduce the leaching of preservatives from treated wood used in ground contact. Postsaver is a wrap with an internal coating that adheres to wood commodities (*i.e.*, posts or lumber) with slight pressure and heat. In addition to reducing leaching from treated wood, Postsaver can be applied to a durable heartwood species, like cedar or cypress, and then this wood will last as long as a non-durable wood treated with preservatives in ground contact use. Postsaver will extend the service life of treated commodities when only a fraction of the expected amount of preservative typically specified for ground contact has been applied. It is possible that this technology will also allow the use of more leachable, but less toxic chemicals, like borates, in exterior ground contact uses where these preservatives currently cannot be utilized. Postsaver is unlike typical wood preservative groundline remedial treatment wraps in that it does not contain additional toxic preservatives to supplement any preservatives that have already leached from the wood in service. Instead, the product is applied by use of a mechanical applicator to new wood prior to the wood being installed in service. Postsaver has been submitted for consideration for an USEPA Presidential Green Chemistry Challenge Award. Postsaver use would result in longer service life for wood products in ground contact, thereby cutting down less trees to make those wooden items, in addition to also reducing the overall chemical usage and ultimate introduction of biocides into the environment.

232. Efficient molecular simulations for environmentally benign products and processes

Saadet Ulas and Urmila Diwekar, Vishwamitra Research Institute & University of Illinois at Chicago, Westmont, IL

Octanol-water partition coefficients (K_{ow}) are useful for the estimation of biological and toxicological properties such as, LC_{50} , LD_{50} , bioaccumulation and bioconcentration factor useful for designing environmentally benign products and processes. The reasoning behind this is that the partitioning of a compound between a polar aqueous environment and a non-polar organic environment is often the rate determining step in biological and environmental processes and K_{ow} is an excellent indicator of this step. Although experimental data is available for a great number of solutes, since new molecules are synthesized every day, efficient methods of prediction for K_{ow} are needed. Furthermore, there is considerable variability among the tabulated experimental values for octanol-water partition coefficients. Molecular simulations can play a significant role in enhancing the accuracy of predictions for K_{ow} and they provide predictive capabilities where experimental data is not available. However, molecular simulations are computationally very intensive requiring large sample sizes and long simulations. Since there is no universal criteria where to stop the simulation, uncertainties may arise from inefficient sampling of the configurational space. In this work, an efficient sampling technique namely the Hammersley Sequence Sampling (HSS) based on quasi-random numbers is applied to molecular simulations. Due to its k -dimensional uniformity properties, this sampling technique reduces the computational intensity and converges faster as compared to the conventional Monte Carlo method based on pseudo-random numbers. The results show that the HSS technique increases the accuracy of predictions for K_{ow} and provides about 3-fold gain in efficiency and reduces the number of cycles required to reach equilibration.

233. Novel lignocellulose fractionation by cellulose- and organic solvents

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Lignocellulose, the most abundant biological resource, is a recalcitrant composite mainly containing cellulose, hemicellulose, and lignin. Production of cellulosic ethanol and biobased products from renewable lignocellulose would bring benefits in economy, environment, and national security. Overcoming the recalcitrance of lignocellulosic materials is one of the largest technical obstacles to emerging biobased products and bioenergy industries.

Here we invented a novel lignocellulose fractionation technology using sequential treatment by cellulose solvent (concentrated phosphoric acid), organic solvent (acetone) and water. This technology can fractionate lignocellulose to amorphous cellulose, hemicellulose sugars, lignin, and acetic acid. Modest reaction conditions (50°C, atmospheric pressure) can avoid any sugar degradation and inhibitor formation; the resulting high reactivity amorphous cellulose requires less enzyme use and highest sugar yields can be obtained. For example, hydrolysis results of pretreated corn stover showed that ca. 97% cellulose was digested after 24 hours of hydrolysis at an enzyme loading of 15 filter paper unit/gram glucan.

An important lesson from oil refineries and corn-wet-milling ethanol refineries is co-utilization of different components in feedstocks for improving the economy of whole process. Any of separate co-products (hemicellulose, acetic acid and lignin) from lignocellulose has much higher (5~10 fold) selling prices based on weight that glucose from cellulose fraction. This technology would offer several potential economic benefits: 1) an increase in total revenue, 2) a decrease in processing costs, 3) better economy of scale, 4) low capital investment for small biorefineries, and 5) lower transportation costs for feedstock.

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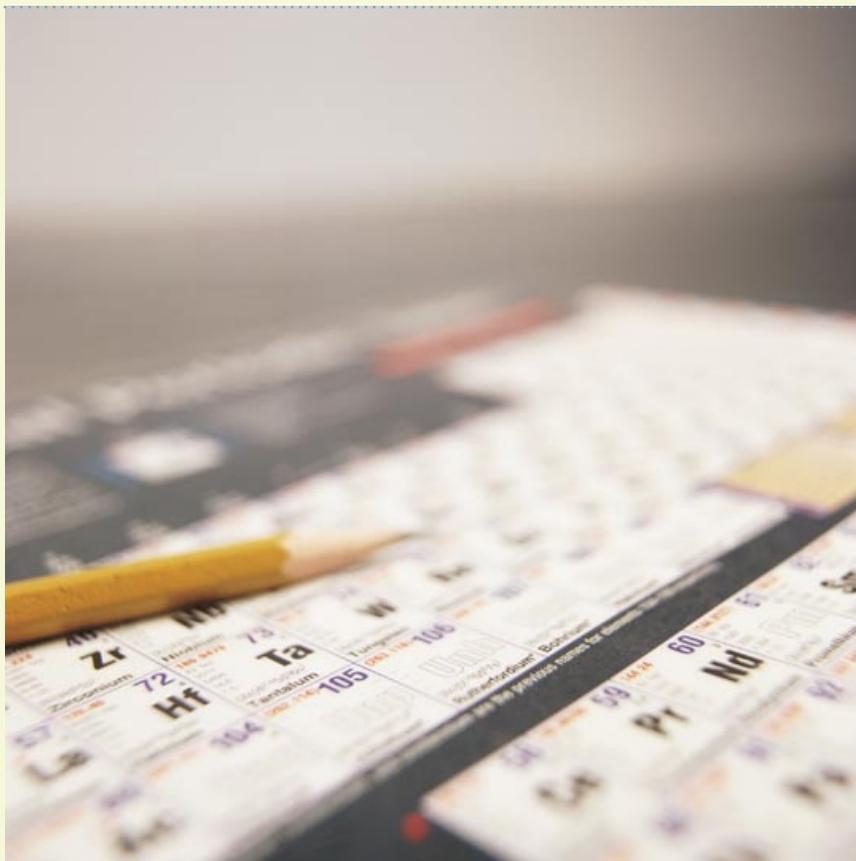
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