

American Chemical Society
Division of Industrial and Engineering Chemistry
ABSTRACTS

228th ACS National Meeting

Philadelphia, PA
August 22-26, 2004

R. M. Chamberlin, Program Chair; M. A. Gonzalez, Program Secretary

SUNDAY MORNING

• **Workshop on Green Chemistry for Graduate Students (Sponsored by Green Chemistry and Engineering Subdivision)**

M. M. Kirchhoff, Organizer; P. T. Anastas, Presiding

Papers 1-4

SUNDAY AFTERNOON

• **Preparative-Scale Chiral Separations (sponsored by Separation Science & Technology Subdivision)**

G. B. Cox, Organizer

Papers 5-10

SUNDAY EVENING

• **Industrial and Engineering Chemistry Posters**

H. K. Jacobs, Organizer

Papers 11-24, 25-31

MONDAY MORNING

• **Sustainability and the Chemical Industry: Plenary Session**

J. R. Zoeller, Organizer

Papers 32-35

MONDAY AFTERNOON

• **Sustainability and the Chemical Industry: Plenary Session**

J. R. Zoeller, Organizer

Papers 36-39

MONDAY EVENING

• **Sci-Mix**

H. K. Jacobs, Organizer

Papers 13, 15-18, 20, 24, 26, 28

TUESDAY MORNING

• **Polymers from Biobased Feedstocks (sponsored by Industrial Bio-based Technology Subdivision)**

R. Narayan, Organizer

Papers 40-45

TUESDAY AFTERNOON

• **Young Industry Innovators Forum**

R. M. Chamberlin, Organizer, Presiding

Papers 46-52

WEDNESDAY MORNING

• **Green Chemistry and Engineering: From Bench to Pilot Scale (sponsored by Green Chemistry & Engineering Subdivision)**

M. A. Gonzalez, Organizer

Papers 53-58

WEDNESDAY AFTERNOON

• **Green Chemistry and Engineering: From Bench to Pilot Scale (sponsored by Green Chemistry & Engineering Subdivision)**

M. A. Gonzalez, Organizer

Papers 59-65

DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY

1. GREEN CHEMISTRY: DEFINITION AND PRINCIPLES. *Paul T. Anastas, White House Office of Science and Technology Policy, Washington, DC 20502*

Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and/or generation of hazardous substances. This innovative approach to the protection of human health and the environment has been found to be beneficial both economically and to the biosphere. The Twelve Principles of Green Chemistry provide a framework for chemists to design chemical products and processes in an environmentally benign way.

2. IF NOT YOU, WHO ELSE IS GOING TO SAVE THE WORLD? *John C. Warner, Department of Chemistry, University of Massachusetts, Boston, 100 Morrissey Boulevard, Boston, MA 02125, Fax: 617-287-6127, john.warner@umb.edu*

Current training of chemists in the research laboratory as well as the classroom does not fully take advantage of the opportunities that Green Chemistry enables. With government providing limited funding for this new area of research, academia needs to work in partnership with industry both to train the next generation of scientists as well as discover the next generation of products and processes. In examples ranging from photovoltaics to new polymers, scientists at the Center for Green Chemistry at the University of Massachusetts Boston are working with the U.S. Green Chemistry Program and industry to develop models for how research and education can be combined in the pursuit of economic and environmental prosperity. Real-world examples of Green Chemistry from the research lab to industrial implementation will be presented.

3. SUSTAINING A HIGH TECHNOLOGY CIVILIZATION. *Terrence J. Collins, Department of Chemistry, Institute for Green Oxidation Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, Fax: 412-268-1061*

The idea that our civilization is not sustainable has far-reaching implications that encompass most areas of scholarship including ethics and science, especially chemistry, and calls for a deeper unity among the classical fields of scholarship. Many crucial sustainability-oriented adaptations of the technology base will require the participation of chemists. We have the ability to thoughtfully create new compositions of matter and processes specifically to cope with the technological problems of sustainability. The three biggest sustainability challenges confronting us pertain to developing new technologies for solar energy conversion, pollution elimination, and renewable chemical feedstocks. With major breakthroughs in these fields, chemists could revolutionize the technology base in favor of sustainability. The challenges inherent in the advancing broader issues of sustainability science will be reviewed. Efforts at Carnegie Mellon University's Institute for Green Oxidation Chemistry to contribute to the advancement of green chemistry will be described.

4. INTEGRATING GREEN CHEMISTRY INTO YOUR TEACHING. *Mary M. Kirchoff, American Chemical Society, Green Chemistry Institute, 1155 16th Street NW, Othmer 323, Washington, DC 20036, Fax: 202-872-6206, m_kirchoff@acs.org*

Environmental, human health, and economic benefits are realized when new and existing products and processes are developed using green chemistry principles. Yet green chemistry concepts, principles, and applications are largely absent from the curriculum at all levels. One of the best ways to accelerate the adoption of green chemistry by industry and academia is to train students to design their reactions in terms of pollution prevention. Environmentally benign alternatives are available for many traditional reactions and processes, but chemists and engineers may be unaware of them due to their curricular focus on classic methodologies. By reinforcing green chemistry concepts throughout the curriculum, students become aware that the choices they make in designing a reaction have consequences. This presentation will focus on strategies for

incorporating green chemistry concepts into the curriculum and highlight green chemistry materials for the lecture and laboratory.

5. SOME RECENT APPLICATIONS OF PREPARATIVE CHIRAL CHROMATOGRAPHY TO THE EXPEDITED PREPARATION OF PRECLINICAL PHARMACEUTICAL CANDIDATES. *Christopher J. Welch, Process Research, Analysis and Preparative Separations, Merck & Co., Inc, Rahway, NJ 07065, christopher_welch@merck.com*

Several recent examples will be presented illustrating the utility of preparative chiral chromatography in the synthesis of preclinical pharmaceutical candidates. The use of preparative chromatography offers a number of time and labor saving benefits in pharmaceutical development. Several recent examples will be presented illustrating method development, scale up, and execution of HPLC or SFC preparative resolutions on multikilogram scale.

6. UNEXPECTED PARTIAL RACEMIZATION OF SUBSTITUTED BENZODIAZEPINONE ENANTIOMERS. *Robert J. Rafka and Teri L. Shanklin, Separation Science Group, API Manufacturing, Pfizer Global Research & Development, Groton, CT 06340, robert_j_rafka@groton.pfizer.com*

A request was made to the Pfizer Separation Science group to resolve a significantly functionalized, racemic benzodiazepinone. Numerous chiral stationary phases were evaluated and S,S Whelk-O1 was eventually determined to be the most advantageous. Solubility of the racemate was very poor in all solvents but tetrahydrofuran. Trial separations were performed on the above chiral phase in mixtures of methyl tert-butyl ether and tetrahydrofuran in which the latter solvent was the major component. A clean enantiomeric separation was effected and a facile scale-up in the pilot plant was anticipated. However, re-analysis of the desired cuts after storage indicated the re-appearance of a small proportion (~3%) of the undesired enantiomer. Surprisingly, the ratio of forms in the resulting scalemic mixture then remained completely stable. It did not appear that the diminution in chiral purity was dependent on solvent, temperature or the presence of a contaminant. Subsequent studies eventually showed that partial racemization was linked to restricted rotation (atropisomerism) of the benzodiazepinone ring and an unfortunate ability of the high energy form of the undesired enantiomer to co-elute with the low energy form of the desired. The talk will delineate the analytical methods we used to unravel the conundrum of partial racemization. It will also describe the successful large-scale separation of the racemate that recently occurred in our pilot plant.

7. PREPARATIVE CHIRAL SFC SEPARATION OF BASIC COMPOUNDS USING ALKYL SULFONIC ACID ADDITIVES. *Rodger Stringham, Chiral Technologies, Inc, 730 Springdale Drive, Exton, PA 19341, rstringham@chiraltech.com*

Chiral separation of basic compounds in supercritical fluid chromatography (SFC) is complicated by putative interactions between amines and carbon dioxide, as well as protonation-deprotonation equilibria. The end result of these complications is severely spread or absent peaks. Addition of ethanesulfonic acid (ESA) to the mobile phase alcohol modifier and sample diluent allows the separation of ESA salts of primary, secondary and tertiary amines as well as amino acids, amino acid esters and beta-blockers. A large number (>50) of basic analytes that had not been separated by SFC were tested with additive. About 80% of these materials were easily separated. Preparative separations and successful isolation of various enantiomers will be presented.

8. APPLICATION OF MULTICOLUMN CONTINUOUS CHROMATOGRAPHY FOR A CHIRAL INTERMEDIATE ISOLATION. *Leo C. Hsu¹, John Filan², Patricia Hong², Alex Fridman², Grazyna Gracyk-Milbrandt², Zheyuan Luo², and Gerald Terfloth³.* (1) Analytical Science, SmithKline Beecham Pharmaceuticals, 709 Swedeland Road, King of Prussia, PA 19406, Fax: 610-270-4829, Leo.Hsu@gsk.com, (2) GlaxoSmithKline Pharmaceuticals, (3) Chemical Development, GlaxoSmithKline Pharmaceuticals

Chiral chromatography is currently the only way to separate the desired enantiomer from the racemic mixture. Previously, dynamic kinetic resolution had been used but this proved to be non-robust on pilot plant scale. The isolation of 3 Kg chiral intermediate was performed by the multicolumn continuous chromatography (MCC) on a six-ChiralPak AS column Varicol configuration. We encountered stability issue of the desired enantiomer during the preparative campaign. The tactic to compensate the stability issue will be discussed.

9. SCALE-UP DIFFICULTIES FOR LARGE SCALE CHROMATOGRAPHIC PROCESS. THE IMPORTANCE OF IMPURITIES. *Olivier Dapremont, Manager SMB Operations, Aerojet Fine Chemicals, P O Box 1718, Rancho Cordova, CA 95741, olivier.dapremont@aerojet.com*

The development of chromatographic method is often conducted using high purity material produced by the R&D chemist in the lab in small quantities. The chromatographer runs a number of experiments and then calculates the production rate at larger scale using this material. It is well known that scale-up in chromatography is linear with the square of the column diameter and quality performance and reliability of packing material allows great confidence in the scale-up process. However, when the time comes to perform the separation at pilot scale, the feed supplied is not necessarily as clean as the material used for development. Several type of impurities even at trace level can affect the performance of the system. Identification of these impurities and evaluation of their effect on the performance of the separation is a key to the success of the scale-up and the future of the project. We will discuss the effect of impurities and on the separation performance through examples.

10. COMBINATION OF UNIT OPERATIONS FOR THE PRODUCTION OF ENANTIO-PURE DRUGS. *Wilhelm Hauk, Novasep Inc, 23 Creek Circle, Boothwyn, PA 19061, Willy.Hauk@novasepinc.com*

Performing purification at large scale by means of chromatography is emerging as a key option for the purification of intermediates and active pharmaceutical ingredients (APIs) during chemical development. The main advantages are speed, simplicity of automation, high yield and straightforward scale-up. Even the tightest purity specifications can be obtained for the target compound. A global optimization of purification processes is proposed by integrating various technologies at an early stage of the development process. The performance of the chromatography are predicted and optimized by software modeling the physical parameters. Coupling chromatography with crystallization can significantly enhance the overall throughput of the global process. For chiral systems, often a mixture enriched in one enantiomer is all that is needed to perform the further purification by crystallization. However, the enriched mixture of enantiomers has to be within acceptable thermodynamic limits in the binary phase diagram to yield the pure enantiomer during the crystallization step. The determination of the crystallization mode of the racemic mixture is therefore carried out prior to the optimization of the global process. To this ultimate purification step can be added the screening for polymorphs during the crystallization step using the right solvent or mixture of solvents. Therefore, the pure enantiomer of an API can be obtained not only at higher purity but also under the desired crystalline form, which can then be directly formulated without any further recrystallization step. A global process optimization is presented for a chiral separation.

11. INTRODUCING THE NOVEL CHEMISTRY WITH INDUSTRIAL APPLICATIONS SUBDIVISION. *Joseph R. Zoeller, Research Laboratories, Eastman Chemical Company, P.O. Box 1972, Kingsport, TN 37662-5150, Fax: 423-229-4558, jzoeller@eastman.com*

The Industrial and Engineering Chemistry Division approved the formation of the new Novel Chemistry with Industrial Applications subdivision in the Fall of 2002.

The subdivision was formed to provide a forum for the wide variety of newly emerging chemical and material science technologies which may ultimately have industrial relevance and which increasingly involve multidisciplinary components that defy easy classification into the traditional disciplines and often lie outside of the traditionally defined chemical sector. Additionally, it provides a forum for discussion of new manufacturing methods, new applications of chemistry, and new marketing techniques. This poster will present an overview of the division and its efforts to date as well, as provide an opportunity to join the division or be added to the mailing list.

12. JOIN THE GREEN CHEMISTRY AND ENGINEERING SUBDIVISION! M.A. Matthews, Department of Chemical Engineering, University of South Carolina, 300 Main St., Columbia, SC 29208, Fax: 803-777-0973, matthews@engr.sc.edu

The Green Chemistry and Engineering Subdivision is dedicated to the promotion of sustainable chemical and materials manufacture through the techniques of green process chemistry and design. GC&E encourages industrial chemists, chemical engineers, and academic researchers to join the subdivision. Examples of recent and upcoming programming and activities will be presented.

13. KINETIC STUDY OF SYNTHESIZING DIALLYL ETHER BISPHENOL A IN A PHASE-TRANSFER CATALYTIC REACTION. *Maw Ling Wang, Department of Environmental Engineering, Hung Kuang University, No. 34, Chung-Chie Road, Shalu, Taichung County 433, Taiwan, Fax: 886-4-2652-9226, chmmlw@sunrise.hk.edu.tw, and Ze Fa Lee, Department of Chemical Engineering, National Chung Cheng University*

For synthesizing diallyl ether bisphenol A from bisphenol A and allyl bromide, the liquid-liquid mode of operation catalyzed by quaternary ammonium salts was carried out in an alkaline solution/organic solvent two-phase medium. In this work, rotational reaction mechanism and kinetic model were built up. The apparent rate constant of the organic-phase reaction was obtained via experimental data. It is found that no agitation effect is observed when the agitation speed exceeds 800 rpm. The order of the relative reactivities of the solvents are: dibutyl ether < cyclohexane < benzene < toluene < cyclohexanone < 1,4-dioxane < chlorobenzene. Examination of seven quaternary ammonium salts revealed that tetraoctylammonium bromide exhibited highest activity. The presence of 1 mmol of catalyst in the chlorobenzene/water system produces over 3-fold rate larger than that of the reaction without containing catalyst. The presence of alkali promoted the alkoxide forming and the extractive efficiency. The existence of sodium cation would decrease the reaction rate. An appropriate amount of organic solvent, potassium hydroxide and water is recommended in order to obtain a higher yield of product. The present etherification via phase transfer catalyst could operate in lower temperature to avoid Claisen rearrangement.

14. ADSORPTION EQUILIBRIA AND TRANSPORT RATES FOR A RANGE OF PROBE GASES IN MOLECULAR SIEVING CARBON. *Steven William Rutherford and James E. Coons, Engineering Sciences and Applications Division, Los Alamos National Laboratory, Mail Stop C926, Los Alamos, NM 87545, Fax: 505-665-7836, stevenr@lanl.gov*

Pressure swing adsorption (PSA) has been become a useful process for commercial separation and purification operations. A variety of adsorbent material are employed for PSA processes with carbon molecular sieve (CMS) chosen for air separation due to its high kinetic selectivity. In this study, measurements of adsorption equilibria and transport kinetics for argon, oxygen and nitrogen at 20°C, 50°C and 80°C on commercially derived Takeda carbon molecular sieve (CMS) have been undertaken in an effort to elucidate fundamental mechanisms of transport. Results indicate that micropore diffusion which is modeled by a Fickian diffusion process, governs the transport of oxygen molecules and the pore mouth barrier controls argon and nitrogen transport which is characterized by a linear driving force (LDF) model. For the three temperatures studied, the pressure dependence of the diffusivity and the LDF rate constant appear to be well characterized by a formulation based on the chemical potential as the driving force for transport. Isothermic heat of adsorption at zero loading and activation energy measurements are compared with predictions made from a previously proposed molecular model for characterizing CMS.

15.

AUTOMATED ATOMIZER FOR EVALUATING AEROSOLS. *Heather D. Willauer¹, John B Hoover¹, George W. Mushrush², and Frederick W Williams¹.* (1) Chemistry Division Code 6180, Naval Research Laboratory, 4555 Overlook Avenue, SW, Washington, DC 20375, (2) Department of Chemistry, George Mason University and Naval Research Laboratory

The ability to reduce the flammability characteristics of jet fuel aerosols is critical to the development of fire resistant fuels. Our laboratory is focusing on a series of chemical additives that when added to the fuel will significantly reduce its ability to ignite. In our efforts to design and characterize fire safe fuels, an automated rotary atomizer has been developed to produce fuel aerosols and measure their flammability properties. A particle analyzer has been coupled to the atomizer to provide information on the size distribution of the aerosol produced by this type of atomizer. This presentation will focus on the ability to evaluate water aerosols as a function of disk speed and additive concentration by this instrumental design.

16.

SYNTHESIS AND CHARACTERIZATION OF NEW TYPES OF IONIC LIQUIDS. *Sharon I. Lall-Ramnarine¹, Delroy Coleman², Annu Ipe¹, Carolyn Spence¹, Wadson Miranda², Robert Engel², and James F. Wishart³.* (1) Chemistry, Queensborough Community College, CUNY, 222-05 56th Avenue, Bayside, NY 11364, Fax: 718-997-5531, slall@qc1.qc.edu, (2) Chemistry and Biochemistry, Queens College and the Graduate school of the City University of New York, 65-30 Kissena Boulevard, Flushing, NY 11367, Fax: 718-997-5531, (3) Chemistry Department, Brookhaven National Laboratory

We have previously reported on the synthesis and characterization of liquid ionic phosphates (LIPs) and polyammonium ionic liquid sulfonamides (PILS). We report here on the synthesis of yet another category of ionic liquids. In particular those containing ether substituents and pyrrolidinium cations. These cations are combined with phosphate and dicyanamide anions to form new ionic liquids. Physical characterization includes measurement of water content by Karl Fischer titration, conductivity and viscosity. Preliminary results indicate that these new species conduct on the order of 0.1 to 10 mS/cm.

17.

HYDRODECHLORINATION OF CCL₂F₂ USING Pd SUPPORTED ON G-AL₂O₃ CATALYSTS. *Chandra Shekar Sridara, National Risk Management Research Laboratory, US Environmental Protection Agency, 26 W. Martin Luther King Dr, MS 443, Cincinnati, OH 45268, Fax: 513-569-7677, shaker.sridara@epa.gov, K. S. Rama Rao, Catalysis Division, Indian Institute of Chemical Technology, and Endalkachew Sahle-Demessie, National Risk Management Research Laboratory, U.S. Environmental Protection Agency*

Chlorofluorocarbons, have been implicated in the accelerated depletion of ozone in the Earth's stratosphere. Research groups have been working for effective conversion of the CFCs in to useful compounds. Selective hydrodechlorination of CFCs has been identified as a useful process for their transformation as it yields either HCFCs or HFCs that have low or almost zero ozone depletion potential value. Hydrofluorocarbons (HFCs), potential replacements for CFCs that contain no chlorine, have been evaluated for potential effects of fluorine compounds on ozone destruction. Selective hydrodechlorination of CCl₂F₂ (CFC-12) yields CH₂F₂ (HFC-32). In the selective hydrogenolysis of CCl₂F₂, Pd supported on g-Al₂O₃, active carbon, etc were used. In this study, alumina supported palladium catalysts are prepared by wet impregnation technique with varying Pd loading. The catalysts after drying are calcined at 400°C for 4h in hydrogen flow to obtain Pd in poorly dispersed state. These catalysts are tested for their activity and selectivity in the hydrogenolysis of CCl₂F₂ to CH₂F₂. Low dispersed Pd/g-Al₂O₃ catalysts are obtained by H₂ reduction of the catalysts at 400°C. Transmission electron microscope revealed that there is a strong redispersion of palladium is taking place during the reaction. Studies on the effect of palladium loading on the activity and selectivity in the conversion of CCl₂F₂ to CH₂F₂ and CH₄ have shown that 8wt% Pd on g- Al₂O₃ is optimum in giving maximum CH₂F₂ yields.

18.

HYDROGENATION OF OLEFINS USING PALLADIUM NANOPARTICLES PREPARED WITH PULSE ELECTROCHEMICAL DEPOSITION. *Bizuneh Workie¹, Ayuk Obale¹, Unnikrishnan R Pillai², and Endalkachew Sahle Demessie².* (1) Chemistry Department, Delaware State University, 1200 N. DuPont Highway, Dover, DE 19901, Fax: 302-857-6538, bworkie@desu.edu, (2) Office of Research and Development National Risk Management Research Laboratory, US EPA

Electrochemistry has been used to synthesize nano-structured materials. In this project, we have conducted the application of electrochemistry for the synthesis of nano-palladium catalysts that may have application in the area of green chemistry. The electrochemical technique used was pulse galvanostatic electro-deposition. The efficiencies of the palladium catalysts were tested for the hydrogenation of olefins. The palladium particles were deposited from PdCl₂/(NH₄)₂SO₄/H₃C₅H₅O₇.H₂O/NH₄OH, PdCl₂/HCl, and PdSO₄/H₂SO₄ baths. Palladium particles deposited from PdCl₂/HCl bath at a temperature of 60 °C shows fairly good amount of catalytic properties for the hydrogenation of olefins at mild conditions.

19.

HOW DIMETHYL CARBONATE IS SYNTHESIZED FROM METHYL CARBAMATE AND METHANOL VIA CATALYSIS. *Tinghua Wu, Zhuoqun Zheng, Ya Liu, Fulin Mao, Qineng Zhang, and Fei Chen, Institute Of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China, Fax: 086-579-2282595, wth3907@163.com, zhengzhuoqun1980@yahoo.com, sky48@mail.zjnu.net.cn, mflchina@163.com, zpy22@163.com, xinyue9877@163.com*

When dibutyl tin oxide was used as catalyst, the effects of several factors on the conversion and selectivity of the synthesis in which methyl carbamate reacted with methanol to produce dimethyl carbonate were intensively investigated. Particularly, the influences of reaction temperature, reaction time, initial pressure, mole ratio of methyl carbamate to methanol, and mass ratio of dibutyl tin oxide to methyl carbamate on the catalytic properties of dibutyl tin oxide have been evaluated. Based on our study, the optimum operating conditions as follow have been obtained: reaction temperature of 200°, reaction time of 4 h, initial pressure of 1.4 MPa, mole ratio of methanol to methyl carbamate 9:1, mass ratio of dibutyl tin oxide to methyl carbamate 1:10. The yield of carbonate reaches 38.1%. This study provides the industrializing production of dimethyl carbonate with reliable data.

20.

HOW METHYL CARBAMATE IS SYNTHESIZED THROUGH ALCOHOLYSIS OF UREA. *Tinghua Wu, Fulin Mao, Ya Liu, Zhuoqun Zheng, Qineng Zhang, and Fei Chen, Institute Of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China, Fax: 86-579-2282595, wth3907@163.com, mflchina@163.com, sky48@mail.zjnu.net.cn, zhengzhuoqun1980@yahoo.com, zpy22@163.com, xinyue9877@163.com*

The environment-friendly synthesis of methyl carbamate(MC) from urea and methanol in an autoclave was systematically investigated. A better understanding of the effect of the reaction temperature, reaction time, mole ratio of the feeds and initial pressure and other appropriate reaction conditions on the reaction results has been obtained. Based on our study, when the reaction started with a methane-MC mole ratio of 4:1 takes place at an initial pressure of 1.4 MPa and temperature of 363.15 K for 1.0 h, the yield of MC is up to 85.1%, which is enhanced by 24.6% compared to the report written by Saleh et al. Besides, the selectivity for MC is close to 100%. Therefore, we think the data we have obtained from our study may be useful to the further research on this novel process of MC.

21.

TRANSFORMATION OF AGRICULTURAL WASTES INTO VALUABLE PRODUCTS BY FAST PYROLYSIS. *See Hoon Lee¹, Young Chan Choi¹, Jae Ho Kim¹, Jae Goo Lee¹, and Kyung Seun Yoo².* (1) Gasification Application Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, South Korea, Fax: 82-42-860-3134, donald@kier.re.kr, (2) Dept. of Environ. Eng, Kwangwoon University

The fast pyrolysis characteristics of agricultural wastes such as chest nutshell, ginko nutshell, wood chips, and chaff have been determined in a thermobalance reactor (0.055 m-I.D. x 1.0 m-high) consisting of preheater, reactor, basket and

electronic balance and a bubbling fluidized bed (0.2m I.D. × 2.0 m-high) consisting of preheater, windbox, bubbling bed, cyclone, heat exchanger, and electrostatic precipitator. The experiments were carried out to determine the effects of temperature, L/D ratio and bed particle diameter on carbon conversion, ratio, yield and gas composition. In the thermobalance reactor, the bed temperature affected the pyrolysis characteristics (pyrolysis ratio, time) with increasing of bed temperature(350-500°C) but its effect was almost gone over 550°C. In the experiments of the bubbling fluidized bed, the oil yield had maximum value (near 450-500°C) and decreased with increasing of temperature. The oil yield increased with increasing L/D, however there was no effect of bed particle size.

22.

STUDY OF WASTE GASIFICATION CHARACTERISTICS WITH ADIABATIC EQUILIBRIUM MODEL.

Jaeho Kim, *Gasification application research center, Korea Institute of Energy Research, 71-2 Jang-dong, Yousung-gu, Daejeon 305-343, South Korea, Fax: 82-42-860-3134, jaeho@kier.re.kr, Hong G. Im, Department of Mechanical Engineering, University of Michigan, and Choon Han, Department of Chemical Engineering, Kwangwoon University*

To provide a guidance to predict the waste gasification process and to identify the optimal operating conditions, a simple equilibrium model based on the CHEMKIN 3.7 software is developed. The primary goal of the study is to determine the ideal equilibrium composition, adiabatic final temperature, and the cold-gas efficiency of the gasifier in which standard waste material reacts with various amounts of the input water and oxygen. The results are reported for a wide range of the water/waste and oxygen/waste ratio, for which the overall product temperature and composition are investigated and discussed. For the type of waste material and under the assumptions used in this study, the optimal operating conditions are achieved for the water/waste ratio at 0 ~ 1kg/kg-waste, the oxygen/waste ratio at 1.0 ~ 1.2 kg/kg-waste, for which the operating temperature ranges about 800 ~ 1200°C. It is anticipated that the results presented in this study serve as a baseline guide to determining the operating input conditions for the waste gasification process.

23.

LIAGDS FOR RHODIUM-BASED CATALYSTS IN MIXED OLEFIN

HYDROFORMYLATION. **Jong Ki Jeon¹**, *Sang Gyun Noh¹, Seung Tae Koh¹, Won Hee Han¹, Jung Ho Cho¹, and Young Kwon Park². (1) Department of Chemical Engineering, Dongyang University, Youngjou, Kyungbook, 750-711, South Korea, Fax: 82-54-636-8523, jkjeon@phenix.dyu.ac.kr, (2) Faculty of Environmental Engineering, University of Seoul*

A rhodium catalyst containing the phosphine ligands exhibits a markedly low activity in the hydroformylation of the mixture of internal and/or branched-olefin which can be obtained through oligomerization of low olefin. Recently, a Rh catalyst modified with triphenyl-phosphine oxide has been commercialized for hydroformylation of mixed olefins. However, the addition of phosphine is necessary to stabilize the rhodium catalyst before the distillation step for catalyst recovery. In the present work, we aimed to develop a new ligand to increase catalyst stability as well as to maximize activity and selectivity. Phosphorous compounds such as tri-*t*-butyl phosphine, triphenyl phosphine, tris(2,4-di-*tert*-butylphenyl) phosphite, triphenyl phosphine oxide, tertiary bisphenyl dioxide, and tetrakis-(2,4-di-*tert*-butylphenyl)-4,4'-biphenylphosphonite were examined as a ligand for rhodium-based catalysts in mixed olefin hydroformylation. Rh-based catalyst containing tetrakis-(2,4-di-*tert*-butylphenyl)-4,4'-biphenylphosphonite ligand exhibits an excellent catalytic activity as well as stability for the hydroformylation of mixed olefins in the present work, indicating the nature of ligand is very important for the catalyst design.

24.

EFFECTS OF CHEMICAL ADDITIVES ON THE SELECTIVE NON-CATALYTIC REDUCTION OF NOX IN A PILOT SCALE FLOW REACTOR.

Kyung Seun Yoo¹, **Soo Youp Park¹**, *Nam Chan Kim¹, Joong Gee Lee², Seung Do Kim³, Jong Ki Jeon⁴, Young Kwon Park⁵, and Jong Hyeon Jung⁶. (1) Department of Environmental Engineering, Kwangwoon university, 447-1, Wolgye-Dong, Nowon-Gu, Seoul 139-701, South Korea, Fax: 822-911-2033, yooks@kw.ac.kr, psy@kw.ac.kr, (2) Korea Institute of Science and Technology, (3) Hallym University, (4) DongYang University, (5) University of Seoul, (6) Seorabol College*

Selective non-catalytic reduction (SNCR) of nitrogen oxides by injecting N-containing reducing agent into a high temperature zone of combustors is a

convenient way to remove NOx in flue gas. One of the drawbacks of SNCR processes is a narrow temperature window in which the effective reduction of NOx occurs. It has been reported that chemical additives (hydrocarbons, alcohols, metal species) could enhance the performance of SNCR reaction. In this study, synergistic effect between metals and organic chemicals on NOx reduction efficiency has been experimentally investigated in a pilot scale flow reactor (160 KWth). Effect of NSR ratio, reaction temperature, oxygen concentration, additives species (surfactants, sodium salts, alcohols) and residence time of flue gas on NOx removal efficiency has been determined in a pilot scale flow reactor. Among the tested additives, anionic surfactant of LAS (linear alkylbenzene sulfonate) showed the highest NOx removal efficiency at around 1000-1300K.

25.

WITHDRAWN.

26.

SIMPLE AND RAPID DETERMINATION OF BORON IN WASTEWATER USING

ION-SELECTIVE ELECTRODE. **Seiichi Ohyama**, *Hitoshi Ohsumi, Satoshi Kudo, and Masahiro Sakata, Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko-shi 270 1194, Japan, Fax: +81-4-7182-1181, sei@criepi.denken.or.jp*

A simple and rapid determination method of boron concentration in wastewater using an ion-selective electrode has been developed. By adding H₂SO₄ and HF to a H₃BO₃ solution, H₃BO₃ is converted to BF₄⁻, which can be measured with a commercial BF₄⁻ ion-selective electrode. The BF₄⁻ formation rate obeys the first-order kinetics with respect to the H₃BO₃ concentration. Approximately 1 hour is usually required for the complete conversion of H₃BO₃ to BF₄⁻. The authors found that by applying the rate equation to a BF₄⁻ profile in the initial 10 min of the reaction, the original boron concentration in wastewater can be determined from the curve fitting, which leads to a considerable reduction in the measurement time. They also found that NaF can replace toxic HF as a fluorine source in the determination. The proposed method covers a range of 1-300 mg-B dm⁻³ without any pretreatments; this range covers the Japanese wastewater standards for boron.

27.

ELECTROKINETIC REMEDIATION OF 2,4-DNT CONTAMINATED SOILS.

Amid P. Khodadoust, *Krishna R. Reddy, and Omprasad Narla, Department of Civil and Materials Engineering, University of Illinois at Chicago, 842 West Taylor Street, Chicago, IL 60607-7023, Fax: 312-996-2426, akhodado@uic.edu*

The removal of 2,4-dinitrotoluene (2,4-DNT), a munitions waste constituent and an industrial intermediate, from contaminated subsurface soils is evaluated using enhanced electrokinetic (EK) remediation. Two spiked soils are selected for the EK experiments. The spiked soils are kaolin, a low-buffering clayey soil, and glacial till, a high-buffering silty soil. The glacial till is obtained from a field site and contains 2.3 percent organic matter. Both soils are spiked with approximately 480 mg/kg of 2,4-DNT.

Water and cyclodextrin solutions are used as the electrode conditioning solutions. Two aqueous solutions of hydroxypropyl β-cyclodextrin (HPCD) at concentrations of 1 and 2 percent are used for kaolin and glacial till, respectively. These HPCD concentrations have been selected based on results for batch extraction of 2,4-DNT from the same soils. The HPCD solutions enhance the extraction of 2,4-DNT from the soils. After the completion of the EK experiments, the soils in the EK cell are extracted for remaining 2,4-DNT levels.

Overall, higher removal of 2,4-DNT is obtained from the kaolin soil than from the glacial till. Higher amounts of 2,4-DNT (approximately 80 percent of the spiked level) remained in the glacial till than in the kaolin (as low as 6 percent of the spiked level). For kaolin, a lower amount of 2,4-DNT remained in the soil after EK with HPCD solution than EK with water. For glacial till, comparable levels of 2,4-DNT remained in the soil for both EK solutions. Since little or no 2,4-DNT is detected in the effluents from the EK cells, the removal of 2,4-DNT is attributed to electrochemical transformations of 2,4-DNT to other species.

28.

USING ALUMINUM OXIDES AS CARRIERS FOR CARBON NANOTUBES TO REMOVE LEAD AND OTHER HEAVY METALS. *Jao Jia Horng, Su Hwei Hsieh, and Cheng Kuo Tsai, Department of Safety, Health, and Environment, National Yulin University of Science and Technology, 123 University Road Section 3, Touliou 640, Taiwan, Fax: 886-5-532-6202, horngjj@yuntech.edu.tw*

Using carbon nanotubes (CNTs) to remove lead and other heavy metals from water were proved to have high adsorption capability and efficiency. In actual applications, the separation might be problematic due to the need for the separation of CNTs and water which require ultra fine filtration process. This study proposes a fabrication process to deposit CNTs on aluminum oxides as carriers. The multiwalled CNTs had diameters around 80 to 100 nm and about 32% (w/w). Without acid washing, the CNTs exhibit good lead adsorption with capacity at 60 mg/g. The adsorption isotherms could be well described by both Langmuir and Freundlich models. The CNTs/Al₂O₃ also contained Ni/Fe bimetal at around 12%. Since Ni/Fe bimetal were often used to break down chlorinated pollutant such as chloroforms, the CNTs/Al₂O₃ might be able to use at complex contamination sites to remove metallic and organic pollutants at one process.

29.

VERY HIGH RATE CHEMICAL REACTION: A BREAKTHROUGH FOR FUTURE OF CHEMISTRY AND CHEMICAL ENGINEERING. *Ashis K Das, Independent Petroleum Engineer, Independent Researcher, 176 Falton Way NE, Ground Floor, Calgary, AB T3J 1K5, Canada, calgadas@hotmail.com*

Chemical reactions for long have been associated with a limitation described by what is commonly known as Le Chatelier's Principle. It is stated as: If a stress is brought upon to bear a system in chemical equilibrium, a reaction occurs which displaces the equilibrium in the direction which tends to undo the effect of the stress. The consequence of this in simple explanation can be observed in following. When two reactants A and B react reversibly to products C and D the products piling (diffusion control) offer pressure to force the reverse reaction and the forward reaction can be altered by altering concentrations of the piled up products or the remaining reactants at any time. The author came upon this concept during a chemical enhanced oil recovery independent research (in crude oil industry area) in early 1980s at University of California, Berkeley when in-situ surfactants were produced in relatively profuse quantity at early times from accelerated hydrolysis of polyacrylamide polymer due to two reasons one of which was this withdrawal of reaction products and suppression of reverse reaction consequent to which Le Chatelier barrier was broken to significant extents. This led to a lot of surfactants production in-situ and additional mobilization action and production of residual crude oil. More reasons for reaction rate upgrading has since been derived out of this work. In this paper, I try to present as vividly and as simply as possible following: (a) till early 1980s status of reaction rate studies in chemistry and chemical engineering, (b) significant differences in my research derived conceptions from earlier research (c) design of my pointers in form of sound mathematical treatment of the subject and (d) a realistic assessment of intellectual property matter value of this concept for inventors and application industries worldwide.

30.

FAST TRANSIENT PROCESSES AT INFINITE RELAXATION. *Kal Renganathan Sharma, Formerly Principal, Mathur Post, Anna University - Sakthi Engineering College, Mount, Ramapuram (opp. MGR Gardens), Chennai 602105, India, Fax: 2526019, jyoti_kalpika@yahoo.com*

During short time scales the system may be far from equilibrium and the high rate unsteady state transient processes cannot be fully described using Fourier's heat conduction law, Fick's mass diffusion law, Newton's law of viscosity. Alternate expressions are being evaluated in the literature to fully describe transient events. The Cattaneo and Vernotte non-Fourier heat conduction and relaxation equation was applied to the 1 dimensional energy balance equation. The resulting governing equation was hyperbolic damped wave Partial Differential Equation in two variables. At the limit of infinite relaxation time it was shown that the equations reduced to the Wave Equation. The D'Alambert solution was applicable for the Wave Equation at this asymptotic limit. The non-Fourier equation can be traced back to the statistical mechanical derivation of physical properties such as thermal conductivity, viscosity, diffusivity. The accumulation of energy, mass, momentum at the surface may be included and this may later become the storage term in the modified constitutive equation.

31.

EXERGY ANALYSIS FOR DOMESTIC HEAT RECOVERY SYSTEMS. *Kal Renganathan Sharma, Formerly Principal, Mathur Post, Anna University - Sakthi Engineering College, Mount, Ramapuram (opp. MGR Gardens), Chennai 602105, India, Fax: 2526019, jyoti_kalpika@yahoo.com*

Cost effective domestic use heat recovery unit for hot water discharge from sewer system from sinks, showers, and laundry rooms are needed. Present Heat Recovery units are cylindrically shaped measuring about 3 feet in length. These units are connected to drains where hot water is discharged into the sewer system. Recovering and using discharged hot water to pre-heat water for conventional water heaters will decrease the amount of natural gas and electric power consumed. Currently, there are heat recovery units commercially available but because of bulk and volume they are not suitable for either retrofit or new construction. By using exergy analysis the available energy that can be recovered was calculated. A countercurrent design from preheating the cold water was evaluated. A heat pipe design was explored. The feasibility study indicate developmental costs, prototyping costs, production costs, and market prices for these new heat recovery systems. A user data package is suggested.

32.

SUSTAINABILITY, STOICHIOMETRY, AND PROCESS SYSTEMS ENGINEERING. *Jeffrey J. Sirola, Eastman Research Division, Eastman Chemical Company, PO Box 1972, 200 South Wilcox Drive, Kingsport, TN 37662-5150, Fax: 423-229-4558, sirola@eastman.com*

There is clearly much interest in environmental protection, greener chemistry, and the general notion of responsible sustainability within the chemical processing industries. But what does this mean really? In this presentation some elementary process systems engineering principles are applied to help elucidate what sustainability issues and metrics actually imply in practice. Simple concepts from systems theory, chemical structure and oxidation state, stoichiometry, thermodynamics, and kinetics are shown to be useful for screening among alternative sources of raw materials and process energy, and among alternative products, chemistries, and environmental footprint and other, especially greenhouse gas, impacts. Such analyses can provide significant guidance for evaluating and optimizing overall sustainability performance.

33.

SUSTAINABILITY: A CHEMICAL INDUSTRY VIEW. *John Carberry, Director: Environmental Technology, DuPont, Wilmington, DE 19801, john.b.carberry@usa.dupont.com*

The leading issues of "sustainability" will be identified from the point of view of a major chemical industry, along with representative examples about products and processes. Concepts covering "green" survival, "green" prosperity, and "green" futures will be discussed. Particular attention will be given to searching for cost effective renewable energy and looking at product ideas and operating concepts for needed renewable energy technologies of the future. Key cooperative technology development efforts will be reviewed.

34.

RESEARCH IN SUSTAINABILITY: AN EPA PERSPECTIVE. *Subhas Sikdar, Sustainable Technology Division, US Environmental Protection Agency, Mail Stop 497, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, sikdar.subhas@epa.gov*

With the rise of concerns for sustainable development among leaders in industry and Government, and among the public, it is time to invest in research that provides a scientific face to sustainability. Clearly the question, "sustainability of what?" leads us towards system definition and sustainability metrics development. Solutions to problems that can be called sustainable begin with system definition and metrics must be used to show progress from a sustainability viewpoint. This approach is a significant departure from the previous approaches commonly known as waste minimization and pollution prevention. This presentation will present a common sense approach to system classification and dwell on the kinds of metrics that could be used, and others that must be developed. The Office of Research and Development within the Environmental Protection Agency is currently developing a research strategy that will identify significant issues that would require such sustainable solutions. Included in the strategy is the need to approach the issue from a practical perspective and to

develop collaborative approaches among various Government, industry, and private organizations.

35.

ECO-EFFICIENCY IN THE CHEMICAL INDUSTRY AND BEYOND. *Charlene A. Wall-Markowski, Eco-efficiency - North America, BASF Corporation, 3000 Continental Drive North, Mail Stop 5-013, Mount Olive, NJ 07828, Fax: 973-426-2622, wallc1@basf-corp.com, and Andreas Kicherer, Eco-efficiency, BASF AG*

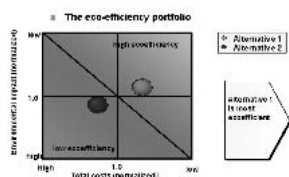
This presentation will explain BASF's eco-efficiency analysis tool and highlight a case study of how it has been used to support sustainability.

Six environmental categories are evaluated:

- Raw materials
- Energy consumption
- Land use
- Emissions
- Toxicity potential
- Risk potential

Life-cycle data are compiled for each of these categories, a weighting scheme is used to aggregate the results, and they are normalized in order to generate the ecological fingerprint. The fingerprint depicts the relative impacts of the alternatives in each of the environmental categories.

An economic analysis is also done to address costs over the life-cycle of the product. The economic results are then combined with the environmental results to obtain the portfolio. The portfolio depicts the relative environmental impacts of the alternatives on one axis, and similarly, the relative economic impacts on the second axis. Thus the relative eco-efficiencies of the alternatives are concisely shown.



36.

HYDROGEN: AN ECONOMICALLY COMPETITIVE FUEL THROUGH TECHNOLOGY DEVELOPMENT. *C. Lowell Miller, COAL FUELS & INDUSTRIAL SYSTEMS, U.S. Department of Energy, FE-24/Germantown Building, 1000 Independence Ave., S.W, Washington, DC 20585-1290, Fax: 301-903-2238, Lowell.Miller@hq.doe.gov*

Like electricity, hydrogen is not a naturally occurring fuel. It must be chemically separated from some other source. Currently, hydrogen is produced predominantly by steam reforming of natural gas and as a byproduct from naphtha reforming. Concerns over global climate change and eventual resource depletion of fossil fuel resources have revived the concept of the hydrogen economy where hydrogen is used as an energy carrier. This concept would use hydrogen to provide energy to all sectors of the economy including electric power (both central station and distributed power), industrial, residential and transportation. The successful transition to this hydrogen economy will require technologies that can be used to produce large volumes of hydrogen at a cost that is competitive with other energy choices available to the consumer. Comparative analyses of hydrogen production processes featuring innovative technology now part of the fossil energy research, development and demonstration program support the potential of these advanced processes to produce hydrogen, not only at a competitive cost, but with minimum or no impact on the environment.

37.

TAKING CUES FROM NATURE: INTEGRATING METABIOLOGY WITH CHEMISTRY AND ENGINEERING TO DRIVE DEVELOPMENT OF CHEMICALS AND FUELS FROM RENEWABLE SOURCES. *Bill Baum, Executive Vice-President, Diversa Corporation, 4955 Directors Place, San Diego, CA 92121, Fax: 858-526-5558, bbaum@diversa.com*

Carbon and energy drive the chemical industry. Current industrial processes leverage inexpensive petrocarbon as both a feedstock and a source of energy. Biomass-based green chemicals and sustainable energy are not a broadly available because economics are poor. Existing fermentation processes have

relied too heavily on a few standard fermentation organisms and enzymes to convert sugar to chemical intermediates or fuel. Discovery of new organisms and optimized catalytic enzymes provide a new base but aligning this new biology with chemistry and engineering is providing even greater efficiency. Millions of previously unknown microbes and billions of new genes will be discovered in the near future using advanced techniques emerging from metabiology and metagenomics. These discoveries will align with complementary chemistry and engineering steps to create green and energetically sustainable processes for making chemical intermediates and fuel from biomass.

38.

DESIGNING GREEN OXIDATION TECHNOLOGIES. *Terrence J. Collins, Department of Chemistry, Institute for Green Oxidation Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, Fax: 412-268-1061*

In the Institute for Green Oxidation Chemistry, we develop green catalytic oxidation systems designed to move the elemental composition of oxidation technology away from chlorine and toxic metal ions toward the natural oxidants, hydrogen peroxide and oxygen. We have designed and developed nontoxic iron catalysts called "TAML[®] activators" that have unprecedented technical performance in large-scale oxidation applications. There are more than twenty examples with different lifetimes and reactivities. They have molecular weights of ca. 500 u and are capable of thousands of turnovers per minute with H₂O₂ in certain reactions. I will briefly sketch the design history and reactivity considerations of TAML activators and the research aspects of their reduction to practice for selected uses. These will include applications in the pulp and paper and textile industries, disinfection and homeland defense (spore killing), the destruction of priority organochlorine pollutants and thiophosphate pesticides, and the desulfurization of gasoline and diesel.

39.

GREEN CHEMISTRY AND GREEN ENGINEERING FOR SUSTAINABILITY. *Paul T. Anastas, Green Chemistry Institute (GCI), 1155 16th St. NW, Othmer Suite 330, Washington, DC 20036, Fax: 202-872-6206, gci@acs.org*

There is widespread attention to the goals of sustainability throughout the chemical industry. Now that there is beginning to be a realization the sustainability and competitiveness are often, if not always, overlapping goals, the question becomes how do you accomplish the move toward sustainability. While complex issues such as supply chains, marketing and regulatory frameworks all enter into the equation, the central and essential elements still center on the chemistry and engineering and its design for sustainability. The concepts, principles and methodologies of Green Chemistry and Green Engineering are fundamental in integrating sustainability throughout the system of our chemical enterprise. By incorporating these Green Chemistry approaches in the research and development, scale-up and commercialization stages in industry and by ensuring that training of both established and next generation chemists and engineers includes Green Chemistry and Engineering, large strides can and are being made in sustainability in the chemical industry.

40.

WHAT'S DRIVING BIOBASED PRODUCTS? A PANEL PRESENTATION. *Ramani Narayan, Department of Chemical Engineering & Materials Science, Michigan State University, 2527 Engineering Building, East Lansing, MI 48824, narayan@msu.edu*

Sustainability, industrial ecology, and green chemistry are new principles that are guiding the development of the next generation of materials, products and processes. Biobased products hold great promise for achieving the goals of sustainable development and implementing the principles of industrial ecology and green chemistry.

The U.S. Government has set the goal of tripling U.S. use of bioenergy and biobased products by the year 2010. Meeting this goal could create an additional \$15-20 billion a year in new income for farmers and rural America, and reduce the environmental impact associated with annual greenhouse gas emission by an amount equal to as much as 100 million metric tons of carbon. The U.S. Congress passed the U.S. Farm Security and Rural Investment Act of 2002 (P. L. 107-171), Title IX Energy, Section 9002 (FARM BILL) that requires the Federal Government to give preference to purchasing biobased products, and charges the USDA with: · developing guidelines for designating biobased products · publish a list of biobased products for federal purchase; · issue

criteria for being placed on the Designated Biobased Products List (DBPL) · establish a voluntary USDA labeling program

In this session, a panel of representatives will address the contents and status of this Federal procurement of biobased products. Panel representatives will brief on ASTM standards developed and under development for biobased products — namely the definition of biobased product, identifying and quantifying biobased content, Life Cycle Assessment (LCA) of biobased products. The session will highlight biobased product technologies that are commercial and under development.

41. BIOPOLYMER NANOCOMPOSITES CONTAINING NATIVE WHEAT STARCH AND NANOCCLAYS. *Bor Sen Chiou, Emma Yee, Gregory M Glenn, William J. Orts, Dellah F. Wood, and Syed H. Imam, Bioproduct Chemistry and Engineering, United States Department of Agriculture, 800 Buchanan Street, Albany, CA 94710, Fax: 510-559-5675, bschiou@pw.usda.gov*

We formed bio-based polymer nanocomposites made from renewable resources by adding montmorillonite nanoclays to native wheat starch. We produced these polymer composites by using a twin-screw extruder and characterized their properties by using rheology, x-ray diffraction, tensile, water absorbance, and water vapor transmission tests. We first examined the interactions between the nanoclays, wheat starch, and water by measuring the formulation's rheological properties during gelatinization. The sample with the most hydrophilic nanoclay, Cloisite Na+, had the largest elastic modulus, indicating the Cloisite Na+ nanoclays became better intercalated than the other nanoclays. We then produced the nanoclay and starch composites by using a twin-screw extruder. From X-ray diffraction results, the solid to liquid ratio had the greatest effect on the nanoclay intercalation. Adding the nanoclay reduced the water absorbance by as much as 29% for some samples. In addition, the samples had higher modulus and lower stress and strains at break.

42. ELASTOMER FROM RENEWABLE RESOURCES: SYNTHESIS AND CHARACTERIZATION. *Lin Zhu and Richard P. Wool, Department of Chemical Engineering, University of Delaware, Academy Street, Newark, DE 19716, Fax: 302-831-1048, zhul@che.udel.edu*

Bio-based elastomers present environmental advantages over conventional petroleum based synthetic rubbers. The objective of this research is to develop new elastomers from plant oils, which are suitable for elastomer processing and have properties similar to conventional synthetic rubbers. Acrylated oleic methyl ester (AOME) was synthesized from the triglycerides. Different strategies have been developed to generate an elastic network based on AOME. Ethylene glycol dimethacrylate was used as crosslinker to crosslink AOME through bulk polymerization. High temperature and room temperature curing were both carried out and the latter resulted a network with better properties. Methyl methacrylate was used to further modify the network structure. 0.35 MPa tensile strength and 143% elongation at break were achieved. In addition to in situ crosslinking method, a high molecular weight linear polymer was obtained through miniemulsion polymerization and then compounded with curing agent to generate a crosslinked network. Finally, carbon black was added as a filler to study the filler effects. The network structure was studied and related to the thermal and mechanical properties, which in turn gives us the idea of controlling the elastomer properties by modifying the network structure i.e. molecular weight and crosslink density.

43. ENZYMATIC GRAFTING AND CROSSLINKING FOR ADDING VALUE TO BIOPOLYMERS. *Gregory F. Payne and Li Qun Wu, Center for Biosystems Research, University of Maryland Biotechnology Institute, 6134 Plant Sciences Building, College Park, MD 20742-4450, Fax: 301-314-9075, payne@umbi.umd.edu*

Biology serves as a model for the construction of high performance and environmentally benign materials. Typically, these materials are constructed from proteins and polysaccharides through biocatalytic routes. We are examining how enzymes can be exploited to graft side groups and side chains onto the polysaccharide chitosan. Specifically, natural phenols, peptides, and proteins can be grafted onto the chitosan backbone using the enzyme tyrosinase. These grafted polymers offer a variety of interesting properties. For instance, protein-

chitosan conjugates have been observed to have pH-responsive properties characteristic of chitosan. Also, we are examining the crosslinking of proteins using the enzyme transglutaminase. This enzyme is capable of converting protein-based solutions into three-dimensional hydrogel networks. Thus, enzymes can add value to renewable biopolymers by upgrading their functional properties.

44. PROCESSING AND PROPERTIES OF STARCH-POLYACRYLAMIDE GRAFT COPOLYMERS PREPARED USING REACTIVE EXTRUSION. *J. L. Willett and Victoria L. Finkenstadt, Plant Polymer Research, USDA, ARS, National Center for Agricultural Utilization Research, 1815 N. University St., Peoria, IL 61604, willetjl@ncaur.usda.gov*

Graft copolymers of starch and polyacrylamide (PAAm) can be readily prepared using a twin screw extruder. Initiator type and concentration significantly affect the properties of the PAAm. Ammonium persulfate (APS) gives PAAm with molecular weights exceeding 500,000, while Fenton's reagent (ferrous iron-hydrogen peroxide) gives molecular weights in the range 75,000 to 300,000 under comparable conditions. APS also gives higher conversions of monomer to polymer (90%) and higher grafting efficiencies (75%) than Fenton's reagent. Effects of increasing monomer content and decreasing initiator content are in general agreement with free radical polymerization kinetics. PAAm molecular weights are lower with Fenton's reagent due to chain termination by ferric ions. Since grafted PAAm molecular weight and graft frequency both depend on the level of initiator used, some degree of control over the properties of the starch graft copolymer is possible. After saponification, the starch-PAAm graft copolymers absorb between 150 and 250 times their weight in water at pH 7.

45. ECONOMICS OF EXTRACTING CELLULOSE FROM CORNHUSKS FOR INDUSTRIAL APPLICATIONS. *Narendra Reddy, Department of Textiles, Clothing and Design, University of Nebraska, Lincoln, NE 234, East Campus, P.O. Box 830802, Lincoln, NE 68583-0802, Fax: 402-472-0640, nreddy2@unlnotes.unl.edu, and Yiqi Yang, Department of Textiles, Clothing and Design and Department of Biological Systems Engineering, University of Nebraska- Lincoln*

Cellulose fibers with lengths from 2 mm to 20 cm have been extracted from cornhusks. These fibers are suitable for various applications such as textiles, composites, and fiber reinforced foams and also as a source for ethanol. A unique fiber extraction process using chemicals and enzymes has been developed which is low cost and eco friendly. The extracted fibers contain about 80 % cellulose and about 25 % fiber yield can be obtained from the cornhusks. The cost of fiber extraction including the cost of cornhusks (\$ 35 per ton) will be about \$0.30 per pound of fiber. Longer fibers (> 2 cm) extracted from cornhusks have properties required for textile applications. A value addition of at least \$0.50 per pound of the fiber is possible by using the fibers for textiles. This paper will evaluate the economics of producing cellulose from cornhusks in relation to the various end use applications.

46. NEW APPROACH TO IDENTIFYING LIGANDS FOR THE TYPE-1 PARATHYROID HORMONE RECEPTOR. *Percy H Carter, Rui Qun Liu, William R. Foster, Joseph A. Tamasi, Qihong Zhao, Vanessa Dell, Michele H. French, Ada Staal, Margaret Favata, Ramakrishna Seethala, Zhengping Ma, Mark Cunningham, Jean H. M. Feyen, Carl P. Decicco, and James M. Trzaskos, Pharmaceutical Research Institute, Bristol-Myers Squibb Company, P.O. Box 4000, Princeton, NJ 08543-4000, Fax: 609-252-7410, percy.carter@bms.com*

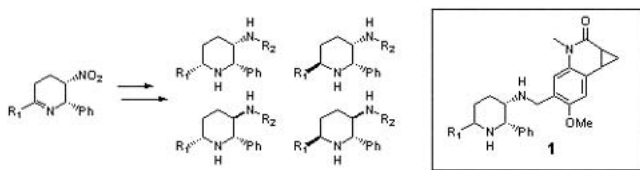
Osteoporosis is a disease in which bone loss arises from inappropriate regulation of the bone resorption and bone formation processes that occur as a normal part of bone remodeling. Parathyroid hormone (PTH) is an eighty-four amino acid peptide hormone that plays an important role in calcium homeostasis/bone remodeling through its direct actions on osteoblasts (bone forming cells) and indirect actions on osteoclasts (bone resorbing cells). In animal models of osteoporosis, continuous administration of PTH exerts catabolic effects on bone, whereas intermittent administration gives rise to anabolic effects. Consistent with this latter observation, once-daily subcutaneous administration of recombinant human PTH(1-34) provides for dramatic increases in bone mass in women with postmenopausal osteoporosis. We will discuss our initial efforts to identify orally bioavailable, small molecule equivalents of PTH,

which have focused on developing a new approach to screening for ligands of the PTH receptor. The design, validation, and implementation of a new screening strategy will be presented.

47. POTENT NEW NK1 ANTAGONISTS FROM A MODIFIED PIPERIDINE TEMPLATE: DIASTERESELECTIVE SYNTHESIS OF 2,3,6-TRISUBSTITUTED PIPERIDINES.

Thomas A. Chappie, Pfizer Global Research and Development, Groton Laboratories, Eastern Point Rd., MS 8220-4074, Groton, CT 06340, Fax: 860-686-1059, thomas_a_chappie@groton.pfizer.com

Modification of the 2-phenyl-3-benzylaminopiperidine series of NK-1 antagonists via alkyl substitution at the piperidine 6-position yields potent new compounds and interesting SAR. The requisite piperidine templates are available in good yield and without chromatography through parallel synthetic routes originating from a common intermediate. Stereoselective synthesis of the various piperidine isomers presents a challenge, particularly with respect to the 2,6-trans relationship. Two successful methods for establishing this stereochemistry will be presented. Also highlighted will be an efficient thermodynamic resolution of a key crystalline intermediate. The synthesis of various diastereomers of structure **1** will be presented in detail, and select biological data and SAR within this new series will be discussed.



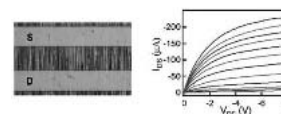
48. REACTOR BLOCKS: CATALYSTS FOR SHIFTING THE CULTURE OF A PHARMACEUTICAL DEVELOPMENT ORGANIZATION TOWARD PARALLEL EXPERIMENTATION. A. Erik Rubin, Process Research & Development, Bristol-Myers Squibb, One Squibb Drive, New Brunswick, NJ 08903, Fax: 732-227-3002, erik.rubin@bms.com

The key to success for any pharmaceutical process development organization is the generation of sufficient process knowledge. Process knowledge is a broad understanding of the factors affecting the quality and yield of the target chemical product and the tolerances of the process to variability in those factors. Process knowledge also refers to the series of incremental advances in the efficiency of a process that enables the delivery of the product faster and cheaper. Prior to the late 1990's, the capture of process knowledge was accomplished by examining a small set of "stressed" reaction conditions or by changing one process variable at a time and documenting the observations. Over the last five years the rising use of parallel experimentation and design of experiments has catalyzed a paradigm shift in many process development organizations to empower scientists to explore a greater experimental space more effectively and earlier in the development cycle. At the start of this paradigm shift and for a period thereafter, good tools to facilitate parallel experimentation did not exist. Process Development at Bristol-Myers Squibb (BMS) made the important decision to initiate its own internal technology development effort to meet the needs of its scientists. This presentation will recount one success of this technology effort through the story of the development of a novel reactor block for parallel small scale solution phase organic chemistry and the role this device is playing in changing the way process research and development is accomplished at BMS.

49. SEMICONDUCTOR NANOWIRES AND NANORIBBONS: FROM NANO-ELECTRONICS TO HIGH PERFORMANCE MACROELECTRONICS: A VISION FOR FUTURE AND IMMEDIATE APPLICATIONS. Xiangfeng Duan, Nanosys, Inc, 2625 Hanover Street, Palo Alto, CA 94304, Fax: 650-331-2101, XDuan@nanosysinc.com

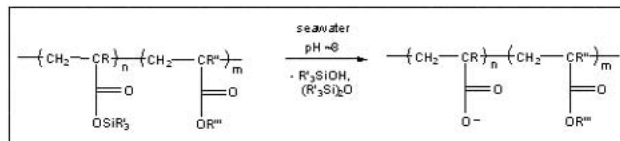
Semiconductor nanowires and nanoribbons are attractive building blocks for assembly of functional electronic systems. Individual nanowires can be used to fabricate nanoscale field-effect transistors with electronic performance comparable to that of the highest-quality single-crystal materials. Furthermore, a broad

range of functional nanocircuits including logic gates and computational circuits have also been assembled. These nanocircuits promise to push the Moore's law to the ultimate limit with unprecedented performance, but are currently difficult to implement for immediate production-scale nanoelectronics due to the complicated and limited scalability of the device fabrication processes. In this talk, we present a paradigm-shift in nanomaterial-enabled electronics, exploiting nanomaterials not for next generation of nanoelectronics, but for high performance macroelectronics on flexible substrate. In macroelectronics, functional devices are distributed yet integrated over large area substrate. Thin film transistors (TFTs) are the fundamental building blocks for current macroelectronics. Plastic is emerging as preferred substrate for macroelectronics due to economic and performance advantages. Current poly-Si, amorphous Si and emerging organic semiconductor TFT technologies are limited by high process temperature and/or low carrier mobility. Here we present a new concept of high performance TFTs on various substrates including glass and plastics. These TFTs have a conducting channel consisting of multiple single crystal nanowires in parallel, or a single crystal nanoribbon, spanning the full distance from source to drain. Unlike amorphous-Si or poly-Si TFTs in which carriers have to travel across multiple grain boundaries, our TFTs have conducting channels formed by multiple parallel single crystal NW paths, thus charges travel from source to drain within single crystals ensuring high carrier mobility. Both p- and n-channel TFTs have been demonstrated with carrier mobility approaching that of single crystal materials, on-off ratios greater than 10^7 and subthreshold swing as small as 70 mV per decade.



50. HIGH THROUGHPUT APPROACH TO DISCOVERY AND PROCESS DEVELOPMENT: TRIORGANOSILYL ACRYLATE-BASED MARINE ANTIFOULANT COATINGS. Mark A. Aubart¹, Michael B. Abrams¹, Rob T. Boaron², Marisa Hull¹, Dana Kobeda¹, David Mountz¹, Ron Siebenlist², Gary S. Silverman¹, Scot A. Swan¹, and Kenneth Tseng¹. (1) Atofina Chemicals, Inc, 900 First Avenue, King of Prussia, PA 19406, Fax: 610-878-6261, mark.aubart@atofina.com, (2) Atofina Vlissingen B.V., Haven 9850, 4389 PD Vlissingen Oost, Netherlands

This paper focuses on two challenging areas of the commercial development of environmentally friendly alternatives for triorganotin-based binders in marine antifoulant paints. These paints rely on the seawater-induced erosion behavior of polymeric binders (see example below) to control the release of added biocides. Both basic product development and optimization of the monomer synthetic process will be described for a series of tin-free triorganosilyl (meth)acrylate-based polymers. Initially, identification of silyl monomers and polymers that effectively balance chemical reactivity and macroscopic physical properties in the final polymer film will be discussed. In the second area of focus, the dehydrogenative coupling of triorganosilanes to unsaturated carboxylic acids will be presented as an economic route to key silyl monomers. The use of high throughput, parallel synthetic techniques as a tool to realize these goals will be a common theme.



51. ALL JET-PRINTED POLYMER THIN FILM TRANSISTOR ACTIVE-MATRIX BACKPLANES. Ana C. Arias, Steve Ready, Rene Lujan, William S. Wong, Kateri E. Paul, Michael L. Chabinyk, Alberto Salleo, and Robert A. Street, Electronic Materials Laboratory, Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304, Ana.Arias@parc.com

The use of solution-processed materials in combination with simple printing technologies offers the promise of inexpensive fabrication of active matrix

backplanes for large area flexible displays. We report additive jet-printing of regioregular polythiophene thin film transistors (TFT), and a printing process to fabricate complete prototype active matrix TFT arrays. We integrated metals and inorganic dielectric materials processed at low temperatures with a polymeric semiconductor to allow the use of flexible substrates. Patterning of metal gate, source and drain features and address lines uses digital lithography to jet-print a wax etch-mask. Once the wax mask is printed, the metal layer is patterned by etching and the wax is removed. The polymer solution is printed from a piezo-jet printhead. Additive jet printing was chosen as the preferred method of polymer deposition in order to achieve semiconductor isolation and reduce the cross talk leakage between transistors in the array. The jetted polythiophene semiconductor exhibits TFT mobility of $\sim 0.1 \text{ cm}^2/\text{Vs}$, on/off ratios of 10^7 , and minimal bias-stress, showing that the process of jet-printing results in the same electronic properties as in spin-coated films. These TFT parameters approach the performance of amorphous silicon transistors and meet the requirements for addressing displays. We fabricated 128X128 pixel active matrix backplanes with 340 micron pixel size, corresponding to 75 dpi display resolution, on glass and flexible substrates. This is the largest number of printed transistors and the highest display resolution reported by ink jet printing. We show that pixel design benefits from the registration accuracy of jet-printing and that the electrical performance is suitable for addressing capacitive media displays. Integration of display media to the array will be discussed.

52. MATERIALS DEVELOPMENT FOR HIGH-PERFORMANCE POLYMER THIN-FILM TRANSISTORS.

Yiliang Wu, Beng Ong, Ping Liu, Yuning Li, and Sandra Gardner, Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, ON L5K 2L1, Canada, Fax: 905-822-7022, Yiliang.Wu@crt.xerox.com

Polymer thin film transistors (TFTs) offer possibilities for creating low-cost transistor circuits for large-area devices such as flat-panel displays, and low-end electronics such as radio-frequency ID tags. Major effort in recent years has been devoted to the development of ambient stable, solution processable materials to enable simple solution-based deposition techniques such as printing in a non-sterile environment. This presentation will discuss our progress in the development of solution-processable materials, including semiconductor polymers, conductors and dielectric materials, for the design of high-performance organic TFTs. We will discuss the materials properties, effects of processing conditions, and nature of dielectric materials on device performance. The integration of all solution-processed materials into a high-performance TFT device will be presented.

53. DEVELOPMENT OF INSTRUCTIONAL MODULES TO INCORPORATE GREEN ENGINEERING CONCEPTS INTO THE CHEMICAL ENGINEERING CURRICULUM.

C. Stewart Slater and Robert P. Hesketh, Department of Chemical Engineering, Rowan University, 201 Mullica Hill Road, Glassboro, NJ 08028, Fax: 856-256-5242, slater@rowan.edu

This paper describes an EPA funded initiative to assist faculty in incorporating green engineering concepts in the chemical engineering curriculum. Instructional modules have been developed that consist of problem sets for use by faculty teaching a broad range of chemical engineering courses, e.g., material and energy balances, transport phenomena, thermodynamics, separations, reaction engineering, process design as well as those that impact multiple disciplines. Faculty from universities across the country are involved in the development of these modules that consist of problem sets, examples, cases studies that can be easily used with traditional course materials. A web site developed to assist faculty in incorporating green engineering concepts into the chemical engineering curriculum has also been launched. It is more effective 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. Using green engineering principles at the start of the design process can lead to processes and products of a sustainable future.

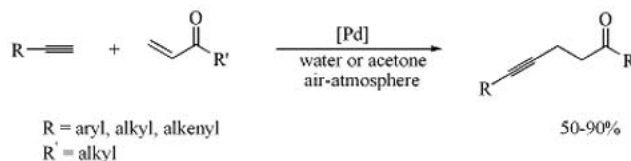
54. DESALINATION OF BRACKISH WATERS USING ION EXCHANGE MEDIA. Jason D. Pless¹, Mark L. F. Phillips¹, Diana L. Moore¹, James A. Voigt¹, J. L. Krumhansl², and Tina M. Nenoff¹. (1) Chemical and Biological Technologies, Sandia National Laboratories, P.O. Box 5800, 0734, Albuquerque, NM 87185-0734, Fax: 505-844-1840, (2) Geochemistry Division, Sandia National Laboratories

The desalination of brackish waters is a potential supply of potable water. We report on an entirely new method of desalination involving the in-situ ion exchange removal of salt ions. Column studies on brackish inland water, TDS=1957 ppm. Water flows through an anion exchange column (hydrotalcite) and into a cation exchange column (permutite). The resultant water contains TDS=25 ppm, pH=5.5. Coal-bed methane produced water, with bicarbonate concentration of 8300 ppm and TDS=10,990 ppm, was also treated. This process uses lime softening to remove the carbonate hardness. The resultant water is treated with hydrotalcite and permutite, resulting in TDS less than 100 ppm. This process is environmentally favorable because the ion exchange materials are either regenerated, or disposed without resultant brine waste.

Sandia is a multiprogram laboratory operated by Sandia Corporation, Lockheed Martin Company, for US DOE's NNSA, Contract DE-AC04-94-AL85000.

55. SYNTHESIS OF γ , δ -ALKYNYL KETONES FROM TERMINAL ALKYNES ADDITION TO VINYL KETONES CATALYZED BY PALLADIUM IN WATER AND IN ACETONE. Chao Jun Li, Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 2K6, Canada, cj.li@mcgill.ca, and Liang Chen, Department of Chemistry, Tulane University, New Orleans, LA 70118

The addition reaction is an atom-economical method to construct more complex molecules from simpler units. Recently, there has been an increased interest in developing reactions that allow for the addition of terminal alkynes to sp² carbons, namely to C=O bonds, C=N bonds. However, there are only a few reported examples (catalyzed by Ru, Rh, and Cu) of the addition of terminal alkynes to alkenes. Additionally, as far as we know, palladium catalyzed conjugated addition of alkynes to enones has never been reported. Therefore, as part of our continued interest in developing organic methodologies in aqueous media, we wish to report a simple and highly efficient Pd-catalyzed addition of terminal alkynes to C=C double bonds such as conjugated enones, either in water or in acetone under an air atmosphere.



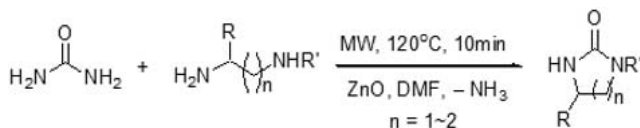
56. HETEROGENEOUS CATALYTIC ACYLATION REACTIONS IN SUPERCRITICAL CARBON DIOXIDE. Y.G. Adewuyi and Jonathan Mbah, Chemical Engineering Department, North Carolina Agricultural and Technical State University, Greensboro, NC 27411

The acylation of aromatics is of considerable industrial importance for making intermediates, which are used in the production of pharmaceuticals, insecticides, perfumes, agrochemicals and other fine chemicals. The acylation of anisole and toluene was studied in a high-pressure 25 ml batch stainless steel (SS 316) reactor using beta zeolite catalysts (with Si/Al ratio = 75-300) in the absence and presence of supercritical carbon dioxide at varying temperatures (60-150°C) and pressures (1200 - 3000 psig). The effects of reaction conditions on the conversion of reactants and product yield/selectivity, reaction kinetics and mechanism will be presented. The results of this study indicate that the zeolite and carbon dioxide based approach shows promise as a greener and more cost-effective alternative to the inherently dirty and highly polluting traditional Friedel-Crafts acylation processes, which uses typically nonrenewable Lewis acid like aluminum chloride as catalyst and nitrobenzene as solvent.

57. MICROWAVE-ASSISTED PREPARATION OF CYCLIC UREAS FROM DIAMINES.

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Cyclic ureas are useful intermediates for a variety of pharmaceuticals and pesticides. One of the attractive approaches for the synthesis of cyclic ureas uses condensation of diamines with urea as a carbonyl source under dynamic evacuation. A direct synthesis of cyclic urea is presented that proceeds expeditiously in the presence of ZnO. The reaction is accelerated upon exposure to microwave irradiation resulting in a shortened reaction time and eliminating the formation of side products when compared to methods involving conventional heating. Various reaction parameters influencing this condensation reaction will be presented including the extension of this work to related cyclic urethanes.



58. ACIDIC IONIC LIQUIDS AS GREEN CONVERSION AGENTS FOR ARENE CARBOXYLATION.

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Chloroaluminate ionic liquids formed from 1-butyl-3-methylimidazolium chloride (BMIC) were examined as conversion agents for toluene carbonylation at room temperature and at pressures between 150 and 1100 psig. The effect upon the toluene conversion and selectivity for changing the ratio of AlCl₃/BMIC from ½ to 2 mol/mol at a constant HCl partial pressure of 30 psig was examined as well as the effect of changing the HCl partial pressure from 0 to 30 psig at a constant value of AlCl₃/BMIC = 2. The effect upon reactivity was also determined for changing the Al₃/toluene ratio at a constant value of AlCl₃/BMIC = 2 when the PHCl was 30 psig for total pressures of 150 and 1100 psig.

59. SLURRY DESIGN FOR A "DRY" CO₂-BASED COPPER CHEMICAL MECHANICAL PLANARIZATION PROCESS. Pamela M. Visintin¹, Ginger M. Denison¹, Carol A. Bessel², Sergei S. Sheiko¹, Cynthia K. Schauer¹, and Joseph M DeSimone¹. (1) Department of Chemistry, University of North Carolina at Chapel Hill, CB #3290 Venable and Kenan Laboratories, Chapel Hill, NC 27599-3290, (2) Department of Chemistry, Villanova University

Chemical mechanical planarization (CMP) is an indispensable technology for fabricating integrated circuits with copper as the interconnection material. Current processes use an aqueous-based CMP slurry leading to technical and environmental difficulties. A typical slurry contains chemicals and abrasive particles to remove the copper metal overburden. We are developing a "dry" CMP process based on liquid or supercritical CO₂ as an alternative to aqueous solvents. Homogenous peroxide/β-diketone etchant solutions oxidatively dissolved copper metal in CO₂ media. Silica and alumina particle surfaces were modified with fluorosilyl groups as potential abrasive particles. Control studies established that the etchant solution with the modified particles did not result in cleavage of the fluorosilyl chains within 24 h. The steric stabilization of these modified particles in condensed CO₂ was quantified with turbidimetry. Hardness measurements and interaction forces between the modified particles and a copper surface were determined using Atomic Force Microscopy.

60. NEWER APPROACHES TO KILOGRAM SCALE SYNTHESIS OF DRUGS AND INTERMEDIATES. Ajay K. Bose¹, Maghar S. Manhas², Subhendu Ganguly², and Arun Mandadi². (1) George Barasch Bioorganic Research Laboratory, Department of Chemistry and Chemical Biology, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, Fax: 201-216-8240, abose@stevens.edu, (2) George Barasch Bioorganic Research Laboratory, Department of Chemistry and Chemical Biology, Stevens Institute of Technology

With the goal of redesigning such classical methods as the Perkin (1868), Biginelli (1893), Knoevenagel (1898) and Knoevenagel/Doebner(1900) reactions,

we have studied efficient approaches to Green Chemistry involving microwave enhanced reactions and "Grindstone Chemistry." Several preparations requiring many hours described in "Organic Syntheses" have been investigated and our techniques were found to lead to superior yield and purity of the same target compounds in 5 – 30 min of processing. Widely used pharmaceuticals and their intermediates (viz, aspirin, tylenol, antipyrine, dapsone, coumarins, arylidenemalonamic acids, etc.) have been prepared on a large scale with high yield and low chemical waste. Our methods can be extended to multiple kilogram preparation in pilot plants. These safe and rapid techniques are suitable for process development for many pharmaceuticals or their intermediates with reduced time of operation and limited use of solvents.

61. SOLVENT FREE PREPARATION OF PHARMACEUTICAL CO-CRYSTALS: SYNTHESIS, SCALE-UP AND PROPERTIES. Magali B. Hickey, Matthew L.

Peterson, Julius F. Remenar, Sherry L. Morrisette, Hector R. Guzman, J. Michael MacPhee, and Örn Almarsson, Pharmaceutical Chemistry, TransForm Pharmaceuticals, 29 Hartwell Ave., Lexington, MA 02421, mbhickey@transformpharma.com

Co-crystals present an interesting opportunity to improve the physico-chemical and performance properties of pharmaceutical compounds. Such materials may be prepared by a variety of techniques, including solvent re-crystallization, melt crystallization and grinding. In this presentation, exploration of co-crystal formation by grinding will be presented, where components were ball milled in the presence or absence of catalytic amounts of pharmaceutically acceptable solvents. Several case studies will be reviewed (i.e., itraconazole and carbamazepine). For example, several co-crystals of itraconazole exhibit four to twenty fold higher solubility relative to the free base. These results demonstrate the utility of this green chemistry approach to the discovery of these novel materials, as well as the impact on performance relative to the parent compound or salts thereof.

62. COPPER CHEMICAL MECHANICAL PLANARIZATION PROCESSES IN CARBON DIOXIDE: SLURRY DESIGN. Ginger M. Denison¹, Renee Smith¹, Carol A. Bessel², Royce W. Murray³, and Joseph M. DeSimone⁴. (1) Department of Chemistry, University of North Carolina, B-5 Venable Hall, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, denison@email.unc.edu, (2) Department of Chemistry, Villanova University, (3) Department of Chemistry, University of North Carolina at Chapel Hill, (4) Department of Chemistry / Department of Chemical Engineering, University of North Carolina at Chapel Hill / North Carolina State University

Water-based chemical mechanical planarization (CMP) faces several industrial challenges as the semiconductor industry implements porous low k inorganic and organic interlayer dielectrics. We propose a carbon dioxide-based CMP process, which takes advantage of the unique intrinsic properties of CO₂, such as excellent surface wetting, low viscosity, tunability (by varying T and P), and ease for recycling. Our current research includes the development of both a homogenous and a heterogeneous (water-in-CO₂) carbon dioxide-based CMP process. Copper etchant studies using CO₂ soluble peroxides and ligands indicate that increasing the fluorine content of the ligand enhances the solubility of the resultant copper species due to the strong interaction between fluorine and carbon dioxide. Copper surface analyses have been accomplished by X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy, Secondary Ion Mass Spectrometry, and Atomic Force Microscopy. The thermodynamics of the copper ligand systems have been studied electrochemically in the form of Pourbaix diagrams.

63. NEW DOWNSTREAM DEHYDROGENATION-POLYMERIZATION PROCESS WITH WASTE MINIMIZATION. SAVVAS Vasileiadis, CHEMISTRY & CHEMICAL TECHNOLOGY, ZIVATECH, 15549 DEARBORN STREET, North Hills, CA 91343, Fax: 818-893-4292, svas150@aol.com

This research reports on improved membrane systems for production of specialty chemicals with waste minimization. New improved reaction and reactor designs with parameter selection and optimization for best process operation are discussed. The described processes are of current significance in hydrocarbon (paraffins) processing and conversion operations to valuable chemicals because of their unique design characteristics. Among other equipment,

permeable catalytic reactors (carriers) are utilized which deliver increases in conversion and yield by using a unified in-situ catalysis, reaction, and separation zone. In the downstream, the reaction products such as olefins and hydrogen are used for direct production of specialty chemicals in a downstream reactor. Such an example includes olefin polymerization to polyolefins (e.g., propylene to polypropylene, ethylene to polyethylene).

Simultaneously, these processes eliminate the use of organic solvents and byproducts in polymerization and achieve reaction operation at lower temperature which favors longer catalyst and reactor lives.

64. ENGINEERING FABRICS FROM CORNHUSK FOR HIGH VALUE APPLICATIONS.

Narendra Reddy, *Department of Textiles, Clothing and Design, University of Nebraska, Lincoln, NE 234, East Campus, P.O.Box 830802, Lincoln, NE 68583-0802, Fax: 402-472-0640, nreddy2@unlnotes.unl.edu, and Yiqi Yang, Department of Textiles, Clothing and Design and Department of Biological Systems Engineering, University of Nebraska- Lincoln*

Natural cellulosic fibers with properties required for textile applications have been extracted from cornhusks. In comparison to common natural cellulose fibers, cornhusk fibers have high elongation with moderate strength, other properties being between cotton and linen. These fibers have been processed on the conventional textile machinery and made into fabrics useful for apparel and industrial applications. Cornhusk fabrics can be used for various fibrous applications such as textiles, fiber reinforced foams and for composites. Stress /Strain behavior of fibers indicate that fabrics made from cornhusk fibers will be soft and flexible due to the low modulus of the fibers but will be tougher than cotton, linen and jute. In this paper, the processability of cornhusk fibers on the

conventional textile machinery and the properties of the yarns and fabrics will be discussed in relation to various end use applications.

65. GREEN TRACTORS AND HOUSES FROM SOYBEANS. **Richard P. Wool**, *Department of Chemical Engineering, University of Delaware, ACRES Program, Center for Composite Materials, University of Delaware, Newark, DE 19716-3144, Fax: 302-831-8525, wool@ccm.udel.edu*

Composite resins derived from plant oil such as soyoil, cornoil and canola can be utilized to make high performance materials for agricultural equipment such as tractors, round hay balers and harvesters. Such bio-based composites also have application in housing, electronic materials, automotive, aerospace, defense and civil infrastructure. In bridging lab-scale to mass production of new bio-based materials, consideration must be given for the the multidisciplinary components involving (a) genetic engineering of plants, (b) oil refining for optimal fatty acid distributions (FAD), (c) chemical modification of the oils to make reactive resins, (d) fabricator manufacturing requirements, and (e) end-user property requirements. The optimal FADS can be selected with regard to the chemical pathways which control the molecular architecture of the reacted resin, which in turn dictate the thermal and mechanical properties through vector percolation relations. Green engineering optimization involves waste reduction through use of renewable materials, integration of chemical synthesis with biofuel refinery waste (e.g. glycerol), air pollution reduction through elimination of volatile reactants, and reduction in fossil fuel consumption via low energy manufacturing processes. For the highest volume potential application of these new bio-based materials, significant changes in housing design permits significant energy savings and resistance to hurricane and tornado damage.