

IEC 1

The discovery of an innovative and very green one-step synthesis of tetronic acid

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Tetronic acid is an important key intermediate for different products (e.g. (+)-Biotin and Losigamon) of the fine chemical and pharmaceutical industry. The industrial production of tetronic acid can be achieved in a multi-step gas phase process, starting from 4-chloro aceto-acetate. It was found, that addition of 4-chloro acetoacetate to a cold, aqueous solution of sodium hydroxide yields a mixture of sodium chloroacetate and sodium acetate. In addition, the resulting yield of sodium tetronate is less than 30%. Based on these findings, an innovative one-step process for the synthesis of tetronic acid was targeted. Therefore, the pH and temperature dependency of this reaction was studied in a parallel, automated set of experiments.

This investigation was resulting in a innovative process, which saves several chemical steps over the pre-existing industrial synthesis of tetronic acid, and may result in major cost savings in the production of this important intermediate.

This and other relevant examples, presented herein, impressively support the enormous value of a parallel and automated High Output Experimentation approach.

Therefore, equipment, which originally has been designed for the HTS approach in the pharmaceutical industry today also is established in the laboratories of Process R&D groups. This transition has caused increased technical demands on automated synthesis workstation capabilities. Only highly modular, flexible and scalable systems, those that can easily be configured to meet the needs of chemists, have a chance of covering a broad range of complex and demanding applications.

IEC 2

Polysulfobetaine-grafted surfaces as environmentally benign nonfouling marine coatings

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Biological fouling settlement and growth of vegetable and animal organisms are among the most important problems affecting a structure immersed in seawater. Existing antifouling methods include (a) biocide-based coatings which release toxicants to kill target or non-target microorganisms and (b) fouling-release coatings which are effective when vessels move at high speeds. In this study, superlow biofouling polysulfobetaine polymers were applied to develop nonfouling marine coatings. Poly(sulfobetaine methacrylate) (polySBMA) brushes were grafted on glass surfaces using surface-initiated atom transfer radical polymerization (ATRP). The settlement, growth and attachment strength of *Ulva* spores were investigated on the polySBMA-grafted glass slides. Results showed that spore settlement density was extremely low on the SBMA coatings. Attached spores were bound more weakly to SBMA coatings than reference PDMS coated slides or bare glasses. Biomass of sporelings on SBMA surfaces was much lower than on PDMS or glass. Sporelings were attached very weakly to SBMA surfaces. In order to improve the long-term stability of these coatings, several analogues of polySBMA were also synthesized and evaluated for their long-term degradation using X-ray photoelectron spectroscopy (XPS). The polysulfobetaine-based coatings present several great advantages over current marine coatings for their effectiveness and friendliness to the environment.

IEC 3

Identifying environmentally friendly chemicals for gas absorption

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In a gas absorption process large amounts of solvent chemicals are utilized, and loss of chemicals to the environment is a concern. Gas absorption is an important technology in the processing of natural gas, and a candidate technology for large scale capture of CO₂. The present work deals with finding solvents that are environmentally friendly while at the same time meeting process requirements. A central challenge is that while high solvent stability is desirable under process conditions, high degradability is desired in the environment.

Ecotoxicity results for a series of solvents for absorption are presented. Likely degradation mechanisms and degradation products are discussed. Initial findings on the correlation between marine biodegradation and degradation under process conditions are discussed. Finally the extent to which different solvents meet all requirements is discussed.

IEC 4

Acrylic thermosets: A novel catalytic green chemistry alternative to formaldehyde resins

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Catalysis is a cornerstone Green Chemistry principle affecting the rate and environmental impact of an industrial process. Acrylic thermoset technology is an excellent example of a Green Chemistry by design. This technology relies on the catalytic transformation of a thermoplastic into a durable thermoset. The unique incorporation of a phosphorus catalyst into the polymer backbone is the critical design feature that provides the superior performance, distinguishing acrylic thermosets from other thermosets. Extensive polyester crosslinking is obtained from an environmentally benign formulation. Acrylic thermosets technology offers a safer, less toxic alternative to traditional formaldehyde-based resins. Water is the only cure byproduct from reaction of a stable formulation consisting of a polycarboxylate, polyol and phosphorous catalyst. The features of acrylic thermosets are presented as an example of Green Chemistry by design. The mechanical properties and uses of acrylic thermosets will also be discussed.

IEC 5

Designing and formulating environmentally benign pressure sensitive adhesives

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Pressure sensitive adhesive (PSA) contaminates post consumer waste impeding its processing and limiting the use of recovered cellulose fiber. An approach for reducing the impact of PSA on recycling operations is to redesign pressure sensitive (PS) label systems to inhibit fragmentation of adhesive films. This results in residual PSA particles that are more easily removed from the process with conventional mill contaminant control equipment. In this presentation findings are reviewed from research aimed at the development of PSA films that are resistant to fragmentation and are removed from recycling operations with high efficiencies. Both thermoplastic (hot-melt) and emulsion (water-based) formulations were examined, which combined, account for much of the PSA label

market. Studies involved the characterization and testing of commercial products to identify potential controlling factors and the development of model systems to better identify their role in determining fragmentation behavior. It is demonstrated that through prudent choices in monomer and additive composition, the impact of PSA products on recycling operations can be significantly reduced or eliminated. And that this can be achieved without increasing costs or sacrificing performance.

IEC 6

You are what you measure: Key considerations in the creation of green metrics

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The creation of appropriate metrics for green technologies is a complex endeavor. Substantial progress has been made in several areas where scientific and technical knowledge is linked to the ability to achieve broader sustainability goals. The Harvard-Yale-ACS GCI Green Chemistry Project's research on the industrial implementation of green chemistry has shed some light on the current status of green metrics in a variety of industrial and regulatory contexts. The strengths and weaknesses of these will be presented. This, combined with more general work such as the National Academy of Science's Roundtable on Linking Knowledge with Action for Sustainable Development, will then provide a context for a discussion of future, broader approaches towards green metrics.

IEC 7

Selective oxidation of cyclohexene to cis-1, 2-cyclohexanediol over MO_x(M=V, Nb, Cr, Mo, W) with t-butyl hydroperoxide as an oxidant

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Selective oxidation of cyclohexene to cis-1,2-cyclohexanediol, where cyclohexene oxide, cyclohexenol, cyclohexenone and 2-hydroxycyclohexanone were formed as by-products, was performed over V₂O₅, Nb₂O₅, Cr₂O₃, MoO₃

and WO₃ with 75% t-butyl hydroperoxide (TBHP) as an oxidant. The results show that the catalytic performance of those catalysts are in the order of MoO₃ >VO₅> WO₃> Nb₂O₅> Cr₂O₃. In the presence of MoO₃, the influence of reaction temperature, reaction time as well as catalyst amount on the reaction were also systematically investigated so as to obtain the maximum yield of cis-1,2-cyclohexanediol. It was thus found that the conversion of cyclohexene and the selectivity to cis-1,2-cyclohexanediol reached 99% and 96% respectively when the reaction was carried out at 90 °C for 12 h using 100 mg MoO₃ as catalyst.

IEC 8

Water recycling from dyeing effluent using nanofiltration and diverse osmosis membranes

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Abstract

The textile manufacturing processes are not only heavy consumers of energy and water, but also produce a substantial amount of undegradable hazardous chemical wastes. Dyeing effluents from textile industry usually contain high concentrations of inorganic as well as organics which are very complicated, and therefore are difficult to treat by conventional physical chemical and biological methods. In this paper, cross flow nanofiltration (NF) and reverse osmosis (RO) using thin film composite polysulfide and cellulose acetate membranes were used to recover the electrolyte solution and remove the COD pollution from the textile wastewater. The characteristics of three kinds of NF membranes and two types of RO membranes were compared and assessed under different temperature, transmembrane pressure and operating time. The NF membranes were found to be easier to operate under lower pressures such as 0.6 MPa with a relatively higher flux of permeate and a lower retention rate of COD and inorganic salts around 50%, while the RO membranes operating in the range of 1.8- 2.8 MPa could easily obtain a higher rejection of COD and salinity above 90%. Further, with the increasing of temperature, the rejection of COD and salinity reduced slightly, but the permeate flux increased in the meantime, which indicated some membrane fouling. The stability of membrane system proved that it was well suited for the treatment of high dye and salt concentrations, and the decolorized permeates was very suitable for industrial reuse or further polishing. Finally, a theoretical model was developed to predict the flux of the membranes and showed good agreement with the relative experimental results.

Keywords Nanofiltration; Reverse osmosis; Membrane; Textile wastewater; Reuse

IEC 9

Recovery of valuable components from wastewater in glycine production by solvent extraction

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With a rapid development in glycine production, processing its wastewater has become very important, because there are chloroacetic acids in the effluent, and monochloroacetic acid is one of the restricted discharging effluent, which allowance concentration is 0.1mg/L. Therefore, an efficient technology for recovering the valuable components from wastewater of glycine production is strongly desired.

Extractive recovery of carboxylic acids from dilute aqueous solutions has attracted scientists' attentions for a decade, because it is an environment-friendly technology for separating and concentrating solutes (metals, organics, etc.) from leachate, fermentation broths, or industrial waste solutions. However, few studies on recovering multiple organic acids from the aqueous solution have been reported. Recovery of valuable components in wastewater of glycine production is very difficult, because acetic acid, monochloroacetic acid and dichloroacetic acid in the effluent have similar properties..

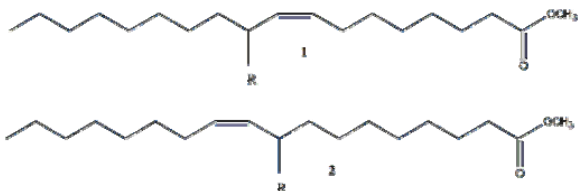
In previous study, some typical extractants have been used to recover the carboxylic acid, e.g. long-chain aliphatic tertiary amine, trioctylamine (TOA) or Alamine 336. phosphorus-bonded oxygen-containing extractant, trialkyl phosphine oxide (TRPO) and tri-butyl-phosphate (TBP). According to the properties of monochloroacetic acid, dichloroacetic acid and acetic acid, TBP was selected as the extractant, and kerosene was used as the diluent in this work, the extraction behavior of monochloroacetic acid, dichloroacetic acid, acetic acid and their mixture from aqueous solution were investigated. The suitable mathematic model was proposed to describe the extraction equilibrium of organic acid with TBP on the basis of mass action laws. The optimal operation conditions of extracting acetic acid, monochloroacetic acid and dichloroacetic acid from wastewater of glycine production was obtained, and the flow diagram was proposed also.

IEC 10

Synthesis and characterization of branched-chain derivatives of methyl oleate

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Oleic acid and linoleic acid are the most abundant fatty acids of cottonseed oil. As part of a project to develop new value-added industrial applications for cottonseed oil (such as biodiesel, fuel additives, and lubricants), studies were conducted in the synthetic conversion of oleic acid to branched-chain fatty acids. In these studies, methyl oleate was brominated in the allylic position and subsequently treated with organocuprate reagents to produce novel branched-chain derivatives 1 and 2 (R = methyl, n-butyl, sec-butyl, phenyl). Details of the syntheses, characterization, and properties of the products (with emphasis on low-temperature properties) will be discussed.



IEC 11

Synthesis and properties of fatty acid 2-hydroxyl-3-sulfo propyl ester

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A novel surfactant, fatty acid 2-hydroxyl-3-sulfo propyl ester as sodium salt, was synthesized. Firstly, fatty acid glycerincydil ester was synthesized with epichlorohydrin and fatty acid in toluene at 373K. A series of fatty acid glycerincydil ester were sulfonated to fatty acid 2-hydroxyl-3-sulfo propyl ester as sodium salt by the NaHSO₃ in aqueous solution at 353K. The yield is 85%. The structures of the surfactants were characterized by IR, ¹H-NMR and MS. In order to find the relation of properties and structure, especially hydrophobic carbon chain, the thermodynamics properties, such as ΔG and ΔS of micellization and absorption at air/water surface, of the surfactants were studied. For lauryl acid derivative, α cmc is 29.5mN/m, cmc is 0.0078 mol/L. The results showed that this

series of surfactants have excellent interfacial properties and a good market foreground.

IEC 12

Glycerin as a renewable feedstock for epichlorohydrin production

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The Dow Chemical Company is currently the world's largest producer of epichlorohydrin, a key building block in the synthesis of liquid epoxy resins. In August 2006, Dow announced its intent to manufacture epichlorohydrin in China (100 kTpa) via a novel, acid-catalyzed hydrochlorination process using glycerin. The increasing availability of glycerin stems from the production of biodiesel. The hydrochlorination process not only utilizes a renewable feedstock, but forms the basis of an economically attractive alternative to an existing process. We will discuss the catalytic attributes and advantages of the Dow Glycerin to Epichlorohydrin process (GTE) over existing process routes. These include faster reactions, the ability to produce more concentrated dichlorohydrin streams, high regioselectivity to 1,3-dichlorohydrin, formation of low levels of chlorinated byproducts, and solventless processing. These features combine to make the process more sustainable by reducing the number of unit operations, environmental footprint and manufacturing costs.

IEC 13

Hydrothermal conversion of biomass to fuels: Effect of interactions between carbohydrates and proteins

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Hydrothermal technologies have the promise of being among the most energetically efficient means of producing fuels from wet biomass. These technologies can accept a wide variety of biological materials, and are not, in general, constrained to specific biomolecules such as glucose or fatty acids. A

variety of fuels can be made with these technologies, from hydrogen and methane to diesel and “biocrude”, a complex mixture of refinable organic compounds. However, while the kinetics and reaction mechanisms of a limited number of pure components are known in hydrothermal media, interactions between them are largely uncharacterized and could provide unexpected results. In particular, reactions between carbohydrates and proteins can cause undesirable polymerizations under certain hydrothermal processing conditions. We have examined glucose and glycine, as model compounds, to better understand and quantify reaction pathways and rates. A strong interaction resulting in higher rates of conversion has been observed under hydrothermal conditions.

IEC 14

Platform chemicals from cellulose, saltwater and microwaves

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α -Crystalline cellulose is the most recalcitrant portion of biomass carbohydrates. Under the usually severe and acidic conditions required for digestion of this fraction, most of the desired aldose platform chemical (glucose) reacts further to undesired mixtures. However, replacing the usual Bronsted acid catalyst with certain salts, which are sensitive to microwave heating, enhances the relative rate of cellulose dissolutions and allows some selectivity of product. Thus, various salt-microwave methods afford good conversions of α -crystalline cellulose to certain platform chemicals. Separation and recycle of the saltwater may assist the economics of such processes.

IEC 15

Production of hydroxymethylfurfural (HMF) from glucosamine and glucosamine-rich renewable materials

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Chitin is a structural polymer of arthropod exoskeletons and fungal cell walls and is considered as the second most abundant biomass on earth. However, it is extremely underutilized and ignored as a renewable resource. Chitin is easily

deacetylated to chitosan and/or hydrolyzed to glucosamine. Our data showed that the yield of HMF from glucosamine exceeds 3 times levels produced from fructose. Additionally, significantly higher HMF concentrations were achieved in organic acids compared to hydrochloric acid. Contrary to the production of HMF from fructose that requires extremely harsh conditions (pH below 1), the maximum yield from glucosamine was accomplished at pH~4. We also found that addition of DMSO may suppress rehydration degradation of produced HMF and thus increased its yield. We believe that hydroxymethyl furfural and its derivate, levulinic acid, can be efficiently produced from glucosamine, which, in turn, can be easily obtained from crustacean shells and fungal biomass.

IEC 16

Stability and friction-reducing properties of epoxidized oleochemical methyl esters

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The use of oleochemicals as biobased replacements for petrochemical lubricants is an important area of study. Physical properties of the epoxidized fatty esters derived from vegetable oil are reported and compared to their olefinic counterparts. Overall the frictional behavior of epoxy methyl oleate (EMO), epoxy methyl linoleate (EMLO), and epoxy methyl linolenate (EMLN) in hexadecane solution were studied and found to reduce friction better than the corresponding olefins. Adsorption coefficients were calculated and the corresponding trends were elucidated. Additionally, the materials have been shown to have improved oxidative stability by Pressure Differential Scanning Calorimetry (PDSC) and Thin film Micro Oxidation (TFMO). The flow properties of the compounds are also favorable for use as in the lubricant industry. Application of a lubrication fluid of this type is especially useful in areas where a bio-based and environmentally friendly lubricant, such as forestry, would be advantageous.

IEC 17

Electrooxidation of ethanol and methanol using heterobimetallic catalysts

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The heterobimetallic Ru/Pd, Ru/Pt, and Ru/Au complexes $\text{Cp}(\text{PPh}_3)\text{Ru}(\text{-X})(\text{-dppm})\text{PdY}_2$, $\text{Cp}(\text{PPh}_3)\text{Ru}(\text{-X})(\text{-dppm})\text{PtY}_2$, $\text{Cp}(\text{PPh}_3)\text{RuX}(\text{-dppm})\text{AuY}$ and $[\text{X} = \text{Cl, Br, I; Y} = \text{Cl, I}]$ function as catalysts for the electrochemical oxidation of methanol and ethanol. Product selectivities, catalyst efficiencies and the effects of structural modifications on catalyst performance will be discussed.

IEC 18

Olefin metathesis of biorenewable feedstocks: Discussion of commercial applications of these novel compositions

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This talk will describe our progress to date in the commercialization of metathesis modified renewable feedstocks. Olefin metathesis has been used to convert natural oils (corn, canola, soybean) into novel value-added compositions and is the basis of a platform of performance additive products. Technological progress has resulted in the reduction of ruthenium metathesis catalyst loadings and increased turnover numbers. This commercialization effort is a result of a co-development program with Cargill and The California Institute of Technology. The first products being marketed are metathesis modified soy-based waxes with applications in paints, coatings and personal care products. The catalyst and process chemistry will be discussed as well as numerous commercial applications.

IEC 19

Organometallic carbohydrate chemistry: Metal nucleophiles in the Ferrier reaction

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In contrast to nonrenewable carbon feedstocks, the lack of chemical transformations involving biomass feedstocks represents a limiting factor in their commercial application. Catalytic production of fuels, chemicals, materials, etc. on an industrial scale is accomplished with transition metal complexes. Thus understanding the interaction of organometallic complexes with carbohydrates is essential for transitioning to a renewable carbon-based economy. While transition metal chemistry involving sugars has been reported, this still remains a largely unexplored field. We have found that the Ferrier reaction of KFP with triacetylglucal (TAG) and a Lewis acid catalyst (BF_3 etherate, I_2) affords a highly

air and solution sensitive complex. In contrast, the analogous Ferrier reaction employing $\text{Li}[\text{Mn}(\text{CO})_5]$ and either TAG or the corresponding triacetylxlal and -galactal affords relatively stable complexes. This paper will report the synthesis, reactivity and characterization of some carbohydrate-transition metal complexes prepared using the Ferrier reaction.

IEC 20

A new process for glycerol transformation to acrolein

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The transesterification process for biodiesel production leads to larger amount of glycerol as a by product. Therefore there is great interest to use glycerol as starting material for the transformation in highly valuable intermediates for the chemical industry. The development of new route for the production of acrolein starting from glycerol in the presence of heterogeneous catalysts can be considered as potential solution for the following problems at once:

- Sustainable valorisation of glycerol
- Environmentally responsible production of valuable intermediates
- Sustainable process development

The catalytic performance in the dependence of the reaction parameters will be discussed as well as the up scale of this process.

IEC 21

The reduction of polyols to diols

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For biodiesel biorefineries to be successful on a long-term basis, they must produce biodiesel and a portfolio of high value products and chemicals. Some soy processors convert the soybean oil into biodiesel by treating the oil with methanol and a catalyst. For every gallon of biodiesel that is produced, a pound of glycerol is generated. The price of glycerol is expected to plummet to almost five cents per pound as biodiesel capacity grows across the Midwest. In order to optimize the overall profitability of the biodiesel operation, glycerol must be

converted into higher-value chemicals that can replace petrochemicals. One such chemical could be 1,3-propanediol(PDO), which is used in textiles and fabrics, such as DuPont's Sorona. Currently over one million pounds of PDO are produced each year; much of this from fossil fuels. Iowa State University Center for Catalysis researchers have developed an ionic hydrogenation reaction to convert glycerol into 1,3-propanediol.

IEC 22

Cracking of oleic and acyl glycerides acid using a superacid or zeolites

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Relatively high petroleum prices and global warming concerns have led to an increase in annual production of renewable fuels such as biodiesel and ethanol. For example, biodiesel production has increased from 500,000 in 1999 to 75 million gallons in 2005. Biodiesel is a mixture of fatty acid alkyl esters produced from vegetable oils and animal fats. It has to comply with the ASTM D6751 standard. The increase in biodiesel demand over the last 6 years has demonstrated the sensitivity of the fuel cost to the market price of vegetable oils, the need for a more robust oil conversion process, and the difficulties associated with handling glycerine, a by-product of biodiesel production. A new biofuel is needed that can utilize a wider variety of lipids while minimizing the generation of unwanted byproducts. Green diesel is a diesel-liked mixture generated from the catalytic cracking of vegetable and microbial oils, and animal fats. The conversion process is similar to that used by petroleum refineries for producing diesel and gasoline. In this study, oleic acid, a major fatty acid component of many potential lipid feedstocks, was reacted at 0°C using triflic acid (super acid) as the protonating catalyst. Oleic acid was found to crack into liquid and gaseous products. Liquid products were analyzed by NMR, FTIR, and GC/MS. The liquid fraction was composed of a mixture of C9 – C14, C16 and C18 free fatty acids. Both, straight and branch chain saturated isomers were formed for many of the carbon-lengths. These results were used in combination with heterogeneous catalysis to develop cracking mechanisms of oleic acid and selected acyl glycerides.

IEC 23

Biopetrochemicals made available by gold-catalyzed oxidative esterifications: From biorenewable feedstocks to polymer building blocks

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As a society, we are highly dependant on fossil resources, as transportation fuels as well as for cheap feedstocks for the chemical industry. A shift from conventional petrochemical feedstocks towards biopetrochemicals appears inevitable since an increased demand for fossil resources will most likely increase the price of commodity base chemicals dramatically. In fact, the Roadmap for Biomass Technologies in the U.S. predicts that by 2020, 18% of all manufactured chemicals will originate from biomass. However, this vision is currently impeded by the availability of technology for large-scale chemical processing of biorenewable feedstocks into commodity base chemicals. Recently, we have developed an oxidative esterification process by which biorenewable downstream chemicals such as hydroxymethyl furfural and 1,3-propanediol can be transformed into high-value polymer building blocks. The production of polymer building blocks from biopetrochemicals is intriguing, since the polymer industry by far is the largest consumer of petrochemical feedstocks in the chemical industry.

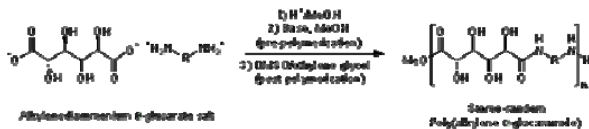
IEC 24

Synthesis and characterization of higher molecular weight stereo-random poly(D-glucaramides) from 1:1 alkylenediammonium D-glucarate salts

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Poly(alkylene D-glucaramides) are a class polyamides produced by the condensation polymerization of alkylene diamines with esterified D-glucaric acid from oxidation of D-glucose. Due to their renewable origins and biodegradable nature, these polyhydroxypolyamides are attractive from both sustainable and environmental perspectives. Their development is now progressing due to application of new methods to significantly increase their molecular weights. With regard to poly(alkylene D-glucaramides), a new polymerization method has been developed originating from 1:1 alkylenediammonium D-glucarate salts (analogous to the nylon 6,6 precursor salt). Polymerization of the salts is carried out by activation of the glucarate moiety through esterification followed by liberation of the diamine with a base. The molecular weights of the resulting polymers are significantly influenced by the base employed in the deprotonation

step. The polymers are extended further by a post polymerization reaction in a mixed solvent system. The synthesis of poly(alkylene D-glucaramides) and their molecular weight characterization by NMR end-group analysis and gel permeation chromatography will be presented.



IEC 25

Market situation, need for action and potential capacity from biopolymers

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The irreversible conversion of petrochemical resources in different energy sources and polymers is not sustainable. Due to the increasing environmental awareness, modified political conditions and the restricted disposability of petrochemicals resources with increasing commodity prices, the biogenous hydrocarbon becomes a stronger interest in the politic, public, chemistry industry as well as in the plastic industry. Due to this development different research on biopolymers were intensified during the last years. Furthermore biopolymer affords a lot of waste disposal advantages. Biopolymers could be composted as well as CO₂-neutral combustion is possible. By this way petrochemical resources can be saved on the field of resources on the one hand and through energetic usage/disposal on the other hand. Nevertheless no one succeeded to establish materials and products based mainly on renewable primary products on an industrial scale which would have fulfilled the high expectations that grew out of very promising prognoses. The lecture will give an overview about the market situation, bottle necks and the potential of biopolymers. The following topics will be covered: How many biopolymer producers and how many biopolymer types are available on a global scale? Who produces which biopolymers? Where are the biopolymers produced? How much production capacity is available? Where are needs for action? The biggest problem of the biopolymers is the missing, non-standardised availability of actual material data. The main goal of the project will be to collect complete information about available Biopolymers, using uniform standards and to generate comparable and complete material data. The result will be a database, which is compatible with the international accepted CAMPUS® system and will be accessible through the internet. The project started at the end of last year and will be finished in the middle of 2009.

IEC 26

Alkyl and aryl substituted polylactides

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Polylactides have become important thermoplastic material for applications ranging from fibers to packaging materials. The L-lactic acid used to prepare polylactide is derived from corn. We have been interested in exploring other sources of α -hydroxy acids that would lead to renewable materials that have physical properties different from polylactides. In particular, we have prepared a family of alkyl-substituted polylactides that ultimately can be obtained from saturated fatty acids. These polymers have a comb-like structure and low glass transition temperatures. Interestingly, the long alkyl chains induce side chain crystallization with melting points near room temperature, suggesting potential applications as breathable packaging materials. Another class of monomers has an aromatic or saturated cycloalkyl ring as a part of their structure. Their polymers resemble polystyrene, both in terms of their chemical structure, glass transition temperatures, and their mechanical properties.

IEC 27

Polylactides derived from oleic acid and furfural

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The diversity of physical properties that can be obtained from polylactides can be broadened by developing new monomers from renewable resources. We recently synthesized two new lactide monomers that provide polylactides with additional chemical functionality and properties. Benzyloctylglycolide, an AB glycolide monomer that places a benzyl protected primary alcohol eight methylene units from the polymer backbone was synthesized from oleic acid. Copolymerization of the AB monomer yielded high molecular weight polymers with low polydispersities. Quantitative de-protection of the alcohol followed initiation of lactide polymerization from the primary alcohols provided branched polylactides with excellent control over the polymer architecture. We also synthesized a lactide monomer derived from furfural that provides a polylactide analog where the pendent methyl group of polylactide is replaced with a tetrahydrofuran ring. Compared to polylactide, incorporation of the THF ring increases the glass transition temperature and increases its hydrophilicity.

IEC 28

Low cost, highly reactive biopolyols for the urethane industry: A coproduct of the emerging biodiesel economy

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Over several billion pounds of petroleum-derived polyols are consumed in the U.S annually in myriad polyurethane applications such as foams, coatings and adhesives. There is an increasing need and interest in the industry to develop alternate polyols based on renewable resource-based raw materials that offer potential advantages in reduced price volatility and dependence on sustainable source of raw materials with a more favorable environmental foot print compared to current petroleum-derived polyols.

The concept of bio-refinery as part of the emerging bio-based economy to provide alternate fuels and chemical products from biomass is gaining momentum. A good example of this trend is the dramatic increase in the number of bio diesel plants that have been built or planned to be plant in the US and other parts of the world. One of the co-products from biodiesel production is glycerin and according to a recent Department of Energy study, supply of glycerin is expected to increase significantly and be available to the chemical industry at attractive prices.

At Battelle, we have been developing low cost biopolyols with enhanced reactivity of value in typical polyurethane applications by using glycerin and vegetable oils such as soybean oil as feed stocks. In this paper, we will highlight key features of our technology and its potential applications in high performance urethane coatings by comparing and contrasting them against current petroleum polyols and recently introduced soy polyols.

IEC 29

Chemistry and physical properties of melt processed- and solution- cross linked corn zein

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Corn zein was cross linked with glutaraldehyde(GDA) and glacial acetic acid(HAc) as catalyst with the objective to enhance the mechanical properties of poured films which were compared with the physical properties of compression molded tensile bars from melt processed zein with GDA. A reaction mechanism for acid catalyzed GDA cross linking of zein is proposed based on results from IR spectroscopy, DSC and DMA. Insolubility of tensile bars in HAc from either process defined cross linking of zein. Mechanical properties of tensile bars cut from film or compression molded from melt processed zein/GDA yielded similar results when tested for their respective mechanical properties using an Instron Universal Testing Machine. The reacted samples from either process showed increased tensile strength, ductility and stiffness when compared with controls. The reacted samples retained their integrity when tensile bars from either process were subjected to boiling water for 10min or soaked for 24h.

IEC 30

Recent development of biodegradable network polyesters obtained from renewable natural resources

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The current technological interests of chemistry have involved the renewable carbon to supply the world's chemical needs. Renewable and natural resources-based biodegradable polymers are environmentally useful for the establishment of the recycled systems. Recently, we have developed biodegradable polyesters of gluconolactone with citric acid. Both reagents are derived from natural resources. In the last decade, we have also developed novel network polyester and films of glycerol with dicarboxylic acids with various length of methylene units and reported their favorable properties of enzymatic degradability and biodegradability. Furthermore, optically active network polyesters from malic acid has prepared and investigated their biodegradability. In this symposium, we discuss the preparation and biodegradability of these network polyesters for future technological interest.

IEC 31

Gamma-valerolactone: A sustainable liquid for energy and chemicals

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It was recently proposed [1] that gamma-valerolactone (GVL), a naturally occurring chemical in fruits and a frequently used food additive, exhibits the most important characteristics of an ideal sustainable liquid, which can be used for the production of both energy or carbon-based consumer products. GVL is renewable, easy and safe to store and move globally in large quantities, has low melting (-31oC), high boiling (207oC) and open cup flash (96oC) points, and a definitive but acceptable smell for easy recognition of leaks and spills. GVL is miscible with water assisting biodegradation. We have now established that its vapor pressure is remarkably low even at high temperatures. We have also shown by using 18O-labeled water that GVL does not hydrolyze to gamma-hydroxypentanoic acid under neutral conditions. In contrast, after the addition of HCl the rapid incorporation of 18O-isotopes was observed, as expected. GVL does not form measurable amount of peroxides in a glass flask under air in weeks. The preliminary evaluation of GVL as a fuel additive, performed by adding it to 95-octane gasoline, shows very attractive properties, comparable to bio-ethanol. The development of selective catalytic processes for biomass conversion to gamma-valerolactone will be also discussed. Finally, it is important to recognize that the use of a single chemical entity as a sustainable liquid instead of a mixture of compounds could significantly simplify its worldwide monitoring and regulation.

[1] Horváth, I. T. 10th Annual Green Chemistry & Engineering Conference, Washington, DC, July 26-30, 2006, abstract number 27.

IEC 32

Expressing tyrosine-rich peptide genes in poplar: Facilitating lignin removal

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Biotechnology research efforts directed at facilitating lignin removal from lignocellulosic materials have taken one of two approaches: facilitating lignin removal by changing lignin monomer ratios, or via reducing total lignin content. However, altering lignin content or composition can lead to mutations with pleiotropic effects and undesirable phenotypes. Rather than decreasing the total

lignin content or altering monomer ratios, we have taken a novel approach of introducing lignin-peptide cross-links. By replacing a fraction of lignin-lignin linkages with peptide linkages, we hypothesize that plant fitness will not be compromised, but that the introduction of peptide linkages will facilitate the “cracking” of lignin such that the cellulosic components are more easily accessed.

We have generated several hybrid poplar transgenic lines with a high tyrosine-content peptide gene. This transgene was driven by a promoter from a poplar phenylalanine ammonia-lyase gene (PAL2) to facilitate transgene expression in lignifying tissues. Preliminary data indicated that introduction of the tyrosine-rich peptide into hybrid poplar did not change lignin content and morphology in stems. The effects of transgene product on lignin digestibility and wood tensile strength are being evaluated. If this approach is feasible, it will help increase the feed value of lignocellulose for livestock, reduce the use of harsh chemicals for lignin removal in pulp and paper industry, and facilitate production of biofuels.

IEC 33

D-galacturonic acid catabolism in fungi

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D-galacturonic acid is the major component of pectin and consequently an important carbon source for microorganisms living on decaying plant material or for biotechnological processes where cheap raw materials such as sugar beet pulp are used. A bacterial catabolic pathway has been described while a eukaryotic pathway has remained unknown. For *E. coli* a pathway was described consisting of five enzymes converting D-galacturonic acid to pyruvic acid and D-glyceraldehyde-3-phosphate. The enzymes of this pathway are uronate isomerase, NADH-utilizing D-galacturonate reductase, altronate! dehydratase, D-erythro-3-deoxy-D-hexulose-6-phosphate kinase and D-erythro-3-deoxy-D-hexulose-6-phosphate aldolase. We show that a fungal pathway exists that is distinctly different from any previously described pathway. In this pathway D-galacturonic acid is converted to pyruvate and glycerol. The intermediates are L-galactonate, L-threo-3-deoxy-hexulose-6-phosphate and L-glyceraldehyde. The pathway contains four enzymes, NADPH-utilizing D-galacturonate reductase, L-galactonate dehydratase, L-threo-3-deoxy-hexulose-6-phosphate aldolase and a glycerol dehydrogenase that converts L-glyceraldehyde to glycerol in the reverse reaction. All the of the enzymes of this pathway have been cloned, expressed in a heterologous host and their kinetic properties determined. We will present potential biotechnological applications of this novel pathway.

IEC 34

Cellulose nanoparticles: Can they be a value added coproduct to bioethanol

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One approach to lessening the cost of cellulosic ethanol is through the development of value added co-products. In this paper we shall review the current status of cellulose nanocrystals, a potential biodegradable reinforcement particle for use in eco-nanocomposites and demonstrate that these particles are generated as a residual from enzymatic breakdown of cellulose. Problems of interfacing this product into a working biorefinery will be explored as will the potential economic benefits.

IEC 35

Hemicellulose extraction prior to processing wood-strand composite panels

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Currently 41 oriented strandboard (OSB) composite wood plants across the country consume an estimated 2.1 billion tons of wood, annually. Extracting a percentage of the available carbohydrate component from the flakes prior to panel processing could generate value-added chemical feedstock for renewable materials. In this work, various parameters such as temperature, pressure, and time are tested to optimize the extraction of hemicellulose from wood strands prior to panel manufacture. The resulting chemical, physical, and mechanical properties of the flakes correlating to the degree of hemicellulose extraction will be discussed.

IEC 36

New polymeric processes from lignin using integration of steam explosion and carbonization technologies

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Steam exploded lignin or lignocellulosis are self-binding plastics. The carbonization of such plastics in special conditions convert mentioned renewables in carbon materials or wood ceramics. It is possible to obtain in steam explosion conditions not only cellulose nanofibrils but also lignin nanofractals. The cellulose can be used as polymers reinforcement but lignin is useful as a filler. One of advanced perspectives may be application of lignin fragments as a source for dendritic nano structures, e. g., use of lignin as a macromonomer cores for branched dendrimers. Modified lignin can act as medicals and heavy metal ions sorbents too. Some lignans are very active as biological substances. Reference: J. Gravitis Green Biobased Chemistry Platform for Sustainability. Eds W. L. Filho et al. Environmental Education, Communication and Sustainability, Peter Lang, Frankfurt am Main, ..., vol.23, 2006, 145-160.

IEC 37

Deep desulfurization of model oil using surfactant-type decatungstates as catalysts

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A series of surfactant-type decatungstates such as [C₁₆H₃₃N(CH₃)₃]₄W₁₀O₃₂, [C₁₄H₂₉N(CH₃)₃]₄W₁₀O₃₂, [C₁₂H₂₅N(CH₃)₃]₄W₁₀O₃₂, [C₁₀H₂₁N(CH₃)₃]₄W₁₀O₃₂, [(C₄H₉)₄N]₄W₁₀O₃₂ have been synthesized and characterized by IR, UV-Vis, gravimetric determination and TG/DSC. With the above decatungstates as catalysts, we have studied the oxidative desulfurization of dibenzothiophene (DBT) in model gas oil with aqueous 30% hydrogen peroxide. The catalysts also perform as the surfactant, making a promising improvement on the removal of sulfur. In the experiments, n(DBT) : n(H₂O₂) : n(catalyst) = 1 : 10 : 0.01, the results show that the catalytic ability increases with increasing length of the substituted alkane. Of all the decatungstates, [C₁₆H₃₃N(CH₃)₃]₄W₁₀O₃₂ exhibits highest activity. After the reaction with [C₁₆H₃₃N(CH₃)₃]₄W₁₀O₃₂ at 70°C for 3h, the sulfur content was reduced from 1000 ppm to 14 ppm, reaching a sulfur removal of 98.6%.

IEC 38

Oxidative desulfurization of fuels catalyzed by peroxotungsten complexes in ionic liquids

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Peroxotungsten and peroxomolybdenum complexes such as $[\text{WO}(\text{O}_2)_2 \cdot \text{Phen} \cdot \text{H}_2\text{O}]$ and $[\text{MoO}(\text{O}_2)_2 \cdot \text{Phen}]$ (Phen: 1, 10-phenanthroline monohydrate) have been synthesized and characterized. Catalytic oxidation of dibenzothiophene (DBT) remaining in n-octane with H_2O_2 in 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}]\text{BF}_4$) and 1-n-octyl-3-methylimidazolium tetrafluoroborate ($[\text{Omim}]\text{BF}_4$) has been investigated. When $[\text{Bmim}]\text{BF}_4$ only was used as an extractant for DBT-containing model oil, a sulfur removal of 16.5% was obtained. After addition of 30wt. % H_2O_2 in $[\text{Bmim}]\text{BF}_4$, a sulfur removal of 30% was given via chemical oxidation. When catalyst, H_2O_2 and $[\text{Bmim}]\text{BF}_4$ were employed together, the sulfur removal increased sharply. In the case of the $\text{H}_2\text{O}_2/\text{WO}(\text{O}_2)_2 \cdot \text{Phen} \cdot \text{H}_2\text{O}/[\text{Bmim}]\text{BF}_4$ system, extraction and catalytic oxidation decreased the S-content from 1000 ppm to 14 ppm, reaching a sulfur removal of 98.6%. However, the oxidative desulfurization system containing $\text{WO}(\text{O}_2)_2 \cdot \text{Phen} \cdot \text{H}_2\text{O}$ and H_2O_2 only led to a sulfur removal of 50.3% in the absence of IL. The experiments demonstrated that a combination of catalytic oxidation and extraction in IL can deeply remove DBT from model oil. This result also indicated the remarkable advantage of this process over the desulfurization of model oil by mere solvent extraction with IL or mere catalytic oxidation without ionic liquids.

IEC 39

Extending secondary nucleation models to the crystallization of polymorphic systems

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A large number of substances, including high-value added pharmaceutical products, crystallize in more than one distinct crystal structure. These structures termed polymorphs, display different physical properties (solubility, dissolution rate, crystal form, density, compressibility, etc.) and consequently pharmacological activities. Regulatory pressure for the development of consistent production processes, dictates the need for a better understanding of all the

crystallization steps involved in the process. Primary nucleation has been appreciably clarified since Ostwald advanced his “Rule of Stages” more than a hundred years ago, which stated that the stable morph has the lowest solubility and yet the form of higher solubility nucleates spontaneously first. Various works have showed that this rule does not apply to all systems and why it does not. The picture, however, is not as clear for the case of Secondary Nucleation. This work will attempt to clarify it. The work involves two stages: an experimental and a modeling one. The experimental part utilizes the polymorphic L-glutamic acid, which has two morphs: the stable beta morph and the unstable alpha morph. Solutions of L-glutamic acid were prepared at different supersaturations. These solutions were not nucleating spontaneously. However, when seeds were introduced secondary nucleation was observed. The morphicity of the resulting new crystals was determined and was compared with that of the seed. The results were sometimes unexpected. The objective of the modeling part is to explain those results. The current models of secondary nucleation, i.e. Contact Secondary Nucleation (CSN) and Embryos Coagulation Secondary Nucleation (ECSN), which have been developed for single systems, were extended to supersaturated solutions of polymorphic systems. Independent embryo size distributions for each morph in a polymorphic system were identified. As the supersaturation increases, the distributions of embryos of the different morphs shift, affecting thus the outcome of the secondary nucleation.

IEC 40

Rapid determination of lignin content in lignocellulosic biomass through the use of ionic liquids

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Bio-fuels produced from lignocellulosic feedstocks are gaining interest as an alternative to traditional petroleum based fuels. Initial compositional analyses of these feedstocks are essential for assessing their potential value. The currently employed protocol for determining the composition of lignocellulosics, i.e., the weight fraction of glucan, xylan, lignin, ash, and other components, is tedious. Ionic liquids (ILs), due to their ability to solubilize many of the components of biomass, are being explored in our laboratories as a vehicle to improve simplicity and safety for the chemical analysis. This presentation describes the successful determination of lignin in biomass solubilized in ILs via UV-visible and FTIR spectroscopies. The analysis focused upon three sources of lignin solubilized in 1-Butyl-3-methylimidazolium chloride, or [Bmim][Cl] at ~0.22 w/w. Acetonitrile has served as a dilution agent for the UV-Visible spectroscopic approach.

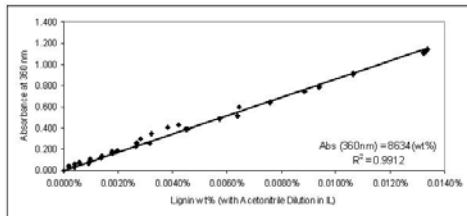


Figure 1. UV-VIS analysis of hydrolytic lignin solubilized in IL (0-0.22 wt%) with acetonitrile dilution

IEC 41

Pyrolysis characteristics and kinetics of pine trees

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Pine trees are one of the renewable resources in Korea, which can be converted to bio-oil, gas and char through pyrolysis. In this research, pyrolysis characteristics of pine trees were investigated using thermogravimetric analysis (TGA) at heating rates of 5~20°C/min. Most of the materials were decomposed at the temperature range from 330°C to 370°C depending on the heating rate. Apparent activation energies increased from 145 kJ/mol to 302 kJ/mol, respectively, when the pyrolytic conversion increased from 5% to 95%. The kinetics of pine trees have been studied experimentally and mathematically. Experiments were carried out in a tubing reactor at a temperature of 330 ~ 370°C and reaction times of 2 ~ 10 minutes. A lump model of combined series and parallel reactions for bio-oil and gas formation was proposed. Conversion data fitted first order kinetics for gas, bio-oil and pine (char). The kinetic parameters were determined by nonlinear least-square regression of the experimental data. It was found from the reaction kinetic constants that the predominant reaction pathway was A (pine) to gas (C1 ~ C4) formation rather than A to bio-oil formation at a temperature of 330~370°C.

IEC 42

Bioethanol analysis of the mixture of gasoline and ethanol using low-level liquid scintillation counter

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Alternative fuels to petroleum derived fuel are being sought in order to reduce the world's dependence on fossil fuel in the view of sustainable resources. Ministry of Commerce, Industry and Energy in Korea has a plan to introduce bio-ethanol as a transportation fuel in the range of E3, E5 and/or E10. The TAX of gasoline is 257%, while those of solvents such as syn-ethanol and methanol are very low compared to gasoline. Therefore, the development of analysis methods for bio-ethanol is an urgent issue to protect illegal circulation in the transport market. Low-level liquid scintillation counter (LSC) can analyze carbon isotope (C14) within biomass derived organics. E0 (sub-octane gasoline), E5 and E10 were analyzed by LSC at the energy channel of 50 and 650, and peak intensity was increased with increasing bio-ethanol. CPM value of E0, E5 and E10 were 1.51, 3.21 and 5.04, respectively.

IEC 43

Catalytic decarboxylation of naphthenic acid with metal oxide catalyst

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Naphthenic acid is a complex of carboxylic acids (various low-molecular-weight fatty acids believed to have cyclopentane ring mainly) present in acid crude oils. They often cause serious problems such as pipeline corrosion in processing crude oils. As oil price has rapidly increased recently, utilization of acid crude oil has become rather active across the world. Thus, finding an economic way to reduce naphthenic acids from crude oil turned out to be very important for oil refinery industries to make the cost balanced. Among the technologies, catalytic decarboxylation of naphthenic acids seems promising and may provide a solution for that purpose. It has been reported that various metal oxides are active toward the decarboxylation. However, their reaction kinetics and long term stability have not been reported in the literature. In this study, activities of alkaline earth metal oxides, prepared in various ways, and their long term stabilities were compared and the possible causes of the deactivation of the catalysts were investigated using surface characterization.

IEC 44

Biofuel production from corn residues by thermochemical conversion

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Declining fossil oil reserves, skyrocketing prices, unsecured supplies, and environmental pollution are among the many energy problems we are facing today. It is our conviction that renewable energy is a solution to these problems. The objective of this research is to study and develop thermochemical processes for converting bulky and low-energy-density biomass materials into biofuels and value-added bio-products. In our study, a Parr high-pressure-reactor was used for the hydrothermal process. Supercritical water condition was created at high pressure (374C, 22.1MPa). Corn residue was used as a model feedstock. Process variables to be studied include temperature, time, catalysts, solid loading, gas composition, and liquid composition. The products from the supercritical water assisted reactions consist of three phases: water soluble phase, heavy oil phase and gaseous phase. The yields and chemical properties of individual phases were also determined. On the other hand, a novel pyrolytic process for the recovery of fuel gas and liquid from agricultural wastes was developed. This new process is an environmental-friendly technique in which energy transfer to the waste occurs by microwave radiation; it has shown several advantages over conventional pyrolytic processes and represents a new opportunity to use pyrolysis to treat solid wastes as it overcomes the major difficulties that arise from other alternative methods.

IEC 45

Liquefaction of corn components: Heat transfer and process

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The corn components, corn stalk, corn leaf, corn cob, corn stover, and corn stover pellet, were liquefied in a batch pressure vessel equipped with an induction heating system, which allows the reduction of heat-up times by about two orders of magnitude. Various corn components show different densities, but similar compositions, and do not seem to affect the yield and composition of bio-crude oils. The direct conversion of corn stover pre-treated with dilute acid and lignin extracted from corn stover, were also studied to evaluate suitability as the raw material for producing bio-crude oil. Liquefaction process of corn stover was optimized using the following treatment variables: heating rate (5-140°C /min), cooling rate (4-80°C /min), reaction temperature (300-450 °C, corresponding to a pressure range of 3000-5000 PSI), reaction time (1-30 min), particle sizes, and catalysts. The yields of bio-crude oil were found to depend on heating rate, final liquefaction temperature, the length of reaction time. The major compounds from

biomass liquefaction were identified by GC-MS. The mechanism of liquefaction reactions was proposed.

IEC 46

Multifunctional epoxy resin/metal oxide nanocompositions for electronics applications

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It is known that differences between the coefficients of thermal expansion (CTE) of circuit boards and dies contribute to early fatigue failure of solder interconnects. In flip-chip packaging, the CTE mismatch is mitigated by the use of underfill which is a highly filled epoxy resin system. Micro-scale filler particles used traditionally in adhesive compositions have been effective in providing the desirable low CTE underfills for electronic packaging. However, high concentration of large filler particles in these underfills is problematic. Nano-scale filler particles can produce similar large improvement in properties yet at much lower concentrations primarily because of their large surface to volume ratio. We report here on epoxy resin nanocompositions that have exceptional thermal and mechanical properties as well as excellent processing characteristics. They are partly based on multifunctional low viscosity epoxy resins containing functionalized nanoparticles of Boehmite or silica. We will show that nano-scale particles are key to the development of these properties.

IEC 47

Investigation of ionic liquids based on diphenyl phosphate

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Ionic liquids are salts that have melting points below 100 °C and in general exhibit little vapor pressure, are non-flammable, thermally stable and can exhibit high conductivities. We have developed a new series of ionic liquids based on the diphenyl phosphate anion. The goal of this study was to develop ionic liquids which are more hydrophobic, than those ionic liquids we have previously

developed and continue to investigate, based on the phosphate anion. Cation types include those based on 1-methyl imidazole, 1-methylpyrrolidine, 4-dimethylaminopyridine (DMAP) and pyridine. Preliminary results indicate that in comparison to phosphate ionic liquids, these salts have lower melting points and are not as hydrophilic. We report here on the synthesis and physical properties of these new materials. This work was supported in part at BNL by the U. S. DOE Office of Basic Energy Sciences under contract # DE-AC02-98CH10886.

IEC 48

Mass culture of microalgae on wastewater and gases from sludge burning for production of biomass feedstock for biodiesel

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Sustainability is an essential aspect of biobased economy. The development of biofuels, an important component of biobased economy, must conform to sustainable behaviours. The work is centered on development of a new biofuel strategy, in which production of high oil content microalgae for biodiesel fuel is coupled with wastewater treatment and flue gas emission control, and thus provides significant environmental benefits and improves the economic feasibility. The work addresses the two priority areas defined “Development of new biofuel resources or technologies” and “Biofuels, the environment, and the economy”, and will involve expertise in multiple areas including algae production, biology, waste treatment, water quality, engineering, biomass processing, and biofuel production. Management of wastewater and associated gaseous emission is very costly and technically challenging. With increasingly stringent regulations and limits on wastewater discharge and gaseous emission, modification of current conventional processes must be made to meet these new limits. These process modifications will require substantial capital investment and would also likely substantially increase operating costs. The present proposed project takes a creative approach in which microalgae is grown on nutrients supplied from wastewater and gaseous emission from wastewater treatment plants, harvested and extracted for oil that is converted to biodiesel fuel. This would create a win-win situation where water and air conditions are preserved while renewable energy is generated. Furthermore, savings/credits from the wastewater and emission treatments will significantly improve the economic feasibility of microalgal biodiesel.

IEC 49

Microwave assisted heterogeneous catalysis with manganese octahedral molecular sieves

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Microwave heating has recently emerged in heterogeneous catalytic reactions by reducing the reaction time, enhanced conversion, and selectivity. Many Octahedral Molecular Sieve (OMS) catalyzed reactions have been reported in our lab which involve conventional heating. Some of the reactions had required longer reaction times. Herein, we report the use of microwave heating as an alternative to conventional heating for OMS catalyzed reactions. The conversions and selectivities obtained via microwave and conventional heating are compared. In addition, scale –up of these reactions will be explored.

IEC 50

Microwave pyrolysis of corn stover: Process development and reaction kinetics

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The present study was to investigate the microwave-assisted pyrolysis of corn stoves in nitrogen gas environment. The yields of syngas, bio-oils, and solid residue obtained at different input power were determined. Under our experimental conditions, a power input level above 300 W was necessary to initiate thermal pyrolysis of corn stover. The degradation of solid corn stover increased with increasing microwave power. A higher power input also favored syngas production. Adding 1% pyrolytic residue to the corn stover pyrolysis increased the yields, particularly the liquid fraction yield. Addition of sodium hydroxide (NaOH) to the corn stover as catalyst increased the syngas yield greatly. The chemical profiles of the syngas and bio-oils were determined using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). A thermogravimetric analysis (TGA) including determination of kinetic parameters was performed over the temperature range of 373-1073 K at controlled heating rates of 10 - 30 K/min and with various particle sizes. Under the conditions studied, the heating rate has a significant effect on the pyrolysis process while the particle size has little effect on it. One-step global model was developed to simulate this pyrolysis of corn stover and to determine the kinetic parameters. Although various chemicals were released during pyrolysis, one-

step global kinetic is looked to as offering a clue to the key mechanistic steps in the overall degradation process.

IEC 51

Removal of ammonium from New York City rejection water using a nitritation/Anammox process

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The removal of ammonium-nitrogen (NH₄-N) from wastewater is of great importance to reduce the nitrogen loading to receiving water bodies. Liquid streams (rejection water) generated by the dewatering of anaerobically-digested sludges in New York City wastewater treatment plants contain ammonium-nitrogen in the range of 400mg/L – 1000 mg/L and can contribute a significant ammonium load to the wastewater plant. A biological process utilizing bacteria capable of the Anaerobic Ammonium Oxidation (ANAMMOX) reaction has proven to be capable of removing high levels of NH₄-N from rejection water to acceptable levels. In the ANAMMOX reaction, ammonium and nitrite are converted to NO₃⁻ and N₂ gas. In the treatment process, the ANAMMOX bacteria are coupled with aerobic ammonium-oxidizing bacteria (nitritation) in a sequencing batch reactor operated with pH-controlled intermittent aeration. During the aerated phase of the reaction cycle, a low dissolved oxygen concentration is maintained to only partially convert ammonium to nitrite and to restrict nitrite oxidation to nitrate. In the subsequent anoxic portion of the reaction cycle, the ANAMMOX bacteria perform the reaction shown above. Coupling nitritation and the ANAMMOX reaction reduces the oxygen requirements compared to a conventional biological nitrification process, which leads to lower energy demand and reduced operating costs. Since the ANAMMOX bacteria do not require an organic substrate as an electron donor, the nitritation/ANAMMOX process further reduces operating costs by eliminating the need for an external organic carbon source. This poster presents results of a 2000-gallon pilot reactor study in which the nitritation/ANAMMOX process was used to remove ammonium from rejection water generated at the NYC 26th Ward wastewater treatment facility.

IEC 52

Assessing As, Hg and Se speciation and transport in flue gas desulphurization material and drywall

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The risk associated with the reuse of flue gas desulphurization (FGD) material in drywall manufacture is largely determined by the distribution or mineralogical fractionation of mercury (Hg), arsenic (As) and selenium (Se). During coal combustion, FGD material is enriched in volatile Hg, Se and As, which are known to be potent neurotoxins. With the replacement of natural gypsum with FGD for wallboard manufacture, exposure to workers can occur via soluble metal release or its volatilization (especially for Hg). Thus, the speciation or form of trace metal present is the most critical factor to whether exposure will cause disease in fish, animals or humans.

In this paper, we report the chemical characteristics and speciation of As, Se and Hg in FGD (dry) and drywall material. We also attempt to assess the potential groundwater (leaching) metal release from FGD and drywall products. Trace metal speciation was determined via sequential chemical extraction techniques and the findings complimented with X-ray Absorption Spectroscopy (EXAFS). The data indicated that As, Se and Hg in FGD and drywall material appeared to be mostly associated with the iron oxide matrix. Less than 1 % of the total As and Se content was water soluble. Association of As, Se and Hg with sparingly or acid soluble oxide fractions provided better environmental stability. Based on EXAFS data, Hg speciation can be characterized as Hg (I) in a high Fe matrix; perhaps a direct association with Fe oxides or an Hg-C-Fe oxide ligand bridge. However, possible concentration of the metals via water separation in an easily mobile lighter fraction can result in serious environmental contamination of natural settings.

IEC 53

Application of Nickel/Kieselguhr catalysts to C9-aldehyde hydrogenation in trickle bed reactor

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The objective of the present study was to select the optimal catalyst and operating conditions for the manufacture of C9-alcohol, using C9-aldehyde and

hydrogen, in a trickle bed reactor. When CaO, Ce₂O₃ or MgO was added as a promoter to the Ni/kieselguhr catalyst, the BET and Ni surface areas were increased. In the reaction for the manufacture of C₉-alcohol, using C₉-aldehyde and hydrogen in a batch reactor, a Ni-MgO/kieselguhr catalyst showed the highest activity. In addition, the catalyst using Na₂CO₃ as a precipitant showed the highest activity. According to the result of an experiment to find the optimal reaction conditions for C₉-alcohol synthesis, using C₉-aldehyde and hydrogen in a trickle bed reactor loaded with Ni-MgO/kieselguhr catalyst, the highest yield of C₉-alcohol was 91.5 wt% at 130°C, 400 psi and WHSV = 3. The C₉-aldehyde hydrogenation performance of the Ni-MgO/kieselguhr catalyst was similar to that of a Cu/ZnO/Al₂O₃ catalyst, but superior to that of Cu-Ni-Cr-Na/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts. In a long-term catalysis test, the Ni-MgO/kieselguhr catalyst showed higher stability than the Cu/ZnO/Al₂O₃ catalyst.

IEC 54

Conversion of chlorinated hydrocarbon over mesoporous catalysts

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Dioxins, known as persistent organic pollutants (POP), are mainly by-products of industrial processes. In terms of dioxin release into the environment, solid waste incinerators are the worst culprits due to incomplete combustion. Well known examples are the highly toxic polychlorinated dioxins (PCDDs) and dibenzofuranes (PCDFs) formed in municipal incinerators. Significant efforts have been made in order to reduce POP emissions (especially of chlorinated compounds) at the international level, which were translated in a series of protocols signed within the framework of several international conventions. Such materials have been considered to be human carcinogens for decades. Previous works were conducted to decompose chlorinated compounds by various methods, such as catalytic oxidation, catalytic hydro-dechlorination, UV irradiation, ozonation, pyrolysis, and electron beam treatment. Among them, catalytic oxidation is one of the most promising technologies for the removal of organic compounds from waste gas. Metal oxides or supported noble metals (platinum and palladium) are the most investigated catalysts for the destruction of organic pollutants. Performances of Pt/Al₂O₃ catalysts for chlorobenzene oxidation have been widely investigated. Also, zeolites have been considered as effective alternative catalyst to noble metal and metal oxide catalysts used in most commercial applications for air pollution control. However mesoporous

materials has not been investigated for 1,2-dichlorobenzene decomposition. In this study, the catalytic activities of Pt/mesoporous catalysts such as Pt/Al-MCM-41, Pt/Al-MCM-48, Pt/Al-SBA-15 were compared with Pt/fx-Al₂O₃. The catalytic activity of Pt/Al-MCM-41 is higher than that of Pt/fx-Al₂O₃. As Si/Al ratio increases, the catalytic activity increased. This implies that acidity is very important factor for oxidation of 1,2-dichlorobenzene. Catalytic activities of Pt/Al-MCM-48, Pt/Al-SBA-15 are also presented. This work was supported by the grant number (R01-2006-000-10786-0) from the basic research program of the Korea Science and Engineering Foundation.

IEC 55

Recovery of lactic acid from model fermentation broth using thermostable amine adsorbents

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Recovery of lactic acid using reversible chemical complexation with solid adsorbents has been found to be a promising alternative to the conventional precipitation process by calcium salts. The use of adsorbents could reduce chemical consumptions substantially and offer the high contacting area for extraction. Polymeric anionic resins are generally used for this purpose, but organic solvent or strong basic agents are necessary for back extraction of lactic acid from these adsorbents. Therefore, the recovery process involves multiple steps including leaching of lactic acid from the acid-adsorbent complex, regeneration of adsorbents; and purification of lactic acid from organic solution or acidification of carboxylate salt solution. To address this problem, an active carbon-based adsorbent has been synthesized and applied to adsorption/desorption system in aqueous lactic acid solution in this study. Adsorbent having amine functional group was prepared simply by surface modification reaction on activated carbon. Adsorption behavior of lactic acid into the adsorbent was similar to that using polymeric adsorbents. On the other hand, since the adsorbent synthesized are based on thermostable active carbon, lactic acid-adsorbent complex could be thermally decomposed easily, thus allowing reduction of process steps.

IEC 56

Adsorption of sulfur compounds in light cycle oil on activated carbon and multicomponent metal oxide

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As the environmental regulation imposed by government has tightened, demand on clean fuel has increased gradually. Light cycle oil (LCO) is a complex combination of hydrocarbons produced by the distillation of products from the fluidized catalytic cracking process with carbon numbers in the range C9 to C25. Previously, LCO was used as bunker fuel because it contained high concentration of sulfur and aromatic compounds. However, bunker fuel market is expected to be shrunken rapidly due to the environmental regulation. Thus, LCO must be converted to clean fuel or chemical feed stock. Thus, desulfurization is a mandatory process for LCO treatment. In this study, sulfur compounds were selectively removed from LCO using a series of activated carbons and multi-component metal oxides as adsorbents. When a series of activated carbons were used as adsorbents, surface area, surface properties of activated carbon and concentration of aromatic compounds in LCO were closely related with the sulfur adsorption capacity. When multi-component metal oxides, which contained zinc oxide, ferrite, cerium oxide and nickel oxide, were applied as adsorbents, the composition of metal oxides and adsorption temperature affected the sulfur adsorption capacities.

IEC 57

Study on carbon dioxide absorption into ammonia water using high-efficiency packed column

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As a post-combustion carbon dioxide separation and recovery process, absorption has been investigated by many researchers over the world. Successive operation process can be achieved by using effective absorption solvents. Currently, the most commonly used solvents are alkanolamines. However, alkanolamines still have many unresolved problems, such as expensive material price, absorbent degradation by oxygen and sulfur compounds in gas phase, and high regeneration energy required. Thus, various absorption solvents have been developed to provide economic and stable carbon

dioxide separation and recovery process. Among the solvents, recently, ammonia water was proposed as the most effective and economic solvent for carbon dioxide separation and recovery process because of its low material cost and energy requirement for regeneration, and high reactivity with carbon dioxide. However, little information about its reaction characteristics with carbon dioxide is available so far. In this study, carbon dioxide absorption into aqueous ammonia solution was investigated with an absorption column packed with structured packings. Overall mass transfer coefficient was obtained from the absorption tests at different gas and liquid flow rates using ammonia water with various carbon dioxide loadings. Concentrations of carbon dioxide in gas phase and temperatures at several points along the absorption tower were collected and used for interpreting mass transfer performance of carbon dioxide into ammonia water.

IEC 58

Decolorization of crude polysaccharides from *Cyclocarya paliurus* (Batal.) Iljinsk by ultrasound/H₂O₂ process

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An advanced oxidation process, ultrasound/H₂O₂ oxidation was used for the decolorization of crude polysaccharides from *Cyclocarya paliurus* (Batal.) Iljinsk. The decolorization efficiency is strongly dependent on concentration of initial crude polysaccharide solution, dosages of hydrogen peroxide, temperature, pH value of solution and ultrasonic irradiation. The effects of these operating parameters on decolorization of the crude polysaccharides have been evaluated and the optimum operational conditions of the process were studied. FTIR spectra method was used for the analysis of change in the macromolecular structure of polysaccharides. The results showed that ultrasound/H₂O₂ oxidation process represented good decolorizing ability on decolorization of crude polysaccharides. The optimum operational conditions for decolorization were determined as follows: concentrations of the polysaccharide solution: 0.5mg/mL, H₂O₂: 0.623mmol/L, T=40°C, pH=9.0 with a constant ultrasound of 40 kHz and at sonic power of 100 W. Under these conditions, the results were obtained with a decolorization rate of 84.0% and a polysaccharides holding rate of 80.9%. The FTIR spectra indicated that ultrasound/H₂O₂ oxidation process did not result in any significant change in the macromolecular structure of polysaccharides. Supported financially by Program for Changjiang Scholars and Innovative Research Team in University (No: IRT0540).

IEC 59

Deep desulfurization of oil by extraction with ionic liquids

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Recently, deep desulfurization of gasoline and diesel oil has attracted much attention, due to the increasing demand of lower S-content diesel oil and gasoline, because sulfur-containing compounds are a source of SO_x. Current hydrodesulfurization (HDS) process, however, has a limitation in removing S-compounds such as DBT and 4,6-dimethyl-dibenzothiophene. In this regard, extraction of S-compounds from oil by ionic liquids (ILs) could be a promising alternative to conventional HDS. Sulfur-containing compounds which are hard to remove by HDS have been successfully removed under mild condition using various imidazolium-based ionic liquids.

IEC 60

Oxidative carbonylation of aniline with polymer-immobilized alkylselenites

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Polymer-immobilized selenites, poly(1-ethyl-3-vinylimidazolium) methylselenite and poly(1-ethyl-4-vinylpyridinium) methylselenite were synthesized and tested for their activities in the oxidative carbonylation of aniline. FT-IR (NMR) and DSC studies clearly showed that methylselenites are tightly immobilized on the imidazolium and pyridinium polymers. These polymer-supported heterogeneous catalysts exhibited comparable activities to their corresponding homogeneous analogues, 1-ethyl-3-vinylimidazolium methylselenite and 4-vinylpyridinium methylselenite. The catalyst recycle tests showed that the immobilized catalysts can be reused at least up to five times without serious deactivation.

IEC 61

Polymerized room temperature ionic liquids as gas separation membranes

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Room temperature ionic liquids (RTILs) possess many desirable properties for CO₂ separation and capture. The versatile chemistry of imidazolium-based RTILs allows for the design of tailored polymers, which may be implemented as solid, poly(RTIL) gas separation membranes. Poly(RTIL) monomers can be configured in a number of ways. Novel single and "gemini" (tethered cations) type systems have been studied for their performance relating to CO₂ separations involving H₂, N₂ and CH₄. The substituents on the cation play an important role in determining the permeability and selectivity of the polymer films. For example, a polymer from a single cation monomer with a methyl group substituent exhibits CO₂ permeability of ~7 Barrers with CO₂/N₂ = 31 and CO₂/CH₄ = 40. An analogous polymer with a hexyl group substituent shows CO₂ permeability of 28 Barrers with CO₂/N₂ = 28 and CO₂/CH₄ = 16. CO₂ flux can be improved by tailoring the cation with little sacrifice to CO₂/N₂ selectivity. On the other hand, "gemini" systems exhibit almost barrier-like behavior to light gases, with permeabilities of N₂ and CH₄ << 1 Barrer, but with lower separation factors for CO₂/N₂ and CO₂/CH₄ than observed in single cation polymers. The inclusion of polar substituents such as oligo(ethylene glycol) units on the imidazolium cation serves to enhance separation selectivity with similar CO₂ permeability. Synthetic methods, characterization and structure-property relationships for gas separations in these novel polymers will be discussed.

IEC 62

Preparation of polyurethane foam from microwave pyrolytic bio-oils

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Currently biooils from thermochemical conversion of biomass are mainly used as fuels. The goal of the present research is to use biooils as feedstock for making biomaterials, and therefore to contribute to the expansion of the biooil market. Our specific research objective was to evaluate the feasibility of preparing polyurethane foam from biooils made from microwave pyrolysis, a novel thermochemical conversion process being developed in our lab. Biooils obtained under different microwave pyrolysis conditions were used in the experiments. The underlying principle of preparing polyurethane foam is to crosslink the hydroxyl groups in biooils with the isocyanate group. The number of hydroxyl

groups in the biooils was analyzed, which was used to calculate how much crosslinking agents were needed for complete reactions. The crosslinking agents used were MDI, TDI, PPI and other commercial available isocyanate such as Papi 27 and Isocyanate 181. The tensile strength, the elongation, stability and biodegradability of the prepared polyurethane foam are being analyzed. The effects of microwave pyrolysis and crosslinking conditions on the properties of the polyurethane foam are also evaluated.

IEC 63

Separation of olefin/paraffin mixtures using multifunctional zwitterionic compounds as carriers

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Various types of multi-functional zwitterionic compounds containing both an ester and a sulfonate group were prepared and their silver nitrate salts were tested as carriers for facilitated olefin transport membranes in the separation of ethylene/ethane and propylene/propane mixtures. Ester group-containing multi-functional zwitterionic silver compounds exhibited much higher performances in comparison with methyl group-containing zwitterionic compounds. FT-IR study showed that ester-containing zwitterionic compounds interact with silver ions through both sulfonate and ester functional groups.

IEC 64

Comparison of microwave-assisted extraction and conventional extraction of polysaccharides from *Ganoderma atrum*

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A new method of microwave-assisted extraction (MAE) was evaluated for the extraction of polysaccharides from fruiting bodies of *Ganoderma atrum*, which have been reported to have medicinal bioactivity. The extracts were directly determined by phenol sulfuric colorimetric method without any further treatment. In the first stage of the microwave extraction process optimization, the single factor experiments as the preliminary trials were performed to evaluate the

effects of many related factors on polysaccharides extraction, including irradiation time, temperature, extraction times and ratio of solvent to material. It was found that irradiation time, temperature and ratio of solvent to material significantly affected the extraction of polysaccharides. Subsequently, a uniform experiment design was applied and validated by parallel tests to analyze influences of factors and to further optimize extraction technology. Optimal conditions of MAE of polysaccharides from *Ganoderma atrum* can be concluded as follows: 5 min at 135°C, the ratio of solvent to material of 35:1, purified water as the solvent, extraction stages of 2. Experiments on different extraction techniques were also conducted. The results show that MAE method demonstrates several advantages, such as higher extraction yield, less extraction time, lower energy consumption and higher purity of extracts, compared with other extraction techniques including heat reflux, ultrasonic, and enzyme hydrolysis-reflux extraction. The time used in MAE is only 15 min with 6.64% extraction rate, while heat reflux and enzyme hydrolysis-reflux extraction need several hours with only about 2.04% and 3.75% extraction rate respectively. Ultrasonic extraction gives the lightest color of extractive but lowest extraction rate. (Supported financially by the Program for Changjiang Scholars and Innovative Research Team in University (No: IRT0540) and Jiangxi Provincial Department of Science and Technology).

IEC 65

MBR for treatment of wastewater from olefins and polyolefins processes

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Feasibility study on treatment of wastewater from olefins and polyolefins processes has been conducted using a bench scale submerged membrane bioreactor (MBR). An anoxic/aerobic concept and flat sheet MF membranes were used in the study. The MBR system was operated continuously (24-hour) under different membrane fluxes over two months. Effects of hydraulic retention time (HRT) and aeration on nitrification were investigated. The results showed that a membrane flux of 12.5 L m⁻² h⁻¹ (LMH) was sustainable and HRT of 13 hrs was applicable. Membrane permeability could be fully recovered after chemical cleaning. The effluent quality consistently met the requirement for discharge while segregation of the streams with high TDS was required to reclaim the water for reuse. In addition, there was no observation of foaming in the process. It was concluded that it was feasible to treat the wastewater using submerged MBR technology.

IEC 66

Pilot studies for reclamation of municipal used water: Comparison of MBR-RO and ASP-MF-RO process

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The membrane bioreactor (MBR) is a combination of activated sludge process (ASP) and membrane separation. MBR has advantages of small foot-print, producing consistently high quality of effluent and less sludge disposal, etc. The objective of the pilot studies was to compare a new MBR-RO process to ASP-MF-RO process for reclamation of municipal used water. The pilot results showed that the new MBR-RO process demonstrated the capability of producing the same or more consistent product quality (in terms of TOC, NH₄ and NO₃) compared to the conventional ASP-MF-RO process in reclamation of domestic sewage. RO membranes in the MBR-RO process could be operated at 22 Lm⁻²h⁻¹ without CIP during the whole study period of five months, which was 30% higher than that (17 Lm⁻²h⁻¹) in the ASP-UF-RO process. It was concluded that the MBR-RO process could be a better option for production of high grade water from municipal used water.

IEC 67

Scale-up process study for aniline bisphosphonates: EBP

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Bisphosphonates have found significant use in pharmaceutical industry as well as in ion sequestering and detergent applications. Blockbuster osteoporosis drug, sodium alendronate, is currently commercialized by several pharmaceutical companies. Cabot is interested in making aniline derivatized bisphosphonates for its applications. Herein we present scale-up process study of one particular molecule, EBP, 2-(4-aminophenyl)-1-hydroxyethylidene-1,1-bisphosphonic acid, mono sodium salt. The synthesis of EBP involves the reaction of 4-aminophenylacetic acid (APAA) with phosphorous trichloride (PCl₃) and phosphorous acid in the presence of methane sulfonic acid (MSA). This is followed by hydrolysis and subsequent precipitation of EBP at a pH of around 4.3. A 12 factor, 22 experiment, screening design of experiments (DOE) was

performed by varying the concentrations of all the starting chemicals, additional water, temperatures, times at various stages of the reaction, and hydrolysis conditions. Results from screening DOE showed that increasing amounts of all the reactants relative to APAA, adding PCl_3 at a slower rate, reacting at higher temperature and reducing water of hydrolysis increased yield of EBP. The reaction hold times could be reduced from 16 to 8 hours without impacting yield. Yields could be increased from about 27% to 65% and results validated. Characterization and level reduction of major impurities from the reaction are also discussed.

IEC 68

Scale-up process study for aniline bisphosphonates: EDP

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Bisphosphonates have found significant use in pharmaceutical industry as well in ion sequestering and detergent applications. Blockbuster osteoporosis drug, sodium alendronate, is currently commercialized by several pharmaceutical companies. Cabot is interested in making aniline derivatized bisphosphonates for its applications. For carbon black and color pigments, surface modification with various bisphosphonates has lead to new generation pigment based inks with significantly better optical density, color saturation and other properties. Herein we present scale-up process study of one particular molecule, EDP, 2-(4-aminophenyl)-ethylidene-1,1-diphosphonic acid, mono sodium salt. Previous literature procedure (Benedicts et al, US patent 4830847) for the preparation of EDP has been found not suitable for large-scale production. We have come up with more improved and reliable synthesis. The synthesis of EDP involves several steps starting from tetraalkylmethylenediphosphonate (MDP). Coupling MDP with 4-nitrobenzaldehyde in the presence of TiCl_4 at low temperature afforded vinyl diphosphonate, which is first reduced and then hydrogenated to an aniline phosphonate ester derivative, which is hydrolysis to afford the final product. Alternatively, the vinyl diphosphonate can be hydrolyzed and then hydrogenated to give EDP. The optimized conditions for the coupling reaction and the pros and cons of two follow-up processes are discussed.

IEC 69

Synthesis and characterization of poly(*N*-isopropylacrylamide) particles in supercritical carbon dioxide

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The temperature responsive poly(*N*-isopropylacrylamide) (PNIPPA_m) have been widely used in biomedical applications, such as drug controlled release systems, drug carrier and so on. We carried out polymerization of *N*-isopropylacrylamide with AIBN as the initiator and *N,N*-methylenebisacrylamide (MBIS) as the crosslinking agent using dispersion polymerization method in supercritical carbon dioxide. The polymerizations were prepared in scCO₂ at various monomer concentration, temperature, pressure ranges and weights of crosslinking agent. Fluorinated and siloxane-based surfactants were used for spherical particles of NIPPA_m in scCO₂. The resulting polymer was characterized by FE-SEM, DSC, TGA and ¹H-NMR etc.

IEC 70

Dispersion polymerization of 2-hydroxypropyl methacrylate (HPMA) in supercritical carbon dioxide and in compressed liquid dimethyl ether in presence of siloxane-based surfactant

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Dispersion polymerization of 2-hydroxypropyl methacrylate (HPMA) has been successfully performed in compressed liquid dimethyl ether (DME) with siloxane-based PDMS-g-pyrrolidone carboxylic acid (Monasil PCATM) polymer as the surfactant and with 2,2'-azobisisobutyronitrile (AIBN) as the initiator. The spherical and relatively uniform poly(2-hydroxypropyl methacrylate) (PHPMA) particles could be produced even at 20 bar, with a narrow particle size distribution. The effect of two continuous phases, which are supercritical carbon dioxide (scCO₂) and compressed liquid DME, as a polymerization medium, the surfactant types such as fluorine-based surfactants, i.e., poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate) [poly(HDFDA)], poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) [poly(HDFDMA)] and poly(HDFDMA-co-MMA) and siloxane-based surfactants, i.e., PDMS-g-pyrrolidone carboxylic acid (Monasil PCA), SS-5050KTM and KF6017TM, and the concentration, initiator concentration, and

monomer concentration on the morphology and size of the polymer particles was also investigated.

IEC 71

Optimization of spray-drying conditions for β -mannanase stability by response surface methodology

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In this work, the effects of four additives (NaCl, sucrose, amylum, and dextrin) on the stability of β -mannanase (an important industry enzyme) during spray drying were discussed and the operational conditions were also optimized by response surface methodology (RSM). The experimental results of the above additives with various concentrations were shown that the addition of sucrose and dextrin might greatly enhance the thermal stability of enzyme during spray drying, and the maximum activity of β -mannanase was increased about 50 % when dextrin was 50 mg/ml. Furthermore, RSM was applied to optimization of three significant spray-drying parameters: feed flow rate, heated air flow rate and inlet temperature when dextrin was constant (50 mg/ml). Through RSM, the optimal conditions of spray drying were calculated as follows: feed flow rate of 4.3 mL/min, heated air flow rate of 31.3 L/h, and inlet temperature of 177 °C. Under these conditions, β -mannanase activity of 3734.9 U/g was experimentally obtained, which increased about 21.9 % comparing with that before optimization.

IEC 72

Study on direct electrosynthesis conditions of p-aminophenol from nitrobenzene

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p-Aminophenol (PAP), also known as 4-aminophenol, is an important medicine, rubber and dye intermediate with wide uses and optimum application prospects. It is manufactured through several chemical methods. An alternative method is the electrolytic method, which has mild reaction conditions, high product purity and reduced waste. In this study, using Nafion 427 cation-exchange membrane as membrane, Monel alloy as cathode and Pb-Sb alloy as anode, the technology conditions for synthesizing PAP were investigated in a self-made plate and frame electrolyzer. The optimum technological conditions were that current density 500 A.m⁻², reaction temperature 185 F, catholyte sulfuric acid concentration 20%

(mass fraction, the same below), nitrobenzene apparent concentration 6.75%, emulsifying agent content in catholyte 0.12%, electric quantity 100 A.h. Using the optimum technological conditions, parallel test results showed that the mean current efficiency was over 78% and the mean yield of PAP was 80% or more, which were higher than the reported values in some references.

IEC 73

Kinetic measurements using catalyst coatings

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Conventional micro structured reactors consist of channels with admeasurements in both dimensions within the micro meter scale. Using slits with a width of less than 1 mm gives the chance for simple and economical fabrication. Due to the slit geometry other than usual coating technologies become feasible. Using the spray technology porous coatings with high thickness, planarity and excellent mechanical strength can be achieved. Reaction kinetics of coated catalysts are the base for the design of microstructured production reactors. A laboratory tool for kinetic measurements are gradientless recycle reactors. In contrast to conventional measurements in recycle reactors catalyst coatings rather than powder-shaped catalysts have to be evaluated. Data for the acetoxylation of ethylene using coated catalysts will be shown. Prearrangements comprise the adaption of the reactor inlet, the verification of reactor ideality and the elimination of diffusion limitation. Afterwards the experimental realisation and interpretation of kinetic measurements can be performed.

IEC 74

Synthesis of trimesic acid by catalytic oxidation of mesitylene in a loop bubble reactor

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With a novel loop bubble reactor, and the solvent of acetic acid, and the catalytic system of cobalt acetate, manganese acetate, and the initiator of

tetrabromoethane, the preparation of trimesic acid from mesitylene by gas-liquid phase catalytic oxidation using air was studied. The effect of reaction conditions (temperature, pressure, solvent ratio, catalyst ratio, water content in solvent) on the yield of trimesic acid under semibatch operation, was investigated and the optimum results were obtained as followed: 215~220°C, 2.0MPa, mesitylene:Co (weight ratio) is 100:0.7~1.0, Co:Mn:Br (weight ratio) is 1:0.6:3, solvent:mesitylene (volume ratio) is 5.5:1, water content in solvent is 6~7%. These optimum reaction conditions were used in continuous operation, and also gave good results: reaction weight yield (mesitylene as calculate base) is over 140%, and the acid value of product is greater than 780.

IEC 75

Biobased solvents for quick-drying cosmetics

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Investigations to find alternative solvents for air-drying coatings represent an important stake to meet both environmental concerns and technical requirements such as volatility. Several natural-based solvents have been synthesized from fusel oil. This ethanol fermentation co-product is a mixture of short alcohols which contains principally isoamyl alcohol. Due to the fast-growing production of ethanol, the availability of fusel oil has widely increased during the last few years, thus offering a cheap and renewable source of isoamyl alcohol. Acetates, carbonates, ethers and isovalerates have been prepared by green processes, preferring specific catalyst use and external solvent-free reactions, leading to minimum waste. Both environmental and economical assessments have been carried out. Calculations performed from the simulation of a cosmetic production plant supplied with these biosolvents showed a reduction of Volatile Organic Compounds emissions by at least 50%.

IEC 76

Benzaldehydes from propenylbenzenes and cinnamic acid derivatives

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Propenylbenzenes and cinnamic acid derivatives yield correspondingly substituted benzaldehydes when oxidized by lead-ruthenium pyrochlore oxide

under heterogeneous conditions. Reaction of terminal and internal aliphatic alkenes under similar conditions gives no aldehydes.

IEC 77

On the molecular modeling of dilute multicomponent systems in near-critical media: Formal results and thermodynamic pitfalls

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Truncated series expansions for the species partial molar fugacity coefficients in ternary and quaternary dilute systems are derived for the systematic study of mixed solutes in pure and mixed solvents at near critical conditions. Then, explicit molecular-based expressions for the expansion coefficients are drawn in terms of direct and total correlation function integrals associated with the actual system's microstructure. Finally, these self-consistent formal expressions are used (a) to interpret the potential synergistic effects on the solubility enhancement caused by the presence of either a co-solute, a co-solvent, or both in terms of the solvation behavior of the dilute species, and (b) to highlight, and illustrate with examples from literature, some frequent pitfalls in the molecular modeling of these mixtures leading to serious thermodynamic inconsistencies. *This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.*

IEC 78

Viewing the cybotactic structure in gas-expanded liquids (GXLs)

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A synergistic collaboration between experiment and microscopic molecular dynamics simulations has provided a view of the heterogeneous environments surrounding solutes in GXLs. The former are essential in validating the computational model which relies on the metastability of the liquid phase in contact with a CO₂-rich phase. The cybotactic structure of CO₂-expanded methanol and acetone has been seen to be sensitive to CO₂ overpressure. In particular, solutes are preferentially solvated in solvent-rich regions. This is consistent with the corresponding solvatochromic measurements of dissolved chromophores, though only the molecular dynamics simulations reveal the typical structure of the solvent around the probe.

IEC 79

Phase equilibrium, structure and transport properties of carbon-dioxide expanded liquids: A molecular simulation study

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Carbon-dioxide expanded liquids (CXL's) are mixed solvents composed of carbon dioxide condensed into an organic solvent that have potential application as environmentally benign catalyst support media. We present molecular-simulation studies of the phase equilibrium, structure and transport properties for a number of CO₂-expanded organic solvents, including acetonitrile, acetone, acetic acid, toluene, methanol, ethanol and 1-octene. In these studies, the CO₂ mole fraction was varied by changing the pressure at a constant temperature. Gibbs ensemble Monte Carlo (GEMC) was used to obtain phase equilibrium (volume expansion) and structural information. In addition, Molecular-Dynamics simulations were used to determine translational diffusion coefficients, rotational correlation times and shear viscosities for some of these mixtures. The GEMC results for the volume expansion were found to be superior to the predictions based on the Peng-Robinson equation of state. The MD simulation results for the transport properties are in good agreement with the available experimental data for the pure components and provide interesting insights into the largely unknown dynamical properties of these mixtures.

IEC 80

Solvation and solvatochromism in CO₂-expanded liquids

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A combination of electronic spectroscopy and molecular dynamics (MD) simulations are used to investigate the equilibrium properties as well as dynamical aspects of solvation in a set of gas-expanded liquids (GXLs) including cyclohexane + CO₂, acetonitrile + CO₂, and methanol + CO₂. Electronic absorption and emission spectroscopy using the probe solutes 10-bis(phenylethynyl)anthracene (PEA) and coumarin 153 (C153) reveal a non-linear dependence of spectral frequencies on the composition of these mixtures suggesting substantial preferential solvation of both solutes. Corresponding computer simulations show that the commonly used assumption of a linear relation between spectral shifts and local compositions grossly exaggerates the extent of preferential solvation in these mixtures. The dependence of solvation dynamics on GXL composition for the solute trans-4-(dimethylamino)-4'-cyanostilbene (DCS) has been measured using Kerr-gated emission spectroscopy and also computed using MD simulations. Simulation-experiment comparisons offer an interpretation of the observed dynamics.

IEC 81

Oxygen solubility in CO₂-expanded acetone, methanol, acetonitrile and 1-n-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide

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CO₂-expanded liquids are attractive media for reactions and separations. However, investigations of the solubility of oxygen and other reactant gases in CO₂-expanded acetone, methanol and acetonitrile over a range of compositions and at 40 C and at pressures to 90 bar show very little enhancement, if any, in the solubility of the oxygen. While the oxygen solubility is greater than for 1 bar of pure oxygen, it is not significantly greater than the pure gas at the same oxygen partial pressure. In many cases, the solubility is less than if the entire applied pressure was pure oxygen. The situation is very different for the ionic liquid 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, where the presence of CO₂ does significantly increase the solubility of oxygen, especially at total pressures above 30 bar. Comparison at the same thermodynamic conditions of temperature and pressure reveals the significant differences between the phase behavior of the molecular and ionic solvents.

IEC 82

Phase behavior and equilibria of r-134a in room-temperature ionic liquids

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The global phase behavior and phase equilibrium have been determined for several ionic liquids with the refrigerant R-134a (1,1,1,2-tetrafluoroethane) in imidazolium based ionic liquids. Low-pressure solubility measurements of R-134a in imidazolium based ionic liquids have been performed using a gravimetric microbalance at temperatures of from about 283-345 K and pressures up to about 2 MPa. High-pressure solubility measurements have been measured using a static stoichiometric method from about 313 to 373 K and pressures up to about 25 MPa. Both low and high-pressure solubility (pressure-temperature-composition) data have been well correlated with an equation-of-state (EOS) model. The EOS has predicted Type-V phase behavior according to the Konynenburg-Scott classification for some of the ionic liquids. In order to prove this prediction, liquid-liquid equilibrium (LLE), vapor-liquid-liquid (VLLE) and critical point measurements have been measured experimentally to confirm the phase behavior classification. In addition, large negative excess molar volumes have been observed for the ionic liquid-rich solutions.

Keywords: ionic liquid, equation of state, solubility, hydrofluorocarbon, liquid-liquid separation, vapor liquid equilibria, vapor liquid liquid equilibrium, critical points.

IEC 83

Ion pair association in aqueous hydrochloric acid solutions along near-critical isotherms

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The main goal of this work is the molecular-based determination of the ion-pair association constant in model near-critical aqueous *HCl* solutions. The radial profiles of the potential of mean force for the $H_3O^+Cl^-$ pair are determined by

constraint molecular dynamics of infinitely dilute aqueous solutions along near-critical isotherms and from steam-like to liquid like densities. The ion-pair association constant are consequently calculated and compared with those obtained from the most accurate recent electrical conductance experiments [Ho, P. C.; Palmer, D. A.; Gruszkiewicz, M. S. *Journal of Physical Chemistry B* **2001**, *105*, 1260-1266] at corresponding states. Resulting equilibrium constants between contact and solvent-shared ion-pair configurations are then used to estimate the distribution between contact and water-mediated ion-pair configurations. The adequacy of some simple fully electrostatic models to represent ion-pair association behavior in high temperature aqueous solutions is also discussed.

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IEC 84

Switching solvents and surfactants using CO₂ at 1 atmosphere

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While elevated pressures of CO₂ gas can be used to modify solvent properties by expansion, it is possible to modify the properties of some solvents with only atmospheric pressure CO₂. 1 atm of gaseous CO₂ causes certain low polarity liquids to change into more polar liquids (ionic liquids). The effect can be reversed by the application of N₂. The different liquids, their polarities, and example applications will be described. Surfactants are widely used in the mining, energy and manufacturing industries to stabilize emulsions for a stage in the process, after which the emulsion is no longer required. Because breaking the emulsion is made more difficult by the presence of the surfactant, it would be preferable if the surfactant can be turned off. "Switchable surfactants" will be described which are "turned on" (become able to stabilize emulsions) by an atmosphere of CO₂; when the CO₂ is removed, the emulsion breaks.

IEC 85

In situ alkylcarbonic acid catalysts formed in CO₂-expanded alcohols

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We demonstrate catalysis using self-neutralizing alkylcarbonic acids formed from carbon dioxide and alcohols. These are acid catalysts generated in situ which can be easily neutralized via depressurization. Alkylcarbonic acids combine a medium with good organic solubility with acid catalysts that do not require neutralization, thus completely eliminating the solid wastes associated with many acid processes. We examine the origins and characteristics of alkylcarbonic acids by comparing reaction rates of acid-sensitive probes in different CO₂-expanded alcohols, elucidating the effect of CO₂ pressure, and demonstrate the use of alkylcarbonic acids for acetal formation, the hydrolysis of beta-pinene and the formation of reversible ionic liquids. The effect of CO₂ pressure on the formation and dissociation of alkylcarbonic acids is discussed in light of dielectric measurements performed on the gas-expanded liquid systems.

IEC 86

Chemical engineering insights toward carbon-nitrogen bond formation in CO₂-expanded liquid media

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For several years, the MIT Departments of Chemistry and Chemical Engineering have engaged in a collaboration dedicated to the investigation and optimization of synthetic transformations in environmentally-benign media. Our groups have extensive experience in measuring and modeling kinetic rate constants and physico-chemical properties under a variety of conditions, most notably high-temperature and supercritical water (scH₂O), liquid and supercritical carbon dioxide (scCO₂), and mixtures of these with conventional organic solvents.

Given the importance of nitrogen-bearing compounds in specialty-chemical and pharmaceutical industries, we are currently exploring a wide range of carbon-nitrogen bond-forming reactions in CO₂-based media. The successful development of these processes relies heavily on the application of fundamental chemical engineering principles. Using illustrative carbamate and amide-forming reactions, this presentation will discuss some essential chemical engineering analyses required for the optimization of these and many other reactions in CO₂-based media. Specific emphasis will be placed on the modeling and visualization of phase behavior in CO₂-expanded liquid systems.

IEC 87

Catalytic oxidation reactions in carbon dioxide expanded liquids using the green oxidants oxygen and hydrogen peroxide

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Carbon dioxide expanded liquids, CXLs, provide transport and safety advantages for catalytic oxidation reactions using the green oxidants, oxygen and hydrogen peroxide. These benefits have been explored for the oxidation of various substrates, including alternatives for important reactions: p-xylene to terephthalic acid, cyclohexane to adipic acid, p-nitrotoluene to p-toluic acid, phenols to quinones, and replacement of chromium(VI) oxidants for benzylic alcohols and alkyl benzenes. Catalysts range from transition metal salens and porphyrins, to that for the venerable MidCentury process, cobalt/manganese acetate/bromide, the more recent Shell catalyst, cobalt and zirconium acetates, and cobalt acetate catalysts with organic radical sources such as N-hydroxy imides, aldehydes and ketones. Hydrogen peroxide, runner-up to oxygen as a green oxidant, is disadvantaged for CXLs by the immiscibility of water and carbon dioxide and the safety benefits of water. When achieved, monophasic hydrogen peroxide oxidations show substantial improvements over their phase transfer counterparts.

IEC 88

β-Pinene hydrolysis by in situ acid catalysis in reversible smart solvents

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Smart solvents are materials that change properties when exposed to certain external stimuli. Activating this stimulus will change the process environment, allowing for reaction and easy separation. For example, gas-expanded liquids are smart solvents that use pressure as a dial to alter solvent and transport properties. For this research, we changed the stimulus from a “dial” to a “switch”. We created a smart molecule with a thermoresponsive on/off switch, enabling rapid property changes. This smart solvent is a reversible, dimethylsulfoxide analog. The thermoresponsive switch enables decomposition of the solvent to volatile components which are separated and recombined easily. We used this molecule to facilitate in-situ acid catalyzed reaction and separation by utilizing the thermodynamics of our solvent. We tested this technique on the hydrolysis of β -pinene, an industrial reaction for making flavoring compounds. Our results show excellent yields and selectivity, indicating comparable rates to industrial systems while avoiding acid neutralization.

IEC 89

Hydrogenation of polycyclic aromatic compounds using Ni supported on Hf⁺-zeolite as catalysts in supercritical carbon dioxide

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The primary rationale for the use of supercritical carbon dioxide (sc-CO₂) as a solvent for the hydrogenation is the elimination of mass transfer limitations, through enhancement of the solubility of hydrogen at the reaction locus. Hydrogenation of anthracene was performed using Ni/Hf⁺-zeolite catalyst and sc-CO₂ as a solvent. Optimization of the reaction parameters were carried out for best tuning of the solvent properties of carbon dioxide. The conversion of anthracene increases from 32 to 60 % on increasing the temperature from 80-130C. The effect of metal loading was studied from 5-30-wt% and metal loading of 20-wt% was found to be optimum. The conversion of anthracene found to be slightly increased on increasing reaction pressure from 5.5 MPa to 12.4 MPa and remained constant there after. We are also studying the effects partial pressure

of hydrogen, effect of various supports and metal-support interactions, and effect of catalyst properties on hydrogenation of anthracene.

IEC 90

Hydrogenation of CO₂-expanded liquid terpenes: Phase equilibrium-controlled kinetics

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Abstract. The hydrogenation of liquid terpenes α -pinene and limonene was carried out in the presence of high-pressure carbon dioxide, using carbon-supported Pt and Pd catalysts. Phase equilibrium data on terpene + CO₂ + hydrogen were used to interpret the kinetics of hydrogenation in liquid + vapour systems, close to the critical lines of the mixtures.

IEC 91

Hydroformylation in CO₂-expanded media

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Carbon dioxide-expanded solvents are useful media for rhodium-catalyzed hydroformylation reactions. For example, performing hydroformylation in CO₂-expanded 1-octene leads to improved catalyst activity as well as higher n/i selectivity. Moreover these reactions occur at mild temperatures (30°-60°) and pressures (10-60 bar). These efforts as well as efforts toward catalyst recycle will be described.

IEC 92

Catalysis, phase equilibria and mass transport in biphasic ionic liquid-compressed CO₂ systems

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Efficient platforms for reactions, catalysis and separations remain a key issue for the implementation of industrial processes. A new biphasic approach has been proposed based upon ionic liquids (ILs) and compressed or supercritical CO₂. An IL/CO₂ system has many advantages over each individual technology. This study will show quantitatively the beneficial effect of CO₂ on the various properties of ionic liquids, including phase equilibria and mass transport. In the literature, there are a several studies that offer contradictory results on the effects of CO₂ on reaction rates in IL/CO₂ systems. Some indicate that CO₂ may enhance reactivity and selectivity in catalyzed reactions in IL/CO₂ systems and others indicate that there is no effect or a slower reaction rate. However, little quantitative data exists on the kinetics, mass transport, and phase equilibria of these type of systems. This presentation will illustrate the mechanism of CO₂ on Rh-catalyzed hydrogenation and hydroformylation of 1-octene in a biphasic ionic liquid/CO₂ system. The effects of phase equilibria will be shown to largely control the apparent reaction rates and are thus critical to understanding this reaction platform.

IEC 93

Sulfur trioxide containing caprolactamium hydrosulfate: An extended ionic liquid for large scale production of caprolactam

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Ionic liquids are among the solvents which can be used to fine tune the performance of chemical systems, mostly to facilitate high yields for chemical reactions or facile separation of product(s) from reagents or catalysts. The ultimate success of these solvents depends whether they will be used commercially in small or larger scale applications. While ionic liquids have been used in smaller processes, large scale application has not been reported. We have discovered during the investigation of the mechanism of the Beckmann rearrangement of cyclohexanone oxime to caprolactam in sulfuric acid or oleum that the rearrangement medium, used by all caprolactam manufacturers, is actually an ionic liquid, the caprolactamium hydrosulfate. We will report the characterization of this ionic liquid including its remarkable capability to keep the vapor pressure of dissolved sulfur trioxide below 10 kPa even at 150 C, allowing its safe use in large scale processes for a long time.

IEC 94

Synthesis of polytetrafluoroethylene in carbon dioxide expanded solvents: Practical approaches to avoid the use of pfoa

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According to the EPA's 2010/15 PFOA Stewardship Program, participating companies will eventually eliminate the use and emission of PFOA in fluoropolymer synthesis by 2015. This demands more environmentally benign alternative processes. Supercritical CO₂ has been successfully used in production of Process-G fluoropolymers by DuPont but improvement on the process is needed. In this study, we report the synthesis of polytetrafluoroethylene in CO₂ expanded organic solvents. Both precipitation and emulsion polymerization of tetrafluoroethylene (TFE) conventional hydrocarbon surfactant in scCO₂ expanded organic solvents were successful. A number of CO₂ expanded organic solvents have been explored and proven to be effective solvent mediums for polymerization of TFE. Among them, carbon dioxide expanded acetic acid is considered to best balance the environmental benefits of supercritical CO₂ and practicality for industrial use. In the polymerization, the ratio of acetic acid could be up to 60 vol% without significantly compromising molecular weights and thermal properties of so-obtained PTFE. Our results on the polymerization of TFE in various carbon dioxide expanded organic solvents, especially acetic acid, will be discussed in detail. The preparation of colloidal PTFEs using SDS, a conventional hydrocarbon surfactant in CO₂ expanded acetic acid will also be presented.

IEC 95

Supercritical fluids: Enhancing polymerization and processing

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There has been intense interest in the use of supercritical fluids, particularly supercritical carbon dioxide (scCO₂) as a solvent for polymerization and processing. But scCO₂ has a reputation as a relatively poor solvent. There have been many approaches to overcoming this limitation. Heterogeneous polymerization and the development of stabilizers for dispersion, emulsion or suspension processes have perhaps raised most interest. However, there are

many processes where this may not be appropriate. In this paper we describe polymerization and processing routes where scCO₂ acts to plasticize a polymer phase and to facilitate novel and clean preparation of desirable new materials from block copolymers to composites and scaffolds for tissue engineering and drug delivery applications.

IEC 96

Green processing for creating low-k metalizable polymer films using supercritical carbon dioxide

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This report presents that low-density polymer layers created by supercritical carbon dioxide (scCO₂) exposure can be exploited to enhance metallization of the polymer surface. Spun-cast polymer thin films were exposed to scCO₂ within a narrow temperature/pressure regime known as the "density fluctuation ridge", where the excess swelling was induced, and the swollen structures could be frozen by quick evaporation of CO₂. X-ray reflectivity technique showed that the "expanded" films resulted in the large interfacial broadening at the polymer/metal interface regardless of the polymer film thickness and types of polymers during vapor deposition process, providing potential benefits for next generation microelectronics. A significant effect of nanoparticles embedded in a polymer matrix on polymer metallization will be also presented.

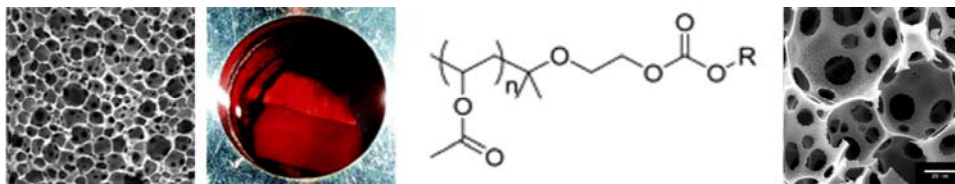
IEC 97

Emulsion-templated porous materials using concentrated carbon dioxide-in-water emulsions and inexpensive hydrocarbon surfactants

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We present here a versatile methodology for producing highly porous cross-linked polymer materials by templating concentrated CO₂-in-water (C/W) emulsions. Poly(vinyl alcohol) (PVA), blended PVA/PEG, and naturally derived chitosan materials were produced via this route, as was porous emulsion-templated poly(acrylamide). The technique can be carried out at moderate

temperatures and pressures (25 C, <120 bar) using inexpensive hydrocarbon surfactants such as poly(vinyl acetate)-based block copolymers which are composed of biodegradable blocks. This methodology opens up a new solvent-free route for the preparation of porous biopolymers, hydrogels, and composites, including materials which cannot readily be produced by foaming. In addition, the development of biodegradable surfactants for C/W emulsion formation is relevant in areas such as extraction and biphasic catalysis. We also show that PVAc oligomers with a single hydroxyl end-group can be used to solubilize a variety of species in liquid and supercritical CO₂.



IEC 98

Hollow polymer shells through emulsification/freeze drying followed by near critical solvent processing

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A novel process will be described for producing micron-sized hollow polymer shells or microcapsules. In the first step, a polymer/solvent emulsion in water is freeze dried to form hollow polymer particles with a small hole open on one end. These hollow particles are suspended in water/ethanol mixtures and exposed to near critical CO₂ solvent or solvent mixtures to plasticize the polymer. Under appropriate conditions, the solvent exposure causes the hole on the surface of the particle to close, forming a microcapsule. The factors influencing the formation of hollow particles and microcapsules will be examined and discussed. Water-soluble compounds can be encapsulated inside the hollow polymer particles. When formed from biodegradable polymers, the microcapsules are attractive for controlled release of the encapsulated material. Processing with near-critical CO₂ offers a route to form microcapsules without solvents that are undesirable for drug delivery and biotechnology applications.

IEC 99

Fractionation of metal and semiconductor nanoparticles using CO₂-expanded liquids: Experiment and theory

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This paper presents an environmentally friendly and efficient process for size selective fractionation of polydisperse metal and semiconductor nanoparticle dispersions into multiple narrow size populations (± 0.5 nm) using the pressure tunable physico-chemical properties of CO₂ gas expanded liquid solutions. Our work shows that metal and semiconductor ligand stabilized nanoparticles can be size selectively precipitated by controlling the addition of CO₂ antisolvent to an organic nanoparticle dispersion. This CO₂-expanded liquid approach provides fast and efficient size separation, a reduction in organic solvent usage, tunable size selection, and controllable deposition. The efficiency of process was investigated on several types of metallic (Ag, Au, Pd, Pt) and semiconductor (CdSe/ZnS) nanoparticles to both illustrate the general applicability and to provide fundamental information on the effects of processing parameters. In addition, a thermodynamic model was developed to improve our understanding of the size selective fractionation process. Osmotic energy and Hamaker constant expressions were developed to estimate the maximum nanoparticle size that could be dispersed by equating the total interaction energy to the Boltzman threshold stabilization energy.

IEC 100

Nanoparticulate metal complexes prepared with compressed carbon dioxide: Structural correlations and nitric oxide binding

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Nanoparticles of metal complexes are rare because of the limited methods for their preparation. We have used precipitation with compressed antisolvent (PCA) to process nanoparticles of neutral metal-salen complexes (*N,N'*-salicylidiene)-1,2-ethylene-di-aminato(2-)). PCA is a semi-continuous technique utilizing supercritical carbon dioxide (scCO₂) as the precipitant. The scCO₂ dissolves into

a solution of the complex and simultaneously extracts the solvent, resulting in formation of nanoparticles of uniform morphology. Spectroscopic and analytical methods were used to support the assignment that the nanoparticles are composed of metal complexes. Scanning electron microscopy reveals that planar complexes, such as [Ni^{II}salen], afford rod-like particles with average diameter and 85 nm. In contrast, complexes with non-planar molecular structures produce nanoparticles with varied structures: these findings suggest a correlation between the structures of the molecular precursors and the morphology of the processed particles. Furthermore, we have investigated the ability of the nanoparticles to absorb nitric oxide (NO). This talk will describe the processing, nanoparticle morphologies, and functional properties of NO binding.

IEC 101

Development of a novel precipitation technique for the production of highly respirable powders: The atomized rapid injection for solvent extraction (ARISE) process

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In the ARISE process, organic solutions containing dissolved pharmaceutical actives are delivered into supercritical carbon dioxide as a single bolus injection under quasi-isothermal and isochoric conditions to effect homogenization and solvent extraction. With the energized rapid release of organic solutions into the anti-solvent environment, the ARISE process eliminates the use of capillary nozzles and low solution flowrates for atomization, thereby reducing processing times significantly. By effecting precipitation over a larger volume, the ARISE process is also capable of processing with increased nucleation homogeneity, decreased nucleation densities and hence, decreased bulk densities. The feasibility and tunability of the ARISE process was successfully demonstrated with the generation of dry powders of insulin. At different operating conditions of the ARISE process, insulin generated was either of very narrow particle size distributions or of extremely low bulk densities. In-vitro analyses of low bulk density products indicated excellent aerodynamic properties and dry dispersibility.