Direct Capture of Products from Biotransformations

Chemical Industry VISION2020 Technology Partnership

Organizers:

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Report Team

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OAK RIDGE NATIONAL LABORATORY

Vision 2020 Advanced Separations

- Program Objective:

  Identify & initiate R&D opportunities and potential programs to address key challenges for commercializing new separations technology to improved energy efficiency, economics, environment and sustainability

Reported located at:
http://www.chemicalvision2020.org/pdfs/direct_capture.pdf

Advanced Separations Team -- Start

- Air Products: **Robert Miller**
- Cargill: **Tim Oolman**
- DOE OIT: **Charles Russomanno, Dickson Ozokwelu**
- Dow: **George Killat**
- Dow Corning: **Keith Hayes**
- Dupont : **Vidya Pai, Raymond Zolandz, Tucker Norton, Robert Sylvester**
- Eastman Chemical: **Chester Sink**
- ExxonMobil: **Bal Kaul**
- GlaxoSmithKline: **David Constable**
- OLI Systems: **David Linz**
- Praxair: **Jack Solomon**
- Practical Sustainability: **Earl R. Beaver**
- Tate & Lyle: **Marion Bradford**
- Fairfield Resources: **Francis Via (Co-Chair)**
- ORNL: **Sharon Robinson (Co-Chair), Brian Davison**
- ANL: **Jim Frank, Seth Snyder, Jamie Hestekin**

Advanced Separations Topics

Initial Focus: Direct Capture of Products

Alternative Candidates:

Synthesis Matching Criteria	Biocatalyst
Foams and Emulsions	Analytical
CO_2 Separations	Selective Separations
Alternative Solvent Separations	Adv Electrodialysis
Oxygen/Nitrogen Separations	**Water Removal**

Advanced Separations Team -- Bioseparations

- Dow: **George Killat**
- Dupont : **Vidya Pai, Raymond Zolandz**
- Eastman Chemical: **Chester Sink**
- OLI Systems: **David Linz**
- Tate & Lyle: **Marion Bradford**

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Chemical Plus Project Charter

- Direct Capture of Products
  - Highly selective, up-front separation
  - Small molecules
  - Remove product without cell separation & de-watering
  - Low-level, high-value by-products e.g. Vitamin E

- Water Removal
  - Fermentation Broths (product now only 2% of mix)
  - Low cost water removal to expand bioprocessing in the chemical industry
  - Aqueous-based processing of chemical & Ag products
  - Technology to displace evaporation

Executive Summary

Membrane technology offers some of the most promising breakthroughs if selectivity could be enhanced without reducing flux.

Much of the improvements in separations technologies will develop from **new materials or new modifications** of commercial materials

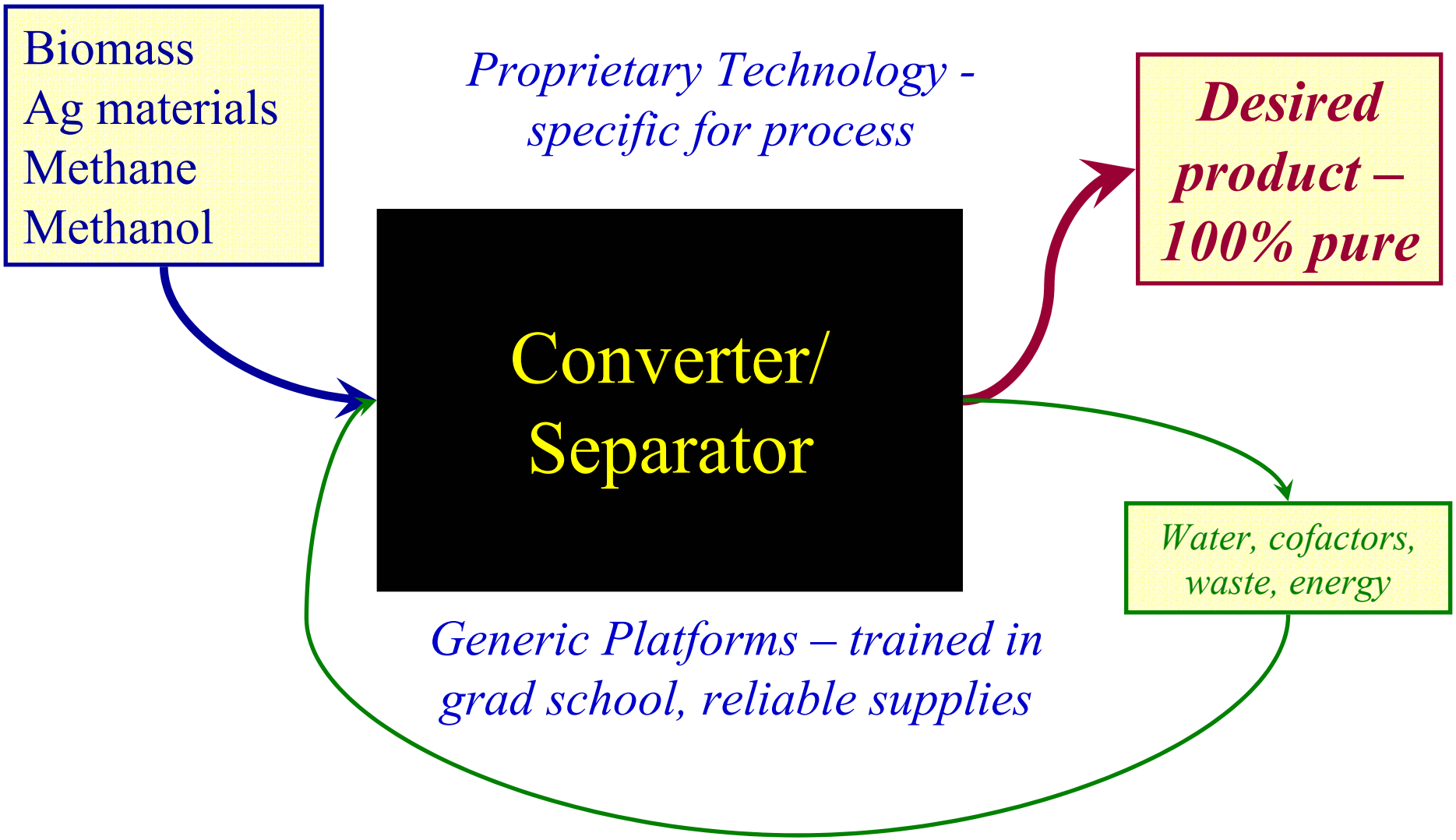
Removal of impurities such as cell debris, proteins, sugars, and salts improves all subsequent separations technologies and should be considered in all processes.

R&D in biocatalysis are: 1) working with **minimal fermentation media to reduce impurities**, and 2) **enhancing microorganism tolerance** to products

Integrating biocatalysis with separations
pH control of fermentations and **continuous removal of products.**

R&D tools for **screening, and modeling**, in processes and materials.

Ideal System – Second Generation

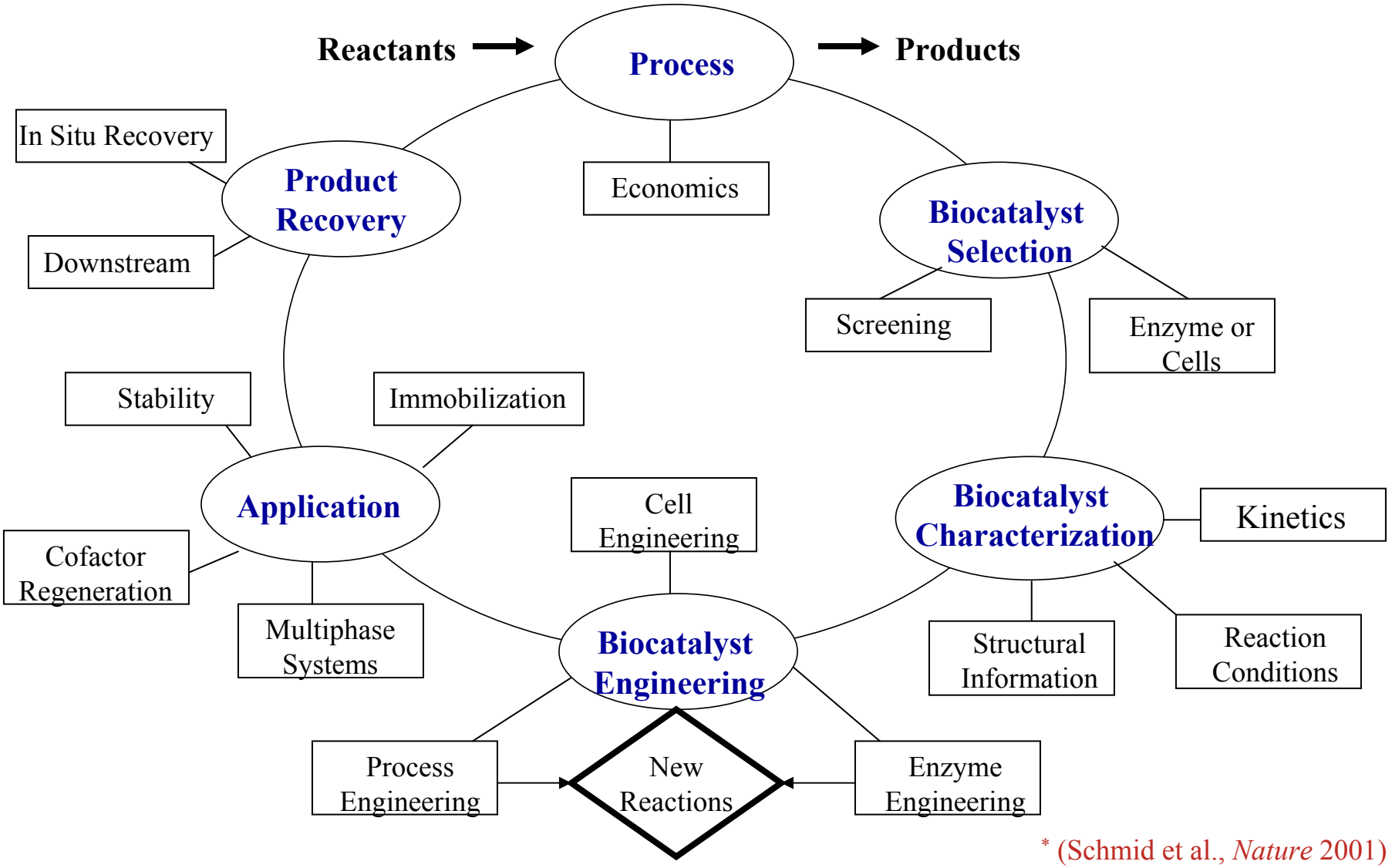


Three model systems that represent important commercial processes

- **Organic acids (and esters)**
  - Major metabolic products and platforms for other products
  - Processes to control pH
  - Simultaneous fermentation and separation
  - General Separation not necessarily biocompatible – highly selective

- **ABE – acetone:butanol:ethanol**
  - A significant example of solvent systems
  - Simultaneous fermentation and separation
  - Change distribution
  - Not necessarily biocompatible
  - Pervaporation, Hollow-fiber reactors, Liquid extraction, Membrane-assisted
- **Chemicals from biobased oils (biodiesel and biolubricants)**
  - Important potential targets as a representative of fat-soluble products
  - Continuous
  - Separation media development for recycle of enzymes
  - Separations for caustic recycle – e.g. Membrane development for glycerol

The Biocatalysis Cycle*



* (Schmid et al., *Nature* 2001)

Technical areas considered ripe for discovery R&D

- **Removal of impurities** – For example removal of proteins, sugars, and salts from organic acids can prevent fouling of membrane-based and ion exchange separations.
- **New materials** – Resins, membranes, and solvents that provide higher selectivity, specificity, or flux with increased stability and robustness
- **Modification of existing generic materials** –Modification of existing generic materials to meet performance requirements
- **New approaches to screening** –Computational modeling and database comparisons to existing materials and processes are required to extrapolate data and supplement screening for desired performance.
- **Advancements in biocatalysis and fermentation** – The revolution in genomics, proteomics, and bioinformatics enables new approaches to biocatalysis and fermentation.

New highly selective materials

Extraction-Based Separations

Liquid-liquid extraction is a fairly mature technology

An extraction process using a membrane contactor

- Provide surface area where the two immiscible phases can exchange the product.
- New materials for membrane contactors

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New highly selective materials

Adsorption/Ion-Exchange

Columns containing resin beads that separate the product based on affinity.

- ***pH control with ion exchange***

  Ion-exchange/adsorption research for the ABE and biodiesel processes.

  Adsorbent concentrate butanol selectively, and be regenerated easily

  Adsorbent to remove glycerols from the water stream in biodiesels

Adsorption and ion exchange that are economical for dilute separations.

Disadvantages

- Regeneration (pressure, temperature, solvent stripping)
- Relative size of the column (large footprint)
- Non-specific binding of proteins (fouling)

Electrosorption, may have promise for easier regeneration

Modification of existing materials

The most promising strategies are:

- Attachment of chelating groups onto ion-exchange resins for better adsorption and EDI applications

- Use of traditional organic solvents for liquid-liquid extraction spiked with highly-selective extracting agents

- Modification of the surfaces of pervaporation and ED membranes to allow for a higher concentration of the transporting component on the surface.

Biocatalytic approaches

One way to deal with separation challenges is to minimize or avoid them.

- Defined media (reduce problems with impurities)
- High product tolerant microbe
- Novel biocatalysis

Biocatalyst improvement: increase product titer

Genetic engineering

- Culture optimization
- Process configuration (e.g., immobilized cells)

In situ product removal or simultaneous fermentation and separation (SFS)

- Vacuum distillation, pervaporation and the use of hollow-fiber reactors, solid adsorbents and an immiscible extractive solvent

- SFS → higher conversions, higher rates and sometimes higher yields when the inhibitory product is removed from the ongoing bioconversion.

Separations & Biocatalytic approaches

Organic acids

pH control, the pH drops rapidly and conversion is halted.

- Neutralization increases separation complexity

Microorganisms with improved pH tolerance need to be developed.

Simultaneous fermentation and separation

- Bioreactor combined with the separation of the organic acid.

Biocatalytic approaches

ABE

Butanol is primary product of fermentation of sugars by various bacteria (*Clostridium acetobutylicum)*

Products and the lowered pH inhibit continuous fermentation

→ limits final butanol concentrations

R&D Needs

- Higher butanol tolerance
- Decrease in organic acid production
- Control of spore formation and culture degeneration.

Biocatalytic approaches

Biobased oils & specialty chemicals

One biocatalysis goal:

Replace the caustic transesterification process with a biocatalytic method (e.g. lipases)

Advantages of enzymatic conversion

- Lower energy and capital costs
- Decreased caustic costs and the need to neutralize.

Difficulties

- Cost of the enzyme
- Need for minimum water content, pH control, and high conversions from an equilibrium reaction
- Enzymes may also be destabilized at oil-water interfaces.
  - Potential solutions:
    - Immobilized forms.
    - Lipases modified catalyze reactions directly in an organic phase

Stretch goals

- A perfect simultaneous fermentation/separation process with for highly selective, high capacity separation.
- A method to fractionate narrow MWt ranges (e.g., to <10% for small molecules & 10-100 Da for large molecules range) of closely related organics, proteins, or lipids of similar functionality
- Membrane transport of dilute components (e.g., <10 ppb of butanol by pervaporation) at similar flux/selectivity as concentrated streams.
- Membrane flux increase of >500% at current selectivity and fouling characteristics
- Sorbents with extremely high affinity (ppb) with comparable usable capacity (>0.1 g/g) and with easy regeneration.
- Remove proteins completely from fermentation broth
- Modify a robust low cost mass separation media
- Eliminate whole cell fermentation by use of an effective “artificial cell” or nanocomposites using “in vitro” multistep enzymes or biomimetic pathways
- Microorganisms designed to augment separation.

Potential impact of "Direct Capture" R&D

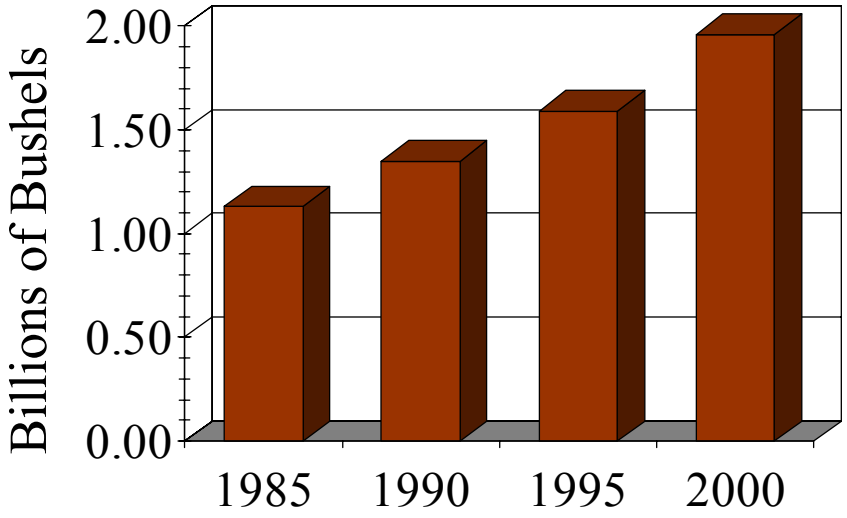
Two areas of impact

- Biobased products to compete with fossil fuel-based feedstocks
- Bioprocessing to compete with chemical catalysis
  - Reduced solvent usage
  - Reduced heat, pressure, etc. needs
  - More benign waste streams

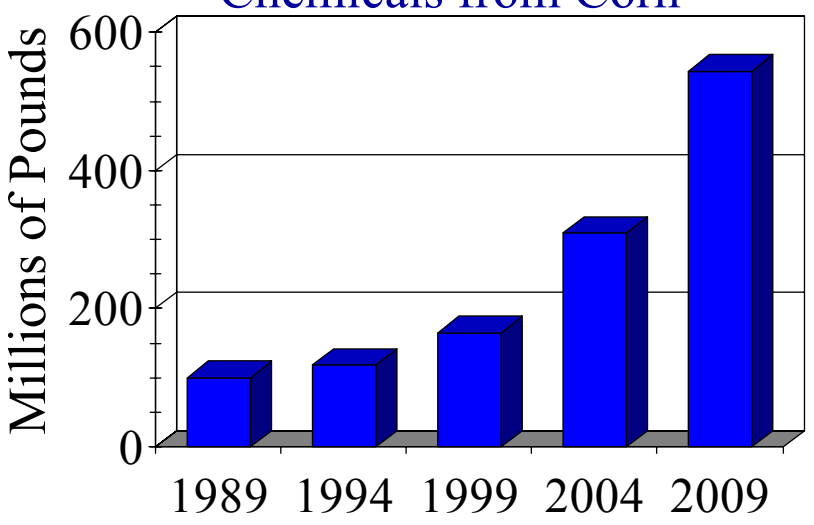
Biobased Products and Bioenergy Vision: Feedstocks

Feedstocks & Technology → **Value-added products** → **Reduced petroleum dependence**

Growth in Total U.S. Corn Utilization*



Growth in U.S. Chemicals from Corn*



- **Using corn as one example**

Outcomes…..

- Proposal to OIT Chemistry Is Funded
  - Membranes for selective removal of organic acids
    - *ANL with a membrane and petrochemical company*
    - *Production and separation of acids using pervaporation membranes*
- Proposal to ORNL State Partnership Project for bioseparations using ionic liquids
- Provided Input for BioEnergy and BioProducts 2003 SBIR solicitation
- Provided Input for 2003 Chemicals IOF RFP
- Program Proposal Development

  Leads under study with

  Amalgamated Research Inc.

  Materials Methods, Inc.

DOE-EE SBIR Solicitation – due Jan. 2003

22. BIOMASS

… Grant applications are sought only in the following subtopics:

a) Advancements in Biocatalysis and Fermentation

b) Separation Technology for the Direct Capture of Bioproducts and Biofuels from Fermentation and Other Biotransformations or from Thermochemical Transformations

c) Feedstock Densification and Handling

d) Drying of Biomass

Developed by Charlie Russomanno (DOE-OIT Chemicals)

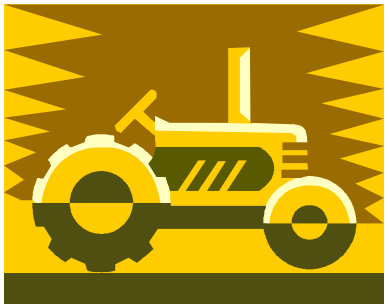
Separations 2020 AIChE Session

- Vision2020 Research Collaborations, **Jo Rogers**, AIChE
- Direct Capture of Products from Biotransformations, **Seth Synder**, ANL
- Advanced Vapor Liquid Contactor Model Development, **Bruce Eldridge**, University of Texas
- Plasticization-Resistant Membranes for Propylene/Propane Separation, **Andre De Costa** Membrane Technology and Research
- Pressure Swing Absorption for Gas Separation, **Keith Ludwig**, Air Products
- Bioseparations Using Fractal Technology, **Mike Kearney**, Amalgamated Research

Presentations from Argonne and Oak Ridge report team at AIChE

Michelle Arora, et al. (Networking Session, Tues & Wed, 5:00)

- *Controlled Immobilization of Biocatalytic Enzymes in Separative Bioreactors*



Jamie Hestekin, et al. (Session 134g, Friday, 10:30)

- *Production and Recovery of Organic Acid Using a EDI Separative Bioreactor*

Brian Davison, et al. (Session 329, Friday, 10:24)

- *Variation of S/G/ ratio and Lignin in a Populus Family Influences the Release of Fermentable Sugars by Dilute Acid Hydrolysis*

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Advanced Separations Plan Forward

Target: **Separations associated with Natural Gas, Fuel Cells, Refinery Hydrogen and the Hydrogen Economy**

Interested Participants:

Air Products

Praxair

BP

ExxonMobil

Shell Chemical

Membrane Technology and Research, Inc

Ceramatec

Equistar Chemicals, LP

CeraMem Corporation

Potential Targets:

CO_2 and CH_4

N_2 and CH_4

H_2O and CH_4

H_2S and CH_4

O_2 and N_2 from Air for liquefying CH_4

CO and H_2

CO_2 and H_2

C_1 and C_3; from reforming gas streams

H_2 from reforming gas streams

H_2S from reforming gas streams