National Science Foundation Workshop Report on

Catalysis for Biorenewables Conversion

Marriott Crystal Gateway Hotel
Arlington, Virginia
April 13 and 14, 2004

Dennis J. Miller, Workshop Chair, Michigan State University
James E. Jackson, Workshop co-Chair, Michigan State University

Workshop website: www.egr.msu.edu/apps/nsfworkshop

Sponsors

Dr. Glenn Schrader
National Science Foundation
Division of Chemical and Transport Systems
Catalysis and Biocatalysis Program

Dr. Mike Clarke
National Science Foundation
Division of Chemistry
Inorganic, Bioinorganic, and Organometallic Chemistry Program

Dr. Fred Heinekin
National Science Foundation
Division of Bioengineering and Environmental Sciences
Biochemical Engineering and Biotechnology Program

Cover: A collage of images from workshop presentations

This work supported by NSF grant CTS – 0423954.

TABLE OF CONTENTS

Executive Summary

This report describes the outcomes of a two-day workshop held in April, 2004 near the National Science Foundation headquarters in the Washington, D.C. area to identify U.S. capabilities, needs, and strategies for using catalysis to produce value-added fuels and chemicals from biorenewable feedstocks. The workshop brought together approximately 45 scientists and engineers from academia, industry, and national laboratories, all involved in state-of-the-art chemical catalysis and biocatalysis research relevant to chemicals production from biorenewables. These workshop attendees listened to presentations mainly on heterogeneous catalysis for biorenewables and participated in informal working groups to discuss specific ideas and formulate directions and challenges for future research.

The general objectives of the workshop were set forth as follows:

1) to identify and communicate critical needs for building scientific and engineering capabilities in catalysis to convert biorenewables to chemical and other value-added products;
2) to assess the current state of chemical (heterogeneous and homogeneous) catalyst and biocatalyst science and technology that is applicable to biorenewables;
3) to identify curricular and workforce needs to prepare engineers and scientists for a biorenewables-based chemicals industry;
4) to develop and prioritize goals and directions for the development of effective catalysts and catalytic processes for biorenewables conversion, including the integration of chemical and biochemical catalysis in the future "biorefinery."

These objectives pertain directly to the broader goal of the workshop, and that is to prepare U.S. industry and academia for the massive, inevitable transition from petroleum to biorenewables as the raw materials for fuels and chemicals production. While an exact time frame for this transition is impossible to predict, there is no doubt that it will occur, and that its occurrence will take place gradually as petroleum becomes more expensive and the technologies for biorenewables conversion advance. In a more concrete sense, this workshop was intended as an initial gathering to identify several specific directions for catalysis research at the National

Science Foundation and elsewhere in the U.S. and to set the stage for future workshops that will more fully define the research effort required to facilitate the petroleum-to-renewables transition.

The outcomes of the workshop stress the need for a reinvigoration and redirection of U.S. catalysis research for the purpose of developing fuels and chemicals production from biorenewables. Several key themes surfaced in presentations and discussions at the workshop that together form the foundation for the recommended directions and strategies. These themes reflect the nature of molecular species derived from biorenewable sources and the fact that most catalyst science and engineering in the U.S. has historically focused on petroleum. Petroleum substrates typically have high thermal stability, high volatility, and low functionality; biorenewable species, in contrast, have generally poor thermal stability, low volatility, and excess functionality. Thus a key theme for biorenewables is the need for catalysts that 1) can selectively alter or remove functionality from biorenewable molecules; 2) can function without degradation in water and other liquid phases at a variety of pH conditions; and 3) have high activity at low temperature (where selectivity and thermal degradation are less problematic).

A second theme of the workshop stresses the need for chemical catalysis to integrate with biocatalysis and microbial processes for biorenewable chemicals production. The future biorefinery will be composed of unit operations that involve both biological and chemical conversions, yet very little research has been conducted at the interface between the two fields. There are needs for catalysts that selectively convert only one component of the biomass stream, that have tolerance to biogenic impurities in the intermediate streams, and that can mimic biological conversion pathways.

A third theme arises around the needs for appropriate analytical and simulation tools for biorenewable catalysis. Because many reactions take place in the liquid phase, spectroscopic techniques utilizing classic high vacuum, submonolayer analyses are not suitable. Instead, analytical methods must be developed that facilitate observation and characterization of adsorbed species, that characterize the role of solvent in reaction, and that ascertain the actual state of catalyst metal surface at reaction conditions. Computational studies related to biorenewables must account for the presence of solvent, for the stereochemistry of reactant and product species, and for complex interactions of large, highly functionalized molecules with the catalyst surface.

A fourth theme of the workshop relates to catalytic reactor design for biorenewables conversion. Conversion of feedstocks dissolved or suspended in a liquid phase requires more complex reactor systems than those used in classic heterogeneous catalysis; multiple phases are almost always present including gases and one or more liquid and solid phases. Thus, effective mass transport between phases is an important design consideration, as are hydrodynamics, choice of solvent, and thermal considerations. Multiphase reactors exist and have been used for liquid-phase catalytic systems, but they have not been fully characterized. Reactors such as bubble columns, three-phase fluidized beds, trickle beds, and suspended solids reactors thus require study to better understand flow patterns, species contact times, and mass transfer rates, so that reliable and accurate mathematical models of their behavior can be constructed for design.

This report relates details of the workshop proceedings in light of these themes, with primary emphasis given to recommendations and needs pertinent to the workshop objectives. Relevant background on biomass feedstocks, biological conversions, reaction engineering, and catalyst characterization is included, but no attempt has been made to rigorously describe the state-of-the-art of chemical catalysis beyond that needed to communicate needs for future work.

The workshop organizers wish to thank Dr. Glenn Schrader, Director of Chemical Catalysis and Biocatalysis at NSF for his support of the workshop. Thanks are also due to the speakers at the workshop, and to all those who attended and provided ideas and insights into the future role of catalysts in biorenewables conversion. Their participation made the workshop both worthwhile and enjoyable.

Workshop Overview and Objectives

This workshop was held on April 13 and 14, 2004 near the National Science Foundation headquarters in the Washington, D.C. area for the purpose of identifying U.S. capabilities, needs, and strategies for using catalysis to produce value-added chemicals from biorenewable feedstocks. The workshop brought together approximately 45 scientists and engineers from academia, industry, and national laboratories, all involved in state-of-the-art chemical catalysis and biocatalysis research relevant to chemicals production from biorenewables. The list of workshop attendees and their affiliations is given in Appendix A. These workshop attendees listened to presentations describing recent work in heterogeneous catalysis for biorenewables and participated in informal working groups to discuss specific ideas and formulate directions and challenges for future catalysis work in the field of biorenewables conversion. The full workshop program is reproduced in Appendix B, and the presentations made at the workshop, along with other documentation, are available at the workshop web site at www.egr.msu.edu/apps/nsfworkshop.

The objectives of the workshop are

1) to identify and communicate critical needs for building scientific and engineering capabilities in catalysis to convert biorenewables to chemical and other value-added products;
2) to assess the current state of chemical (heterogeneous and homogeneous) catalyst and biocatalyst science and technology that is applicable to biorenewables;
3) to identify curricular and workforce needs to prepare engineers and scientists for a biorenewables-based chemicals industry;
4) to develop and prioritize goals and directions for the development of effective catalysts and catalytic processes for biorenewables conversion, including the integration of chemical and biochemical catalysis in the future "biorefinery."

These objectives pertain directly to the broader goal of the workshop, to prepare U.S. industry and academia for the massive, inevitable transition from petroleum to biorenewables as the raw materials for fuels and chemicals production. While an exact time frame for this transition is impossible to predict, there is no doubt that it will occur, and that its occurrence will take place gradually as petroleum becomes more expensive and the technologies for biorenewables conversion advance. In a more concrete sense, this workshop was intended as an initial gathering to identify several specific directions for catalysis research at the National Science Foundation and elsewhere in the U.S. and to set the stage for future workshops that will more fully define the research effort required to facilitate the petroleum-to-renewables transition.

Summary Recommendations

The major recommendations from the workshop for continued development of catalysts for biorenewable fuels and chemicals are presented here. The recommendations are listed by subtopics – these subtopics were formulated in setting the workshop program and constitute the major emphasis areas of breakout groups and presentations at the workshop. Greater detail regarding each subject area is presented in the remainder of the report, but the key recommendations are summarized here.

Feedstocks and Intermediates

Catalysts must be developed that facilitate selective conversion of all biomass components including carbohydrates (cellulose and starch), hemicellulose (and associated C5 platform carbohydrates), lignin, proteins, and oils to useful products.

There is a need to identify suitable platform intermediates for producing families of product species. Better collaboration between industry and academic/national laboratory scientists and engineers will aid in targeting specific platform species.

Direct catalytic conversion of carbohydrate feedstocks to products with high selectivity is an important goal. The ability to selectively functionalize or defunctionalize carbohydrates at a specific carbon site using heterogeneous catalysts is required. Direct modification of natural polymer chains (starch, cellulose, etc...) without first destroying the carbon backbone will lead to new and useful materials; heterogeneous and homogeneous catalysts that facilitate such transformations are desired.

There are needs for tighter integration of chemical catalysis with biocatalysis and biological processes. For example, the catalytic conversion of organic acid salts, formed in fermentation, directly to value-added products would be of significant value.

Reactor Design and Process Considerations

There is a need for better design and modeling of multiphase reactor systems for biorenewables conversion. This includes better characterization of mass and heat transfer and better understanding of fluid hydrodynamics and residence time distributions. Design of catalyst particle size, shape, and pore size distribution must be integrated into the design of multiphase reactors.

New processing strategies and modeling capabilities are required to handle the diverse combinations of feedstock properties, fluid rheology, solids handling, and biological processes associated with biorenewables conversion.

New separation methods, including combined simultaneous separation and catalytic reaction such as reactive distillation, must be developed and encouraged for biorenewables conversion.

Catalysis for Energy and Fuels

The universal catalyst requirements for biorenewables conversion to fuels are the abilities to 1) selectively remove excess oxygenate functionality from biomass feedstocks, and 2) form products with liquid or gas properties suitable for fuel utilization.

A complementary need exists for catalysts that take advantage of inherent functionality to improve fuel yield and quality – including selective condensation to larger molecules and selective C-C or C-O bond cleavage.

There is a need for more effective heterogeneous catalysts and processes for reforming biomass to hydrogen and alkanes with high yields.

Stable and effective heterogeneous acid and base catalysts are needed for the development of continuous biodiesel production schemes.

Novel Catalyst Oxides and Support Materials

Aqueous phase reactions involving biorenewables require catalysts and supports that are hydrothermally stable over a wide range of pH and temperature. While carbons have been primarily used in prior work for aqueous phase catalysis, metal oxides such as zirconia and other non-traditional materials should be examined as candidate supports because they can offer superior properties in some circumstances.

There is a need to develop support materials with appropriate texturing or surface modification to control the reaction environment in the pore, particularly the degree of hydrophobicity.

Carbon support materials with controlled pore structures and pore size distributions must be developed to facilitate better mass transfer, make possible shape selectivity, and to better control reaction environment in the pore.

Highly porous polymeric supports should be examined as supports for low-temperature biorenewables conversion processes. Inorganic-organic hybrid supports and catalyst systems should be designed to take advantage of synergistic properties not attainable with single-component catalysts or supports.

Integrating Biocatalysis and Chemical Catalysis

There is need for better collaboration between researchers in chemical catalysis and biocatalysis.

The issue of biogenic fermentation impurities in downstream catalytic processes must be addressed – both through design of impurity-tolerant catalysts and through “process-friendly” fermentations developed in collaborative efforts.

Catalysis in the biorefinery would be aided by advances in biological processes that include 1) organisms with improved production rates; 2) organisms that function at extreme pH and temperature ranges, particularly low pH fermentations; 3) organisms with improved product specificity via genetic manipulation; and 4) improved fungal fermentations and aerobic fermentations.

Methods for selectively withdrawing and recovering a single component from fermentation media would enhance the ease of conducting downstream catalysis and thus increase overall biorefinery viability.

The concept of "one-pot" combined chemical and biological conversion reactions needs to be explored.

Substrate-catalyst specificity: Chirality and Biomimetic Character

The development of inorganic "synthetic enzyme" catalysts is a long-term goal. Such catalysts would facilitate highly selective conversions with potential advantages over real enzymes of improved thermal stability, lower cost, viability in a wider variety of reaction media, and the ability to carry out reactions for which biological enzymes do not exist or are not well-suited.

There is need for chiral catalyst materials – for methods to develop intrinsically chiral catalyst surfaces and to transfer chirality from the catalyst surface to substrate products.

There are opportunities to advantageously apply and control the natural chirality of biorenewable feedstocks to catalytically convert them to products of specific functionality. For example, polymer properties are controllable via appropriate manipulation of feedstock chirality and polymer tacticity.

Analytical Tools for In-situ Catalyst and Reaction Characterization

There is great need to develop and apply high-resolution *in-situ* characterization techniques to observe and quantitate adsorption and reaction at solid surfaces in liquid media, particularly water. Surface-sensitive spectroscopies that can discriminate between compounds in bulk solution and those bound at the catalyst-liquid interface will be critical and merit substantial new investment.

Understanding reactivity of biorenewable molecules requires spectroscopic and labeling methods that can distinguish among similar sites within complex molecules, such as different hydroxyl groups on sugars. Spectroscopic characterization of activation of specific C-H, C-O, and C-C sites in biorenewable substrates will be critical in developing selective conversion chemistry. Similarly, detection of selectivity among chiral and prochiral sites will be the key to practical catalytic processes yielding (typically high-value) optically active products.

Time-resolved methods (IR, Raman, EXAFS) and hardware to follow the sequence of reactions at catalyst-liquid interfaces will be key complements to classical kinetic studies of mechanism. For fast reactions, new strategies for coherent reaction initiation will be needed as well.

Heterogeneity of catalytic sites multiplies the above spectroscopic challenges enormously. Identification and characterization of structurally and chemically well-defined model catalyst surface-substrate systems representative of biorenewable systems would simplify analysis of the complex conversion reaction chemistry of catalytic biorenewables processing.

As with heterogeneous catalysts, there is a need for spectroscopic tools to characterize enzyme structures and active sites. Exploration of structural and catalytic equivalencies and complementarities between enzymatic and heterogeneous catalytic mechanisms would also help to accelerate both fields' progress.

Computational methods for biorenewables

Closer coupling between theory and experiment in the resolution of surface intermediates, surface structure and their *in-situ* changes during reaction must be facilitated**.**

The modes of physisorption and chemisorption of platform chemicals and their potential products onto catalyst surfaces must be established, including the understanding of functional group orientation on the catalyst surface, the identification of sites to which functional groups attach, and the preference for adsorption on different crystal faces and on different metals. Adsorption energies at different orientations, conditions, and on different metals must be calculated.

The surface reaction chemistry of platform feedstocks, including identification of stable reaction intermediates and the elementary reaction steps involving activation of specific C-H, C-C, or C-O bonds, must be examined. Catalyst surface features that activate specific reactions such as dehydration, hydrogenolysis, oxidation, and condensation reactions must be identified.

There is need to computationally distinguish the features of adsorption and surface reaction that retain, disrupt or add chirality.

The effect of reaction medium on surface adsorption and reaction intermediate formation and stability must be examined.

Correlations between metal/support properties and chemisorption affinity/reactivity must be elucidated, including the influence of bimetallic and multi-metal catalyst compositions and the influence of the support in catalyzing reactions and in affecting the pore reaction environment.

The modeling of enzyme structures and enzymatic reactions must be initiated. The use of computations to identify promising biomimetic analogues and the means to encapsulate or immobilize enzymes in heterogeneous frameworks are also pertinent objectives.

<u>Curricular and workforce needs</u>

To prepare professionals for a biorenewables fuels and chemicals industry, chemical sciences and engineering educational programs must place greater emphasis on

- biology, bioprocessing, fermentation, and enzymatic systems
- carbohydrate, protein, and lipid chemistry
- plant science

- “green” processing, sustainability, and life science assessment
- Homogeneous catalysis, acid-base catalysis, shape selectivity, and other diversified aspects of catalyst science

Universities must develop closer ties with the biorenewables industry to facilitate communication of workforce needs to the academic environment so that they can be addressed in a timely manner.

Students must develop improved capability for generating and managing intellectual property, including 1) patent searching and analysis; 2) data collection and recording; 3) writing patent applications and understanding licensing and IP transfer mechanisms.

Graduate programs should encourage graduate students working in biorenewables research to take more industrial internships and to work in research teams as part of their graduate education.

Grand Challenges

Three ‘grand challenges’ for catalysis research and development in biorenewables are presented here. These research challenges describe broad, far-reaching problems that when successfully addressed will greatly enhance the prospects for successful emergence of biorenewables-based fuels and chemicals industries in the U.S.

1. Develop catalysts to selectively alter or remove functionality at specific molecular sites of biorenewable feedstocks – thus making possible a wide variety of products ranging from slightly modified (e.g., based on existing biomass structure) to fully deoxygenated chemicals and fuels.

2. Develop catalysts and process concepts to utilize all components of biorenewable feedstocks, including the selectively disassembly of complex biomass species such as lignin, protein, and chitin to useful chemical building blocks.

3. Develop spectroscopic techniques to elucidate the nature of the catalyst-fluid interface for liquid phase biorenewable conversion reactions, including the identification of active catalyst surface structures, adsorbed substrates and reaction intermediates, and solvent effects on reaction.

Background

Environmental and national security concerns, global political instability, and a diminishing supply of fossil fuels are leading our nation to search for alternative sources for fuels and chemicals. The use of renewable plant biomass to generate alternative fuels and chemicals is appealing, but comes with significant and as yet unmet technical and economic challenges. Nevertheless, fuels and chemicals derived from biomass are ultimately greenhouse gas-neutral and renewable, and thus offer a viable, sustainable solution to our long-term energy and materials needs.

Domestically available biomass resources provide an opportunity to reduce our dependence on fossil fuels; however, more energy- and cost-efficient processes are needed to convert biomass into fuels and chemicals. At present, renewable resources are used as raw materials for only about 3% of fuels and chemicals produced in the U.S. This percentage is expected to grow: according to the U.S. DOE Vision 2020 statement, 10% of chemicals should come from renewables by the year 2020, and 50% by the year 2050. The Roadmap for Biomass Technologies (1), authored by 26 leading experts from academia, industry and government agencies, has predicted a gradual shift from a petroleum dependent infrastructure to a more biorenewables-based economy. They estimate that by 2030, 20% of transportation fuel and 25% of chemicals will be produced from biomass. This shift is already transpiring in Europe, where it has been mandated that 10% of the fuel consumption in the European Union be replaced by alternative fuels by 2020 (2).

Significant economic barriers exist to replacing mature petroleum-based technology with a biorenewables industry. It is certain that shifting away from a petroleum-based economy will have a tremendous impact on the environmental and political issues currently affecting the United States; however, it is still unclear what the cost of renewable processes will be to consumers and society. The current delivered cost of biomass is $20-36 per boe (barrel of oil energy equivalent), which is below the current price of crude oil ($45-55 per boe). Much research is being done on developing high yield biomass growth crops; it has been predicted that crops will soon be available that have yields twice that of current crops. In addition, a large amount of low-cost (or even free) biomass, with an energy content of 14.3 quads/yr (U.S.), is currently available as waste material. Thus, sufficient biomass resources are available at costs competitive with petroleum – the challenge remains to efficiently convert those biorenewable resources to useful products. The potential impact of the sustainable production of energy and valuable materials (e.g., chemical intermediates for polymers, fibers, pharmaceuticals, etc.) from biomass is enormous, and would lead to a considerable decrease of U.S. dependence on imported fossil fuels. The development and availability of efficient conversion processes, some of them based on catalysis, is a critical component that will drive the transition from petroleum to a sustainable, bio-based economy.

The U.S. currently produces approximately 140 billion kilograms of industrial chemicals each year, consuming somewhere around 900 million barrels, or about 10%, of total U.S. crude oil use. Current bio-based chemicals production, which as stated above accounts for about 3% of total U.S. chemicals production, is dominated by corn wet milling, which is responsible for both fuel ethanol production, processed foods such as sweeteners and starches, and fermentation products such as lactic acid and citric acid. Fuel ethanol production from corn is growing very rapidly in the U.S., and there are indications that momentum for biobased chemicals production is building as well. Ventures such as Nature Works' polylactic acid production and DuPont's recent announcement of an integrated 1,3-propanediol – ethanol biorefinery, as well as enhanced participation by large U.S. industries in commercially-driven federal grant programs, are all signs of expanded biorenewables chemical production. Beyond corn, some biorenewables-based chemicals production from other crops exists, but on a much smaller scale except for biodiesel production from soybeans and other oil seeds. Currently, there are no commercial facilities producing monomer carbohydrates from cellulosic biomass for fuels or chemicals production. Fortunately, the biomass source for carbohydrate-based chemicals production is, for the most part, unimportant since any carbohydrate can eventually be converted to glucose.

At maturity, a biorenewables-based industry will consist of a series of production facilities or "biorefineries," with fuels and chemicals production integrated such that energy requirements of each process are balanced with those of other processes and chemical intermediates of one process are either separated as final products or utilized elsewhere in the biorefinery. In this way, the future biorefinery will be analogous to the petrochemical refinery of the present: a highly integrated system of processes optimized for energy efficiency and resource utilization. However, whereas the petrochemical refinery has reached its present state of efficiency by continuous improvement over the past 50 years, the biorefinery is in its infancy.

For the biorefinery to come about, a diverse range of processing capabilities, including both chemical conversions and separations, must be available. In particular, the ability to selectively transform biomass feedstock materials to specific products, using both biocatalytic and chemical catalytic routes, is required. Biocatalysis, with its intrinsically high selectivity, will be primarily used to convert carbohydrate raw materials to low-cost intermediates such as organic acids, and to produce high-value fine and specialty products via secondary pathways. Heterogeneous catalysis, with its versatility and robustness, will play a key role in secondary conversions of intermediates to higher-value products as well as in direct conversion of feedstocks. Homogeneous catalysis will play a role in applications directed primarily at high-value products. These catalysts and catalytic processes must be developed in order to provide the biorefinery the capability and flexibility to adjust and optimize performance in response to feedstock changes and market demands. One objective of the workshop was to begin to more clearly define the roles of heterogeneous and homogeneous chemical catalysis and their interplay with biocatalysis for the production of fuels and chemicals from biorenewables.

There is a tremendous knowledge base pertaining to catalytic reactions of hydrocarbon-based materials, and many recent scientific advances provide powerful tools for new catalyst discoveries. Using spectroscopic and associated analytical tools, researchers can characterize catalysts at the nanoscale level under actual reaction conditions. Theoretical methods such as density functional theory have been developed over the past 10 years to elucidate the surface chemistry for existing catalytic processes and to predict the performance of new materials for new catalytic applications. High-throughput techniques allow rapid screening of a large number of catalytic materials. New synthesis techniques are being used to develop innovative catalytic materials. Bimetallic catalysts are being developed which are cheaper and more active, selective and stable than monometallic catalysts. These recent advances in synthesis, characterization, and design of new materials at the nanoscale can now be applied to develop new catalysts and catalytic processes for the biorefinery of the future.

The feed materials and conversion pathways required for the biorefinery are for the most part fundamentally different than traditional petroleum-based conversions for which much of catalyst science has been applied. In contrast to hydrocarbon feedstocks that exhibit substantial thermal stability and volatility, bio-based feedstocks are characterized by a high degree of oxygenation, thermal fragility, and low volatility. Reactions must therefore be conducted at lower temperatures and in condensed phase: these conditions require different catalyst compositions and structures to facilitate reaction selectivity and alleviate mass transport constraints, and different characterization, analytical, and spectroscopic methods to gain information about catalyst properties, reaction mechanisms, and surface intermediates. At present, the understanding of condensed phase catalysis for biorenewables is underdeveloped, and there thus exists need to build capabilities ranging from fundamental catalytic chemistry to process optimization. This workshop constitutes an initial effort to meet that need by setting directions for research in catalysis applied to biorenewables conversion.

References

1. Biomass Research and Development Technical Advisory Committee, "Roadmap for Biomass Technologies in the U.S.", U.S. Government Report (December 2002).
2. J. Rostrup-Nielsen, “Fuels and Energy for the Future. The Role of Catalysis”, Plenary Lecture #4, 13th International Congress of Catalysis, Paris France (2004).

I. Feedstocks and Intermediates

The replacement of petroleum with biorenewables for fuels and chemicals requires the identification of feedstock, intermediate, and product species that replace their fossil counterparts. Feedstock species must be identified that are consistently available at low cost, chemically and thermally accessible, and consistent in composition. Current choices include corn and cellulosic biomass for C5 and C6 monomer carbohydrates, soy, canola, rapeseed, palm, and others for oils (triglycerides), and numerous other plant components for specialty products used as flavorings, nutraceuticals, and cosmetic additives. For carbohydrate feedstocks, from which it is generally agreed most biorenewable commodities and many specialty chemicals will be generated, a significant infrastructure exists around corn processing. Starch from corn, which contains α-1,4 glucose linkages, is readily hydrolyzed to glucose monomer, thus making possible the current advances in biorenewable chemicals production. It must be noted, however, that the cost of corn, resulting from the agriculturally intensive methods used in its production, constitutes an economic barrier for entry into many chemical markets. Many believe that the cellulosic component of biomass, which has β-1,4 glucose linkages and exists in crystalline form, will be the ultimate biorenewable feedstock, but efficient breakdown of cellulose to glucose is still a challenge after twenty-five years and several billion dollars of effort. Some progress has been made toward low-cost enzymatic hydrolysis of β-1,4 linkages, but chemical hydrolysis routes generally have yielded disappointing rates and selectivities. Outside of cost, the source of C6 carbohydrate for chemicals production via chemical catalysis has little impact, as catalysis is typically implemented downstream of feedstock processing.

All plant-based feedstocks include multiple classes of chemical compounds or structures; e.g. protein, fiber, and starch in corn, and cellulose, hemicellulose, and lignin in woody biomass. For maximum economic advantage, all components of the raw material must be converted to value-added products. For instance, at present lignin is burned to provide energy for cellulose hydrolysis process; the ability to produce and develop markets for products from lignin, whether specific chemical species or mixtures of species, would be a major step forward in biorefinery economic viability. Similar needs exist for the protein and fiber components of corn, for the C5 (hemicellulosic) carbohydrate stream from woody biomass, and for other complex biorenewable materials such as chitin. The application of catalysis and biocatalysis to the problem of successfully disassembling these complex materials into useful products represents a significant and underdeveloped area of research.

An example of catalysis for separation of biomass components is given in Figure I.1, in which the selective oxidation of lignin is carried out via use of a catalyst that effectively undergoes a red-ox cycle in the course of reaction. The applicability of catalysts and processes such as that shown should extend to agricultural wastes (manure, etc.) and industrial and municipal wastes (paper, sawdust) to provide relatively higher purity materials at lower cost than is currently possible.

The second major challenge in charting the future biorefinery is identifying platform intermediates and their corresponding product families. As in petroleum refining, platform species must be developed as building blocks based on carbon number – examples of biorenewable building blocks are shown in Table I.1. Production of these platform species will take place via biological or chemical conversion pathways or a combination of the two

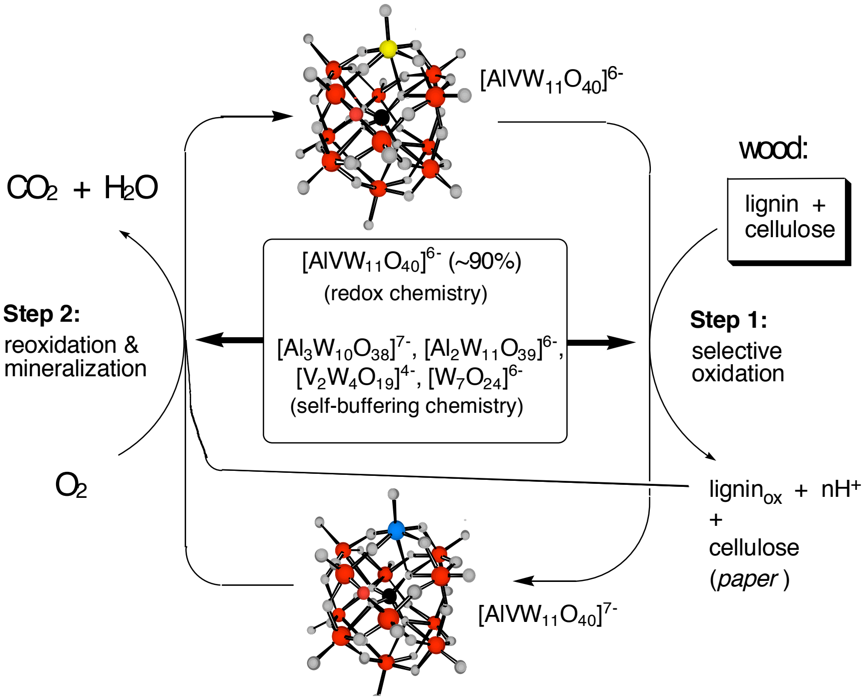


Figure 1.1 Selective, thermodynamically stable, self-buffering system for selective use with O_2 as the oxidant and H_2O solvent (C. Hill, Emory Univ.)

Table I.1 Chemical building blocks from biorenewable feedstocks

Carbon No.	Petroleum	Biorenewables
1	methane	CO, CH_3OH
2	ethane, ethylene	acetic acid, ethanol
3	Propane, propylene	lactic, 3-HP acids, glycerol, 1,3-propanediol
4	Butane, isobutylene	succinic, levulinic, hydroxybutyric acids
5		xylose, arabinose
6	benzene, adipic acid	glucose, fructose
>6	toluene, xylenes	triglycerides

The platform species must be relatively easy and economical to produce and must have functionalities that facilitate their conversion into multiple products of commercial interest. Identifying potential new platform species remains a problem of significant importance and uncertainty, as there is limited understanding of the links between molecular structure, applications, and economics. In the corporate world, economics drive the commercial viability of specific targets, but identification of applications, market potential, and processing concepts for broader classes of compounds are strengths of large corporations that non-industrial scientists have little familiarity with or expertise in. Collaboration between industrial scientists and universities and national laboratory researchers will provide a route to better focusing catalysis research on viable platform species from biorenewables. Better communication and integration of the biological processing community and the catalysis community must also be facilitated in order to target the most attractive platform species.

Carboxylic acids, produced primarily by microbial fermentation from carbohydrate feedstocks, constitute a class of chemicals that has received substantial attention as biorenewable platforms. Essentially theoretical yields of organic acids such as lactic acid and succinic acid from glucose have been achieved, and the 300 million lb/yr lactic acid plant at Cargill's Blair, Nebraska facility signals the arrival of lactic acid as a biorenewable commodity. Fermentation typically requires addition of nutrients and pH adjustment to maintain production rate, resulting in a raw product stream with substantial impurity content and the organic acid in salt form. Acidification and several purification steps are thus required to isolate the desired product – adding substantial cost and often reducing product yield. Improvements in these steps, either through microorganism modification to lower nutrient requirements and increase tolerance to low pH, or through more efficient processing, including novel desalting (e.g. via ester formation) and selective reaction of impurities, would of course enhance economics. An even more attractive alternative would be the development of catalysts, reactor configurations, and reaction conditions that would facilitate direct conversion of organic acid salts and would tolerate the presence of low concentrations of residual carbohydrates, proteins, and other byproducts without loss of performance. Such catalyst development requires fundamental research that accounts for reaction thermodynamics (acids vs. salts), adsorption behavior of various biogenic species onto the catalyst surface, and familiarity with biological processes producing the platform species.

An interesting example of an organic acid as a platform species is levulinic acid; a simple “family tree” of products that can be produced from levulinic acid (Manzer, DuPont) is presented in Figure I.2. A process for levulinic acid production via thermochemical/catalytic transformation of glucose is currently under development by Biofine, Inc.

A second platform species is 3-hydroxypropanoic acid (Cameron, Cargill) produced from glucose via a genetically modified microbial pathway. Cargill is making a major push to develop 3-HP as a versatile route to several products that will replace petroleum-derived feedstocks. The family tree of chemicals from 3-HP is given in Figure I.3.

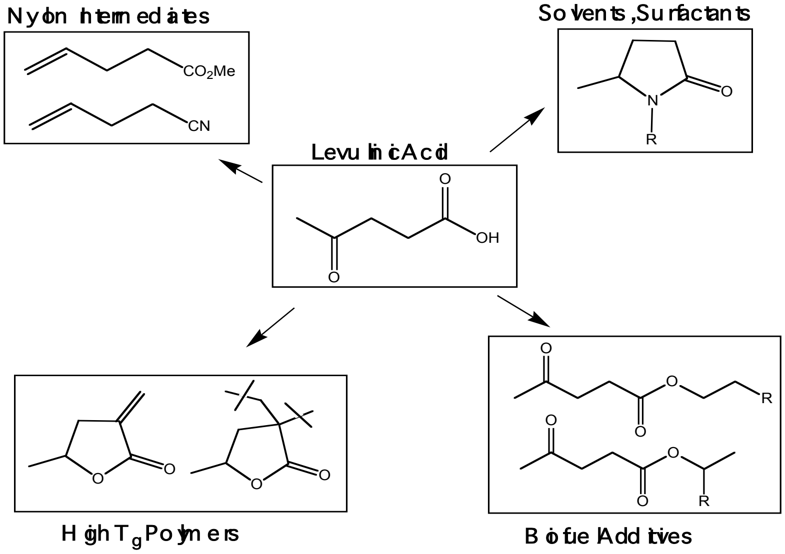


Figure I.2. Levulinic acid as a platform for biorenewable chemicals production (L. Manzer, DuPont, USA)

For both of these feedstocks, as with other biorenewable platforms, effective catalysts and processing conditions for a variety of selective conversion pathways including hydrogenation, oxidation, condensation, and polymerization reactions are required. For more details on these specific systems, the reader is referred to the respective presentations at the workshop web site.

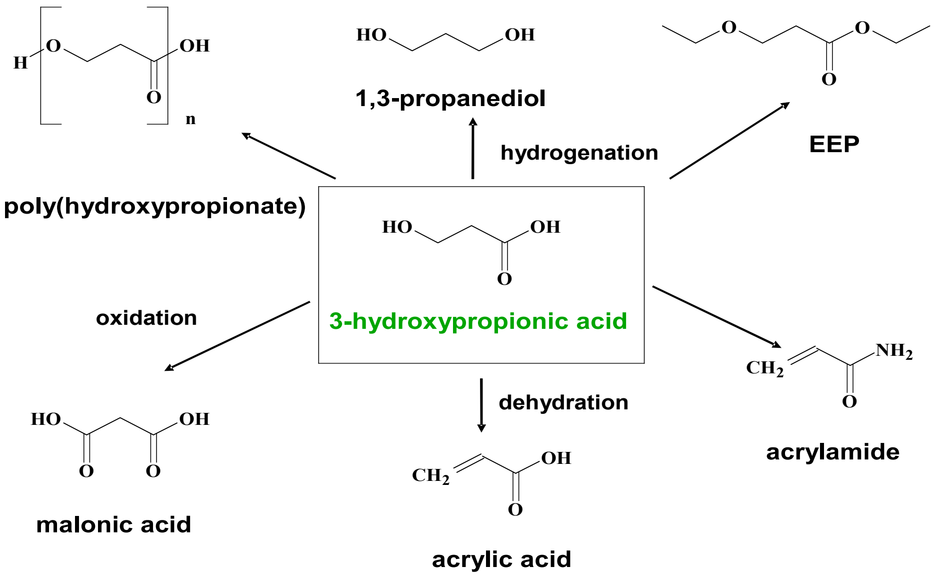


Figure I.3. The chemical products of 3-hydroxypropionic acid (D. Cameron, Cargill, USA)

Another class of platform species suitable for direct catalytic conversion is the C5 and C6 carbohydrate monomers. Potential conversion routes include substitution at a specific hydroxyl group on the sugar, C1 hydrogenation to sugar alcohol, C1 oxidation to acid (glucose to gluconic acid), and hydrogenolysis to produce a mixture of C2, C3, and C4 alcohols, diols, and polyols. There is need to develop catalytic chemistry that selectively involves each of the carbons of the carbohydrate monomer (e.g. selective substitution at C2 vs. C3). Selective functionalization of the sugar molecule could greatly advance the use of carbohydrate monomers such as glucose for chemical feedstocks, an attractive proposition because they are the least expensive class of biorenewable platform species.

The direct use of biorenewable feedstocks with only modest modifications constitutes another route to biorenewable chemicals. More specifically, the use of plant-based polymers in products without first breaking them down into monomer represents a potentially fruitful route to new products. In Figure I.4, the concept of directly modifying starches (Gallezot, CNRS, France) is presented. The ability to functionalize and derivatize biorenewable raw materials such as starches, cellulosics, oils, lignins, and biopolymers such as PHAs, would constitute an important advance for the biorenewables chemical industry, as the backbone chemical structure is already in place and only relatively straightforward substitutions that do not involve the breaking of carbon-carbon bonds would be required.

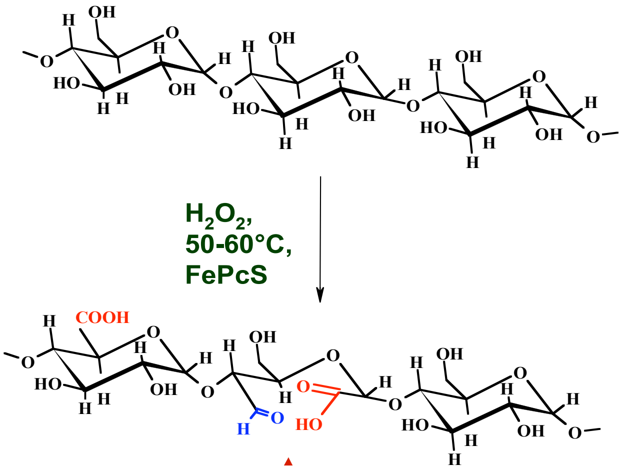


Figure I.4. Increased starch hydrophilicity via catalytic oxidation of vicinal diols to carboxylic acids and aldehydes (P. Gallezot, IRC-CNRS, France).

II. Reactor Design and Process Considerations

The development of the future biorefinery hinges on attractive chemical and catalytic routes for product formation. While biological processes provide high selectivity to targeted species, the robust and flexible nature of inorganic chemical catalysis makes it a critical link in development of product families that will make the biorefinery viable. The nature of these catalytic processes will likely be fundamentally different than those historically used in petroleum processing, as properties of biorenewable feedstocks are fundamentally different than those of traditional petroleum-based species. The low volatility and/or thermal fragility of substrate carbohydrates, proteins, and oils; the importance of water as the medium of necessity or choice in most reacting systems; and the presence of solids and multiple fluid phases throughout processing – all of these are primary considerations in the development of catalysts and processes for efficient conversion to fuels and chemicals.

Reactor Design: Application of multiphase reactor systems are common throughout the chemical industry, with products valued in excess of $600 billion produced each year from processes involving these reactors. For biorenewables, the properties of reactive species involved in producing chemicals call for multiphase reactor configurations and separation concepts that are markedly different than those used in traditional petrochemicals production. In most cases, some level of design and modeling of these less-familiar reactor and separation processes is possible, but the understanding of their behavior is by no means complete. A broad need for the biorenewables industry is thus the capability to design multiphase reactor systems and the catalyst geometries that accommodate the attributes of biorenewables mentioned above: low volatility, preferential solubility in water, thermal fragility, and multiple reaction phases.

While some reactions involving biorenewable substrates, for instance condensation reactions, disproportionations, and acid-base catalyzed conversions, take place within a single fluid phase (along with a solid catalyst), there are significant classes of reactions (for example, oxidation and hydrogenation) that necessitate liquid and gaseous fluid phases or multiple liquid phases in addition to the solid catalyst phase. These reactions require heterogeneous reactors such as trickle beds, spouting beds, bubbling beds, fluidized beds, and entrained liquid reactors to facilitate adequate contact between fluid phases and with the catalyst. Even with the prior work with these reactor systems, there is a need for better correlations of mass and heat transfer properties and for better characterization of reactor operation that can lead to better control of the reaction temperature, flow patterns, and substrate residence times. Thus, significant effort is required in building more rigorous models and new modeling approaches for multiphase reactor systems, and in developing new experimental methods to gain further insight into the details of the reactor properties.

One such approach to better understanding reactor behavior involves characterization of flow patterns in multiphase reactors via particle trajectories (Dudukovic, Washington Univ.). The method is represented in Figure II.1, in which a neutrally buoyant radioactive tracer particle is inserted into a bubble column reactor and its trajectory is followed by gamma-ray detection. The fundamental information acquired by this method facilitates a better understanding of fluid flow patterns and residence time, all necessary for suitable design of multiphase systems.

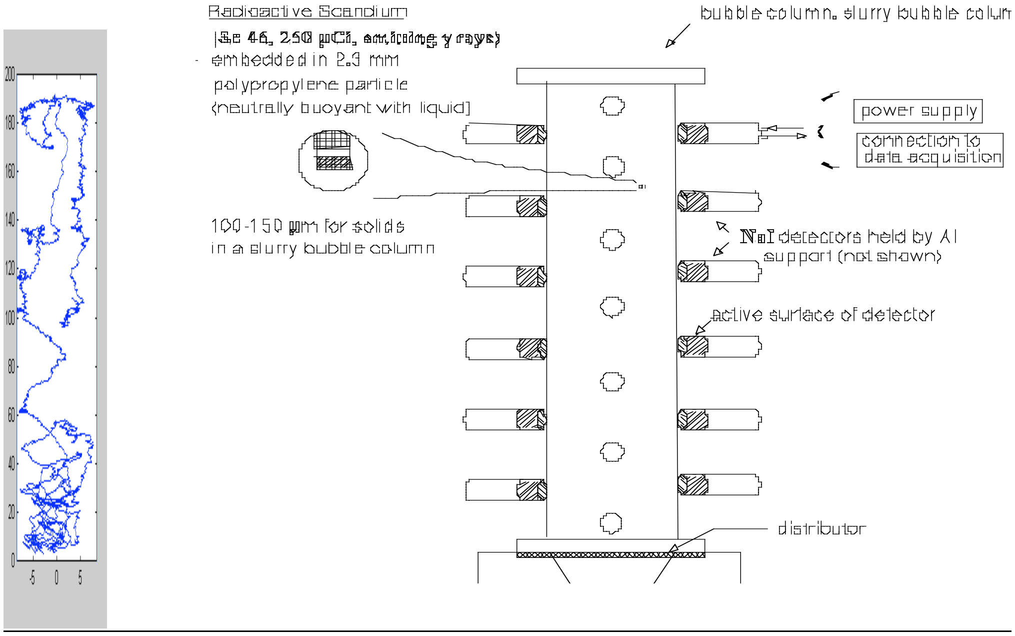


Figure II.1. Schematic of computer-aided radioactive particle tracking (CARPT) for characterizing flow patterns in multiphase reactors. The experimental reactor and analysis is shown on right, and a typical particle trajectory within the vessel is given on the left. (M. Dudukovic, Washington University, St. Louis, USA)

Similar techniques that probe details of reactor behavior are needed for more reliable design of biorenewable reactor systems.

In addition to systems where the catalyst is the solid material present, there is a need for reactor designs that facilitate the conversion of reactive solids to desired products. In this case, hydrodynamic and shear considerations are paramount along with mass and heat transfer between fluid and solid phases. In addition, solids handling and transport, including size reduction, feeding, filtering, and dewatering, are key aspects of these processes that must be better characterized.

More generally, mass and heat transfer rates play key roles in the overall conversion efficiencies in multiphase heterogeneous reactors, often dominating reaction kinetics as the rate-limiting steps in the system. A pertinent example is catalytic hydrogenation, which is particularly important in biorenewables conversion as the primary means of deoxygenating biomass substrates to their more petrochemical-like analogs. In hydrogenations involving three-phase systems, it is well-documented that gas-liquid hydrogen mass transfer and low hydrogen solubility in aqueous solutions dictate overall conversion rates. Lack of awareness of this phenomenon has led to improper commercial three-phase reactor designs that end up operating at conversions far below the desired design values.

Finally, the design of reactors for biorenewables must account for specific fluid and species properties in order to achieve a successful outcome. For example, high concentrations of biorenewable substrates, which may be advantageous for reactivity, can result in high viscosities that pose challenges in heterogeneous systems. Many fluids associated with biorenewables processing, such as starch solutions, exhibit highly non-Newtonian behavior that can radically alter design criteria. At the other extreme, very low substrate or impurity concentrations must often be dealt with. Biomass-derived feedstocks often contain a dizzying array of impurities in low concentrations; these impurities can have deleterious effects on catalyst performance. Thus selective removal techniques or means of efficiently concentrating the desired species must be developed so that practical reaction rates can be realized.

In regards to reaction media, the use of solvents other than water must be considered when possibly advantageous. Not only should “green” solvents readily available in the biorefinery (such as ethanol and acid esters) be considered, but media such as supercritical CO_2, ionic liquids, liquid polymers, and traditional organic solvents derived from petroleum should be contemplated if they provide unique or significant chemical or economic advantage over their “green” counterparts. Such solvent systems may provide advantages by facilitating miscibility of insoluble liquids, easing solvent removal and recovery, and exerting a favorable influence on reaction selectivity. An example is given in Figure II.2, in which a homogeneous hydrogenation catalyst is recovered and recycled through the use of supercritical CO_2 which is used to extract the product at the end of reaction (Jessop, Queens University). Finally, solventless reaction systems must be given consideration wherever possible, as they can result in the highest possible reaction rates and obviate the need for product purification in some cases.

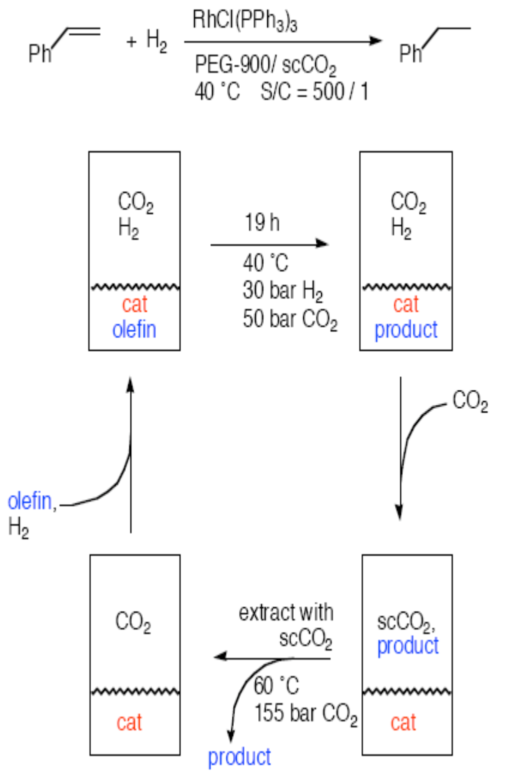


Figure II.2. The use of supercritical CO_2 to facilitate recovery and recycle of homogeneous hydrogenation catalysts (P. Jessop, Queens Univ., Canada

Process considerations: The development of catalysts and catalytic processes for biorenewables conversion must go beyond surface science and chemistry. Only through rigorous process synthesis and evaluation can the biorefinery become a viable source of fuels and chemicals for the 21st century. In that regard, there are needs to better define and more generally disseminate information on the unit operations that will prevail in the biorefinery. While many, including the reactors described above, are familiar to the engineering profession, there are others such as centrifugation, ion exchange, chromatography, and membrane separations that are less well-known. More widespread educational materials dealing with these separations, including workshops, short courses, textbooks, and published articles, would better prepare the workforce for biorefinery design.

Another class of operations for the biorefinery that requires further development is that in which chemical reaction and separation are carried out simultaneously. Reactive distillation, reactive extraction, and membrane systems can all provide advantages in biorenewables processing, particularly for the numerous equilibrium-limited reactions (isomerization, esterification, etc...) and product-inhibited reactions that occur in the biorefinery. Their application must be further explored and encouraged to optimize biorefinery operations. Somewhat more specifically, the ability to selectively remove one product or a class of products (e.g. protein fragments or carbohydrates) from a process stream or a reaction medium would have broad application in biorefinery operations, where actual feedstocks can contain an array of biogenic impurities. In a broader sense, recycling and in-situ product removal from chemical and biological reactors will all play a growing role, and research and development to examine these and the above combined reaction/separation processes is needed to best ascertain their role in the biorefinery.

In addition to familiarization with process operations, there is a need to develop standard methods of economic evaluation and life cycle analysis (LCA) of biorefinery processes. Reliable economics, grounded in a common database of equipment and raw materials costs, energy costs and utilization, and market analysis, would significantly enhance the ability of inventors and investors to evaluate the potential viability of new catalytic reactions and processes. In addition, the availability of unbiased LCA methodologies that give a realistic picture of process feasibility and impact would be a great step forward in the evaluation of these new processes.

In all of the above scenarios, process design, reactor design, and catalyst design must be carried out in an integrated fashion. The catalyst design must not only facilitate highly selective conversion of substrate to desired product, it must be compatible with the reaction environment and present in a physical form suitable for the reactor configuration. The reactor design must provide adequate mass and heat transfer, residence time, and flow patterns so that the catalyst performs as designed. Finally, the process must provide feedstocks of suitable composition to the reactor and must incorporate efficient product recovery to make the process economical.

III. Catalysis for Energy and Fuels

Production of ethanol via fermentation of biomass carbohydrates is currently the primary route for generating fuels from renewable biomass resources. Because of federal tax credits that have subsidized large-scale production, ethanol production from corn is a mature technology in which chemical catalysis plays a negligible role. On the other hand, ethanol production from cellulosic/woody biomass has yet to reach commercial viability despite twenty years of fairly intensive research, primarily because of the difficulty in liberating carbohydrate monomer from the cellulosic structure by either catalytic or biocatalytic means. In either case, fuel ethanol from biomass does not compete with petroleum gasoline on an equivalent energy basis, although recent spikes in crude oil prices certainly narrow the economic gap between the two.

Biodiesel is gaining attention as a renewable fuel in the U.S. and Europe; the recent biodiesel Federal tax credit of $1.00 per gallon will certainly accelerate the pace of research in U.S. biodiesel production. Acid and base catalysis plays an important role in biodiesel production, particularly for the transesterification reaction of the plant oil feedstock (triglyceride) to the fatty acid ester that is the primary component of biodiesel. To date, most biodiesel processes use soluble base as the transesterification catalyst, but this complicates product recovery and purification. There is a clear need for continuous biodiesel production using heterogeneous catalysts instead of soluble catalysts – this would significantly enhance the economic viability of biodiesel production. There are additional needs for catalytic routes to convert byproduct glycerol to value-added chemicals – disposal or sale of glycerol as the byproduct of biodiesel formation is a major challenge to large-scale biodiesel utilization in the U.S.

The continued development of cleaner, more efficient combustion schemes for biorenewable fuels is a target for future work. Strategies such as lean burn of fuel, alternative engine configurations, and reduction in particulate emissions from diesel vehicles are all areas of research for biorenewable fuels in which catalysis could play a role.

Catalysis for Fuel Cell Reforming: A significant advancement in renewable fuels and reduction in fossil fuel dependency can be made with the realization of fuel cell technology. The current fuel cell technology ranges from solid oxide fuel cells (SOFC) for high temperature applications to proton exchange membranes fuel cells (PEM) at temperature near 80°C. The fuels employed depend on the type of fuel cell, but include hydrogen, methanol, and ethanol. The ability to produce these fuels from renewable feedstocks is perhaps the greatest opportunity to reduce our dependence on fossil fuels. Currently, hydrogen and methanol production occurs via the formation of synthesis gas (H_2 + CO), which can either be further processed using Fischer-Tropsch technology (methanol) or purified (H_2) through CO elimination reactions including water gas shift and CO oxidation. The syngas generation steps involve high temperatures and pressures, with significant CO_2 production, and are only economically viable on large scales.

Recently it has been shown that syngas, CO-free hydrogen, and alkanes can be produced by reforming/partial oxidation of domestically available biomass-derived oxygenated hydrocarbons, ethanol, and biodiesel (1-5). Biomass-derived oxygenated hydrocarbons can be converted to hydrogen and/or alkanes by aqueous-phase reforming (APR), which is a single-step, low-temperature process (1-3) represented pictorially in Figure III.1. These studies indicate Pt-based catalysts are effective for producing hydrogen via APR. Various reaction pathways may occur, depending on the nature of the catalyst, support, feed and process conditions. Accordingly, it is possible to control the selectivity of the process to make hydrogen versus alkanes. Moreover, the catalyst and process conditions can be manipulated to control the molecular weight distribution of the product alkane stream.

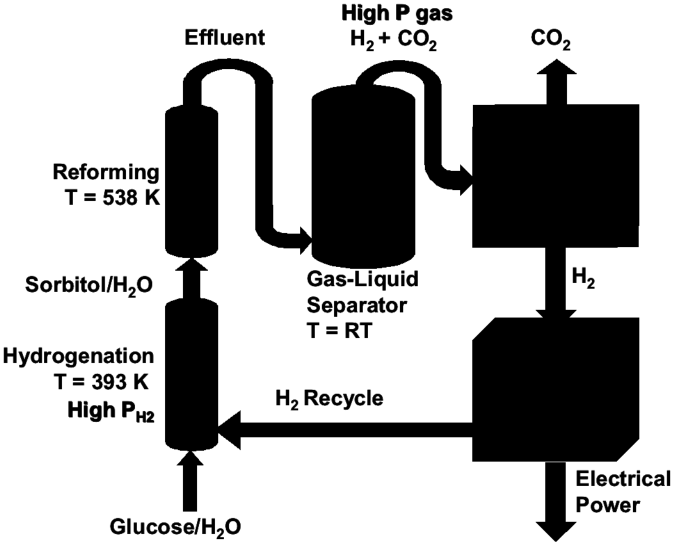


Figure III.1. Direct aqueous phase reforming (APR) of biomass sugars to produce hydrogen and ultimately electrical power (Dumesic, University of Wisconsin-Madison, USA)

Beyond its role as a motor fuel, ethanol must be considered an attractive candidate for reforming and hydrogen production. As seen in Figure III.2, essentially all combustion energy in glucose is retained in ethanol produced by fermentation, with the bonus that ethanol only retains 52% of the weight of the feed glucose. Autothermal reforming of ethanol has been demonstrated (4) with 100% selectivity and > 95% conversion over Rh/Ceria catalyst in millisecond contact time reactors. These reactions occur in the vapor phase with the addition of the fuel via an automotive injector. Similar to APR of biomass-derived oxygenates, the autothermal reforming reaction conditions were found to have a significant impact on the products generated. Only at low residence times and low temperatures could carbon, acetaldehyde, ethylene, CO_2 and H_2O formation be minimized. Haldor-Topsoe (5) recently reported a process in which they use a dual function dehydration/hydrogenation catalyst to convert ethanol and water in to ethane and ethylene, and then further convert these products via a reformer/shift/purification process to produce H_2 (5). The process uses recycled H_2 for the hydrogenation reaction; the recycle ratio was found to significantly impact the ethylene concentration. Although this process does not address the needs of portable power due to the necessity to further purify the hydrogen after the reforming reactor, they do demonstrate that ethanol can be converted to hydrogen simply and with high efficiency. Furthermore, the high energy cost currently associated with the water removal during the production of ethanol can be significantly reduced if the ethanol is to be reformed to produce hydrogen.

A figure analogous to Figure III.2 can be drawn for the reforming of biomass carbohydrates to liquid alkanes – showing that essentially all combustion energy from the carbohydrate feed is retained in the alkane product, but with less than one-half the weight. Catalysts to efficiently and completely convert carbohydrates to liquid alkanes via reforming are currently being sought.

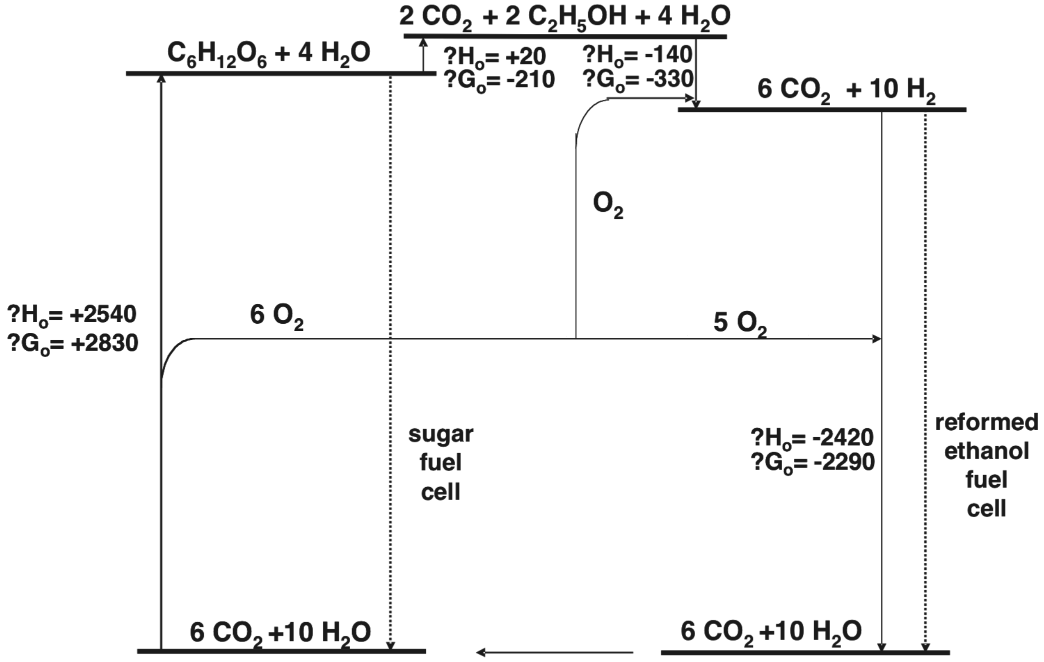


Figure III.2. Energy diagram showing challenges and opportunities for converting combustion energy in glucose (left) to useful power (fuel cell). Nearly all available combustion energy in glucose is retained in ethanol and is recoverable via the reformed ethanol fuel cell (L. Schmidt, Univ. Minnesota, USA).

<u>New Directions in Catalysis for Energy and Fuels</u>: The past 50 years of catalysis research have primarily addressed how to add functionality to non-renewable fossil fuel resources (e.g., partial oxidation). In contrast, biomass-derived compounds, such as carbohydrates, have excess functionality for use as fuels. Therefore, an important catalytic challenge for fuels applications is to identify new catalytic processes that allow the effective utilization of renewable biomass-derived compounds by: (i) taking advantage of the high inherent functionality of these compounds, and (ii) selectively removing the excess functionality of these compounds. Catalytic processes that take advantage of the high inherent functionality of biomass-derived oxygenated hydrocarbons for fuels applications are

1. Selective cleavage of C-C bonds versus C-O bonds
2. Selective oxidation of specific -C-OH groups to –C=O groups
3. Selective condensation processes, such as aldol condensation

Catalytic processes that selectively remove the excess functionality of biomass-derived oxygenated hydrocarbons for fuels applications are

4. Selective dehydration
5. Selective hydrogenation of specific C=C, C=O groups, and hydrogenolysis of C-OH sites

It is essential to develop new catalysts for the above processes that are stable under the high temperature aqueous conditions needed to process biomass-derived oxygenated compounds (e.g., 400 – 500 K), or that possess the functionality required to do the vapor phase reforming of ethanol and other biorenewables at lower temperatures . Furthermore, it is essential to develop new catalyst supports and active phases that do not sinter and are not leached into an aqueous environment. These and other desirable attributes are required for biorefinery catalysts for producing fuels and chemicals.

References

1. R. D. Cortright, R. R. Davda, J. A. Dumesic, Nature 418 (2002) 964.
2. G. W. Huber, J. W. Shabaker, J. A. Dumesic, Science 300 (2003) 2075.
3. G. W. Huber, R. D. Cortright and J. A. Dumesic, "Renewable Alkanes by Aqueous-Phase Reforming of Biomass-Derived Oxygenates", Angewandte Chemie International Edition 43, 1549 (2004).
4. G. A. Deluga, J. R. Salge, L. D. Schmidt, and X. E. Verykios, Science, 303 (2004) 993.
5. K. Asber-Petersen, S. Dahl, J. Jacobsen, and C. S. Nielsen, “Ethanol Reforming for Fuel Cells”, Paper 13f, AIChE Annual Meeting, Austin, TX, (2004).

IV. Novel Catalyst Oxides and Support Materials

The catalytic conversion of biorenewables introduces reaction conditions that are distinctly different than those typically encountered in the catalytic conversion of petrochemical feedstocks. In particular, the higher level of functionality in biorenewable-derived molecules necessitates lower temperature reaction conditions than used in petrochemical processing. Due to this lower temperature processing and the low volatility of many biorenewable feeds, conversions will usually have to be performed in the liquid phase with water being the most common solvent for solubilization of typically polar, high-molecular-weight biorenewable-derived species. The reaction conditions imposed upon biorenewable catalytic conversions will provide new constraints and opportunities for the support materials to be used for solid catalysts relative to the standard materials used for petrochemical catalysts. Perhaps most important is the need for aqueous-phase processing, which necessitates that the catalyst support must have adequate hydrothermal stability at the reaction temperature and solution pH. Also, the combination of liquid-phase processing and large reactant molecules will accentuate the mass transfer effects for these reactions. The mass transfer considerations will be further compounded in reactions such as hydrogenation in which the bio-based substrate and hydrogen must both have access to the catalytic sites. While liquid-phase conditions place reactivity constraints on support materials, the lower reaction temperatures decrease the thermal stability requirements compared to applications in higher temperature gas-phase processes.

The higher level of functionality present in bio-based feedstocks will likely necessitate a high level of reaction environment control at the active site to achieve high selectivities. This tight reaction environment control can be clearly seen with enzyme catalysts in which the amino acid residues not directly associated with the catalytic sites play an important role in modulating the reaction environment around the active site. Conceptually, the pores in the catalyst supports could play a somewhat analogous role in the creation of a favorable reaction environment. To achieve this goal, pore structure at the nanometer level and surface chemistry would need to be carefully controlled. Recent advances in materials synthesis could potentially be exploited to provide these well-defined porous networks.

Metal oxide supports, primarily alumina and silica, are widely used in petrochemical catalysts. This wide usage has led to well-characterized methods for tailoring the textural and surface properties of aluminas and silicas. The broad base of knowledge on these types of metal oxide supports would be advantageous to access in the development of catalysts for biorenewables. However, these materials will typically have poor textural stability under aqueous-phase conditions when reaction temperatures exceed about 150ºC, which can be further exacerbated by high or low solution pH. While some biorenewable conversions can be achieved at temperatures low enough that aluminas and silicas can be used, new strategies will be needed to improve their hydrothermal stability before they can be widely used in aqueous-phase reactions. Alternatively, different metal oxides with better inherent hydrothermal stability such as titania and zirconia will likely need to be explored. Multi-metal oxides must also be examined to ascertain desirable properties achievable as a function of composition. These materials may offer better hydrothermal stability, but they will be more expensive and will require additional research to achieve the understanding needed to tailor textural properties for target characteristics.

Carbon supports hold significant promise as catalyst supports that have the requisite stability in aqueous-phase systems. Historically, carbon supports have been synthesized by the processing of naturally occurring precursors such as coconut shells. While providing relatively reproducible textural properties, the design of specific textural properties could not be achieved. Recent advancements in synthetic carbons have allowed significantly better control over textural properties making them improved candidates for catalyst supports. Additional work is needed on the application of these synthetic carbons as catalyst supports as well as improvement of the mass yields of designed carbons from polymeric precursors.

The lower temperatures needed in the conversion of many bio-based feedstocks creates the opportunity for more extensive direct use of polymers as catalyst supports. Polymer supports can be stable in the aqueous phase and can be synthesized with controlled composition and structure. The polymer matrix can be used to support metal crystallites or to anchor homogeneous catalysts. Further work is needed to understand swelling of these materials under reaction conditions to insure the desired porous network maintains its integrity.

Other potential catalyst support materials are organic-inorganic hybrid materials and natural occurring materials. Organic-inorganic hybrid materials provide the opportunity to carefully tune textural and surface properties and can be used at higher temperatures than polymer supports. These materials, however, can suffer from the same hydrothermal stability problems experienced with some metal oxides. In contrast, natural occurring materials such as diatomaceous earth, calcium carbonate, hydrotalcites, and apatites have the requisite hydrothermal stability, but offer limited control over textural and composition properties.

V. Integrating Chemical Catalysis and Biocatalysis

An important aspect of the biorefinery is that both biological catalysts and chemical catalysts will be involved in the conversion of raw materials to final products. Yet in biorenewable conversion concepts to date, biological conversions and chemical conversions have been developed separately, with little collaboration or even communication between the communities of scientists and engineers working in the respective areas. One of the goals of this workshop is to initiate communication between the two fields, with the goal of understanding challenges and opportunities in each area and defining directions for future collaboration. This section addresses the process aspects of integrating biocatalysis and chemical catalysis in the biorefinery; the more fundamental issue of biomimetic catalysis is addressed in the next section of the report.

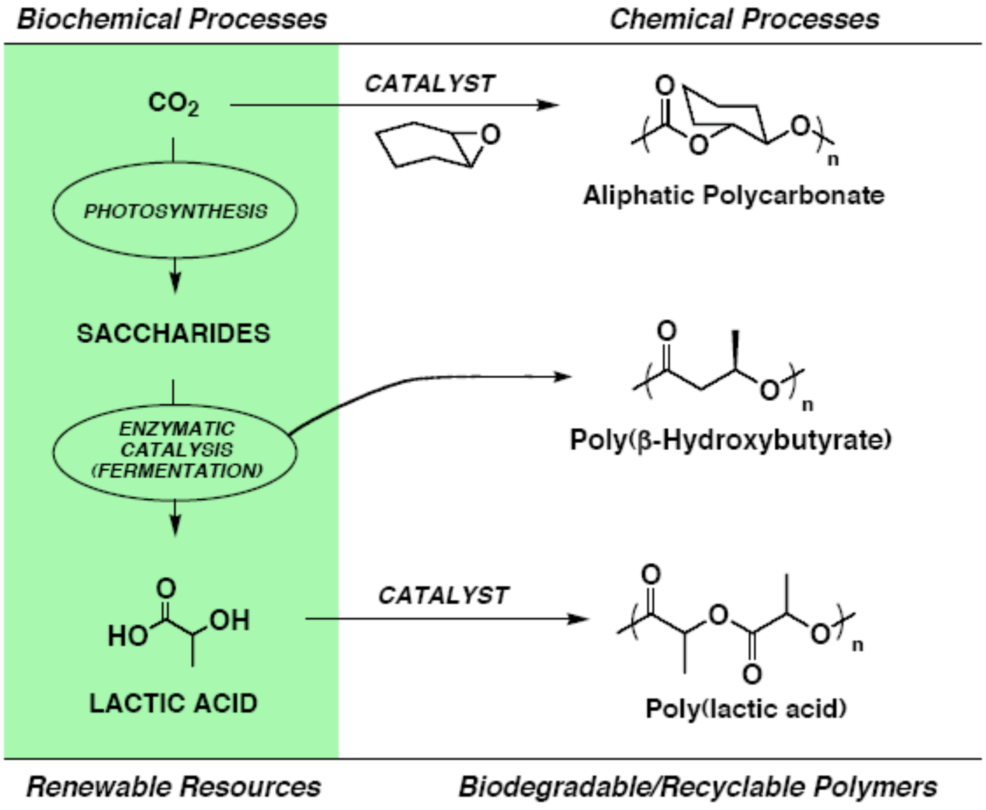


Figure V.1. Integration of chemical and biochemical pathways for the production of biorenewable polymeric materials (J. Coates, Cornell Univ., USA).

Figure V.1 gives an illustration of the synergy that can arise upon the integration of biological and chemical processes. While the Figure specifically illustrates formation of several polymer families from biorenewables, the same concept applies to nearly all biomass conversions in that biological and chemical conversions are closely linked. Clearly, the innovative integration of chemical and biological processes can lead to a far greater spectrum of value-added products than either of the processes alone.

In the above illustration and in many other biorefinery process concepts, the role of chemical catalysis is predominantly in the secondary conversion of intermediates produced by fermentation. A major challenge for chemical catalysis is gaining an understanding of the influence on catalyst performance of the complex mixtures of nutrients and biogenic impurities generated along with the desired product in a typical fermentation. These impurities can include carbohydrates, cell fragments, color bodies, proteins, amino acids, salts, and other minerals. As an example, Figure V.2 shows the effect of the addition of a small quantity of a model protein (bovine albumin) on the steady state performance of a Ru/C catalyst for the hydrogenation of lactic acid to propylene glycol in a trickle bed reactor. The decline in conversion over time corresponds to the protein filling the pore volume of the catalyst, physically blocking the substrate from reaching the active sites of the metal. Similar effects on catalyst performance, including irreversible poisoning of the catalyst by sulfur-containing amino acids such as methionine and cysteine, are observed for other impurities. In the worst case, these impurities have to be removed from the fermentate prior to subsequent catalytic conversions. However, with collaboration between catalysis and biological scientists, poison-resistant catalysts may be developed or, even more attractively, a more “catalyst-friendly” set of additives (nutrients, pH adjustor, etc.) may be developed for fermentation. All too often, these additives are simply scaled up from standard laboratory practice without concern for overall process viability; simplifying the nutrient mix could circumvent costly intermediate purification.

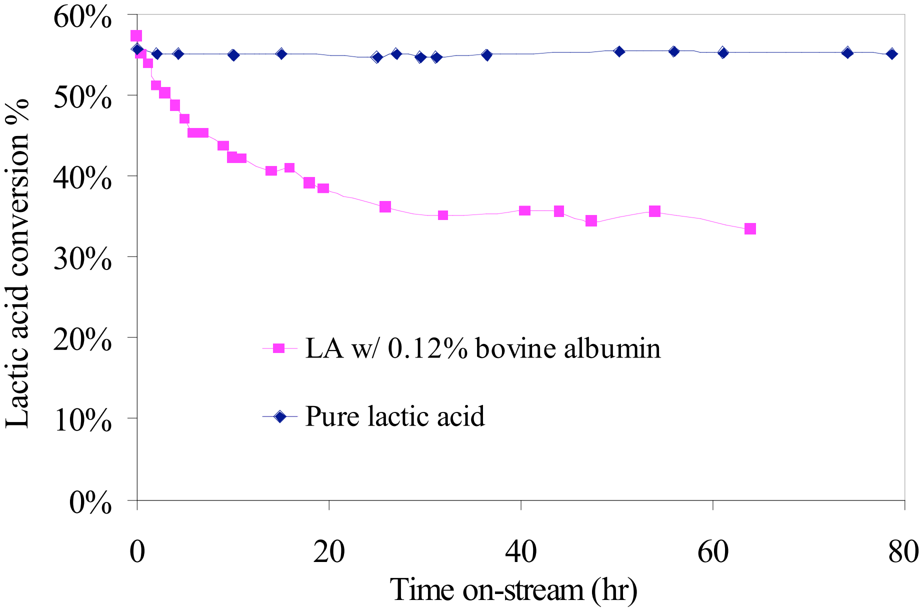


Figure V.2. Effect of protein addition on catalyst performance in lactic acid acid hydrogenation to propylene glycol - 150°C, 8.3 MPa H_2, catalyst: 5 wt% Ru on activated carbon. (D. Miller, Michigan State Univ., USA).

A complete discourse on research needs in biocatalysis is well beyond the scope of the workshop and this report; nevertheless several recommendations have come forth that are pertinent to overall biorefinery development and to the availability of fermentation products for downstream chemical catalysis. These include the global need for improved microorganisms with more rapid production rates and the ability to function in extreme environments (high temperature, elevated pressure, high shear or flow conditions), genetic modification of organisms to facilitate better specificity to desired products, better designs for fungal fermentations, better facilitation of aerobic fermentations, and development of low-pH tolerant organisms. This last point is particularly critical in organic acid production, where the requirement of neutralization during fermentation followed by downstream acidulation leads to large waste streams (in the classic case of lactic acid, nearly 1 kg of waste $CaSO_4$ per ton of lactic acid produced) and high product cost.

Beyond microbial requirements, the ability to selectively and efficiently withdraw product from the fermentation medium would have a great impact on overall process economics. Such withdrawal would allow fermentation to be operated continuously and would provide a product stream free from many of the biogenic impurities present in classic batch fermentation effluents. While membrane separations and extraction have been examined in some detail, there remains a significant opportunity for further work in recovering fermentation products without treating and disposing of the entire fermentation medium.

There are also research needs to examine the potential of simultaneously employing chemical and biological catalysis in a single reaction vessel. While complicated when considered in light of the above discussion on the effects of impurities, the "one-pot" synthesis of a product involving several processing steps would be a major leap in process intensification. A further step would be to develop surfaces that are hybrids of biological and chemical moieties – with reactivity and selectivity that are a synergistic combination of individually desirable properties. There are many unexplored avenues for moving toward integrated processing that may involve immobilizing microorganisms or enzymes, homogeneous or heterogeneous catalysis, electrochemical conversions, or continuous product removal, but to date very little if any work has been done.

VI. Substrate-Catalyst Specificity: Chirality and Biomimetic Character

Biomimetics is the science of imitating nature. For chemical catalysis, biomimetics involves the development of materials that imitate natural catalysts – that is, enzymes. Enzymes are remarkable materials – possessing nearly 100% selectivity for a particular chemical reaction and exhibiting high activity at low temperatures. These are, ultimately, the desired attributes of all catalysts – hence the interest in developing synthetic materials that behave like enzymes.

The field of biomimetic catalysis is in its infancy – there are relatively few systems that have been extensively investigated and there is a growing but still small community of researchers. The primary barrier to developing "synthetic enzymes" is the complexity and subtlety of the actual enzymatic structure and the difficulty in characterizing and then transposing the key aspects of that structure to a synthetic structure. One general strategy employed in the development of biomimetic catalysis is that of imprinting, shown pictorially and described in Figure VI.1 below (Katz, UC Berkeley).

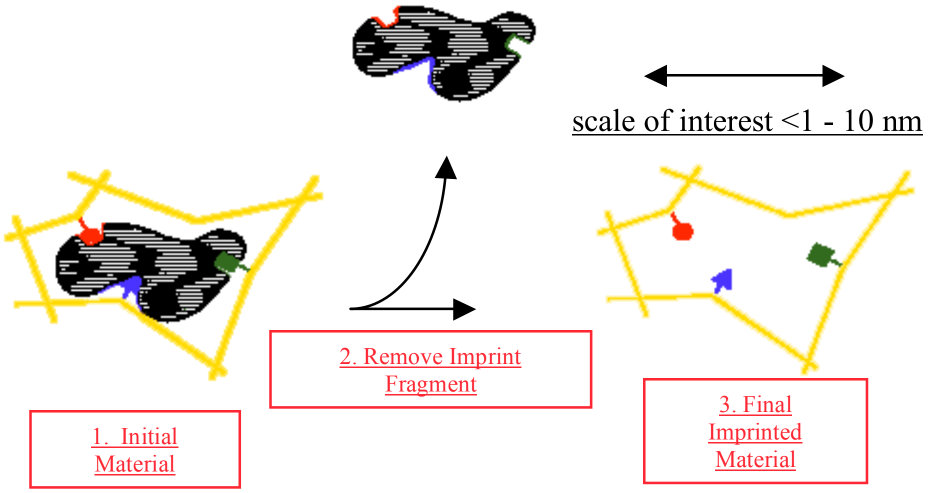
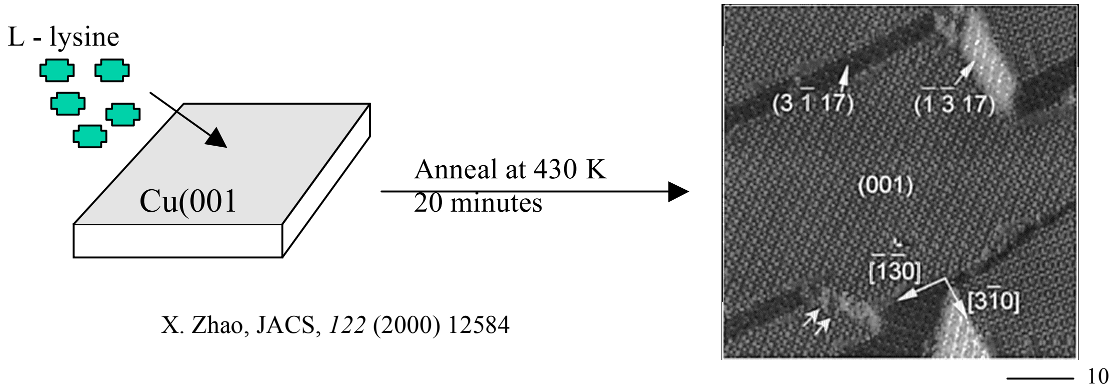


Figure VI.1. Imprinting is a concept for organizing chemical functional groups in heterogeneous catalysts. The imprint positions chemical functional groups (different shapes above) and creates porosity in their immediate vicinity. It is the "rubber stamp" of the active site. A scaffolding material framework, which can be either a crosslinked organic polymer or an inorganic oxide such as silica (broken lines), maintains the integrity of the imprinted site organization once the imprint has been cleaved from the framework. (A. Katz, Univ. California Berkeley, USA).

Enzymatic conversions obviously play an important role in the biorefinery, so there are many opportunities to enhance biorefinery performance by introducing successful biomimetic technologies. There are several reasons why biomimetic materials would be preferred to "natural" enzymes for biorenewable conversions: 1) an inorganic (biomimetic) enzyme could be much more thermally stable than its natural counterpart and thus could provide higher activity by operating at a higher temperature; 2) inorganic materials may be less expensive than the biological material; and 3) with experience, it may become possible to design synthetic "enzymes" that catalyze reactions not activated by natural enzymes. This may include the ability of using biomimetic structures to control stereochemistry in a way not possible with natural enzymes or chemical catalysts. This concept has already been implemented in biological systems in the form of catalytic antibodies, protein molecules raised to recognize synthetic templates that simulate the transition states of the reactions of interest. But a truly general approach to production of low-cost, robust, heterogeneous, selective catalytic materials with engineered active sites remains to be developed. Clearly this is an area of great need for future research collaboration between chemists, biochemists, materials scientists, and engineers.

A second major area for biorenewable catalysis, although again one not well characterized, is the formation and interaction of chiral species with the catalyst surface. In Figure VI.2, intrinsically "chiral" surfaces are prepared by adsorption of chiral L-lysine onto a Cu(001) crystal face. Once formed, the surfaces catalyze asymmetric hydrogenation of a (prochiral) C=O bond to form a chiral alcohol product.



X. Zhao, JACS, *122* (2000) 12584

Figure VI.2. Development of intrinsically chiral surfaces via adsorption of chiral templating agents. (D. Sholl, Carnegie-Mellon Univ., USA).

The development of catalysts to impart desired chirality into chemical products would be a major breakthrough in advancing our ability to produce tailored products from biorenewables. For example, the chiral purity of biorenewable monomers such as lactic acid essentially dictates the properties of the resulting polymer. In general, the desire to control polymer properties via control of monomer chirality and polymer tacticity is a field of significant opportunity in biorenewables. Similar effects are observed in specialty and fine chemicals used in pharmaceutical and pesticide applications.

VII. Analytical Tools for In-Situ Catalyst and Reaction Characterization

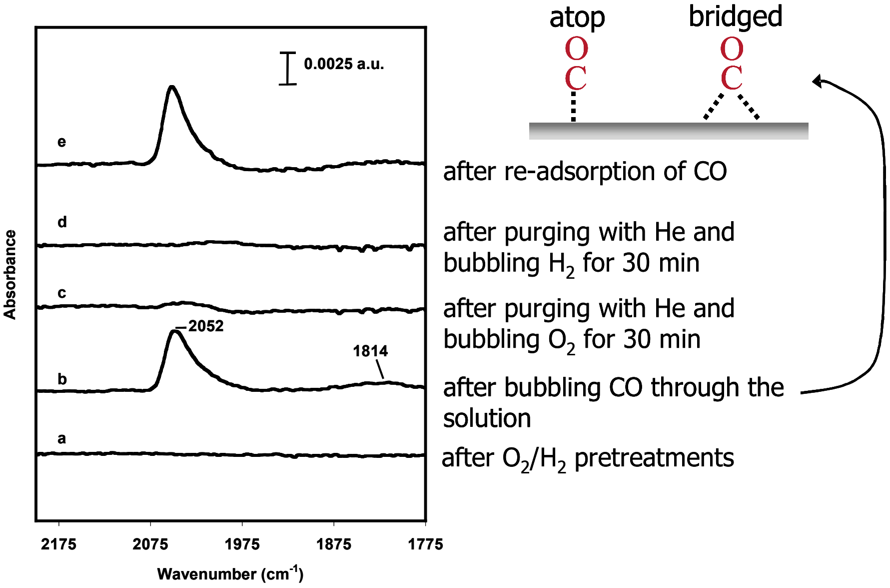


Figure VII.1 Attenuated total reflectance IR (ATR-IR) spectroscopy image of carbon monoxide adsorbed onto Pt from aqueous solution at 25^{o}C. (C. Williams, Univ. South Carolina, USA)

Systematic development of the specificity and efficiency necessary for practical catalytic renewables-based processes will require an approach more sophisticated than the traditional Edisonian empirical search; fundamental insights into the details of complex reacting systems will be needed, calling for new and expanded tools for in-situ analysis of solution chemical composition, substrate-catalyst adsorption, and interfacial structures including surface-bound species and catalyst/support materials. Yet even simple chemical analysis of renewables-based feedstocks and products is significantly more challenging than in the petroleum-based industries. As noted earlier, the difficulties arise from these systems' typical characteristics, specifically:

(a) complexity and diversity in structure, stereochemistry, and (poly)functionality
(b) involatility and thermal sensitivity
(c) strong preference for aqueous environments

For study of heterogeneous catalytic reactions, the above issues are further complicated by

(d) the multiple-phase nature of the relevant reaction systems
(e) the fact that the regions of main interest are interfaces between condensed phases, and
(f) the heterogeneity of pore sizes and reactive sites.

In line with the observations above, workshop discussion of challenges in this area centered around complexity: the structural complexity of renewables-based feedstocks; the multi-step nature of most reactions of value; the diversity of reactive sites on catalysts; the fact that in an overall conversion, key steps likely occur in different phases (e.g. on surfaces and free in solution). These issues all point to the need for high-resolution probes of the systems of interest. Surface sensitive vibrational spectroscopies offer the most immediate potential for yielding detailed insights into chemical structures at metal surfaces under water.[1] As exemplified by the attenuated total reflectance-IR (ATR-IR) spectra in Figure VII.1, methods are beginning to emerge that can probe simple surface-bound species even under liquid water.[2] Several techniques used in electrochemist try to study solute adsorption at electrode-electrolyte interfaces appear particularly promising. For instance, subtractively normalized interfacial FTIR spectroscopy (SNIFTIRS) has been used to probe phenylalanine adsorption on an Au surface.[3] Exploitation of the orienting effect of surface adsorption allows the use of polarized light in methods such as polarized modulation infrared reflection absorption spectroscopy (PM-IRRAS) to selectively probe bound species in the presence of free (non-oriented) solutes.[4] Signal enhancement via interaction of adsorbed species with certain metal surfaces, primarily Au, has long been the key to surface-enhance Raman spectroscopy (SERS), but recent developments in this area suggest that via special surface preparation, SERS is becoming possible on catalytically important metals.[5] Surface enhancement is also the key to the related sum frequency spectroscopy (SFS) method.[6] Simulations methods are also now being profitably applied to interpretation of surface spectra.[7]

Though impressive progress has been made, most of the above tools have been used to probe noncovalent adsorption on non reactive metal surfaces, and substantial work remains to be done to extend their utility to catalytic reacting systems. In particular, combination of spectroscopic probes with techniques analogous to solution fast kinetics methods for probing the time course of reactions on surfaces would be especially valuable. As with electrochemically modulated IR spectroscopy (EMIRS), manipulation of catalytic metal surface potential may provide one strategy to control reaction timing, both for study and potentially for applications.[8] Step-scan FTIR is another time-resolved method beginning to show potential in this area. “Real” catalysts are often much less uniform and spectroscopically accessibly than idealized metal surfaces on an electrode. Thus, the additional work needed to understand the diversity of reactive sites and how they each contribute to a real reaction's progress will be a further challenge for the partnership between spectroscopic analysis and catalyst synthesis.

Some of the spectroscopic methods with the potential to address the above needs involve multiple wavelength laser light sources and specialized sample cells. Typically such equipment requires operators with specialized expertise as well. – Such techniques, where the instruments and infrastructure are too expensive for individual universities to routinely purchase and maintain may better be located and shared in regional centralized user facilities for spectroscopy. This approach would be reminiscent of the early days of high-field NMR and advanced Mass Spectrometry centers.

References

1. "*In-Situ* Investigation of Solid-Liquid Catalytic Interfaces by Attenuated Total Reflection Infrared Spectroscopy," I. Ortiz-Hernandez and C. T. Williams, *Langmuir* ,**19** , 2956 (2003).

2. "Probing Buried Interfaces with Non-Linear Optical Spectroscopy," C. T. Williams and D. A. Beattie, *Surf. Sci.,* **500** , 545 (2002).

3. "Electrochemical and FTIR studies of L-phenylalanine adsorption at the Au(111) electrode" H.-Q. Li, A. Chen, S. G. Roscoe, J. Lipkowski, *J. Electroanal. Chem.* **500**, 299–310 (2001).

4. "Electrochemical and PM-IRRAS studies of the Effect of the Static Electric Field on the Structure of the DMPC Bilayer Supported at a Au(111) Electrode Surface" X. Bin, I. Zawisza, J. D. Goddard, J. Lipkowski, *Langmuir* **in press** (2005).

5. "Adsorption and reaction at electrochemical interfaces as probed by surface-enhanced Raman spectroscopy" Z. Q. Tian, B. Ren, *Ann. Rev. Phys. Chem.* **55**, 197-229 (2004).

6. "Total-Internal Reflection Sum-Frequency Spectroscopy: A Strategy for Studying Molecular Adsorption on Metal Surfaces," C. T. Williams, Y. Yang, C. D. Bain, *Langmuir* **16** , 2343.

7. "Simulations of SNIFTIRS experiments" B.Pettinger, J.Lipkowski and M.Hoon-Koshla, *J. Electroanal. Chem.* , **500**, 471-478 (2001).

8. "An in situ IR reflectance spectroscopic study of the electro-oxidation of D-sorbitol on platinum" L. Proenca, M. I. S. Lopes, I. Fonseca, F. Hahn, C. Lamy, Electrochimica Acta **44**, 1423-1430 (1998).

VIII. Computational Methods

Background: Ab initio theory and simulation have advanced to the stage where they can not only complement experimental efforts but offer suggestions for potentially more active and selective materials. As applied to heterogeneous catalysis, theory has predominantly been used to examine catalytic reactions that occur at the vapor/solid interface. More specifically, it has been used to probe the modes and the strength of adsorption for a range of different oxygenates relevant to biorenewables including maleic anhydride[1-2], maleic acid[3], succinic acid/anhydride, acetic acid[4-6], and gamma-butyrolactone on various metal surfaces (Pd, Re, Ru, Cu, Pd/Re alloys). Theory has also been used to calculate the reaction energies and activation barriers for hydrogenation, hydrogenolysis and dehydration reaction channels that convert these species into other surface intermediates and reaction products, and in addition, to establish plausible reaction mechanisms. Ab initio studies focused on the hydrogenation and hydrogenolysis of acetic acid over ideal Pd, PdRe, and Cu surfaces have all been reported in the literature as a model systems for understanding the potential mechanisms for succinic, maleic as well as other organic acids.[4-6] An example of the pathways and the mechanism involved as predicted from ab initio simulation is presented in Fig.VIII.1.

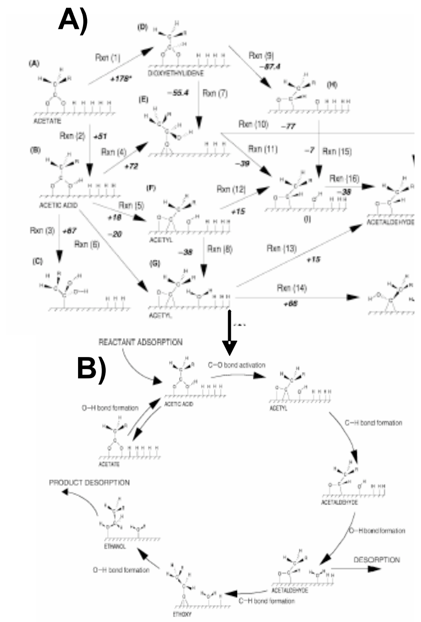


Fig. VIII.1 The conversion of (A) DFT calculated reaction energies for different reaction paths into (B) a plausible mechanism for the hydrogenolysis over acetic acid over Pd.[4] (M. Neurock, Univ. Virginia, USA)

Theory is currently being used to not only understand potential reaction mechanisms but also begin to develop structure-property relationships that may be used toward the prediction of optimal metals as well as metal alloys.[7-14] The results presented in Fig. VIII.2, for example, show the

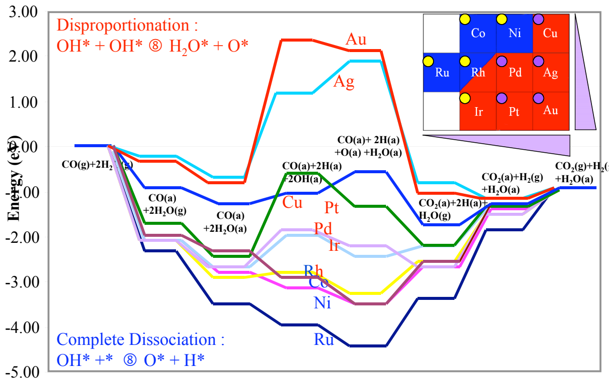


Fig. VIII.2. Periodic trends in the thermochemistry for water-gas shift reaction over model closed-packed metal surfaces. (M. Mavrikakis, U. Wisconsin, USA)[7] .

differences in the overall potential energy diagram for the water gas shift reaction carried out over different model closed-packed metal substrates.[7] The mechanism can change as one moves from one metal to another so it is necessary to evaluate all of the proposed steps as shown in Fig.VIII.2.

The current state of the art in theory has extended the efforts on model substrates to the preliminary design of catalytic features including the optimal composition and spatial location of bimetallic alloys, surface structure, promoters, and supports in order to improve catalytic performance.[8-14] The results from ab initio calculations are also being used in both deterministic[15] and stochastic methods[13,16] to simulate how changes in the surface structure influence the overall kinetics and catalytic performance which then provides a direct link with experimental efforts.

Solution Phase Effects: Modeling of aqueous catalytic hydrogenation and hydrogenolysis will require the ability to simulate catalytic reactions which occur at the aqueous solution/metal interface since the solution can influence the kinetics as well as the mechanism. Ab initio energetics and molecular dynamics have been used to begin examining different physicochemical phenomena that occur at the metal/solution interface including the dissociation of acetic acid[17], the hydrogenation of formaldehyde over Pd in water[18-19], the oxidation of CO to CO_2 [20-21], and the oxidation of methanol[22]. These are very CPU intensive calculations since they involve simulating the metal surface, the adsorbates, and a very large ensemble of water molecules. The aqueous solution phase, however, significantly changes the thermodynamics as well as the kinetics for many elementary processes including adsorption, diffusion, desorption and surface reactions. The steps that undergo charge

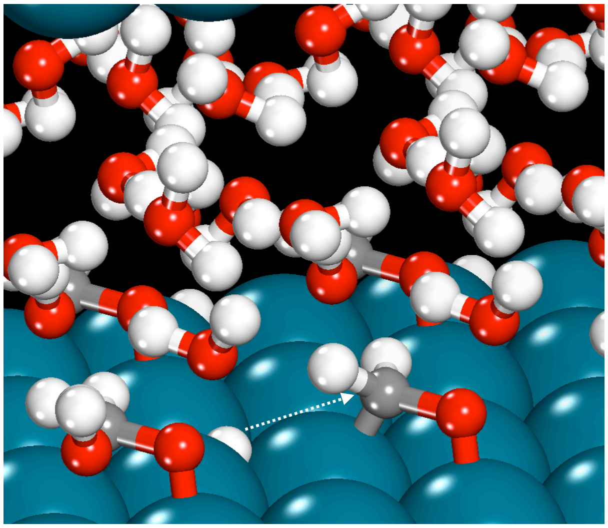


Fig. VIII.3. The optimized reactant state for the hydrogenation of formaldehyde over Pd(111) in the presence of water. Hydrogen can attack at either the carbon or the oxygen end forming either the methoxy or the hydroxymethyl surface intermediates respectively. (M. Neurock, University of Virginia, USA)[18-19].

transfer are most critically affected by the presence of an aqueous medium. In addition to the classical effects of solvation, the solvent can directly participate in and catalyze the actual mechanism. For example, in formaldehyde hydrogenation over Pd, studied as a probe of aldehyde and ketone hydrogenation,[18-19] the aqueous medium reduced the activation barriers for the hydrogenation at both the carbon and the oxygen ends of the molecule.

Previous Workshop Recommendations: The general computational needs for computing in catalysis have been the focus of previous workshops. Rather than repeat these same discussions, we used them as a starting point to build from in the discussions on applications to biorenewable systems.

The results from the NSF workshop on the *Future Directions in Catalysis: Structures that Function on the Nanoscale* held in June, 2003 (23) identified the following major computational needs and developments necessary to aid in the design of novel catalytic materials:

- Improve theoretical and simulation method accuracy.
- Improve the accuracy and size of the models used to identify active sites.
- Develop multiscale methods that span disparate time and length scales.
- Identity of the active site along with its environment for metastable molecular and nanoscale assemblies.
- Elucidate the dynamics of the active site and its environment along with the resulting catalytic kinetics.
- Design and optimization of active sites and their environments.
- Understand the elementary processes which lead to catalyst deactivation and control catalyst lifetime.
- Provide a tighter coupling of theory and experiment.

Needs for Computational Developments for Biorenewables Catalysis: The conversion of biochemically-derived platform compounds into value added chemicals requires the ability to selectively remove or add functionality to the functionalized carbon backbone. At present, there is little fundamental understanding of elementary steps that control the conversion of these reactants into specific products, thus hindering the design of more selective catalytic materials. Biorenewable feeds and platform chemicals are more complex systems than have been studied in the past; their multifunctional molecules that can adsorb and react on supports as well as catalytic surfaces, and in a number of different binding configurations. In many cases the functional groups are the same or similar with little to distinguish one from another, thus hampering selective formation of specific products. Catalytic conversion of feedstocks is typically carried out over supported metal or metal oxide nanoparticles in aqueous solution. That catalytic metal and support can participate in reactions increases the complexity in elucidating these systems, but at the same time, offers more opportunities for design optimization. In addition to surface chemistry, solution reactions may also compete with or complement the surface catalyzed processes. The properties of the solution phase can also influence the kinetics as well as the overall thermodynamics of surface catalyzed processes. The pH of the reaction solution, for example, can considerably influence the dominant surface reaction paths and their kinetics. The presence of minor products such as sulfur-containing molecules that are the resulting by products from the biochemical production of these feeds can significantly deactivate the catalyst.

While the complexity of these systems presents a number of challenges for theory they also present a number of opportunities for the design of advanced materials with improved catalytic properties. Therefore a fundamental understanding of each of these areas could lead to important advances.

1. Establish the modes of physisorption and chemisorption for platform chemicals and their potential products. How do the functional groups orient the molecule to the surface? Which sites on the surface do they adsorb to? How does this change in moving to different single crystal surfaces and different metals surfaces? What dictates the strength of the adsorbate surface bonding?

2. Determine the surface reaction chemistry of platform feedstocks, their potential reaction intermediates and products over different metals, metal oxides and supported materials. Is it possible to selectively activate specific hydroxyl groups? How do the elementary steps of C-

H, C-O, C-C bond-breaking and bond-making proceed? What sites are necessary for dehydration, hydrogenolysis, condensation and oxidation?

3. Distinguish the features from adsorption as well as surface reaction that retain, disrupt or add chirality.

4. Determine the influence of the support and its role in catalyzing specific reactions.

5. Establish the effects of the aqueous medium on the controlling reaction chemistry and kinetics. What reactions are better carried out in the solution rather than on a surface? What is the influence of pH?

6. Elucidate the effects of local hydrophobicity and hydrophilicity on the surface reaction chemistry. Can we design nanoporous systems which might impart optimal environment into pore framework?

7. Distinguish the modes of catalyst deactivation. What are the effects of small amounts of fermentation products in the feed?

8. Develop structure-property relationships which relate changes in the metal as well as the support to the chemisorption, hydrogenation, hydrogenolysis, condensation reactions.

9. Design novel material systems based on the fundamental principles. What are the best metals? Can we devise bimetallic systems with improved reactivity? What are potential bifunctional systems that could efficiently separate specific surface reaction steps to improve overall activity and selectivity?

10. Model how enzymes catalyze similar conversions. Can we develop biomimetic analogues? Can we support or encapsulate enzymes in heterogeneous frameworks?

11. Establish a closer coupling between theory and experiment in the resolution of surface intermediates, surface structure and their in-situ changes during reaction conditions**.**

From Carbohydrates to Platform Chemicals: The conversion of carbohydrates which are rich in oxygen but fragile feedstocks typically requires aqueous phase processing. The size of the molecules as well as the complexity of dealing with a complex multicomponent mixture presents a number of challenges which have thus far prevented modeling of such feeds. Modeling, however, is reaching the stage where it can begin to answer some very basic questions as to which bonds are susceptible to attack during aqueous phase processing and what are the potential product distributions. The issues and challenges outlined above for the catalytic conversion of platform chemicals also hold for the conversion of carbohydrates. The modest size of the systems that can be examined computationally may limit the scope of the work in this area and its value. In addition, many of these conversions are typically carried out biochemically, which prevents most modeling efforts.

From Biorenewable Oils and Fats to Polymer Precursors: Similarly, the conversion of triglycerides present in plant oils and animal fats into polymers or polymer building blocks via transesterification, metathesis and other conversion routes has important prospects. Theory and simulation can provide an elementary understanding of the mechanisms that occur over metal, metal oxide, porous materials. The size of these systems may limit full-scale simulations. Model molecular substrates could, however, offer very valuable information on how specific functional groups interact with catalytic surfaces, how specific elementary processes proceed and what are the potential mechanisms governing the conversion of more complex macromolecular structures. In addition to probing the catalytic conversion of these renewable-based feeds into traditional polymer building blocks, atomistic simulations could aid in predicting and elucidating the properties of the polymer products, guiding the design of desirable new polymers and hence the choice of feedstocks and processes that have yet to be explored.

References

1) V. Pallassana, M. Neurock, Chem. Eng. Sci. 1999, 54 (15-16).3423-3431.

2) V. Pallassana, M. Neurock, G.C. Coulston, J. Phys. Chem. B 1999, 103 (42).8973-8983.

3) V. Pallassana, Theoretical investigation of reaction pathways in the selective hydrogenation of maleic acid to tetrahydrofuran over Pd-Re surfaces; University of Virginia, 2000.
4) V. Pallassana and M. Neurock, J. Catal. 2002, 209, 289-305.
5) R.D. Cortright, M. Sanchez-Castillo, and J.A. Dumesic, Appl. Catal. B, Env., 39, 2002, 353.
6) M. A. Natal-Santiago, M.A. Sanchez-Castillo, R.D. Cortright, and J.A. Dumesic, J. Catal. 193, 2000, 16.
7) M. Mavrikakis, University of Wisconsin, 2004.
8) C. Jacobsen, S. Dahl, B. Clausen, S. Bahn, A. Logadottir, and J.K. Norskov, J. Am. Chem. Soc, 123, 8404, 2001.
9) F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Norskov, and I. Stensgaard , Science, 279 (5358) 1913-1915, 1998.
10) J.K. Norskov, J. Phys. Chem. B, 107, 11013 (2003).
11) J. Greeley and M. Mavrikakis, Nat. Mater., 3, 810 (2004)
12) Y. Xu, A.V. Ruban, and M. Mavrikakis, J. Am. Chem. Soc., 126, 4717, 2004.
13) M. Neurock, J. Catal., 216, 73 (2003).
14) L. Kieken, D. Mei, and M. Neurock, J. Phys. Chem. 2004, in Press.
15) P. Liu P, A. Logadottir A, J.K. Norskov, Electrochim. ACTA 48 (25-26): 3731-3742, 2003
16) E.W. Hansen, and M. Neurock, J. Catal., 196 (2): 241-252, 2001.
17) S.K. Desai, P. Venkataraman, M. Neurock, J. Phys. Chem. B 2001, 105, 9171-9182.
18) S.K. Desai, Ph.D. Thesis University of Virginia.
19) S.K. Desai, and M. Neurock, 2004
20) S.K. Desai, and M. Neurock, Electrochim. Acta, 48 (25-26), 3759-3773, 2003.
21) S.K. Desai, S.K., and M. Neurock, Phys. Rev. B, 68, 075420, 2003.
22) M. Neurock, Chem. Eng. Sci., In Press, 2004.
23) M. Davis, and D. Tilsey, NSF Workshop Report on “Future Directions in Catalysis: Structures that Function on the Nanoscale”, June 2003.

IX. Educational and Workforce Needs

The emergence of biorenewable feedstocks as fuel and chemical sources for the U.S. will require a significant adjustment of technical curricula across the chemical sciences and engineering. Gone or greatly reduced in scope will be the classic petroleum-based chemical engineering and chemistry curricula, replaced by chemistry programs that cross into the biological and plant realms and by chemical engineering curricula that facilitate competence in the greatly diversified environments in which biorenewable processing takes place.

In the short term, students at both the undergraduate level and graduate level must be made more aware of the emergence of biorenewables as raw materials and of current and forthcoming processing schemes for biorenewables conversion. Thus, biology and biological processing must gain greater emphasis in the curriculum, along with plant science, carbohydrate, protein, and lipid chemistry, and the concepts of "green" processing. With regard to catalysis, the classic treatment of heterogeneous catalysis in two-phase systems must expand to include catalysis in the liquid phase, homogeneous chemical catalysis, acid-base catalysis, and enzymatic biocatalysis. In many cases, these concepts can be used as example problems, assignments, and projects in existing courses for the purpose of illustrating classic principles. However, there are many instances where more in-depth study is warranted, and thus dedicated courses addressing biorenewables-related issues must be developed. The principles of sustainability and methods of life cycle assessment must be invoked in evaluation of new and existing technologies. In the broader sense, the goal of a sustainable world, both from resource utilization and environmental standpoints, must be integrated across the curriculum as the foundation of all aspects of education pertaining to manufacturing and society. Such integration will require addressing the philosophical, economic, and societal issues regarding sustainability that are well beyond the scope of this report.

Beyond redirecting the curriculum to incorporate biorenewables-related concepts, faculty at U.S. universities must work more closely with corporations having biorenewables interests. Examples of such relationships include industry participation on university technical advisory boards, presentation of lectures and courses by industrial instructors, and opportunities for student internship and cooperative education experiences and faculty sabbaticals at biorenewables industrial sites. Developing such partnerships will strengthen the academic research effort and, in many cases, generate opportunities for collaboration through the growing number of federally-funded joint university-industry programs. Closer relationships will also open communication regarding the technical workforce needs of U.S. industry and how the academic community can work to meet those needs. Such needs for new or redirected skills and knowledge are described to some extent earlier, and may range from fundamental sciences to understanding rural economies. When structured properly, long-term industry-academic partnerships are mutually beneficial and can lead to broader dissemination of key challenges and opportunities in biorenewables utilization.

For the academic community to play a major collaborative role with the corporate world in development of a biorenewables industry, students and faculty must gain a more thorough understanding of the concepts of intellectual property and patenting. The ability to properly collect and record experimental data, to write an invention disclosure, to search and interpret the patent literature, and to understand the protection of an invention are central requirements for the modern industrial researcher – and should be standard practice for academic graduate students and postdoctoral associates as well. Clear training in developing and handling intellectual property will both enhance the attractiveness of academic researchers to industry and equip future industrial scientists for their work.

Graduate education in chemical sciences and engineering must continue to evolve in response to needs of the forthcoming biorenewables industry. Graduate students must develop and take advantages of opportunities for internships with corporations, in order to gain hands-on experiences and perspective useful in academic biorenewables research and coursework. Further, the interdisciplinary nature of research related to biorenewables, often involving concepts from genetic engineering to distillation, requires that graduate students interested in biorenewables gain breadth in their graduate education and interact effectively in multidisciplinary research teams. These interactions and experiences will prepare advanced degree students to be immediately effective upon entry to a biorenewables industry setting.

Appendix A. Workshop Attendees

Name	**Affiliation**
Bentley, Bill	University of Maryland
Bloom, Paul	Archer Daniels Midland
Bozell, Joe	National Renewable Energy Laboratory
Buchholz, Stefan	Degussa AG
Cameron, Doug	Cargill
Cardona-Martinez, Nelson	University of Puerto Rico
Cavalcanti, Fernando	Rohm and Haas
Coates, Geoff	Cornell University
Cooper, Adrienne	Temple University
Davis, Robert	University of Virginia
Dudukovic, Milorad	Washington University, St. Louis
Dumesic, Jim	University of Wisconsin
Foley, Hank	Pennsylvania State University
Gallezot, Pierre	CNRS, France
Giroux, Thomas	Engelhard
Hill, Craig	Emory University
Holladay, John	Pacific Northwest National Laboratory
Jackson, James	Michigan State University
Jessop, Philip	Queens University, Ontario
Katz, Alex	U.C. Berkeley
Kelley, Steve	National Renewable Energy Laboratory
Ladisch, Mike	Purdue University
Manzer, Leo	DuPont
Marinangeli, Richard	UOP
Mavrikakis, Manos	University of Wisconsin
Miller, Dennis	Michigan State University
Miranda, Raul	Department of Energy, BES
Neurock, Matthew	University of Virginia
Ogden, Kim	University of Arizona
Payne, Gregory	University of Maryland
Ribeiro, Fabio	Purdue University
Schmidt, Lanny	University of Minnesota
Schrader, Glenn	National Science Foundation
Scott, Susannah	U.C. Santa Barbara
Shanks, Brent	Iowa State University
Sholl, David	Carnegie Mellon University
Smith, Pat	Dow Chemical
Thompson, Levi	University of Michigan
Tsobanakis, Paris	Cargill
Turner, Howard	Symyx
Wang, Ping	University of Akron
White, Jim	Pacific Northwest National Laboratory
Williams, Chris	University of South Carolina
Williams, Susan	Kansas University

Appendix B. Workshop Program

Tuesday, April 13, 2004

7:00 - 8:00 a.m. Continental Breakfast (provided)

8:00 – 8:15 a.m. Welcome and Introductions (D. Miller)

8:15 – 8:30 a.m. NSF Welcoming Remarks

Dr. Esin Gulari, Director
Chemical and Thermal Systems, NSF

8:30 – 8:45 a.m. Workshop objectives and goals (D. Miller)

8:45 – 10:00 a.m. Targeting feedstocks, products, and processes (M. Neurock moderate)

Doug Cameron	Cargill	Catalysis for the biorefinery – an overview
Leo Manzer	DuPont	Levulinic acid derivatives: a case study on biomass conversion
Questions, discussion		

10:00 - 10:15 a.m. Break

10:15 a.m. – 12:00 Targeting feedstocks, products, and processes (B. Shanks moderate)

P. Gallezot	IRC-CNRS, France	Catalytic processes for the transformation of renewables. A European perspective
James Dumesic	U. Wisconsin	Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water
Questions, discussion		
Short presentations		
Lanny Schmidt	U. Minnesota	Ethanol reforming
D. Miller	Michigan State Univ.	Catalyst deactivation from biogenic impurities

12:00 - 1:00 p.m. Lunch (Speaker: Stefan Buchholz, Degussa - Biocatalysis at Degussa)

1:00 – 2:45 p.m. Fundamental catalyst science for biorenewables (S. Williams moderate)

Chris Williams	U. South Carolina	Bridging the liquid gap: in-situ vibrational spectroscopy of solid-liquid catalytic interfaces

Matt Neurock	U. Virginia	Computational catalysis towards elucidating the catalytic conversion of renewable resources

Questions, discussion

Short presentations

Bob Davis	U. Virginia	In-situ spectroscopic methods
Manos Mavrikakis	U. Wisconsin	Water-gas-shift reaction mechanism
Ned Jackson	Michigan State U.	Surface binding in aqueous-phase hydrogenation

2:45 – 3:00 p.m.	Break
3:00 – 4:00 p.m.	Breakout discussions – i) biorenewable feedstock, product, and process challenges; ii) analytical tools for in-situ catalyst and reaction characterization; iii) interfacing catalysis and biocatalysis; iv) catalysis for energy and fuels
4:00 – 5:00 p.m.	Reports from breakout groups, discussion, identification of research priorities
5:00 – 6:30 p.m.	Break
6:30 – 8:00 p.m.	Dinner

Wednesday, April 14, 2004

7:00 – 8:00 a.m.	Breakfast
8:00 – 8:15 a.m.	Review objectives, schedule, progress, logistics (D. Miller)
8:15 – 10:00 a.m.	Novel catalyst materials (N. Jackson moderate)

Geoff Coates	Cornell Univ.	Synthesis of biodegradable polymers from renewable resources
Craig Hill	Emory University	Pollution-free conversion of trees to paper. Stable, equilibrating, self-buffering catalysts for selective O_2-based oxidations in water
Alex Katz	U. C. Berkeley	Imprinting functionality in silica catalysts

Questions, discussion

10:00 – 10:15 a.m.	Break
10:15 – 11:15 a.m.	Novel catalyst materials (R. Davis moderate)

Brent Shanks	Iowa State Univ.	Design of metal oxide-based catalysts for biorenewables conversion
Hank Foley	Penn State Univ.	Nanoporous carbon membranes for transport and catalytic reactions

Questions, discussion

11:15 – 12:00 noon Short presentations

S. Scott	U.C. Santa Barbara	Heterogeneous olefin metathesis catalysts
D. Sholl	Carnegie-Mellon	Methods for producing chiral catalysts
Ping Wang	Akron Univ.	Enzymatic biocatalysis for polymers

12:00 – 1:00 p.m. Lunch

1:00 – 2:15 p.m. Reaction/process engineering for biorenewable feedstock conversion (J. Dumesic moderate)

Phil Jessop	Queens Univ.	Homogeneous catalysis and catalyst recovery using environmentally benign solvents
M. Dudukovic	Washington U.	Multiphase reaction engineering in biomass conversion processes

Questions, discussion

2:15 – 2:30 p.m. Break

2:30 – 3:30 p.m. Breakout groups – i) Reaction/process engineering, ii) novel oxide and support materials, iii) catalyst-substrate specificity: chirality and biomimetic character

3:30 – 5:00 p.m. Reports of breakout groups, identify research priorities and challenges, summary discussion

Appendix C. Organizing Committee and Workshop Website

Organizing Committee

Dennis J. Miller,Workshop Chair
Dept. Chemical Engineering and Materials Science
Michigan State University
2527 Engineering Building
East Lansing, Michigan 48824
(517) 353-3928
millerd@egr.msu.edu

James E. “Ned” Jackson, Workshop Co-chair
Department of Chemistry
Michigan State University

Robert Davis
Chemical Engineering Department
University of Virginia

James Dumesic
Department of Chemical Engineering
University of Wisconsin – Madison

Matthew Neurock
Chemical Engineering Department
University of Virginia

Fabio Ribiero
Department of Materials Science
Purdue University

Brent Shanks
Department of Chemical Engineering
Iowa State University

Susan Williams
Chemical Engineering Department
Kansas University

Workshop website www.egr.msu.edu/apps/nsfworkshop