BASED ON
THE JUNE 25-26,
2007 WORKSHOP
WASHINGTON, D.C.

A RESEARCH ROADMAP FOR MAKING
LIGNOCELLULOSIC BIOFUELS
A PRACTICAL REALITY

UNIVERSITY
OF
MASSACHUSETTS
AMHERST

Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels:

Next Generation Hydrocarbon Biorefineries

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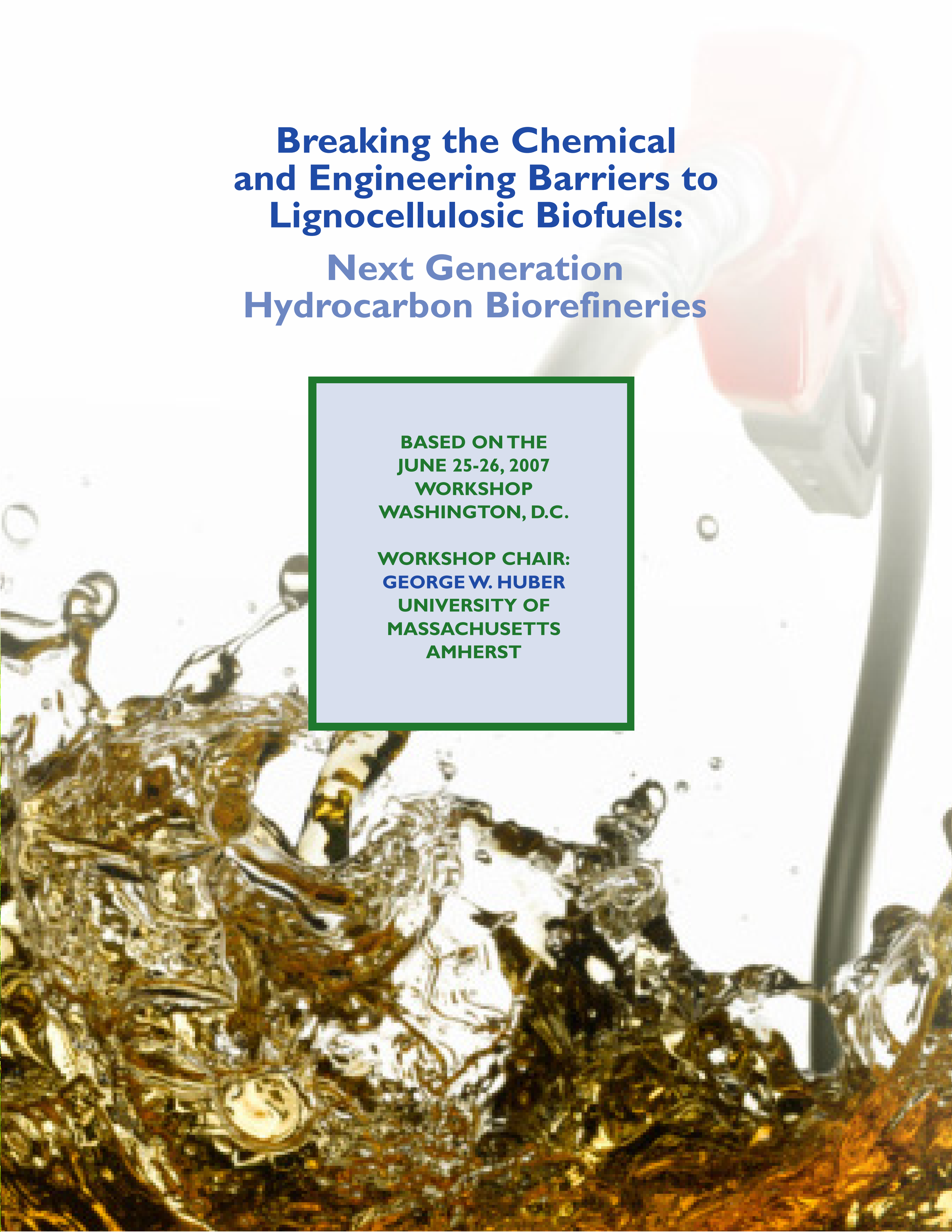

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WORKSHOP CHAIR:
GEORGE W. HUBER
UNIVERSITY OF
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Executive Summary

Liquid biofuels produced from lignocellulosic biomass can significantly reduce our dependence on foreign oil, create new jobs, improve rural economies, reduce greenhouse gas emissions, and improve national security. There has been deep bipartisan support for measures such as the Vehicle and Fuel Choices for American Security Act. In his 2006 State of the Union address, the President noted that "With America on the verge of breakthroughs in advanced energy technologies the best way to break the addiction to foreign oil is through new technologies."

> *"With America on the verge of breakthroughs in advanced energy technologies – the best way to break the addiction to foreign oil is through new technologies."*
>
> - President George W. Bush
> State of the Union
> Address/January 31, 2006

Advances in agriculture and biotechnology have made it possible to inexpensively produce lignocellulosic biomass at costs that are significantly lower (about $15 per barrel of oil energy equivalent) than crude oil. Significant amounts of lignocellulosic biomass can be sustainably produced on US agriculture and forestry land with the energy content of 60 % of the current US petroleum consumption. The key bottleneck for lignocellulosic-derived biofuels is the lack of technology for the efficient conversion of biomass into liquid fuels.

While the U.S. has made a significant investment in technologies focusing on breaking the biological barriers to biofuels, principally ethanol, there has not been a commensurate investment in the research needed to break the chemical and engineering barriers to hydrocarbon fuels such as gasoline, diesel, and jet fuel.

The production of hydrocarbon fuels from biomass has many important advantages. First, "green" hydrocarbon fuels are essentially the same as those currently derived from petroleum, except that they are made from biomass. Therefore, it will not be necessary to modify existing infrastructure (e.g. pipelines, engines) and hydrocarbon biorefining processes can be tied into the fuel production systems of existing petroleum refineries. Second, biomass-based hydrocarbon fuels are energy equivalent to fuels derived from petroleum. In contrast to the lower energy density of E85 flex fuel, there will be no penalty in gas mileage with biomass-based hydrocarbon fuels. Third, hydrocarbons produced from lignocellulosic biomass are immiscible in water; they self-separate, which eliminates the need for an expensive, energy-consuming distillation step. Fourth, biomass-based hydrocarbon fuels are produced at high temperatures, which allows for faster conversion reactions in smaller reactors. Thus, processing units can be placed close to the biomass source or even transported on truck trailers. Fifth, the amount of water needed for processing hydrocarbon fuels from biomass can be greatly reduced, compared with the dilute sugar solutions to which enzymes are constrained. This is because organic or heterogeneous catalysts work well in concentrated water solutions or even in the absence of water if ionic liquids are used. Finally, heterogeneous catalysts are inherently recyclable. So they can be used over the course of months and even years, which significantly reduces costs compared to biological catalysts. The elimination of energy-intensive distillation, the higher reaction rates, and the much smaller process footprints can also lead to lower biofuel costs than are possible using currently available biological pathways for producing cellulosic ethanol.

To articulate the essential role of chemistry, chemical catalysis, thermal processing, and engineering in the conversion of lignocellulosic biomass into green gasoline, green diesel and green jet fuel, the National Science Foundation and the Department of Energy convened a workshop entitled *"Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels"* on June 25-26, 2007 in Washington D.C., ancillary to the 2007 ACS Green Chemistry and Engineering Conference. Over 70 participants from 24 academic institutions, 20 petroleum, chemical and biofuel companies, and 7 national laboratories contributed expertise in chemical catalysis, chemistry, petroleum refining, nanotechnology, quantum chemistry, and engineering. This document is the result of that workshop.

This roadmap to *"Next Generation Hydrocarbon Biorefineries"* outlines a number of novel process pathways for biofuels production based on sound scientific and engineering proofs of concept demonstrated in laboratories around the world. Roadmap highlights are as follows:

- Selective thermal processing of lignocellulosic biomass to produce liquid fuels (bio-oils) in distributed biorefineries (Chapter 1).
- Utilization of petroleum refining technology for conversion of biomass-derived oxygenates within existing petroleum refineries (Chapter 2).
- Hydrocarbon production by liquid phase processing of sugars to a heretofore "sleeping giant" intermediate, hydroxymethylfurfural (HMF), followed by HMF conversion to "green" diesel and jet fuel (Chapter 3).
- Process intensification for diesel and gasoline production from synthesis gas (CO and H_2) by Fisher-Tropsch synthesis (FTS), which dramatically decreases the economically viable size compared to traditional FTS processes with petroleum derived feedstocks (Chapter 4).
- Conceptual design of biorefining processes in conjunction with experimental studies at the beginning of research projects to allow rapid development of commercial biofuel technologies (Chapter 5).
- Design of recyclable, highly active and selective heterogeneous catalysts for biofuel production using advanced nanotechnology, synthesis methods and quantum chemical calculations (Chapter 6).

Years of engineering research and design went into the development of the modern petroleum industry. A similarly expansive and sustained effort must also be applied to develop hydrocarbon biorefineries. Advances in nanoscience over the last several decades have given us an unprecedented ability to understand and control chemistry at the molecular scale, which promises to accelerate the development of biomass-to-fuels production technologies. As the tremendous expertise of the chemistry, catalysis and engineering communities—which was so instrumental in the development of petroleum refining technologies—is brought fully to bear on this field as well, there is every reason to believe that we can rapidly develop cost-effective hydrocarbon biorefineries.

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Introduction

A CONCERTED EFFORT TO ACCELERATE THE DEVELOPMENT OF DOMESTICALLY PRODUCED ALTERNATIVE TRANSPORTATION FUELS PROMISES TO REDUCE OUR NATIONAL DEPENDENCE ON FOREIGN OIL, SPUR ECONOMIC DEVELOPMENT, AND IMPROVE ENVIRONMENTAL QUALITY IN THE UNITED STATES. In his 2007 State of the Union address, President Bush proposed to increase the domestic supply of alternative fuels to 35 million gallons annually over the next 10 years [White House 2007]. The U.S. Department of Energy has determined that more than 1 billion dry tons of biomass could be sustainably harvested from U.S. fields and forests, enough to displace 30 percent of the nation's annual petroleum consumption for transportation fuels [Perlack, et al. 2005]. The Natural Resources Defense Council has further projected that an aggressive plan to produce lignocellulosic biofuels in the US could produce the equivalent of nearly 7.9 million barrels of oil per day by 2050, or more than 50 percent of current total oil use in the transportation sector, and more than three times total Persian Gulf oil imports alone [Greene, et al. 2004].

The promise of these domestic fuel production goals, strategies, and projections will only be realized through technological advances derived from concerted and long-term programs in interdisciplinary science and engineering. As President Bush himself said, "With America on the verge of breakthroughs in advanced energy technologies the best way to break the addiction to foreign oil is through new technologies."

In order for biofuels to emerge as a viable alternative to petroleum-based fuels we must develop cost-effective production technologies. The obvious national imperative of the problem has produced a groundswell of research activity in laboratories across the country. The range of high-tech analytical tools, sophisticated software, and powerful computers now available to the scientific community allow researchers to "see" chemical reactions as they unfold. This unprecedented analytical capacity presents exciting opportunities to fine tune biomass conversion reactions and engineer efficient and economical processes for biofuels production. Today, we have both the incentive and the technical means to solve this problem. Through concerted effort and a sustained investment in research we will solve it.

> *"In challenge, there is great opportunity. We must seize the initiative – as past generations of Americans have done – and harness the unique American ingenuity that has made us the world leader in innovation, invention and technology. If we do, we can achieve real energy independence that strengthens our national security, boosts our economy, creates more jobs and protects our environment for future generations."*
>
> -Steny Hoyer, Majority Leader
> U.S. House of Representatives.
> March 1, 2007

0.1 JOINT WORKSHOP CHALLENGES THE INTERDISCIPLINARY COMMUNITY OF BIOFUEL SCIENTISTS AND ENGINEERS

On June 25th and 26th 2007 more than 70 leading biofuels scientists and engineers representing industry, academia, and government agencies gathered in Washington D.C. to develop a roadmap for making lignocellulosic biofuels a practical reality. The objective of the workshop was to articulate the critical role that chemistry, chemical catalysis, thermal processing, and engineering play in the conversion of lignocellulosic biomass into liquid transportation fuels including "green" gasoline, diesel, and jet fuel. Workshop participants included a range of academic, government, and industry scientists and engineers with backgrounds in petroleum and petrochemical production, catalysis, chemistry, process design and engineering, and biorefining. An array of companies participated in the workshop, including representatives from the following industries: oil (Conoco-Phillips, Exxon-Mobil, British Petroleum, Chevron, UOP), chemical (Dow, Dupont, GE Plastics, ABB Lumus, Symyx), venture capital (Khosla Ventures), agriculture (Cargill), engine (United Technology) and small businesses (Virent Energy Systems, Renewable Oil International). The following five national laboratories were also represented: National Renewable Energy Laboratory (NREL), Pacific National Northwest Laboratory (PNNL), Oak Ridge National Lab, Brookhaven National Lab, and Savannah River National Lab. Attendees also included professors from twenty-four U.S. universities. Each workshop thrust area was co-led by a professor and a national laboratory representative . The substantial interest in this workshop, evidenced by the diversity of participants, demonstrates the vital importance of this topic to our nation.

SECTIONS OF INTRODUCTION:

The following roadmap report paints a picture of concerted, transformational science. It outlines a far-reaching research program focused on the development of fundamental knowledge about biomass feedstock properties and reaction products, which will lay the groundwork for the biorefineries of the future. At this stage, there are many more questions than answers, but the tremendous potential for domestic production of essential fuels and products compels us to work diligently to develop the technologies necessary to realize this potential.

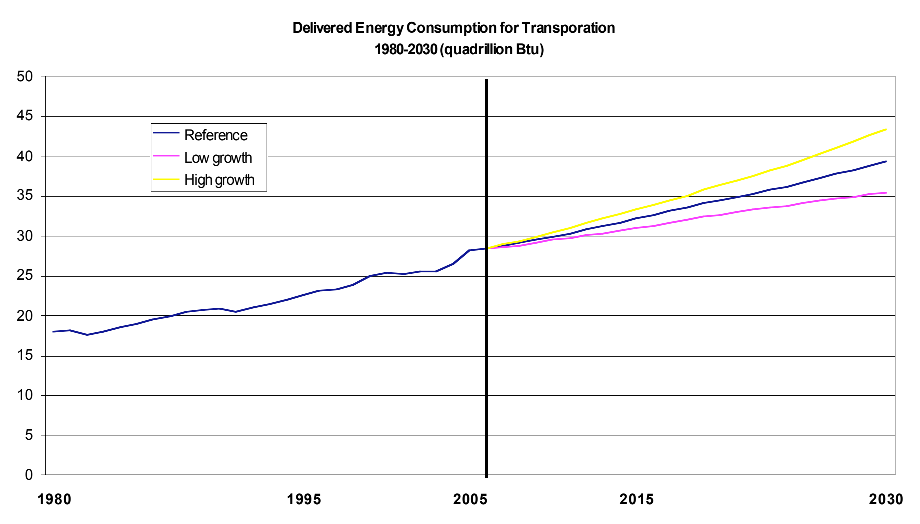
0.2 AMERICA'S ENERGY CHALLENGE

It is now widely acknowledged that the current U.S. energy supply-demand problem and the myriad environmental, economic, and social challenges associated with global climate change are urgent. Our increasing demand for energy, especially transportation fuels, far outstrips our domestic production capacity, leaving the nation vulnerable to the political, economic, and national security consequences of importing foreign oil. The greenhouse gas emissions produced in large part by fossil fuel combustion may cause unprecedented climactic upheavals worldwide. To head off the potentially severe consequences of these trends a new national energy research program must be initiated with the intensity and commitment of the Manhattan Project or President Kennedy's Apollo lunar landing challenge. Then, this research must be sustained until the problems are solved.

World demand for oil now stands at 85.9 million barrels a day [International Energy Agency 2007]. The U.S. Energy Information Administration expects it to reach 117.6 million barrels a day by 2030 (Figure 0.1) [Energy Information Administration 2007]. That extra 31.7 million barrels of daily production is the equivalent to the oil production of three Saudi Arabias. Transportation accounts for 94 percent of the projected increase in liquid fuel consumption.

With crude oil prices currently approaching $100 per barrel, and projections for continued heavy use of petroleum for transportation fuels, it is imperative to develop alternatives fuels that can be used in existing cars, trucks, boats, and planes. Through chemical processing and upgrading, the full range of transportation fuels including gasoline, diesel, and jet fuel can be produced from biomass feedstocks.

Figure 0.1: Projections of Petroleum Consumption for Transportation through 2030 [Energy Information Administration 2007]



Plant biomass is the only sustainable source of organic carbon currently available on earth, and biofuels, are the only sustainable source of liquid fuels [Wyman et al 2005, Klass 2004]. However, the complex nature of biomass and the currently ill-defined issues related to biomass-to-biofuels conversion pose a substantial, but not insurmountable, challenge to the large-scale production and widespread use of biofuels.

0.3 THE PROMISE OF LIGNOCELLULOSIC BIOFUELS

Abundant and inexpensive, lignocellulosic biomass does not compete with the production of food crops.[1] As such, it can serve as a source of fungible fuels to fill the gap between demand and availability of petroleum. The current delivered cost of lignocellulosic biomass is significantly cheaper than crude oil. However, the cost of biomass in the U.S. varies according to type and region, ranging from $5 to $15 per barrel of oil energy equivalent [Huber, et al. 2006]. Furthermore, the price difference between biomass and petroleum would be even greater if the expense of confronting negative geopolitical challenges was added to the total cost of crude oil.

Biomass is abundant, inexpensive, and does not compete with the production of food crops. Economically, lignocellulosic biomass has an advantage over other agriculturally important biofuels feedstocks such as corn starch, soybeans, and sugar cane, because it can be produced quickly and at significantly lower cost than food crops [Klass 2004]. Lignocellulosic biomass is also an important component of the major food crops listed above; it is the non-edible portion of the plant, which is currently underutilized, but could be used for biofuel production. In short, lignocellulosic biomass holds the key to supplying society's basic needs for sustainable production of liquid transportation fuels without impacting the nation's food supply.

Availability of domestic lignocellulosic biomass is not a limitation. In fact, the U.S. has a large amount of underutilized biomass (Table 0.1). In fact, non-food biomass, including trees, grasses and agricultural residues, constitutes more than 80% of the total biomass in the U.S. A 2005 study determined that 1.3 billion dry tons of this non-food biomass could be available for large-scale bioenergy and biorefining industries by the middle

Table 0.1: Potential U. S. Biomass Resources (adapted from Perlack, et al. 2005)

Biomass Resources	*Million Dry Tons per Year*
FOREST BIOMASS	
Forest Products industry residues	145
Logging and site-clearing residues	64
Forest thinning	60
Fuelwood	52
Urban wood residues	47
Subtotal for Forest Residues	*368*
AGRICULTURAL BIOMASS	
Animal crop residues	428
Perennial crops	377
Misc. process residues, manure	106
Grains	87
Subtotal for Agricultural Resources	*998*
TOTAL BIOMASS RESOURCE POTENTIAL	*1,366*

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[1] Lignocellulosic biomass is the fibrous, woody, and generally inedible portions of plants that are composed of hemicellulose, and lignin—key structural components of plant cell walls. Cellulose and hemicellulose are complex carbohydrates (i.e. long chains of sugar molecules). Lignin is a complex, noncarbohydrate polymer that binds cellulose and hemicellulose and gives plant cell walls their rigidity. Dry cellulosic biomass consists of about 75% carbohydrates (including cellulose, the most abundant form of carbon in the biosphere and hemicellulose, polymers of 5- and 6-carbon sugars) and 25% lignin (a complex ringed aromatic structure).

of the 21st Century [Perlack, et al. 2005]. This much biomass has the energy content of 3.8 billion barrels of oil; an amount equivalent to approximately half the oil consumed in the U.S. in 2006. Lignocellulosic biomass feedstocks for biofuels production can be derived from both forest and agricultural resources. Forest resources include residues such as tree bark and scrap wood, the logging and site clearing debris that is usually left on site or burned, and urban wood residues consisting mainly of municipal solid waste. Agricultural resources consist mainly of crop residues, which are mostly leaves and stems (e.g. corn stover), from crops grown for food and fiber such as soybeans, corn, and wheat. Additionally, the study included grasses (e.g. switchgrass) and fast-growing trees (e.g. poplars) grown specifically for bioenergy. The results of the so-called "billion-ton study" illustrate that ample lignocellulosic biomass resources are readily available for sustainable extraction from U.S. fields and forests.

The limiting factor to biofuels production is simply that low-cost processing technologies to efficiently convert a large fraction of the lignocellulosic biomass energy into liquid fuels do not yet exist.

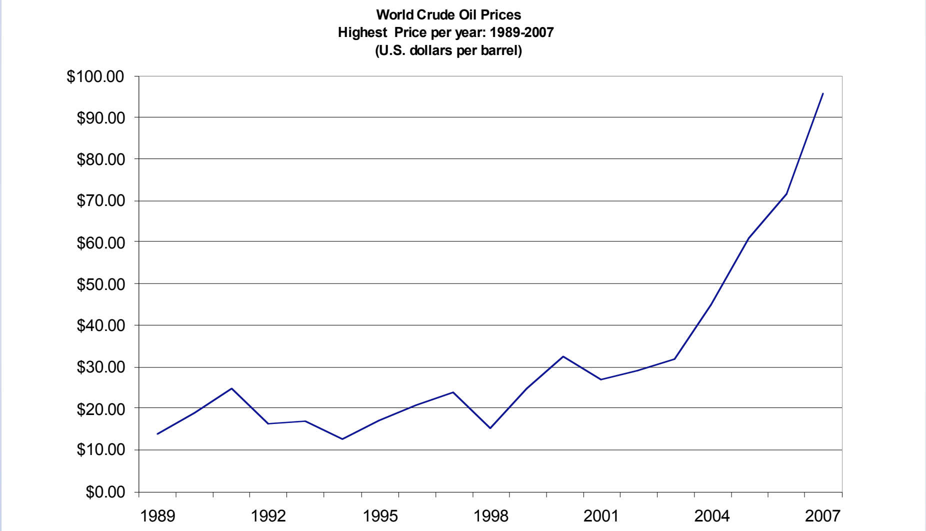
0.4 A NATIONAL MANDATE FOR DOMESTIC BIOFUELS PRODUCTION

Today, the American public overwhelmingly supports the development of technologies to produce alternative fuels and reduce greenhouse gas emissions [Saad 2007]. The environmental and geopolitical challenges resulting from the nation's dependence on fossil fuels, combined with diminishing petroleum resources, have spurred our society to search for renewable sources of liquid fuels and chemicals.

> *"When it comes to energy, we must think big and lead the future. We must be bold; we must declare independence from yesterday's thinking and invest in energy solutions of tomorrow"*
>
> - Nancy Pelosi, Speaker
> U.S. House of Representatives
> June 28, 2007

In 2005, the United States consumed about 874 million gallons of petroleum per day of which 385 million were consumed as gasoline, more than any other country. The 3.9 million gallons of ethanol produced domestically in 2005 represents just 1 percent of our country's annual gasoline consumption [Renewable Fuels Association 2007]. Clearly, achieving the President's goal of reducing the nation's gasoline usage 20 percent by 2017 will require substantial fuel efficiency and conservation efforts in combination with increased domestic biofuels production.

Figure 0.2: World Crude Oil Prices, Annual Highs
[Energy Information Administration 2007b]



In the last six years, the average annual price of regular gasoline has risen from $1.46 to $2.70 per gallon. The price of a crude oil per barrel has more than doubled from $21-$32 in 2000 to a record high of nearly $100 in the fall of 2007 [Energy Information Administration 2007b] (Figure 0.2). From 2003 to 2025, U.S. energy demand is projected to rise by 35%, an increase much greater than the projected growth in domestic production [Energy Information Administration 2007]. The current level of petroleum consumption in the United States, and projections for ever-increasing demand, has wide-ranging environmental consequences and leaves the country vulnerable to severe economic and social impacts resulting from disruptions in oil supplies.

In the challenges associated with our national dependence on oil there is also great opportunity. Today, the United States is fundamentally a petroleum-based economy. The daily consumption of 874 million gallons of petroleum that is used to produce a vast range of fuels, chemicals, and products represents about 3 gallons of petroleum each day for every man, woman, and child in the country. Given the enormous demand for petroleum-based transportation fuels and consumer goods in the U.S. and around the world, the opportunity to develop alternatives cannot be overstated. Ultimately, the solution will be many solutions and will require creative use of existing infrastructure in parallel with development of a new biorefinery infrastructure.

The benefits of moving toward domestic production of fuel from lignocellulosic biomass sources will also yield valuable benefits for national security, the economy, and the environment.

National Security Benefits of Biofuels

Achieving independence from foreign oil, and thereby making the country less vulnerable to political instability in the oil producing regions of the Middle East, is perhaps our foremost energy issue. America's oil consumption accounts for approximately 25 percent of the global total, yet America holds only 3 percent of the world's known oil reserves. Roughly 60% of the 319 billion gallons of petroleum consumed in the U.S. annually is imported, with about 13% (~42 billion gallons) coming from Persian Gulf countries [Energy Information Administration 2007c]. The United States primarily imports crude oil but also imports petroleum products including gasoline, aviation fuel, and fuel oil. A concerted effort to develop the chemical and engineering methods for cost-effective production of biomass-derived alternatives to conventional transportation fuels could significantly reduce our dependence on foreign oil.

Economic Benefits of Biofuels Production in the United States

According to the U.S. Council on Competitiveness, energy security and sustainability are key U.S. competitiveness issues because of the direct impact they have on the productivity of U.S. companies and the standard of living of all Americans [Council on Competitiveness 2007]. A vibrant lignocellulosic biofuels industry would create a large amount of high paying domestic jobs in the agricultural, forest management, and oil/chemical industries.

The U.S. Bureau of Labor Statistics (BLS) has stated that production workers in chemical manufacturing, which would be similar to those in a biorefinery, earn more money ($820 weekly) than in all other manufacturing sectors ($659/week) [US Department of Labor 2005]. The BLS has further stated that the median hourly wages in 2004 were more than $19/hour for plant operators, maintenance and repair workers, chemical technicians, and chemical equipment operators and tenders. Thus, jobs created in the biofuel industry are likely to be good-paying jobs for skilled workers.

Because of the variable nature of biomass resources, small-scale, geographically localized plants are likely to be prevalent in the biofuels production industry. In contrast to fossil fuels, the quantity of biomass is not confined to certain localities and the resource cost of biomass is much lower than that of crude oil. Therefore, conversion to fuels or fuel precursors must be done on a local level to eliminate the expense of transporting low-cost biomass, which would likely limit biomass harvest to a radius of 50-75 miles around the conversion plant; such a plant would produce the liquid fuel equivalent of 10,000-20,000 barrels of oil/day. Distributed production of fuels from domestically grown biomass would reduce infrastructure vulnerability by not consolidating all extraction and production activities in single geographic area. This paradigm of distributed production will create good jobs in biorefineries and may offer the opportunity to found new bio-based industries that will benefit rural economies across the nation.

Biofuels and Food

Biofuels can and should be produced sustainably with food and animal feed as co-products. Ethical and moral questions arise when edible biomass products are converted into biofuels. Therefore, conversion of non-edible biomass is the preferred strategy for long-term, large-scale biofuels production in the U.S. However, the economics are currently more favorable for conversion of edible biomass (e.g. corn starch, soybeans) into fuels due to their chemical structure, which can be more efficiently processed. Therefore, it is important to continue developing technologies for the cost-effective conversion of non-edible lignocellulosic biomass into fuels.

Agricultural practices in the U.S. and other industrialized countries are very advanced, and most industrialized regions produce more than enough food for domestic consumption. Farmers do not pick the crops based on how efficiently they produce edible food products. Instead farmers' goals are to grow crops that maximize their income, even though more efficient crops can be grown. Therefore, to the extent that bioenergy crops can be produced economically and dependably command a good price, they can provide farmers another market for their products, which could improve the economic situation of agricultural communities.

■ Environmental Benefits of Biofuels

One of the biggest benefits of biofuels is the associated reduction in net emissions of CO_2. The release of CO_2 into the atmosphere is directly related to an increase in temperatures worldwide. According to a landmark report released by the United Nation's Intergovernmental Panel on Climate Change (IPCC), an international body comprised of representatives from 113 world governments, "Most of the observed increase in globally averaged temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations." [Climate Change 2007]. The IPCC report further states that burning fossil fuels is one of global warming's main drivers.

Projections of rising sea levels and more frequent episodes of severe weather have prompted policy makers and the general public to demand action to stabilize atmospheric CO_2 concentrations. Over the long term, stabilizing CO_2 concentrations in the atmosphere means reducing emissions close to zero. Fossil fuel combustion releases CO_2 into the atmosphere. While the biofuels combustion also releases CO_2, it is consumed during subsequent biomass re-growth. Thus, biofuels made from lignocellulosic biomass can be carbon-neutral transportation fuels if efficient processes for biomass conversion are developed (i.e. the amount of CO_2 produced during fuel production and combustion is equal to the amount of CO_2 consumed by the biomass during its growth).

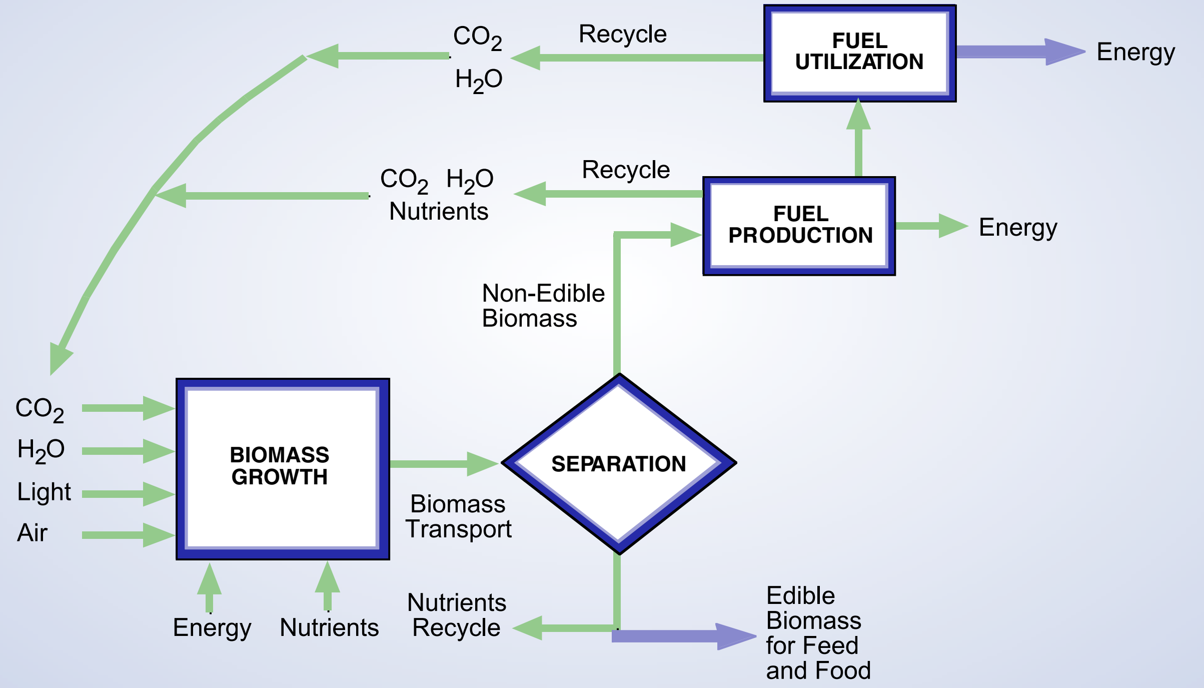
0.5 THE FEASIBILITY OF PRODUCING FUELS FROM LIGNOCELLULOSIC BIOMASS

The objective of the research program outlined in the following sections of this roadmap report is to develop biomass-to-biofuels conversion technologies and processes that are cost- and performance-competitive with petroleum-based fuels. The nation's non-food agricultural and forest biomass provides an ample and underutilized resource base for development of these technologies. A gradual shift from our petroleum-based economy to a biomass-based economy is possible.

As this workshop report illustrates, it is technologically feasible to convert lignocellulosic materials and organic wastes into biofuels. However, costs have to be lowered and new technologies must be demonstrated at a commercial scale (i.e. greater than 150,000 metric tons per year). If this is achieved, second-generation biofuels (i.e. fuels made from non-food biomass feedstocks) will secure a higher market share by allowing the use of a wider range of raw materials. Moreover, the cultivation process for bioenergy crops could be environmentally less intensive than for ordinary agricultural crops, with corresponding cost decreases and lower greenhouse gas emissions.

A concerted program of scientific research based on the recommendations described herein, will set biofuels on a trajectory toward becoming a major U.S. industry sector during the first half of the 21st Century. The projections for development of a mature biofuels industry resembles an accelerated version of the petroleum industry's development over the 20th Century. As with the petroleum industry, the biofuels production sector will be driven by intensive research and development, but

Figure 0.3 The three primary needs (biomass growth, fuel production and fuel utilization) for the biofuel economy.



growth of this new bio-based industry will be accelerated by the innovative and powerful tools now available.

In the past two decades, many new techniques have become available to probe the catalyst and catalyst-reaction medium interface, including various high-resolution electron microscopies, laser spectroscopies, and high field nuclear magnetic resonance spectroscopy. Such techniques have elevated our understanding of the structure-property relationship of biomass-conversion catalytic reactions to a higher level. Together, these and other related tools are helping researchers to unravel the secrets of chemical reactions at the molecular scale. These analytical tools, combined with powerful computer simulations of catalytic reaction conditions, can be used to elucidate reaction mechanisms and design new catalysts with the necessary properties to create high-performance biofuels from a range of biomass feedstocks. However, the complexity of the reaction systems for biomass conversion to fuels has posed new challenges that can be met only by stretching the limits of these tools and techniques and developing new ones.

The projections for accelerated growth and maturation of the emerging biofuels industry must begin with a prolonged period of investigation into the fundamental properties of biofuels feedstocks and their chemical intermediates. This foundational work must then be followed by construction of the necessary infrastructure and/or adaptation of existing petroleum refining and transportation infrastructure for biofuels production.

Carbon dioxide, water, light, air, and nutrients are the inputs for biofuel production. Energy to power transportation vehicles and food are the outputs. The three main technology areas that need to be improved in order to realize this vision of a mature biorefining industry are: (1) growth of the biomass feedstock; (2) biomass conversion into a fuel; and

(3) fuel utilization. (Figure 0.3) [Huber, et al. 2006]. Although the other areas are clearly important, this report focuses exclusively on technologies for the conversion of biomass into fuels.

0.6 BIOFUELS FROM CATALYTIC PROCESSING OF BIOMASS

Biomass can be converted into different types of hydrocarbon fuels, such as "green" gasoline, diesel, and jet fuel. Via the conversion technologies

THE WIDE RANGE OF BIOFUELS FROM LIGNOCELLULOSIC BIOMASS

A biofuel is a liquid transportation fuel made from biomass. Feedstocks suitable for conversion into biofuels include starches such as corn, sugar, animal or vegetable oils, lignocellulosic materials such as trees, grasses or corn stover, waste paper, etc. Unlike fuels derived from fossil sources such as crude oil, biofuels are renewable and have a smaller carbon footprint. A wide variety of biofuels are possible and include single chemical fuels or additives, as well as traditional, complex mixtures of chemicals:

Single molecule fuels or additives:

ETHANOL or ethyl alcohol (C_2H_5OH) can be made from cellulosic biomass via fermentation routes. Polysaccharides are depolymerized to yield monomeric sugars, which are then enzymatically fermented into ethanol. In addition, new technologies are emerging for the synthesis of ethanol and other higher alcohols from biomass-derived syngas via non-biological catalysis.

BUTANOL or butyl alcohol is a four-carbon alcohol. This biofuel can be made from cellulosic biomass via fermentation routes or synthesized from syngas.

HYDROXYMETHYLFURFURAL (HMF) or Furfural is derived from biomass and does not have to be biocatalytically processed via fermentation to make fuels. Sugars can also be dehydrated via chemical catalysis to yield HMF (from 6-carbon sugars like glucose) and furfural (from 5-carbon sugars like xylose). These molecules are building blocks for transformation into potentially viable transportation fuels such as ethyl levulinate (ELV), dimethylfuran (DMF), and γ-valerolactone (GVL). Routes to prepare **DIMETHYFURAN** (DMF), a 6-carbon cyclic ether, from sugars in high yields have recently been reported. DMF is a molecule that has many appealing properties for potential use as a transportation fuel [Roman-Leshkov et al. 2007]

γ-VALEROLACTONE (GVL) is similar to DMF and can be synthesized from decomposition products of sugars. Processes exist for the production of levulinic acid in high yield from monomeric sugars, as well as for the catalytic transformation of levulinic acid into GVL [Manzer 2005]. GVL has recently been suggested to have numerous properties that make it suitable for use as a transportation fuel [Horvath, 2008].

ETHYL LEVULINATE (ELV) is made by the reaction of ethanol and levulinic acid to make an ester. EVL has been suggested as a fuel additive by numerous parties [Manzer 2005].

Mixture of compounds – classical fuels:

"GREEN" GASOLINE OR DIESEL can be synthesized from lignocellulosic biomass by catalytic deoxygenation. Technologies such as biomass reforming can be used to provide hydrogen for reduction of components of cellulosic biomass, such as sugars, as well as lignin fractions of biomass, into gasoline or diesel range hydrocarbons. In some cases, the small biomass fragments need to be coupled to allow for proper molecular weights [Huber, et al. 2005]. Green diesel can also be prepared via the catalytic deoxygenation of fatty acids derived from virgin or waste vegetable or animal oils. These same oils can be transformed into biodiesel by a transesterification reaction with methanol.

described in this report, hydrocarbon fuels derived from biomass are virtually indistinguishable from petroleum-based hydrocarbons with respect to their energy density. Additional advantages of biomass-derived hydrocarbons include their capacity to self separate, which removes the great expense of distillation, and their compatibility with the current fuel utilization infrastructure – no need for engine modifications or new distribution systems.

Catalytic processing is the technique by which liquid fuels and chemicals are made from petroleum-based feedstocks. Catalytic processing can also be applied to the production of liquid hydrocarbon fuels derived from lignocellulosic biomass. However, just as it is impossible to convert all the energy in crude oil into gasoline and diesel fuels, it is equally impossible to convert all the energy of biomass into a fuel. Different conversion technology methods have a wide range of efficiencies. Further advances in conversion technologies and process integration will ultimately improve overall energy and economic efficiency of biofuels.

Liquid biofuels can be produced through a wide range of processes (Figure 0.4).The two main types of catalysts used in these processes are either biological or chemical (Table 0.2). Biological catalysts, such as the yeast used to produce ethanol, are homogeneous catalysts, meaning they are in the same liquid phase as the biomass feed. Chemical catalysts range from homogeneous acids to solid heterogeneous catalysts. As shown in Figure 0.4, the majority of the pathways to biofuels production use chemical catalysts. While mankind has been using biological catalysts in fermentation (i.e. ethanol production) for thousands of years, heterogeneous catalysts have only recently been

Figure 0.4: Routes to Make a Biofuel, adapted from Huber et al. [2006].

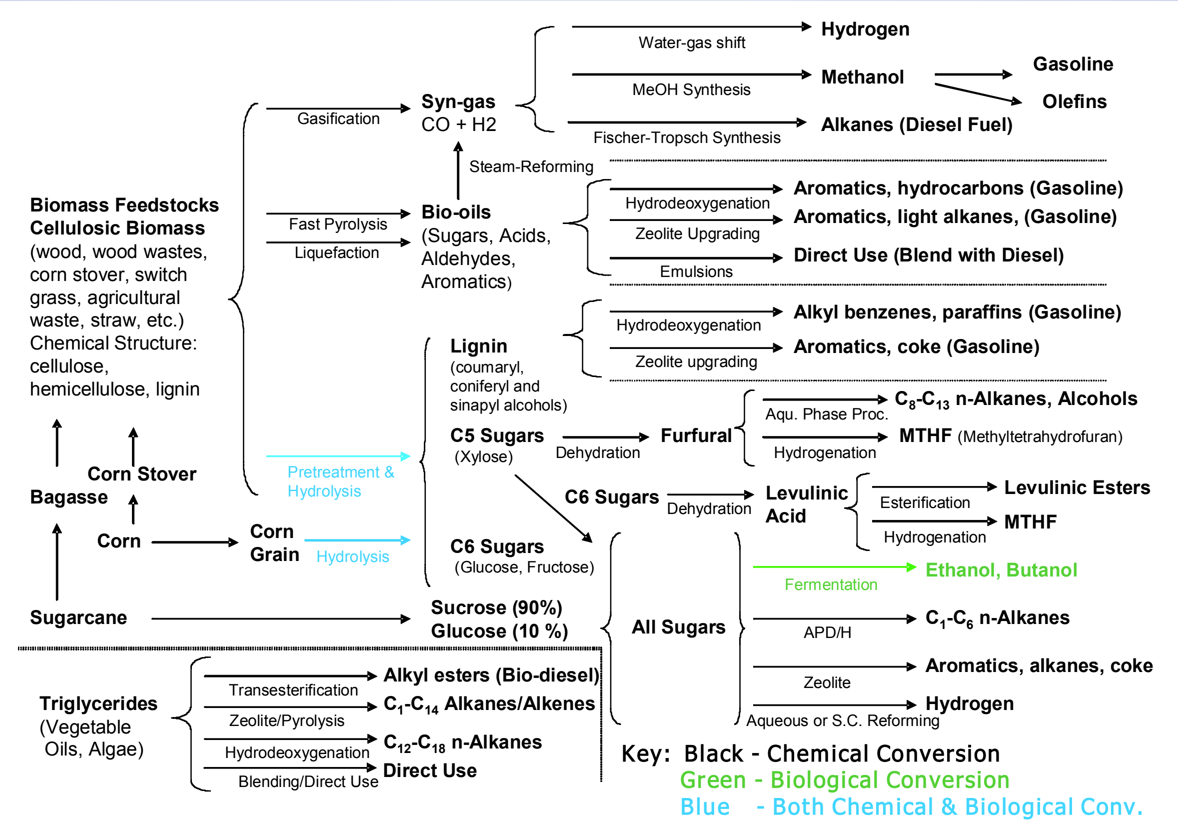


Table 0.2: Comparison of Biological and Chemical Catalysts for Making Fuels from Lignocellulosic Biomass

	Biological Catalysts	*Chemical Catalysts*
Products	Alcohols	A Wide Range of Hydrocarbon Fuels
Reaction Conditions	Less than 70°C, 1 atm	100-1200°C, 1-250 atm
Residence Time	2-5 days	0.01 second to 1 hour
Selectivity	Can be tuned to be very selective (greater than 95 %)	Depends on reaction. New catalysts need to be developed that are greater than 95 % selective.
Catalyst Cost	$0.50/gallon ethanol *(cost for cellulase enzymes, and they require sugars to grow)* *$0.04/gallon of corn ethanol*	$0.01/gallon gasoline *(cost in mature petroleum industry)*
Sterilization	Sterilize all Feeds *(enzymes are being developed that do not require sterilization of feed)*	No sterilization needed
Recyclability	Not possible	Yes with Solid Catalysts
Size of Cellulosic Plant	2000-5000 tons/day	100-2000 tons/day

applied to many of these biofuels production pathways.

Chemical catalysts differ from biological catalysts in a number of respects (Table 0.2). Chemical catalysts can operate at significantly higher temperatures and over a broader set of conditions than biological catalysts. Thus, the residence time for a reaction using biological catalysts is measured in days compared with seconds or minutes for chemical catalysts. Biological catalysts are very selective for certain classes of reactions such as hydrolysis and fermentation. Chemical catalysts can also be selective for certain classes of reactions, and new classes of chemical catalysts will be developed expressly for use with specific biomass-derived feedstocks. Biological catalysts are also more expensive than most chemical catalysts. For example Department of Energy projections indicate that the cost of cellulase enzymes for ethanol production is between $0.30-.50 per gallon of ethanol [EERE 2007]. In contrast, the cost of chemical catalysts in the petroleum industry ranges around $0.01 per gallon of gasoline. The majority of biological catalyst-based processes require feedstocks to be sterilized prior to enzymatic conversion. No sterilization step is required for chemical conversion. Solid chemical catalysts can be recycled, lasting for weeks and even years. In contrast, it is difficult to recycle biological catalysts because they cannot easily be separated from aqueous media once fuel is produced. Furthermore, chemical catalysts present an opportunity for small-scale distributed biorefineries, which may not be possible for processes that utilize biological catalysts exclusively because of the need to scale up the process in order to make it economical. While most research in biofuels to date has focused on development of biological catalysts it should be emphasized that future biorefineries will likely use a combination of biological and chemical catalysts to make biofuels.

WHAT MAKES A GOOD FUEL?

If you ask most drivers what they want when it comes to fueling their cars or trucks you will hear that they want low cost, good mileage, and wide availability. Some, more thoughtful, drivers will add low impact on the environment and improved engine maintenance. While this sounds easy enough, the particulars of providing a fuel that can meet these requirements are quite intricate and involve detailed specifications derived from environmental regulations and engine requirements.

New biomass-derived fuels that can meet these requirements while minimizing the impact on current vehicle engines, fueling infrastructure, and the environment, will have a significant advantage over fuels that require new engines, new tanks, or new types of fueling stations. For example, ethanol and bio-diesel fit into the current transportation infrastructure, which explains why these fuels have had greater commercial success than previous attempts at introducing less compatible fuels, such as compressed natural gas or liquid propane gas.

Engine, fuel, and environmental technologies change with time. Fuels that were excellent for engines of the past would destroy catalytic converters, pollute our air, and give poor driving performance in today's engines. While it is impossible to know the exact details of future fuel specifications since both engines and environmental regulations will continue to evolve, a number of key fuel properties are certain to be important to future fuels.

IMPORTANT GASOLINE PROPERTIES

Some of the most important properties of a "green" gasoline, made entirely of chemicals derived from processed biomass or blended with petroleum products, are: cost; fuel economy; volatility; water tolerance; material compatibility; and environmental impact.

Fuel Economy

Fuel economy is commonly calculated as the number of miles traveled on a gallon of gasoline — miles per gallon (mpg). Some drivers also think of it in terms of fill-up frequency. Although Brazil's experience with substituting fuel ethanol for petroleum-derived gasoline has shown that consumers can cope with more frequent fill-ups when fuels have reduced energy content. However, a new fuel component with high volumetric energy density would be more desirable.

Volatility

The rate at which a liquid vaporizes into the air is its volatility. Fuels only burn once they have vaporized into the air. When a liquid appears to be burning, actually it is the invisible vapor above the surface that is burning.

It is important to note that there is no single best volatility for gasoline. In cold weather, gasoline is blended to vaporize easily. This allows an engine to start quickly and run smoothly until it is warm. In warm weather, gasoline is blended to vaporize less easily in the vehicle to prevent vapor lock or other hot-fuel handling problems and minimize evaporation, which contributes to air pollution.

Three properties are used to measure gasoline volatility in the U.S.: vapor pressure, distillation profile, and vapor-liquid ratio. A fourth property, driveability index, is calculated from the distillation profile. Instead of a vapor-liquid ratio, a Vapor Lock Index (VLI) is used outside the U.S. to control hot-fuel-handling problems.

Octane

Fuels with poor octane rating can damage engines when the fuel ignites prematurely. The measure of a fuel's propensity to pre-ignite is called the octane number. The minimum acceptable octane number for a fuel varies with engine design. Work is being done to redefine the minimum octane requirements for

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modern vehicles based on a measure of acceleration performance.

Heating Value

Heating value is usually thought of as the amount of energy in a gallon of fuel. Conventional fuels vary in heating value. One cause is the formulation differences among batches and among refiners. A 1990–1991 survey of conventional gasolines found that the heating value of summer gasolines varied over an 8 percent range. The heating value also varies by grade and by season. On average, the heating value of premium-grade gasoline is about 0.7 percent higher than regular-grade because premium-grade, in general, contains more aromatic hydrocarbons — the class of hydrocarbons with the highest densities. The heating value of winter gasoline is about 0.5 percent lower than summer gasoline because winter gasoline contains more volatile, less dense hydrocarbons. Since ethanol has less energy per gallon than gasoline, the heating value of ethanol/gasoline blends decreases as the amount of ethanol increases.

Water Tolerance

Fuels always come into contact with water. New fuel blending components that do not absorb water or split into separate phases when mixed with water are highly desirable. Conventional gasoline can dissolve up to 150 parts per million (ppm) water at normal conditions. Oxygenating gasoline by adding ethers to it can increase water solubility to 600 ppm. Bringin either conventional gasoline or ether-oxygenated gasoline into contact with additional water will not affect the properties of the gasoline but can make it hazy in appearance. In contrast, ethanol/gasoline blends can phase separate when they come into contact with too much water.

Material Compatibility

New biomass-derived fuel blending components must not corrode fuel system metal components or dissolve polymers used in fuel tanks and lines. Oxygenates can swell and soften natural and synthetic rubbers (elastomers). Oxygenated gasolines affect elastomers less, the extent of which also depends on the hydrocarbon chemistry of the gasoline, particularly the aromatics content. The effect is of potential concern because fuel systems contain elastomers in hoses, connectors ("O" rings), valves and diaphragms. The elastomeric materials used in today's vehicles in the U.S. have been selected to be compatible with oxygenated gasolines. Owner's manuals approve the use of gasoline oxygenated with 10 vol % ethanol or 15 vol % MTBE (the compatibility of the other ethers is the same as that of MTBE). New gasoline blending components that do not require additional automobile upgrades would be highly desirable.

Environmental and Safety Impact

New fuel components must be safe for the people that use them and for the environment. Lead additives for gasoline were banned decades ago in the U.S. Limits on the amounts of benzene and aromatics in gasoline have been in effect for several years. Recently safety concerns over methyl t-butyl ether (MTBE) caused the use of this material (as well as higher molecular weight ethers and alcohols) as a fuel additive to be banned in some states. No fuel producer will be willing to consider adding a new component to its gasoline without extensive scientific and regulatory review.

Biomass feedstocks have lower levels of sulfur-containing compounds than either crude oil or coal, resulting in lower levels of SOx emissions. Sulfur poisons catalytic converters and on-board diagnostic equipment in vehicles, leading to increased levels of pollutants, which adversely affect human health and the environment. In 2005, the U.S. government imposed a maximum limit on sulfur in gasoline of 30 ppm; the European Union will require even stricter limits of 10 ppm by 2009. Biomass-derived fuels will be required to meet these sulfur limits as well. These lower sulfur concentrations also eliminate the need for a costly sulfur removal step prior to combustion.

continued next page...

WHAT MAKES A GOOD FUEL?

IMPORTANT DIESEL FUEL PROPERTIES

The properties of fuel economy, low engine wear (lubricity), low-temperature operability, long filter life (stability), ease of startup, and low emissions are important to diesel fuels. Their relative importance depends on engine type and duty cycle (truck, passenger car, stationary generator, marine vessel, etc.). "Green" diesel, comprised at least in part from blend stocks produced from biomass, can be formulated to have a number of these desirable properties.

Cetane Rating

When a cold diesel engine is started, the heat of compression is the only energy source available to heat gas in the combustion chamber to a temperature that will initiate spontaneous fuel combustion (about 750°F [400°C]). A fuel that combusts easily will require less cranking to start an engine. The measure of combustibility is referred to as the cetane number. Thus, all other conditions being equal, a higher cetane number fuel makes starting easier. Modern diesel engines require a minimum cetane number of 40 for adequate cold starting unless temperatures are very low. Future engine design advances may reduce this requirement.

Fuel Economy

As for gasoline, fuel economy is related to heating value. The heating value (also referred to as energy content) of diesel fuel is its heat of combustion (i.e. the heat released when a known quantity of fuel is burned under specific conditions). In the U.S., the heating value is usually expressed as British thermal units (Btu) per pound or per gallon at 60°F. (International metric [SI] units are kilojoules per kilogram or per cubic meter at 15°C.)

Lubricity

Some moving parts of diesel fuel pumps and injectors are lubricated by the fuel. To avoid excessive wear, the fuel must have some minimum amount of lubricity. (Lubricity is the ability to reduce friction between solid surfaces in relative motion.) Many diesel fuel components are good lubricants. This is not due to the hydrocarbons that constitute the bulk of the fuel. Instead it is attributed to trace amounts of oxygen- and nitrogen-containing compounds and certain classes of aromatic compounds. Evidence for the role of trace quantities is the fact that the lubricity of a fuel can be restored with the addition of as little as 10 ppm of an additive.

0.7 DESIGNING BIOFUELS PRODUCTION PROCESSES

A comprehensive understanding of the fundamental chemistry, science and engineering underpinning the chemical catalytic production of lignocellulosic biofuels is necessary to build on the many advances that have already been made in the development of biofuels production processes. Empirical "know-how" must be translated into sound theory in order to advance the science and engineering of the biorefinery.

Process optimization is critical to the success of scaled-up biofuels production operations. This requires the combination of process models derived from known feedstock and reactant properties and application of property prediction methods in tandem with laboratory-based research. Through careful process design and engineering using reliable data, 80 percent of biomass-to-fuel production facility can be locked in at the end of the process design phase.

An economic process model is also critical to the development of cost-effective, large scale biofuels production processes. Process economic

WHAT MAKES A GOOD FUEL?

Acidity

Organic acids in diesel fuel can also cause corrosive wear of the fuel system. While this may be a significant wear mechanism for high sulfur diesel, it is less significant for low sulfur diesel because hydrotreating to reduce sulfur also destroys organic acids.

Low Temperature Operability

Low temperature operability is an issue with middle distillate fuels because they contain straight and branched chain hydrocarbons (paraffin waxes) that become solid at ambient wintertime temperatures in colder geographic areas. When this happens, the wax may plug the fuel filter or it may completely gel the fuel, making it impossible for the fuel system to deliver fuel to the engine. This has also been a concern with the current generation of bio-diesels comprised of fatty acid methyl esters. The ability to remain liquid at low temperature is a highly desirable characteristic of diesel blend stocks.

Emissions

Regulated emissions are hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NOx), and particulate matter (PM). Unlike gasoline powered engines, diesel engines don't have much trouble meeting the HC and CO standards. The standards for NOx and PM are much more challenging and are affected by fuel components. Gums in the fuel are deposited on the injectors, causing sticking, which interferes with fuel metering.

Petroleum residue or inorganic salts in the fuel result in injector tip deposits that prevent the injector from creating the desired fuel spray pattern. Excessive abrasive contaminants, organic acids in the fuel, or inadequate fuel lubricity cause abrasive or corrosive injector wear.

IMPORTANT JET FUEL PROPERTIES

Jet fuels are comprised of materials that distill in the temperature range between gasoline and diesel. The specifications are more wide accepted internationally since airplanes cross international borders more frequently than cars and trucks. The important properties of jet fuels are energy content, lubricity, combustion characteristics, stability, distillation range, corrosivity, density, cleanliness, fluidity, and electrical conductivity.

The ASTM specifications for several jet fuels are shown in Table S-0.1 on page 22.

bottlenecks include the needs to: reduce hydrogen requirements; demonstrate catalyst stability; and increase product value. Experiments in chemical engineering and theoretical chemistry should be carried out in tandem with process engineers in order to develop methodologies and processes that are both thermodynamically efficient and economical.

However, a lack of fundamental information about the chemical properties of various biomass feedstocks hinders the development of essential production process models. Detailed models of the chemical and thermodynamic properties of these biostreams would enable the development of advanced bioprocessing systems to create fuels and valuable organic chemicals. The lack of basic understanding about the reaction system limits the ability to draw general relationships between biomass composition, pyrolysis conditions, condensation conditions, and bio-oil composition. The creation of a feedstock and reactant properties database, which will enable the development of properties prediction methods, is essential to the design of cost-effective biofuels production processes.

WHAT MAKES A GOOD FUEL?

Table S-0.1 Summary of ASTM D 1655 Table 1 Requirements*

Property	*Jet A or Jet A-1*	*Jet B*	*ASTM Test Method*
COMPOSITION			
Acidity, total, mg KOH/g, max	0.10	–	D 3242
Aromatics, % vol, max	25	25	D 1319
Sulfur, mercaptan, % mass, max	0.003	0.003	D 3227
Sulfur, total, % mass, max	0.30	0.3	D 1266, D 1552, D 2622 D 4294, or D 5453
VOLATILITY			
Distillation, ºC	D 86		
Volume percent recovered			
10, max	205	–	
20, max	–	145	
50, max	Report	190	
90, max	Report	245	
Final boiling point, max	300	–	
Distillation yields, % vol:			
Residue, max	1.5	1.5	
Loss, max	1.5	1.5	
Flash point, ºC, min	38	–	D 56 or D 3828
Density, 15ºC, kg/m3	775 to 840	751 to 802	D 1298 or D 4052
Vapor pressure at 38ºC, kPa, max	–	21	D 323 or D 5191
FLUIDITY			
Freezing point, ºC, max	– 40 (Jet A) – 47 (Jet A-1)	– 50	D 2386, D 4305, D 5501, or D 5972
Viscosity at –20ºC, mm2/sec max	8.0	–	D 445
COMBUSTION			
Net heat of combustion, MJ/kg, min	42.8	42.8	D 4529, D 3338, or D 4809
One of the following requirements:			
1. Luminometer number, min	45	45	D 1740
2. Smoke point, mm, min	25	25	D 1322
3. Smoke point, mm, min and	18	18	D 1322
naphthalenes, % vol, max	3.0	3.0	D 1840
CORROSION			
Copper strip, 2 hr. at 100ºC, max	No. 1	No. 1	D 130
STABILITY			
Thermal stability, 2.5 hr. at 260ºC:			
Filter pressure drop, mm Hg, max	25	25	D 3241
Tube deposit, less than	Code 3	Code 3	
CONTAMINANTS			
Existent gum, mg/100 mL, max	7	7	D 381
Water reaction, interface rating, max	1b	1b	D 1094

** See the current version of D 1655 for complete requirements.*

0.8 NEXT GENERATION BIOREFINERIES FOR PRODUCTION OF LIQUID FUELS

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic bio-based industry. By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock.

A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but high-volume liquid transportation fuel, while generating electricity and process heat for its own use, and perhaps enough for sale of electricity. The high-value products enhance profitability, the high-volume fuel helps meet national energy needs, and the power production reduces costs and avoids greenhouse-gas emissions [NREL 2007].

PICKING A WINNER!

There are many different types of biofuels to choose from, including fuels currently in use and those that are still on the drawing board. In terms of "picking a winner", we strongly advocate that science should determine the best possible solution. Whether bio-based fuels are best fit for gasoline (spark ignited engines), diesel (compression ignited engines) or jet fuel (turbines) is not critical. While we are not advocating that the end product application be completely ignored, research should be encouraged to facilitate the best possible opportunity for a fuel technology breakthrough that could fit into any of these end-product areas.

As the governmental, academic, and industrial communities debate technology options to develop preferred bio-based fuel pathways, a frequently raised question is, "What fuel or fuel properties do we want to design for?" While this is a key long term question, the immediate issues that deserve prioritized attention include: reducing the oxygen content (lower oxygen content increases energy density in the context of liquid-phase catalytic processing of biomass-derived streams), ensuring that the molecular weight is within the range of fuels compatible with internal combustion engines, and that the end product is designed to optimize compatibility with conventional hydrocarbon fuels.

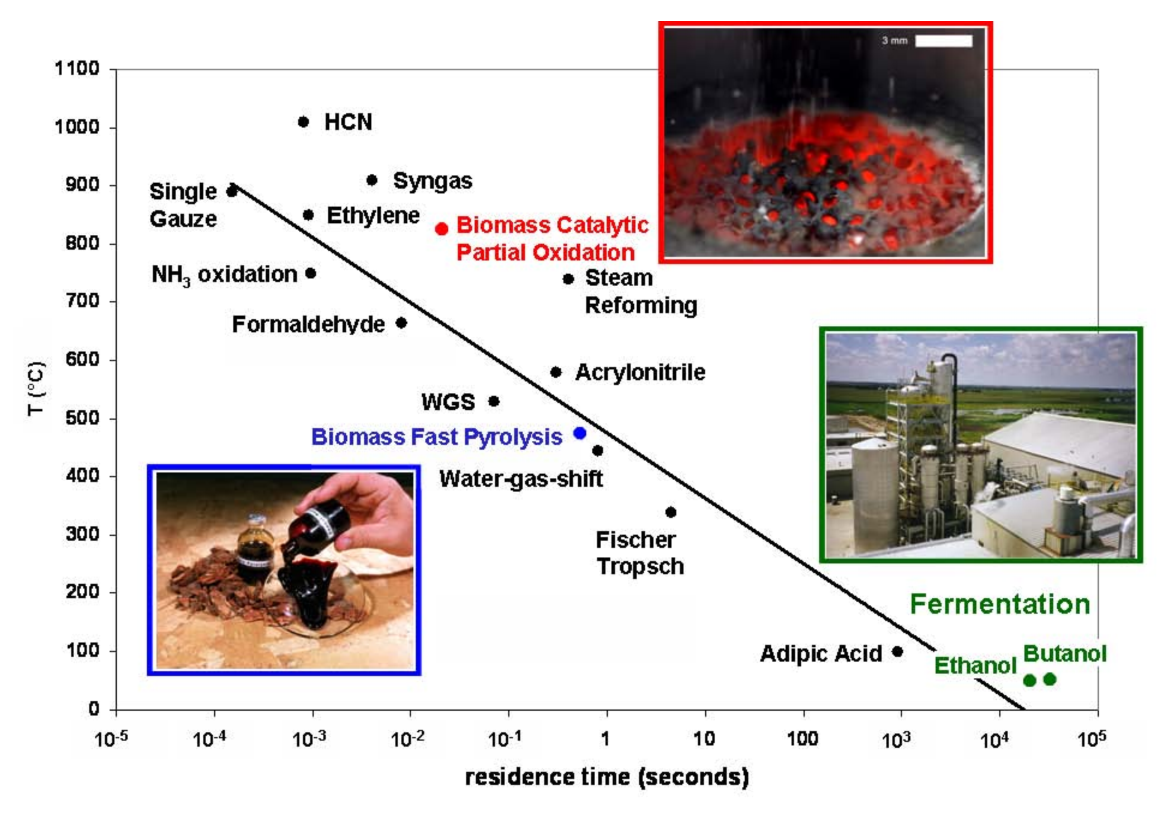
In the global fuels market, advances in biofuel technology would be welcomed in any of these areas. Furthermore, the use of conventional hydrocarbon processing facilities is an option that would exploit the availability of existing fuel processing and distribution infrastructure for the production of biofuels. To summarize, maximum liberty to research and develop a desirable, cost-effective bio-based fuel product should be encouraged and we should not limit ourselves to a "designer fuel" specification mentality that hinders creativity or opportunity.

RAPID BIOFUELS PRODUCTION USING HIGH-EFFICIENCY, SMALL-SCALE REACTORS

The heart of any biorefinery is the reactor (or reactors) where the biomass is converted into a fuel or fuel precursor. The residence time is the time a reactant or product is in the chemical reactor. Ideally the residence time should be as low as possible since this leads to a smaller reactor and lower capital and operating costs. Chemical reactions exhibit a clear, well-understood relationship between temperature and residence time as shown in Figure S-0.1. This figure shows a range of industrial processes, which use both chemical and biological catalysts. Chemical catalysts can be used over a wide range of temperature from 50-1100°C (black dots in Figure S-0.1). In contrast, biological catalysts are only stable at a very limited temperature range (20-50°C), which is required to preserve organic enzymes and microorganisms [Schmidt and Dauenhauer 2007]. Figure S-0.1 also contains two chemical routes to make biofuels. A technique called "biomass fast pyrolysis" (blue dots in Figure S-0.1) rapidly heats wood chips to about 500°C to produce a brown liquid called "bio-oil" in about one second. This transformation of biomass to fuel occurs four to five orders of magnitude faster than biological routes, permitting reactor systems that are several thousand times smaller.

(continued next page)

Figure S-0.1: The residence time of a reaction versus the reaction temperature. Processes that operate at higher temperature require smaller reactor residence times. By selecting a higher temperature process, or adding catalyst, the residence time of chemicals in a reactor can decrease by orders of magnitude.



Chemical routes to biofuels occur even faster by the addition of chemical catalysts combined with higher operating temperatures. It has recently been shown that catalysts can be added to biofuel reaction at high temperature in a process called "catalytic partial oxidation of biomass" (red in Figure S-0.1) permitting particles of biomass to be converted to a liquid fuel precursor called "synthesis gas" as fast as 0.05 seconds residence time [Salge, et al. 2006]. The catalyst also reduces the amount of waste byproduct significantly improving the overall efficiency of the biomass-to-liquids process. As shown in Figure 0.5, white particles of biomass directly impact the bright orange metal catalyst at about 800 °C where they rapidly convert to a gaseous mixture [Dauenhauer, et al. 2006]. The gaseous mixture flows into the catalyst where it undergoes reactions producing predominately liquid fuel precursors. The reaction sustains the necessary high temperatures without a heat source permitting the reaction to operate independently of extra equipment. Small, independent chemical reactions of this nature have the potential to permit production of liquid fuels from biomass at locations as small as individual farms and homes.

The biorefinery of the future will be analogous to the petroleum refinery of the present: a highly integrated system of processes and chemical mechanisms at a fundamental level. Detailed process analysis made the unprecedented efficiencies of the petrochemical industry possible. Similarly, there is a great need for extensive data collection and the development of computer models representing the reactants, products and intermediates involved in the conversion of biomass feedstocks into valuable fuels.

0.9 OVERVIEW OF ROADMAP AND WORKSHOP

This workshop builds on the success of four previous programs:

- **Catalysis for Biorenewables Conversion**
  (2004; Chair: Dennis Miller)
  http://www.egr.msu.edu/apps/nsfworkshop/
- **Design of Catalyst Systems for Biorenewables (report)**
  (2005; Chair: Brent Shanks)
  http://www.nsf.gov/eng/cbet/workshops/catalysis_for_biofuels_workshop_2005.pdf
- **Breaking the Biological Barriers to Cellulosic Ethanol**
  (2005; Chair: Sharlene Weatherwax)
  http://genomicsgtl.energy.gov/biofuels/b2bworkshop.shtml
- **Thermochemical Conversion of Biomass**
  (2007; Chair: Paul Grabowski, David Dayton)
  http://www.thermochem.biomass.govtools.us/

A wide range of experts from industry, governmental agencies and academic research institutions were invited to participate in the workshop:
- 71 invited participants
- 27 academics from 24 universities
- 19 companies represented
- 13 representatives from 5 national laboratores
- 10 program managers (NSF, DOE, USDA)

The workshop was divided into six thrust areas (below). The first four thrusts cover different technical strategies to convert lignocellulosic biomass into biofuels. The last two strategies address important cross-cutting areas which affect all of biomass conversion. Figure 0.5 shows a general scheme that illustrates the overall approaches to the conversion of lignocellulosic biomass to fuels. This scheme also provided the organization structure of the workshop.

- **1. Selective Thermal Processing of Lignocellulosic Biomass**
- **2. Utilization of Petroleum Refining Technologies for Biofuel Production**
- **3. Liquid-phase Catalytic Processing of Sugars and Bio-oils**
- **4. Catalytic Conversion of Syn-gas[2]**
- **5. Process Engineering and Design**
- **6. Cross Cutting 21st Century Science, Technology, and Infrastructure for a New Generation of Biofuel Research**

The Key Findings of the workshop are outlined in the following sections. We have identified the basic research needs and opportunities in catalytic chemistry and materials science that underpin biomass conversion and fuel utilization, with a focus on new, emerging and scientifically challenging areas that have the potential for significant impact. The report illuminates the principal technological barriers and the underlying scientific limitations associated with efficient processing of biomass resources into finished fuels. Major developments in chemistry, biochemistry, materials and other disciplines associated with biomass-to-fuels processing are underscored and strategies to overcome the long-term grand challenges are outlined.

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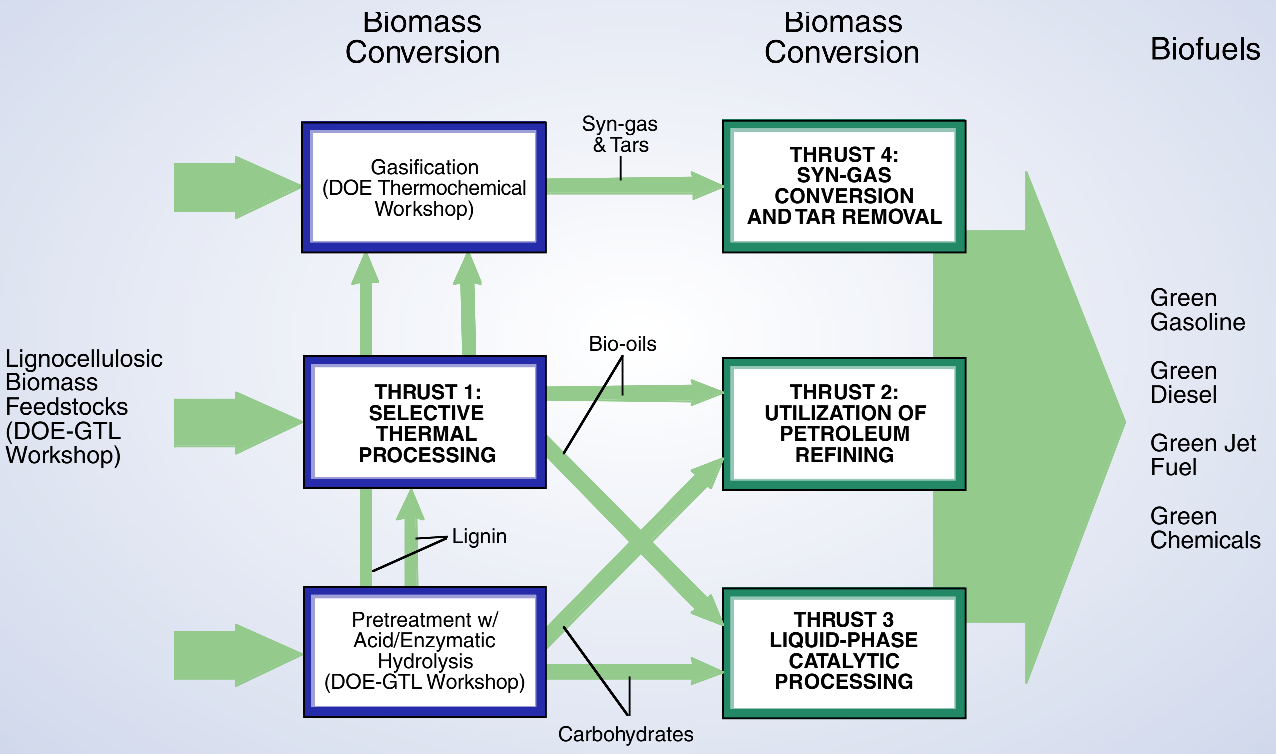
[2] Biomass gasification was not discussed because it was the primary focus of a previous DOE workshop held in January 2007. (www.thermochem.biomass.govtools.us/).

Figure 0.5: Overview of Workshop



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An Integrated Chemical and Engineering Platform for Overcoming the Barrier to Cellulosic Biofuels…

1. Selective Thermal Processing of Cellulosic Biomass and Lignin

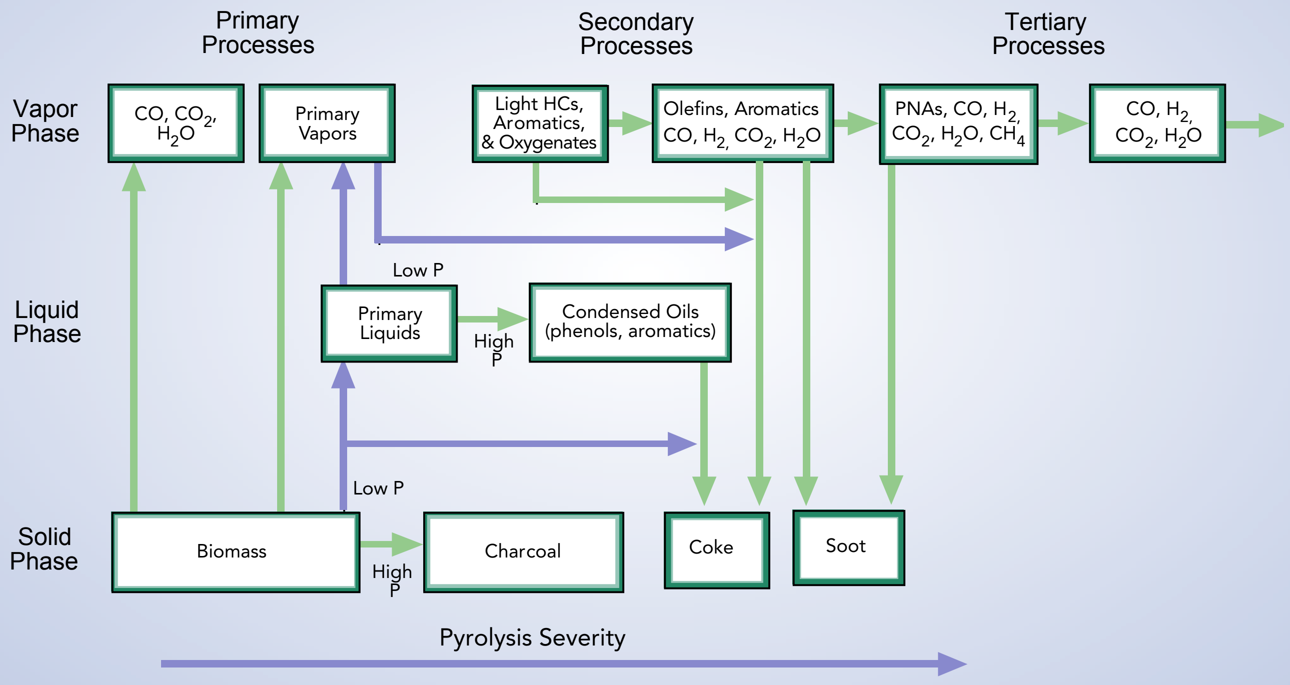
OVERVIEW:

The production of bio-oils, through thermal processing of biomass, is a versatile and economical first step in the fabrication of liquid transportation fuels. Bio-oils are multi-component mixtures comprised of different sized molecules derived primarily from depolymerization and fragmentation reactions of the three key biomass building blocks: cellulose, hemicellulose, and lignin. Bio-oils production technologies are relatively low cost and suitable for small-scale applications. Several types of thermal processes for producing bio-oils are in the commercial pilot plant stage, demonstrating that the economics of these processes are competitive. However, current bio-oils production technology is not very selective, resulting in a bio-oil composed of more than 300 chemical species. New techniques for increasing the control of bio-oil composition are needed to make this technology more attractive. Among the technological advances needed are better characterizations of the thermal reactions and an examination of how catalysts may be incorporated into the reaction environment to produce the preferred bio-oil compositions.

1.1 INTRODUCTION

Lignocellulosic biomass is difficult to deconstruct into easily utilized sub-fractions because of its heterogeneous composition. The approaches used for lignocellulose deconstruction can be broadly lumped into three classes: gasification, hydrolysis, and selective thermal processing. Of these three approaches, gasification creates a primary product with the simplest chemical distribution, but this synthesis gas ("syngas") product must be subsequently reconstructed into fuels and chemicals, as discussed in Chapter 4. Hydrolytic processes, particularly if performed with

Figure 1.1 A schematic showing the chemical products resulting from the thermochemical conversion of biomass in the absence of any catalytic materials.



biocatalysts (as in fermentation), provide a mixed sugar and a lignin product with slightly higher chemical species complexity than with gasification. Of these three approaches, selective thermal processing results in a product with the highest level of chemical complexity. In spite of the chemical complexity of the resulting bio-oil, the advantage of this approach is the simplicity of the process.

The complexity of the chemical products resulting from thermal fractionation is illustrated in Figure 1.1. Depending on the severity of the pyrolysis conditions the product slate can access a range of chemical processes; increased severity is defined as higher temperature and/or longer reaction times. These chemical processes, which are a function of pyrolysis severity, can be lumped into primary, secondary and tertiary reactions. Primary processes represent the first products produced when lignocellulosic biomass is thermochemically treated. However, these primary products can go through subsequent conversion to secondary products. Finally, as the process severity increases, the secondary products can react again. Products from the tertiary processes represent those obtained via gasification. It is important to note that the chemical products shown in Figure 1.1 represent only the products produced by thermal reactions. Incorporating catalytic materials into this process provides an opportunity to further alter this chemical landscape.

The liquid bio-oil produced by thermal fractionation processes requires requires downstream catalytic upgrading, discussed in Chapter 2 and 3. The current chapter and the following chapters on upgrading are inherently linked because the composition of chemical products obtained by a given thermal fractionation process will drive the type of processing needed to upgrade the resulting bio-oil. However, the inverse problem of determining what thermal fractionation products are most amenable to upgrading is also tremendously important. Substantial process optimization can only achieved by concerted work in both the areas of thermal fractionation and upgrading.

SECTIONS OF THRUST 1:

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1.2 OVERALL PROCESS DESCRIPTION

■ 1.2.1 Fast Pyrolysis

Biomass pyrolysis is the thermal depolymerization of biomass at modest temperatures in the absence of added oxygen. The slate of products from

DISTRIBUTED BIOFUELS PRODUCTION USING FAST PYROLYSIS

A fundamental challenge to cost-effective biomass-conversion is the expense of transporting low energy density biomass feedstocks. An advantage of fast pyrolysis is that this technology is economical for use on a small scale (i.e. 50-100 tons-biomass/day) where fast pyrolysis systems are built on portable units and distributed close to the biomass source. This can significantly reduce costs. For example the cost of biomass has been reported to be $22/dry-ton for a 24 tons/day biofuel facility, which is half the cost of a 1000 ton/day facility which would be $44/dry-ton. This contrasts with other biofuel technologies, such as cellulosic ethanol, where bigger is usually better due to economies of scale.

Another advantage of the distributed technology is that it may create more jobs, compared with other large-scale biofuel technologies. The distributed technology has lower capital cost investment, but a higher operating cost than other biofuel technologies such as cellulosic ethanol. The higher operating cost is because more operators are needed than with a larger scale processing facility. The chemical industry is one of the highest paying industries for skilled labor. The U.S. Bureau of Labor Statistics (2005) has stated that production workers in chemical manufacturing (which would be the same as those who work in a bio-refinery) earn more money ($820 weekly) than in all other manufacturing industries ($659/week) and than in private industry ($529/week). They further state that in 2004 the median hourly wages were above $19/hour for plant operators, maintenance and repair workers, chemical technicians, and chemical equipment operators and tenders.

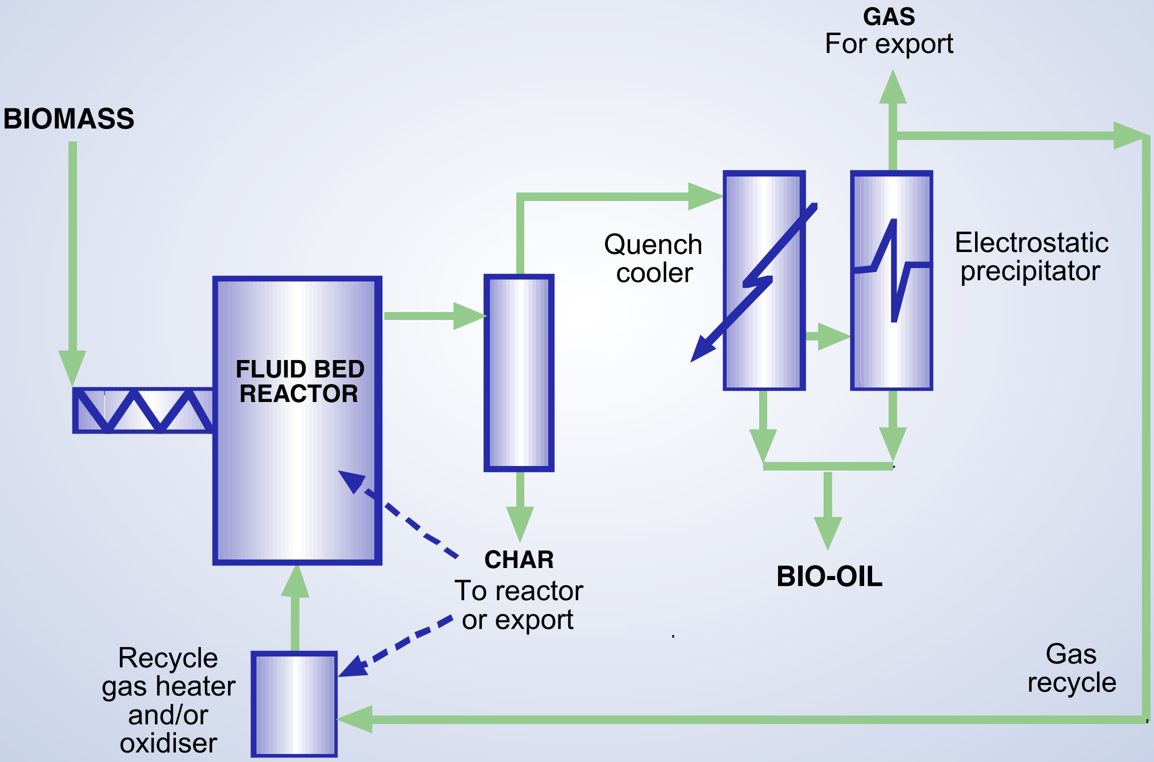
Utilization of small mobile or modular pyrolysis reactors is a concept that is currently being developed to produce liquid biofuels close to the biofuel location. Figure S-1.1 illustrates a fast pyrolysis reactor that is built on a truck bed. One of the most successful tests of this concepts was the Canadian Waterloo Fast Pyrolysis Process comprising a mobile trailer with a production capacity of 200 kg/hr that was tested successfully to process several fuel types. Several small companies, including Renewable Oil International® LLC, are focusing on development of smaller mobile or modular pyrolysis reactors.

Figure S-1.1 A Small scale portable reactor for liquid fuel production by distributed fast pyrolysis.

1.2.1 Fast Pyrolysis continued

biomass pyrolysis depends on the process temperature, pressure, and residence time of the liberated pyrolysis vapors (Bridgwater, 1999; Bridgwater and Peacocke, 2000; Czernik and Bridgwater, 2004; Yaman, 2004). Production of the bio-oil products is maximized by fast pyrolysis, which is typically performed at temperatures of 450 to 500°C at atmospheric pressure (Czernik and Bridgwater, 2004). High heating rates (i.e., 500°C/s) and short residence times (1-2 s)

Figure 1.2: A diagram of the key process components for a representative fast pyrolysis process utilizing a fluidized bed reactor (used with permissions from Bridgwater et al., 2001)

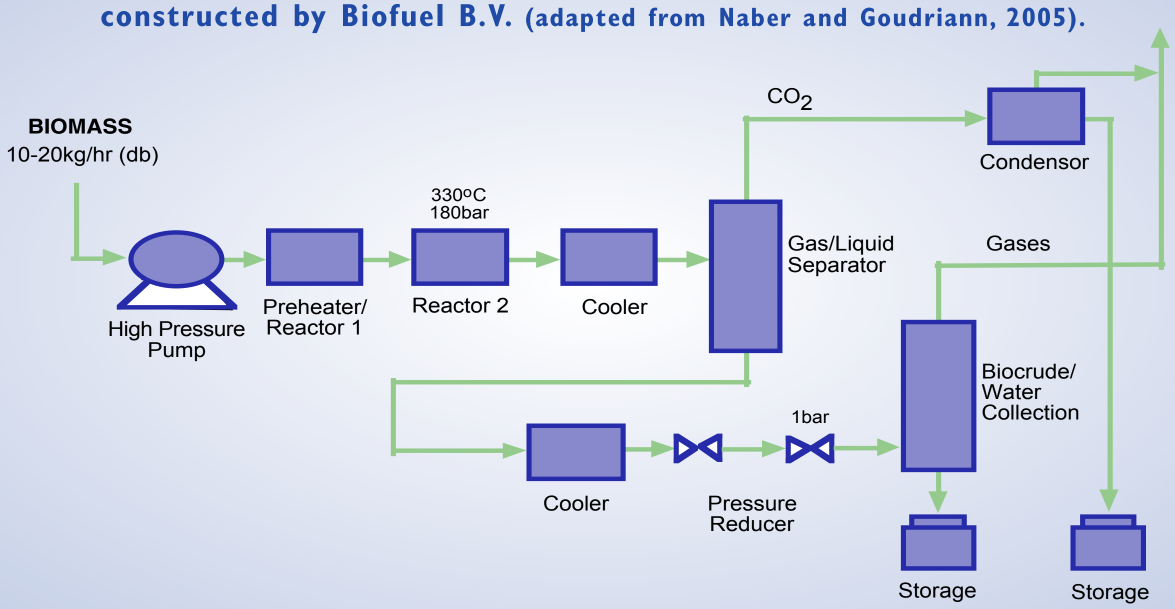


produce substantial yields of bio-oils that retain up to 70% of the energy present in the biomass feedstock prior to processing .

The products from the fast pyrolysis process include gases, bio-oil, and char. A representative distribution of products from a fast pyrolysis reactor, operated to maximize the bio-oil liquid, is: 65 wt% organics, 10 wt% water from the reaction, 12 wt% char, and 13 wt% gas. However, the relative ratios of three of these fractions is highly dependent on reaction conditions, reactor design, and biomass alkali content.

Bio-oil consists of water soluble and insoluble fractions. The water-soluble fraction, which is high in oxygen content, is derived from the cellulose and hemicellulose fractions of the biomass. The water insoluble fraction, which has lower oxygen content, is derived primarily from the lignin fraction. The chemical species in the bio-oil exit the pyrolysis reactor in either the vapor form, as a free radical precursor, or in an aerosol form.
A schematic of a fast pyrolysis process is shown Figure 1.2. The schematic shows a fluidized bed reactor, but a number of different reactor designs, which can provide high biomass heating rates and short product residence times, have been studied (Scott et al., 1999). A key feature in the subsequent utilization of the bio-oil is effective separation of the solid char so as to minimize its presence in the liquid bio-oil.

Figure 1.3 A process diagram for an aqueous liquefaction pilot plant constructed by Biofuel B.V. (adapted from Naber and Goudriann, 2005).



1.2.2 Liquefaction

Bio-oils can also be produced by liquefaction, which occurs in the presence of a solvent at high pressure (120-200 atm) and relatively mild temperatures (300-400 °C). Addition of catalysts to the liquefaction process can improve the quality of the bio-oil produced. The most commonly used solvent in liquefaction studies is water (Moffatt and Overend, 1985; Naber et al., 1997; Goudriaan and Peferoen, 1990). A biomass solids loading of about 40% by weight can be used in the process. One attractive feature of this process is that wet biomass can be used directly. In contrast to the bio-oil from fast pyrolysis, the liquefaction product has lower oxygen content. The difference is due to a significant amount of decarboxylation that occurs during the liquefaction process. The removal of oxygen via decarboxylation leaves a more favorable C/H ratio in the bio-oil product and makes the product water insoluble.

Table 1.1 Properties of bio-oils and heavy fuel oil
(compilation from Czernik and Bridgwater, 2004; Elliott and Schiefelbein, 1989; Huber et al., 2006).

Property	*Pyrolysis oil*	*Liquefaction oil*	*Heavy fuel oil*
Moisture content, wt%	15-30	5.1	0.1
pH	2.5		
Specific gravity	1.2	1.1	0.94
Elemental composition, wt%			
-carbon	54-58	73	85
-hydrogen	5.5-7.0	8	11
-oxygen	35-40	16	1.0
-nitrogen	0-0.2		0.3
-ash	0-0.2		0.1
Higher heating value, MJ/kg	16-19	34	40
Viscosity (50°C), cP	40-100	15,000 (at 61°C)	180
Solids, wt%	0.2-1		1
Distillation residue, wt%	Up to 50		1

The products from the liquefaction process include gases, water-insoluble bio-oil, and an aqueous phase with water soluble products. A representative product composition by weight basis of the initial biomass feedstock is: 45% bio-oil, 25% gas (with >90% of gas being CO_2), and 30% aqueous phase (with the aqueous phase consiting of 66% water, and 33% soluble organics) (Naber and Goudriann, 2005). Several aqueous liquefaction pilot plants were operated until the 1980's (Moffatt and Overend, 1985; Elliott et al., 1991), but are no longer in use. Biofuel B.V. is a startup company located in the Netherlands that is still actively pursuing aqueous liquefaction of biomass. Shown in the Figure 1.3 is a schematic of the Biofuel B.V. liquefaction pilot plant known as the HTU® process.

1.3 RESULTING FUELS

The biomass-derived fuels produced from both the fast pyrolysis and liquefaction processes are highly dependent on the feestock properties as well as the process conditions, making precise definitions of the resulting products problematic. Nonetheless, the chemistries associated with these two processes is somewhat different and have distinguishing characteristics. Table 1.1 compares the compositions and properties of representative bio-oils from fast pyrolysis and liquefaction versus that of heavy fuel oil (Czernik and Bridgwater, 2004; Elliott and Schiefelbein, 1989; Huber et al., 2006).

1.3.1 Fast Pyrolysis Product Analysis

Bio-oil has significantly different physical and chemical properties compared to the liquid from slow pyrolysis processes, which is more like a tar. Bio-oils are multi-component mixtures comprised of different sized molecules derived primarily from depolymerization and fragmentation reactions of the three key biomass building blocks: cellulose, hemicellulose, and lignin. Therefore, the elemental composition of bio-oil resembles that of biomass rather than that of petroleum oils.

Table 1.2 A general breakdown of the components in fast pyrolysis bio-oil (Bridgwater et al., 2001).

	Wt%
Water	20-30
Lignin fragments: insoluble pyrolytic lignin	15-20
Aldehydes: formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal	10-20
Carboxylic acids: formic, acetic, propionic, butyric, pentanoic, hexanoic	10-15
Carbohydrates: cellobiosan, levoglucosan, oligosaccharides	5-10
Phenols: phenol, cresol, guaiacols, syringols	2-5
Furfurals	1-4
Alcohols: methanol, ethanol	2-5
Ketones: acetol (1-hydroxy-2-propanone), cyclopentanone	1-5

Most of the phenolic compounds are present as oligomers having a molecular weight ranging from 900 to 2500. The presence of oxygen in many oil components is the primary reason for differences in the properties and behavior seen between hydrocarbon fuels and biomass pyrolysis oils. The high oxygen content results in a low energy density (heating value) of 50% of conventional fuel oils. An even more important consequence of the organic oxygen is the instability of bio-oil.

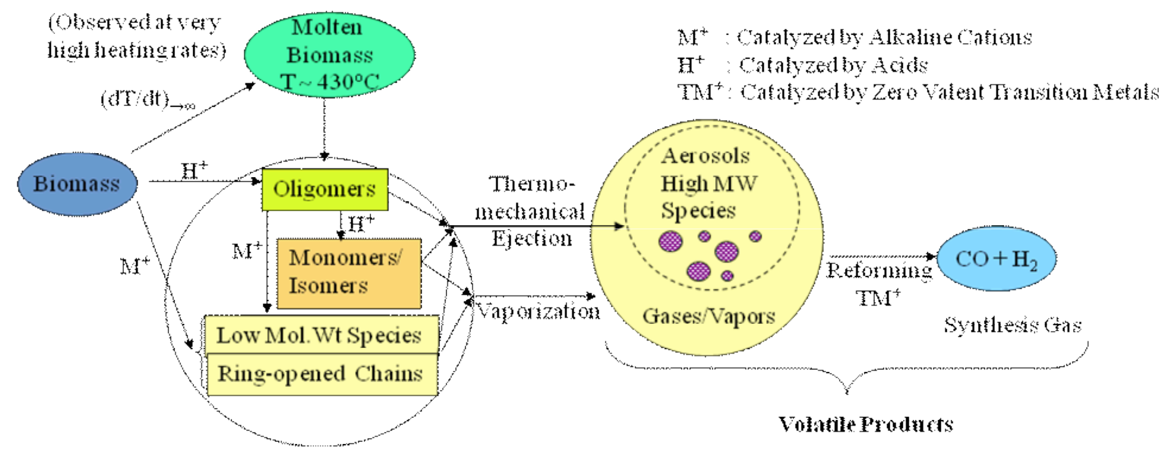
Liquid bio-oil can be transported and stored. Czernik and Bridgwater (2004) reviewed the research in this field, which demonstrates that direct application of bio-oils for heat and power generation is possible requiring only minor modifications of the existing equipment. Bio-oil has been successfully used as boiler fuel and has also showed promise in diesel engine and gas turbine applications (Elliott et al., 1991; Solantausta et al., 1992; Grassi and Bridgwater, 1993; Peacocke and Bridgwater, 1994; Wornat et al., 1994; Czernik et al., 1995; Solantausta et al., 1995; Oasmaa and Czernik, 1999; Boucher et al., 2000; Shihadeh and Hochgreb, 2000; Ganesh and Banerjee, 2001; Vitolo et al., 2001; Chiaramonti et al., 2003; Gayubo et al., 2004; Gayubo et al., 2004; Yaman, 2004). Several technical challenges need to be overcome in order to upgrade bio-oil to a quality of transport liquid fuel that would be broadly adopted and economically attractive (Bridgwater and Cottam, 1992; Cottam and Bridgwater,,1994; Williams and Horne, 1995; Williams and Horne, 1995; Horne and Williams, 1996; Vitolo et al., 2001; Yaman, 2004).

Though over 300 compounds have been identified in wood fast pyrolysis oil, they are found in small amounts. Therefore isolation of specific single compounds is seldom practical or economical because it usually requires complex separation techniques. Some chemicals produced from the whole bio-oil or by its fractionation are already commercial products, for example liquid smoke used as a food-flavoring component. A few others, such as pyrolytic lignin as phenol replacement in resins or bio-oil based slow-release fertilizer, have a chance for short-term commercialization, especially if a bio-refinery concept based on a fast pyrolysis process is implemented.

1.3.2 Liquefaction Product Analysis

In contrast to fast pyrolysis, significantly less work has been reported on the chemical species analysis of liquefaction oils (Elliott 1981, Elliott 1981, Schirmer et al, 1984, Elliott 1985). Since a large amount of decarboxylation and dehydration occurs under liquefaction conditions, the bio-oil product has much lower oxygen content, and consequently a higher heating value, than bio-oils from fast pyrolysis. Of the total oxygen removed during

Figure 1.4 Pyrolysis pathway model (adapted from Radlein, 1999).



liquefaction, more than 50% has been attributed to decarboxylation (Goudriaan et al., 2001). The water-insoluble bio-oil derived from the Biofuel B.V. HTU® process is a heavy organic liquid that solidifies at 80°C and has a H/C of 1.1 (Naber and Goudriann, 2005). The lower oxygen content in liquefaction bio-oil makes it a more attractive fuel than fast pyrolysis bio-oil from the standpoint of energy density, but the high viscosity associated with the liquefaction bio-oil limits its utility without some amount of upgrading.

1.4 SUMMARY OF PREVIOUS RESEARCH

1.4.1 Fast Pyrolysis

Several published reviews provide extensive accounts of previous research on fast pyrolysis (Bridgwater and Peacocke, 2000; Bridgwater et al., 2001; Mohan et al., 2006). The key to maximizing the yield of bio-oils in a fast pyrolysis reactor are: rapid heating, high heat transfer rates, a reactor operating temperature of ~500°C, and rapid cooling of the pyrolysis vapors. In addition to these processing variables, the biomass alkali content has significant impact on the bio-oil composition because the alkali salts catalyze cracking to lower molecular weight species in the pyrolysis reactor. Due to the complexity of the reaction system, most of the studies have been empirical and highly dependent on the reactor system and specific feedstock used in a given study. As a result detailed comprehensive models for fast pyrolysis have not been developed. Nonetheless, some high level models exist that can explain gross trends.

Radlein (1999) has proposed the pyrolysis pathways shown in Figure 1.4. There are several important features of this model that significantly impact the products from the fast pyrolysis reaction. As noted in the figure, acid catalyzed reactions are thought to depolymerize the biomass to oligomers that can be subsequently converted to monomers. The acids in the reaction, which are carboxylic acids, are generated from the reaction and then participate in the conversion of other reaction intermediates. Alkaline cations, which are present in lignocellulosic feedstocks, catalyze reactions to lower molecular weight species as well as catalyzing ring opening reactions. Some pretreatment work has been performed in which the alkaline cations are removed from the feedstock prior to pyrolysis. The pretreatment leads to increased anhydrosugars in the bio-oil product.

Products from the fast pyrolysis reaction leave the reactor in three states: volatile gases that contain condensable and noncondensable fractions, liquids that are present as aerosols, and solids that consist of the char and some condensed liquid. The char is first removed from the effluent stream with a cyclone. While a cyclone will remove much of the char, some solid particles are not removed at this point and end up in the bio-oil, which has implications on the resulting bio-oil quality. The condensable gases are then quenched and collected as the bio-oil. The method used to quench these gases influences the chemical species ultimately present in the bio-oil.

The bio-oil produced from fast pyrolysis contains hundreds of chemical species making full characterization of the bio-oil quite challenging. As such, many studies have only characterized bio-oils by properties such as those given in Table 1.1. Unfortunately, this level of detail provides limited insight into the reactions taking place through the fast pyrolysis process. Reactions influencing the final bio-oil product occur in the fast pyrolysis reactor through the range of processes given in

Figure 1.1 as well as through char-facilitated reactions and alkali-facilitated reactions. Another set of reactions occur during the condensation process. Finally, bio-oil in the condensed state is still reactive and undergoes further conversion. Diebold (2002) suggested that the range of reactions that can occur in fast pyrolysis bio-oil after it has been condensed include esterification of organic acids with alcohols, transesterification of esters, homopolymerization of aldehydes, hydration of aldehydes or ketones, hemiacetal formation of aldehydes and alcohols, acetalization and transacetalization of aldehydes and alcohols, phenol/aldehyde reactions to form resins, polymerization of furan derivatives, and dimerization of organic nitrogen from proteins. The high level of acidity in bio-oil can catalyze a number of these reactions. The addition of methanol or ethanol to fast pyrolysis bio-oil at the 10 wt% level was found to be effective in largely retarding these condensed phase reactions (Diebold and Czernik, 1997).

A number of different reactor types have been examined to optimize the fast pyrolysis reactions including, fluidized beds, circulating fluidized beds, ablative pyrolyzers, and vacuum pyrolyzers (Scott et al., 1999). In all cases, the goal is to maximize heat transfer to the biomass and minimize the residence time of the pyrolysis products in the reactor. While each of these reactor systems has advantages and disadvantages, fluidized bed reactors appear to be the most economical and readily scalable option.

1.4.2 Liquefaction

While Biofuel B.V. continues the commercial development of liquefaction, it has received significantly less attention in the technical literature recently (Elliott 1981, Elliott 1981, Schirmer et al, 1984, Elliott 1985). Several reviews provide an overview of the liquefaction process through 1990 (Moffatt and Overend, 1985; Elliott et al., 1991). To an even greater extent than with fast pyrolysis, there is little information available to compare reaction products of different liquefaction conditions because the reaction products have typically only been evaluated at a very general level as given in Table 1.1. Even the limited chemical speciation work done with fast pyrolysis bio-oil has not been replicated in the literature for liquefaction bio-oil. Therefore, prior work has focused on the empirical correlation between liquefaction conditions, primarily temperature, pressure, and residence time, with high level properties of the resulting bio-oil.

1.4.3 Sub and Supercritical Catalytic Reforming of Biomass

One important subset of biomass liquefaction is the catalytic reforming of biomass in sub and supercritical water. Sub and supercritical reforming of sugars and biomass-derived feedstocks can produce H_2 and/or methane (Matsumura, Minowa et al. 2005). Supercritical water conditions occur at conditions above the supercritical point of water (temperatures above 375°C and pressures above 217 atm). Modell showed that supercritical reforming of wood sawdust was able to produce gaseous products and avoid coke formation (Modell 1977; Modell, Reid et al. 1978). Thus, supercritical reactions can be used to efficiently gasify glucose (and other biomass components) without coke formation. Heterogeneous catalysts have been used in subcritical reactions and have been shown to greatly change the product selectivity. The Battelle single-step subcritical gasification reactor produces gas with high methane levels at temperatures around 350°C and pressures 21 MPa with Ru or Ni catalysts supported on TiO_2, ZrO_2 or carbon (Elliott, Neuenschwander et al. 2004; Elliott, et al, 2006). Higher reaction temperatures (600°C and 34.5 MPa) for supercritical reactions have been able to produce H_2 from supercritical reforming of glucose (Matsumura, Minowa et al. 2005). Xu et al. showed that activated carbon is an efficient catalyst for supercritical gasification of glucose (Xu, Matsumura et al. 1996). At a WHSV of around 20 h-1 close to 100 % of the glucose feed was gasified with a molar gas composition of 22% H_2, 34 % CO, 21% CO_2, 15 % CH_4, 6% C_2H_6, and 2% C_3H_8.

Other biomass feedstocks including whole biomass can also be used for supercritical gasification. The advantages of supercritical reforming are that high reaction rates are obtained, impure feedstocks can be used, wet feedstocks can be processed with high thermal efficiencies, product gas is produced in a single reactor, and the product gas is available at high pressure. The disadvantages of supercritical reforming are the high capital cost of a high-pressure reactor and that H_2 can be selectively produced only at high temperatures where large amounts of CO are also produced. Supercritical reforming is an excellent way to produce product gases from aqueous biomass mixtures.

1.5 ECONOMICS AND POTENTIAL OF TECHNOLOGY

The most recent direct comparison of the economics of the fast pyrolysis versus the liquefaction process was presented by Elliott et al., 1990 and is given in Table 1.2. The results are presented in 1990 U.S. dollars and assume a 1000

Table 1.2 A comparison in 1990 U.S. dollars of the economics of producing bio-oil from wood chips using either a fast pyrolysis or liquefaction process (table adapted from Huber et al., 2006).

	Fast pyrolysis		*Liquefaction in solvent*	
	Present	*Potential*	*Present*	*Potential*
Total capital requirement ($US millions)				
primary liquefaction	49.8	26.4	84.2	48.4
crude upgrading	46.6	34.3	26.8	26.0
product finishing	14.5	0.7	15.3	0.7
total	110.9	61.4	126.3	75.1
Production costs ($US million/year)				
fixed operating costs	14.48	10.77	14.48	10.03
variable operating costs	25.74	23.67	33.44	33.60
(feedstock costs)	(20.00)	(20.00)	(20.00)	(20.00)
capital charges	12.96	7.17	14.75	8.78
total production cost	53.18	41.61	62.67	52.39
Minimum selling price ($US/GJ)				
bio-oil	9.32	6.91	13.44	12.27
refined bio-oil	16.24	12.99	19.54	14.77
Process thermal efficiency (energyliquid products/energyfeed+inputs)				
primary liquefaction prod.	0.61	0.68	0.55	0.48
finished product	0.52	0.53	0.48	0.49

** See the current version of D 1655 for complete requirements.*

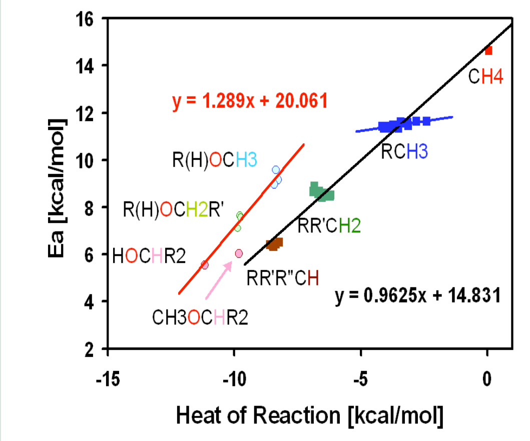
DEVELOPMENT OF DETAILED KINETIC MECHANISMS FOR MODEL BIOMASS COMPOUNDS

The full potential of biomass as a resource for transportation fuels, fine chemicals or syngas can only be reached through improved understanding of the underlying conversion chemistry. This in turn means the development of predictive models, which will support the process design and optimization of a conversion process. Given the complexity of biomass, highly detailed model predictions will be impossible in the foreseeable future. However, taking gasification applications as an example, such mechanisms should at least be able to reliably predict hydrogen to carbon monoxide ratios as well key reactive species and byproducts. Similarly, a good model should be able to support the search for the reaction conditions that will result in more valuable reaction products in bio-oil upgrading.

While development of such a kinetic mechanism is a formidable challenge, several factors suggest significant progress is possible: (1) Despite the overall complexity of biomass, it consists largely of just a few chemically relevant units (e.g., lignin has many phenyl, alcoholic and ether groups and bio oil has acid groups); (2) The reaction chemistry is thought to be analogous to the chemistry of well-studied hydrocarbon systems. Thus, one expects that the same reaction types (H abstraction, β-scission and isomerization) will dominate, even though the specifics will differ to reflect the weakening of C–H bonds next to the oxygen functionalities in biomass. (3) Well-established theoretical tools (e. g., electronic structure methods) are readily available and can be applied either directly or with minor modifications for oxygenated substances such as biomass.

Building on Colorado School of Mine's expertise in developing accurate detailed kinetic models of hydrocarbon systems, a joint CSM/NREL research program is getting underway to apply this approach to biomass conversion. This research project is focused on a quantitative characterization of oxygenated model species that have been selected to represent the classes of compounds found in biomass. It is based on high-level electronic structure calculations combined with statistical mechanics methods to calculate thermodynamic properties of reactants, products and intermediate species as well as transition states. Transition state theory provides rate constants at the high pressure limit. QRRK theory with the modified strong collision assumption yields pressure-dependent rate expressions. We can generalize these results in "rate rules" that allow us to assign rate expressions to reactions that cannot directly be treated by ab initio methods. These results, validated against experimental data if possible, will be used to extend existing chemical kinetic mechanisms to include biomass. Initial results for hydrogen abstraction reactions by H-atoms (Figure S-1.2) suggests that the connection between reaction exothermicity and activation energy for the oxygenates is different than for hydrocarbons. Furthermore, these results also suggest the importance of steric effects (e.g., the exothermicity of abstraction of a tertiary H in CH_3OCHR_2 is less than expected).

Figure S-1.2 Comparison of the computed activation energies for H abstraction reactions by H atoms from (A) hydrocarbons (black line, squares) and (B) alcohols/ethers (red line; circles) as a function of the reaction energetics.



dry metric ton/day of biomass processed using a biomass basis of wood chips with 50% moisture at a cost of $30/metric ton. The best estimate for the state of each technology in 1990 as well as the estimated potential for the technology with further advancements is shown. The table includes the cost associated with fast pyrolysis and liquefaction portions of proposed processes as well as the costs associated with upgrading the resulting bio-oil to a more useable refined state. Due to the high pressures associated with liquefaction, the capital cost for a fast pyrolysis unit would be significantly less expensive. The difference diminishes to some extent when bio-oil upgrading is also considered, since the bio-oil from fast pyrolysis will require more significant upgrading. However, the side-by-side assessment as presented in Table 1.2 suggests that the fast pyrolysis process currently enjoys a significant economic advantage over liquefaction. The "potential" columns of this table depict how additional technological advancements are expected to increase the economic attractiveness of fast pyrolysis-derived fuels even further. For this reason, liquefaction processing is generally focused on biomass feedstocks that have high water content, which are more problematic for processing through fast pyrolysis. Additional economic assessments of fast pyrolysis can be found elsewhere (Bridgwater et al., 2000; Bridgwater et al., 2002) as well as for liquefaction (Naber et al., 1999).

1.6 CURRENT TECHNOLOGY LIMITATIONS AND RESEARCH/ DEVELOPMENT NEEDS

1.6.1 Fast Pyrolysis

An important challenge to the use of fast pyrolysis bio-oil for production of liquid transportation fuels is its high oxygen content. To make the bio-oil more compatible with the existing transportation fuels infrastructure, much of the oxygen needs to be removed.

The high oxygen content issue is particularly acute for the fraction of the bio-oil that comes from the cellulose and hemicelluloses fractions of lignocelluloses. The bio-oil fraction from lignin is significantly lower in oxygen content.

In previous studies, the bio-oil was hydrotreated at high pressures (2000 – 2500 psi) and low space velocities (0.1 – 0.2 LHSV). The resulting hydrotreated oil was then cracked in a fluid catalytic cracker, or hydrocracker, to produce gasoline. At these high pressures and low space velocities, hydrodeoxygenation predominates. However, large quantities of hydrogen are required during hydrodeoxygenation due to the high level of oxygen in the bio-oil. Alternative strategies that require the use of less hydrogen to remove oxygen would be quite attractive. It is possible that these alternative strategies would work better with a certain product distribution in the bio-oil. Processing to upgrade bio-oil is intimately linked with how the fast pyrolysis unit is operated. Therefore, research is needed to establish the bio-oil characteristics that would be most desirable to obtain from the fast pyrolysis reactor system.

Another serious problem for fast pyrolysis processing is the high acid number of the bio-oils, which will cause corrosion in standard refinery units. Although the bio-oils can probably be processed using 317 stainless steel cladding, this material is not standard in refinery units making it difficult to introduce bio-oil into the existing refinery infrastructure. Therefore pyrolysis bio-oils require pre-processing to reduce the acid number before processing in typical refinery units. Research is needed to understand how to accomplish this pre-processing in an efficient manner. There is an opportunity to introduce chemical transformations during this pre-processing that would not only reduce the acid number, but also decrease the oxygen content,

thereby addressing two bio-oil challenges.
Due to the complexity of the biomass pyrolysis reaction system, the underlying chemistry is not well understood. Therefore, the correlations that have been developed between bio-oil composition and pyrolysis and condensation conditions are empirical. The lack of basic understanding of the reaction system limits the ability to draw general relationships between biomass composition, pyrolysis conditions, condensation conditions, and bio-oil composition. Therefore, research is needed to develop better foundational chemistry knowledge about the fast pyrolysis reaction, which can drive the process to more desirable product compositions.

As mentioned above, the alkaline cations in the lignocellulose feedstocks serve as a catalyst for reactions in the pyrolysis reactor. While this result is understood empirically, little work has been done on the intentional manipulation of these alkaline cations. Instead, research has largely focused on examining how their naturally varying levels in native lignocellulose result in different bio-oil properties or on their removal in a pre-processing step. There is a need for a more systematic understanding of the role of different alkaline cations, as well as the alkaline cation concentration, on the pyrolysis reaction. Additionally, the intentional introduction of different catalytic moieties could be used to alter the product bio-oil composition.

1.6.2 Liquefaction

Due to its lower oxygen content, bio-oil from liquefaction has more desirable properties than bio-oil from fast pyrolysis. However, the high pressure conditions required in the liquefaction process makes the capital requirement significantly higher than for a fast pyrolysis process. Since this limitation is intrinsic to the process, there is significantly less work ongoing in the liquefaction area than the fast pyrolysis area. Some work has been performed with solvents other than water, which would potentially allow operation at somewhat lower pressures. However, liquefaction systems using alternative solvents create a myriad of new problems, so none are currently in development.

As with fast pyrolysis, the chemistry in biomass liquefaction is complex. So, thus far, investigators have attempted to draw only empirical relationships between reaction conditions and biomass composition. In addition, significantly less work has been reported on analyzing the chemical composition of liquefaction bio-oil than fast pyrolysis bio-oil. Therefore, further advancement in this process area needs to be supported by a more fundamental understanding of the chemical reactions that occur during the liquefaction process. There is also an opportunity to modify this chemistry by introducing a catalyst into the process.

1.7 RECOMMENDATIONS

Research needed to advance the technology of selective thermal processing of lignocellulosic biomass can be grouped into six topics: overarching technical needs, plant characteristics, feedstock preprocessing, deconstruction selectivity, bio-oil recovery (fast pyrolysis), and alternative deconstruction approaches.

1.7.1 Overarching Technical Needs

- Development of more detailed thermal deconstruction microkinetic models that can account for a broad range of chemical reactions. These can be used to provide a basis for choosing which reactions should be enhanced to increase selectivity for desired chemical

BIOMASS CATALYTIC CRACKING

One of the key technical problems that must be solved in order to achieve cost-effective conversion of the non-edible biomass is the problem of how to open up the inaccessible solid fibrous 'woody' material, so that it can be effectively transformed by catalysts. Cellulose, the main component of wood, is a very pure polymer of glucose, and once 'unlocked' the woody structure can be converted into high quality bio-oils as shown in Figure S-1.3.

The challenge is to find a simple non-energy intensive way to make the woody biomass accessible to reactive media, catalysts and/or enzymes. Biomass catalytic conversion (BCC), demonstrated in Figure S-1.4, is an improvement to classical biomass pyrolysis, whereby catalytically accessible biomass is converted into a bio-crude suitable for further processing in new or existing oil refineries to gasoline and/or diesel fuel.

Because of the enhanced accessibility of the biomass to the catalyst, the catalyst in BCC does not only improve the secondary tar cracking, like in classical catalytic pyrolysis, but the catalyst also enhances the kinetics and selectivity of the primary conversion of the solid biomass. This allows for conversion at lower temperatures (improved energy efficiency), while producing improved quality products. BCC can build on the long history of fluid catalytic cracking (FCC) technology the low cost workhorse of the oil refining industry. BCC is a new innovation of the FCC process based on low cost and environmental friendly synthetic catalyst technology developed by KIOR, a privately funded venture.

Figure S-1.4 Pathways for conversion of lignocellulosic biomass to bio-oils, gases, and chars

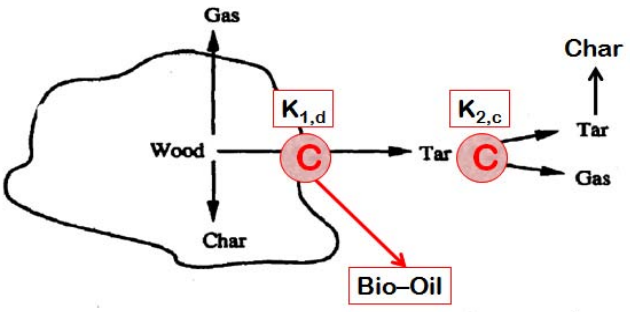
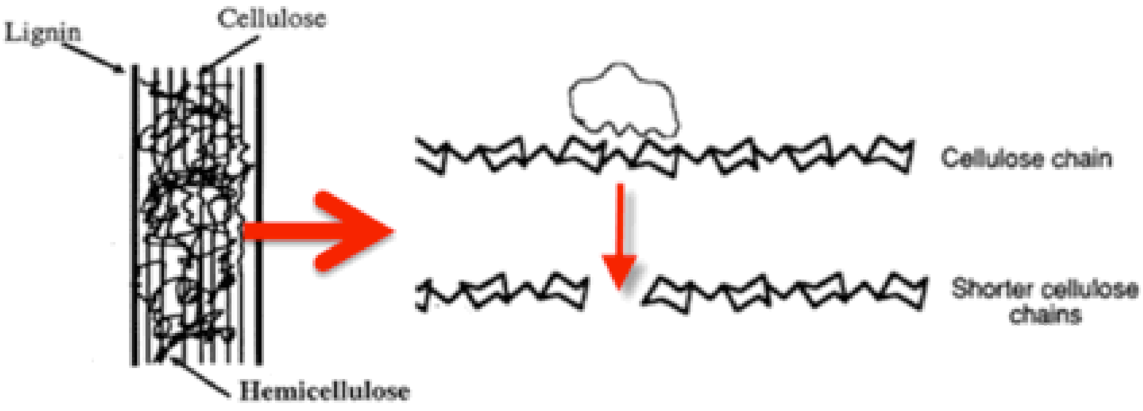


Figure S-1.3
Unlocking the woody structure



species in the resulting bio-oil.

- Better characterization of the catalytic pathways that occur due to acid generation in the thermal processing and the presence of alkalis.

- To complement the kinetic modeling, there is a need to determine the thermodynamic and physical properties of key chemical species present in thermal processing, since little data are currently available for these species.

- The chemical complexity of the bio-oils produced by selective thermal processing necessitates the development of analytical techniques that can give chemical speciation. Without this information, experimental work can only focus on lumped property effects as given in Table 1-1, which provides little insight into the underlying chemistry. The lack of analytical characterization has historically caused many thermal processing studies to be highly empirical.

1.7.2 Plant Characteristics for Thermal Processing

- For thermal processing, the lignin fraction of the plant biomass is decomposed into chemical species that are lower in oxygen content than those from cellulose or hemicelluloses. Therefore, plant feedstocks with higher lignin content and lower hemicellulose content would likely be preferred for selective thermal processing. The desire for higher lignin-containing feedstocks is in opposition to the plant composition desired for biological deconstruction, which seeks to diminish the lignin content.

- For fast pyrolysis-type processing, there is a desire to decrease the water content in the biomass feedstocks.

- Diminished mineral content in the plant material would potentially simplify the selective thermochemical processing.

- Designing plants with higher oil/wax content could lead to bio-oils that require less oxygen removal during the subsequent bio-oil upgrading.

1.7.3 Biomass Feedstock Preprocessing

- Development of preprocessing methods to efficiently remove alkalis from the biomass could provide better control over thermal deconstruction process.

- The lignin and cellulose/hemcellulose fractions yield distinctly different chemical species after thermal processing. Therefore, improved bio-oil chemical specificity could be accomplished if a biomass separation process was available.

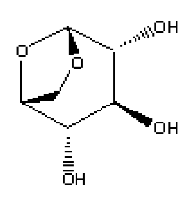
- Catalyst incorporation as a preprocessing step that could improve selectivity to desired species in the subsequent thermal processing.

- Torrefaction is a low temperature process (300°C) that removes volatile species from biomass. It would be useful to evaluate whether this preprocessing step, which also densifies the biomass, leads to a feedstock with improved thermal processing characteristics.

- There is a need to better understand the relationship between biomass particle morphology and its thermal processing characteristics to determine what is the optimal size and shape to create during preprocessing.

- The pretreatment of biomass, which is being developed for the biological conversion process, enhances the accessibility of the biomass to enzymatic hydrolysis. How would this pretreatment procedure affect biomass deconstruction through thermal processing?

BIO-OIL FERMENTATION



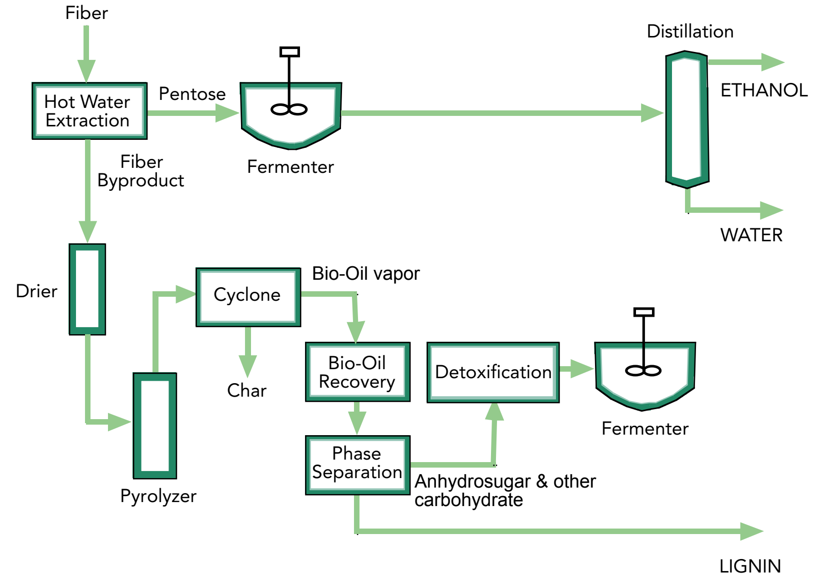
Under rapid pyrolytic conditions, pure cellulose yields levoglucosan, an anhydrosugar with the same empirical formula as the monomeric building block of cellulose: $C_6H_{10}O_5$ (Evans and Milne, 1987). A "dehydrated" sugar, it can be hydrolyzed to glucose. Thus, fast pyrolysis presents an alternative approach to enzymatic hydrolysis for liberating simple sugars from biomass. However, most biomass contains small amounts of alkali, which promotes the formation of hydroxyacetaldehyde instead of levoglucosan, with the result that bio-oil typically contains only a few percent of levoglucosan and other anhydrosugars. Scott and coworkers at the University of Waterloo discovered that by dilute acid washing of wood before pyrolysis levoglucosan can be produced at very high yields (Scott et al., 1989).

Brown and his collaborators evaluated the effect of several treatments to remove alkali on the pyrolytic products of cornstover (Brown et al., 2001). These were able to increase the yield of anhydrosugars from less than 3 wt-% to as high as 28 wt-%. Acid hydrolysis of this anhydrosugar yielded 5% solutions of glucose and other simple sugars. The resulting glucose solutions can be fermented (Prosen et al., 1993). However, the resulting substrate derived from the bio-oil contains fermentation inhibitors that must be removed or neutralized by chemical or biological methods

A biorefinery based on fermentation of bio-oil (shown in Figure S-1.5) would include several unit operations that are reminiscent of those used in a biorefinery based on enzymatic hydrolysis. Fibrous biomass is pretreated with dilute acid to simultaneously remove alkali and hydrolyzes the hemicellulose fraction to pentose. The remaining fraction, containing cellulose and lignin, is dried and pyrolyzed at 500°C to yield bio-oil, gas, and char. The bio-oil is separated into a levoglucosan-rich aqueous phase and pyrolytic lignin through a simple precipitation process. The levoglucosan is acid-hydrolyzed into glucose. After detoxification, the hexose and pentose recovered from the biomass are separately fermented to ethanol. The lignin, char, and gas are burned to generate steam for distillation and other process heat requirements of the plant.

So and Brown (1999) have compared the capital expense and operating costs for a bio-oil fermentation biorefinery. The total capital investment for an ethanol plant based on fermentation of bio-oil producing 95 million liters of ethanol was estimated to be $69 million, while the annual operating cost was about $39.2 million, resulting in an ethanol production cost of $0.42/L. The production cost was comparable to that of acid hydrolysis and enzymatic hydrolysis of woody biomass to produce ethanol for the year of the analysis.

Figure S-1.5: Cellulosic ethanol plant concept based on fermentation of bio-oils.



1.7.4 Thermal Deconstruction Selectivity

- While some work on catalyst incorporation directly into the thermal deconstruction has been performed, there is a need to more systematically evaluate the product selectivity possible with different types of catalytic materials.
- Process condition optimization has largely been based on empirical studies, to date. Improved microkinetic and reactor models will allow a more detailed understanding of the optimal process conditions.
- In addition to microkinetic models for individual reactants, improved understanding of the depolymerization reaction mechanisms is needed.
- Both hydrolysis and cracking reactions play important deconstruction roles. More research is needed to understand the appropriate balance between these reactions in thermal processes.
- Catalytic materials will need to be designed that provide high selectivity, but also maintain their physical integrity in the thermal process and be readily recovered from the product.
- Aerosol formation is an important mechanism for nonvolatile bio-oil components to pass out of the pyrolysis reactor, there is a need to better understand this mechanism.
- Research is needed to explore the possibility that the selectivity of the deconstruction process can be altered by the introduction of co-reactants.
- While torrefaction has the potential to be a useful preprocessing step, there might instead be the possibility to improve the selectivity of fast pyrolysis by operating under staged reaction conditions.

1.7.5 Bio-Oil Recovery (Fast Pyrolysis)

- In the fast pyrolysis process bio-oil is recovered through condensation. The bio-oil composition is influenced by the condensation approach used, so there is a need to better understand the reactions occurring during bio-oil condensation.
- Improved downstream separation would improve the capability to segregate bio-oil fractions derived from the lignin or carbohydrate fractions, which have very different chemical characteristics.
- It is desirable to remove as much of the char from the bio-oil as possible. Introduction of a catalytic filter downstream from the char-removal cyclone could serve the dual purpose of particulate removal and conversion of the bio-oil vapor to alternative products prior to condensation.
- Bio-oil stabilization will be needed if the bio-oil is to be produced at one location but shipped to another for upgrading. Stabilization strategies could include catalytic reactions.

1.7.6 Alternative Deconstruction Approaches

- Alternative solvents to water could be considered in the liquefaction process.
- Elimination of alkalis from lignocellulosic feedstocks increases the production of anhydrosugars in the fast pyrolysis process. These anhydrosugars could be fermented to fuels and chemicals thereby making a coupled chemical/biological process.
- Ionic liquids have potential for selective thermal

deconstruction of biomass.

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2. Utilization of Petroleum Refining Technologies for Biofuel Production

2.0 UTILIZATION OF PETROLEUM REFINING TECHNOLOGIES FOR BIOFUEL PRODUCTION

OVERVIEW: Liquid biofuel precursors produced through pyrolysis or hydrothermal liquefaction of biomass can be converted to hydrocarbon fuels including "green" gasoline, diesel and jet fuel by utilizing the same refining technologies applied to petroleum and coal-liquid conversion. Specific technologies covered include hydrotreating, hydrocracking and catalytic cracking. A major research challenge associated with this thrust is how to efficiently remove oxygen from biomass-derived feedstocks while minimizing the consumption of expensive hydrogen. The complex nature of biomass and the ill-defined issues related to biomass-to-biofuels conversion pose a substantial, but not insurmountable, challenge to the large-scale production and widespread use of biofuels. The following chapter provides data, descriptions, and schematic comparisons of the various technologies that can be used to produce fuels from biomass within the existing infrastructure of petroleum refineries. We also identify the outstanding research and engineering issues related to biomass conversion that must be addressed in order to realize the tremendous potential economic and environmental rewards of large-scale domestic biofuels production.

2.1 INTRODUCTION

Biomass-derived fuels have the potential to help meet the increasing global demand for transportation fuel while reducing greenhouse gasemissions by closing the carbon cycle loop; CO_2 emitted by combustion of biofuels is subsequently removed from the atmosphere during biomass re-growth

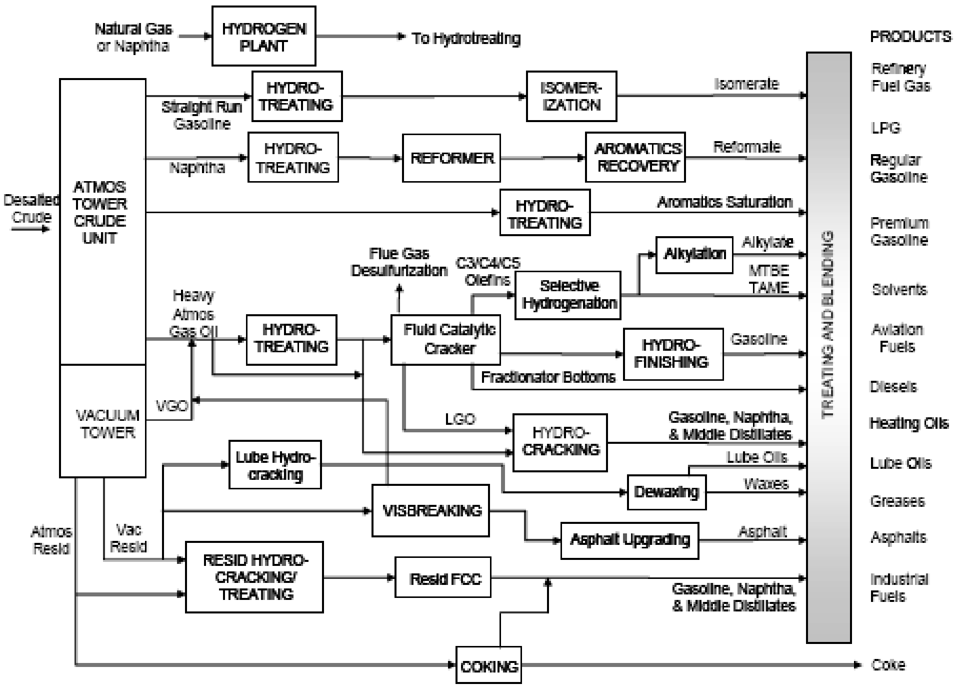

Figure 2.1 A representative flow diagram of a petroleum refinery
[Energetics, 2006]

[Song 2006]. Bio-oils can be produced through the selective thermal processing of a wide variety of lignocellulosic biomass feedstocks, as described in Chapter 1. Bio-oils can be used for the production of both fuels and chemicals [Czernik and Bridgwater 2004]. However, bio-oils are inherently complex, acidic, and thermally instable. Therefore, they must be upgraded before they can be used as a transportation fuel.

The objective of this thrust is to identify promising pathways towards clean liquid hydrocarbon transportation fuels using technologies similar in principle to those employed in fossil fuels refining. The advantage of this approach is that it exploits known technological processing schemes and takes advantage of the existing petroleum refining infrastructure [Huber and Corma 2007 and Marinangeli et al. 2006].

2.2 OVERALL PROCESS DESCRIPTION

The petroleum refining technologies for biofuel production discussed in this chapter include hydrotreating, hydrocracking, catalytic cracking, and hydrodeoxygenation, which are similar to the technologies used in petroleum refining, coal liquid upgrading, and Fischer-Tropsch product refining (Figure 2.1). The reasons for considering these processes are two-fold. First, these processes could take advantage of existing infrastructure. Second, such processes produce clean liquid hydrocarbon fuels that can be transported through exisiting pipelines and used in current and next-generation internal combustion engines for land, sea and air transportation. (See Sidebar on next page)

SECTIONS OF THRUST 2:

PARTICIPANTS:

Phillip Badger; Calvin H. Bartholomew; André L. Boehman; Curt Conner; Steven Czernik; Anthony Dean; Burt Davis; Douglas Elliott*; Kristi Fjare; Manuel Francisco; Bruce Gates; James Goodwin; Harold Kung; Leo Manzer; Richard Marinangeli; Chunshan Song*; Don Stevens; Philip Steele; Tiffany Westendorf; Phil Westmoreland
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2.3 RESULTING FUELS

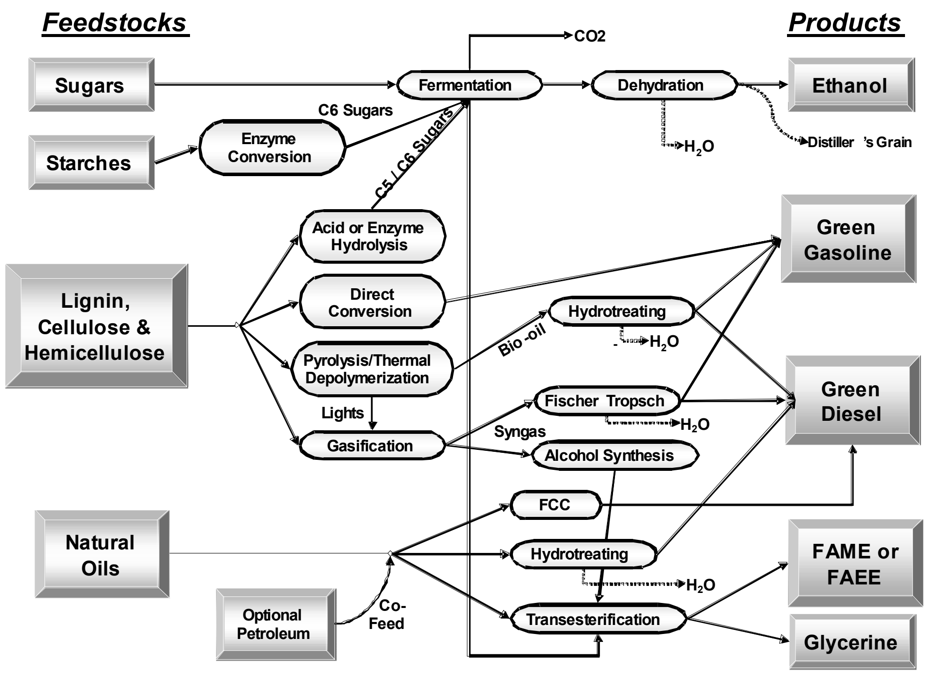
The technologies discussed in this chapter are able to convert bio-oils and other biomass derived feedstocks into clean hydrocarbon-based liquid biofuels for transportation including "green" gasoline, jet fuel and diesel as well as organic chemicals. The feedstocks that can be processed with petroleum technology include organic liquids derived from selective thermal processing of lignocellulosic biomass. Examples of such

OPPORTUNITIES FOR BIORENEWABLES IN PETROLEUM REFINERIES

Use of existing infrastructure would significantly decrease the ramp-up time for economical, large-scale production of advanced biofuels. However, despite the heightened interest in the potential for domestic biofuels production, there has so far been little integration of biofuels into the existing infrastructure of petroleum refineries. Using the existing infrastructure of petroleum refineries could significantly reduce the cost of biofuels production. Instead of the five years it normally takes to build a new fuel plant, existing petroleum refineries could be updated to accommodate biofuels production in less than a year.

If economical opportunities for blending or co-processing them within traditional petroleum refineries were identified and developed biofuels could quickly and substantially alleviate the increasing demand for petroleum. Indeed, many current petroleum refineries are already starting to commercialize biofuels produced using existing petroleum refinery technology. For example, Conoco-Phillips and Tyson Foods recently signed an agreement to produce diesel fuel through hydroprocessing of waste vegetable oils. In addition UOP, the National Renewable Energy Laboratory, and the Pacific Northwest National Laboratory completed a U.S. Department of Energy-funded evaluation of the economics of producing biofuels within petroleum refineries [Holmgren 2005; Marker, et al. 2005]. The purpose of this project was to identify economically attractive opportunities for biofuels production and blending using petroleum refinery processes. Economic analyses were conducted to assess a variety of potential processes and configurations using process modeling and proof-of-principle experiments.

Figure S-2.1 Overview of Biofuel Production



The DOE study identified many promising and profitable options for integrating biorenewable feeds and fuels into existing refineries. Figure S-2.1 shows a schematic of several options for biofuels production from different biomass sources. Some of the routes are already in commercial practice, such as ethanol from the fermentation of corn or sugar cane. Several routes have a considerably more distant commercialization horizon due to the

related scientific and technical challenges and limited feedstock availability. However, new nanotechnology, quantum chemical and molecular engineering methods developed over the last 10 years that will help accelerate these processes into reality.

One of the most promising options for lignocellulosic-derived biofuels is the use of petroleum refineries for upgrading bio-oils. Bio-oils are produced by fast pyrolysis, a thermochemical process with the potential to convert large volumes of lignocellulosic biomass into liquid fuels. In this process a solid biomass feedstock is injected into a fluidized bed with high heat transfer capability for short contact times, followed by a quenching process to condense a liquid bio-oil in 50-75% yields, with gas and char making up the balance. The bio-oil contains the thermally cracked products of the original cellulose, hemicellulose, and lignin fractions present in the biomass. It also contains a high percentage of water, often as high as 30%.

Many economically attractive opportunities for the integration of biorenewable feedstocks and biofuels in petroleum refineries were identified in this study, including pyrolysis oil to produce "green gasoline". However, this technology is still in its infancy. In order to become a viable production technology, pyrolysis oil processing will require additional scientific and technical development. Over the long term, however, the potential volume of pyrolysis oil could rapidly and economically replace global shortages of petroleum fuel and help alleviate the environmental, economic and social problems related to petroleum dependence and greenhouse gas emissions.

feedstocks include bio-oils produced through fast pyrolysis of biomass and liquids from hydrothermal liquefaction of lignin and cellulose in biomass.

To meet government regulations for fuel sulfur and aromatic contents, petroleum-based fuels must be "cleaned" through a process called deep desulfurization [Song 2003]. In contrast, the cleaning process for hydrocarbon fuels produced from biomass feedstocks involves the deep removal of oxygen, because bio-oils produced through pyrolysis and hydrothermal liquefaction of biomass are more oxygen-rich than conventional petroleum-based feedstocks [Elliott 2007, Czernik and Bridgwater 2004]. (See Thrust 1, Table 1.1.)

2.4 SUMMARY OF PREVIOUS RESEARCH

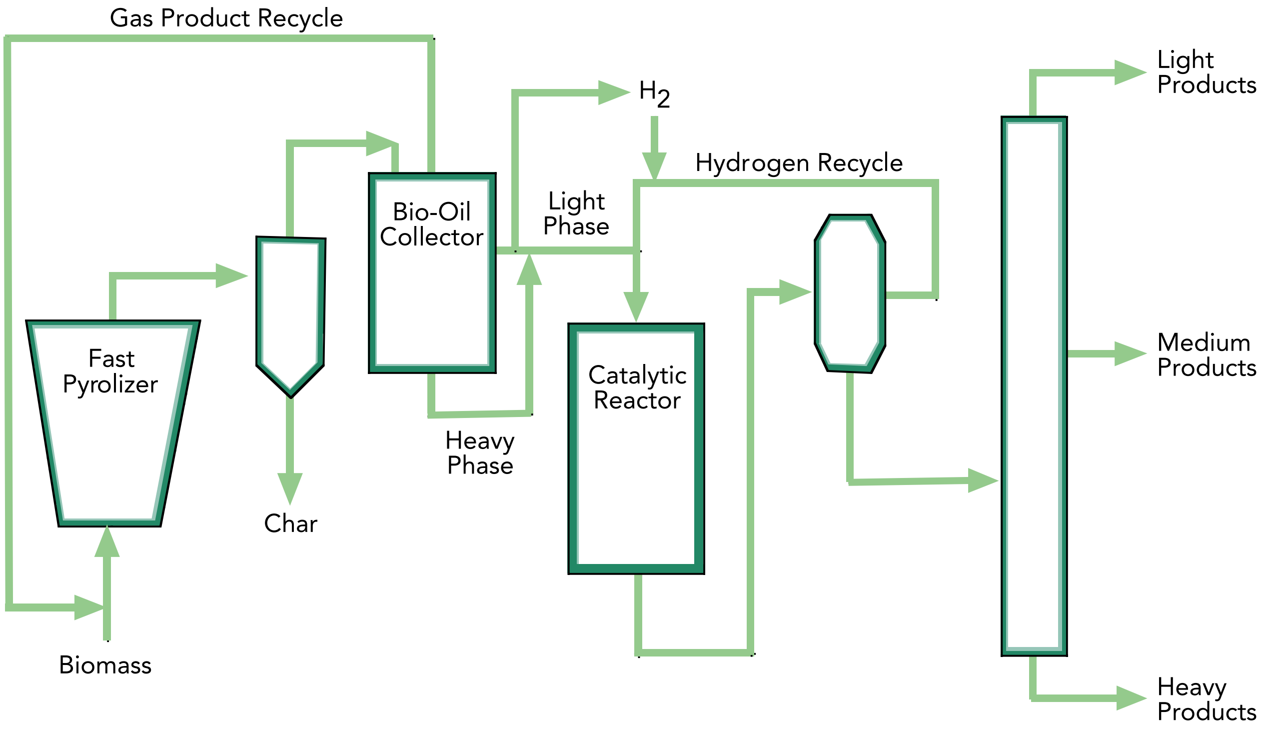
The technology for producing the biomass-derived feedstocks, such as bio-oils and liquefaction oils are described in Thrust 1. However, the liquid products generated through selective thermal processing are not useful as fuels, other than direct boiler firing and possibly for some types of turbine and large diesel applications, and then only after significant modifications. In order for the biomass liquids to be useful as transportation fuels they must be chemically transformed (i.e. upgraded) to increase volatility and thermal stability and to reduce viscosity. These changes can be accomplished through oxygen removal and molecular weight reduction by methods similar to those used in the petroleum refinery. A useful summary of the early work in this field has been published [Elliott et al. 1991]. Upgrading biomass-derived oils to hydrocarbon fuels can be accomplished by one of two catalytic methods: hydroprocessing or catalytic cracking.

BIO-OIL HYDROPROCESSING

Bio-oil hydroprocessing refers to the conversion processing of liquids from biomass using pressurized hydrogen. Work has been underway, primarily in the U.S. and Europe, in catalytic hydrotreating and hydrocracking of biomass-derived liquids (bio-oils) in both batch-fed and continuous-flow bench-scale reactor systems. A range of heterogeneous catalyst materials have been tested, including conventional sulfided catalysts developed for petroleum hydroprocessing and precious metal catalysts. The important processing differences identified require adjustments to conventional hydroprocessing as applied to petroleum feedstocks. This application of hydroprocessing is seen as an extension of petroleum processing and system requirements are not far outside the range of conventional hydroprocessing. The technology is still under development, but can play a significant role in supplementing increasingly expensive petroleum.

Upgrading fast pyrolysis bio-oils to hydrocarbon fuels requires oxygen removal and molecular weight reduction. As a result, there is typically a formation of an oil-phase product and a separate aqueous phase product by hydroprocessing. To minimize hydrogen consumption in hydroprocessing, hydrodeoxygenation (HDO) must be emphasized, without saturation of the aromatic rings. Hydroprocessing biomass-derived oils differs from processing petroleum or coal liquids because of the importance of deoxygenation, as opposed to nitrogen or sulfur removal. At the time that researchers

Figure S-2.2 Pyrolysis Bio-oils Upgrading Approach



began to evaluate the HDO of biomass-derived oils, it had received only limited attention in the literature [Furimsky 1983]. In the course of more than 20 years a wide range of efforts has been reported, as described in a recent literature review [Furimsky 2000]. A large portion of the body of work addresses the catalytic chemistry by hydrotreating model compounds containing oxygen. Many of these models, such as phenolics and aromatic ethers, are relevant to bio-oil hydroprocessing.

Extensive work in the field of hydroprocessing biomass-derived liquids has been undertaken during the past 25 years [Elliott 2007]. This work extends from small-batch reactor tests in universities to demonstration-scale processing in petroleum refining laboratories. The processing potential, measured by these results, is shown to be relatively more expensive than conventional petroleum processing at traditional prices, as shown by the most recent economic studies, now 10 years old [Grange, et al. 1996]. The same study found that pyrolysis-derived oils are more economical than other biomass-to-liquid fuel processing, such as ethanol or biodiesel.
In light of recent inflation in petroleum prices the increasing potential for biofuels to be cost-competitive with conventional fuels, should be carefully evaluated.

Hydroprocessing of biomass-derived oils differs from processing of petroleum or coal liquids because of the importance of deoxygenation, as opposed to nitrogen or sulfur removal. At the time that research began to evaluate the hydrodeoxygenation (HDO) of biomass-derived oils, HDO had received only limited attention in the literature [Furimsky 1983]. Over the past 20-plus years, a range of efforts in the field has been reported in the literature, as described in a recent review [Furimsky 2000]. A large fraction of this body of work addresses the catalytic chemistry of hydrotreating by using model compounds containing oxygen. Many of these model compounds are relevant to bio-oil hydroprocessing, such as phenolics and aromatic ethers, while others, such as aromatic heterocyclics like benzofuran or benzoquinone, are not. In addition, there are many other oxygenated functional types, important to the composition of bio-oil, which have received much less attention, such as ketones, organic acids or mixed functional types.

Work is underway, primarily in Europe and a small amount in the US, in catalytic hydrotreating and hydrocracking of bio-oil in both batch-fed and continuous-flow bench-scale reactor systems. A recent review by Elliot collects and summarizes the data from experiments involving the handling and upgrading bio-oils by catalytic hydroprocessing [Elliott, 2007]. A range of heterogeneous catalyst materials have been tested, including conventional sulfided catalysts developed for petroleum hydroprocessing and precious metal catalysts. Important processing differences were identified, which required adjustments to conventional hydroprocessing as they would normally be applied to petroleum feedstocks. This application of bio-oil hydroprocessing is seen as an extension of petroleum processing and system requirements are not far outside the range of conventional hydroprocessing. The technology is still under development, but will play a significant role in future biofuels refining schemes.

A primary concern related to hydroprocessing fast-pyrolysis oil is its thermal instability. The tendency of bio-oil to further react upon heating, to increase in viscosity, and even form coke, precludes conventional catalytic processing methods of the kind applied to petroleum. A lower temperature hydrogenation can be used to stabilize the bio-oil and allow its subsequent catalytic hydroprocessing to be performed at more conventional temperatures [Elliott and Baker 1989]. The subsequent processing step can result in efficient conversion to high yields of liquid hydrocarbons within the distillation range appropriate for transportation fuels.

In parallel developments, several laboratories around the world have investigated catalytic cracking of bio-oils based on the technology currently used for petroleum fractions. The use of acidic catalyst for cracking petroleum hydrocarbon structures to lower molecular weight material and reforming it into aromatic structures is well-known. This atmospheric pressure process has been found to produce hydrocarbon liquids from bio-oils as well, but with high yields of coke. A short summary of the results can be found in a recent review of biomass conversion to transportation fuels [Huber, et al. 2006; Huber and Corma 2007].

The use of zeolitic acid catalysts can maximize the yield of aromatic hydrocarbons in the cracking process. The catalyst HZSM-5 has been demonstrated to be particularly useful in this regard, producing aromatic yields with up to 5 times the aliphatic content. Other zeolites produce an aromatics to aliphatics ratio of about 1 to 1. Coke yields typically range from 30- to 50-weight percent. Coke formation by itself is not necessarily bad because the petroleum catalytic cracker is traditionally operated in a circulating fluidized bed in which the coke is periodically burned off to stimulate catalyst regeneration and provide heat for the process. However, a good heat balance has not yet been demonstrated for bio-oil catalytic cracking.

Compared to fast pyrolysis oil, hydrothermal liquefaction oil has lower oxygen content and, due to differences in chemical composition, it is more thermally stable. These desirable properties are the result of more severe processing conditions involved with hydrothermal liquefaction (i.e., longer residence time at high pressure). Subsequent hydrodeoxygenation can be accomplished through a catalytic hydrotreatment at conventional conditions. This process also results in high yields of hydrocarbon products.

If the objective is to produce a finished hydrocarbon product, eliminating the need for the first stabilization step gives an important economic advantage to hydrothermal liquefaction, compared with fast pyrolysis. Nevertheless, detailed chemical analysis of a limited number of samples suggests that these products would both be useful as feedstocks in a petroleum refinery setting.

Determination of catalyst stability is a key shortcoming of the hydroprocessing research undertaken to date. No long-term processing of more than a few days has been reported for hydroprocessing the product from hydrothermal liquefaction. In the longest test (8 days) catalyst deactivation was also identified as a limitation for hydroprocessing fast pyrolysis bio-oil. Catalyst deactivation has also been reported in the catalytic cracking application, such that the useful catalyst lifetime would be limited to only a few cycles. The deactivation of the catalysts is not well understood, but can be attributed to either the effect of high amounts of water on the oxide structures, the presence of trace contaminants (e.g. the minerals, derived from the biomass feedstock), or both of these things.

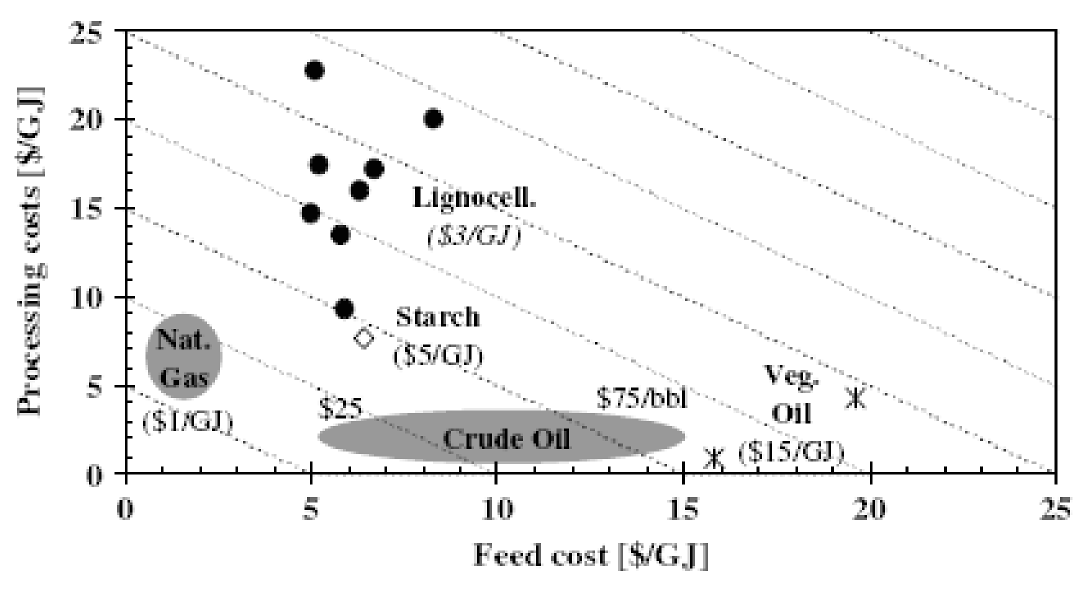
2.5 ECONOMICS AND POTENTIAL OF TECHNOLOGY

The production of bio-oils by fast pyrolysis has been conducted by several industrial groups. However, the economics of producing clean hydrocarbon fuels from bio-oils remain uncertain since little work has been done in a manner that allows for reliable economic evaluation of a large-scale operation. The production cost of biofuels based on current technoloies, including feedstock costs and processing costs, is estimated to be in the range of $60–120/barrel of oil equivalent [Lange 2007]. This cost will significantly decrease as new technologies for biomass conversion are developed further.

The end cost of biofuels derived from vegetable oils are currently dictated by feed cost because vegetable oils already command a premium in the marketplace, whereas the cost of fuels derived from inexpensive lignocellulosic biomass is dominated by technology [Lange 2007]. Figure 2.2 on the following page illustrates the economics of various technologies for transportation fuel production with processing cost plotted against the feed cost. The alternatives depicted include producing transportation fuels from biomass and petroleum feedstocks (i.e. from lignocellulose, starch and vegetable oil as well as from crude oil and natural gas), as reported in a study by Shell [Lange 2007]. The Shell report illustrates that the cost of crude oil refining is dominated by feed cost whereas the costs of gas conversion (e.g. MeOH or Fischer–Tropsch synthesis) are dominated by technology. The report describes the trade-off between feedstock cost and plant cost, which is also applicable to analysis of the options for biofuels production.

Solid lignocellulosic biomass is inexpensive ($2–4/GJ or $34–70/t dry), but very difficult to convert. Nevertheless, implementation of the strategies outlined in this roadmap will significantly reduce the cost of producing fuels from cellulosic biomass. The low cost of processing crude oils has been achieved thanks to advances in petroleum chemistry and catalysis over the last 80 years. It is likely that similar advances anticipated over the coming years will also significantly decrease the cost of processing biomass. The factors that affect the process economics include the cost and type of the biomass feedstock at the plant gate, the conversion efficiency, the scale of the process, and the value of the end product (e.g. fuel, electricity or chemicals).

Figure 2.2. Feed and processing cost of transportation fuels derived from lignocellulose and fossil resources (the biofuel plants are set at 400 MW intake, which corresponds to 680 kt/a of lignocellulose) [Lange 2007].



2.6 CURRENT TECHNOLOGY LIMITATIONS AND RESEARCH/ DEVELOPMENT NEEDS

There are no large-scale commercially available technologies for biofuel production from petroleum refineries. The physical and chemical properties of bio-oils are fundamentally different from petroleum feedstocks, and these differences account for the challenges associated with upgrading biomass-derived feedstocks using petroleum refining technologies. Bio-oils are generally characterized by the following features:

- Bio-oils from fast pyrolysis are acidic, oxygen-rich mixtures of organic components from thermal decomposition of lignocellulosic biomass at 450-550 °C under rapid heating-short residence-time conditions.
- Bio-oils produced through liquefaction processes are mixtures of organic components from hydrothermal conversion of lignocellulosic biomass at 300-400 °C under pressurized conditions, which are less acidic and less oxygen-rich compared to pyrolysis oils.
- The compositions and properties of both fast pyrolysis bio-oils and liquefaction bio-oils depend, to some degree, on the feedstock type and the processing conditions.

2.6.1. Feedstock-related Bio-oil Processing Issues

The complex and ill-defined issues related to biomass conversion pose a huge challenge to the production and widespread use of biofuels. A wide variety of feedstocks are used to make the bio-oils (including hardwoods, softwoods, switchgrass, and agricultural residues). Each of the feedstocks produces different levels of impurities and desired products. Bio-oils are like heavy oils in appearance. The challenges associated with processing them like heavy oils are their acidity, instability, and partial volatility. About 50% of the bio-oils are non-volatile.

Bio-oils may need treatments, such as hydrodeoxygenation, before they can be sent to the refinery for processing. Hydrogen is needed to remove oxygen in hydrotreatment. The limited availability and high cost of hydrogen can be a limiting factor. However, hydrogen could be made by steam reforming of some fractions of bio-oils or biomass.

2.6.2. Scientific Issues Related to Bio-oils Conversion

Not surprisingly, processing whole bio-oils is far more challenging than processing model compounds. The major challenge is how to design a catalytic process such that it can selectively remove targeted oxygen and minimize hydrogen consumption. Bio-oil conversion includes water formation (hydrogen consumption), CO_2 and CO formation (carbon rejection), and retention of an oxygen fraction in the fuel.

Priorities for future research related to bio-oil conversion include the following important issues:

- Improvement of upstream processes (i.e. pyrolysis and liquefaction), to make the resulting bio-oils more amenable to downstream processing.
- Development of methods to increase the overall efficiency of the process. For example, perhaps process chars can be used as energy for the pyrolysis and the water-soluble products used for hydrogen production via reforming.
- Techniques for effective removal of acidity. Decarboxylation would be desirable, but the most efficacious route (e.g. catalysis, reaction chemistry) is currently unclear. It may be possible to make use of the acids in bio-oils by reacting them with alcohols, present in the bio-oils or produced during processing, to make esters that could become useful products.
- Identification of desirable oxygen compounds that improve the fuel properties.
- Development of technologies that produce fuels compliant with sulfur specifications, while preserving only the desirable oxygen compounds in the biofuels. There may be advantages in leaving certain oxygenated compounds in the fuel for lubricity. There are multiple ways to improve lubricity. One way is to use vegetable oil-based biodiesel and another way is to use lubricity additives [Knothe and Steidley 2005]. The addition of 1% ethyl levulinic acid to fuel in Canada was found beneficial. The possible benefits of some oxygenates in fuels are increased lubricity and higher cetane number and in some cases the improved reactivity in the soot [Song, et al. 2006].
- With respect to C-O bond cleavage, the bond energy distributions for bio-oils must be determined. The less stable bonds must be identified. Molecular-level detailed composition information will be necessary to determine bond energy.

Molecular compositions of bio-oils from pyrolysis and liquefaction remain ambiguous. Detailed analytical characterization work must be undertaken to understand the molecular composition and the type of bonds in the bio-oils and the intermediate products. Mass balance will also need to be established on different fractions and on hydrogen consumption during the conversion processing of bio-oils.

2.6.3. Technology Routes for Biofuels from Bio-oils

There is a variety of options for the implementation of biofuels-to-bio-oils technology. One option is the grassroots refinery, but mis-match in scale may be a major issue. Additionally, it may not be economically feasible to build a large-scale grassroots refinery exclusively for bio-oils.

Bio-oils may or may not be processed to the exclusion of crude oil in the petroleum refinery, since the high oxygen content, high acidity and instability of bio-oils present problems. Thus, blending bio-oils from pyrolysis with petroleum refinery streams may be an option.

Bio-oils may possibly be produced directly through hydroprocessing. However, this depends on the quality of the feedstock and the hydrogen balance. A common processing challenge is the miscibility of bio-oils with petroleum streams.

The impacts of bio-oils processing on the total energy balance and hydrogen balance in the refinery, and on the consumption of imported petroleum, is not straightforward, but must be considered. How bio-oils are processed depends, to a large degree, on their source. For example, some processing technologies, such as decarboxylation, can reduce hydrogen consumption, while hydrodeoxygenation would saturate the feed and increase hydrogen consumption.

Regulated fuel specifications include sulfur and nitrogen contents, not oxygen contents. Thus considerations for oxygen removal would be different than considerations for the other heteroatoms in biofuels.

2.6.4. Research Needs for Using Petroleum Refining Processes with Bio-oils

HYDROTEATING PROCESSES/ FUNDAMENTALS

- Model reactions should be conducted to establish a baseline for understanding the fundamentals of hydrotreating processes. The reactions of model mixtures should be undertaken to elucidate the reaction network, including catalytic and non-catalytic reactions. The questions related to free-radical reactions and other reactions need to be understood at a fundamental level. Computational analysis using models that are currently available could augment this understanding.
- In order to understand the fundamentals of bio-oils processing, model compounds should include the following classes: acids, aldehydes, ketones, phenols, alcohols, anhydrosugars, furans, furfurals, olefins, and ethers.
- The intermediate and final products of model reactions should be carefully characterized.
- Selected tests could be conducted by blending small amounts of bio-oils into the existing refinery streams.
- To some extent, bio-oils are similar to heavy oils. So, tar sands processing and the issues related to solid formation from heavy oils should be studied and characterized for their relevance to bio-oils processing.
- It is worthwhile to test whether bio-oils should be blended with refinery heavy oils or crude oils with some surfactants to ensure the miscibility. There has been some related industrial testing. However, a published report is not available.

- The competition between oxygen compounds with sulfur and nitrogen on the catalytic surface should be examined.

CRACKING PROCESSES

Fluid catalytic cracking (FCC) converts bio-oils to liquid fuels without hydrogen consumption. However, catalytic cracking currently gives lower liquid yield, higher gas yield, and a higher yield of chars.

- The higher water yield, higher char yield and the trace alkali metals in the 100-1000 ppm range may lead to serious catalyst deterioration or deactivation, which needs to be evaluated.
- Compared to hydrotreating, FCC is a process that conserves hydrogen. This savings is related to the hydrogen and carbon balance, since there are more oxygen atoms per carbon atom in liquid bio-oils (e.g., 1 O per 4 C) when compared to liquids from coal (about 1 O per 6 or 7 C).
- NREL has conducted fixed-bed catalytic cracking. Catalytic cracking of bio-oils has been reported from studies in Spain and the University of Massachusetts, in the Sustainable Energy Center, in the Mississippi State University, and in the Chemical Engineering department at University of Saskatchewan, Canada.
- UOP has compared the different processes in a DOE-supported study, and the report from DOE [Marinangeli et al. 2006].

HYDROCRACKING PROCESSES

- Bio-oils contain high molecular weight (MW) substances, but do not have long hydrocarbon chains as in the petroleum feed. Hydrocracking technologies will have to be adapted to accommodate this difference.
- Hydrocracking has been conducted in some research labs, PNNL with metal sulfides and PGM.
- The proper balance in catalytic functions such as metal, acid sites, base sites, as reflected in hydrogenation and C-C and C-O bond breaking must be determined.
- Average MW of bio-oils is on the order of 800. Components from lignin in the bio-oils include monomers and oligomers of substituted phenols.

FISCHER-TROPSCH RELATED PRIOR WORK

It may be important to consider prior work in the area of Fischer-Tropsch Synthesis (FTS) since non-hydrocarbon products in FTS have some similarities to some biomass-derived oxygen-containing products. There is some similarity to the deoxygenation of low-temperature FTS liquids which contain acids and alcohols.

2.6.5. Issues in Development of Future Fuels for Next-Generation Internal Combustion Engines

There is a need to consider fuel utilization efficiency as we imagine how to incorporate lignocellulosic biofuels into refinery operations. The composition and properties of ideal fuels for future engines/vehicles are still unclear. So, the biomass conversion processing schemes must have the flexibility to meet uncertain future demands and criteria.

Variable fractionation of liquid fuels into “green” diesel, jet fuel and gasoline can be envisioned as part of biorefinery operations. Flexibility of a biorefinery to adjust the proportions of fuel types produced is advantageous. One can imagine a scenario in which the demand for diesel fuel grows, driven by the public’s preference for the efficiency of diesel engines. This, combined with advanced combustion engine technology, would compound the benefits of using biofuels, vis-a-vis energy security and sustainability.

■ 2.6.6. Some Barriers

Bio-oils are complex mixtures with molecular diversity; molecules in biomass feedstocks contain cellulose and hemicellulose in 6- and 5-membered carbon rings. To some degree, there are similarities in bio-oils from different source materials, but with different distributions of compounds. To what extent the types of molecules and specific compounds of heteroatoms present in the bio-oils and intermediate products from bio-oils impact the processing scheme and product quality is unclear. We do not currently have a sufficient supply of the range of bio-oils and biofuels needed for wide-spread studies. It is also problematic that we do not have enough bio-oil-derived biofuels for engine testing. Some fuels will have to be produced at pilot scale to have sufficient samples for engine testing.

■ 2.6.7. Needs for Collaborative Research

We see a need for international collaboration involving industrial, academic, and national laboratories. Researchers in many countries outside the U.S. are actively involved in bio-oils conversion studies. We see the need for more collaboration between industrial, academic, and national laboratories that play different roles in promoting the development of science and technology.

2.7 RECOMMENDATIONS

A large-scale fundamental research program focused on the chemistry and catalysis involved with upgrading bio-oils to clean liquid hydrocarbon-based transportation fuels using processing schemes that are in principle similar to petroleum refining technologies should be initiated immediately.

We recommend that future research programs address the issues and needs discussed in Section 2.6 for conversion of bio-oils to hydrocarbon fuels using petroleum refining technologies. Some of the unresolved cross-cutting issues related to biofuels production science and engineering are listed below:

- The chemical reaction processes of petroleum refining that are most suitable for producing hydrocarbon fuels from bio-oils must be identified. In particular, the best processes for producing specific transportation fuels, including gasoline, jet fuel, and diesel fuel, need to be determined.
- The types of chemistries and catalysts most effective for dexoygenation of bio-oils in a petroleum refinery need to be studied. Technologies for efficient removal of oxygen during the process of bio-oils to hydrocarbon fuels conversion must be developed further
- Selective catalytic oxygen removal from bio-oils should be carefully studied.
- With respect to C-O bond energy and bond cleavage, the bond energy distributions for bio-oils, and identification of which bonds are least stable, must be determined.
- Work is needed on a detailed analytical characterization in order to understand the molecular composition, bond type, and bonding energy distribution of bio-oils and

the intermediate products of conversion processing. The type of sulfur and nitrogen compounds need to be identified and quantified.

- Detailed mass balance will need to be established on different fractions and on hydrogen consumption during the conversion processing of bio-oils. Hydrogen management and good mass balance, including direct measurement of hydrogen consumption, should be taken into consideration.
- Technologies for effective acid removal must be developed. Decarboxylation would be desirable, but the most efficacious way (e.g. catalysis, reaction chemistry) to accomplish this is unclear. If there are any desirable oxygen compounds that improve fuel properties, they must be identified. Biofuels upgrading techniques designed to meet fuel sulfur specifications while leaving the desirable oxygen compounds would be desirable.
- Mechanistic study of the chemical transformation from the bio-oils derived from lignocellulosic biomass to the hydrocarbon-based liquid biofuels is needed.
- A range of catalytic materials need to be tested to identify suitable catalysts. A systematic investigation of catalyst deactivation, including guard bed design and associated fundamental engineering issues, should be studied. In particular, used catalysts at different stages of deactivation need to be characterized. The impacts that metals in bio-oils have on catalyst deactivation need to be evaluated. The type of metals (alkali at 100 ppm range, sulfur from 10 ppm range in feeds from wood to 500 ppm range from agricultural resides) in bio-oils is determined, to some degree, on the type of bio-oils production process. For example, bio-oils from pyrolysis are more acidic and can leach out some metals.
- It is more challenging to process whole bio-oils than to convert single model compounds, like those used in laboratory studies. Therefore, conversion processing using both model compounds and the real bio-oils should be conducted in basic studies to ensure relevance and applicability of the research results.
- Strategic planning for basic research is needed in order to reach the stage where fundamental understanding can drive the development for cost-effective and chemically efficient processes for biofuels production using petroleum refining technologies.
- Graduate fellowships in the bio-fuels area, if established in government agencies, will be a major step forward to facilitate the research and training of talented young researchers at U.S. universities.
- Government-funded research programs and collaborative programs involving academic, industrial and national laboratories are needed to bridge fundamental gaps in knowledge in order to pave a path forward. We must elucidate the fundamental reaction processes, types of processing steps and operations necessary to produce bio-oils in a manner that will make their use as biorefinery feedstocks for transportation fuels cost competitive with petroleum feeds.

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3. Liquid-phase Catalytic Processing of Biomass-derived Compounds

3.0 LIQUID-PHASE CATALYTIC PROCESSING

OVERVIEW: Biomass-derived oxygenates typically have a high-degree of functionality and a low-thermal stability making it difficult to process them in the gas phase where traditional petroleum reactions occur. Catalytic processing in the liquid-phase allows thermally unstable molecules to be selectively converted into a range of fuels and chemicals. Liquid-phase processing has many advantages including higher thermal efficiencies, high reaction rates per reactor volume, and exclusion of an energy intensive distillation step. However, new catalyst and reactor systems need to be designed specifically for conversion of biomass-derived feedstocks in the liquid-phase in order to realize the full potential of this technology.

3.1 INTRODUCTION

The overarching goal of liquid-phase catalytic processing of biomass-derived compounds (e.g., sugars) is to produce next-generation liquid transportation fuels that: (i) can be used with the existing infrastructure; (ii) do not involve energetically-intense distillation steps; and (iii) have high rates of production per reactor volume. One strategy for achieving this goal is to convert sugars to liquid alkanes, such that the liquid fuel derived from biomass is identical, with respect to chemical composition and energy density, to the current liquid fuels currently derived from petroleum (e.g., gasoline, diesel, jet fuel). Another strategy is to produce unconventional types of fuels by precisely engineering molecules with well-defined amounts of oxygen such that the desired volatility and combustion properties are optimized without adversely affecting the energy density or the hydrophobicity of the fuel.

3.2 PROCESS DESCRIPTION AND RESULTING BIOFUELS

Liquid-phase catalytic processing of biomass-derived compounds offers unique opportunities for achieving high yields of specific, and well-defined, liquid fuels from biomass. For example, liquid-phase catalytic processing of sugars is typically carried out at lower temperatures (e.g., 500 K) compared to biomass pyrolysis, liquefaction, or gasification. However, whereas these latter process can operate with complex biomass feedstocks (e.g., containing cellulose, hemicellulose, and lignin components), liquid-phase catalytic processing typically involves feedstocks containing specific biomass-derived compounds, such as sugars or polyols. Thus, an advantage of liquid-phase catalytic processing is that high selectivities and yields to targeted fuel compounds can be achieved, but a disadvantage of such processing is that real biomass feedstocks must be pretreated to prepare a feed solution that for subsequent liquid-phase catalytic processing.

Because of the high level of functionality (e.g., -OH, -C=O, -COOH groups), biomass feeds have low volatility and high reactivity, and these feeds must typically be processed by liquid-phase technologies. In addition, in view of their hydrophilic properties, liquid-phase processing of carbohydrate feeds is typically carried out in the aqueous phase, or under biphasic conditions employing an aqueous and an organic phase. In general, a variety of fuels and chemical intermediates can be produced from these biomass feeds by employing various types of reactions including: hydrolysis, dehydration, isomerization, C-C coupling (e.g., aldol-condensation), reforming, hydrogenation, oxidation, and hydrogenolysis. The heterogeneous catalysts used for these reactions can include acid, base, metal, and metal-oxide catalysts. Several types of reactions typically occur during a given process, allowing the opportunity for the use of multi-functional catalysts.

The production of ethanol by fermentation of glucose is also a liquid-phase process that produces a liquid transportation fuel. This process has been practiced for many years (e.g., by the brewing industry), which has led to its wide-scale implementation in the production of bioethanol as a transportation fuel. However, fermentation has several disadvantages. One disadvantage is the rather high energy costs associated with the distillation of ethanol from the aqueous solution in which it is produced. Another is the low rates of production per volume of reaction vessel. In contrast to bioethanol, next-generation fuels derived from liquid-phase processing should have higher energy densities per volume and properties that are nearer to those of gasoline and diesel fuels.

3.3 FEEDSTOCKS

Biomass may be made amenable for liquid phase catalytic processing by a variety of means. First, the raw biomass feedstock may be fed directly to a liquid phase catalytic reactor. In this case, usually relatively simple feeds such as vegetable oils, starch or cellulose are utilized. For processing more complex, lignocellulosic feeds, the biomass is usually pretreated to produce a liquid stream that is amenable to catalytic upgrading. Bio-oils and bio-oil components can also be used as feeds for liquid-phase processing. Bio-oil generation by fast pyrolysis or liquefaction processes has been discussed in detail in Thrust 1. The most common biomass feed sources along with a few of their key advantages and disadvantages are listed below:

CELLULOSE can be solvated by aqueous acidic, basic, or ionic liquid mediated processes. Glucose monosaccharides and degradation products can be sourced from cellulose for liquid phase upgrading. Hemicellulose can be easily liberated from lignocellulose by mild aqueous acid treatment, yielding a mixture of C5 and C6 sugars and degradation products. Pure hemicellulose as a starting feedstock is difficult to obtain.

LIGNIN can be separated from the sugar fractions of the holocellulose portion of biomass by multiple means including kraft pulping, organosolv pulping, or aqueous acid hydrolysis.

SECTIONS OF THRUST 3:

PARTICIPANTS:
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Different treatments leave the solid lignin fraction with different degrees of cross-linking and condensation. Black liquor is a waste stream produced via kraft pulping that contains lignin and several inorganic chemicals from the pulping process. The aromatic rich stream represents a possible feedstock for further catalytic upgrading.

STARCH and sucrose are common food sources but are also possible feedstocks for fuels. Starch is a glucose polymer that can be treated to yield glucose and degradation products. Sucrose is a simple disaccharide containing a glucose and fructose unit.

Plant and animal **GLYCERIDES** are amenable to liquid phase catalytic processing for the synthesis of gasoline and diesel range fuels. Both virgin oils and waste oils can be feedstocks for such processes. However, the relative amounts of these feeds are too limited to make a large impact on transportation fuels needs in the US.

PROTEINS represent another class of renewable raw materials for liquid phase catalytic processing. However, they do not represent a viable feedstock for fuels, but maybe useful for chemical production.

3.4 REVIEW OF CATALYTIC REACTIONS FOR LIQUID-PHASE PROCESSING

3.4.1 Liquid-phase Processing vs. Gas-phase Processing

Petroleum feeds usually have a low extent of functionality (e.g., -OH, -C=O, -COOH groups), making these feeds directly suitable for use as fuels after appropriate catalytic processing (e.g., cracking to control molecular weight, isomerization to control octane number). In contrast, functional groups must be added to petroleum-derived feeds to produce chemical intermediates, and the challenge in this field is to be able to add these groups selectively (e.g., to add -C=O groups without complete oxidation of the organic reactant to CO_2 and H_2O). Unlike petroleum which contains limited functionality, biomass-derived carbohydrates contain excess functionality for use as fuels and chemicals, and the challenge in this field is to develop methods to control functionality in the final product.

Figure 3.1 is a qualitative illustration of the temperature and pressure regimes at which petroleum and carbohydrate feedstocks are typically processed. Petroleum processes are usually conducted at elevated temperatures, and many of these processes are carried out in the vapor phase. Thermochemical processing of biomass-derived feedstocks, such as gasification, liquefaction, pyrolysis, and supercritical treatments, also involve high temperature treatments of biomass. As an alternative, biomass-derived carbohydrate feeds can also be treated at mild temperatures in the liquid phase. The potential advantage of this approach is to be able to control the catalytic chemistry and reaction conditions to achieve high yields of desired products, without the undesirable formation of chars and tars that occurs

Figure 3.1 Comparison of reaction conditions for petroleum versus biomass processing

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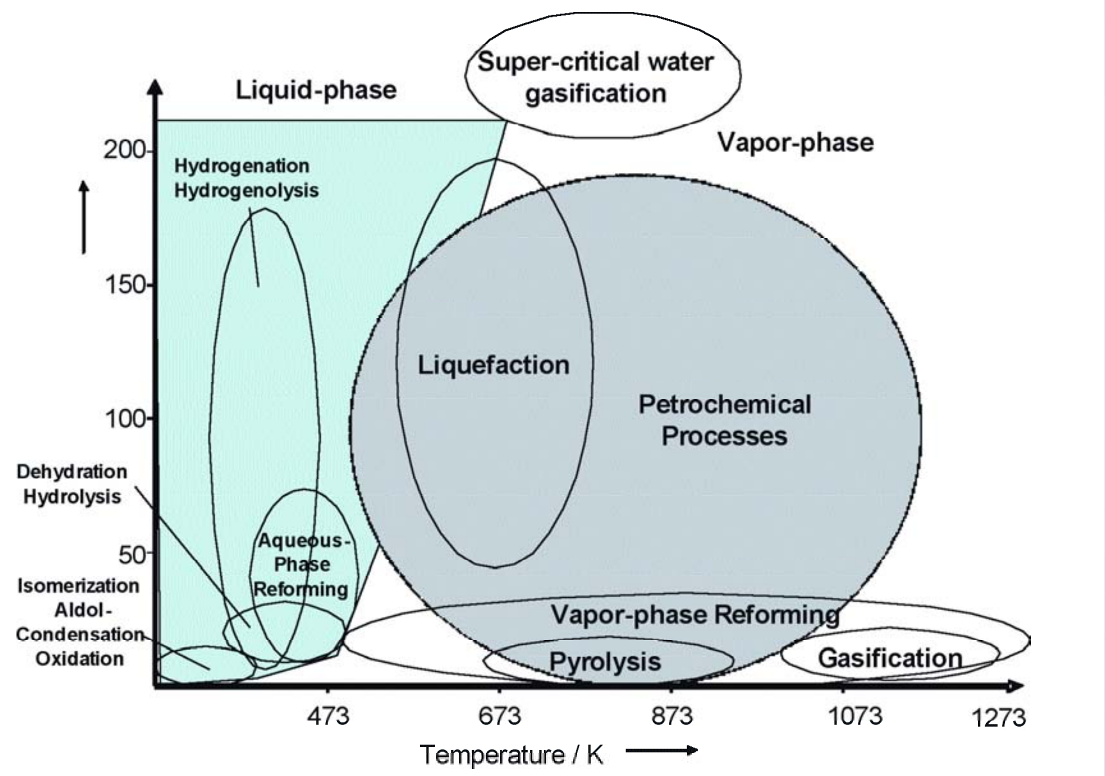

at elevated temperatures. Reactions such as hydrolysis, dehydration, isomerization, oxidation, C-C coupling (e.g., aldol-condensation), and oxidations are often carried out at temperatures near or below 400 K. Hydrogenolysis and hydrogenation reactions are usually carried out at higher temperatures (e.g., 470 K), and aqueous-phase reforming is carried out at slightly higher temperatures (e.g., 500 K) and at higher pressures to maintain the water in the liquid state (> 50 atm). Vapor-phase reforming of oxygenated hydrocarbons can be carried out over a wide range of temperatures and at modest pressures (e.g., 10 atm).

■ 3.4.2 The Thermodynamics of Liquid-phase Thermal Processing

The conversion of biomass-derived oxygenates to fuels and chemicals involves the combination and/or coupling of various types of reactions, including hydrolysis, dehydration, reforming, C-C hydrogenolysis, C-O hydrogenolysis, hydrogenation, C-C coupling (e.g., aldol condensation), isomerization, selective oxidation, and water-gas shift. Figure 3.2 presents a schematic representation of the energy changes associated with the aforementioned reactions at 300 K and 1 atm for selected examples, where exothermic reactions (i.e., negative changes in enthalpy) are represented as moving toward the bottom of the figure and endothermic reactions (i.e., positive changes in enthalpy) are represented as moving toward the top of the figure.

Figure 3.2 Standard enthalpy changes for typical reactions involved in biomass processing.
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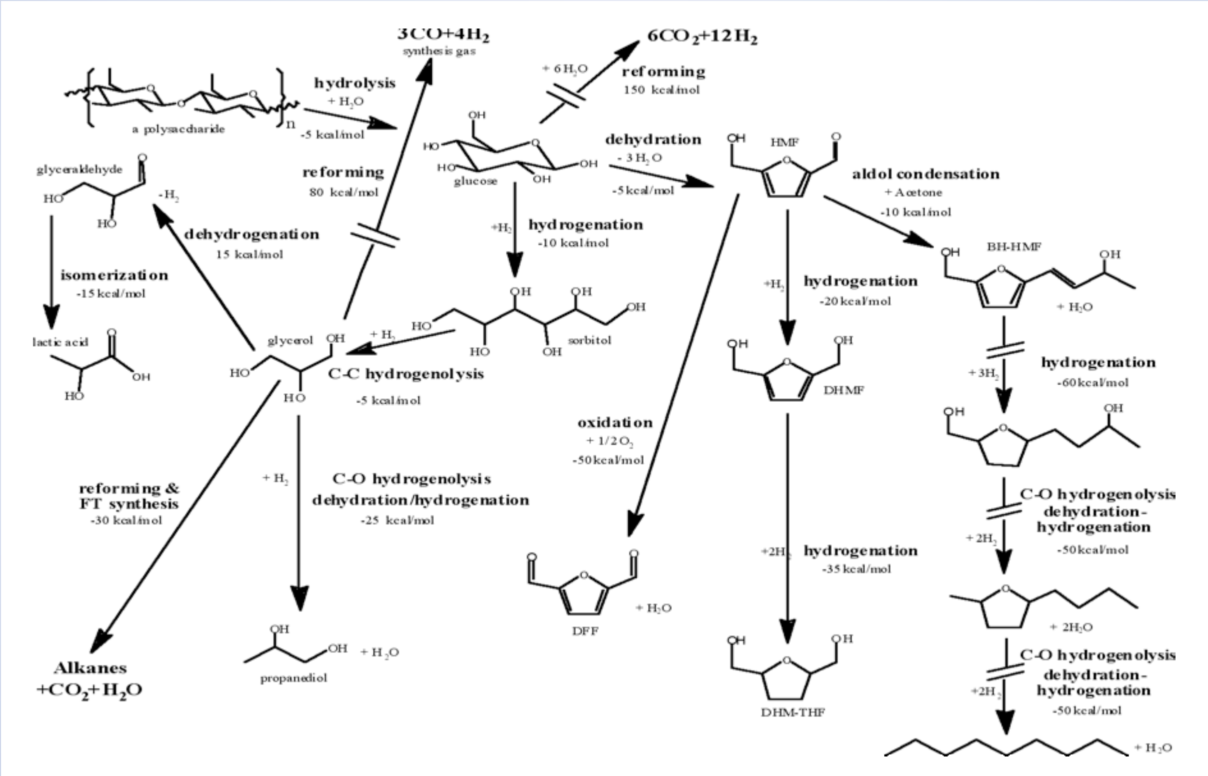

Hydrolysis of a polysaccharide to monosaccharides is nearly neutral energetically (e.g., equal to -5 kcal/mol for the hydrolysis of sucrose to glucose and fructose), as is the subsequent dehydration of glucose to form hydroxymethylfurfural (HMF). In contrast to these steps where water is added or removed from biomass-derived carbohydrates, the reforming of glucose with water to form CO_2 and H_2 is a highly endothermic reaction (150 kcal/mol of glucose). This formation of CO_2 and H_2 may be considered to be a catalytic decomposition of the sugar to form CO and H_2, combined with the conversion of CO and H_2O to produce CO_2 and H_2 (i.e., the water-gas shift reaction, CO + H_2O → CO_2 + H_2, which is exothermic by 10 kcal/mol). In this respect, half of the H_2 is derived from the sugar molecule and the other half is derived from H_2O. The change in Gibbs free energy for the overall reforming reaction is favorable at modest temperatures and above (e.g., -50 kcal/mol of glucose at 400 K), because of the large increase in entropy for the reaction.

Hydrogenation reactions are typically exothermic. For example, the enthalpy change for the hydrogenation of glucose to sorbitol is equal to approximately -10 kcal/mol; the hydrogenation of HMF to 2,5-di(hydroxymethyl)furan (DHMF) has an enthalpy change of about -20 kcal/mol; and, the enthalpy change for the hydrogenation of the furan ring in DHMF to produce 2,5-di(hydroxymethyl)-tetrahydrofuran (DHM-THF) is about -35 kcal/mol (or about -18 kcal per mol of H_2). For comparison, we note that the enthalpy change for hydrogenation of a C=C bond in an olefin is about -25 to -30 kcal/mol. Thus, it is thermodynamically more favorable to hydrogenate the C=C bonds in olefins, compared to hydrogenation of C=O bonds or the C=C bonds in the furan ring, and it is thermodynamically more favorable to hydrogenate these latter bonds than it is to hydrogenate a carbohydrate to its sugar-alcohol (e.g., glucose to sorbitol).

Cleavage of C-C bonds in the presence of hydrogen is termed C-C hydrogenolysis, and such reactions are nearly neutral energetically (e.g., equal to – 5 kcal/mol for the hydrogenolysis of sorbitol to produce two molecules of glycerol). In contrast, C-O hydrogenolysis reactions are highly exothermic. As an example, the enthalpy change for C-O hydrogenolysis of glycerol to produce propanediol and water is about -25 kcal/mol. It is important to note that C-O hydrogenolysis can also be accomplished by a two-step process involving dehydration (catalyzed by an acid or a base) followed by hydrogenation (catalyzed by a metal). Because dehydration reactions are energetically neutral and hydrogenation reactions are highly exothermic, the combination of dehydration followed by hydrogenation is a highly exothermic process.

Another type of reforming reaction is the production of CO:H_2 gas mixtures (called synthesis gas) from biomass-derived oxygenated hydrocarbons. This route for production of synthesis gas is carried out by minimizing the extent of the water-gas shift reaction, for example, by minimizing the concentration of water in the feed. As seen in Figure 3.2, the formation of synthesis gas from glycerol is highly endothermic, with an enthalpy change of about 80 kcal/mol. This formation of synthesis gas is highly beneficial for the biorefinery, because synthesis gas can be used as a source for fuels and chemicals by various synthesis gas utilization steps, such as Fischer-Tropsch synthesis or methanol synthesis. As an example, the conversion of synthesis gas to alkanes (along with CO_2 and water) is highly exothermic (e.g., -110 kcal/mol), such that the overall conversion of glycerol to alkanes by the combination of reforming and Fischer-Tropsch synthesis is mildly exothermic, with an enthalpy change of about -30 kcal/mol of glycerol (Soares, Simonetti et al. 2006).

A useful synthetic reaction that can be employed to produce C-C bonds between biomass-derived molecules is aldol-condensation. For example, aldol condensation of HMF with acetone leads to a C9 species (1-buten-3-hydroxylhydroxymethylfuran, BH-HMF) (Huber, Chheda et al. 2005).
This step is mildly exothermic, with an enthalpy change of about -10 kcal/mol. The subsequent hydrogenation and C-O hydrogenolysis (or dehydration-hydrogenation) steps involved in the conversion of BH-HMF to a C9-alkane are highly exothermic (with enthalpy changes of about -20 to -25 kcal/mol of H_2).

While the production of fuels from biomass-derived carbohydrates involves reduction reactions, the production of chemical intermediates may involve oxidation reactions, such as the conversion of alcohols to aldehydes and carboxylic acids. These oxidation reactions are highly exothermic, as illustrated in Figure 3.2 by the oxidation of HMF to form 2,5-diformylfuran (DFF), with an enthalpy change of -50 kcal/mol.

Another class of important reactions for biomass conversion involves isomerization processes. For example, the conversion of glucose to fructose is of importance for the production of HMF, because higher rates and selectivities for fructose dehydration to HMF are achieved compared to the case for glucose dehydration. The conversion between these two sugars is nearly neutral energetically. In contrast, the isomerization of a hydroxy-aldehyde (such as a sugar) to a carboxylic acid is highly exothermic. As shown in Figure 3.2, the dehydrogenation of glycerol to glyceraldehyde is highly endothermic with an enthalpy change of about 15 kcal/mol, and the isomerization of glyceraldehyde to lactic acid is exothermic with an enthalpy change of -15 kcal/mol, such that the overall conversion of glycerol to lactic acid is about neutral energetically.

3.4.3 Reaction Classes for Catalytic Conversion of Carbohydrate-derived Feedstocks

The main types of reactions involved in the conversion of biomass-derived feeds to fuels and chemicals are: hydrolysis, isomerization, reforming, C-C coupling (e.g., aldol-condensation), hydrogenation, selective oxidation, hydrogenolysis, dehydration/hydrogenation and olefin oligomerization and metathesis.

3.4.3.1 Hydrolysis

Hydrolysis is one of the major processing reactions of polysaccharides in which the glycosidic bonds between the sugar units are cleaved to form simple sugars like glucose, fructose and xylose, and partially hydrolyzed dimer, trimers, and other oligomers. The challenge is to identify the reaction conditions and catalysts to convert a diverse set of polysaccharides (such as cellulose, hemicellulose, starch, inulin, and xylan) obtained from a variety of biomass sources.

Hydrolysis reactions are typically carried out using acid or base catalysts at temperatures ranging from 370 – 570 K, depending on the structure and nature of the polysaccharides. Acid hydrolysis is more commonly practiced because base hydrolysis leads to more side reactions and thus lower yields. Acid hydrolysis proceeds by C-O-C bond cleavage at the intermediate oxygen atom between two sugar molecules. Often the reaction conditions can lead to further degradation of sugars to products such as furfural and HMF that may be undesirable. Cellulose, the most abundant polysaccharide with β-glycosidic linkages, is the most difficult material to hydrolyze because of its high crystallinity. Both mineral acids and enzymatic catalysts can be used for cellulose hydrolysis, with enzymatic catalysts being more selective. The highest glucose yields achieved for cellulose hydrolysis with concentrated mineral acids are typically less than 70%, whereas enzymatic hydrolysis of cellulose can produce glucose in yields close to 100% (Huber et al. 2006). Hemicelluose is more open to attack at intermediate positions to break down the oligomers to single sugar molecules, thereby requiring modest temperatures and dilute acid concentrations, which minimize further degradation of the simple sugars. Soluble starch (a polyglucan with β-glycosidic linkages obtained from corn and rice) and inulin (a polyfructan obtained from chicory) can be hydrolyzed at modest conditions (340 – 420 K) to form glucose and fructose, respectively (Moreau et al. 1997; Nagamori and Funazukuri 2004).

3.4.3.2 Dehydration

Dehydration reactions of carbohydrates and carbohydrate-derived molecules comprise an important class of reactions in the field of sugar chemistry. Sugars can be dehydrated to form furan compounds such as furfural and HMF that can subsequently be converted to diesel fuel additives (by aldol-condensation and aqueous phase dehydration–hydrogenation) (Huber et al. 2005) industrial solvents (e.g., furan, tetrahydrofurfuryl alcohol, furfuryl alcohol) (Lichtenthaler and Peters 2004) various bio-derived polymers (by conversion of HMF to FDCA) (Werpy and Petersen 2004) and P-series fuel (by subsequent hydrogenolysis of furfural) (Paul 2001). Furfural is industrially produced from biomass rich in pentosan (e.g., oat hulls, etc) using the Quaker Oats technology employing mineral acid as catalyst (Zeitsch 2000).

However, HMF is not yet a high-volume chemical in view of difficulties in cost-effective production, even though many researchers have shown promising results in a wide-range of potential applications (Kuster 1990; Gandini and Belgacem 1997; Lewkowski 2001; Moreau, Belgacem et al. 2004). Production of HMF from sugars is a problem that illustrates the selectivity challenges involved in the processing of highly functionalized carbohydrate molecules. Dehydration of hexoses has been studied in water, organic solvents, biphasic systems, ionic liquids and near- or super-critical water, using a variety of catalysts such as mineral and organic acids, organocatalysts, salts and solid acid catalysts such as ion-exchange resins (Mercadier et al. 1981) and zeolites (Moreau et al. 1996) in the temperature range from 370 – 470K.

Although evidence exists supporting both the open-chain and the cyclic fructofuransyl intermediate pathways, it is clear that the reaction intermediates and the HMF product degrade via various processes (Antal Jr. et al. 1990; Antal Jr. et al. 1990; Moreau et al. 1996; Qian et al. 2005). Similarly, glycerol can be dehydrated to acrolein an important industrial chemical. Acrolein can also be converted to other chemicals including: acrylic acid, used in super adsorbents, and potentially 1,3-propanediol, used in Sorona™ polyester. Ott, et al. have shown promising results using sub- and super-critical water with zinc sulfate salts as catalysts to achieve acrolein yields up to 80%. However, corrosion induced by water and salt at these conditions necessitates use of expensive corrosion-resistant materials for the reaction (Ott et al. 2006).

3.4.3.3 Isomerization

Isomerization of carbohydrates is typically carried out in the presence of base catalysts at mild temperatures and in different solvents. Glucose conversion to fructose is widely practiced for production of high fructose corn syrup. In addition, HMF selectivity from glucose can be improved by isomerization of glucose to fructose.

Isomerization can be carried out in the presence of a base catalyst such as magnesium-aluminum hydrotalcites (Lecomte et al. 2002) at temperatures ranging from 310 to 350 K. Carbohydrates in solution are present in open chain (acyclic) and in ring structures such as α-furanose, β-furanose, α-pyranose, β-pyranose in varying proportions (Collins and Ferrier 1995).

The isomerization reaction involves formation of intermediate enolate species through open chain forms to transform aldo-hexoses to keto-hexoses. The rate of glucose isomerization is thus dictated by the fraction of the glucose molecules that are in the open chain form, which is governed by the solvent medium and temperature. Thus, the reaction rates are higher in aprotic solvents, such as dimethylsulfoxide (DMSO), in which the

GREEN GASOLINE PRODUCTION BY INTEGRATED SYN-GAS PRODUCTION AND FISCHER-TROPSCH SYNTHESIS

Liquid alkanes or green gasoline can be produced directly from glycerol by an integrated process involving catalytic conversion to H_2/CO gas mixtures (synthesis gas) combined with Fischer-Tropsch synthesis (Figure S-3.3). Concentrated solutions of glycerol (e.g., 80 wt%) in water are first passed at low temperatures (548 K) and moderate pressures (1-17 bar) over a catalyst consisting of PtRe nanoparticles supported on carbon, and the products from this catalyst are then contacted at the same temperature and pressure with nanoparticles of Ru supported on titania, leading to the formation of liquid alkanes.

This integrated process has the potential to improve the economics of "green gasoline" by reducing capital costs and increasing thermal efficiency. Importantly, the coupling of glycerol conversion with synthesis gas and Fischer-Tropsch synthesis leads to synergies in the operations of these processes, such as (i) avoiding the highly endothermic and exothermic steps that would result from the separate operation of these processes and (ii) eliminating the need to condense water and oxygenated hydrocarbon byproducts between the catalyst beds.

Figure S-3.1 Integrated catalytic process for production of liquid alkanes (green gasoline).
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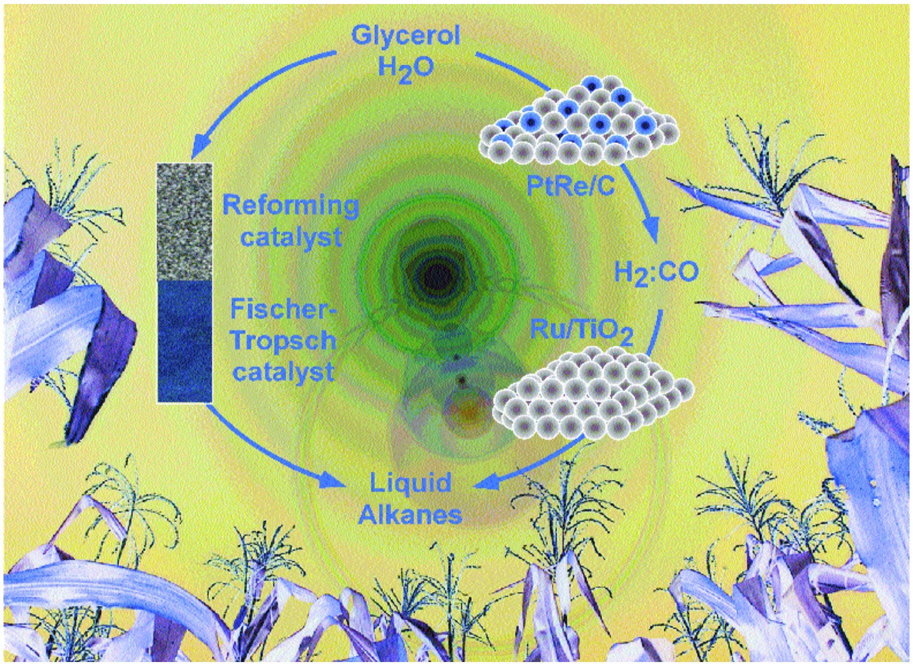


abundance of the acyclic form is about 3% for fructose as compared to in water where it is less than 0.8%. In addition, an increase in temperature to 350 K increases the open chain form, thereby increasing the rate of isomerization (Dais 1987; Franks 1987; Bicker et al. 2005).

3.4.3.4 Reforming Reactions

The production of hydrogen for fuel cells, ammonia synthesis and other industrial operations is an essential element of future biorefineries, similar to current petroleum refineries. Pyrolysis of solid biomass followed by reforming of bio-oils and biomass gasification are known technologies for H_2 production (Huber, Iborra et al. 2006). In addition, it has recently been shown that aqueous phase reforming (APR) can be used to convert sugars and sugar alcohols with water to produce H_2 and CO_2 at temperature near 500 K over metal catalysts (Cortright et al. 2002). Importantly, the selectivity towards H_2 can be controlled by altering the nature of the catalytically active metal sites (e.g., Pt) and metal-alloy (e.g. Ni-Sn) (Huber et al. 2003) components, and by choice of catalyst support (Shabaker et al. 2003).

Various competing pathways are involved in the reforming process. A good catalyst should promote C-C bond cleavage and water-gas shift to convert CO to CO_2, but it should not facilitate further hydrogenation reactions of CO and CO_2 to form alkanes or parallel reactions by C-O bond cleavage to form alcohols and acids (Davda et al. 2005). It has also been demonstrated that APR can be tailored to convert sorbitol to a clean stream of light alkanes (C4-C6) using a bi-functional metal-acid catalyst (e.g., Pt/SiO_2-Al_2O_3), wherein formation of hydrogen and CO_2 takes place on a metal catalyst and dehydration of sorbitol occurs on a solid acid catalyst (Huber et al. 2004). The combination of catalytically active sites, support, solution pH, feed concentration, process conditions and reactor design governs the selectivity of hydrogen and alkane production using aqueous phase processing. It has recently been shown that the APR process can be used to produce H_2 from actual biomass; however, low yields (1.05 -1.41 mmol/g of carbohydrates) were obtained due to coke and byproduct formation (Valenzuela et al. 2006).

3.4.3.5 Carbon-Carbon Bond Coupling Reactions

To convert carbohydrate derived molecules into liquid range alkanes that fit within the diesel and jet fuel range C-C bonds must be formed. Aldol condensation is a C-C bond forming reaction, generally carried out to form larger molecules at mild temperatures (300 – 370 K) in the presence of a base or acid catalyst. It has been shown that various carbohydrate-derived carbonyl compounds such as furfural, HMF, dihydroxyacetone, acetone, and tetrahydrofurfural can be condensed in aqueous and organic solvents to form larger molecules (C7-C15) that can subsequently be converted to diesel fuel components (Huber et al. 2005). Aldol condensation requires at least one carbonyl compound having an α-hydrogen atom, and the reaction is generally carried out in the presence of a base catalyst. At first, the base catalyst abstracts the α-hydrogen from the carbonyl compound to form an intermediate carbanion (enolate ion) species, which can then attack the carbon atom of a carbonyl group from another molecule, that may or may not have an α-hydrogen atom, to form a C-C bond. The aldol-adduct can further undergo dehydration to form an unsaturated aldehyde or ketone. Factors such as reaction temperature, solvent, reactant molar ratio, structure of reactant molecules, and the nature of the catalyst determine the selectivity of the process towards heavier compounds (Barrett et al. 2006).

More generally, C-C coupling reactions typically require an activated site next to the carbonyl functionality or an unsaturated C-C bond which would be either conjugated with the carbonyl functionality or isolated. The main challenges with C-C bond forming reactions are related to: the reagents needed for this chemistry, how to introduce selectively unsaturated C-C bonds, how much of the oxygen content can be removed and how to do that in a selective fashion. Another aspect is that the above mentioned chemistry has mainly been studied in organic solvents using homogeneous catalysis. Several questions arise when these reactions are applied to biofuel related chemistry. How will this chemistry apply to aqueous systems? Will the reagents be soluble in organic solvents? What will their structure be in those solvents? (For example, in water the carbonyl functionality is typically hydrated to a certain extent, and thus may hinder aldol chemistry.) Will the reagents be stable in the conditions required for the transformation to take place?

Other molecular weight enhancing reactions should also be explored. Linking together smaller molecules via C-O bonds also appears to be a promising route. Esterification and etherification reactions appear to be useful approaches, although these methods necessarily introduce (or maintain) oxygen in the end products. This may or may not be feasible for some intended applications. In addition, C-C bonds could potentially be formed by alkylation reactions (aromatic and aliphatic) over acid catalysts. Another route to C-C bond formation would be first to produce olefins, followed by oligomerization. Alternatively, alcohols could be produced from biomass-derived compounds, followed by the formation of higher molecular weight species by MTG (methanol to gasoline) process variants.

3.4.3.6 Hydrogenation

Biomass-derived oxygenates are intrinsically hydrogen deficient molecules. Hydrogenation is one of the key reactions for conversion of biomass-derived oxygenates to liquid alkanes. Aqueous-phase hydrogenation reactions are used for hydrogenation of fermentation products (lactic acid, acetic acid), production of polyols (sorbitol, etc), upgrading of bio-oils, and liquid alkane production by aqueous-phase dehydration/hydrogenation. In these processes a number of functionalities are hydrogenated including acids, aldehydes, C=C bonds, and C-O-C (ether) linkages. Hydrogenation reactions are carried out in presence of a metal catalyst such as Pd, Pt, Ni, or Ru at moderate temperatures (370 – 420 K) and moderate pressures (10 - 30 bar) to saturate C=C, C=O and C-O-C bonds. Selective hydrogenation reactions are important to make biofuels and products. Electrocatalytic hydrogenations offers the means to reduce unsaturated bonds by hydrogen produced at the surface of an electrode made of catalytic metal. In-situ production of hydrogen eliminates the need of high pressures to accumulate enough H_2 in solution, splitting of H_2 on catalyst surface and its mass transport issues in water. Lactic acid reduction using a reticulated vitreous carbon electrode suffused with a Ru/C catalyst, was performed at 70°C in aqueous environment in presence of an electrolyte to selectively produce lactaldehyde in an 80% yield. These conditions are milder than the ones used for batch reactions which typically run at 130°C and 1000 psi H_2. Also one must note the selectivity of the electrochemical process that stops at the first step in terms of reduction, lactaldehyde. The challenges associated with this technique at present are: dilute conditions needed due to mixing issues, stability of the reactants in presence of the electrolyte, reaction rate due to surface limits (Dalavoy et al. 2007).

3.4.3.7 Selective Oxidation

Selective oxidation is conducted to form chemical intermediates having specific functionality, and this reaction is carried out in the presence of aqueous or organic solvents at temperatures from 330 to 420 K and oxygen pressures of 2 to 10 bar in the presence of supported metals (Pt, Pd, Au, Ti, Zr, V) or metal oxides and metal derivatives such as vanadyl phosphate (Carlini, et al. 2005). Catalytic oxidation reactions can form multiple products, and thus the challenge is to direct the reaction pathways to desired products. Selective oxidation of HMF leads to formation of 2,5-diformylfuran (DFF) that has potential applications in the synthesis of drugs, fungicides and in preparing new polymeric materials (Halliday, Jr. et al. 2003). The product distribution for this reaction depends on the type of solvent, pH, partial pressure of oxygen, temperature and nature of the catalyst. High temperatures and almost neutral pH in the presence of a Pt/C catalyst lead to oxidation of the hydroxymethyl group to give DFF, while low temperatures and basic pH lead to oxidation of both the formyl and the hydroxyl groups of HMF to form 2,5-furandicarboxylic acid (FDCA)(Carlini et al. 2005). Similarly, acidic conditions in glycerol oxidation favor oxidation of the secondary alcoholic group to dihydroxyacetone (DHA), while under basic conditions the primary alcoholic groups are oxidized to form glyceric acid. Addition of Bi promotes the Pt/C catalyst in the presence of base to a mechanism involving oxidation of the secondary alcoholic group to dihydroxyacetone (Bianchi et al. 2005). In a recent study of glycerol oxidation, researchers found that bimetallic catalysts (Au-Pt, Au-Pd) are more active than monometallic catalysts (Au, Pt, Pd), indicating a synergistic effect existing between Au and Pd or Pt. (Bianchi et al. 2005). A recent study has shown that glycerol can be converted to dihydroxyacetone (DHA) by an electrochemical route (Ciriminna, 2006).

3.4.3.8 Hydrogenolysis

The hydrogenolysis of C-C and C-O bonds in polyols occurs in the presence of hydrogen (14 – 300 bar), at temperatures from 400 to 500 K, usually under basic conditions, and with supported metal catalysts including Ru, Pd, Pt, Ni, and Cu (Zartman and Adkins 1933; Tronconi, Ferlazzo et al. 1992; Lahr and Shanks 2003; Chaminand, Djakovitch et al. 2004; Dasari et al. 2005; Lahr and Shanks 2005; Saxena et al. 2005; Miyazawa et al. 2006). The objective of hydrogenolysis is to selectively break targeted C-C and/or C-O bonds, thereby producing more valuable polyols and/or diols. These lower polyols such as ethylene glycol (EG), 1,2-propanediol (1,2 PDO) and 1,3-propanediol (1,3 PDO) have potential applications in the polymer industry (Chaminand, et al. 2004).

The hydrogenolysis of glycerol has received recent attention, (Lahr and Shanks 2003; Chaminand et al. 2004; Dasari et al. 2005; Lahr and Shanks 2005; Miyazawai et al. 2006) because the cost of glycerol as a byproduct is projected to decrease significantly as biodiesel production increases (McCoy 2005).

Glycerol can undergo dehydration reactions to form acetol or 3-hydroxypropionaldehyde, which are then hydrogenated on the metal catalyst to 1,2 propanediol and 1,3 propanediol, respectively. It has been proposed that OH-species on Ru catalyze the dehydration reaction to produce 3-hydroxypropionaldehyde, whereas the production of acetol occurs on amberlyst sites.(Miyazawa, Kusunoki et al. 2006) The reactivity of 1,3 propanediol is high, and it undergoes C-O or C-C bond cleavage, where C-O bond cleavage occurs through a dehydration/hydrogenation pathway. Alternatively, glycerol can undergo C-C bond cleavage to produce ethylene glycol and methanol.

In contrast to hydrogenolysis of glycerol, C-C bond cleavage is a desirable reaction for hydrogenolysis of large polyols (such as sorbitol). The addition of a base catalyst (e.g., NaOH) increases the rate of C-C hydrogenolysis. Wang, et al. have proposed that carbon-carbon bond cleavage occurs by retro-aldol condensation, and they have studied hydrogenolysis of 1,3 diols with Raney Ni and Cu catalysts (Wang, Hawley et al. 1995). They propose that the first step in C-C bond cleavage is dehydrogenation, followed by retro-aldol condensation. The products from retro-aldol condensation are then hydrogenated. The forward aldol condensation can also occur under these conditions.

3.4.3.9 Aqueous-Phase Dehydration/ Hydrogenation

The conversion of biomass-derived molecules into liquid alkanes involves removing the oxygen functionality from the feedstock. This can be done by aqueous-phase dehydration/hydrogenation (APD/H) which involve bifunctional catalysis containing both metal and acid sites. One example of APD/H is alkane production directly from sugar alcohols by APD/H (Equation 1) with a catalyst containing metal (e.g., Pt or Pd) and acid (e.g., SiO_2-Al_2O_3) sites to catalyze dehydration and hydrogenation reactions, respectively. Equation 1 requires the addition of hydrogen, which can be produced from sorbitol by aqueous-phase reforming (APR) (Equation 2). The net reaction (Equation 3) is exothermic, in which approximately 1.5 moles of sorbitol produce 1 mole of hexane.

$$C_6O_6H_{14} + 6H_2 \rightarrow C_6H_{14} + 6H_2O \qquad (1)$$

$$C_6O_6H_{14} + 6H_2O \rightarrow 6CO_2 + 13H_2 \qquad (2)$$

$$\frac{19}{13}C_6O_6H_{14} \rightarrow C_6H_{14} + \frac{36}{13}CO_2 + \frac{42}{13}H_2O \qquad (3)$$

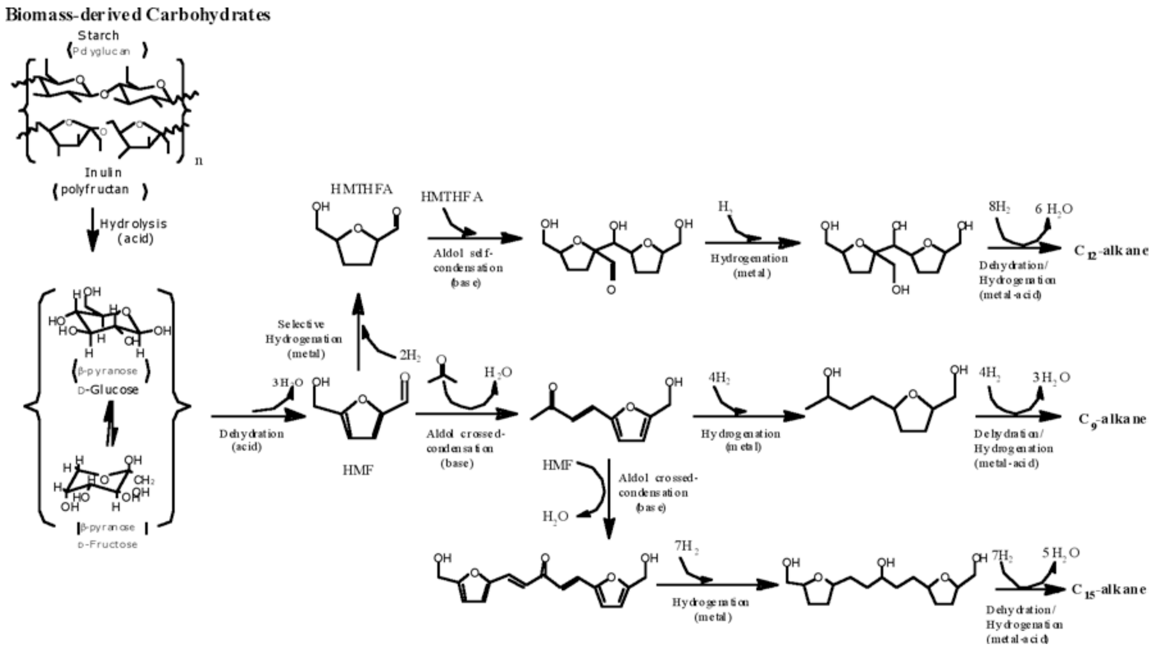
The essential features of the bi-functional reaction scheme for production of alkanes from sorbitol involve: (1) hydrogen production on metal catalytic sites by cleavage of C-C bonds followed by the water-gas shift reaction, (2) dehydration on acid sites, and (3) hydrogenation of the dehydrated species on metal sites. Repeated cycling of dehydration and hydrogenation reactions in the presence of H_2 leads to heavier alkanes (such as hexane) from sorbitol. Formation of lighter alkanes takes place by cleavage of C-C bonds compared to hydrogenation of dehydrated reaction intermediates. One method to produce more valuable compounds is to combine the APD/H process with a base catalyzed aldol condensation step to produce larger alkanes ranging from C7 to C15 as recently reported by Huber et al. (Huber et al. 2005). Optimization of the APD/H systems involves choosing the proper: (1) metal catalyst, (2) acid catalysts, (3) ratio of metal to acid sites, (4) reaction conditions and (5) proper reactor design. This example illustrates how bifunctional catalysts can be used to selectively produce targeted products.

GREEN DIESEL AND JET FUEL RANGE ALKANES BY AQUEOUS-PHASE PROCESSING

Aqueous-phase processing can be used to selectively produce liquid alkanes from carbohydrate-derived compounds that can be used as "green" diesel or jet fuel (Huber et al., 2006). This is a multi-step process that requires acid catalysts for dehydration reactions, base catalysts for aldol-condensation, metal catalysts for hydrogenation reactions, and bifunctional metal/acid catalysts for dehydration/hydrogenation reactions (Figure S-3.1)

The first step in this process is biomass deconstruction to furfural and HMF. These compounds are then reacted with acetone over base- catalysts to form C-C bonds. The final step in this process involves converted these large biomass-derived oxygenates into liquid alkanes by dehydration/hydrogenation. This requires a four-phase reactor involving: (1) a gas phase containing H_2; (2) a solid phase composed of a bifunctional heterogeneous catalyst containing metal and acid sites; (3) an aqueous phase containing the sugar reactant; and (4) a liquid alkane phase used to remove hydrophobic species from the catalyst surface before then react further to form carbonaceous deposits that deactivate the solid catalyst. The alkanes are easily separated from the aqueous feed, significantly improving the process thermal efficiency. This example illustrates how chemistry and catalysts can be used to selectively make targeted fuels from biomass-derived feedstocks.

Figure S-3.1 Reaction pathways for conversion of polysaccharides into liquid alkanes by aqueous-phase processing. Analogous chemistry can be depicted for conversion of C5 polysaccharides to C10, C8 and C13 alkanes, respectively, via furfural as reaction intermediate. (Reprinted with permission from Chedda, Huber, Dumesic 2007. Copyright 2007 Wiley).



3.5 ADVANTAGES OF LIQUID-PHASE PROCESSING

■ 3.5.1 The Potential to Design New Generations of Nanostructured Catalysts

Heterogeneous catalysis has largely been developed in concert with the conversion of fossil fuel feedstocks, which are predominantly processed at elevated temperatures. This processing paradigm has placed constraints on the catalyst systems to be used. In particular, supported metal catalysts or metal oxide catalysts are almost exclusively used. However, liquid-phase processing, which will generally occur at temperatures below 525 K, opens the potential for catalytic moieties beyond metals and metal oxides. A number of the reactions to be performed on biomass-derived molecules will exploit acid/base catalysis. In addition to traditional catalytic materials, organic acids and bases can be used as catalysts. These species can be immobilized on polymer or metal oxide supports for use as heterogeneous catalysts. Use of these organic acids and bases will allow the synthesis of materials with well-defined catalytic sites. Additionally, the properties of these catalytic moieties can be systematically adjusted. For example, organic acids with a range of pKa values can be explored (e.g. carboxylic, phosphonic, sulfonic) or the pKa value for say sulfonic acid can be modified by changing the chemistry of the tethering group (e.g., alkyl, arene, perfluorinated).

Compared to petroleum feeds, the carbohydrates in biomass-derived feeds are highly reactive and can be processed at mild temperatures (e.g., < 500 K). Accordingly, the catalysts employed for these processes need not be subjected to high temperatures, potentially allowing a greater degree of flexibility in the design and synthesis of these materials. In fact, this ability to operate at relatively low temperatures offers unique opportunities for applications of nano-synthetic techniques. In particular, recent advances in nanotechnology have provided the concepts and tools required to synthesize new materials with unprecedented control at the nanometer length scale. However, while many of these materials may not be stable under the harsh conditions required for the processing of petrochemical feeds, it is likely that sophisticated materials prepared by nano-synthetic techniques may be more appropriate for low-temperature catalytic reactions employed in the processing of biomass-derived carbohydrates.

■ 3.5.2 Ability to Process Thermally Unstable Molecules

A key advantage of liquid-phase catalytic processing is that thermally unstable reactant molecules, such as sugars, can be processed at low temperatures, where undesirable thermal degradation reactions are slow, leading potentially to high selectivities for targeted products. Clearly, a variation on this theme is that liquid-phase catalytic processing can be used to convert reactant molecules having low volatility, such as sugars. In particular, by processing these molecules in the liquid phase we eliminate the need to employ high temperatures to evaporate these molecules into the vapor phase, and operation at lower temperature minimizes the contributions from degradation reactions, leading again to high selectivities for targeted products. This effective processing of non-volatile reactants also applies to the processing of feeds containing non-volatile impurities and contaminants (e.g., ash). For example, the presence of ash in a biomass feed would deposit on and accumulate within the pores of a solid catalyst for a vapor-phase reaction, whereas it is possible that the ash would be swept from the catalyst by the flowing solvent for a liquid-phase catalytic reaction.

3.5.3 Reaction Control through Solvent Selection

A key attribute in liquid-phase processing is the choice of solvent, and this choice is dictated by consideration of how the solvent affects the solubilities and reactivities of the reactants, products and intermediates of the liquid-phase process, as well as upstream and downstream processes that interface with the liquid-phase process. For example, the upstream reactant for the overall process may be a highly polar, hydrophilic molecule such as a sugar or a polyol, and a logical solvent for this molecule would be water. In the overall processing of this molecule to a liquid fuel, oxygen atoms will be removed leading to a less polar, hydrophobic molecule. Accordingly, this change in physical properties leads to opportunities for biphasic liquid-phase processing, wherein the hydrophobic product is transferred, without vaporization, from the aqueous phase to an organic solvent phase. In this respect, the solvent properties are chosen to optimize the partition coefficients of the reactants, products and intermediates between the aqueous and the organic phase. Moreover, the interactions of the solvent with liquid-phase species, with the catalyst surface, and importantly with the transition states for the rate-determining steps control the reaction activity and selectivity.

The choice of the solvent for liquid-phase catalytic processing can be of critical importance, and there is much that can be learned from the pulp and paper industry, such as is involved in Organosolv and kraft pre-treatment processes. Also, the choice of the solvent will be influenced by availability at the biorefinery location, and solvents of particular merit in this respect would be butanol, ethanol, biodiesel, ethyl acetate, acetone, and gasoline itself. It is noteworthy that ionic liquids have recently been shown to have unique properties for the selective conversion of biomass-derived compounds, such as the conversion of hexoses to HMF. Moreover, these ionic liquid solvents have very low vapor pressures at elevated temperatures, offering effective strategies for separating volatile products from the reactive solution by distillation. In addition, the low volatilities of these solvents make it possible to use vacuum techniques (e.g., XPS, TEM) to characterize these reactive systems under reaction conditions. *(see sidebar on next page)*

3.5.4 Biphasic Reactions

The possibility of conducting reactions having multiple phases offers challenges in reaction engineering, but it also opens new avenues for developing new catalytic processes that take advantage of synergies between reaction kinetics and thermodynamics. For example, if a desired reaction intermediate or product undergoes side-reactions with a reactant, then the production of this species can be optimized by conducting the reaction in a bi-phasic reactor containing the reactants in one liquid phase plus a second liquid phase that preferentially extracts the desired intermediate or product. In a variation on this theme, a four-phase reactor can be used to carry out a hydrodeoxygenation conversion of a sugar to produce an alkane, involving (1) a gas phase containing H_2, (2) a solid phase composed of a bifunctional heterogeneous catalyst containing metal and acid sites, (3) an aqueous phase containing the sugar reactant, and (4) a liquid alkane phase used to remove hydrophobic species from the catalyst surface before they react further to form carbonaceous deposits that deactivate the solid catalyst. If the feed stream also contains solid biomass components, then the aforementioned reactor becomes a five-phase system. The concept of a bi-phasic reactor can also be used to couple an aqueous-phase reaction leading to deconstruction of polysaccharides to form reaction intermediates (e.g., H_2, sugars, polyols, furans), combined with an organic phase in which these

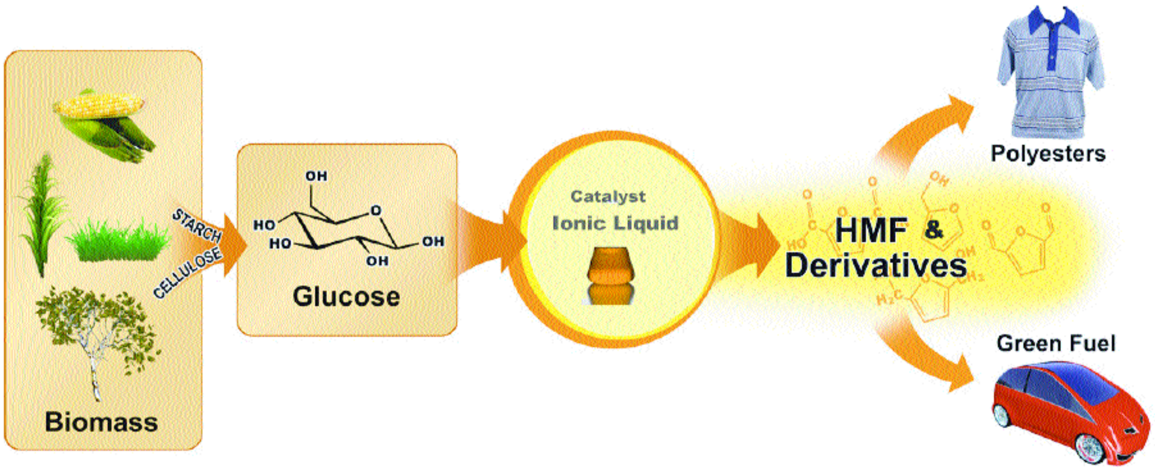
LIGNOCELLULOSIC BIOMASS DECONSTRUCTION TO FUEL PRECURSORS WITH IONIC LIQUIDS

Ionic liquids are often defined as salts that have a melting point below 100°C; many are liquids at normal ambient temperatures. The properties of these salts present a wide range of opportunities for their use as solvents and as catalysts.

Most ionic liquids exhibit practically no measurable vapor pressure and are highly polar, and yet non-coordinating, which is ideal as solvent for catalytic reactions. Some ionic liquids are immiscible with water; others are immiscible with organic solvents. Therefore, many ionic liquids are suitable for catalytic processes. Their application can improve reaction rates and selectivity, and importantly reduce the cost of product separation. Using ionic liquids to replace water and organic compounds as solvents offer potential advantages, such as reduced waste disposal and improved process economics, provided that ionic liquids are reused. The non-volatile nature, thermal stability, and higher density of most ionic liquids compared with water and organic solvents make their reuse readily achievable in most processes.

For biomass processing, a highly attractive property of some ionic liquids is their capability to swell and disperse the polymeric structure of biomass components, creating a desirable condition that allows appropriate catalysts to perform depolymerization and chemical transformation in the same media. For example, lignocellulosic materials have been shown to be soluble in ionic liquids with strong hydrogen acceptor (Fort et al. 2007). Ionic liquids that are capable of dissolving carbohydrates have been demonstrated to enable catalytic transformation of the carbohydrates to a versatile platform chemical, like hydroxymethylfurfural (Zhao et al. 2007). The process from biomass to end products is illustrated in Figure S-3.2

Figure S-3.2 Schematic view of ionic liquid application in biomass



intermediates are used to form liquid fuel components (e.g., by reactions such as hydrogenation, hydrogenolysis, aldol-condensation, and Fischer-Tropsch synthesis).

3.5.5 Ability to Vary Ionic Strength

An advantage of processing a biomass-derived reactant in the liquid-phase is that it is possible to control the reaction chemistry by altering the pH and ionic strength of the solution. Furthermore, it is possible to take advantage of salt effects that change the bonding and electrostatic interactions of the solvent with the reactants, products and intermediates of the reaction. In addition, it may also be possible to utilize electrochemical effects to control the rates and selectivities of reactions taking place in the liquid phase. Furthermore, it may be possible to use microwave energy to deliver heat specifically to the active sites of a catalytic reaction in the liquid phase, without extensive heating of the bulk liquid phase, thereby accentuating the contribution of the catalytic reaction and minimizing undesired side-reactions taking place in the bulk liquid phase.

3.5.6 Faster Reaction Rates

Compared to the production of bioethanol by fermentation, the production of next-generation liquid fuels by liquid-phase catalytic processing offers the possible advantage of being carried out at faster rates. For example, while the time-scale of a fermentation process may typically be measured in days, the time-scales of liquid-phase catalytic reactions are typically of the order of minutes. These higher rates translate to potentially lower capital costs versus cellulosic ethanol. In addition, the very high selectivity for fermentation of glucose to ethanol comes at the cost of being very sensitive to the nature of the feed (e.g., high preference for C6 compared to C5 sugars, and high sensitivity to the presence of contaminants inhibitory to the organisms). In contrast, whereas the catalysts used in liquid-phase catalytic processing typically achieve modest selectivities (e.g., 80%), they are not typically dependent on the detailed structure of the reactant (e.g., glucose versus xylose, or sorbitol versus xylitol), and the negative effects caused by contaminants are either small or can be reversed by appropriate catalyst regeneration procedures. This difference in specificity leads to potentially higher versatility in accepting feedstocks for liquid-phase catalytic processing. As an example we consider the hydrolysis of polysaccharides to form sugar monomers in aqueous solution. Compared to fermentation, liquid-phase catalytic processing should have the potential ability to handle a broader range of biomass, including C5 sugars. Also, while the presence of organic byproducts during the hydrolysis step (such as furan compounds or levulinic acid) is highly detrimental for the subsequent fermentation of glucose to ethanol, these species may play a small role in the catalytic conversion of glucose to liquid alkanes by the combination of dehydration and hydrogenation steps over heterogeneous catalysts. In this respect, it may be possible to push the hydrolysis pretreatment step to more severe conditions for subsequent liquid-phase catalytic processing, which may reduce the need for expensive enzymes required for cellulose.

3.5.7 Lower Capital Costs

Finally, we note that liquid-phase catalytic processing may lead to lower capital cost versus gas phase processing at elevated pressures, in view of the lower energy cost associated with compressing a liquid versus a gaseous feed. Also, liquid-phase catalytic processing does not require vaporization of the feed and typically takes place at lower temperatures compared to gas-phase processes, leading to potential savings in heats of vaporization and minimizing the need for heat integration.

3.6 CURRENT TECHNOLOGY LIMITATIONS AND RESEARCH/ DEVELOPMENT NEEDS

3.6.1 Analytical Challenges with Biomass-derived Feedstocks

An evaluation of any reaction system or separation step requires a knowledge of the components present in the feed goint into and the products coming out of the process. In some cases, a bulk compositional analysis is sufficient while in other cases a detailed compositional breakdown of individual components is required. Incoming biomass is typically characterized by bulk compositional analysis, including the proportions of the feed that consist of cellulose, hemicellulose, lignin, ash, and extractable material. The ash fraction may be further characterized to determine the concentrations of specific metals present. In general, the analytical techniques developed for evaluating solid biomass feeds are well established, if time consuming.

As biomass is routed through various liquid phase processing steps, the degree of compositional complexity may increase, primarily due to the complex chemistry of oxygen functional groups. Often this complexity may prohibit a detailed analysis of what occurs during a reaction step. One way to address this issue is to use a model compound, such as purified sugar, polyol, or a process intermediate, as a feedstock to a given reaction step. Even in these cases, the products emanating from a reaction step may not be able to be fully characterized due to non-specific reactions. Nonetheless, studies using model compounds offer insights into catalyst performance that would not be possible to understand if a complex, incompletely characterized feedstock were used. As oxygen is rejected during the course of processing, the degree of compositional complexity eventually decreases because the elimination of oxygen reduces the number of functional groups that are present. The complexity of the final liquid fuel product should be similar to that of conventionally produced fuel. Decades of research by the petroleum industry have led to analytical techniques that are well suited to final product analysis, although some methods will need to be updated to reflect the unique nature of these products.

The composition of the intermediate process streams, then, poses the greatest analytical challenge for liquid phase processing. For aqueous streams, high performance liquid chromatography (HPLC) can identify and quantify many of the components present. However, HPLC has limited capability to identify unknown compounds and the resolution of HPLC methods lag behind that of gas chromatography (GC), making it difficult to deconvolve complex mixtures. GC can be used for aqueous streams containing non-volatile organic components if a derivatization step is utilized to increase the volatility of normally non-volatile compounds (such as sugars). In addition, volatile compounds present in aqueous streams such as alcohols, carbonyl compounds, esters, ethers, and furans, can be analyzed directly by GC, as can any organic phases produced in the process. These methods suffer from a problem with compound identification and quantitation. The use of gas chromatography – mass spectrometry (GC-MS) can improve matters by identifying many relatively low molecular weight compounds. Even with this powerful compound identification capability, higher molecular weight compounds are not easily identified by GC-MS due to inconclusive fragmentation patterns and, often, the absence of compounds from spectral databases.

Continued effort will be necessary to increase the capability for analyzing intermediate process streams. For kinetic and mechanistic studies, a high degree of compositional identification completeness is necessary to identify both the rates of desired product formation and the rates and selectivity towards less desirable components, often present at trace levels. When process development is at a more advanced stage, a less detailed analysis, with incomplete identification of components may be acceptable, or even necessary, given that complex feedstreams will lead to a more difficult challenge for both the feed and intermediate product streams.

3.6.2 Developing Activity Structure Relationships

A fundamental challenge for liquid-phase processing of biomass is the ability to selectively and efficiently break and make C-H, C-O, and C-C bonds on a catalyst submerged in the solvent. The catalysts employed for various liquid-phase reactions have by and large been selected based on empirical evidence. Although impressive activity and selectivity have been demonstrated several questions are unknown: Why do certain catalysts work well and others poorly? What effect if any will the choice of solvent and the presence of impurities have? What room for improvement is present? This reduces the engineer's ability to adapt to different feeds and to maximize the economic advantage of liquid-phase processing. To begin to address these important questions, multiple, complementary sets of tools, including *in situ* spectroscopic techniques and computational modeling techniques, need to be applied in concert to unraveling the secrets of chemical reactions at the molecular scale, and electronic structure-based theoretical methods are particularly powerful tools for this purpose. These methods, particularly density functional theory, have been successfully applied to elucidating reaction mechanisms and increasingly to designing new materials with desired catalytic properties. Nonetheless, some important obstacles lie in the way of applying theory to elucidate reactions at the liquid-solid interface. One is to accurately capture the nature of the catalytic material. For instance, while transition metal catalysts tend to have simple structures, solid acid and base catalysts as well as functional catalyst supports may be structural complex. Another level of complexity enters through how catalytic materials respond to a liquid environment: It is conceivable that, when exposed to a dense layer of water and ionic species, even under mild temperature and pressure, the exterior of the catalyst may no longer be as prepared, and the transformation may be connected to its catalytic activity. Another major obstacle is to understand whether and how the liquid phase affects reactions, for which there are known examples. There is yet no well-established methodology for describing reactions across the liquid-solid interface under the influence of the dynamics of the liquid, with quantum chemical accuracy. Ad-hoc or highly simplified models can be found in the literature that attempt to capture the effect of water on adsorption and reaction. Some of them may well be effective to some degree and can possibly be used beneficially, but no calibration of results is yet available, and better theoretical development is very much needed.

3.6.3 Spectroscopy and Imaging of Catalytic Materials under Liquid-Phase Conditions

An important challenge for advancing the understanding and practice of liquid-phase catalytic processing is to develop advanced *in situ* and *operando* methods to observe the catalyst structure and surface properties under controlled conditions and preferably to do so under real reaction conditions. This task is made difficult by the presence of the solvent. However, techniques such as attenuated total reflectance infrared spectroscopy, polarization modulation infrared spectroscopy, sum frequency generation, X-ray spectroscopy, sum frequency generation, X-ray absorption measurements (EXAFS, XANES), and X-ray diffraction, appear to be well positioned in this respect. Also, it is possible that high resolution imaging techniques (e.g., AFM, SEM, TEM) will make advances to contribute to this important area.

3.6.4 Design of Integrated Catalyst Reactor Systems

A current limitation in the development and optimization of liquid-phase catalytic processing of carbohydrate feeds is that the sugar breakdown chemistry (with competitive reaction rates unknown) is complicated and difficult to control, especially in aqueous solution. A strategy that has proven to be effective in this respect is first to convert the sugar to a sugar-alcohol by a hydrogenation step, thereby suppressing the rates of degradation reactions at elevated temperatures in solution. However, another approach would be to develop catalyst support packings and reactor configurations that minimize the volume of heated solution at elevated temperature and maximize contact of the liquid phase with active sites on the surface of the catalyst. These support packings will also have to deal with the flow of insoluble biomass impurities (e.g., ash) through the catalytic reactor, or these impurities will have to be filtered from solution upstream of the reactor.

Related to catalyst engineering are reactor engineering challenges of working in aqueous systems. One challenge is the low solubility of reactive gasses such as hydrogen and carbon dioxide. This results in the need for high reactor pressure and temperature. The ionic nature of water at elevated temperatures leads to reactor corrosion issues. As corrosion occurs dissolved metals can plate out on the catalyst and impact performance.

3.6.5 Engineering a New Generation of Liquid-phase Catalytic Materials

The need to work in aqueous environments produces a suite of unique opportunities and challenges that have not yet been dealt with in conventional catalysis, which are often either gas phase or organic solvent-based. This field is rapidly evolving – especially in the area of heterogeneous catalysis in aqueous environments. The richness of the chemistry involved in liquid-phase processing is evident in aspects -such as choice of acid effecting product selectivity and reaction rate, affect of organic additives such as DMSO, DCM, on the reaction (i.e. glycosidic hydrolysis, aldol condensation, and dehydration).

These aspects offer unequivocal proof that effects above and beyond bulk effects such as pH are critical for controlling liquid-phase processing of biofuels, and argue therefore, in turn, that the microscopic environment surrounding the catalytic active site is critical. There are emerging examples in the realm of synthetic homogeneous catalysis of how control of the microenvironment around a divalent zinc cation via choice of alcohol substituents on the ligand can greatly accelerate (over 100 fold) the rate of phosphate esters hydrolysis in water as solvent. This subsequently allows the operation of the process under sufficiently mild conditions for avoiding degradation reactions. These observations suggest an approach for liquid-phase processing in which the active site is surrounded by a preferable microsolvation environment. This approach is inspired by the intricacy observed in biological active sites, but reduces the complexity of these sites into the simplest possible scenario of an active site and its immediate surroundings. This could employ emerging methods of anchoring acid and base catalytic active sites on silica, such as amines, alkyl and aryl sulfonic acids developed by Mbaraka and

Shanks, 2005, while placing these active sites within an outer-sphere that surrounds each and every one of them, enforcing a favorable dielectric and bifunctional cooperative environment for catalysis (Shanks, et al). Such an approach has been successfully demonstrated, for example, in the nitroaldol condensation using primary amines as active sites. Organizing amines within a nanoscale environment of cyano-terminated functional groups synthesized a catalyst that produced 99% of a beta-nitroalcohol product in the nitroaldol reaction, whereas a catalyst in which the cyano groups are replaced with methyl groups produces the same product in fifty-fold lower rate as well as a nitroolefin product, which arises from a completely different mechanistic pathway. Finally, amines surrounded by a silanol-rich environment produce predominantly the nitroolefin product. This example clearly demonstrates how control of microenvironment surrounding a catalyst active site can significantly impact catalyst selectivity and activity for nitroaldol catalysis. These concepts can be extended to the many other reactions involved in liquid-phase processing for biofuel synthesis.

3.6.6 Overcoming Catalyst Stability Problems

When working with biomass feedstocks, catalyst stability (deactivation) issues are substantial. Chemistry that works well with pristine systems (such as purified glucose) fails when using actual biomass feeds because of the rich mixture of various impurities present. Impurities include inorganic salts and other products in ash; protein components rich in sulfur; phosphorus containing impurities; and other unknowns. Some impurities act as inhibitors; when the purity is removed catalyst performance returns. Other impurities permanently damaged the catalyst. One challenge faced by researchers is that impurities have a different effect on a catalyst to catalyst basis. However, some impurities cause problems in a more general or universal way. Engineering approaches to solve this problem can include new separation techniques to process crude biomass. Selective adsorption of substrates and products (particularly on carbon supports which have a strong affinity for organics) is another issue that should be addressed.

Catalyst systems that have been developed for petroleum and petrochemical refining in general are unstable under aqueous conditions. The most common supports used in petroleum-based catalytic processes are based on metal oxides of alumina, silica and alumina silicates. These supports are unstable under hydrothermal conditions. The issue is compounded when reactions are run under high or low pH. For these reasons catalyst supports for processes run under hydrothermal conditions commonly consist of carbon, monoclinic zirconia, rutile titania, and to a lesser extent on niobia, tin oxide, and barium sulfate.

One of the challenges is avoiding leaching of active sites. New techniques are necessary for permanently anchcoring active sites so that they can be used without leaching in a continuous process. One of the promising approaches that can be used for this purpose is based on the concept of using hydrophobic calixarenes as scaffolds for active sites, because these molecules are not soluble in water. Attaching promoters to anchored calixarenes is a promising way therefore to permanently anchor promoters to the surface. These anchored sites could either be used in and of themselves to enhance the activity and selectivity of a reaction, or they could be used within the context of an outer sphere surrounding an active site. Another challenge related to leaching has to do with loss of inorganic active sites, such as those involved in aldol condensation for biofuel synthesis when using MgO/OH materials, in water. Choice of support and changing the composition of the support may be important here. For example, emerging methods of "hydrophobizing" the surface may prevent water from interacting with these sites and can be used to reduce their leaching.

A key issue in the use of heterogeneous catalysts for liquid-phase processing is that the catalysts can be recycled for re-use in batch-reactor applications or that can be regenerated readily for flow-reactor processes. In this respect an important part of the overall process will be pretreatment of biomass to remove poisons and deactivators, and this removal will require the development of new materials and processes for effective separations.

3.7 RECOMMENDATIONS

IN SUMMARY, the following issues appear to be of critical importance for the successful application of liquid-phase catalytic processing of biomass-derived compounds:

- Achieving selective transformations with good carbon balances
- Achieving good energy balances (e.g., minimizing energy-intensive distillation steps)
- Controlling pathways for oxygen management (decarbonylation versus hydrogenation)
- Controlling hydrogen management (hydrogen production and captive use)
- Controlling carbon and coke management
- Addressing lignin utilization (heat production versus chemical production, such as aromatics and cyclohexanes)
- Utilizing solvent effects to achieve desired catalyst performance, especially in multiphasic reactors
- Developing effective methods for feedstock conditioning
- Developing catalysts that are tolerant to biomass impurities (inorganics and ash, protein-sulfur, phosphorus)

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4. Catalytic Conversion of Syngas

4.0 CATALYTIC CONVERSION OF SYNGAS

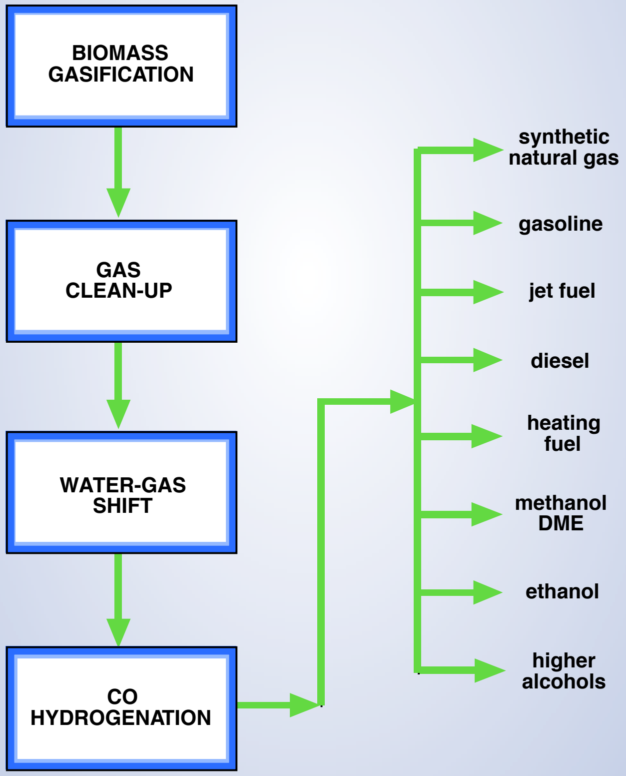
OVERVIEW: Biomass gasification is a flexible, energy efficient, and "green" way to produce low-to-medium energy fuel gases, synthesis gas, and hydrogen for fuel cell applications. Syngas, produced by gasification, can be converted to electric power, hydrogen, steam and/or a wide variety of fuels/chemicals depending on location requirements. This thrust area focuses on the cleanup and conversion of syngas derived from lignocellulosic biomass. The actual gasification process, while not the focus of this thrust area, is addressed to a small degree to provide context for discussions of subsequent syngas conversion. Clean up of the gases exiting the gasifier and water-gas-shift reactions are considered heavily. A major focal point of this thrust is on the conversion of CO and H_2 to fuels (and accompanying chemicals).

4.1 INTRODUCTION

Currently, the best defined and technically proven route for producing alternative fuels from lignocellulosic biomass involves gasification/reforming of biomass to produce syngas ($CO + H_2$), followed by syngas cleaning, Fischer-Tropsch synthesis (FTS) or alcohol synthesis, and some product upgrading via hydro-processing. This section of the report focuses on cleanup and conversion of the syngas produced through the gasification of lignocellulosic biomass. The actual gasification process will be considered only insofar as necessary to provide context for the subsequent cleanup and conversion reactions. In particular, clean-up of the raw syngas exiting the gasifier (consisting primarily of H_2, CO, CO_2, and H_2O with significant amounts of tars, ammonia, and H_2S as impurities) and water-gas-shift will be considered. A major focus of this section will be on CO hydrogenation to fuels and accompanying organic chemicals, which provide the source material for a broad range of synthetic products (e.g. vinyl, polyester, rubber, and plastic).

FTS reactions that produce paraffinic hydrocarbons primarily are a subset of potential CO hydrogenation reactions. CO hydrogenation reactions can also produce synthetic natural gas and alcohols, as shown in Figure 4.1, as well as olefins and other compounds (not shown). Synthetic diesel and jet fuels produced using FTS are sulfur-free and have been shown to work well in conventional engines with essentially no design modifications. On the other hand, ethanol and

Figure 4.1 A typical process based on syngas conversion would consist of a biomass gasifier, a biomass gas clean-up unit, a water-gas-shift reactor in certain cases, and finally a reactor for syngas conversion (i.e., CO hydrogenation).



higher alcohols generated from biomass by alcohol synthesis, are better suited for gasoline blending

The required H_2/CO ratio is different for each of the target products named in Fig. 4.1 (e.g., about 1.0 for Fe-catalyzed FTS, and 2.0 for Co-catalyzed FTS and methanol synthesis). The actual H_2/CO ratio of the clean syngas produced using different feedstocks and processes can vary significantly. For example, the ration can be 0.7 to 1.5 with coal or biomass based processes and > 3 with natural gas, The following techniques can be used to modify the H_2/CO ratio up or down as necessary. In the case of syngas with a low H_2/CO ratio, the ratio can be adjusted up by combining the syngas from the gasification unit with a methane reformer having a high H_2/CO ratio or alternatively by employing a water-gas-shift (WGS) reactor. When the H_2/CO ratio is higher than required, it is usually lowered by passing the syngas through a H_2-selective membrane unit. Physical separation using a membrane or simple blending is usually more economical and impurity-tolerant than a catalytic WGS step.

4.2 OVERALL PROCESS DESCRIPTION

4.2.1 Gasification of Biomass

The gasification technology involves high temperature (600-900°C) partial combustion of biomass in the presence of a gasification medium (e.g., oxygen, air, steam) in a gasifier. Fluidized-bed biomass gasifiers are best suited for large-scale operations and, for this reason, they are the gasifiers of choice. Biomass gas from a gasifier consists of syngas containing mostly H_2, CO, CO_2, and H_2O but with important amounts of tars, ammonia, H_2S, and particulates as impurities [Torres et al., 2007]. These impurities are the primary barrier to direct use of gasification gas for producing fuels, chemicals, or electricity. They must be removed before the syngas can be used in an engine, turbine or fuel cell for producing power, or in a catalytic reactor for producing liquid fuels and chemicals. In addition to these contaminants, the gas may contain trace quantities of HCN, halogens (e.g., HCl), alkali metals, and other metals (Hg, As, Pb). Tars, in particular, can coat surfaces downstream and gum up power producing devices [Reed et al., 1999].

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4.2.2 Biomass Gas Clean-up

Syngas must be cleaned up prior to CO hydrogenation since H_2S can poison metal catalysts, tars can cause fouling of such catalysts, and ammonia can block catalyst sites as a result of

BIOMASS GASIFICATION

Biomass gasification is a complex thermochemical process that consists of a number of elementary chemical reactions, beginning with the partial oxidation of a lignocellulosic fuel with a gasifying agent, usually air, oxygen, or steam. Volatile matter, which is released as the biomass fuel is heated, partially oxidizes to yield the combustion products H_2O and CO_2, plus heat to continue the endothermic gasification process. Water vaporizes and biomass pyrolysis continues as the fuel is heated. Thermal decomposition and partial oxidation of the pyrolysis vapors occur at higher temperatures, and yield a product gas composed of CO, CO_2, H_2O, H_2, CH_4, other gaseous hydrocarbons (including oxygenated hydrocarbons from some processes), tars, char, inorganic constituents, and ash. A generalized reaction describing biomass gasification is as follows:

(1) biomass + O_2 (or H_2O)
$\rightarrow$ CO, CO_2, H_2O, H_2, CH_4 + other hydrocarbons
$\rightarrow$ tar + char + ash
$\rightarrow$ HCN + NH_3 + HCl+ H_2S + other sulfur gases

The actual composition of the biomass gasification product depends heavily on the gasification process, the gasifying agent, and the feedstock properties [Beenackers and van Swaaij, 1984; Hos and Groeneveld, 1987]. Various gasification technologies have been under investigation for their potential to convert biomass into a gaseous fuel. These include gasifiers where the biomass is introduced at the top of the reactor and the gasifying medium is either directed co-currently down (downdraft) or counter-currently up (updraft) through the packed bed. Other gasifier designs incorporate circulating or bubbling fluidized beds. Tar yields can range from 0.1% (downdraft) to 20% (updraft) or greater (pyrolysis) in the product gases. The energy content of the gasification product gas ranges from 5 MJ/Nm^3 to 15 MJ/Nm^3 and is considered a low to medium energy content gas compared to natural gas (35 MJ/Nm^3). If air is used as the gasifying agent, then roughly half of the product gas is N_2 [de Bari, et al. 2000]. The relative amount of CO, CO_2, H_2O, H_2, and hydrocarbons depends on the stoichiometry of the gasification process. The air/fuel ratio in a gasification process generally ranges from 0.2-0.35 and if steam is the gasifying agent, the steam/biomass ratio is around 1. The actual amount of CO, CO_2, H_2O, H_2, tars, and hydrocarbons depends on the partial oxidation of the volatile products, as shown in equation (2).

(2) $C_nH_m + (n/2+m/4)\ O_2 \rightarrow nCO + (m/2)\ H_2O$

The char yield in a gasification process can be optimized to maximize carbon conversion or the char can be thermally oxidized to provide heat for the process. Char is partially oxidized or gasified according to the following reactions:

(3) $C + 1/2O_2 \rightarrow CO$

(4) $C + H_2O \rightarrow CO + H_2$

(5) $C + CO_2 \rightarrow 2CO$ (Boudouard reaction)

The gasification product gas composition, particularly the H_2/CO ratio, can be further adjusted by reforming and shift chemistry. Additional hydrogen is formed when CO reacts with excess water vapor according to the water-gas shift reaction

(6) $CO + H_2O \rightarrow CO_2 + H_2$

Reforming the light hydrocarbons and tars formed during biomass gasification also produces hydrogen.

Steam reforming and so-called dry or CO_2 reforming occur according to the following reactions and are usually promoted by the use of catalysts.

(7) $C_nH_m + nH_2O \rightarrow n\,CO + (n+m/2)\,H_2$

(8) $C_nH_m + nCO_2 \rightarrow (2n)\,CO + (m/2)\,H_2$

Catalytic steam reforming of hydrocarbons has been extensively studied, especially in the context of methane reforming to make syngas ($H_2/CO = 2:1$) for methanol and Fisher-Tropsch liquid synthesis. The basic mechanism of steam reforming is the dehydrogenation of a hydrocarbon fuel and the associated carbon deposition on the active sites of a catalyst. Gasification of the carbon deposits via reactions (3)-(5) yields additional CO and maintains the catalyst activity. Similar catalysts have been applied to biomass gasifier tar reforming with varied success. Catalytic conversion of unwanted hydrocarbons is applied for both product gas purification and to adjust the composition of the product gases for a particular end use. Tar reforming also maintains the chemical energy content of the product gases because, instead of being physically removed, tars are converted to H_2 and CO.

competitive adsorption. The target level of cleanup depends on the contaminant tolerance of the downstream conversion catalyst. The first approach to minimize the impurities listed above is to optimize properties of the biomass gasifier and its operating conditions (primary treatment). The second approach is to remove these impurities in a downstream cleaning system based on physical (scrubbers, filters) or catalytic strategies (secondary treatment). This secondary treatment is also known as hot gas clean-up of biomass gasification gas.

4.2.3 Water-Gas-Shift

The H_2/CO ratio from a typical biomass gasifier is below 1. Therefore, a separate water-gas-shift reactor may be required to bring the ratio in line with the necessary stoichiometry for production of alcohols or of hydrocarbons using a cobalt catalyst. However, since iron FTS catalysts simultaneously catalyze both WGS and FTS reactions, a separate WGS reactor is in that case unnecessary.

4.2.4 Syngas Conversion

The syngas is converted to liquid fuels via CO hydrogenation. The type of liquid fuel produced depends on the type of catalyst used and reaction conditions.

4.3 RESULTING FUELS

A wide variety of fuels can be produced from syngas, including gasoline, diesel fuel, heating fuel, jet fuel, synthetic natural gas, methanol, di-methyl ether, ethanol, and higher alcohols. With the exception of methanol, di-methyl ether and synthetic natural gas (primarily methane), it is impossible to make any of the other fuels with 100 percent selectivity. Instead, it is best to plan further processing for the range of fuels and chemicals that result from syngas conversion. In this biorefinery model the products of biomass gasification are “cleaned up” in a manner that is analogous to petroleum upgrading. A range of products are formed via gasification and subsequent catalytic upgrading, although the range is typically less broad than the product slate resulting from petroleum refining. Some products may require multiple processing steps. For example, if diesel fuel is preferred, the typical approach is to make long carbon chain paraffins (C_1-C_{100}) and then to use cracking or hydrocracking, as in oil refining, to maximize the production of hydrocarbons in the diesel fuel range.

Biofuels produced by conversion of biomass-based synthesis gas, commonly referred to as biomass-to-liquids (BTL), are similar to the fuels produced from petroleum and very similar to those produced by coal-to-liquids (CTL) or gas-to-liquids (GTL). Using any of these four routes, it is possible to produce gasoline, diesel, and jet fuels. However, diesel fuel is more readily produced by low-temperature BTL, CTL, and GTL. Moreover, this synthetic diesel is superior to petroleum-based diesel since it contains essentially no sulfur, is cleaner burning, and consists largely of linear paraffins. It is important to be clear that diesel produced by BTL processes is not the same as so-called “biodiesel”, which is made from plant oils or animal fats and consisting of methyl or ethyl esters of free fatty acids.

From a more comprehensive process-system perspective, it is also feasible to combine BTL, CTL, or GTL with electric power production using various combinations of low-temperature (LT) and high-temperature (HT) FTS reactors, and different separation and recycle streams to optimize thermal and carbon efficiencies and process economics for a desired product slate [Dry and Steynberg, 2004; Bartholomew and Farauto, 2006].

4.4 SUMMARY OF PREVIOUS RESEARCH

4.4.1 Biomass Gas Clean-Up

Syngas from a biomass gasifier typically contains 10,000-15,000 ppm of tars, 2000-4000 ppm of ammonia, and 100-500 ppm of H_2S (Torres et al., 2007). Tars are a complex mixture of condensable hydrocarbons, but a unique definition is lacking (Biomass Technology World, 2004). Some definitions include "the mixture of chemical compounds which condense on metal surfaces at room temperature" and "the sum of components with boiling points higher than 150°C." One of the better definitions is “organic contaminants with a molecular weight greater than that of benzene” [Abatzoglou et al., 2000].

The number of compounds in tar can range from hundreds at high temperature to thousands at low temperature. The total amount of tar leaving with the syngas is a function of fuel type and gasification conditions. Increasing the air-to-fuel ratio, bed temperature, and freeboard temperature in a fluidized bed gasifier reduces the tar amount [Narvaez et al, 1996; Gil et al., 1999]. Also, the addition of dolomite to the bed reduces the amount of tar made. However, tar cannot be reduced below 1 g/m^3 by varying these parameters. Increasing the bed temperature to >900^{o}C is not a good option, especially for biomass containing alkali metals as they can promote slagging and result in increased alkali vapor in the gas. Also, increasing the temperature requires more O_2, resulting in more fuel loss as CO_2.

Substantial research has been conducted on the removal of tars and ammonia from biomass gas at temperatures greater than 500°C. Cleaning systems based on condensation alone or systems combining hot-gas cleanup with downstream condensation have been researched in the past. The removal of tars and ammonia from biomass gasifier gas is typically approached in one of several ways. One way is by choosing operating conditions that minimize tar and ammonia formation. This helps but has never been able to reduce the production of those compounds to tolerable levels.

The second way of removing tars is to add dolomite to the gasifier to reduce the production of tars. Gil et al. [1999] found that use of dolomite in the gasifier reduced tar from 20 to ca. 2 g/Nm^3 at 800-820^{o}C. They hypothesize that dolomite acts as a base catalyst and catalyzes steam reforming of the tars. However, use of dolomite in the gasifier to reduce tars has been reported to increase the formation of ammonia [Berg et al., 2001]. Also, because of poor attrition resistance, the dolomite can lead to production of dust entrained in the syngas. In addition, although the concentration of tars is significantly decreased (down to 1-8 g/Nm^3 depending on gasifier operating conditions), it is still too high.

The third way of removing tars is by placing reactors after the gasifier for cracking or steam reforming of the tars. Steam reforming of hydrocarbons to produce CO + H_2 (i.e. syngas) is highly endothermic [Kochloefl, 1997]. Materials that can effectively crack tars include nickel-based catalysts, limestone and dolomite. However, these materials require very high temperatures, on the order of 871-899°C (1600-1650°F), that are typically not available at the gasifier exit. Long-term durability of these materials is also not confirmed. Attempts at scrubbing (cold cleaning) the tar without a cracking step have largely met with failure because of the tendency of tar to form an aerosol. Catalysts studied for tar removal include acidic catalysts (e.g., zeolites, silica-alumina, sulfated metal oxides), iron catalysts, and supported Ni catalysts. The Battelle/FERCO gasification process [Paisley et al., 2001] that produces up to 16,000 mg/Nm3 of tar in the gas makes use of a cracking catalyst (DN-34).

Dolomites ($CaMg(CO_3)_2$) are the most extensively researched basic catalysts for the purpose of tar removal mainly because of their low cost. Use of dolomite in a reactor after the gasifier results in a decrease in the concentration of tars in the effluent stream. CaO appears to also catalyze steam reforming of higher hydrocarbons [Simell, 1997]. However, steam reforming of tars is normally accomplished using a Ni reforming catalyst in 1-2 reactors after the gasifier [Caballero et al., 2000; Hepola and Simell, 1997; Aznar et al., 1998]. Ni is supported on thermo-resistant Si-free supports such as α-alumina, MgAl spinel, or ZrO2. Ni catalysts for steam reforming may contain promoters of Fe, Mn, K, or Ba. Caballero et al. [2000] were able to get the tar content down to as low as 2 mg/Nm^3 using dolomite in the gasifier and 2 reactors containing Ni catalysts at 900°C to clean up the gas. Tar contents as low as 10 mg/Nm3 were obtained without noticeable deactivation of the Ni catalyst over a 50-hour run. Nickel catalysts, however, can be poisoned by sulfur in the syngas (requiring the level of sulfur be kept below 10 ppm) or by carbon deposition.

The main problem in catalytic tar removal is coke accumulation resulting in catalyst deactivation and sulfur poisoning of catalysts due to H_2S present in the stream. Currently, there are no cleaning systems that have demonstrated consistent cleanup (in particular, tar removal) on a long-term basis from an updraft fluidized-bed biomass gasifier at its practical exit temperature, which is less than 800°C (1472°F).

Ammonia and hydrogen cyanide formation in biomass gasification increases in proportion to the amount of fuel-bound nitrogen. [Zhou and

Masutaui, 2000; Leppälahti and Koljonen, 1995]. Using pressurized fluidized-bed gasification, de Jong et al. [2003] found fuel-nitrogen conversion to ammonia to be >50% for a gasifier operated at 1 to 7 atm and a maximum temperature of 900°C. Again as mentioned above, such temperatures are not practical for biomass gasification. The effect of temperature on NH_3 formation is complicated. Zhou et al. [2000] reported a significant decrease in NH_3 formation with increasing temperature. Leppälahti et al. [1995] reported an increase in NH_3 formation with temperature until most of the volatile matter was released, followed by a decrease with increasing freeboard temperature. A pressurized top-fed fluidized-bed reactor appeared to convert a lower amount of fuel-nitrogen content to NH_3 than did bottom fed reactors [Chen, 1998]. This appears to be due to differences in the environment in which the initial flash pyrolysis takes place.

The preferred methods for ammonia removal is to decompose it to N_2 and H_2. The traditional catalysts for ammonia decomposition include supported Ru, Ni, Fe catalysts. Carbides and nitrides of W, V, and Mo can also be used for this purpose. Calcined dolomites and supported Ni catalysts are efficient in both NH_3 and tar removal. Also, if not removed, it is expected that more than 50% of the ammonia will be converted to NO_x in an engine or turbine.

There are a wide variety of metals and metal oxides/carbides/nitrides that can catalyze the decomposition of ammonia. These include Group Ib (Cu, Ag), Group IIb (Zn), Group IIIa (La, Ce), Group IIIb (Al, Ca), Group IVa (Ti, Zr), Group IVb (Ge, Sn), Group Va (V, Nb), Group VIa (Cr, Mo, W), Group VIIa (Mn, Re), and all of Group VIII (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) [Bera and Hegde, 2002; Cholach et al., 1981; Grosman and Loeffler, 1983; Nakatsuji et al., 1996; Papapolymerou and Bontozoglou, 1997; Sheu et al., 1997; Sugishima and Mitsuharu, 1995]. Although the Group VIII metals tend to be more active than many other elements, carbides and nitrides of Groups Va and VIa can be especially active for ammonia decomposition. For example, Mo_2C is about twice as active as the vanadium carbides that are 2-3 times more active than Pt/C [Choi et al., 1997]. Vanadium nitrides were found to be comparable or superior catalytically to Ni supported on silica-alumina [Choi et al., 1997]. LaNi alloys are also very active due to the formation of a nitride phase [Dinkov and Lazarov, 1993]. CaO [Chambers at al., 1996], MgO [Kagami et al., 1984], and dolomite (CaO-MgO) are all active. MgO will decompose ammonia to N_2 and H_2 at temperatures as low as 300°C. Group VIII metals seem to be active mainly in the metallic state [Friedlander et al., 1977]. Even though reaction is noted for oxides of Group VIII metals in gases containing H_2 or CO, this is likely only due after reduction of the metal surface. Activity for ammonia decomposition on smooth metal surfaces has been reported to fall in the following order: Co > Ni > Cu > Zr [Artyukh et al., 1963].

Gas phase composition can significantly impact catalyst activity. For example, CaO is deactivated almost totally when CO, CO_2, and H_2 are present [Kong et al., 2001; Chambers, et al., 1996] – probably due to the reaction of CO_2 with the CaO. Ni on the other hand, does not seem to be affected by the presence of such gases [Hepola and Simell, 1997]. Small quantities (< 2000 ppm) of H_2S, were not found to lead to severe poisoning of calcined dolomite, CaO or, surprisingly, Fe for decomposition of 2000 ppm quantities of ammonia [Kong et al., 2001; Hepola and Simell, 1996]. Not surprisingly, since ammonia synthesis has been found to be highly structure sensitive, the ammonia decomposition activity of Fe has also been found to be highly dependent on particle size (20-50 nm)

[Ohtsuka et al., 2004]. NH_3 decomposition catalysts in the presence of syngas with and without H_2S have been extensively evaluated in the past [Gangwal et al., 1992; Gangwal et al., 1997; Jothimurugesan and Gangwal, 1998]. When H_2S is less than 10 ppmv, commercial reforming catalysts work reasonably well, even at 650°C, for NH_3 decomposition.

The sulfur content of biomass is typically very low compared to fossil fuels. Biomass gasification results in approximately 20 to 600 ppmv H_2S + COS in the syngas. However, even this low sulfur content is too high because it can rapidly deactivate downstream catalysts, typically nickel-based, used for tar removal [Hepola and Simell, 1997] and ammonia decomposition [Krishnan et al., 1988]. Deactivation may be overcome by the use of very high temperatures (≤ 900°C) for the nickel-based hot-gas cleanup reactor. But such high temperatures create material-of-construction issues and also result in accelerated deactivation of the catalyst due to sintering. Also, as mentioned above, such high temperatures are not practical in syngas leaving fluidized-bed biomass gasifiers. Removal of sulfur to very low levels is also necessary if the goal is to use the syngas in a fuel/chemical synthesis reactor or a fuel cell.

Sulfur can be removed down to low levels using an amine scrubbing process or chilled methanol (Rectisol Process). These are expensive, equipment intensive, low temperature processes. A more attractive option would be to use a high temperature regenerable sorbent or solid reactant. One such material is a zinc oxide-based sorbent [Gangwal et al., 2002] that functions as follows:

$$ZnO + H_2S \rightarrow ZnS + H_2O \text{ (sulfidation)}$$

$$ZnS + 3/_2\, O_2 \rightarrow ZnO + SO_2 \text{ (regeneration)}$$

Zinc ferrites and zinc titanates are also effective as H_2S removal sorbents.

Although hot gas clean-up has been studied for many years, a recent review paper [Torres et al., 2007] and references cited therein indicate that considerable additional R&D will be necessary before full commercialization of biomass gas clean-up.

■ 4.4.2 Water-Gas-Shift

The water-gas-shift (WGS) is a well-known and highly practiced commercial process. This reaction can be written as:

$$CO + H_2O = CO_2 + H_2$$

Commercial catalysts are available for low, medium and high temperature ranges - Cu/Zn based catalysts at 225 to 250°C, Co-Mo catalysts at 350 to 375°C, and Fe-Cr catalysts at 450-475°C. The Cu-Zn catalyst is easily poisoned by syngas contaminants, especially sulfur; thus, removal of H_2S in syngas down to less than 60 ppb is required. On the other hand the high temperature Fe-Cr catalyst is known to withstand sulfur at moderate levels of around 50-100 ppm. The Co-Mo catalyst, which is actually used in the sulfided form, can be used in sour gas at H_2S levels of several thousand ppm. In fact, it requires the presence of H_2S in syngas to maintain its sulfidation level. The choice of the water-gas-shift catalyst for a biomass-derived syngas would be site specific depending on the sulfur level in the biomass and the overall process design. In general, since the sulfur is typically low for woody biomass, a Fe-Cr catalyst may be a good option. Tars would perhaps remain vapor in this temperature range and may not affect the catalyst. It would be useful to evaluate the effect of tar on the Fe-Cr catalyst in order to determine what levels of tar it could tolerate.

CARBON CHAIN GROWTH IN FISCHER-TROPSCH SYNTHESIS

The distribution of hydrocarbon chain length in FTS is governed by a parameter called the Anderson-Schultz-Flory chain growth probability, α. This parameter is borrowed from a similar concept in polymerization chemistry. The synthesis of FTS products can be understood by looking at a simplified mechanism where * indicates a catalyst site, and $*CH_x$ represents an adsorbed reaction intermediate (in this case having a single carbon). The mechanism proceeds in a way such that intermediates are either terminated by hydrogenation (chain termination) to a product (represented here in the form of paraffins) or continue to grow as a carbon chain (i.e., polymer) (chain growth). The Anderson-Schultz-Flory chain growth probability is thus a number between 0-1 giving the probability that chain growth will occur rather than termination. This probability is affected by the active catalytic material, the presence of promoters, and the reaction conditions used. The product distributions for different values of this parameter are shown in Figure 4.2.

$$\begin{array}{ll}
CO + 2\,* \longrightarrow *C + *O & \\
*C + x*H \longrightarrow *CH_x + * & \\
*CH_x \xrightarrow{+*H} * + CH_4 & \text{Chain Termination} \\
\quad\downarrow + *CH_y & \text{Chain Growth} \\
*CH_x\text{-}CH_y \xrightarrow{+*H} * + C_2H_6 & \text{Chain Termination} \\
\quad\downarrow + *CH_y & \text{Chain Growth} \\
C_2H_{2x}\text{-}CH_y \xrightarrow{+*H} * + C_3H_8 & \text{Chain Termination}
\end{array}$$

■ 4.4.3 CO Hydrogenation

■ 4.4.3.1 Synthetic Natural Gas

Synthetic natural gas (SNG) production or methanation via CO hydrogenation using a nickel-based catalyst is commercially practiced in the U.S. (e.g. at the Great Plains Coal Gasification complex). Since the currently employed catalyst has sufficient activity to achieve operation at or near the diffusion limited rate, it would seem difficult to produce additional effective catalyst improvements, apart from a longer life for an already robust catalyst. However, since biomass gasification can already produce significant levels of methane, a further increase in methane production via modification of the gasification process (e.g. pyrolysis followed by catalytic gasification) may be a fruitful research area to pursue, depending on site-specific demand for natural gas.

■ 4.4.3.2 Gasoline

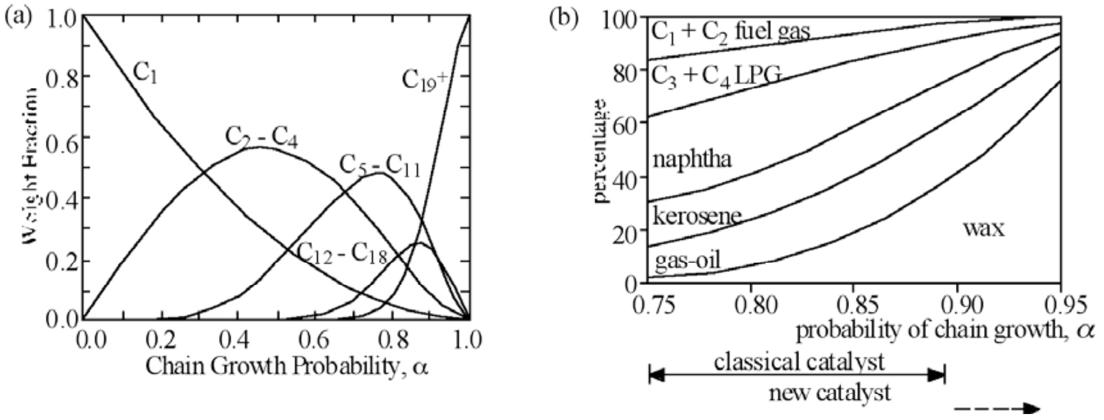
Sasol uses a HT FTS process with a fused-iron catalyst to produce gasoline range hydrocarbons in a bubbling fluidized-bed reactor. LT FTS (Co or Fe catalyst) generally produces a relatively small C_5-C_{12} fraction of mostly low octane n-paraffins; hence this approach by itself would not be efficient for producing gasoline. However, in a large FT complex using both LT and HT FTS, it is possible through a combination of several series/parallel reactions, wax cracking, and separation stages to achieve selectivities of 70–90% for gasoline or diesel products. Mobil developed a process for the conversion of methanol (produced from syngas) to gasoline. However, even though it produced an acceptable octane number, that process is no longer utilized because it made a gasoline with a high aromatic content, which is no longer permitted.

4.4.3.4 Diesel Fuel

FTS is the most effective catalytic process for converting syngas (H_2 + CO) into a variety of hydrocarbons including diesel fuel. FTS results in a wide product slate ranging from C_1 to C_{60}+ hydrocarbons via polymerization reactions ($CO + 2H_2 \rightarrow -CH_2- + H_2O$) (see Figure 4-2). The so-called low temperature FTS process operating in the 200-250°C temperature range is used for jet fuel and diesel production. To produce gasoline range hydrocarbons the high temperature (300-350°C) FTS process is used. The wax (C_{20}+) produced in the low temperature FTS process can be subjected to mild hydrocracking in a separate reactor to further increase the desirable jet fuel and diesel fraction.

Catalysts based on cobalt and iron find wide application in FTS because of their high activities and selectivities for production of higher hydrocarbons (C_5+) and relatively low selectivities for gaseous hydrocarbons (C_1-C_4). Co catalysts are generally 5-10 times more active than iron catalysts for comparable conditions. Moreover, carbon selectivities to C_5+ of Co catalysts are also generally higher relative to Fe catalysts, since Co produces very little or no CO_2. The hydrocarbon chain growth in FTS is largely dictated by the Anderson-Schulz-Flory (ASF) distribution parameter, α, typically ranging from 0.75 to 0.95 and affected by both the catalyst and reaction conditions. A catalyst with α of 0.9 or higher is

Figure 4.2 (a) Weight fraction of hydrocarbon products as a function of chain growth (propagation) probability during FTS. (b) Percentage of different hydrocarbon product cuts as a function of chain growth (propagation) probability showing a range of operation for classical and developing Fischer-Tropsch catalysts and synthesis [Bartholomew and Farrauto, 2006].



preferred as it produces less gaseous hydrocarbons (see Fig. 2b). Fe, due to its low cost and high water-gas-shift (WGS) activity, is the preferred catalyst for unshifted low H_2/CO ratio (typically 0.6 to 1) syngas produced by gasifying coal or biomass. The WGS reaction provides intrinsic hydrogen to overcome the hydrogen deficiency of the syngas from these feedstocks. Co, on the other hand, has low WGS activity and is usually the preferred catalyst for a high H_2/CO ratio syngas (typically 2.0 to 2.2) produced by reforming natural gas or shifting low H_2/CO ratio syngas. However, the choice between Fe and Co catalysts is not totally clear-cut for a high H_2/CO ratio syngas at low FTS conversion conditions.

Reaction mechanisms, kinetics, and design of Co and Fe FT catalysts have been vigorously investigated since1925. Results from representative previous studies of FT mechanisms, reaction kinetics, catalyst preparation, characterization, testing, and design are summarized by Bartholomew and Farrauto [2006].

Since FTS reactions are highly exothermic, heat removal and reactor temperature control are crucial to control product selectivity and prevent thermal degradation of the catalyst. Several reactor types have been developed, including tubular fixed-bed (TFBR), fluidized bed, and slurry bubble column (SBCR) reactors; details of the performance characteristics of these reactors are summarized elsewhere [Bartholomew and Farrauto, 2006]. Each reactor type has its own set of advantages and disadvantages. For example, SBCRs are said to have the following advantages over TFBRs [Jager, 1997]: (i) simpler, cheaper construction; (ii) lower pressure drop; (iii) higher production rate for the same reactor dimensions; (iv) ease of heat removal; (v) lower catalyst consumption (20–30% of the TFBR); (vi) reduced maintenance cost; (vii) on-line replacement of catalyst; and (viii) substantially lower capital cost. For example, Jager [1997] indicated that the cost of a single 10,000 bbl/day SBCR reactor train is 25% of that of an equivalent TFBR system with six reactors! Nevertheless, Shell workers have reported substantially improved performance for their TFBR achieving productivities 2–3 times higher than for their existing commercial plant in Bintulu, Malaysia [Geerlings et al., 1999; Hoek and Kersten, 2004]. This is probably possible through operation at higher pressure (i.e., 40 bar instead of 30 bar) favoring higher heat transfer rates and use of smaller catalyst tubes for which heat transfer coefficients are higher. In fact, Hoek and Kersten [2004] report that the performance of their improved TFBR rivals that of a large SBCR; i.e., both reactors have a production capacity of 19,000 bbl, but the TFBR is smaller (8 m diameter x 21 m height relative to 8–10 m diameter x 40 m height) and has higher C_5+ selectivity, lower CO_2 production, and lower catalyst consumption. Moreover, the 5-year life of the Shell catalysts, combined with the requirement of only one in situ regeneration annually, sets a high standard for catalyst longevity.

Refinery processes can be used for upgrading FTS liquid and wax products, such as oligomerization, catalytic reforming, hydrotreating, and mild hydro¬cracking/hydroisomerization but the combination of these processes needs to be optimized to produce optimum yield of diesel and jet fuel. Jet fuel and diesel produced from FTS are of high quality due to their low aromatic (diesel) and zero sulfur content (both diesel and jet fuel), although, as mentioned above, some aromatics are needed in jet fuel to give it the desired properties.

While much is known regarding FTS catalyst design and performance, there are nevertheless significant improvements that could be made through a more detailed understanding of the nanoscale structure of the catalysts, reaction mechanism and kinetics.

4.4.3.4 Jet Fuel

Aviation turbine fuels (ATF) (i.e., jet fuels) are a complex mixture of C_8 to C_{17} organic compounds and are presently derived from the kerosene fraction of petroleum (crude oil) distillation as well as hydroprocessing of heavier fractions. Petroleum-based ATF (kerosene) represents the optimum fuel for aviation given its high energy density, good combustion characteristics, low cost, excellent thermal and oxidative stabilities, safety characteristics, and fluidity. Of particular importance, given the very low temperatures experienced at high altitude is its fluidity as measured by freeze point (-40 to -47°C).

The petroleum shortages of 1970s led to the search for domestic sources of liquid transportation fuels. Large US reserves of coal and oil shale and Canadian reserves of tar sands spurred the development of conversion processes to produce fuels from these non-petroleum sources. In the 1980s, programs were initiated to demonstrate the suitability of fuel derived from shale, coal and tar sands. Engine tests and flight demonstrations of shale-derived JP-4 indicated no deleterious effects. Jet fuels produced from syngas ($CO + H_2$) via Fischer-Tropsch technology were evaluated in the mid to late 1990s. A thorough study by Southwest Research Institute demonstrated that the properties of a 50/50 blend of petroleum-derived Jet A-1 and iso-paraffinic FT liquids fell well within the Jet A-1 specification range and should have no adverse impact on engine operation. Recent tests in 2005 of the shale-derived JP-4 and JP-8 fuels showed that the fuel still met specifications after 20 + years in storage.

Currently, the most promising route for producing alternative ATF or jet fuels involves gasification-/reforming of coal, natural gas, biomass or other hydrocarbon feedstock to produce a syngas ($CO + H_2$) followed by syngas cleaning, FTS, and FTS product upgrading via hydroprocessing. The synthetic ATF produced using this route is sulfur-free and has been shown to integrate well with present and future aircraft with essentially no modifications to engine design [Dittrick, 2007]. The synthesis of jet fuel is probably best done using a cobalt catalyst to make long chain paraffins followed by the use of hydrocracking to produce paraffins in the desired range. While the price point at which the FTS jet fuel becomes an economically viable alternative to petroleum-based jet fuel remains to be established, experts have indicated crude oil-price thresholds ranging from $38 to $50 per barrel. However, production costs in the United States must be determined, including the financing and amortization cost of the FTS plant (estimated to be in $billions).

One of the principal concerns for the FTS-derived ATF fraction is that it cannot by itself meet the freeze point specifications (-40 to -47 °C) of commercial ATF (Jet A) and military ATF (JP-8). Some aromatics and/or naphthenes need to be present in the FTS-derived ATF fraction in order to meet freeze point and other important specifications. Research is needed to explore possibilities for synthesizing ATF via FTS that meets all the specifications. Such an in-spec ATF might require secondary upgrading of FTS liquids.

4.4.3.5 Heating Fuel

The synthesis of long-chain paraffins using a cobalt catalyst followed by hydrockracking to produce paraffins in the desired range is most likely the best method for producing heating oil from biomass. See the previous section on diesel fuel. See the previous section on diesel fuel.

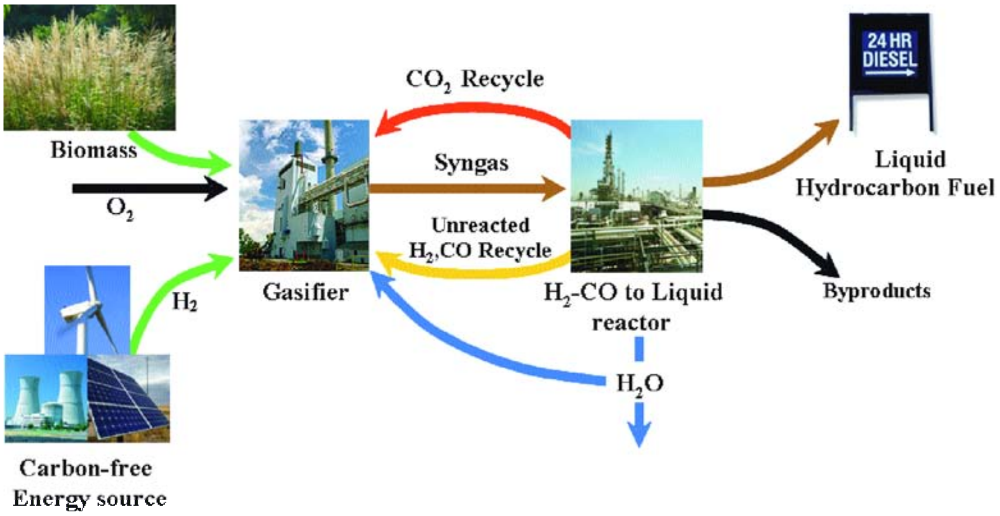
H_2CAR: SUSTAINABLE TRANSPORTATION FUELS FROM BIOMASS

Fuel molecules with the energy density and combustion characteristics of gasoline or diesel can be produced using carbon atoms derived from biomass combined with hydrogen atoms generated through carbon-free energy generation processes – such as wind, solar, or nuclear. Instead of looking to biomass as a source of potential energy and carbon atoms, this hydrogen-carbon (H_2CAR) process exploits only the presence of carbon in biomass, which reduces the amount of biomass needed to produce finished fuels. Even using photovoltaics power systems with 15% efficiency, the annualized average solar energy conversion efficiency for hydrogen generation is more than an order of magnitude greater than it is for biomass growth [Agrawal, et al. 2007].

A unique aspect of this hydrogen-carbon, or "H_2CAR", process, recently described by Agrawal, et al. [2007] and illustrated in Figure S-4.1, is that the biomass gasifier is not only co-fed with the supplemental H_2, but also with CO_2 recycled from the gas-to-liquid conversion reactor. The great benefit of this approach is that CO_2, which is normally lost to the atmosphere as a greenhouse gas or sequestered in conventional approaches, is recycled back to the process. Thus, all the carbon fed to the system is converted into fuel product, minimizing the amount of biomass needed to produce a given amount of fuel and reducing greenhouse gas emissions. Furthermore, the added hydrogen accounts for more than half of the energy content of the liquid product. Thus, the carbon-free production of hydrogen contributes significantly to the overall efficiency of the H_2CAR process.

Through computational modeling, Agrawal, et al [2007] have identified several major advantages of this biomass to liquids process: (1) 40% less land is needed to grow the biomass for fuels produced by

Figure S-4.1 The H_2CAR Process



the H_2CAR process compared with other biofuels production processes that derive all the fuel energy from the biomass itself; (2) because of the decreased land area requirements, the H_2CAR process could potentially meet 100% of the demand for transportation fuels in the U.S. using the 1.37 billion dry tons of domestic biomass that can be substantially harvested, instead of the estimated 30% of total fuel demand that Perlack, et al [2005] calculated could be produced from this amount of biomass using other conversion processes; and (3) this fuel-production solution makes use of existing transportation fuel distribution infrastructure.

Long term implementation of the H_2CAR process will certainly be accompanied by improved methods for carbon-free hydrogen production , but even in advance of these improved methods, the comparatively higher efficiencies involved with producing hydrogen by solar power, instead of biomass-derived hydrogen, is a compelling benchmark for the efficiency advantage of this process. In light of the tremendous potential of this process, new strategies for staged implementation and further development of H_2CAR are urgently needed.

4.4.3.6 Methanol

Methanol synthesis from syngas using a Cu-Zn-based catalyst at about 50-80 atm and 225-250°C is a well-known and highly practiced commercial process [Bartholomew, 2006]. Using this catalyst, methanol can be produced from syngas with nearly 100 percent selectivity. The presence of a small amount of CO_2 (around 4 vol%) in the syngas has been found to increase methanol productivity. Mechanistically, the synthesis reaction is believed to proceed via CO_2 hydrogenation. Typical industrial productivities range between 1.3-1.5 g methanol/g catalyst/h at space velocities on the order of 10,000 scc/cc catalyst/h. Due to thermodynamic limitations, the per pass conversion is low and the unconverted syngas is recycled to increase the overall conversion. Previous work suggests qualitatively that pore diffusional resistance may be significant under commercial reaction conditions for pellet diameters larger than 1.5 mm and temperatures above 240°C.

While low-pressure methanol processes employ a variety of reactor types, all are of the gas-fluid, fixed-bed catalyst type [Bartholomew and Farrauto, 2006]. Reactors are differentiated primarily by the method used for removing heat generated by reaction. Methods include: (1) indirect cooling of catalyst-packed tubes with boiling water (e.g., Lurgi); (2) interstage injection of cold feed (ICI); or (3) cooling with heat exchangers between 3–4 stages of adiabatic reactors. Each of these methods enables the outlet temperature to be controlled to about 220–240°C. There are variations on each of these themes, each with its own set of advantages and limitations. The near isothermal operation of the tubular boiling-water reactor (TBWR) facilitates: (1) high thermal efficiency (defined as energy content of the products divided by the energy content of the reactants); (2) control of temperature; and (3) high conversion, yield, and selectivity with a minimum of byproducts. The temperature profile in the second half of the catalyst bed is close to the locus of maximum rates, thus minimizing the amount of catalyst needed. The low average operating temperature minimizes sintering, leading to the longest catalyst life (5 years) for any of the methanol processes. The choice of reactor for a specific plant depends greatly on plant size and the syngas production process. The TBWR is economically favored for smaller plants characteristic of BTL, while for large, world-class plants (> 2,500 TPD), the economics of series-adiabatic, spherical reactors are favored.

Like the low temperature WGS catalyst, the methanol synthesis catalyst is highly susceptible to poisons, particularly sulfur and arsine. Thus the syngas needs to be cleaned prior to the methanol synthesis reactor.

4.4.3.7 Dimethyl Ether (DME)

Dimethyl ether (DME) is a potential ultra-clean diesel fuel that offers excellent benefits as an alternative fuel in that it can be used at high efficiency and with low emissions, is readily stored and transported, provides high well-to-wheel efficiency and is safe and reliable. DME is easily made from methanol and can be used in a mixture with regular diesel. DME is a compound that has been targeted for future use as a fuel in several countries around the world [Phillips and Reader, 1998; Verbeek and Van der Weide, 1997; Wakai et al., 1999].

Efforts to increase the use of DME as a transportation fuel are motivated by several factors. There has been confirmation that the fuel yields low particulate emissions and possibly lower NOx emissions [Sorenson and Mikkelson, 1995; Fleisch et al., 1995]. Because of these environmental advantages, DME may provide a far more effective means of achieving the "Clean Diesel

Technology" mandated by the US EPA for cars and trucks by 2010.

4.4.3.8 Ethanol and Higher Alcohols

Catalytic synthesis of ethanol and higher alcohols from syngas has been under development since the beginning of the 20th century. Substantial research work has been carried out for developing processes to convert syngas to higher alcohols mainly for the purpose of synthesizing a mixture of methanol and isobutanol as precursors for methyl tertiary butyl ether (MTBE), previously used widely as an octane enhancer.

The recent debate surrounding the use of ethanol as a transportation fuel has been contentious. While there may be many opportunities, there are also many unknowns [Johnson, 2007]. Fermentation-derived ethanol from corn starch is a particularly controversial and politicized issue. On the other hand, gasification of cellulosic biomass from biomass waste and non-food crops followed by catalytic synthesis of ethanol has potential for providing an efficient and economically viable route to transportation fuels or fuel additives. Some consider the development of an effective ethanol synthesis catalyst to be the "Holy Grail."

Because MTBE use has recently been phased out and is being replaced by ethanol, the interest in the synthesis of ethanol from syngas is growing. Ethanol is currently considered as the "fuel of the future" because it can be produced domestically from biomass. Although it offers a lower chemical energy than gasoline, it produces much less pollution and has a higher octane number. It has been estimated that the use of a 10% blend of ethanol and gasoline as a fuel, known as E10 fuel that is commercially available in many of U.S. gas stations, can reduce automobile greenhouse gas emissions by 12-19%. Use of this fuel can also reduce CO emissions by 39% and particulate matter emission by 50%. Consequently, there is a growing worldwide interest in producing ethanol from biomass and using it as an alternative transportation fuel.

The conversion of syngas to ethanol via direct synthesis and methanol homologation pathways has been performed using a wide range of homogeneous and heterogeneous catalysts. Two types of catalysts currently hold promise for the direct synthesis of ethanol from syngas,: Rh-based catalysts and Cu-based catalysts. For Rh-based catalysts, there are reports in the literature of selectivities as high as 50% at higher pressure (Hu et al., 2007). However, most often this high selectivity is obtained at the expense of conversion (i.e., high selectivities are only seen at very low conversions). Depending on the type of catalyst used, both the direct synthesis and indirect

Figure 4.3 Volvo's 2nd Generation Heavy-Duty prototype DME vehicle, developed under the EU-sponsored "AFFORHD" (Alternative Fuel For Heavy-Duty) project in 2005.

synthesis via methanol homologation are accompanied by a host of side reactions leading to methane, C_2-C_5 alkanes and olefins, ketones, aldehydes, esters, and acetic acid. Methanation can be particularly significant via hydrogenation of CO. To increase ethanol selectivity, the catalyst and the reaction conditions need to be better designed to suppress methanation activity.

While not yet commercialized, a few higher alcohol synthesis (HAS) processes have advanced to the pilot scale stage, or conceptual processes based on patented catalysts have been designed.

A review of the literature on the conversion of syngas into ethanol and higher alcohols indicates that:

- Currently, higher selectivity may be achieved with homogeneous catalysts, but commercial processes based on these catalysts require extremely high operating pressures, complex catalyst recovery, and expensive catalysts, making their commercial application impractical.
- Rh-based heterogeneous catalysts preferentially produce ethanol over other alcohols. However, the limited availability of rhodium, high cost of Rh, and insufficient ethanol yield make these catalysts less attractive for commercial application, especially if high metal loadings are required.
- Modified methanol synthesis catalysts based on CuZn-, CuCo-, and Mo have been developed and demonstrated in pilot plant testing. The alcohol production rates of 0.1 to 0.6 g alcohol/g catalyst/h are significantly less than that achieved in methanol synthesis (1.3 to 1.5 g methanol/g catalyst/h). Thus, significant improvements, at least 2-3 fold, in alcohol production rate must be achieved.
- Direct synthesis of ethanol and higher alcohols from syngas is thermodynamically feasible, but kinetically restricted.

Reactor designs employed in the higher alcohol synthesis catalyst R&D have typically adapted standard fixed-bed reactor technology with specialized cooling designs used for methanol or FT synthesis of hydrocarbons. Improved product yield and selectivity could be achieved by performing the reactions in slurry reactors due to efficient heat removal and temperature control. However, for small-scale BTL plants, fixed-bed technology is likely to be more economically favorable and enjoy the same advantages of process intensification as FT and methanol syntheses.

4.5 ECONOMICS AND POTENTIAL OF TECHNOLOGY

The overall syngas conversion plant is capital intensive, consisting of a gasifier or reformer depending on the feedstock, syngas cleanup system, the syngas conversion reactor, product separation equipment, and possibly a hydrocracker for upgrading wax into desired products. The majority of the cost (60-70%) lies in the gasification of the biomass.

The economics of most syngas conversion processes are dominated by the initial plant investment. For example, the investment for a coal-to-liquids FTS plant is now approaching $100,000/daily bbl. Once the FTS plant is built, the operational costs are in the $10-25/bbl range. The issue is how to provide protection for the substantial initial investment in plant construction. Despite the technical feasibility and attractiveness of FTS and the abundant availability of indigenous coal and biomass resources, there is currently no commercial FTS plant operating in the US, although a number of plants are in the planning stages. Nevertheless, there is considerable potential for improving the economics of small plants suitable for BTL through process intensification and module production [Nehlsen et al., 2007]. and Through integration with power generation the economics of CTL plants can also be improved [Robinson and Tatterson, 2007]. It may be possible, for example, to reduce the size and cost of an FBR for FTS in a small BTL plant by a factor of 10, compared to conventional technology.

4.6 CURRENT TECHNOLOGY LIMITATIONS AND RESEARCH/DEVELOPMENT NEEDS

4.6.1 Biomass Conversion to Syngas

A major roadblock is the cost-effective production of synthesis gas from biomass. Since the quantity of biomass is not concentrated at a site as fossil fuels are, gasification must be done on a local level to eliminate the transportation costs of biomass. Due to the high cost of transporting raw biomass, conversion plants would probably service only an area of radius 50-75 miles and would produce liquid fuels equivalent only to 10,000-20,000 barrels/day of oil. Therefore, methods to reduce the cost of syngas generation on a small scale are desperately needed. If this can be accomplished, the next priority will be to either develop economical small-scale FTS plants or to develop a pipeline system to transport the syngas generated in the small plants.

In the present and projected environment of energy supply and demand, it is also reasonable to examine these premises in light of the nation's large and growing need for clean electrical power. Biomass is a low energy density feed stock that may vary with the seasons. There is a need to consider possible co-production of electricity and syngas, with the excess electric power generated exported to the grid while the syngas is converted to liquid fuels.

4.6.2 Biomass Syngas Clean-up

Due to the sensitivities of the equipment, processes, and catalysts downstream, biomass syngas clean-up is critical. The concentrations and nature of impurities in the syngas are feedstock dependent because of the variety of biomass available. Thus, different catalyst formulations may be required for biogas clean-up from different feedstocks.

Besides steam reforming, other ways of conversion of tars need to be researched. Cracking of hydrocarbons is a well-established technology using solid acid catalysts such as silica-alumina and zeolites. In fact, any catalyst with strong acid sites will crack hydrocarbons at temperatures above 100-200°C. Aromatics present during hydrocarbon cracking can lead to higher molecular weight hydrocarbons and coke [Gates et al., 1979].

Since tars are polycyclic aromatics or their precursors, cracking the tars would be expected to extensively deposit coke on the catalyst. The coke could be burned off the catalyst in an air regenerator, and the regenerated catalyst could be returned to the cracker.

An alternate technique for tar elimination is hydrogenolysis and/or ring opening of the polyaromatics. Unfortunately, hydrogenolysis and/or ring opening activity are thermodynamically limited, with conversion decreasing with increasing temperature. At a temperature even as low as 200°C, catalysts such as Rh, Pt, Ir, and Ru have been found to show little ring-opening activity for naphthalene [Jacquin, 2003].

Little is known about the reaction mechanisms and kinetics of different contaminants including H_2S, tars, and others on clean-up catalysts. More research in this area will be required to develop better catalysts and strategies for biogas clean up.

It is known that FTS requires that there be < 60 ppb of H_2S, arsine, HCL, HCN, NH_3, particulates, Se, Hg, alkali, and P. Thus, removal of all of these impurities needs to be addressed. Some impurities may greatly interfere with catalytic removal of other impurities. However, little is currently known about this issue.

4.6.3 Syngas Conversion to Liquid Fuels

The conversion of biomass derived syngas to liquid fuels represents a significant redirection direction for a field that for the past 20 years has concentrated on the conversion of stranded natural gas to liquids, typically in the context of a >60,000 bbl/day plant with assured long term gas supplies. The syngas in these plants has a H_2/CO ratio of about 2. Many of these plant concepts further assume a desired product of paraffinic FTS-based "syncrude" with just enough hydroisomerization treatment to facilitate transportation to a refinery rather than being a directly salable commercial fuel. Since these concepts were based on the idea of stranded gas, the export of electrical power was never considered an option.

Assuming that one can develop a small gasifier, the problem becomes one of defining the reactor type that will be optimum for the small-scale process. Several companies are currently developing microreactor technologies that could lead to a substantial reduction in capital cost for a small plant. However, reactor design and economic studies are not available in the public domain for these alternatives.

A partial list of research needs with regards to the reaction of syngas is provided below.

4.6.3.1 Fischer-Tropsch Synthesis

There are many issues associated with the FTS reactor system that result in poor economics and prevent the widespread commercialization of FTS. Important topics that require significantly more research are the following:

MECHANISMS AND THE ACTIVE CATALYTIC SITES

The exact mechanisms for syngas conversion to the various possible products is still not completely known, especially the synthesis of oxygenates. The structures required for sites to be active for hydrocarbon vs. ethanol synthesis are not known. Both are needed in order to understand and design better catalysts for selective synthesis. Development of active, selective, stable, and attrition-resistant catalyst formulations and a fundamental understanding of FTS reaction kinetics could lead to enhanced reaction yields, desirable product distribution, and improved reactor design and operation.

METHANE FORMATION

Methane is the least desired FTS product. There is a lack of understanding of the paths by which methane is formed during FTS and why the methane fraction of the hydrocarbon products increases as the catalyst ages.

LIMITATION OF CHAIN GROWTH

Deviations from the Anderson-Schulz-Flory (ASF) distribution for a single catalyst are most likely dominated by the operation of the reactor and not by the reaction mechanism. Thus, it is highly unlikely that limitation of chain growth can be achieved with a single catalyst. Bifunctional catalysis can do this, but to date no one has been able to achieve a reasonable catalyst lifetime for at least one of the functions to make it worthwhile. For example, Mobil abandoned the single reactor to adapt a two-reactor system, one for FTS and one for cracking. While there may be combined catalyst/reactor design strategies that enable varying product slates in FTS, very little has been done in this area.

CATALYST DEACTIVATION

Deactivation of FTS catalysts can be significant due to pore plugging by waxes, carbon deposition, partial oxidation, poisoning, and attrition. For example, cobalt catalysts deactivate significantly during the initial reaction period before reaching steady operation. Better understanding of such initial deactivation could lead to better catalyst design and less deactivation resulting in smaller reactors and less capital expenditures. Catalyst attrition can be a big issue in the use of fluidized bed reactors and of slurry phase reactors, which are excellent for heat management. Major problems are observed with catalyst attrition in and wax removal from the catalyst slurry. A currently operational FTS plant in Qatar is having problems with development of fines during wax separation even though they are using a cobalt-alumina catalyst. Relatively little is known about the basic mechanisms of catalyst attrition. For example, how do sudden pressure variations impact the disintegration of the catalyst particle? There is need to define the factors that determine the ease of wax removal from the slurry. Some research on catalyst deactivation has been done, but, in general, especially for FTS, this has not been the focus of many fundamental studies. (see Sidebar on next page).

■ 4.6.3.2 Higher Alcohol "Synthesis" (HAS)

There are other alternatives to liquid fuels besides FTS, such as the synthesis of C_2-C_4 alcohols. Ethanol can be used directly as a gasoline additive. Isobutanol can be de-hydrated and the resulting olefin dimerized yielding iso-octane, a valuable gasoline component. HAS catalysts can incorporate light olefins back into the synthesis process. It is clear that economics and feed stock availability will be essential in choosing the most fruitful route. Methanol synthesis has already reached a high level of commercial development, and federally funded research for methanol synthesis is not recommended. However, the yield of methanol in the commercial process could serve as a target to reach for HAS processes.

Catalytic synthesis of ethanol from syngas suffers from low yield and poor selectivity of the desired alcohol product due to the slow kinetics of the C_1-C_2 linear chain growth and fast chain growth to form C_2+ alcohols. R&D work to improve the ethanol yield and selectivity should focus on developing methodology for increasing the kinetics of the C_1-C_2 chain growth. Homogeneous catalysts are expensive and perhaps should not be considered based on cost and selectivity.

Among the heterogeneous catalysts, the high temperature ZnO/Cr_2O_3 catalyst that uses severe conditions (high temperature and very high pressure) is unattractive because of the following factors:

- Operating pressure is not compatible with the operating pressure envisioned for commercial and developmental biomass gasifiers.
- High operating temperature results in high selectivity for methane and isobutanol but not ethanol.

The low yield combined with high cost and limited availability of Rh makes it less attractive. However, Rh, though expensive, still offers the best possibilities for the design of a selective ethanol synthesis catalyst. Since it is used only in low loadings, if a Rh catalyst could be designed with both high ethanol selectivity and long lifetime, the economics would be acceptable.

CATALYST DEACTIVATION AND REGENERATION IN FISCHER-TROPSCH SYNTHESIS

Catalyst deactivation in Fischer-Tropsch Synthesis (FTS) is a serious, economic- and process-limiting problem [Dry, 2003; Bartholomew and Farrauto, 2006]. In processes using expensive Co catalysts, catalyst life must be extended to a minimum of 3-5 years through purposeful catalyst, reactor, and process design, periodic *in situ* rejuvenation, and either online or offline regeneration. Similar measures are required to extend the lifetime of less expensive Fe catalysts to at least 8-16 months.

Primary catalyst deactivation problems in FTS include: (1) poisoning of catalysts by sulfur and/or nitrogen compounds; (2) fouling by hard waxes and carbon; (3) formation of inactive catalytic phases such as oxides, inactive carbides and metal-support compounds; (4) hydrothermal sintering; and (5) catalyst attrition. Causes of these catalyst deactivation problems and their prevention and/or treatment (e.g. regeneration) are addressed in detail by Bartholomew and Farrauto [2006]. In the case of Co catalysts two general types of deactivation are observed [LeViness et al., 1998]: (i) a short-term, easily-reversible deactivation with a typical half-life of 20–40 days due to reversible oxidation and accumulation of hard waxes, organic acids, and reversible poisons and (ii) a long-term, difficult-to-reverse deactivation with a typical half-life of 100–200 days resulting from irreversible metal-support compound and carbide formation along with accumulation of surface carbons and reversibly-adsorbed poisons.

Rejuvenation, a mild, in situ treatment in H_2 at around 250-300°C is effective in removing waxes and acids, while a more severe *ex situ*, high-temperature regenerative treatments in O_2 and H_2 is required to reverse formation of oxides and carbides. Irreversible poisoning by sulfur compounds and reversible poisoning by nitrogen compounds in reduced by decreasing these poisons to ppb levels in guard beds upstream of the FT reactor(s). Hydrothermal sintering is avoided by (1) choice of hydrothermally stabilized supports and (2) avoiding operation at steam partial pressures above 5-6 atm. Attrition can be a serious problem for catalysts used in slurry bubble column reactors (SBCRs). High attrition resistance is realized through design of strong, dense catalyst spheres typically prepared by spray drying.

Figure S-4.2
Sasol Oryx Plant in Qatar

The serious consequences of severe attrition were dramatically apparent in the recent startup of the Sasol Oryx GTL plant in Qatar (Figure 4S.1). Apparently, the attrition rate was found to be 5 times the design level, a situation that required the plant to be operated at 20% of its full capacity for a period with resulting losses of millions of dollars in potential revenue.

Other heterogeneous catalyst classes for further consideration in HAS are:

- Alkali modified low-temperature methanol synthesis catalyst – Cu-ZnO/Al_2O_3
- Alkali-modified Cu-Co alloy catalysts
- Alkali-modified Mo-based catalysts

It is noteworthy that formulations based on these three classes of catalysts have been used in pilot plants for HAS or are being considered as candidates for pilot plants to be constructed in the future. Among the three classes, the Cu-ZnO/Al_2O_3 catalyst shows the lowest yield of higher alcohols and the Mo-based catalysts show the highest. Thus a logical order of emphasis could be: Mo-based catalysts > Cu-Co alloy catalysts > Cu-ZnO/Al_2O_3 catalysts.

Catalysts of particular interest for further improvement include Cu-Co, unsulfided Co-Mo, and unpromoted and cobalt-promoted MoS_2. Current total alcohol yields from these catalysts are in the 0.1 to 0.6 g/g catalyst/h range as compared to the bench-mark 1.3 to 1.5 g/g catalyst/h methanol yield in the commercially practiced methanol synthesis process. Also, hydrocarbons, especially methane, and CO_2 are produced thereby reducing total alcohol and ethanol selectivities. Modifications could be made to these baseline catalyst formulations using promoters that might improve yield and selectivity of ethanol.

High dispersion of the catalyst, that has been shown to improve activity for HAS, is also a very important consideration in catalyst preparation/modification. Catalysts need to be prepared with high dispersion and with structural promoters to prevent sintering at reaction conditions. Scalability and cost of catalyst preparation/modification is also an important consideration. Exotic methods of catalyst modification/preparation that cannot be easily scaled up using conventional commercial equipment should be avoided.

Since temperature is one of the most important reaction parameters, the temperature of maximum selectivity needs to be determined through experimentation and then closely controlled at this value in a commercial reactor. The requirement of close temperature control can be met by suitable reactor choice and design. Choices include fixed-bed, fluidized-bed and slurry bubble column reactors (SBCR). Shell and tube type fixed-bed reactors can be employed to better control temperature. However, catalyst extrudates (typically 3/16-inch) have to be used for commercial applications whose internal temperature can be quite different from the gas temperature for exothermic reactions. These reactors are also hard to scale up. Fluidized-bed reactors use small catalyst particles and can provide for heat removal using boiler tubes placed in the bed. However, the catalyst particles need to be highly attrition resistant. SBCR could have advantages reactors for a commercial embodiment of an ethanol synthesis and HAS process.

4.6.3.3 Dimethyl Ether “Synthesis”

Further development of fuel system and engine hardware for use with dimethyl ether (DME) in advanced high efficiency clean combustion engine is needed to remove barriers to deployment of DME vehicles in the U.S.

SELECTIVE ETHANOL SYNTHESIS WITH MICROCHANNEL REACTORS

Ethanol synthesis from syngas is a highly exothermic reaction, meaning that there is significant heat released during the reaction. Thus the reaction must be tightly controlled to prevent a detrimental temperature rise in the reactor, especially at high conversions. Hu et al. [2007] recently demonstrated that ethanol can be selectively produced in a microchannel type reactor which allows for efficient temperature control. This work demonstrates how integrated catalyst/reactor design can be used to more efficiently produce syngas products. Ethanol selectivities of 61% at a conversion of 25% were achieved using a $RhMn/SiO_2$ catalyst operated at a H_2/CO ratio of 2, 265^oC, and 50 atm pressure. The only other significant product was methane (34%). The structured catalyst prepared with the same catalyst formulation on a high heat conducting material were able to increase the space velocity up to 7 times (to GHSV = 20,000 h-1) while keeping the conversion at 20+% and the ethanol selectivity only slightly below 60%. The ability to achieve high conversion at this high flow rate was attributed to an improvement in mass transfer, since the catalyst particles were only 0.5-2 microns in diameter on the structured catalyst. Such small particles could never be used in a packed bed reactor because of the pressure drop that they would cause. The results are an indication of the possibilities for process intensification using specially designed chemical reactors such as this microchannel reactor. By increasing the flow through the reactor while keeping the conversion high, the size of the reactor required and hence its cost can be significantly reduced.

4.6.3.4 Development of Improved Product Upgrading Methodology for Optimization of Diesel and Jet Fuel Production

Further work is recommended for optimizing the upgrading processes to maximize the yield of diesel and/or jet fuel. A combination of upgrading processes should be considered including oligomerization of lighter hydrocarbons to produce jet fuel-range compounds, catalytic reforming to produce aromatics to provide the necessary properties to jet fuels, hydrotreating to remove oxygenates and saturate olefins, and mild hydrocracking/isomerization to produce the desired paraffins and iso-paraffins in the desired boiling range.

4.6.3.5 Reactor Technologies for FTS Based on Process Intensification and Catalyst/ Reactor Integration

Prevailing wisdom is that SBCRs will be the reactors of choice for future large-scale FTS plants in the US and abroad. However, for smaller plants (< 500 bbl/d) applicable to BTL, TFBRs probably have the edge because they can be designed with catalyst tubes of small diameter or with thin layers of structured catalyst, an approach which substantially increases heat transfer rates and catalyst productivity, while decreasing reactor size and capital/operating costs. The key here is managing the heat removal, the limiting factor in FTS reactors, through an integrated catalyst/reactor design and modular design [Nehlsen et al., 2007].

The design of a reactor and catalyst go hand in hand. Relatively little has been done to support research on integrated catalyst/reactor systems for FTS or structured catalysts for FTS. Very little has been done to model integrated reactor/catalyst systems. Such systems require new approaches for catalyst preparation and forming - issues that likewise have not been addressed. Novel catalyst and reactor configurations need to be considered that may better fit such smaller plants and result in improved heat management and improved overall operation.

The promise of new step-out technologies using process intensification and structured catalysts can only be realized through additional research and development. Priorities for new research might include studies of:

- Shaped catalysts and combined catalyst/reactor designs. For example, preparation, characterization, testing, and modeling of shaped catalysts including coated ceramic or metal monolithic or skeletal forms or unique extruded forms with an emphasis on heat and mass transport properties and experimental validation of heat and mass transfer models.
- Development and validation of reactor/catalyst models. For example, development of comprehensive robust 1D and 2D models that include reaction thermodynamics and kinetics, pore diffusion, heat transfer, pressure drop for steam reforming, methanol and FT synthesis and

FT REACTORS: THE ECONOMICS OF SCALING DOWN

Conventional wisdom teaches that large plants can produce a product more economically than small plants due to economies of scale (i.e., capital cost of equipment and processes has been found over many decades to scale with size raised to the 0.6-0.7 power). This empirical relation-ship has guided design and construction of syngas conversion plants for more than 50 years.

Prior to 2005, it was widely held that large economies of scale were preferred for GTL plants, for example, the 34,000 bbl/day Sasol Oryx Plant in Qatar (Figure S-4.2). The capital cost for this plant, which began operation in late 2006, was roughly $1.0–1.5 billion or $30,000/bbl/d. By mid-2007, however, escalation of worldwide material and construction costs had driven capital costs upward by 2–3 fold. Thus, the capital cost for a 100,000 bbl/d plant constructed in 2007 could exceed $10 billion!

Given such enormous capital costs, interest has recently shifted to the development of small-scale BTL, CTL, and GTL plants based on structured catalysts and mini-reactor technologies which apparently enable substantial (3–5 fold) reductions in FT reactor size and cost. Moreover, pressures to reduce CO_2 emissions have created incentives to develop processes for converting renewable biomass resources to fuel liquids in small, geographically-dispersed modular plants, producing 500–2,000 bbl/d of fuel liquids in shell-tube fixed-bed reactors. A 500 bbl/d GTL plant incorporating a compact GTL reactor with small-diameter tubes and similar process-intensified modules for syngas conversion, gas purification, and product upgrading could cost as little as $25 million [Bartholomew, 2007].

Figure S-4.3 Reactor for Sasol Oryx Plant in Qatar

A NEW PARADIGM IN SYNGAS CONVERSION PLANT DESIGN: INTEGRATED, COMPACT, MODULAR REACTORS AND PLANTS WITH STRUCTURED CATALYSTS

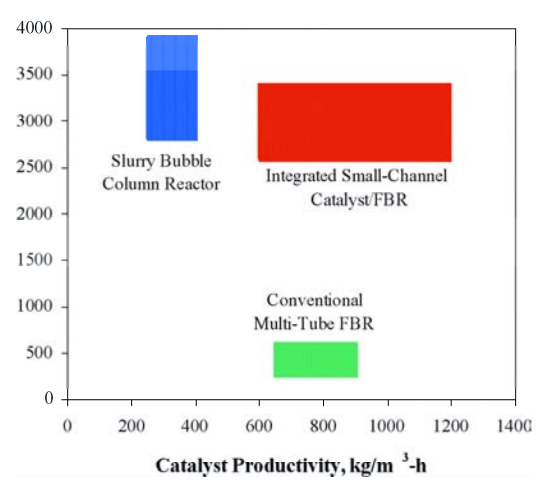
During the past 25 years, improvements in Fischer-Tropsch (FT) catalyst and reactor technologies have enabled 30-40% improvement in the economics for large gas-to-liquids (GTL) plants leading to an estimated capital cost of around $30,000/bbl/d for a 10,000 bb/d plant. However, due to the wide geographical dispersion of biomass or biogas sources, conversion to liquid fuels is logistically favored in small plants (500 to 1,000 bbl/d) close to regional sources of the feedstocks. Scaling by the six-tenths rule, the capital cost of a 500 bbl/day GTL plant would be $180,000/bbl/d or $90 million, an unacceptably high figure. Two important decade-old trends, process intensification or miniaturization based on integrated catalyst/reactor design [Nehlsen et al, 2007] and modular plant construction [Shah, 2007] have considerable potential for reducing the costs of small syngas-conversion plants 3-5 fold.

1. PROCESS INTENSIFICATION. Development of process-intensified reactor technologies or 'micro-reactors' promises to revolutionize many aspects of syngas conversion including: catalyst, reactor and process designs; catalyst and reactor manufacturing; and chemical production/processing [Ehrfeld, 2002; Matlosz and Commenge, 2002; Schouten et al., 2002; Sharma, 2002; Tonkovich et al., 2004]. Such reactors could be produced using high-throughput, low-cost fabrication methods such as those developed in the semiconductor industry. Development of thermally efficient, high productivity, compact reactors is possible for highly exothermic or endothermic reactions due to more effective heat and mass transfer in micro-channel reactors. Indeed, overall reactor size can be reduced by 1-2 orders of magnitude in water-gas-shift, steam reforming, and FT processes. Developing compact reactors typically relies on: (1) integrated design of catalyst and reactor [Nehlsen et al, 2007]; (2) incorporation of new catalysts forms, e.g. "shaped catalysts" such as coated ceramic or metal monoliths or skeletal "sponges"; and (3) targeting improvements in the limiting technical and economic factors (e.g. heat and mass transport or pressure drop).

2. MODULAR DESIGN. Construction of a plant using truly modular mini-plants for BTL, CTL, and GTL could lead to further economic efficiency. While modular design principles are well known [Shah, 2007], they have not been applied widely in energy or chemical industries. Truly modular, mass-manufactured plants could revolutionize manufacturing and refining of products and substantially reduce construction and operating costs of large and small plants. The ideal module is a finished, pre-tested, standardized system which performs a single unit operation (e.g. syngas production, FT reaction, distillation, or hydrocracking) and could in principle be substituted interchangeably in any number of processes or could be combined in parallel with identical modules to enlarge a plant. Substantial savings in capital cost and construction time can be realized due to substantial reduction in equipment, piping, and structural designs; on-site fabrication and construction; and plant shakedown. The cost of updating or enlarging plants can also be substantially reduced.

The promise of these new step-out technologies can only be realized through additional research and development. The application of process intensification is illustrated by recent developments in FT catalyst/reactor technologies [Nehlsen et al., 2007; Bartholomew, 2007] based on (1) heat removal management and (2) incorporation of small catalyst

Figure S-4.3 Performance of conventional and integrated, compact FT reactors [Bartholomew, 2007].



pellets on the inside or outside of small tubes or channels. Some advantages of this approach are illustrated in Figure S-4.3, showing heat transfer coefficient (i.e., normalized rate) plotted against catalyst productivity for conventional technologies and integrated catalyst/reactor technology. Heat transfer in a slurry bubble column reactor (SBCR) is highly efficient and enhanced by its well-mixed characteristic, a factor that also reduces reaction rate and productivity. On the other hand, a conventional fixed-bed reactor (FBR) is characterized by high reaction rates and high productivity but poor heat transfer rate. The new integrated compact catalyst/reactor technology facilitates both efficient heat transfer and high productivity (see Figure S-4.3), while also eliminating the catalyst-product separation problem.

the validation of these models using pilot plant data obtained by industrial partners. Computer codes should be developed in user-friendly platforms such as Visual basic/Excel. Development of microkinetic models would also be a high priority.

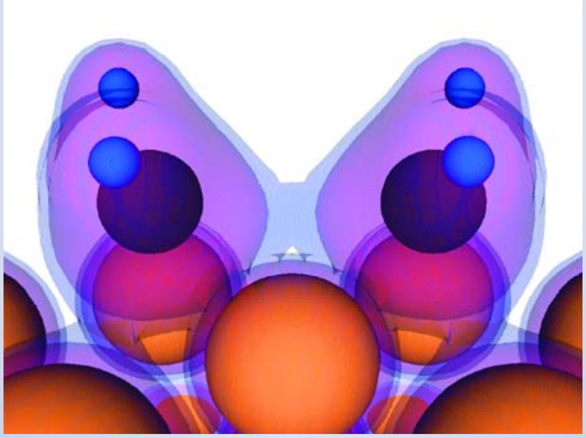
- <u>Process design, synthesis, and simulation.</u> Engineering and economic studies of process design, synthesis, and simulation using process intensified, modular technologies.

4.6.4 Molecular Computation

One way to tackle key issues relating to mechanistic routes, modeling, and catalyst design is through the use of electronic structure-based theoretical methods. These methods, especially density functional theory (DFT), have reached a level of sophistication where they can be used to explain diverse surface phenomena and describe complete catalytic reactions. When combined with modern surface characterization techniques, theory can now afford us the ability to pinpoint the origin of catalytic activity and, thus, open up the possibility of rational catalyst design [Lauritsen et al., 2004; Zhang et al., 2005]. Syngas conversion technologies can potentially benefit a great deal from theory.

Nonetheless, one needs to be aware of the practical challenges facing the theoretical approach to heterogeneous catalysis right now. Chief among them is the difficulty in capturing the coupling between the chemical environment, the nature of the catalytic material, and the reaction mechanism. This coupling can lead to the dynamic transformation of the catalytic material and reaction mechanism during operation, often in unexpected ways.

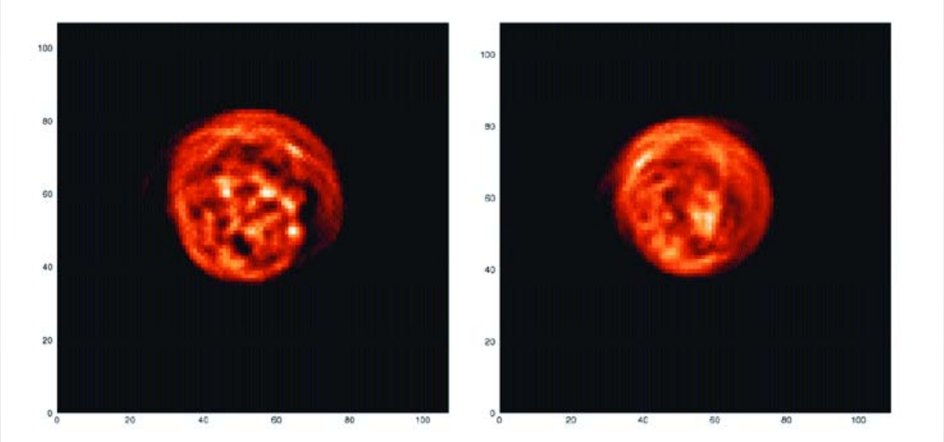
Figure 4.4: "Electron density plot of the transition state of ethylene (C_2H_4) formation from two methylene groups (CH_2) on the Fe(110) surface. Courtesy of Prof. Manos Mavrikakis, University of Wisconsin-Madison."



As a simple example, the active phases of several transition metal oxidation catalysts have recently been identified as oxidic and not metallic. They are stabilized by the reaction conditions, and some exist only on the surface [Bocquet et al., 2003; Ackermann et al., 2005]. The deployment of base metals such as Fe and Co, in an oxygen- and carbon-rich environment under elevated temperature and pressure, generates various oxide and carbide phases or perhaps even mixtures with support materials, which likely possess complex structures [Pentcheva et al., 2005] (many yet to be elucidated) and disparate catalytic properties. Considering how complicated the FTS reaction mechanism is itself, one can see how this added level of complexity can potentially make the theoretician's task much harder. Therefore, at the current state of the art, sustained, concentrated, and smart efforts will be required, most likely tightly integrated with experiments, in order to comprehensively understand the catalytic properties of these seemingly mundane materials and develop an efficient methodology in the process.

At the same time, theory can help tackle some of the technological problems that have been identified in this thrust area now. For instance, the chain growth mechanism and kinetics on Fe and Co, the factors that limit selectivity to ethanol and higher alcohols on transition metals, the effect of promoters, all remain to be better understood and may well be within the reach of simplified models that are expertly constructed and from which

Figure 4.5 Fe distributions in two fluorescence tomographic sections through FT wax showing the variability of catalyst concentration [Jones et al., 2005].



insights of practical value could be generated. Therefore, the possibility of theory making a more immediate impact on syngas conversion must not be overlooked, and efforts along these lines should be encouraged and fostered.

4.6.5 New Experimental Methodologies

In order to address many of the issues raised, new or modified *ex-situ* and *in-situ/operando* experimental methodologies are required, such as micro-X-ray fluorescence (see Figure 4.5), to allow us to develop more understanding of catalyst composition and structure during reaction and the nature of the reaction at the site level.

4.7 RECOMMENDATIONS

The following is a summary of some of the research needed in order to move the conversion of biomass to liquid fuels via biomass gasification towards commercialization.

- Development of more efficient and less expensive biomass gasification processes is crucial, especially given the smaller scale likely to be required for BTL plants.
- Better analytical techniques are needed for the characterization of low levels of syngas contaminants.
- There is a need for better characterization of the composition of biomass feedstocks including the concentration of catalyst poison precursors for predictive purposes.
- Impurities are feed dependent. This may mean that different catalyst formulations must be used for biogas clean-up from different feedstocks. Research is needed to understand the optimal catalyst formulation for different impurities and concentrations.
- Fundamentals of reaction on clean-up catalysts need to be studied using a combination of computational chemistry and *in operando* techniques for removal of
  - H_2S
  - Ammonia
  - Tars
  - Other contaminants
- Syngas needs to have < 60 ppb of H_2S, arsine, HCL, HCN, NH_3, particulates, Se, Hg, alkali, and P for FTS.
  - Some impurities may greatly interfere with catalytic removal of other impurities. Both computation and model experimental studies are needed in this area.
  - Can a one-stage biogas clean-up process be achieved that meets all requirements or are 2-3 stages required?
- There is a need to look at lower temperature clean-up processes such as the venturi scrubber. Much can be learned from coal gasification clean-up studies, but this knowledge will need to be extended to biomass gasification.
- Investigate sorbents and membranes for high temperature CO_2 removal. CO_2 may need to be removed from syngas for catalyst or reaction reasons.
- Better characterization and understanding of active sites for CO hydrogenation and chain growth or termination are needed in order to better design new catalysts that are active, selective, and stable for biomass syngas conversion.
- Increase use of computation for multi-scale modeling for catalyst design and mechanism delineation. Use computation to improve activity and/or selectivity of catalysts.

- Develop better mechanistic understanding of and microkinetic models for FTS and higher alcohol synthesis.
- Improve FTS catalysts and product upgrading methodologies for potentially new formulations of diesel and jet fuel based on new insights gained from experiment and computation.
- Design higher-yield catalysts for ethanol synthesis.
- Develop more understanding of catalyst deactivation and regeneration issues in syngas conversion.
- Attrition of currently available high α Fe FTS catalysts in an SBCR results in plugging, fouling, difficulty in separating the catalyst from the wax product, and catalyst loss. There is a need for more research into the design of attrition resistant catalysts.
- Develop economical reactor technologies for syngas conversion based on process intensification, catalyst/reactor integration, and heat management.
- Develop reactor/catalyst design strategies that enable varying product slates in FTS and higher alcohol synthesis
- Investigate the use of structured catalysts and process intensification
- Develop better catalyst-reactor models.

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5. Process Engineering & Design

OVERVIEW

Process optimization is critical to the success of scaled-up biofuels production operations. This requires the combination of process models derived from known feedstock and reactant properties and application of property prediction methods in tandem with laboratory-based research. In this Thrust area we articulate the role of process analysis for optimization of the biofuels production process.

5.1 INTRODUCTION

Like all large-volume petrochemical production processes, the processes for biofuels production can be designed and optimized using advanced analytical and modeling tools. This requires a combination of models implemented along with databases and development of property prediction methods assembled in parallel with laboratory research. Because this is a low-margin, high-volume business, optimization is critical for the success of chemical or biological processes on a large scale. Unlike the early days in the development of production processes for petroleum-based fuels and chemicals, there are now many excellent computer-aided design and optimization tools available.

The application of design and optimization tools to units and processes for the biofuels production demands new data on the physical, chemical and biological molecules, mixtures, and steps in the processes. Many of these are described and discussed in other sections of the workshop. Furthermore, there are typically many options for the arrangement of process units, as well as for the process conditions to be used. Consequently, a comprehensive and complete database sufficient for the detailed design of all alternatives is not likely to be developed within any reasonable timeframe. Conceptual design is useful alternative to bridge the gap between laboratory research on new process steps and the detailed biofuels production process design and optimization. Biofuels process plants must also be integrated with models for supply and distribution of biofuels and including life-cycle analysis.

5.2 PROCESS ANALYSIS

In the context of lignocellulosic biofuels, the objective of process analysis is to evaluate biofuels and biochemical processes to determine materials and energy balances, product yields, equipment size, capital and operating costs, environmental impacts, and cost of production. Process analysis is the application of scientific methods to the recognition of problems or definition of processes (Himmelblau and Bischoff 1968) and the development of procedures for their solution; it involves an examination of the process, alternative processes, and economics. The steps in process analysis are 1) mathematical specification of the problem or process, 2) detailed analysis to obtain mathematical models describing the problem or process, and 3) synthesis and presentation of results to ensure full understanding of the problem or process. Process analysis is frequently referred to as technoeconomic analysis.

■ Definitions

A number of definitions are useful in discussing process analysis and design:

A PROCESS is the actual series of operations or treatment of materials of interest in the analysis.

A MODEL is the mathematical representation of the real process.

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A SYSTEM is the group of process elements that are tied together by common flows of materials and/or information. It is always important to understand that the model and system are a representation of the physical process, and not always an exact replication of the process. In many cases, the process representation permits a mathematical solution where the exact replication does not.

A PARAMETER is a property of the process or its environment that can be assigned arbitrary numerical values. It is also a constant or coefficient in an equation.

SIMULATION is the study of a system or its parts by manipulation of the mathematical model.

■ Disciplines

Many scientific disciplines are used in process analysis, and include thermodynamics, transport phenomena, phase equilibria, mass transfer, heat transfer, chemical reaction kinetics, catalysis, mathematics such as statistics and multivariate analysis, and economics. The applications of process analysis include reactor design, separations, materials transfer and handling, life cycle assessment, and net energy analysis.

■ Examples of Process Modeling Tools

A number of processing modeling tools are available for process analysis. Examples of theses tools include:

Interpretation of R&D data
– Unscrambler, Matlab

Process modeling and design
– Chemkin (kinetics), Fluent (computational fluid dynamics), FACT (thermodynamics and phase equilibria)

Material and energy balances
– ASPEN

Process cost estimation
– ASPEN Icarus Process Estimator

Data analysis, economics etc.
– EXCEL

Risk analysis
– Crystal Ball, At-Risk

Dynamic modeling
– STELLA

Life cycle assessment
– TEAM, SimaPro, GREET

5.3 PRIORITIES FOR RESEARCH & DEVELOPMENT

Based on the presentations for each thrust in this workshop, the participants in Thrust 5 developed a list of areas that are important for the process engineering and design needed to overcome the chemical and engineering barriers to advancing biofuels technology. Many more detailed individual topics were considered and discussed by the participants. These topics were then rank-ordered and grouped into higher-level areas for research and development. It is important to note that all of the goals in the final list were considered important. The priority is primarily dictated by the precedence order for developing and implementing the new chemical and physical steps considered in this workshop. For example, detailed optimization studies cannot proceed without a proper basis of chemical and physical properties. Table 5.1 lists each of these goals, grouped approximately into three priority groups.

Table 5.1 Goals and Priority Groups Identified for Process Engineering & Design

	Area	*Priority*
1	Analytical Methods	A
2	Physical Properties	A
3	Kinetics	A
4	Conceptual Design Methods	A
5	Life Cycle Assessment	A
6	Separations	A
7	Economic Optimization Studies	B
8	Pretreatments	B
9	Educational Materials	B
10	Hybrid Reaction-Separations	B
11	Byproduct & Co-product & Markets	B
12	Robustness & Process Control	C
13	Reactor Design Models	C
14	Pollution Prevention & Treatment	C
15	Cost of Promoters, Catalysts & Solvents	C

A brief discussion of each area is given in the following subsections:

5.3.1 Analytical Methods

Rapid and reliable methods are needed to characterize not only biomass feeds, but also intermediate streams in the process as well as the products and byproducts. In addition to water content, measurements of the bulk density, ash, and trace elements would be very useful.

5.3.2 Physical Properties

Quantitative information for many physical properties is required for process design and optimization. This should include data from laboratory studies as well as physical property models. Physical property models that can build on a small set of data to describe the complex materials often encountered seem to be essential. Improved information for heats of reaction and phase equilibrium will be needed for many of the process engineering and design activities necessary to reach the goals described here.

5.3.3 Kinetics

A significantly expanded and quantitative description of chemical kinetics is needed for reactor design and potentially for studies of hybrid reaction-separation methods. It is especially important to have reduced-order models for complex reaction networks. These should be sufficiently detailed to describe, not only the rate of the primary reaction(s), but also the product distribution. In many cases, studies and laboratory tests are required to assess and remove transport effects from data or empirical models.

5.3.4 Conceptual Design Methods

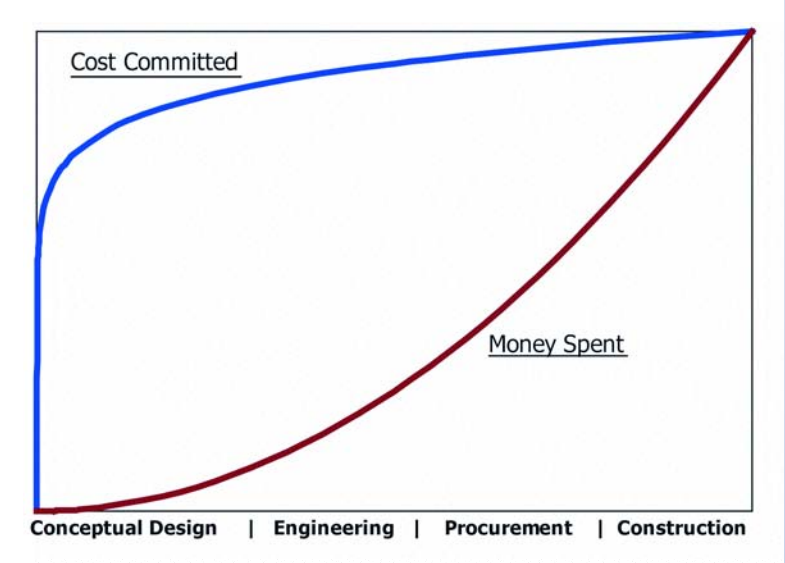
Conceptual design refers to the engineering decision-making that is required to conceive a process from information on the products, feeds, and chemical and physical steps proposed as a basis [Douglas 1989]. There are frequently many processes alternatives that can be chosen and many design variables to specify. Conceptual design approaches practically always include both assumptions and heuristics along with numerical modeling and optimization techniques. The extent to which each of these is useful depends strongly on the databases of physical and chemical properties and the level of detail in the process descriptions. Whatever the combination, the effective use of conceptual design methods in the early stages of process design can have a large impact.

Figure 5.1 is a schematic of the relationship between conceptual design and the more detailed steps in the implementation of a process, in terms of the Costs Committed to and the Money Spent to support the activities required to implement a project. The costs committed represent the best case that can be accomplished with the choice of chemical route, catalyst, conditions, separation and purification, etc. The level of activity and people involved in the Conceptual Design stage is typically small compared to the later stages. However, the decisions made at the conceptual design stage dictate the ultimate performance and costs of the project that can be achieved assuming that detailed engineering design and optimization are used subsequently. That is, even the best downstream engineering can only reduce the costs to a certain level (i.e., the Costs Committed).

Process Engineering and Design is often considered after the basic research and development work to produce a science and technology basis for a process. However, experience shows that conceptual design activities conducted in parallel with the process research and development often yield much better processes and, in fact, will often suggest new types and conditions for experiments on catalysts, process conditions, etc.

Figure 5.1 Impact and Phases of Process and Project Engineering

Early stage decisions about Conceptual Design, such as chemical route, catalyst, and separation and purification technology involve relatively few people and budget, but have a great impact on the project because they dictate the lowest cost that can be attained. Once the design concept is available, process development and optimization are essential to achieving these lowest costs in the Engineering, Procurement and Construction stages.

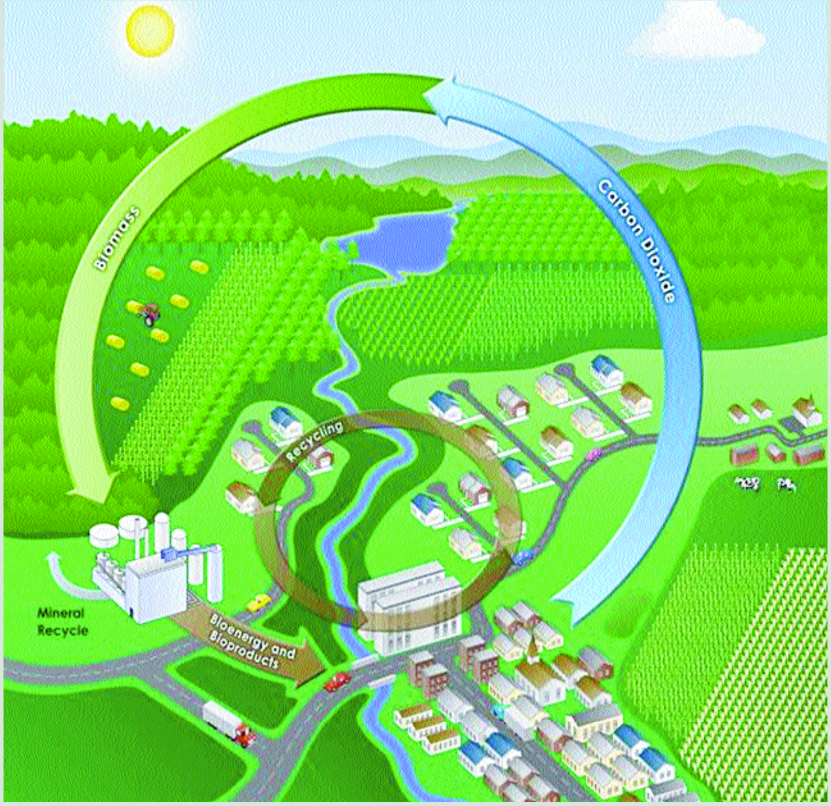


LIFE CYCLE ASSESSMENT

Life cycle assessment is a systematic evaluation of the environmental impacts and resource utilization associated with the production of biofuels, from initial growth of biomass feedstocks (i.e. plants and trees) all the way through the various processing steps to end use of the fuels (Seungdo, 2005a; Seungdo, 2005b). In other words, it is a "cradle to grave" assessment of everything that goes into and comes out of the production and subsequent utilization of biofuels. Life cycle assessment is an important tool for evaluating the impacts of different biofuels production processes utilizing various feedstock types. It provides a methodology that can be used to account for all the energy and resources consumed, as well as all the emissions and waste generated, during the process of producing and refining biofuels compared with the total energy content of the finished fuels.

A comprehensive life cycle assessment includes at least two components: 1) an inventory of raw materials requirements, total energy production and consumption, greenhouse gas emissions, water use and discharge, nutrient return, element cycling, solid waste and agricultural runoff, and release of byproducts during the entire production cycle; and 2) an assessment of the economic, environmental, and public health impacts of findings identified during the inventory. A third component, the life cycle improvement analysis, can be used as a tool to identify opportunities to mitigate the impacts of the production process (Svoboda 1995). Improvement analysis may involve life cycle comparisons based on changes in one or more production parameters, such as: catalyst type; reaction conditions; raw material usage; production scale; end use behavior; waste management; or overall process design.

Figure S-5.1 Life Cycle Assessment for Biofuel Production
(Oak Ridge Nationaly Laboratory).



5.3.5 Life Cycle Assessment

There is currently no validated database of life cycle inventories, including water, nutrient return, total energy picture and element cycling suitable as a basis for decision-making for biofuels development. Such a database would enable studies of feedstock production and processing models, along with identifying and assessing policy issues and constraints. (See Sidebar).

5.3.6 Separations

A systematic quantitative approach should be developed to describe and explain physical and chemical property characteristics and differences that can be used as the basis for separations. Research and development for reduced energy separation methods should be accelerated. These separation studies should include both contaminants and products in feed and intermediate streams. It is particularly important to identify contaminants that can adversely impact catalysts, as well as alternative catalysts that are less sensitive or insensitive to such compounds. Methods to separate catalysts from product or intermediate streams will be essential if the catalyst is not immobilized.

5.3.7 Economic Optimization Studies

Many economic studies have been conducted for alternative biofuels routes. These should be updated and made available in a comprehensive form. A review of the existing studies, widely disseminated, would be particularly useful and timely. Gaps in the studies should also be identified, especially for new technologies, and the studies should be expanded as necessary to close these gaps. Estimates of the optimum plant technology choice, size scale, feed(s) and harvesting footprint, would be very useful. Along with such optimization studies, an estimate of uncertainty in the results to the assumptions and basis are important.

5.3.8 Pretreatments

Many pretreatment methods have been studied for biofuels in general. But further work in support of aqueous-phase processing is important. Improved alternatives such as Organosolv and other approaches should be considered. Alternatives to expensive enzymatic pretreatment are particularly important.

5.3.9 Educational Materials

Chemists and engineers have the science and engineering fundamentals to contribute to the discovery, invention, design and operation of a biofuels industry. A greater emphasis on the application of these fundamentals to address particular biofuels issues would be useful. One route to the development of such educational materials is to provide specific challenge problems for faculty to use in project-based classes. For example, the American Institute of Chemical Engineers distributes a "Students Contest Problem" in a yearly competition that is often used in senior design courses. Student teams often provide excellent solutions as a result of this competition and this has potential not only as an educational vehicle, but also to provide technical insights and solutions.

5.3.10 Hybrid Reaction-Separation Methods & Process Intensification

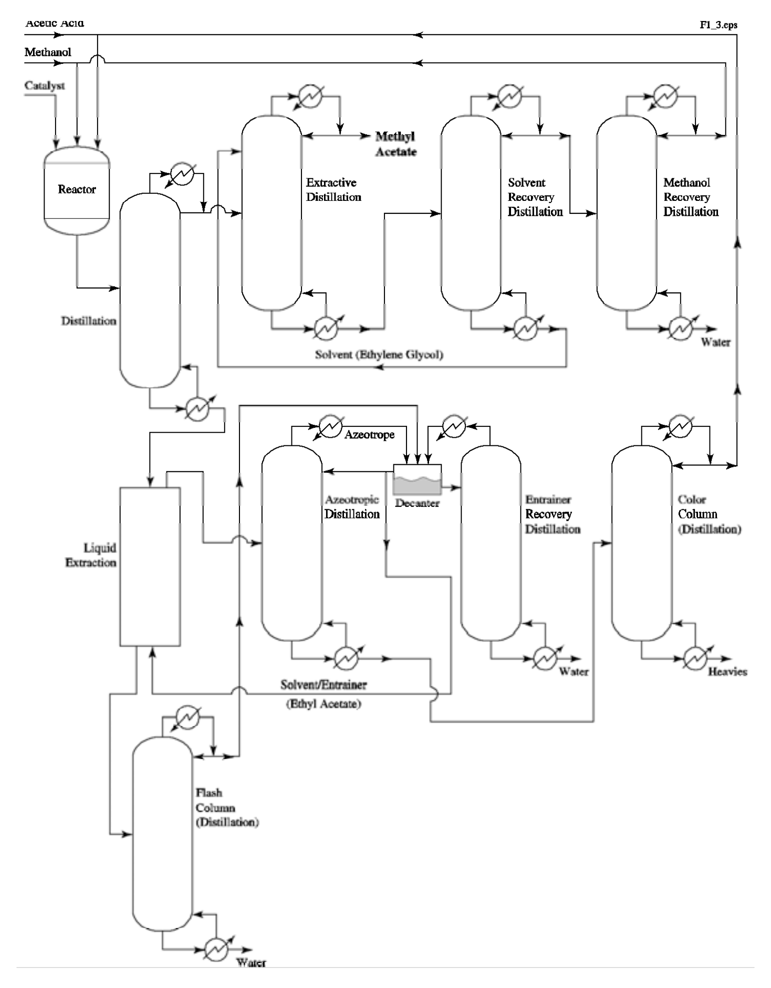
Because the processing costs and sustainability for biofuels are critical to implementing the technology successfully, process intensification is an important area of potential impact. Jenck et al. [2004] discuss sustainability and process intensification in the chemical industry. In fact, process intensification in the chemical industry has found surprising success in the last two decades, especially in reactive distillation as discussed recently by Harmsen [2007]. Some process intensification has been recognized as significant option for biofuels production, e.g., Simultaneous Saccharificaiton and

REACTIVE DISTILLATION

Reactive distillation, sometimes called "catalytic distillation" when a catalyst is present, combines one or more chemical reaction steps with distillation of the reacting mixture. Among many publications, Harmsen [2007] gives a recent review of industrial applications; conceptual design methods and additional examples appear in Doherty and Malone [2001].The best-studied and best-known example is probably the Eastman Chemical Company process for the production of methyl acetate [Agreda et al. 1990]. The traditional process for methyl acetate production used a separate catalytic reaction followed by separation and purification in nine major units as shown in Figure S-5.2. The appropriate combination of chemical reaction with distillation provides a process with a single major (hybrid) unit shown in Figure S-5.3 that requires approximately one fifth of the investment and consumes only one fifth of the energy in the traditional process; see Doherty and Malone [2001], pp. 7-12.

Figure S-5.2 Traditional Process of Reaction Followed by Separation and Purification for the Production of Methyl Acetate.

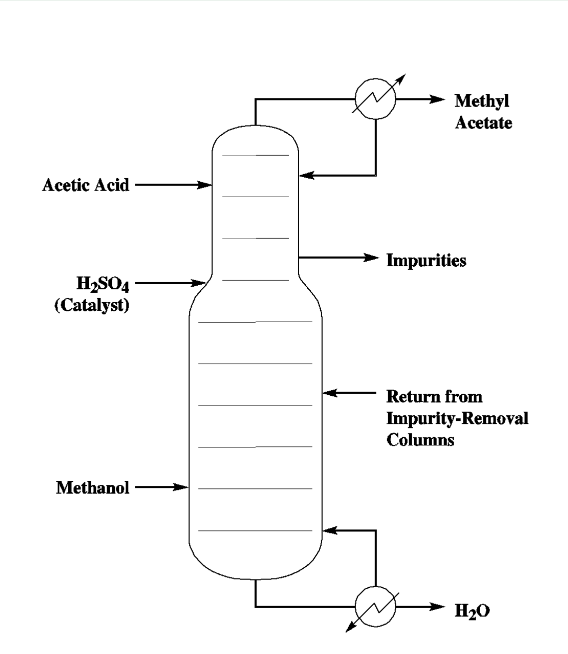
Adapted from Siirola [1996].



The design, development and control of integrated reaction-separation systems such as these are made possible by sophisticated modeling tools, combined with data on catalysts, equilibria and reaction rates.

Figure S-5.3. Reactive Distillation Process for the Production of Methyl Acetate.

Investment and energy use are reduced to 1/5 the values for the traditional process shown in the Figure. Adapted from Agreda and Parten [1984] and Agreda et al. [1990].



Fermentation. Other combinations combining reaction and separation have been considered, but more can be done in this area.

5.3.11 Byproduct and Co-Product Identification & Markets

Byproducts and potential co-products from the chemical and engineering steps discussed in this workshop will have a significant economic and environmental impact. More should be done to identify and develop applications for these materials. For example, there is currently no standard for the incorporation of ash from biomass production into concrete.

5.3.12 Robustness & Process Control

Particularly because of the solid feed streams to the initial steps in biofuels production, and the fact that they are often variable in composition and size, the process robustness to these variations, both chemical and mechanical, is an important consideration in process engineering and design. A small change in the feed stream should not cause a significant upset in the process. So this variability should be characterized early and included in the process design and optimization analysis. Appropriate process analytical methods (see 5.3.1) in support of process control are important and process control studies should be done early in the design activity to identify critical measurements.

5.3.13 Reactor Design Models

Information on the kinetics and physical properties discussed above, along with feed characteristics, should be integrated and used as the basis for reactor design models which include the capability to describe highly non-isothermal conditions, and the presence of multiple phases. In addition to the information in 5.2.2 and 5.2.3, it will be necessary to include transport effects in a manner that is suitable for scale-up from laboratory or pilot scale to commercial operation. Some work has been done in this area, but more attention is needed.

5.3.14 Pollution Prevention & Treatment

Pollution prevention and waste minimization methods should be integrated into process design studies. New options for air pollution control, waste-water treatment and especially solids (e.g., ash) should be explored. It was pointed out that the fate of byproducts is also a critical consideration in Life Cycle Assessment.

■ 5.3.15 Cost of Promoters, Catalysts & Solvents

Process engineering and Design studies, especially conceptual design (See 5.3.4) can guide the selection of promoters, catalysts, and solvents for aqueous phase processing. For example, a quantitative estimate for the benefits of immobilizing catalysts would inform ongoing laboratory studies. The relative costs and benefits of solvent alternatives such as ionic liquids, ethanol, butanol, acetone, ethyl acetate, gasoline or bio-diesel, should be similarly useful.

5.4 SUMMARY

Processes for the production of biofuels can be designed and developed relying in part on advanced modeling tools, databases, and property prediction methods. The development and use of these models for optimization from single plant through the supply chain, distribution and life-cycle analysis is critical for the economic success of biofuels development. Many excellent software tools are available, but new models specific to certain aspects of new chemical or biological steps will also be needed. The application of these models for the development of biofuels demands new data on the physical, chemical and biological molecules, mixtures, and steps in the processes. An effective and efficient approach to biofuels process development demands that the models and the data that drive them be developed in parallel and in close coordination with laboratory studies. Once designs for one or more good candidate processes are understood, these must also be integrated into systems to support decisions concerning the supply and distribution of biofuels.

There are typically many options for the arrangement and selection of process units, as well as for the process conditions to be used. Consequently, a comprehensive and complete database sufficient for the detailed design of all alternatives is not likely to be developed within any reasonable timeframe. In this context, conceptual design is useful to bridge the gap between laboratory research on new process steps and the detailed biofuels production process design and optimization. A variety of open questions important to the design and engineering of processes for the production of biofuels were identified in this workshop. Some of these take a natural precedence over others, and the consensus among academic and industry experts at the workshop is summarized in Table 5-1, on page 126.

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6. Crosscutting Scientific Issues

OVERVIEW

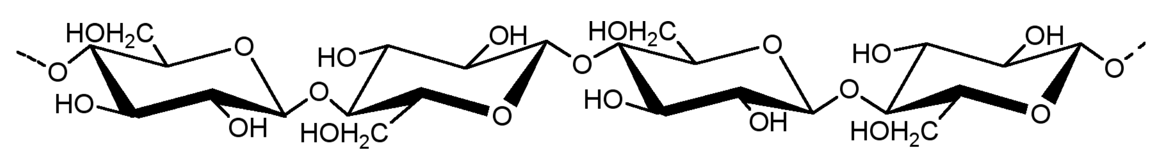
Exhaustive analysis of biomass reactants, intermediates, and products will provide a foundation of data from which biorefinery processing methods can be developed, tested, and optimized. With these data as inputs, powerful computational models will be used to illuminate the thermodynamic and economic efficiencies of biomass conversion reactions, identify prototypical reactant biomolecules and catalysts, and contribute to the discovery and development of novel multiphase biomass conversion reactors. This approach is derived, to a large extent, from the lessons of the petrochemical industry learned over the course of the last century. An important difference is the tremendous variation among biomass feedstocks, compared with the comparatively uniform properties of petroleum feeds. New analytical tools and techniques combined with exceedingly powerful computational methods promise to accelerate the development of biorefinery processing technologies at a rate that would have been inconceivable just a few decades ago.

INTRODUCTION

The concept of a biorefinery is still in its infancy. The ultimate success of biorefineries will depend first on the identification and development of novel processes for the conversion of biomass feedstocks to valuable fuels and chemicals, and second on the integration of these processes such that the biorefinery minimizes the production of undesirable by-products and waste heat. A recurring theme of this cross-cutting area is the parallels drawn between the concept of a 21st Century biorefinery and the advances in production efficiencies achieved through the concerted and sustained efforts of the petrochemical industry over the course of the last century.

Progress in the petroleum and petrochemical industries has been made possible in large part by the development of extensive database of physical properties of reactants, products, and intermediates involved in the conversion of feedstocks to valuable fuels and chemicals and powerful computational approaches used to model their thermodynamic and transport properties during various reactions and under different conditions. This information has been vital throughout all levels of research and development. As occurred during the century-long development and optimization of petroleum refineries, the design, control, and optimization of biorefinery operations will involve detailed process analyses and simulations, which will require extensive knowledge of the physical properties of reactants, products, and intermediates. While there are many parallels, the range of new tools and techniques available today promises to accelerate the development of biorefinery operations at a rate that would have been unattainable petrochemical technology developers just a few decades ago. We begin this thrust with a detailed discussion of

Figure 6.1 Cellulose is a crystalline polymer of glucose connected via beta linkages.



the analytical and engineering challenges involved with thermochemical conversion of biomass to biofuels. Because of the central role that catalysts play in biofuels production, the overarching scientific issues associated with catalyst engineering and characterization are prominently featured. Many aspects of traditional fuel production have been illuminated through computational chemistry. Clearly, the widely applicable cross-cutting tool of chemical modeling will increasingly be used to shed light on the underlying chemistry of biofuels production as well. However, the multi-phase nature of chemical biofuels processing is driving the need for new, more powerful computational methods. Through exhaustive analysis of biomass reactants, intermediates, and products – combined with judicious choice of model systems – development of new computational methods can help us to understand more about conventional biomass refining processes and rapidly develop increasingly efficient processes for the future.

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6.1 ANALYTICAL DATABASE FOR BIOMOLECULES

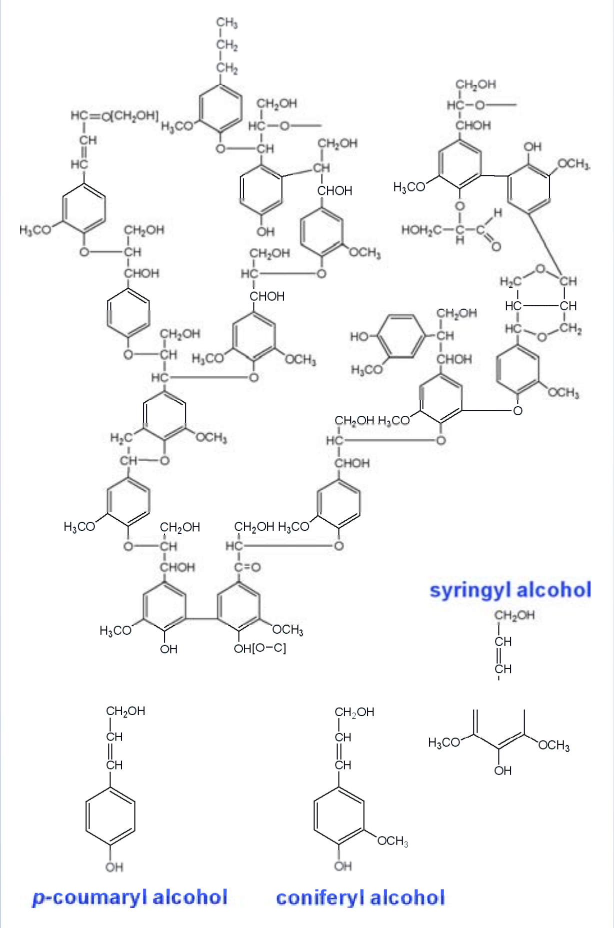
A pillar of modern petroleum refining technology is a comprehensive database that characterizes the individual components of many crude oils and the products of their conversion. This database is valuable for making predictions about the reactivities of various feedstocks and the properties of their refining products; it is a resource worth billions of dollars to refiners who depend on it to guide the optimization of their operations.

The creation of an efficient, economical fuel industry based on biomass will require the development of a similar database for the hundreds of biomass-derived compounds. Such a database does not currently exist, and its absence significantly hinders the fundamental research programs that are exploring new biofuels processing routes.

Of the three main components in cellulosic biomass (cellulose, hemicellulose, and lignin), hemicellulose and lignin are the most difficult to characterize structurally. Cellulose is the crystalline fraction (Figure 6.1) of biomass, which is composed entirely of beta-linked D-glucose units that can be characterized by a variety of techniques including X-ray diffraction methods, 13C MAS NMR spectroscopy, and various other spectroscopies. Lignin is unique in that it is a polyaromatic structure, composed of phenolpropanoids units (Figure 6.2). Although the structure of lignin at the level of atomic connectivities is poorly known, due in part to inter-specific structural variations, the fact that lignin is the only aromatic fraction of cellulosic biomass allows for some characterization of its structure and the concomitant changes that occur during chemical processing of the biomass.

In contrast, characterization of the structure and composition of hemicellulose (Figure 6.3) in the solid state is exceedingly difficult. Unlike cellulose, which is both crystalline and composed of a single monosaccharides unit, hemicellulose exists in biomass in an amorphous structure that contains several different C_5 and C_6 sugars, including xylose, mannose, galactose, glucose, and arabinose. A further structural feature of hemicellulose is the presence of numerous acetyl groups on many of the saccharides. Because hemicellulose is amorphous, characterization methods that rely on crystallinity (such as X-ray diffraction) are not useful. Furthermore, in common spectroscopies (i.e. 13C MAS NMR), the signatures of the different sugar residues are essentially identical, making the cellulose and hemicellulose residues appear identical. Only the presence of acetyl groups is a useful marker for hemicellulose in raw biomass samples. Unfortunately, most mild treatments of cellulosic biomass in aqueous media liberate these acetyl groups, making them essentially useless in the characterization of hemicellulose fractions during chemical processing. Currently, no facile methods exist to monitor the degradation of hemicellulose during chemical treatments, other than to track the formation of non-glucose monosaccharides during the process. Therefore, the development of spectroscopic, or other methods, expressly designed to interrogate the structure of hemicellulose in solid biomass samples is an important research target.

Figure 6.2 Lignin is polyaromatic in structure, consisting of linked phenolpropanoid units. Three lignol building blocks include syringyl alcohol, coniferyl alcohol, and p-coumaryl alcohol.



The complex mixtures of hydrocarbons in crude oils, including even many of the heaviest compounds, have been characterized precisely by mass spectrometry. Gas chromatography/mass spectrometry has complemented this method, and many useful results have been obtained with element-specific detectors.

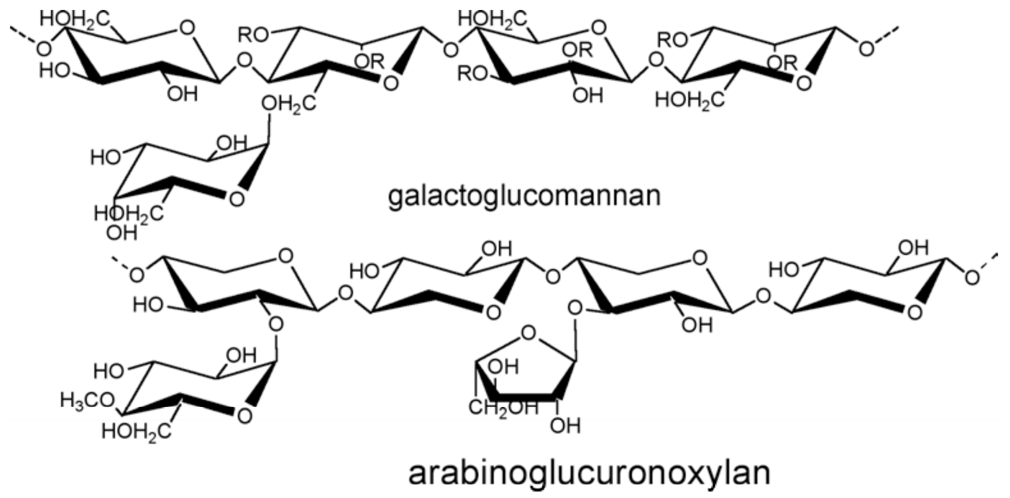
Mass spectrometric analysis is applicable to all but the most intractable components of petroleum, such as asphaltenes. Thus, it can be expected that these techniques would be suitable for analysis of almost all the individual compounds formed from biomass during conversion processes such as pyrolysis and liquefaction. However, many of the compounds in biomass-derived liquid processes such as those described in Chapter 3 are not hydrocarbons; these compounds require development of procedures different from those developed for petroleum.

6.2. THERMODYNAMICS

Major innovations in biorefining will require the identification of new processes, many of these being catalytic in nature. If we follow the lead of the of the petroleum and petrochemical industries, these new processes will be invented by scientists and engineers working with reaction mechanisms, reaction networks, and novel reactors. In addition, these developments will require an understanding of how reactants, products, and intermediates interact with catalyst surfaces, partition between the two phases of a biphasic reactor, are distributed between the gas and liquid (or solvent) phases, or are extracted into specific solvents in separation processes. At present, however, this vital information about the physical properties of biomass-derived molecules is lacking. This dearth of information impedes not only the discovery of new processes, but also the design, operation, optimization and control of emerging technologies.

The unprecedented efficiencies achieved by the petroleum and petrochemical refineries of today would not have been achieved without detailed process analyses, wherein intermediates and heat generated in one process are used in other processes, such that the most effective utilization of the petroleum feed is achieved, both on an atom-efficiency and energy basis. Moreover, the success of the petroleum and petrochemical industries has been achieved through the development and continuous improvement of new chemical processes, most of these processes being catalytic in nature. In this respect, the formulation of a new process or the elucidation of the reaction

Figure 6.3: Hemicellulose is an amorphous polysaccharide containing both 5 and 6 carbon sugars. Examples of hemicelluloses include galactoglucomannans and arabinoglucuronoxylans.



chemistry for an existing process typically involves consideration, at the molecular level, of reaction mechanisms and/or reaction networks. Such analyses also depend on having knowledge of the physical properties of the reactants, products, and importantly the potential reaction intermediates.

Likewise, to advance the field of biofuels production and provide a solid foundation for further work, it is essential that theorists develop new approaches for prediction of the thermodynamic properties (enthalpy, entropy, heat capacity) of biomass-derived molecules in the gas and liquid states, as well as in various solvents. This work should provide not only reliable thermodynamic data for specific biomass-derived molecules of perceived importance in a biorefinery, but should also yield new methods that can be used effectively by practitioners to estimate the thermodynamic properties of new compounds that may appear, for example, in reaction mechanisms, reaction networks, and process flow sheets for new chemical processes.

It is important to note, however, that the vast knowledge on the physical properties of molecules now available from the past decades of research and development in the petroleum and petrochemical industries deals primarily with hydrocarbon molecules that have limited oxygen functionality. Furthermore, most of this information deals with hydrocarbons in the gas phase or perhaps as non-polar liquids. Unfortunately, many of the reactants, intermediates and even some of the products involved in the processing of biomass-derived feeds are highly oxygenated species, and these molecules may well be processed most effectively in water or in polar solvents.

In short, the starting point for any systematic discovery of a new process or for the implementation of an emerging process in a biorefinery is an analysis of the overall thermodynamics, independent of whether the process is a chemical transformation or a separation step. It is for this reason that the lack of thermodynamic data for the biomass-derived reactants, products and intermediates presents a major impediment to further developments in biorefining.

6.3. CHEMICAL REACTION ENGINEERING

6.3.1 Identification of Prototypical Reactants (model compounds)

Much has been learned about catalytic processing in petroleum refining as a result of experimentation with individual compounds that are representative of a larger class of compounds; these are usually referred to as model compounds. Examples are isobutane in catalytic cracking and thiophene in hydrodesulfurization of gas oil. Extensive testing is required to distinguish good from unsatisfactory model compounds, because no model is without limitations in representing a larger group of compounds.

The application of this approach to biomass-derived feedstocks is still in its infancy. The model compounds identified so far have barely been investigated as reactants in conversions intended to mimic biomass conversion. Work is needed to identify appropriate model compounds in biomass-derived feedstocks. A good example of the kind of studies that need to be undertaken is a series of model compounds that were identified as pertinent to the upgrading of pyrolysis oil to hydrocarbons [Gayubo, Aguayo et al., 2004a, 2004b, 2005].

Certain compounds have been shown to be valuable for investigations related to petroleum refining because, being more than representative in their reactivities, they are key components of the conversion reaction because they are the least reactive compounds in the feedstock and, therefore, need to be converted for the product to meet the required purity standards. An example is 4,6-dimethyldibenzothiophene, which must be converted in large measure for the fuel to meet sulfur content specifications.

Work is needed to identify these kinds of key compounds in biomass-derived feedstocks for various upgrading processes.

6.3.2 Lumping of Biomolecules

A useful methodology for representation of complex multicomponent feedstocks in petroleum refining technology is called lumping, whereby a group of compounds that are chemically similar are represented as if they were a single (perhaps fictitious) compound chosen to approximate their reactivity characteristics. The enormous simplification of this procedure (representing, for example, hundreds of compounds in a petroleum residuum with tens of lumps), which is based on an extensive set of analytical results characterizing the feeds and products, makes it possible to accurately predict the reactivities of various feedstocks (even those not yet tested) and the properties of their refining products.

Successful application of the lumping methods to biomass-derived feedstocks will require thorough analysis of these feedstocks and the products of their conversion, primarily by mass spectrometry. It will also require a more fundamental understanding of the reactions that occur in biomass upgrading, which may be obtained in part from investigations of representative model compounds, as described above.

Successful identification of model compounds for the upgrading of biomass-derived feedstocks will also require extensive experimentation so that candidate models can be improved by comparison with experiment. The work will need to be extended to a range of specific catalysts so that generalizations can be made about fundamental catalyst types, such as acids and metals.

6.3.3 Characterization of Activities of Prototypical Catalysts

At this early stage of understanding biomass conversion, there is only fragmentary knowledge about how various feedstocks (or the model compounds representing them) are converted in the presence of different catalysts. To achieve accurate predictions of the best catalysts and reaction conditions for candidate biomass-conversion processes, it will be necessary to generate data that demonstrate the conversion of individual model compounds with catalysts that may be considered protypical, such as acidic zeolites, supported metals, and bimetallic catalysts consisting of metals on acidic supports. Additional work will provide further improved ideas about which catalysts constitute the best prototypes. The initial choices should be based on performance data, and candidate catalysts that are low in activity, poor in selectivity, or poor in stability should be excluded. As testing proceeds, the data should indicate catalyst stability in longer-term tests in flow systems.

Since biomass contains much more oxygen than fossil fuels such as coal, oil and natural gas, catalytic conversion of this renewable resource will necessarily involve processing in aqueous phase systems. Consequently, many of the heterogeneous catalysts that have been developed for hydrocarbon processing are inappropriate for conversion of biomass in aqueous media. Moreover, the chemical reactions and mechanisms involved in the transformation of biomass to transportation fuels are poorly understood.

Transformation of biomass-derived molecules to transportation fuels will involve the removal of oxygen while maintaining, as much as possible, the carbon and hydrogen inventory of the molecules. These transformations necessarily include the selective manipulation of C-C, C-O and C-H bonds. Heterogeneous catalysts and enzymes must be developed to selectively carry out the desired reactions while minimizing the unproductive formation of CO_2 and heavy tars.

The data used to identify prototypical catalysts should include activity and selectivity data, as well as enough information to determine the reaction networks of well-chosen model compounds as reactants. Determination of the networks will require analysis to identify reaction intermediates and experiments with these intermediates as feeds. Experiments should also be done to identify classes of compounds in feedstocks that are significant inhibitors of the various reactions, as well as components (even impurities) that may be catalyst poisons. This work should include long-term tests (some with model compounds as reactants and some with full feedstocks) to determine catalyst deactivation. Analysis of used catalysts will be needed to understand the mechanisms of catalyst deactivation.

Ultimately, data characterizing catalyst performance should be reduced to include fundamental reaction kinetics, with rates of reactions expressed as turnover frequencies. Such determinations require characterization of the catalyst to quantify the numbers of catalytic sites (see section 6.5).

6.3.4 Reactor Engineering

Chemical reactor engineering crosscuts all of the areas through which chemical catalysis will address the conversion of biologically derived feedstocks for fuels production. Basic studies will be required to provide the foundation for implementing these emerging technologies. Mechanisms will need to be determined, if not in atomic detail, at least in the ability to determine kinetic reaction pathways. Once determined, these mechanisms will provide a framework for optimization of yields and selectivities of conversion processes in practical reactors. Only after the complex details of each reaction step are worked out can these processes be compared, and eventually analyzed in scaled-up processes.

Real feedstocks, as opposed to laboratory-grade feeds, often comprise mixtures of reagents, transformed in parallel reaction networks; the formation of biodiesel by the transesterification of vegetable oil is an example. Transesterification is the reaction of triglyceride (or other esters) with alcohols to produce alkyl esters (biodiesel) and glycerol typically in the presence of acid or base catalysts. The oils contain many glycerol tri-esters from C_{13}-C_{19} and each transition of tri- to di- to mono- ester could require individual kinetic expressions, all of which would have to be solved simultaneously. It is far simpler to assume that each of the tri-esters would react with similar rates and to lump these together. This might work well for this sequence, while for other more complex reaction mixtures the rates for specific species, or groups of species, could be considerably different. Therefore, it may be advantageous to identify and classify the reactants and identify those for which the overall rates of reaction are crucial to process success. (In cellulosic liquefaction for example, a class of lignin might prove to be most difficult to solubilize by a specific approach.) The identification of the fundamental reaction classes (lumps) can be determined experimentally by labeling. A similar approach is employed in the petrochemical field and in polymerization kinetic analyses.

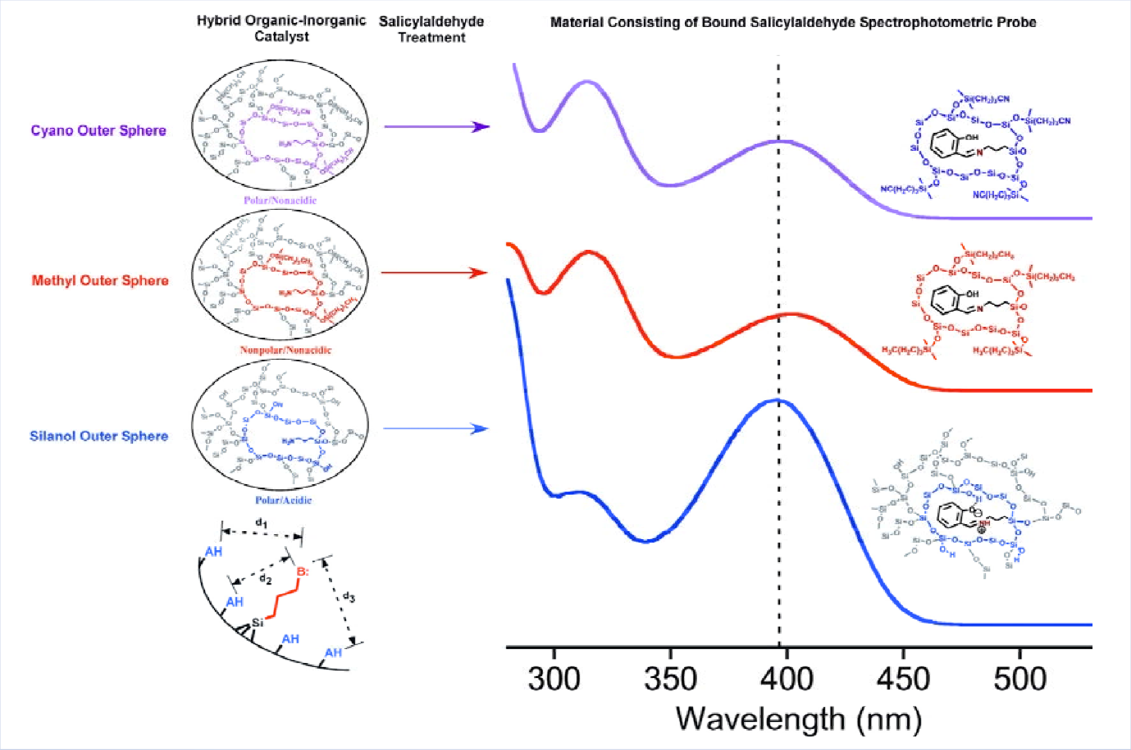
In addition to influencing the overall yields, reactor configurations can provide a method for the collection of basic kinetic data. Stirred tank or plug flow reactor configurations appear as the ideal extremes of mixing. However, many of the reactions involved in the transformation of bio-derived fuels are multiphase. Mixing between the gas, liquid, and solid (e.g. the requirement for the addition of gas to the liquid phase during hydrogenolysis) phases and at the interfaces then controls overall reactivity.

6.4. CATALYST ENGINEERING

Engineering the catalyst itself can be considered over several scales. First, there are rational ways to prepare well-dispersed metal particles over high surface-area supports, based on an understanding of the chemical fundamentals of catalyst impregnation (see sidebar 6.1). Going further, catalyst sites might be designed at the molecular level.

An example of catalyst activity is shown in Figure 6.4. Elucidating how the outer-sphere environment controls heterogeneous catalysis is an important cross-cutting issue that spans both enzyme and abiological catalysts. This can be accomplished by binding a chromaphore that reports on the acidity and dielectric constant surrounding the active site, and is demonstrated for primary amines anchored on silica. By way of illustration, diffuse reflectance UV-Vis spectra of materials treated with salicylaldehyde (more than 80% of the sites are bound with salicylaldehyde) show the acidic outer

Figure 6.4 Treatment of heterogeneous primary amine catalysts with salicylaldehyde synthesizes a bound spectrophotometric probe that reports directly on the acidity and dielectric constant of the environment that immediately surrounds the primary amine active site. This environment in turn strongly affects nitroaldol catalysis activity and selectivity.



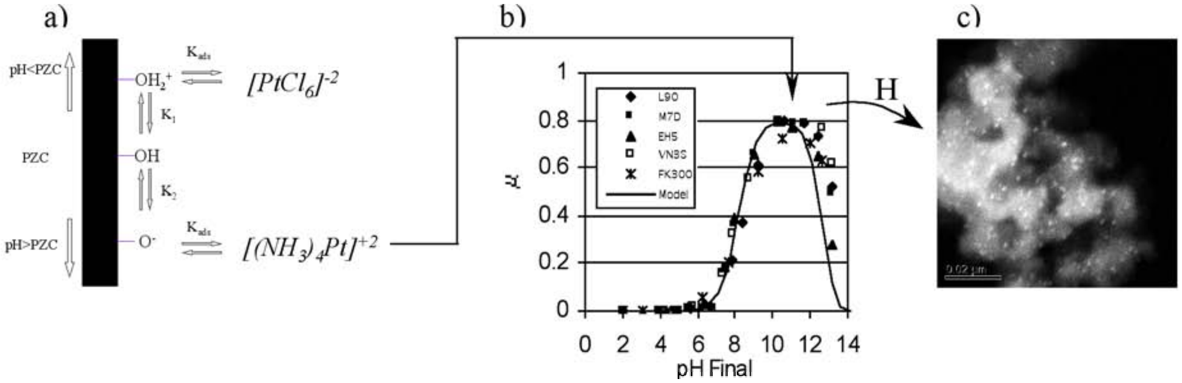
THE NANOSCIENCE OF CATALYST SYNTHESIS

Calls are often heard to "transform the art of catalyst preparation into a science." One arena in which this is occurring is in fundamental studies of catalyst impregnation, the process by which a solution containing dissolved metal precursors is contacted with the high-surface-area catalyst support. In this vein of work, the chemical fundamentals of impregnation are being understood and exploited for simple, rational methods to make metal nanoparticles. Most industrial catalysts are of this sort and employ aluminum oxide or carbon as the support.

The preparation strategy of "strong electrostatic adsorption" (SEA) [Brunelle 1978; Schreier and Regalbuto 2004; Miller, et al; 2004] can yield ultra-small metal particles with a simple contacting process. The electrostatic adsorption mechanism is depicted in Figure S-6.1, part a. At the pH of "point of zero charge" or PZC, which is characteristic of each oxide, the hydroxyl groups populating an oxide or carbon surface are essentially neutral. At pH levels more acidic than the PZC, the hydroxyl groups protonate and the surface charge is positive, while above the PZC, the hydroxyl groups deprotonate, and the surface charge is negative. As an example, silica has a PZC of about 3.5 and preferentially charges negatively at high pH and so strongly adsorbs $[(NH_3)_4Pt]^{+2}$ [Miller et al. 2004].

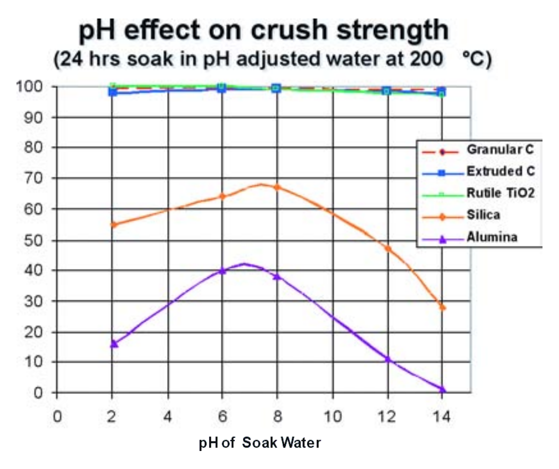
To locate the pH of the strongest interaction, the metal uptake is surveyed as a function of pH at constant metal concentration (Figure S-6.1 part b) [Schreier and Regalbuto 2004]. At the pH of strongest electrostatic adsorption (about 11), the precursor is adsorbed as a monolayer; the high degree of dispersion can be preserved through the catalyst finishing steps as the metal is reduced to its active state. The Pt/SiO_2 material shown in Figure S-6.1 part c contains 1-nanometer Pt particles, in which virtually every Pt atom will contribute to catalytic activity [Miller, et al 2004].

Figure S-6.1 Pt/silica Catalyst Synthesis by SEA a) electrostatic mechanism, b) PTA uptake – pH survey to locate optimal pH over silica, c) reduction of sample prepared at optimum conditions yields ultra-small metal nanoparticles (Figure courtesy of J. Regalbuto).



sphere in the silanol-rich material (blue), which facilitates formation of an iminium cation upon salicylaldehyde binding, and is manifested in a prominent band at around 400 nm [Bass, Katz, 2003, Bass, Solovyov, et al., 2006]. Materials having aprotic outer spheres with varying dielectric constant, ranging from the polar cyano to the non-polar methyl, show a stronger intensity at 325 nm relative to 400 nm, and instead require predominantly neutral imine tautomer upon salicylaldehyde binding (Bass and Katz, 2003). The wavelength of the iminium cation band (~400 nm band) is also sensitive to the local dielectric constant of the environment surrounding the active site, because the excited state of this species is less polar than the ground state. Therefore, the iminium cation band of the methyl-rich outer sphere material (red) appears at slightly higher wavelength than for the respective, higher dielectric, silanol- and cyano-rich (purple) outer sphere materials. This data explains the different reactivities observed in these heterogeneous amine catalysts [Bass, Solovyov, et al., 2006].

Figure 6.5 pH effect on crush strength in water at 200°C (James F. White, PNNL, with permission)



The physically largest scale on which to consider catalyst engineering is in the mechanical and chemical integrity of formed catalyst pellets, which are formed by extruding or otherwise processing powdered material into various shapes. In particular, engineering formed catalysts for the aqueous phase poses numerous fundamental cross-cutting technical challenges. The systems that have been developed for petroleum and petrochemical refining in general are unstable under aqueous conditions. The most common supports used in petroleum-based catalytic processes are based on metal oxides of alumina, silica and alumina silicates. These supports are unstable under hydrothermal conditions. The issue is compounded when run under high or low pH (Figure 6.5). Thus, supports for hydrothermal catalytic processes commonly consist of carbon, monoclinic zirconia, rutile titania, as well as a few others such as niobia, tin oxide, and barium sulfate.

Carbon as a support has a broad range of qualities, which depend on carbon source, processing, and post processing treatments. Catalyst-grade carbons vary in surface properties such as pH or point of zero charge (PZC), porosity, pore volume, and others. These properties can influence carbon interactions with substrate and products. Organic molecules have strong interactions with activated carbon and so selective adsorption of substrate and products can influence catalyst performance (selectivity and rate). In addition to support-substrate/product interactions, there are strong support-metal interactions. The non-covalent interactions of metals on carbon are "less sticky" than those of metal oxides. Hence metal migration, crystallite formation and other forms of sintering are often observed. Metal sintering can be complicated at extreme pH. Catalysts are commonly composed of multiple metals. Fundamental work should be done to understand the metal-metal interactions within a catalyst. In some cases, the second (or additional) metal may not be playing a role in the catalyst at all, but instead be responsible for stabilizing the first metal. In other instances, the second (or additional metal) has a clear role in catalysis by improving reaction rate and product selectivity.

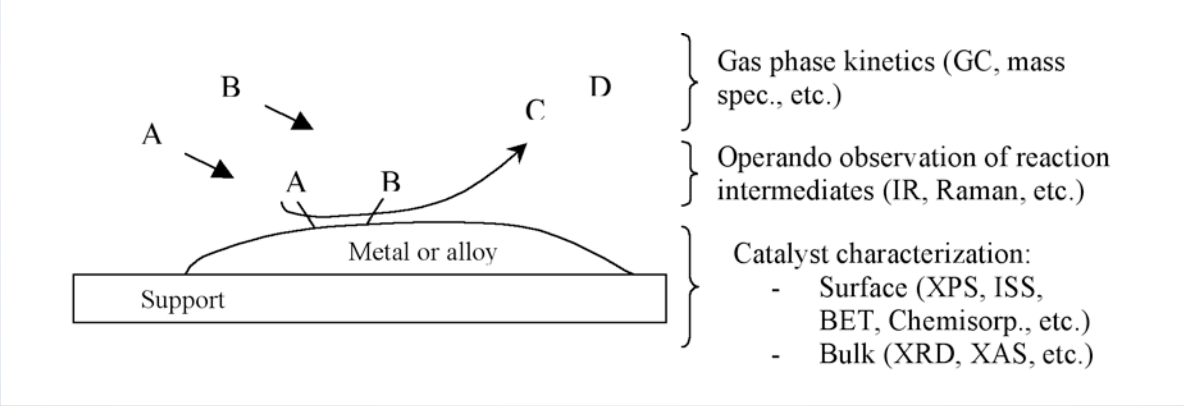
Catalyst stability (deactivation) issues are substantial when working with biomass feedstocks. Chemistry that works well with pristine systems (such as purified glucose) fail when using actual biomass feeds because of the rich mixture of various impurities present. Impurities include inorganic salts or other products in ash, protein containing components, and other unknowns. Some impurities act as inhibitors and catalyst performance returns when the impurity is removed. In other examples, catalysts are permanently damaged by the impurity. One challenge is that impurities have different effects on a catalyst-to-catalyst basis. However, some impurities cause problems in a more general or universal way. Materials containing proteins have sufficient sulfur and similar components that place them in this category.

Related to catalyst engineering are the challenges of reactor engineering in aqueous systems. One challenge is the low solubility of reactive gasses such as hydrogen and carbon dioxide. This results in the need for high reactor pressure and temperature. The ionic nature of water at elevated temperatures leads to reactor corrosion issues. As corrosion occurs dissolved metals can plate out on the catalyst and impact its performance.

6.5. CATALYST CHARACTERIZATION

Fundamental understanding of catalytic chemistry is obtained when the detailed, atomic scale structure of a catalyst and its chemical composition is known and can be correlated to its catalytic activity and selectivity. These qualitative "structure-function" relationships can be derived through detailed characterization of the catalyst, precise measurement of catalytic rates, and *in-situ* or *in-operando* measurement of reaction intermediates over the catalyst surface. A schematic of these three measurement regimes used for deriving structure-function relationships are shown in Figure 6.6.

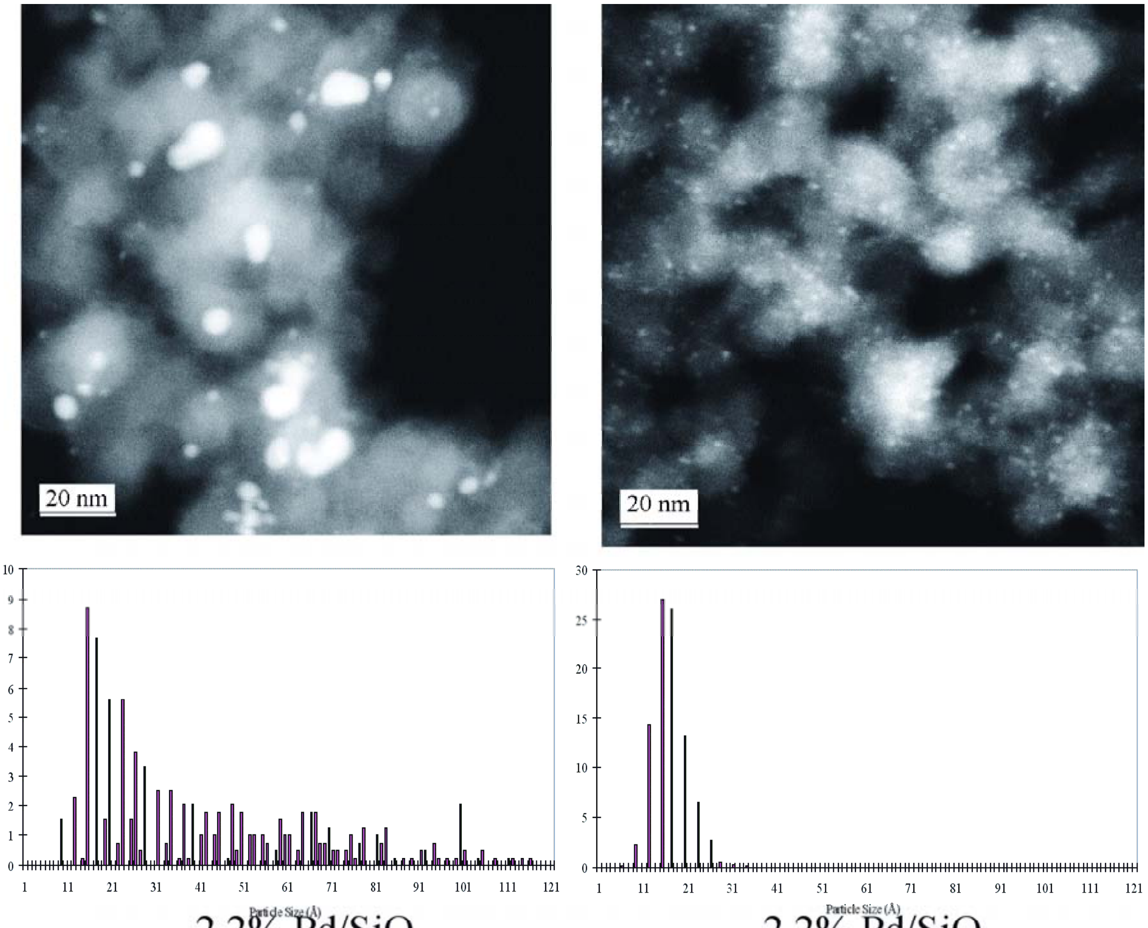
Figure 6.6 The Three Regimes of Measurement for the Derivation of Catalyst Structure-Function Relationships.
(Typical measurement methods in parentheses.)



ELECTRON MICROSCOPY OF SUPPORTED METAL CATALYSTS

One of the most utilized and direct means to evaluate supported metal catalysts is with electron microcopy. High Angle Annular Dark Field, or "Z-contrast" imaging, is one of the workhorse techniques. In this imaging mode, contrast is proportional to the atomic weight of the constituents, making a heavy metal such as palladium on a light oxide such as silica an ideal sample. Virtually all metal particles are imaged and particle size distributions can be readily obtained.

The comparison below shows relatively large particles obtained by a typical "dry" or "incipient wetness" impregnation, versus much smaller particles obtained with a method that optimizes metal precursor – oxide interactions during impregnation. In most catalyst applications, small particles are desired since there is more exposed metal area (active area) per mass of metal. This condition is referred to as ‘high dispersion" and is particularly important for expensive metals such as platinum and palladium.

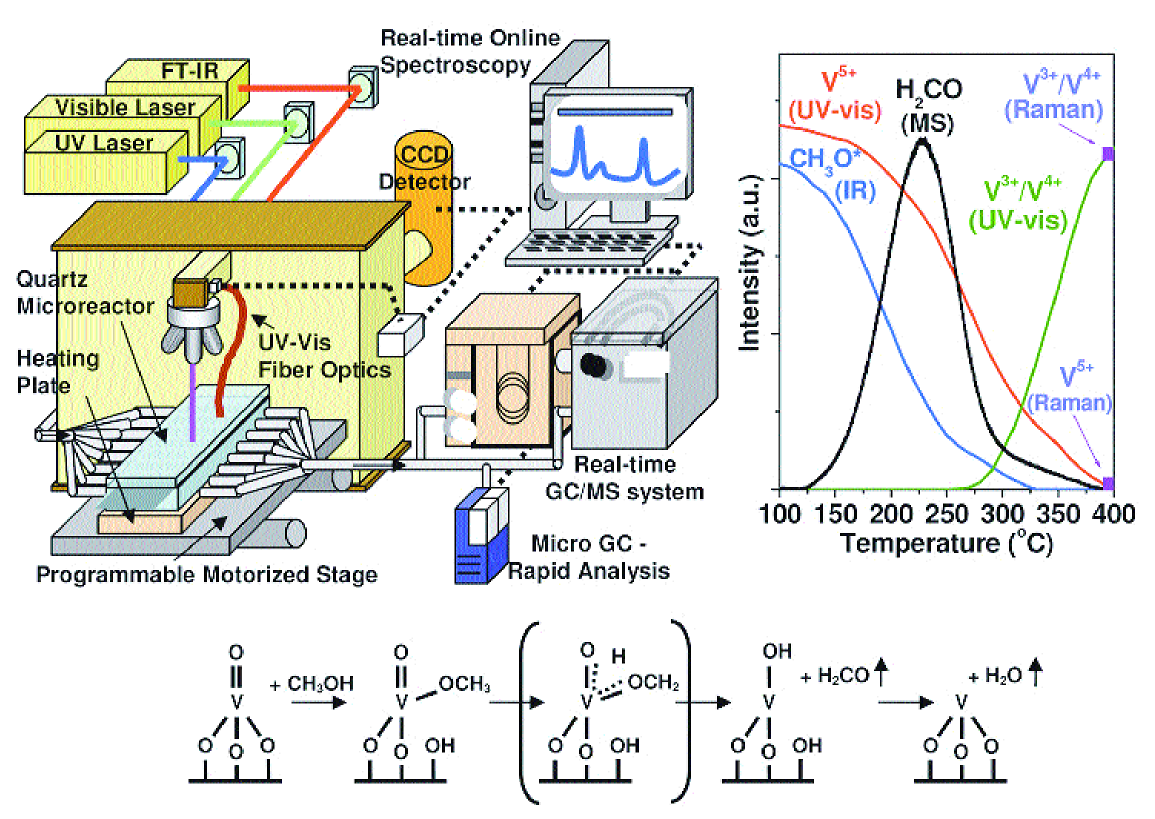


2.2% Pd/SiO_2
Standard preparation
$d_{av} = 55$ Å

2.2% Pd/SiO_2
Optimized preparation
$d_{av} = 16$ Å

Figure courtesy of J. Regalbuto.

Figure 6.7. *In-operando* Spectroscopic Approach to Establishing Molecular/Electronic Structure.
(Catalytic Activity/Selectivity Relationship, courtesy of I.E. Wachs)



Several comprehensive texts review the characterization methods for a host of catalytic materials and applications. These include the Encyclopedia of Catalyst Characterization [Brundle et al., 1992], Spectroscopy in Catalysis [Niementsverdriet, 2000], and Characterization of Catalytic Materials [Wachs, 1992].

Sampling of the gas phase for reactant and product compositions is easily accomplished for common laboratory reactors at atmospheric pressure using gas of liquid chromatography. If the catalyst is deployed in an ultrahigh vacuum setting, mass spectrometers can be used. In a combinatorial setting, a thermal imager may be employed to make parallel measurements of catalytic activity for exothermic or endothermic reactions. Mass spectrometers can also be employed to rapidly scan an array of samples.

A state-of-the-art system for *in-operando* characterization is shown in Figure 6.7. It consists of simultaneous Fourier Transform IR, visible and UV of the catalyst surface, and mass spectroscopy of the reactor effluent. Applied to study the methanol conversion to formaldehyde, the system permits the observation of, not only catalyst intermediates and products, but also catalyst sites. In this case, the changes of the species and catalytic sites are observed as the temperature is increased. From such data, catalytic mechanisms such as those shown in Figure 6.7 can be derived. Raman spectroscopy would enable simultaneous identification of reactive intermediates and measurement of kinetic phenomena [Shao, Adzic, 2005].

Characterization in liquid phase reactions is much more difficult. In these systems, catalytic conversion of biomass-derived molecules to fuel products involves a combination of catalytic steps on solid surfaces and/or enzymes coupled to solution-phase reactions facilitated by H+ or OH-. The lack of information regarding the reactive intermediates involved in these transformations complicates characterization. Classical UHV surface techniques that utilize electron spectroscopies are inappropriate for studies in the aqueous phase because of excessive absorption and scattering of the ejected electrons. Moreover, the vibrational technique IR spectroscopy can suffer from excessive absorption of IR radiation by water. Development of surface-sensitive in-situ spectroscopic tools that are capable of identifying reactive species on catalyst surfaces in aqueous solution are needed. Techniques such as surface enhanced Raman spectroscopy and, in particular, attenuated total reflectance IR spectroscopy may find broad application in this arena [Ortiz-Hernandez, Williams, 2003, McQuillan, 2001, Ferri, Burgi et al., 2001, Ferri, Burgi et all, 2002]. In addition, transient methods to interrogate reaction dynamics at the solid-solution interface should be developed to relate catalyst structure to reactivity. Electro-analytical methods combined with surface spectroscopy would enable simultaneous identification of reactive intermediates and measurement of kinetic phenomena (Shao, Adzic, 2005).

The structure of heterogeneous catalysts and conformation of enzyme catalysts are affected by solution pH, ionic strength, surfactants, impurities, temperature, etc. For example, a supported bimetallic catalyst may experience segregation of the metals, dissolution of the support, disruption of the metal-support interface, and migration of metal particles depending on the nature of the aqueous environment at the interface. Moreover, trace impurities present in biomass feedstocks may selectively poison catalyst surfaces or denature enzyme catalysts thus deactivating the system. For example, polyphenolic structures of lignin and tannin may inhibit catalytic activity by binding to the inorganic or biological catalysts. *In-situ*

Figure 6.8 X-ray absorption near edge spectra of Ru samples as prepared in air (b-e), and following treatment with 40 atm H_2 saturated water at 473 K (g-j); (a) RuO_2 powder, (b,g) Ru/Al_2O_3, (c,h) Ru/C, (d,i) Ru/TiO_2, (e,j) Ru/SiO_2, (f) 17.6 wt% Ru/Al_2O_3 reference sample. Spectra are offset for clarity.

From Ketchie, Maris and Davis [2007], with permission from Elsevier.

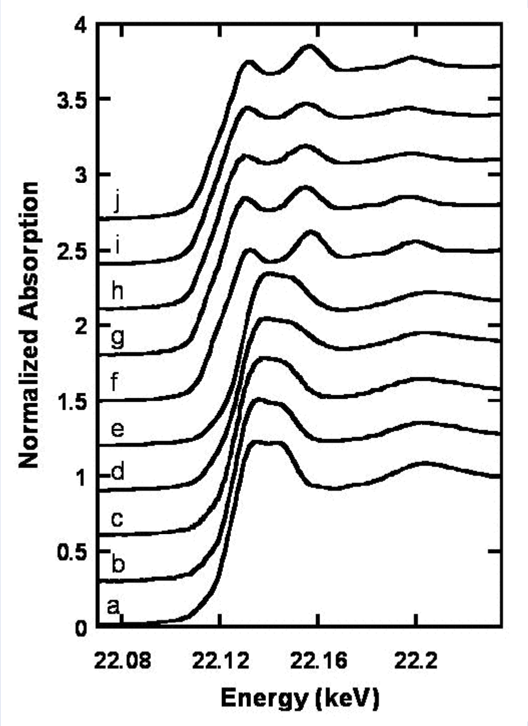


Figure 6.9 Radial structure functions (Fourier transforms of EXAFS) from supported Au-Pd nanoparticles (not corrected for phase shifts) with non-linear least squares fits for bimetallic AuPd catalyst (A) Pd (Pd-Pd and Pd-Au shells) and (B) Au (Au-Au and Au-Pd shells). Data were collected at ambient conditions. From Ketchie, Murayama and Davis [2007], with permission from Elsevier.

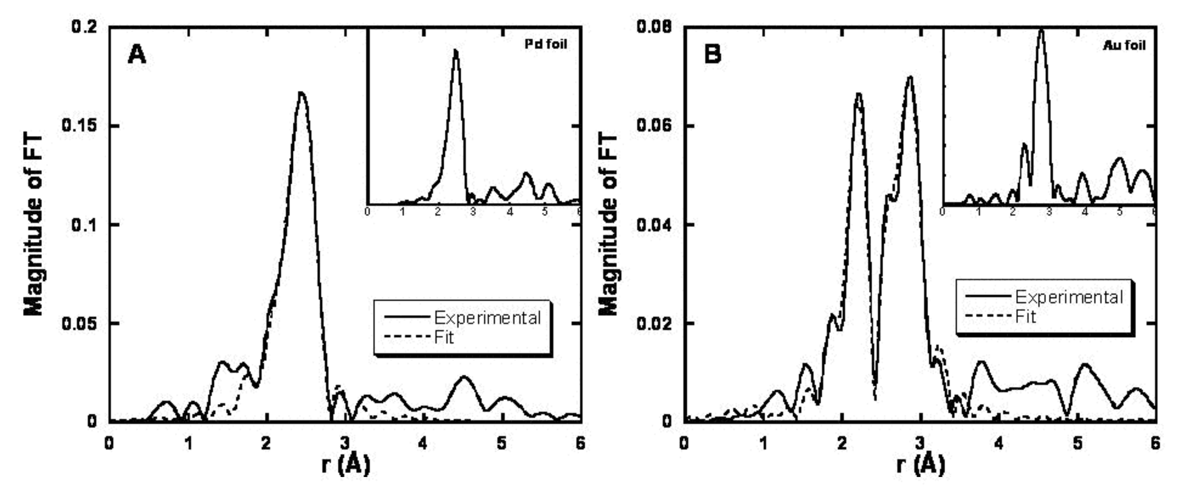
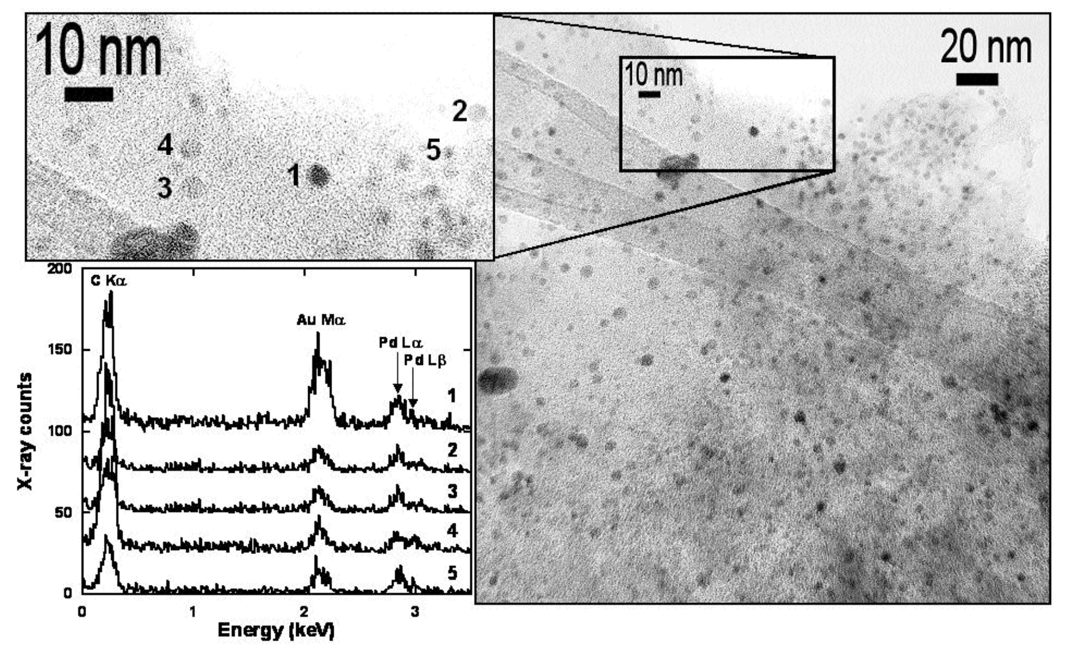


Figure 6.10 Electron micrograph of AuPd bimetallic catalyst with EDS spectra of individual particles (numbers correspond to the particle directly to the right of the number). Spectra are offset for clarity. From Ketchie, Murayama and Davis [2007], with permission from Elsevier.



spectroscopic, scattering and imaging tools need to be developed that allow for real-time monitoring of catalyst structure at the nanometer level. High energy X-ray methods are particularly suitable for studying the structure of catalysts in water [Maris, Ketchie, et al., et al., 2006, Ketchie, Maris et al., 2007, Ketchie, Murayama , et al., 2007, Maris, Ketchie, et al., 2007]. For example, the near edge spectra associated with the K edge of various supported Ru catalysts in air and in liquid water containing hydrogen are shown in Figure 6.8 (previous page). The spectra of the catalysts in air are similar to that of RuO_2 powder, indicating that the supported ruthenium samples were completely oxidized upon exposure to air, regardless of the support. The treatment in H_2-saturated water solution at $473^{o}K$ was sufficient to reduce the oxide to Ru metal.

Combining catalyst characterization results from X-ray spectroscopy with those from analytical electron microscopy is a powerful method to examine multi-component materials. The analysis of a carbon-supported bimetallic Au-Pd catalyst used for glycerol oxidation illustrates the utility of this approach. Figure 6.9 shows the radial structure functions associated with Pd and Au in supported bimetallic catalysts prepared by deposition of Au onto Pd nanoparticles. The results from analysis of the extended X-ray absorption fine structure confirm the selective deposition of Au onto Pd without disruption of the Pd particles. Figure 6.10 presents an electron micrograph together with the EDS spectra for five individual particles of the bimetallic sample, all of which indicate the presence of both Au and Pd, which is consistent with the results from X-ray absorption spectroscopy. Next-generation electron microscopes that allow for imaging of nanometer-sized features in thin liquid layers are needed to explore the structural changes of catalysts in aqueous environments.

The number of active sites in a catalytic material can be determined by estimates of particle size from electron microscopy or by chemical titration methods such as chemisorption or temperature programmed desorption. From detailed characterization of the number of active sites, qualitative, and at times even quantitative, correlations can be derived between the structure and chemical composition of a catalyst and its activity and selectivity. Beyond these correlations, great advances have been made in computational catalysis, which impart an even more detailed understanding of catalyst function.

6.6 COMPUTATIONAL CHEMISTRY

Computational chemistry is a truly cross-cutting tool for the development and optimization of biofuels production reactions. Computational chemistry has shed light on many aspects of traditional fuel production with heterogeneous catalysts. Such calculations have provided microscopic insights into several important areas, including: reactant adsorption-diffusion; chemical reaction and transition state control; and product diffusion-desorption. All of these insights lead to new understanding about the factors that control selectivity in these processes. So too will it be with the burgeoning biofuel production industry. Computational chemistry methods (existing and to-be-developed) can provide new molecular understanding for virtually all stages of biomass-to-biofuel processing.

In the remainder of this section, we describe: the kinds of problems computational chemistry can address today (with examples); the special needs and challenges faced in the computational study of biomass refining; the near-term opportunities for computational chemistry in this area; and finally, the long-term challenges/opportunities that should be pursued in order to fully illuminate the molecular processes involved in making biofuels.

6.6.1 Present Computational Approaches

Quantum Chemistry: Computational chemistry can be broken up into two broad categories: (i) quantum chemical calculations and (ii) classical molecular simulations. Quantum chemical calculations are important for accurately predicting the reaction energies and barriers associated with bond-breaking and bond-making. One typically identifies relatively few important configurations – reactant, transition state, product or intermediate – and computes accurate electronic energies and vibrational frequencies for use in harmonic estimates of equilibrium constants and rate coefficients. These quantities are then fed into micro-kinetic models that predict the time-dependent concentrations of observable species for comparison with experiment [Kandoi, Greeley et al. 2006].

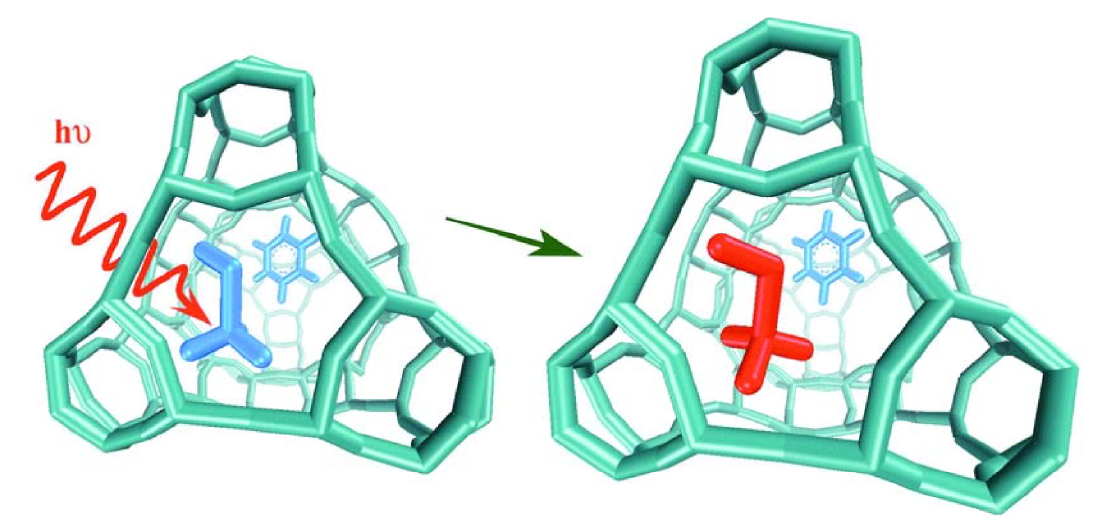
The Hartree-Fock approach provides a useful benchmark theory for quantum chemistry. This approach applies the Pauli exclusion principle exactly, while treating electron-electron repulsions only within mean field theory. The difference between the exact (non-relativistic) energy and the Hartree-Fock energy is defined as "correlation energy," which tends to be important for predictive treatments of reaction kinetics. The most popular method for estimating correlation energy nowadays is density functional theory (DFT), because the electron density is a simpler property than the full many electron wavefunction. Also, theorists have managed to find ways to bundle correlation energy into ever more sophisticated "exchange-correlation potentials" such as that used in the B3LYP approach [Kohn, Becke et al. 1996].

Molecular simulations are applied to systems such as liquids, which exhibit many configurations with nearly equal energy, hence amounting to a calculation of the system entropy [Frenkel and Smit 1996]. Molecular simulations have been applied to understanding the thermo-physical properties of liquids and gases, on their own or in bulk mixtures [Stubbs, Chen et al. 2001]. Simulations have also been performed to study inhomogeneous fluids in contact with solid surfaces such as carbons [Alba-Simionesco, Coasne et al. 2006] and zeolites [Saravanan and Auerbach 1998; Smit and Krishna 2003]. Non-equilibrium simulations have been performed to model mass-transport in nanopores [Maginn, Bell et al. 1993] and microwave heating of zeolites [Blanco and Auerbach 2002; Blanco and Auerbach 2003].

The two main simulation approaches are molecular dynamics (MD) and Monte Carlo (MC). MD is simpler to implement, although it requires not just the potential energy, but also the derivative of the potential (i.e. the force vector). This vector is used to numerically integrate Newton's classical equation of motion. Given the force vector and a system time step, updating the state of the system is trivial, using some integration algorithm such as "velocity Verlet." This approach is particularly convenient for modeling the collective motions of fluid systems, because every particle in the system moves during each MD time step. However, MD suffers from serious time-scale limitations because keeping the algorithm stable requires relatively small time steps, on the order of femtoseconds, limiting most MD runs to nanoseconds.

MC is not limited by time steps in the same way as MD because MC does not numerically solve a differential equation (as does MD). Instead, MC provides stochastic sampling of the fluctuations in a given ensemble such as the canonical or grand

Fig 6.11 Microwave driven zeolite. Figure courtesy of S. Auerbach



canonical ensembles. The main problem with MC is that it requires the modeler to concoct ways of updating the system, which for highly coupled systems such as polymers can be difficult to divine. For example, MC moves of one atom at a time may work well for an atomic fluid, but for a molecular or polymeric fluid, most such moves will be rejected, leading to inefficient sampling of states. Methods such as configurational-bias MC were invented to improve sampling of alkanes in zeolites and polymers in bulk [de Pablo, Yan et al. 1999]. As yet, no method exists to sample the wholesale fluctuations of three-dimensional networks such as amorphous silica.

Auerbach and coworkers have applied non-equilibrium molecular simulations to explore energy distributions that arise during microwave (MW) heating of zeolite-guest systems [Blanco and Auerbach 2002; Blanco and Auerbach 2003]. Experiments suggest that MW-heated zeolites behave in ways that are qualitatively different from conventionally heated zeolites. Auerbach and coworkers have found from their molecular simulations that such "MW effects" can occur because of selective heating, wherein a portion of the system is excited by the MWs and becomes hot, while the rest of the system remains relatively cold (Fig. 6.11). Quasi-elastic neutron scattering experiments are underway to test the microscopic predictions of Auerbach's simulations.

■ 6.6.2 Biomass Refining: Special Needs and Challenges

In comparison with atomistic modeling of petroleum refinement, biomass refining poses special needs and challenges. These can be categorized as pertaining to: (i) solid biomass substrate and (ii) oxygenated compounds.

SOLID BIOMASS SUBSTRATE: In contrast with petroleum, which is a liquid albeit a viscous one, biomass is solid, which poses certain mass transport limitations on attempts to react biomass. If computational chemistry is to provide a deeper understanding of biomass refinement, the first challenge is to provide a microscopic picture of the solid state of cellulose, hemicellulose, and lignin,

COMPUTATIONAL CATALYSIS

Simulating catalytic reactions in the liquid phase presents a number of challenges due to poor understanding of the structure at the aqueous/metal interface, the number of potential reaction intermediates and reaction pathways, and the dynamics of the interface under reaction conditions. Recent theoretical calculations by Desai, Sinha and Neurock [Desai 2003; Desai and Neurock 2003; Sinha, in preparation] have shown that the solution phase can actually stabilize charged transition states in some reactions and can even directly participate in the reaction. Shown here is the lowest energy transition state for the initial hydrogenation of the $C=O$ bond of formaldehyde over a palladium metal surface in the presence of an aqueous solution. Computational catalysis of this sort will complement experimental efforts and begin to suggest potentially more active and selective materials.

The transition state for the hydrogenation of formaldehyde over Pd(111) in aqueous solution. Water molecules were removed to help visualize the surface reaction.

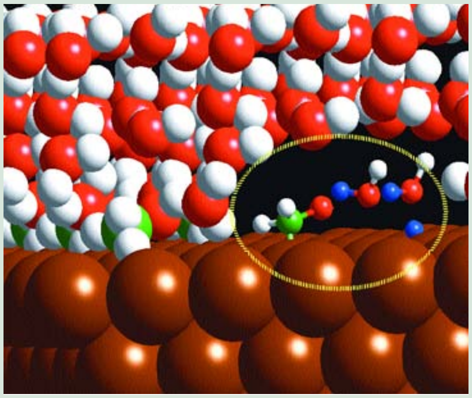


Figure courtesy of M. Neurock.

and how these materials interact. A second challenge is to provide an understanding of how to liquefy, dissolve, and/or vaporize this solid phase without forming excess coke.

OXYGENATED COMPOUNDS: In contrast with petroleum processing, which mostly involves transformations of hydrocarbons (with some trace amounts of sulfur and lead), biomass processing involves the daunting task of removing large amounts of oxygen from biomass-derived feedstocks. This fact has several consequences. First, many of the relevant reactants, intermediates and products of biomass refinement do not have widely tabulated thermodynamic properties, making it difficult to apply the full power of thermodynamic analyses on biomass refining. Second, because of the chemical and thermal instabilities of carbohydrates (relative to hydrocarbons) the processing of biomass-derived species might best be confined to the liquid phase [Chheda and Dumesic 2007]. Any deep understanding of such processing will have to account for solvent effects in addition to the already challenging study of reaction kinetics and catalysis. Third, to avoid complexities associated with liquid phase processing, some researchers are pursuing fast pyrolysis for gas phase processing (and concomitant gas phase modeling). But alas, there is no free lunch, as fast pyrolysis involves strongly non-equilibrium systems.

Gasification of biomass to syngas (CO/H_2) followed by Fischer-Tropsch catalysis is yet another avenue for refining biomass. While still challenging to model by computational chemistry, this approach applied to biomass presents no qualitatively new challenges to molecular modeling, and as such is not discussed further in this section.

In summary, modeling the atomic-level details of biomass processing will require methods that treat: (i) solid substrates; (ii) heretofore uncharacterized oxygenated molecules; (iii) solvent effects in reactions; and (iv) strongly non-equilibrium systems. We note that with the exception of item (ii), these tasks represent "grand challenges" for present-day methods in computational chemistry. As such, significant method development is required for computational chemistry to fully illuminate the atomic-level details of biomass refinement.

6.6.3 Near-Term Opportunities for Computational Chemistry of Biomass Refining

Based on the capabilities of present-day computational chemistry methods, and the particular technological challenges posed by the biomass refining problem, several near-term opportunities exist for computational chemistry to provide fundamental insights into biomass refining. In this section, we outline four specific areas.

6.6.3.1 Calculating Thermodynamic Properties

Thermodynamics provides the foundation for nearly all branches of science and engineering, specifying the constraints of energy conservation and maximal work. For the burgeoning field of biomass refining to be as successful as possible, all possible thermodynamic information must be available for the wide variety of oxygenated compounds likely to arise as reactants, products, and intermediates of the refining process. Quantities such as enthalpies and entropies of formation, and also heat capacities over wide temperature ranges, must be tabulated and made available to the community at large. The first challenge will be agreeing on a useful standard state for these thermodynamic quantities. For example, glucose is a solid, dimethyl ether is a gas, and ethanol is a liquid at standard state. For computational chemistry, gas phase is the most convenient standard state because one avoids the challenge of computing liquid and/or solid equations of state. However, this may not be the most convenient for use by synthetic chemists, reaction engineers and biorefiners. Despite these issues, computational chemistry should be able to contribute important information to help characterize the thermodynamic states of esoteric oxygenated molecules, if only in the gas phase. This might take the form of an expanded "G2-like" database [Curtiss, Raghavachari et al. 1991], which uses a hierarchy of basis sets and levels of theory to provide heats of formation and Gibbs free energies of formation to within 1 kcal/mol (i.e., "chemical") accuracy.

6.6.3.2 Molecular Simulations of Biomass Components

Providing microscopic insights into the structure, dynamics and phase behavior of cellulose, hemicellulose and lignin may facilitate breakthroughs in our ability to refine these biomass components. Because cellulose is a crystalline material, it is amenable to molecular modeling with atomistic detail [Morrison, Chadwick et al. 2002] by analogy with metals and zeolites. Existing forcefields such as AMBER and CHARMM, used for modeling biomolecules such as proteins and nucleic acids, should be readily applicable to cellulose. Computing solid-fluid phase diagrams in the presence and absence of solubilizing species would yield useful information.

In contrast to cellulose, hemicellulose and lignin are both amorphous materials, making atomistic modeling much more challenging. Because much less is known about the structures of these components, and how they interact, coarse-grained modeling would still yield interesting insights into the network connectivities and stabilities of these biomass components. Along these lines, coarse-grained modeling has recently shed some light on silica polymerization to form nanoparticles that are precursors to zeolite growth [Jorge, Auerbach et al. 2005; Jorge, Auerbach et al. 2006]. The three-dimensional network formation in lignin bears resemblance to that of amorphous silica.

6.6.3.3 Thermo-Physical Modeling of Bio-Oil

Bio-oil is a catch phrase for unrefined, liquefied biomass. It can result from fast pyrolysis, high pressure liquefaction, or other means. It is a very complex fluid with hundreds of components, and as a result, very poorly understood thermo-physical properties. Modeling of diffusion and phase behavior of bio-oil could yield interesting insights facilitating its subsequent refinement. Simpler models of bio-oil, containing many fewer components, would have to be developed for use in molecular simulations. Such models could inspire the development of simple bio-oil standards, allowing various laboratories to compare refinement results in meaningful ways.

6.6.3.4 Micro-Kinetic Modeling of Gas-Phase Refining of Biomass-Derived Feedstocks

As a first step towards modeling of solution-phase catalytic processing of biomass-derived feedstocks, modeling the gas-phase refining would yield useful baselines of catalytic activity in the absence of solvent. Indeed, the best way to learn about the effect of a solvent is first to omit it from the model, then later include it and compare the effects. The initial gas phase calculation would yield mechanistic insights that later could be updated by new methods that treat solvent effects as well. This could be applied to the catalytic processing of biomass-derived feedstocks reported by Dumesic and coworkers.

6.6.4 Long-Term Opportunities for Computational Chemistry of Biomass Refining

The holy grail of molecular modeling for biomass refining involves three main application areas: (i) modeling lignocellulose assembly/disassembly, (ii) modeling fast pyrolysis in the absence and presence of catalysts, and (iii) modeling liquid-phase catalytic refining of biomass.

6.6.4.1 Modeling Ligno-Cellulosic Structure and Dynamics

Molecular simulations of lingocellulosic structure and dynamics will require the development of new multi-scale approaches, able to resolve chemical reactions at the atomic scale, while simultaneously treating amorphous structures at nano-scales. This may also require the development of novel reactive simulation methods such as reactive Monte Carlo [Johnson 1999] to account for hydrolysis of carbohydrate chains.

Modeling fast pyrolysis is crucial for providing microscopic insights into the complex chemistry under these rapid heating conditions. This presents another great challenge for computational chemistry because of the strongly non-equilibrium nature of this process. In particular, it is not obvious that transition state theory (TST) applies under such conditions, or even if the concept of temperature remains meaningful at all. TST assumes that all system degrees of freedom remain in thermal equilibrium (i.e., in the canonical ensemble) as the reaction coordinate passes from reactant, through the transition state, and on to product. For systems undergoing heating as rapid as 1000°Celsius per second, as happens during fast pyrolysis, it is unlikely that such an assumption remains valid. Molecular simulations with reactive forcefields, and *ab initio* (Car Parrinello) molecular dynamics [Kuo, Mundy et al. 2004], may yield insights into energy distributions that arise during fast pyrolysis of biomass. Such simulations could be performed on models of bare biomass, and on models that include catalysts such as metals or zeolites.

6.6.4.2 Modeling Solvent Effects in Liquid-Phase Processing

As discussed above, present-day computational chemistry breaks up into two kinds of calculations: accurate calculations of energies for few configurations (chemical interactions), and rather more approximate calculations of energies for many configurations (physical interactions). It remains challenging to model simultaneously coupled chemical and physical effects, such as liquid phase catalytic processing of biomass studied by Dumesic and coworkers, involving biomass-derived molecules such as sugars in aqueous solution reacting in the presence of metal catalysts. Multi-scale computational methods need to be developed to approximate such complex catalytic systems. For example, one could imagine running a DFT calculation on a reactive catalytic system embedded in a classical model of a solvent. Such embedding schemes are now becoming relatively commonplace [Sillar and Purk 2002; Fermann, Moniz et al. 2005]. One could compute minimum energy reactions paths for several fixed solvent configurations to search for solvent effects in the reaction. These calculations appear daunting at present, but will become more feasible with both algorithmic developments and improved computational resources.

While biomass refining remains a series of complicated and poorly understood processes, there is much room for computational chemistry to shed light on and improve the efficiency of such refining. Through the judicious choice of model systems, and the development of new methods, computational chemistry can shed much light on how biomass is refined today, and how it should be refined in the future.

6.7 RECOMMENDATIONS

The cross-cutting scientific needs dealt with in this chapter are summarized in the following recommendations:

- Build an analytical database for biomolecules.
- Compile, by experiment and theory, the key thermodynamic properties of biomolecules.
- Identify prototypical reactant biomolecules as well as lumps of molecules, and prototypical catalysts.
- Discover and develop novel multiphase reactors.
- Engineer catalysts on the micro and macro scales for improved activity and stability, particularly for the demanding liquid phase environment.
- Develop *in-operando* and atomic-scale catalyst characterization methods, particularly for the liquid phase.
- Develop computational methods for gas and liquid phase reactions involving solid biomass substrates and oxygenated compounds.

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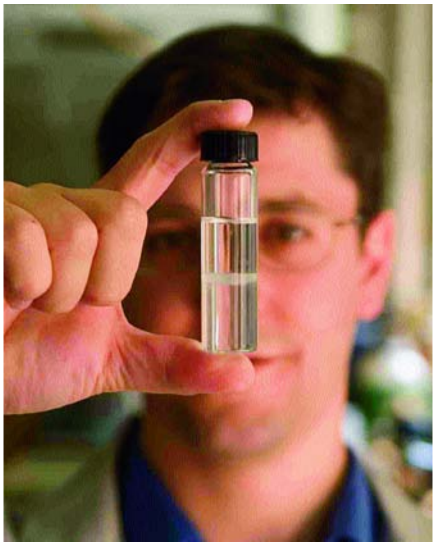

INVITED PARTICIPANT BIOGRAPHIES

Scott M. Auerbach

Scott Auerbach is a theoretical chemist at UMass Amherst, having earned a PhD in physical chemistry at UC Berkeley in 1993. He earned his BS (Summa cum Laude) in chemistry from Georgetown University in 1988, and was an NSF postdoctoral fellow at UC Santa Barbara in chemistry and materials during 1994-1995. Since his arrival at UMass Amherst in 1995, Auerbach has been modeling adsorption, diffusion and reaction in zeolites, as well as self-assembly of zeolites, all with a variety of atomistic modeling methods. The goal of Auerbach's research is to offer a powerful microscope into the factors that control selectivity in shape-selective processes mediated by zeolites. This effort has yielded two books, nearly 70 peer-reviewed articles, over 85 invited lectures, and $1.8MM of extramural research funding.

Two of Auerbach's research areas that are most relevant to biofuel production are microwave processing and functionalized materials. Microwave processing offers the potential to revolutionize both the fabrication and use of heterogeneous catalysts. Despite several reports of remarkably short reaction times using microwaves, controversy remains regarding the actual effects of such microwaves. Auerbach applied molecular modeling to show that non-equilibrium energy distributions are possible and even likely outcomes of using microwaves, especially when ions and dipoles can absorb the radiation. This is especially promising for pre-treatment and reactions of biomass, which contains significant oxygen, making biomass-derived feedstocks highly polar species.

The second biofuel-related area of Auerbach's research is study of shape-selective basic catalysts. Such catalysts are important for controlling carbon-carbon bond-forming reactions of biomass-derived feedstocks. Auerbach has applied periodic density functional theory to show that amine-substituted zeolites may be good candidates for shape-selective basic catalysts. Future research will explore the mechanisms of addition and condensation reactions using such zeolites, and the role of such zeolites during catalytic fast-pyrolysis.

Paul Blommel

Paul Blommel is a lead catalysis researcher at Virent Energy Systems, Inc. He received a bachelor's degree in chemical engineering in 1993 and a doctorate in biophysics in 2007 from the University of Wisconsin, Madison. Between 1993 and 2001, Blommel worked for UOP, conducting research and starting up a diverse number of oil refining, petrochemical, and hydrogen generation processes. His doctoral work focused on high throughput protein production and the characterization of enzyme catalysts. At Virent, he directs research on catalytic upgrading of bio-sourced feedstocks into valuable products.

A. A. Boateng

A. A. Boateng is a research scientist with the Agricultural Research Service (ARS), the intramural research arm of the USDA. He started the ARS thermo chemical program in 2003 and is a lead chemical engineer on their efforts to develop on-farm biorefinery systems for agricultural residues including energy crops. His prior experiences include academic positions at the University of Guyana in South America and at Swarthmore College in Pennsylvania. In 1988 he was faculty Fulbright Fellow from the Caribbean region at the Department of Chemical Engineering, Kansas State University, where he continued his research on the combustion and gasification of rice hulls including the use of rice hull ash as a pozzolan for cement extension. His industrial experiences include process design and operation of high-temperature industrial furnaces used for minerals and materials processing. He spent 10 years in that industry optimizing confined turbulent diffusion flames and the modeling of particulate flows in such operations. He is the author of the book: Rotary Kilns – Transport Phenomena and Transport Processes by Butterworth-Heinemann publishers. He holds a PhD from the University of British Columbia.

André Boehman

André Boehman is a Professor of Fuel Science and Materials Science and Engineering in the Department of Energy & Mineral Engineering in the College of Earth and Mineral Sciences at the Pennsylvania State University, where he has taught courses on Energy, Fuels, Combustion and the Environment since 1994. He holds a BS in Mechanical Engineering from the University of Dayton (1986) and an MS (1987) and PhD (1993) in Mechanical Engineering from Stanford University. He held a two-year postdoctoral fellowship in the Molecular Physics Laboratory at SRI International, Menlo Park, CA.

Prof. Boehman's research interests are in alternative and reformulated fuels, combustion and pollution control. His present research activities are focused on alternative diesel fuels, diesel combustion and diesel exhaust aftertreatment. He was recently appointed the Editor of the journal Fuel Processing Technology and has held executive positions with the American Chemical Society Division of Fuel Chemistry and with the International DME Association. He has received the 2007 Faculty Mentoring Award from the Penn State College of Earth and Mineral Sciences, the 1999 Alumni Achievement Award from the University of Dayton School of Engineering, the 1999 Matthew and Anne Wilson Award for Outstanding

Teaching from the Penn State College of Earth and Mineral Sciences and the Philip L. Walker Jr. Faculty Fellowship in Materials Science and Engineering, from 1995-97. He also received the 1986 Charles T. Main Bronze Medal from the American Society of Mechanical Engineers. He has supervised seventeen MS theses and six doctoral theses at Penn State and he has published more than 40 refereed papers and book chapters. At the Penn State Energy Institute, Prof. Boehman manages the Diesel Combustion and Emissions Laboratory.

Robert C. Brown

Dr. Robert C. Brown is the Bergles Professor in Thermal Science at Iowa State University. He holds the rank of Professor in the Departments of Mechanical Engineering, Chemical and Biological Engineering, and Agricultural and Biosystems Engineering. He is the director of the Biorenewable Programs and the Center for Sustainable Environmental Technologies. Dr. Brown is an expert in thermochemical processing of biomass into energy, fuels, and chemicals. His research in biomass gasification includes studies of carbon conversion, tar measurement and control, hot gas clean-up (particulate matter and inorganic contaminants), hydrogen production, and synthesis of renewable fuels and other biobased products using catalytic and biocatalytic processes. His research in fast pyrolysis includes studies on the evolution and transport of pyrolysis vapors and aerosols, selective condensation of pyrolysis liquids, catalytic and biocatalytic conversion of pyrolysis liquids into fuels and fertilizer, utilization of char byproduct as soil amendment and carbon sequestration agent, and power systems based on pyrolysis liquids. Dr. Brown also performs techno-economic analysis of bioenergy and biofuel systems. In 2003 he published Biorenewable Resources: Engineering New Products from Agriculture, a textbook for students interested in the Bioeconomy. Dr. Brown is a Fellow of the American Society of Mechanical Engineers.

Steven Chuang

Steven Chuang is a professor in the Department of Chemical and Biomolecular Engineering at the University of Akron, Akron, Ohio. He received a Ph.D. in Chemical Engineering from University of Pittsburgh and joined the University of Akron in 1986. His research interest is in the area of catalysis and reaction engineering. His research primarily involves use of in situ infrared spectroscopy and mass spectroscopy to characterize adsorbed species and intermediates under reaction conditions. His current research effort focuses on the development of anode catalysts for the direct hydrocarbon and coal solid oxide fuel cells as well mechanistic studies of photocatalytic reactions, partial oxidation, and CH4 reforming reactions.

Anthony M. Dean

Tony Dean is the W. K. Coors Distinguished Professor in the Chemical Engineering Department of the Colorado School of Mines. He received his bachelor's degree from Spring Hill College and his masters and doctorate in physical chemistry from Harvard University. He joined the Chemistry Department of the University of Missouri-Columbia in 1970, where his research focused on shock tube studies of elementary combustion-related reactions. In 1979 he moved to the Corporate Research Labs of Exxon Research and Engineering, where his efforts focused on the quantitative kinetic characterization of gas-phase reaction systems. In particular, methods were developed to quantitatively characterize both the temperature and pressure dependence of chemically-activated reactions. Detailed kinetic mechanisms were developed and used to develop improved-fuel/advanced-engine concepts to improve efficiency and decrease emissions of internal combustion engines. He joined the CSM faculty in 2000.

At CSM the efforts of his research team focus on the quantitative kinetic characterization of a variety of reaction systems. One such area involves the reactions that occur in high-temperature solid-oxide fuel cells (SOFCs). Gas-phase reactions in the fuel-channel produce intermediates that can profoundly influence fuel cell performance. We seek to understand the detailed chemical pathways that lead to production of the smaller hydrocarbons as well as the molecular weight growth processes that can lead to deposit formation within the anode channels. We also characterize the catalytic reforming kinetics occurring within the porous anode. These reactions are strongly influenced by multiple transport processes including diffusion and reaction of the gaseous hydrocarbons as they migrate through the porous anode. We then include these gas-phase and catalytic reactions, as well as the accompanying electrochemical reactions, into complete fuel cell models that can be used to characterize and optimize SOFC performance.

Another research area, in conjunction with NREL researchers, concerns the production of fuels and power from biomass. The specific thrust of much of this research is to transfer our learnings of free radical chemistry in hydrocarbon systems to biomass systems, especially in the context of the quantitative impact of the weakening of adjacent C–H bonds by the oxygen functionalities in biomass.

Mark Dietenberger

Mark Dietenberger is a Research General Engineer with USDA Forest Service at Forest Products Laboratory in Madison Wisconsin. He received a bachelor degree in Applied Mathematics and Physics at UW-Milwaukee in 1974 and Ph.D. degree in Mechanical Engineering at University of Dayton in 1991, with an emphasis in heat and mass transfer including specialization in combustion. During 1975 to 1992 with the University of Dayton Research Institute he developed specialized computer models that include ice/frost formation on aircraft and space shuttle, air blast propagation over complex terrain, reconstruction of airplane crashes in severe weather, impact damage of various metals and ceramics during armor piercing, heat pipe performance for use in space, and three-dimensional fire growth on an upholstered furniture. After receiving his Ph.D., he won an AFOSR grant to study active control of combustion approaching stoichiometric conditions in a turbine engine. He also developed a computer program to analyze kinetically the thermal destruction of toxic gases.

Since 1992 he became responsible for fire growth research at Forest Products Laboratory. In this capacity he worked with various fire test equipments, improving their performance, developing new hardware, and modifying test protocols. Many in wood industry now consider him as their foremost expert in fire growth modeling and experimentation involving wood products, particularly with fire retardant treatments. His recent work on fundamentals of wood pyrolysis and combustion using specialized tests as performed in the cone calorimeter and oxygen bomb calorimeter resulted in invited presentations within the fire safety science and the thermal analysis communities. Most recently he is applying his fire growth modeling expertise to fire development on exterior building surfaces and ornamental vegetations for the wildland urban interface problems. His publications is provided on-line at http://www.fpl.fs.fed.us

His recent assignment to lead the thermo-chemical lignocellulosic conversion research acknowledges Dr. Dietenberger's expertise and reasserts the laboratory's historical leading role in the field. He has a patent pending on a new gasifier technology that promises to double or even triple the current productivity of syngas. He is currently member of the Int. Association of Fire Safety Science and Society of Fire Protection Engineers.

James A. Dumesic

James A. Dumesic earned his B.S. degree from UW-Madison and his M.S. and Ph.D. degrees from Stanford University. His Ph.D. work was conducted under the supervision of Professor Michel Boudart. Dumesic then conducted post-doctoral research as a U.S.-U.S.S.R. Exchange Fellow at the Institute of Chemical Physics in Moscow and as a NATO Postdoctoral Fellow at the Centre de Cinetique Physique et Chimique of France. Dumesic joined the Department of Chemical Engineering in 1976. He served two terms as department chair. He has been the Shoemaker Professor of Chemical Engineering, and he is currently the Steenbock Chair in the College of Engineering. Throughout his career, Dumesic has used spectroscopic, microcalorimetric, and kinetic techniques to study the surface and dynamic properties of heterogeneous catalysts. Dumesic pioneered the field of microkinetic analysis, in which diverse information from experimental and theoretical studies is combined to elucidate the essential surface chemistry that controls catalyst performance. He has developed microcalorimetric techniques to measure surface chemical bond strengths for adsorbates on metal, oxide, and acidic catalysts. He is actively involved in the use of electronic structure calculations to study the structures and reactivity's of adsorbed species on metal and metal oxide surfaces. Dumesic's research group is currently studying the fundamental and applied aspects of generating of hydrogen and liquid alkanes by aqueous-phase reforming of oxygenated hydrocarbons derived from biomass, as well as the production of intermediates for the chemical industry.

Dumesic has received a variety of awards and honors in the field of catalysis and chemical engineering. He has been recognized with the Colburn Award and Wilhelm Award from the American Institute of Chemical Engineers, the Emmett Award from the North American Catalysis Society, and research excellent awards from the New York and Michigan catalysis societies. In 1998, he was elected to the National Academy of Engineering. He has also been recognized for his excellence in teaching at the University of Wisconsin with a Polygon Award and the 1995 Benjamin Smith Reynolds Award. In 2002, he was given the Byron Bird Award in the College of Engineering for Excellence in a Research Publication, citing his work in the microkinetics of heterogeneous catalysis. His research accomplishments were recognized in 2003 by the Herman Pines Award of the Chicago Catalysis Society. He was named one of the Top 50 Technology Leaders of 2003 by Scientific American, and he received the 2005 Cross Canada Lectureship Award of the Canadian Catalysis Society. In 2006, he received the Somorjai Award for Creative Research in Catalysis from the American Chemical Society, and the Philadelphia Catalysis Club Award for excellence in catalysis research. In 2007, he was awarded the Burwell Lectureship in Catalysis by the North American Catalysis Society.

Dumesic has published more than 300 papers in peer-reviewed journals. Various information about research conducted by the Dumesic group can be found at the following link: http://www.engr.wisc.edu/che/

Douglas C. Elliott

Mr. Elliott has 33 years of research and project management experience in the Battelle system at the Pacific Northwest National Laboratory (PNNL). His work has mainly been directed toward development of fuels and chemicals from biomass and waste. His experience is primarily in high-pressure batch and continuous-flow processing reactor systems. This research has also involved him in extensive study of catalyst systems. In addition to process development, chemical and physical analysis has also been a significant part of his work. While at Battelle, Mr. Elliott's research has involved such subject areas as biomass liquefaction and hydroprocessing of product oils, catalytic hydrothermal gasification of wet biomass and wastewaters, and chemicals production from renewable sources. His work in biomass liquefaction has involved him in the International Energy Agency as a Task representative for the U.S. under the Bioenergy Agreement. He also spent the summer of 1989 under contract working at the Technical Research Centre of Finland in Espoo on oil production from black liquor.

Mr. Elliott is a listed inventor on 15 U.S. patents and numerous related foreign patents. In 2004 he was designated a Battelle Distinguished Inventor. He has been recognized two times with R&D 100 awards for development of notable new technologies and an award from the Federal Laboratory Consortium for Technology Transfer. He was a recipient of a Green Chemistry Challenge Award in 1999. He is the author of over 70 peer-reviewed journal publications and book chapters. In addition, he has made over 30 presentations at national and international meetings and conferences.

Calvin J. Feik

Calvin Feik is a senior engineer with the National Renewable Energy Laboratory (NREL) in Golden, Colorado and currently manages operation of the Thermochemical User Facility (TCUF). He has worked in thermochemical biomass conversion since starting at NREL in 1992 after receiving his Bachelors in Engineering from the Colorado School of Mines. His responsibilities have been in the design of unit operations and integration with automated control and data acquisition. He was instrumental in the development and upgrading of the Thermochemical Process Development Unit (TCPDU), a state of the art 1/2-ton/day pilot plant for the production of syngas and pyrolysis oils from biomass. Current research in the TCUF is focused on developing a catalytic process to remove tars from syngas formed during biomass gasification. Calvin has also been involved in the development of several bench scale systems for biomass conversion research.

Kristi Fjare

Kristi Fjare got her undergraduate degree in Chemistry from St. Olaf college in Minnesota and PhD in Inorganic Chemistry from the University of Minnesota working with Professor John Ellis.

Kristi has spent over twenty years in the petroleum and petrochemical industry, doing research on catalysis, support to manufacturing, and business development at Amoco, BP and ConocoPhillips. She is currently a Principal Scientist at ConocoPhillips in BioFuels R&D, with responsibility for thermochemical projects.

Manuel Francisco

Manuel Francisco received his BS from the Ohio State University in 1977. He attended the Massachusetts Institute of Technology from 1977 to 1981 as an NSF fellow and earned his PhD in Synthetic Organic Chemistrywith Professor George Buchi. After graduation, he joined Exxon Corporate Research Laboratory. Manuel's first seven years were focused on basic research in the conversion and upgrading of heavy oils, resids and bitumens. In 1988 he took a loan assignment at Exxon's Products Research Division and spent three and a half years in basic lubricant research.

Manuel returned to Corporate Research in 1992 then took another loan assignment to the Product Research and Technology Division where he spent a year and a half in applied lubricant research. He returned to Corporate Strategic Research in 2001 and since has worked on high throughput lubricant research and basic research in conversion and upgrading of heavy oils, resids and bitumens.

Anne M. Gaffney

Anne Gaffney joined ABB Lummus Global in 2005 and is currently the Vice President of the Technology Development Center in Bloomfield, N.J. In this role, Anne leads programs to improve upon existing technologies and to provide new innovations in support of the refining, petrochemicals, olefins and JV business groups.

Before joining ABB Lummus Global, Anne held senior technology roles at Rohm and Haas, DuPont and Lyondell in the areas of catalysis, process chemistry, selective oxidation, and materials synthesis & characterization. Anne is the author/co-author of over 100 patents/patent applications and over 50 technical publications. She has held leadership roles in ACS (Chair of the Petroleum Chemistry Division and the Catalysis Secretariat), the North American Catalysis Society (Chair of the 19th NAM and National Representative for the Philadelphia Catalysis Club) and the Organic Reaction Catalysis Society (Director and Editorial Board Member).

Anne received her bachelor's degree in chemistry and mathematics from Mount Holyoke College and her doctorate's degree in physical organic chemistry from the University of Delaware. She is the 2007 recipient of the Tribute to Women in Industry Award, the 2006 DOW/Union Carbide Reaction Engineering and Catalysis Seminar Series Award and the 1999 Catalysis Club of Philadelphia Award.

Dr. Santosh K Gangwal

Dr. Santosh K Gangwal is presently a senior chemical engineer with the Center for Energy Technology at Research Triangle Institute International, Research Triangle Park, NC. He received his PhD in chemical engineering from the University of Waterloo in Canada in 1977. Over the past 30 years, he has procured and successfully managed projects totaling more than $30 million. He is presently responsible for developing and managing projects in cleanup and conversion of biomass- and coal-derived syngas to fuels and alcohols. He is directing experimental studies for the synthesis of novel attrition resistant Fischer-Tropsch (FT) catalysts using a spray dryer and testing these catalysts in microreactor, CSTR and SBCR. He is also scaling up the FT catalyst to a barrel/day plant. He has evaluated modified base-metal oxide catalysts for synthesis of ethanol from methanol and/or syngas. He is also synthesizing novel FCC catalysts and developing a novel triple function FCC-type catalyst and reactor system to remove tar , ammonia, and H2S from biomass gasifier gas. He is also developing a nano-particle iron material for production of hydrogen from syngas via the steam-iron process and a nano-particle nickel hydrogenation catalyst. He is also developing CO2 sorbents for syngas as well as flue gas. He is also assisting in the development of a heterogeneous catalyst-based process for conversion of free fatty acids to biodiesel and has investigated the development of a process to convert vegetable oil to jet fuel.

Previously, he spearheaded the development of an internationally recognized syngas desulfurization program at RTI International that grew into the Center for Energy Technology. He developed fixed-bed, moving-bed and fluidized-bed desulfurization sorbents and ammonia decomposition catalysts. He scaled up a patented zinc oxide desulfurization sorbent to 10,000 lb for testing using a syngas slipstream from the Eastman Chemical Company gasifier. He also developed and tested mixed-metal oxide and carbon-based catalysts for demercaptanization and desulfurization of diesel and jet fuel and prepared and evaluated cobalt- and iron-based catalysts for Fischer-Tropsch synthesis at industrially relevant conditions for more than 20,000 hours. He also evaluated catalysts for deep catalytic oxidation of VOC mixtures and conducted sulfur balances around PC boilers to determine sulfur capture using lime-based materials. He has also been active in University teaching, having taught both undergraduate and advanced chemical engineering courses at University of Maine, University of New Hampshire, and North Carolina A&T State University. He won the prestigious R&D 100 award in 2004 for inventing and scaling up a desulfurization sorbent for syngas. He holds 10 US patents. He has published 45 refereed papers and made over 150 presentations in scientific conferences.

James G. Goodwin, Jr.

Professor James G. Goodwin, Jr., Professor and Chairman of the Department of Chemical Engineering at Clemson University, is an internationally recognized expert in the fields of heterogeneous catalysis and reaction kinetics. He is best known for his research in the areas of Fischer-Tropsch synthesis, the use of isotopic tracing to study reactions at the site level, and now biodiesel synthesis using solid acid and base catalysts. In 1976 he received his PhD in chemical engineering at the University of Michigan. After spending 18 months as an NSF-CNRS exchange scientist at the French Institute of Catalysis and 1 year as an assistant professor of engineering at the University of South Carolina, Professor Goodwin joined the University of Pittsburgh in 1979 where he rose in the ranks to become William Kepler Whiteford Professor of Chemical Engineering. In 2000, he moved to Clemson University to become Chairman of Chemical Engineering. Most of Professor Goodwin's 173 refereed scientific publications are related to supported metal and solid acid catalysis. He is also an author of 12 U.S. (1 pending) and 19 international (3 pending) patents in the area of Fischer-Tropsch synthesis. He has consulted extensively over the past 19 years with Altamira Instruments, Gas-to-Oil (Statoil), Energy

International (Williams), Hampton University, and the U.S. Department of Justice. Dr. Goodwin's research group is internationally known for the study of hydrocarbon catalysis and for the use of isotopic tracing (SSITKA) to study surface reactions. His current research focuses on biomass conversion (biomass gas clean-up, biodiesel synthesis, Fe Fischer-Tropsch synthesis), coal conversion (selective synthesis of ethanol from syngas), and the effect of impurities on PEM Fuel Cell operation.

George W. Huber

George W. Huber is an Assistant Professor of Chemical Engineering at University of Massachusetts-Amherst whose research focus is on Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels. He has authored 25 peer-reviewed publications including two papers in Science and three articles in Angewandte Chemie International Edition. He has five patent applications pending in the area of biofuels and has worked on catalysis projects for Exxon-Mobil, Conoco-Phillips, and Cargill. George's discovery of Raney-NiSn catalyst for hydrogen production from biomass-derived oxygenates was named as one of top 50 technology breakthroughs of 2003 by Scientific America. His research is being commercialized by two different start-up companies (Virent Energy Systems and Bio-e-con).

Prior to his appointment at UMass-Amherst George did a post-doctoral stay with Avelino Corma at the Technical Chemical Institute at the Polytechnical University of Valencia, Spain (UPV-CSIC) where he studied bio-fuels production using petroleum refining technologies. He obtained his Ph.D. in Chemical Engineering from University of Wisconsin-Madison (2005) where he helped develop aqueous-phase catalytic processes for biofuels production under the guidance of James A. Dumesic. He obtained his B.S. (1999) and M.S.(2000) degrees from Brigham Young University, where he studied Fischer-Tropsch Synthesis under the direction of Calvin H. Bartholomew.

Christopher W. Jones

Christopher Jones obtained his BSE degree in Chemical Engineering from the University of Michigan in 1995, followed by graduate studies at Caltech leading to MS and PhD degrees in 1997 and 1999, respectively. During his graduate studies at Caltech, his research activities spanned from the synthesis and characterization of new materials to zeolite catalysis. Following a postdoctoral year at Caltech studying organometallic chemistry and catalysis, he joined Georgia Tech as an Assistant Professor in Chemical Engineering in 2000. Today, he is an Associate Professor and the J. Carl & Sheila Pirkle Faculty Fellow in the School of Chemical & Biomolecular Engineering. At Georgia Tech, Dr. Jones leads a research group that works in the broad areas of materials, catalysis and separations. In particular, his group currently studies (i) the generation of a molecular-level understanding of supported organic and organometallic catalysts, (ii) the conversion of biomass into fuels and chemicals, and (iii) the engineering of materials for low energy adsorption or membrane separations. Working at the interface of synthetic chemistry and chemical engineering, the Jones Group uses advanced organic, organometallic and inorganic synthetic methods to create unique, new functional materials.

In the area of biomass conversion, Dr. Jones' work focuses on the use lignocellulosic biomass as a feedstock for liquid transportation fuels or hydrogen. These biomass resources, particularly softwoods, are being systematically studied to assess their suitability as raw materials for downstream catalytic upgrading. Modern homogeneous and heterogeneous catalytic methods are being used to develop reaction paths to energy-dense, deoxygenated liquids.

Alexander Katz

Alexander Katz received his BS and MS degrees in chemical engineering at the University of Minnesota, and was awarded a Fannie and John Hertz Foundation Fellowship for doctoral work at California Institute of Technology. He conducted postdoctoral studies in supramolecular chemistry in Strasbourg, France as a NSF International Awards Postdoctoral Fellow, and was subsequently appointed Assistant Professor of Chemical Engineering at the University of California, Berkeley in 2000.

Since that time, he has begun an interdisciplinary research program focused on the design and synthesis of functional nanoscale interfaces in hybrid organic-inorganic materials, relying on molecular templating strategies. He has been awarded four patents, covering his different research areas, and a Young Scientist Prize from the International Association of Catalysis Societies for his discovery of grafted calixarene (Cal-Silica) materials. Katz can be reached at katz@cchem.berkeley.edu.

Harold Kung

Harold H. Kung is professor of chemical and biological engineering at Northwestern University. He received his B.S. degree in chemical engineering from the University of Wisconsin, Madison, and his Ph.D. degree in chemistry from Northwestern University. After spending two years at the Central Research and Development Department at DuPont, he started his academic career at the Chemical Engineering Department at Northwestern University. His main research interest has been in the area of heterogeneous catalysis, and is known for work on catalysis for selective hydrocarbon oxidation, deNOx, and hydrocarbon cracking, and catalysis by nanosize Au particles and oxide materials. Recently, his group acquired significant experience in solution preparation of various nanostructures such as dendrimers, vesicles, and 2-D patterns (by lithography), and has synthesized functionalized nanocages as new catalytic structures. He has authored a monograph, Transition Metal Oxides: Surface Chemistry and Catalysis. He is an editor of Applied Catalysis A: General, and recipient of the P.H. Emmett Award and the Robert Burwell Lectureship Award (North American Catalysis Society), the Herman Pines Award (Chicago Catalysis Club), Catalysis Society of South Africa Eminent Visitor Award, and Cross-Canada Lectureship of the Catalysis Division of the Chemical Institute of Canada. He is a fellow of American Association for the Advancement of Science, and has published over 200 papers.

Angelo Lucia

Angelo Lucia earned a Ph.D. in Chemical Engineering at the University of Connecticut and is presently the Chester H. Kirk Professor of Chemical Engineering at the University of Rhode Island, a position he has held since 1996. Prior to that, Professor Lucia was a member of the faculty at Clarkson University in Potsdam, NY for fifteen years. His research interests are in the general area of process engineering, with particular focuses in process modeling, synthesis, design, and optimization and molecular modeling of fuels. Dr. Lucia also has a strong interest in mathematical analysis and current funded research interests in energy conservation and energy efficient design.

Specific areas of applied interest most relevant to the BioFuels Workshop include the design of energy efficient separations by distillation and hybrid separation strategies as well as the molecular understanding and phase equilibrium of lignocellulosic materials.

Devinder Mahajan

Professor Mahajan holds one of the ten joint appointments between Brookhaven National Laboratory and SUNY at Stony Brook. Dr. Mahajan's professional goal is to bridge science and technology for the benefit of mankind. To achieve this goal, his research interests focus on Energy issues that includes a portfolio of projects on Methane hydrates, H2 production, Fuel Cells, natural gas, Biomass and coal utilization via Fischer-Tropsch, Methanol, and mixed alcohol synthesis using soluble (single-site) or slurried (nano heterogeneous or colloidal phase) based catalysts, and extraction of value minerals from geothermal brines. Scientifically, his work in the synthesis of clean fuels is internationally recognized. He has organized symposia and international workshops on issues such as Clean Fuels, Methane Hydrates, and Biomass and has served or now serving as a Guest Editor of three recent special volumes: Topics In Catalysis (2005), Journal of Petroleum Science & Engineering (2006) and Industrial & Engineering Chemistry Research (2006-07). He is the author of over 75 publications including book chapters and encyclopedia articles, 10 patents, and presented over 110 invited lectures at various institutions, conferences and workshops around the globe. His work is constantly covered through press releases. He serves on several national and international energy-related committees. In March 2006, he was recognized with a membership to the prestigious Russian Academy of Natural Sciences (RANS)-US Section and is a recipient of the RANS Crown and Eagle Medal of Honor for service to the field of "Petroleum Engineering".

At Stony Brook University, he was instrumental in setting up the Chemical & Molecular Engineering (CME) Undergraduate program. He is a member of various external and internal committees including the ABET committee at SBU. Professor Mahajan's is playing an active role in setting up the newly funded New York State Advanced Energy Research and Technology Center (AERTC) at Stony Brook. As a Professor and Co-Director of the CME program at Stony Brook U., his priority is to further integrate education and research at both undergraduate and graduate level, foster collaboration within the university with a goal to train students in the next-generation energy technologies.

Leo Manzer

Leo E. Manzer is founder and President of Catalytic Insights LLC, a consulting company in the field of catalysis and process research. His clients cover a number of large and small companies in Europe and North America and he serves on the Scientific Advisory Boards of several startup companies such as Range Fuels and Segetis.

Manzer was born and educated in Canada and after receiving his Ph.D. in chemistry from the University of Western Ontario, he joined the DuPont Company in Wilmington, DE. He retired from the DuPont Company in 2005 as a DuPont Fellow, a position currently held by only 15 out of 3,000 scientists and engineers. During his 30+ year career at DuPont, he founded and directed the Corporate Catalysis Center, led DuPont's R&D effort to replace chlorofluorocarbons (CFCs) with ozone friendly substitutes, led Conoco's Fischer-Tropsch catalysis program, and played a key role in DuPont's efforts to develop chemicals from renewable feedstocks.

Manzer is the author of 89 publications and >114 US patents (> 500 international patents). He has received a number of awards, including: the 1995 ACS Earle B. Barnes Award; the 1997 Catalysis Club of Philadelphia Award; the 1997 ACS Heroes of Chemistry Award; the 1998 Cross-Canada Lecture Tour Award by the Catalysis Division of the Chemical Institute of Canada; the 2001 Eugene J. Houdry Award for Applied Catalysis from the North American Catalysis Society; and the 2003 ACS E.V. Murphree Award. He was also a member of the DuPont team recognized for the 2002 Presidential National Medal of Technology Award for his work in developing CFC Alternatives. He has served on the advisory board on many journals, including the Journal of Catalysis, Catalysis Today and Applied Catalysis.

Richard Marinangeli

Richard Marinangeli has a Ph.D. in Chemical Engineering from Princeton University and a B.S. in Chemical Engineering from the University of Notre Dame. He was a CNRS Fellow in Villeurbanne, France prior to joining UOP. He has 28 years of experience at UOP in Process Development and application of materials for catalysis and adsorption This work has resulted in 18 U.S. patents. Currently, Dr. Marinangeli is Manager of the Renewable Energy and Chemicals Group in the Refining Conversion Development Group.

Steven Phillips

Mr. Phillips has over 22 years of experience in thermochemical process research primarily in the conversion of biomass into fuels and power. In 1993, Steven joined NREL working in biomass conversion to and upgrading of pyrolysis oil. In 1994, he and the Thermochemical Users Facility (TCUF) Team at NREL started design and construction of the Thermochemical Process Development Unit (TCPDU), a state-of-the-art, ?-ton/day pilot plant for producing syngas and pyrolysis oils from a wide variety of biomass feedstocks. Research emphasis has been on developing and demonstrating biomass conversion technologies that will overcome the barriers to successful commercial deployment of renewable biomass energy. In late 2005, Steven moved to the Systems Analysis Team in the National Bioenergy Center. His emphasis over the past two years has been the technoeconomic modeling of biomass-to-liquid fuels processes. Most recently, he was lead author on a biomass to ethanol design report for a 2000 tonne/day process.

Prior to joining NREL, Steven worked at the Dow Chemical Company investigating catalytic fluidized bed processes for making styrene, and at National Semiconductor Corp. developing photolithographic processes for semiconductor production. His graduate school research involved collecting, organizing and characterizing combustion data for evaluating three-dimensional CFD models. He received both a B.S. and M.S. in Chemical Engineering from Brigham Young University.

Kyoung S. Ro, Ph.D., P.E.

Dr. Ro is an environmental engineer at the USDA-ARS Coastal Plains Soil, Water & Plant Research Center, Florence, SC. Before joining the USDA-ARS, he had worked as a faculty member for the Louisiana State University (LSU) and the City College of New York (CCNY) for 13 years. His research focus includes agricultural and municipal wastewater treatment, fate and transport of pollutants and greenhouse gases, and thermo-chemical/biological conversion of biomass and wastes into bioenergy.

Lanny D. Schmidt

Lanny D. Schmidt was born on May 6, 1938 in Waukegan, Illinois. He is married and has two children. He received a Bachelor of Science degree in Chemistry in 1960 from Wheaton College and a Ph.D. degree in Physical Chemistry in 1964 from the University of Chicago, where he was awarded a National Science Foundation Graduate Fellowship. His thesis on alkali metal adsorption was supervised by Robert Gomer.

After a postdoctoral year at the University of Chicago, he joined the Chemical Engineering Department at the University of Minnesota where he is now Regents Professor in the Department of Chemical Engineering and Materials Science.

Professor Schmidt's research focuses on various aspects of the chemistry and engineering of chemical reactions on solid surfaces. Reaction systems of recent interest are catalytic combustion processes to produce products such as syngas, olefins, oxygenates by partial oxidation and NOx removal and incineration by total oxidation. One topic of research is characterization of adsorption and reactions on well defined single crystal surfaces. The second topic is steady state and transient reaction kinetics under conditions from ultrahigh vacuum to atmospheric pressure. The third topic is characterization of small particles and the correlation of catalytic activity with particle microstructure. The fourth topic is catalytic reaction engineering in which detailed models of reactors are constructed to simulate industrial reactor performance, with particular emphasis on chemical synthesis and on catalytic combustion.

Professor Schmidt has published over 300 papers in refereed journals. He has supervised approximately 70 Ph.D. theses and 15 M.S. theses at Minnesota, and 11 of his former students hold university teaching positions. He is a member of the National Academy of Engineering.

Brent Shanks

Brent Shanks is a professor in the Department of Chemical and Biological Engineering at Iowa State University. He received his bachelor's degree in Chemical Engineering at Iowa State University. In 1988, he received a doctoral degree in Chemical Engineering from the California Institute of Technology. Following graduate school, he worked as a Research Engineer and then Department Manager in catalyst research and development for Shell Chemical Company. He joined the faculty at Iowa State University in 1999.

The Shanks research group is working on the design of materials for use as heterogeneous catalysts with particular emphasis on their application to the conversion of biorenewable feedstocks to chemicals and fuels. He is a founding member of the Office of Biorenewable Programs at Iowa State University and has been actively involved in developing interdisciplinary research and education programs focused on biorenewables.

Chunshan Song

Dr. Chunshan Song is a Professor of Fuel Science and Director of the Energy Institute at Pennsylvania State University. His research interests include catalysis and adsorption for fuel processing, desulfurization of fuels, reforming of alcohols and hydrocarbons for fuel cells, shape-selective catalysis for chemicals, CO2 capture and utilization, and conversion of coal, petroleum and biomass.

He has published 160 refereed papers, edited 11 books and special issues of catalysis journals, delivered over 35 plenary or keynote lectures at international conferences, and given 150 invited lectures worldwide. He has won some awards including Herman Pines Award for Outstanding Research in Catalysis from Catalysis Club of Chicago and UOP; Fulbright Distinguished Scholar from the US-UK Commission; Chang Jiang Scholar from Ministry of Education of China; Most Cited Authors 2002-2006 and Top Cited Article Awards in catalysis from Elsevier; Wilson Award for Excellence in Research, and Faculty Mentoring Award at Penn State; Outstanding Scholar Overseas from Chinese Academy of Sciences; Distinguished Catalysis Researcher Lectureship from Pacific Northwest National Lab; Outstanding Service Awards from International Pittsburgh Coal Conference (PCC) and from American Chemical Society (ACS) Fuel Chemistry Division; NEDO Fellowship and AIST Fellowship Awards from Japan; Inventor Incentive Awards and Materials Science and Engineering Service Award at Penn State.

He served as the Chair of ACS Petroleum Division, Chair-Elect (2007) and Program Chair for ACS Fuel Division, Chair of the PCC Advisory Board, Organizing Committee for North American Catalysis Society Meetings, and Chair/Co-chair for 25 national/international symposia. He is on the advisory board for ACS journal Energy & Fuels, international journals Catalysis Today, Research on Chemical Intermediates; Acta Petrolei Sinica-Petroleum Processing, Journal of Fuel Chemistry and Technology, and Coal Conversion. He held Visiting Professorships in Imperial College London, University of Paris VI, Tsinghua University, Dalian University of Technology, and Chinese Academy of Sciences.

Philip Steele

Dr. Philip Steele has been a Professor in the Dept. of Forest Products, College of Forest Resources, Mississippi State University (MSU) for 17 years with both research and teaching duties. He joined MSU after receiving his doctorate in Wood Science and Technology at MSU in 1986. Dr. Steele is Leader of Bio-Oil Research Thrust Area in the MSU Sustainable Energy Research Center (SERC) and is manager of the Bio-Oil Laboratory at MSU. He has directed the development of a unique auger-fed laboratory-scale bio-oil reactor in a cooperative development with the Renewable Oils International, LLC a manufacturer of auger pyrolysis reactors. Based on development of the auger bio-oil reactor researchers in the Bio-Oil Research Thrust Area have attracted substantial funding from USDA and DOE grants to develop fuels and chemical products from bio-oil. The MSU Bio-Oil Research Thrust Area is comprised of 10 on-campus faculty collaborators in the departments of Agricultural and Biological Engineering, Chemistry, Chemical engineering, Forest Products and the Institute for Clean Energy Technology. This group is developing technology for the production of fuels and specialty chemicals from bio-oils made from various types of forestry and agricultural feed stocks. As a researcher in the SERC Dr. Steele is project leader of the research group investigating catalytic upgrading of bio-oils by hydrogenation to transportation fuels and chemicals.

Dr. Steele has won several research awards including the MSU College of Forest Resources Outstanding Research Award and awards for exceptional research papers from both the Hardwood Research Council and the Forest Products Society. He is the author or co-author of over 100 research papers. Dr. Steele holds three patents with one of his patented devices commercialized and marketed internationally.

Jim Stevens

Jim Stevens has worked for Chevron since 1981 and is currently the pathway manager for emerging technology routes for biomass conversion. He received his bachelor's (1973) and doctoral degrees (1977) in chemistry from Rice University. His work in the petroleum industry includes development of processes for production from mined heavy oil sands via solvent extraction and pyrolysis. He has conducted R&D and managed groups involved in carbon dioxide and steam enhanced oil recovery. For the last several years he has been involved in the development of technology needed to commercialize distributed production of hydrogen. Work in this area included catalyst development and evaluation, integration of reforming and separation processes, and sensor development. He is the holder of many U.S. and foreign patents in the area of oil recovery and hydrogen production.

Thomas Henry Vanderspurt

Thomas Henry Vanderspurt is a Fellow at United Technologies Research Center. He earned his B.S., Chemistry, at Lowell Technological Institute, (now U. Massachusetts –Lowell) in 1967 then studied under Prof. John Turkevich and completed his Chemistry Ph. D at Princeton University, in 1972. After the U.S. Army Chemical Officers training and Post-doctoral research at Princeton he joined the Catalyst research group of the Celanese Research Co. in Summit, NJ in 1973. He left Celanese 1979 for Oxirane International; Princeton NJ to build a world class catalysis group, however when Oxirane was sold in 1980 he joined Exxon Corporate Research Laboratories. There as a Research associate/Group Head he was responsible for advanced catalytic routes, including new Fischer-Tropsch catalysts, for converting coal derived syn-gas to hydrocarbons transportation fuels and ammonia.

With the changing economy he then led the development of light virgin naphtha aromatization over Pt/KL zeolite. He was Technical Lead and Section Head for Exxon Basic Chemicals 1985-1988 during the commercializing of EXAR aromatization technology. Returning to Exxon's corporate labs in 1988 he took on numerous assignments investigating non-Fischer Tropsch conversion of stranded natural gas, methane, to liquids. This included methane to light alcohols/isobutanol effort. While at Exxon he co-chaired the 16th Meeting of the North American Catalysis Society in Boston in 1999, served on the Council for Chemical Research Vision 2020 Catalysis Implementation Team, and organization a multi-year, multi-research group, academic study of sulfur tolerant three way catalysts for the Auto-Oil Cooperative Research Council.

In 2000 the rebirth of the Fuel Cell effort at United Technologies Research Center brought him to East Hartford. Presently he is concerned with efforts to discover and commercialize advanced catalytic systems for Biomass conversion, fuel processing, fuel cell electro-catalysts, sulfur tolerant hydrogen separation membranes, UV-photocatalytic oxidation of organic contaminants in air and related technology. He has 41 US Patents, 15 patent applications pending, numerous presentations, publications, and foreign patents.

Bruce Vrana

Bruce Vrana is a Senior Consultant in the Engineering Evaluations and Sustainability Group at DuPont. He earned his B.S. (1980) and M.S. (1982) degrees in Chemical Engineering from the University of Pennsylvania, and his M.B.A. from the University of Houston (1984). He is a registered Professional Engineer in the state of Delaware. Since joining DuPont in 1980, he has worked in research, manufacturing, and in the corporate engineering technology function. For the past 23 years as an internal consultant, he has worked with research and manufacturing teams from a wide variety of DuPont businesses, aimed at transforming research discoveries into commercial successes through technoeconomic evaluations, process conceptualization and process synthesis techniques. For over a decade, he worked on nearly every important program in the nylon intermediates business. In recent years, he has worked on the DuPont cellulosic ethanol(ICBR - Integrated Corn BioRefinery) and biobutanol research and development programs, playing a key role in the engineering team for both projects.

Bruce works with the University of Pennsylvania senior design course in CBE, proposing projects for groups of students to work on, as well as advising student groups working on both his and other projects. He has also served at Rowan University in a similar role. He teaches the internal DuPont course on engineering economics as well as a continuing education course on the same topic at the University of Delaware.

Yong Wang

Yong Wang received his M.S. and PhD degrees in ChE from Washington State University in 1992, and 1993. He joined Pacific Northwest National Laboratory (PNNL) in 1994 as a postdoc fellow. He became a research engineer in 1996, a senior research engineer in 1997, a chief scientist in 2000, and a laboratory fellow in 2005. He currently manages Catalysis & Reaction Engineering team of >20 technical staffs. His research interest is in the development of novel catalytic materials and innovative reaction engineering such as microchannel reactors, structured monolith reactors and membrane reactors for hydrocarbon and biomass conversions to fuels/chemicals; fundamental studies of structural and functional relationship of early transition metal oxide and bimetallic catalysts; novel and durable cathode materials for PEM fuel cell applications. His discoveries in microchannel reaction technology led to the spin-off of Velocys, a wholly owned subsidiary of Battelle in the commercialization of microchannel technology.

Dr. Wang was named as the 2006 Asian American Engineer of the Year by Chinese Institute of Engineers. He has received two R&D100 awards (1997 and 1999) and a Presidential Green Chemistry Award in 1999. He was twice named PNNL Inventor of the Year in 2004 and 2006. He was honored as a Battelle Distinguished Inventor in 2004. He is also a first-time recipient of PNNL Laboratory Director's Award for Exceptional Scientific Achievement in 2005. He is an Adjunct Professor in ChE at Washington State University, a Guest Professor at Tianjin University (China), Sichuan University, Dalian University of Technology, and Dalian Institute of Chemical Physics. He currently serves editorial board of Catalysis Today and Journal of Nanomaterials. He also serves as the Program Committee Chair of ACS (American Chemical Society) Petroleum Division (2006-2008). He has organized numerous international and national conferences. He has more than 100 peer reviewed publications, 48 issued U.S. patents, and one book edited on Microreactor and Process Intensification (published in 2005).

Phil Westmoreland

Phil Westmoreland is Professor of Chemical Engineering at the University of Massachusetts Amherst, temporarily serving at NSF as Program Director for Combustion, Fire, and Plasma Systems in the ENG/CBET division and as co-leader of the division's cyber infrastructure initiatives.

His research activities focus on elementary reaction kinetics in flames and polymer pyrolysis using molecular-beam mass spectrometry, computational quantum chemistry, reactive-flow modeling, and thermal analysis methods. He is using these tools to examine fast pyrolysis methods on biomass and to study combustion chemistry of biofuels. His Pyroprobe/GC-MS instrument developed for studying pyrolysis of synthetic polymers also reveals clues to mechanistic chemistry of biomass pyrolysis. Likewise, his group's Reactive Molecular Dynamics method is very promising for predicting these pathways. In a collaborative project at Lawrence Berkeley National Laboratory, he and his colleagues have mapped concentrations of stable species and free radicals in flat flames burning small-molecule alcohols, ethers, aldehydes, and esters. These results and their modeling provide qualitative and quantitative insights into their reaction kinetics.

He is a Fellow of AIChE; was founding president of AIChE's Computational Molecular Science and Engineering Forum (CoMSEF); serves on the Board of Directors of the Combustion Institute, the Council for Chemical Research, and the nonprofit CACHE Corporation; and has been recognized by AIChE's Lappin Award, Lawrence Berkeley Laboratory's Shirley Award, ASEE Corcoran Award, and the UMass Amherst College of Engineering's Outstanding Senior Faculty Award.

Charles Wyman

Charles Wyman has devoted most of his career to leading the advancement of technology for biological conversion of cellulosic biomass to ethanol and other products. In the fall of 2005, he joined the University of California at Riverside as the Ford Motor Company Chair in Environmental Engineering. Prior to that, he was the Paul E. and Joan H. Queneau Distinguished Professor in Environmental Engineering Design at the Thayer School of Engineering at Dartmouth College where he continues as an Adjunct Professor. Dr. Wyman is also the Chief Development Officer, cofounder, and chair of the Scientific Advisory Board for Mascoma Corporation, a new startup company focused on biomass conversion to ethanol and other products. Before joining Dartmouth College in the fall of 1998, Dr. Wyman was Director of Technology for BC International and led process development for the first cellulosic ethanol plant planned for Jennings, Louisiana. Between 1978 and 1997, he served as Director of the Biotechnology Center for Fuels and Chemicals at the National Renewable Energy Laboratory (NREL) in Golden, Colorado; was Director of the NREL Alternative Fuels Division and Manager of the Biotechnology Research Branch; and held several other leadership positions at NREL, mostly focused on R&D for biological conversion of cellulosic biomass to fuels and chemicals. He has also been Manager of Process Development for Badger Engineers, an Assistant Professor of Chemical Engineering at the University of New Hampshire, and a Senior Chemical Engineer with Monsanto Company. Wyman has a BS degree in chemical engineering from the University of Massachusetts, MA and PhD degrees in chemical engineering from Princeton University, and an MBA from the University of Denver. He has authored over 80 peer-reviewed papers and book chapters, made more than 50 presentations for publication and more than 150 other presentations, many invited, written over 30 technical reports, chaired numerous technical meetings and sessions, edited 9 symposium proceedings, edited a book on biomass ethanol technology, and been awarded 12 patents. He is also on the editorial board of several technical journals and the board of directors or board of advisors for several organizations and institutions.

Ye Xu

Dr. Ye Xu is a member of the research staff of the Center for Nanophase Materials Sciences and the Chemical Sciences Division at Oak Ridge National Laboratory, where he investigates chemical reactions occurring on metals, metal compounds and clusters by using first-principles theoretical methods. His research is focused on gaining fundamental understanding of heterogeneous catalytic processes in order to design and improve catalytic materials.