

AICHE 2006

Topical 4: Sustainable Biorefineries

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Sustainable Biorefineries Plenary (Invited Papers) (T4007)

Wednesday, 15 November 2006 - 3:15 PM

A Research and Market Pathway to Realize the Potential of Ethanol

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1 Introduction

President Bush stated it succinctly in his 2006 State of the Union Address: "America is addicted to oil." In 2004, the United States (U.S.) used almost 21 billion barrels of crude oil per day; approximately 58 percent of this total was supplied by imports. The transportation sector, which receives nearly all of its energy from petroleum products, accounts for two-thirds of U.S. petroleum use. Gasoline is the dominant transportation fuel in the U.S, with a 2004 usage of approximately 140 billion gallons. The Energy Information Administration (EIA) projects that expected increases in total miles traveled will outweigh all vehicle efficiency improvements and lead to a one-third increase in imports of crude oil such that imports will account for 62.5% of total domestic oil use by 2030.

Biomass is the only domestic, sustainable and renewable primary energy resource that can provide liquid transportation fuels. A long-standing question has been "what is the production potential of ethanol, both from starch and cellulosic feedstocks and can it have a significant impact on imported oil displacement and long-term energy security". In response to this question an in-depth study, "Biomass as Feedstock for a Bioenergy and Bioproduct Industry: The Technical Feasibility of a Billion-Ton Annual Supply" (Perlack, R. D., et al., ORNL, DOE/GO-102005-2135, April, 2005) was performed. This study estimated that the U.S. has the potential to produce up to 1.3 billion tons of biomass annually on a sustainable basis without impacting food, feed and fiber uses. To put the ethanol production potential from this amount of biomass plus grain based ethanol in perspective, almost 60% of 2004 motor gasoline demands on a BTU adjusted basis could be met with ethanol from grain and biomass.

Although ethanol both from corn and cellulosic feedstocks shows considerable promise to help lessen our demand on imported oil and increase energy security, a question that needs to be addressed is "What is an appropriate goal for ethanol?" Then given this goal, what needs to be accomplished in what timeframe to achieve this goal. After much discussion and analysis a goal of supplying 30% of the 2004 motor gasoline demand with ethanol by the year 2030 was chosen. This roughly translates to a 60 Billion gallon per year on a BTU adjusted basis target by 2030, herein after referred to as the 30 X 30 goal. This goal was chosen because it represents an aggressive target that translates into a significant positive national impact but well within the maximum potential for ethanol. Also the timeframe of 24 years from the present was considered aggressive but not too short to be overly disruptive to market change dynamics.

2 30 X 30 Goal

This paper presents a scenario for achieving the 30 X 30 goal with ethanol produced from both starch and cellulosic feedstocks. This scenario follows a logical progression to the 30 X 30 goal by determining the market volume potential of grain ethanol and then analyzing the feedstock and technology needs to build upon this grain ethanol with cellulosic ethanol to achieve the 30 X 30 goal. A detailed market assessment is also performed to determine the necessary policy drivers to enable this scenario, as well as an assessment of the distribution and vehicle needs for this level of ethanol production and use.

The goal of this study is to outline a scenario to achieve the 30 X 30 goal that is realistically achievable with a sustained integrated government, academia and private sector effort. The 30 X

30 goal is in essence a market goal and hence this study follows a market driven approach towards achieving the 30 X 30 goal. A fundamental assumption of this scenario is that consumers will behave in a rational manner and choose the fuel that provides the best value on a fuel cost per mile traveled basis. Given this assumption, ethanol fuels must be equal to or less cost than gasoline at the pump on a fuel cost/mile traveled basis in order for consumers to prefer ethanol. Another fundamental assumption is that ethanol fuels must deliver equal or better performance.

Essentially there are two sets of tools that can be used to realize this; technology goals as they relate to production cost targets and, policy and market incentives to make ethanol more competitive in the marketplace. This scenario will analyze the best mix of these tools for achieving the 30 X 30 goal.

2.1 Technology Targets

2.1.1 \$1.07 Target in 2012

The first technology target for cellulosic ethanol in the 30 X 30 scenario is cost competitive with corn-ethanol by 2012. This has been defined as \$1.07 per gal production cost. This value was chosen because it would allow entry into the starch ethanol market. The value can be put in context with the historic ethanol price data as shown in Figure 1. The \$1.07 per gallon value represents the low side of the historical fuel ethanol prices and hence given historical price data, cellulosic ethanol would be commercially viable at this cost of production.

Aden et al. (NREL/TP-510-32438, June, 2002) outlines the technology basis for the \$1.07 market target case and this paper outlines the research pathway towards achieving this target for both biochemical and thermochemical conversion routes. However the goal of \$1.07/gallon in 2012 is not sufficient in of itself to achieve the 30 X 30 goal given DOE's Energy Information Administration (EIA, 2006) crude oil price projections out to 2030. Indeed, preliminary market analysis suggests that, if the goal of a production price of \$1.07/gallon is the ultimate endpoint for the technology, the 30 X 30 goal is not achieved. Hence a second technology target is used in this scenario, an advanced state of technology target of \$0.60/gallon in 2030.

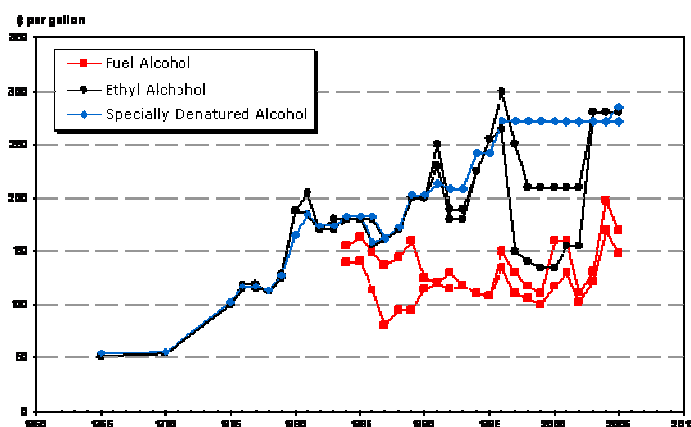


Figure 1. U.S. List Prices for Ethanol

2.1.2 \$0.60 Target in 2030

The target of \$1.07 per gallon in 2012 may be sufficient to gain entry in the fuel market, but further technology improvement is needed to achieve the market penetration implicit in the 30 x 30 goal. To meet the 2030 market goal, the 2030 technology target for cellulosic biomass is to demonstrate advanced conversion technologies capable of producing ethanol at \$0.60/gal.

Specifically, the 2030 goal is to generate sufficient data from the integrated pilot scale process that when extrapolated to a complete a process design and cost estimate of an "nth" plant (an

assumption of “nth plant performance means that all of the potential cost growth and performance penalties of the first-of-a-kind (pioneer) technology have been overcome) shows that an investor will sell the product ethanol for \$0.60/gal and receive an appropriate return on his investment. The target ethanol selling price includes feedstock production, feedstock logistics and conversion cost components. Imbedded in both the 2012 and the 2030 price targets are the following assumptions:

- “Nth plant” cost and performance based on pilot plant scale (2 to 5 tons per day of biomass) data
- A minimum selling price based on a 10% rate of return on investment (ROI)
- A minimum selling price that is not based on availability of tax incentive
- A biomass feedstock cost of \$35 per dry ton.
- A minimum selling price at the plant gate (exclusive of fuel distribution costs, marketing costs and taxes).

However, as the market assessment analysis shows, the proposed targets for ethanol technology improvement are not, by themselves, sufficient to push the ethanol industry to 60 billion gallons/year of capacity—even with higher oil prices. This is because investor attitudes toward new technology risk raise the hurdle of building the first full-scale commercial plant to a higher level. Investors wait until market value for fuel rises enough to overcome their risk-aversion. Hence in addition to technology cost targets, market and policy incentives will be required to achieve the 30 X30 goal.

2.2 Market Incentives

Meeting the 30 x 30 goal calls for strategies that reduce biomass feedstock cost, technology risk, and ethanol price during the early years of industry adoption of lignocellulosic biomass technology after corn ethanol production has reached its peak. Two specific market incentives were evaluated, extending the existing ethanol subsidy by 10 years to 2020 and providing payments (\$15/ton) to lignocellulosic biomass suppliers for residues and energy crops used for fuel production also to 2020. Adding these two market incentives on top of the technology targets was sufficient to achieve the 30 X 30 goal. Additionally the market analysis shows that extending the ethanol subsidy beyond 2020 has no added benefit if progress in R&D continues and is successful in reducing the production price of ethanol to \$0.60/gallon. The same holds true for the biomass feedstock payments. Hence, achieving the \$0.60/gallon target by 2030 is critical in allowing these market incentives to sunset. However if research does not progress towards achieving the \$0.60/gallon by 2030 target, extending the ethanol subsidy until 2030 or whenever the \$0.60/gallon target is achieved provides an additional avenue towards achieving the 30 x 30 goal.

Wednesday, 15 November 2006 - 3:45 PM

Sustainable Energy and Transportation: Engineering the 21st Century

Mark T. Holtzaple, Texas A&M University, Dept. Chemical Engineering, College Station, TX 77843-3122

With the world's population and standard of living rapidly rising, the demand for petroleum-based fuels is increasing at record pace. Given the time required to develop and implement new energy sources, failure to develop sustainable alternative fuels now could mean widespread energy shortages and other economic and ecological problems by mid-century.

This presentation describes the MixAlco process, a novel method for producing fuels from biomass, such as municipal solid waste, agricultural residues, sewage sludge, and manure. In

this process, the biomass is treated with lime and air to enhance digestibility. Then, the lime-treated biomass is fed to a mixed-culture of microorganisms that produce carboxylic acids (e.g., acetic acid). In the fermentor, the carboxylic acids react with calcium carbonate buffer to form carboxylate salts (e.g., calcium acetate). The salts are dried and thermally converted to ketones (e.g., acetone). Finally, the ketones are hydrogenated to alcohols (e.g., isopropanol), which may be used as motor fuel.

In addition, the presentation will include the high-efficiency StarRotor engine, which could triple automotive fuel economy while reducing pollution. It employs the Brayton cycle, the same thermodynamic cycle used in jet engines. It uses a positive-displacement compressor and expander, which gives it more operational flexibility than conventional jet engines.

Wednesday, 15 November 2006 - 4:15 PM

Dupont's Biorefinery Vision in Support of Sustainable Biofuels & Biobased Chemicals

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Sustainable development is core for DuPont, a company that is over 200-years old. DuPont has evolved from its heritage as a premier chemical and materials company to a science company that uses biology across its different platforms. DuPont has set a 2010 objective of having 25% of our global revenues from non-depletable resources and 10% of our energy needs from renewable sources. As part of this transformation, DuPont is creating new products and new business models based on renewable resources and biology. To this end, DuPont has created and staffed a variety of business units to support these new bio-inspired product lines: DuPont BioBased Materials – Energy & Specialties, DuPont BioBased Materials – Sorona® & Bio-PDOTM, DuPont and Tate & Lyle LLC, and DuPont Biofuels.

This talk will focus on the success factors needed for development of world-class bioprocesses and bioproducts that are both cost and investment competitive along with highlighting some of the technical achievements that DuPont has made with the conversion of corn stover to sugar then onwards to biofuels in addition to our market-leading process for making 1,3-propanediol.

Wednesday, 15 November 2006 - 4:45 PM

A Refiner's Perspective on the Future of Biofuels

Scott Mason, ConocoPhillips Company, 864 PB, Bartlesville, OK 74006

Biofuels are hot. Ethanol plant IPO's, E85, 30x30, 25x25. Many companies, including integrated oil companies are entering the renewable fuels area. What does all the press and hype mean?

Scott Mason of ConocoPhillips will speak about the pros and cons of various biofuels options. Scott works in Alternative Energy and Programs in the biofuels area. He will look at market sizes, production costs, and implementation strategies for several options available to a fuel supplier.

ConocoPhillips is an international, integrated energy company. It is the third-largest integrated energy company in the United States, based on market capitalization, oil and gas proved reserves and production; and the second-largest refiner in the United States. Worldwide, of non-government controlled companies, ConocoPhillips has the fifth-largest total of proved reserves; and based on crude oil capacity, is the fourth-largest refiner.

ConocoPhillips owns 12 U.S. refineries, owns or has an interest in six European refineries and has an interest in one refinery in Malaysia. At year-end 2005, ConocoPhillips refineries had a combined net crude oil refining capacity of 2.61 million barrels of oil per day.

Wednesday, 15 November 2006 - 5:15 PM

Technology and Economic Risks Associated with the Forest Biorefinery

Paul Stuart, Professor - Department of Chemical Engineering, École Polytechnique de Montréal, P.O. Box 6079, Station Centre-ville, Montreal, QC H3C 3A7, Canada

Commodity industries such as forestry are characterized by a low R&D intensity, and have transformed from process innovation research to enterprise efficiency research (e.g. achieved through optimization of the supply chain). Investments in enterprise efficiency naturally “align” to existing products, and thus commodity industries and especially those that are capital intensive can create inertia against a model of “punctuated equilibrium” (where punctual innovations result in new products which add significant value to company performance). This innovation challenge is obviously complex for industry sectors such as pulp and paper, which especially in recent years, must respond to stock market metrics in the short term.

There is little argument over whether the North American forestry industry is in crisis. The corporate strategy for many forestry companies in recent years has centered on company mergers and continuous belt tightening. Merger activity has undoubtedly been critical, however it is clear that this is not enough – a new business model is essential. Recent mill closures are permanently removing production and creating price optimism for the near-term, but this too is not a sustainable solution for the cyclical and increasingly global pulp and paper industry.

With this backdrop, the forestry industry leadership has begun to discuss the need for “transformative changes”. Options for successful transformative change are not obvious, and they require the courage necessary to take short-term action for longer-term objectives while in economic crisis.

The Forest Biorefinery

In the 27 January 2006 Science Magazine, Art Ragauskas and his colleagues at Georgia Institute of Technology stated that “in essence, the modern biorefinery parallels the petroleum refinery: an abundant raw material consisting primarily of renewable polysaccharides and lignin enters the biorefinery and, through an array of processes, is fractionated and converted into an array of products including transportation fuels, co-products, and direct energy.”

The forest biorefinery pathway possibilities are large in number, and will depend on many factors such as wood species, production levels, technology in place, and where the mill is located. Forest feedstocks such as woodwaste can be gasified into synthesis gas and transformed into chemicals. Hemicellulose can be extracted from wood chips and converted through enzymatic and chemical transformations. Methanol or DME can be produced via synthesis gas from the gasification of black liquor, and via the Fischer Tropsch Process and otherwise, other fuel products can be made such as diesel, naphtha, and LPG. Pulp and paper mill wastewater is potentially an ideal source of PHB due to high carbon and low nitrogen and phosphorus content. Each of these options implies process technology risks, for example related to limited process yields, process thermal efficiencies, materials of construction, gas cleaning requirements, etc.

On the product side, a company might employ a strategy to enter into the supply chain for biofuels, might pursue a strategy to joint venture with a specialty chemicals company and supply an existing hydrocarbon supply chain with “green product”, or might elect to produce a new fibre reinforced “green plastic” whose market has yet to be developed. Otherwise, products can be made and sold directly within the industry such as resins or dry strength agents.

How can a company mitigate technical and economic risks associated with the implementation of the forest biorefinery, and convince investors that the investment will provide an attractive return? The answer to this question is not obvious, and poses a complex multidisciplinary process engineering problem. This presentation surveys a strategy for achieving this objective.

Product Design Considerations

Using design criteria which are based on business principals incorporating likely prices for feedstocks and products, an important characteristic of the forest biorefinery will be process flexibility. If the forestry industry is to accept the challenge of manufacturing multiple products, it should be able to achieve targeted returns for the biorefinery under a range of volatile market and economic conditions. This will require flexible processes, so that mills can adjust how carbon is consumed to produce pulp and paper, bioenergy, green chemicals or structural material products.

The product opportunity analysis might consist of several steps, starting from the set of possible biorefinery products which has been well-defined by many researchers and authors relative to the biorefinery:

- SWOT and competitiveness analyses of the forest industry in a country are critical relative to a) other countries, and then b) other industry sectors. This analysis serves to remove certain products from the list since they can better be addressed by others, and
- From the remaining product list, a systematic product analysis methodology is needed to identify the most interesting products for specific companies and their mills also by a SWOT analysis, and accounting for such considerations as a) quantities that can be produced based on mass and energy balance constraints, relative to scenarios of future product demand growth and supply-demand, b) product “slates” that can be produced from platforms including design-for-flexibility considerations, c) existing supply chains pertinent to the company's mill locations, etc. The goal of this analysis is to identify that an economic hurdle rate can be met for a range of feedstock and product price ranges, reflected in a business model which would show a marked improvement over the existing business model.

Process Design Considerations

There are numerous complex issues that must be addressed at the process design stage, for example the following:

- Improvements to the existing processes must be made by mills, especially in terms of energy management, as they evolve towards the biorefinery, e.g. for certain process configurations which use lignin as the feed material to the biorefinery, mills must optimize process energy efficiency to maximize carbon availability from the mill. A further energy analysis is required to determine, for a given process pathway, how the energy systems are best integrated and optimized between the biorefinery and the existing mill.
- It is important that following the implemented biorefinery, existing pulp and paper operations continue to operate efficiently, and produce target product qualities. This requires plant-wide analysis techniques. For example, how will contaminants distribute between pulp and paper manufacturing and biorefining operations? Will there be greater or less evaporator scaling issues in pulp and paper manufacture? Will sulphur carry-over with lignin as the biorefinery feedstock and require additional processing steps, or require Na/S ratio adjustments in the pulping process?
- Conversion of hemicellulose sugars extracted from wood chips to ethanol is a promising biorefinery route. However, there are critical technology uncertainties. What are the enzyme costs and pentose conversion efficiencies necessary to have an economically attractive pathway? What will the concentration of the produced ethanol be from various wood feedstocks, and what are the purification and concentration requirements and costs for this?
- What are the most attractive hydrocarbon, carbohydrate or other process platforms that a given mill should consider? How can these be designed to offer maximum production flexibility for different biorefinery products across a product slate?

Summary

Developing a systematic algorithm for analyzing mill biorefinery opportunities is the focus of the NSERC Design Chair at École Polytechnique. We develop validated process and cost accounting models for case study facilities. Process simulation is used to estimate biorefinery quantities for use in market and supply chain analyses. The simulation can be further used to explore mill-wide optimization, and process flexibility. Energy efficiency analysis techniques (such as thermal pinch) are used to explore the potential for minimizing energy use, thereby maximizing carbon availability to produce biorefinery products. Product analysis tools such as supply chain management (SCM) and life cycle assessment (LCA) are used to explore financial and environmental performance of product mixes. Multi-criteria decision-making (MCDM) methods are employed to systematically raise awareness of decision-makers to the key analysis outcomes, followed by a mathematical weighting of stakeholder values for decision-making.

This product and process design methodology is critical for the biorefinery pathways being explored in the proposed program, as well as for analyzing other promising pathways which may emerge in the future as further research into the biorefinery takes place. The global methodology including performance indices for comparing process alternatives has yet to be defined, and implies the application of a range of sophisticated product and process analysis tools in order to be able to extract meaningful evaluation metrics.

Pretreatment of Lignocellulosic Biomass and Interactions with Other Processing Steps I (T4002)

Thursday, 16 November 2006 - 8:30 AM

Comparative Data for Enzymatic Digestion of Corn Stover and Poplar Wood after Pretreatment by Leading Technologies

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Cellulosic biomass must be pretreated to realize high yields of glucose in enzymatic digestion and achieve low enough sugar costs to be economically viable as substrates for production of fuels and commodity chemicals that would open up major new agricultural markets with powerful societal benefits. A Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) among researchers experienced with cellulosic biomass hydrolysis is applying most of the promising pretreatment options on a comparative basis for the first time. Ammonia explosion, aqueous ammonia recycle, controlled pH, dilute acid, flowthrough, lime, and sulfur dioxide steam explosion are being applied to single sources of corn stover and poplar wood, and comparative data are being developed on the digestibility of cellulose in the pretreated solids using a controlled source of enzyme. Application of identical material balance approaches show that all of the pretreatments gave similar high yields of xylose and glucose sugars for corn stover, with xylanase activity being particularly important to releasing residual xylan in the pretreated solids for pretreatments at higher pH. However, consistently high digestion yields are proving to be

more difficult to attain with poplar, with yields from some pretreatments being higher than for others. In addition, results are found to differ between two sources of poplar due to higher lignin content or other variables. This study is also examining how addition of hemicellulase enzymes improves recovery of hemicellulose sugars from the pretreated solids and examining tradeoffs in glucose yields over a wide range of cellulase loadings. Mechanistic models are being developed to relate the observed cellulose digestibility to key substrate features including degree of polymerization, crystallinity, and accessible surface area.

Thursday, 16 November 2006 - 8:50 AM

Modified AFEX Pretreatment Conditions and Enzymatic Hydrolysis of Poplar

Venkatesh Balan, Shishir Chundawat, and Dale Bruce. Chemical Engineering and Materials Science, Michigan State University, 3246, Engineering Building, East Lansing, MI 48824

The search for alternative renewable fuels as replacements for petroleum products is proceeding rapidly. Conversion of plant biomass to fuel is one an attractive source of renewable energy. Among the various sources of biomass, Hybrid poplar (*Populus nigra x Populus maximowiczii*) is of interest due to its wide availability, high density that reduces cost of transport and improves storability and for its high glucan (~ 45%) and xylan (~ 18%) content. Two batches of poplar are being studied in our laboratory containing high lignin (29%) and lower lignin (21%) levels. We present the results of different ammonia fiber explosion (AFEX) pretreatment conditions for both the batches of poplar, including some modifications such as autoclaving the poplar sample prior to AFEX and adding calcium oxide during the AFEX process, followed by enzymatic hydrolysis. We will also discuss additional, inexpensive preprocessing approaches that improve the hydrolysis for pre- and post-AFEX treated samples. Furthermore, optimal combinations of commercially available cellulases and hemicellulases with additives such as surfactants to achieve maximum sugar yields will be discussed. This research is performed as part of the Consortium for Applied Fundamentals and Innovation (CAFI) biomass conversion project.

Thursday, 16 November 2006 - 9:10 AM

Substrate Dependency on the Effect of Pretreatment by Aqueous Ammonia

Rajesh Gupta and Y. Y. Lee. Chemical Engineering, Auburn University, Auburn, AL 36849

Pretreatment of corn stover by aqueous ammonia through ARP process has shown very promising results in terms of digestibility and overall sugar yield. This process achieves high level of lignin removal as well as high level of carbohydrate retention. However, when this process was applied to a different feedstock, hybrid poplar, the pretreatment results were quite different. The extent of delignification was somewhat lower, but the digestibility was far below that of corn stover. Study has also been made with two different batches of hybrid poplar having different sugar and lignin compositions. The effects of pretreatment on the composition of these two batches were similar, yet the digestibilities were significantly different. Lignin content is believed to be one of the major factors affecting the enzymatic digestibility. It appears that not only the gross lignin content but also the properties of lignin and how it is situated in the biomass structure play a role in the enzymatic digestion. To verify this, we have examined corn stover and hybrid poplar feedstocks treated under various ARP conditions by SEM, XRD, and FTIR. The results were organized into physical properties and surface characteristics. Correlations were sought between these factors and the digestibility with emphasis on isolated effect of lignin.

Thursday, 16 November 2006 - 9:30 AM

Lime Pretreatment of Poplar Wood

Mark T. Holtzapple, Texas A&M University, Dept. Chemical Engineering, College Station, TX 77843-3122 and Rocio Sierra, Chemical Engineering, Texas A&M University, Dept. Chemical Engineering, College Station, TX 77843-3122.

Poplar wood was treated with lime only and lime + air at the following conditions: temperature = 25 to 75°C, time = 1 to 12 weeks, lime loading = 0.5 g Ca(OH)₂/g biomass (which is a great excess). At each condition, mass balances were performed to determine the amount of each component (cellulose, hemicellulose, lignin, acetyl, ash, extractives) that was retained in the solid phase. Enzymatic hydrolysis was performed to determine the digestibility at each condition. Conditions were identified that allowed hydrolysis of nearly 100% of the cellulose in the solid phase.

Thursday, 16 November 2006 - 10:00 AM

Integration of Biomass Conversion Processing Steps with Advanced Enzymes

Mohammed Moniruzzaman, Genencor International, Inc, 2600 Kennedy Drive, Beloit, WI 53511

The emergence of lignocellulosic biomass as a renewable energy resource is eagerly anticipated in many countries around the world as a means to decrease dependence on imported oil, reduce air pollution, and quickly and effectively impact greenhouse gas emissions. Biomass-based ethanol technologies are rapidly evolving and bottlenecks are being identified that need to be overcome to achieve widespread commercialization. Current research is driven by the need to reduce the cost of biomass to ethanol production. The preferred method is to thermochemically pretreat the biomass material and subsequently, enzymatically hydrolyze the pretreated material to fermentable sugars that can then be converted to ethanol. Pretreatment research is focused on developing processes that would result in reduced bioconversion time, lower cellulase enzyme usage, and/or higher ethanol yields. Cellulase research efforts are focused on developing a cost-effective, synergistically acting enzyme mixture that would meet the end user's needs. Robust fermentation microorganisms are also being developed for conversion of biomass sugars to ethanol and other bioproducts. This presentation will provide a perspective on biomass processing by highlighting the key elements required for commercializing lignocellulosic biomass conversion, with particular emphasis on some technological advances in cellulase development.

Thursday, 16 November 2006 - 10:20 AM

Effect of Fermentation Inhibitors on the Cofermentation of Glucose and Xylose from Pretreated Lignocellulosic Biomass by Recombinant Yeast

Nathan Mosier, Ryan Warner, Miroslav Sedlak, Nancy Ho, Richard Hendrickson, and Michael Ladisch. LORRE / Agricultural and Biological Engineering, Purdue University, 500 Central Drive, Potter Building, W. Lafayette, IN 47907

Pretreatment of lignocellulosic biomass, while improving enzymatic digestibility, can also produce fermentation inhibitors such as furfural, HMF, and acetic acid. These compounds can decrease the fermentability and the ethanol yields from sugars derived from lignocellulose. This paper reports a systematic study of the effect of furfural, HMF, and acetic acid on the fermentation of both glucose and xylose to ethanol by the recombinant yeast *S. cerevisiae* 424A(LNH-ST). Batch fermentations (30°C, 200 rpm) were conducted with inhibitors in a control solution of YEP with glucose and xylose as co-substrates. Inhibitor concentrations were varied from 0 to 40 g/L. The results show that concentrations of these inhibitors below approximately 5 g/L cause negligible

inhibition for yeast cells in early stationary phase. We confirm that furfural is more inhibitory than HMF and that the toxicity of acetic acid is pH dependent. A preliminary model of glucose/xylose co-fermentation by *S. cerevisiae* 424A(LNH-ST) with the effect of these inhibitors is presented.

Thursday, 16 November 2006 - 10:40 AM

Logistical Support and Modeling Efforts in Pretreatment Research

Tim Eggeman, Neoterics International, 2319 S. Ellis Ct., Lakewood, CO 80228 and Richard T. Elander, NREL, 1617 Cole Blvd, Golden, CO 80401.

The Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) was formed in 1999 as a multi-institutional effort to develop comparative information on cellulosic biomass pretreatment options. Our prior work focused on a comparative evaluation of corn stover feedstock for five leading pretreatment technologies (dilute acid, hot water, ammonia recycle percolation, ammonia fiber explosion and lime). Our current efforts, known as the CAFI II project, have been expanded to cover hybrid poplar as the feedstock and an additional pretreatment (SO₂). This paper will describe the logistical support and modeling efforts that the National Renewable Energy Lab has provided to the consortium in the CAFI II project. Model updates include a more current costing basis for the economic models, the development of a graphical user interface, and the incorporation of a woody biomass (hybrid poplar) feedstock handling system. In addition, initial pretreatment and saccharification data on hybrid poplar for each pretreatment process has been incorporated into the economic models. Progress toward the incorporation of hydrolyzate fermentation performance and the inclusion of any necessary hydrolyzate conditioning processes into the economic models will also be reported.

Biological Conversions and Processes for Renewable Feedstocks (T4005)

Thursday, 16 November 2006 - 12:30 PM

Alternative Routes for Conversion of Biomass to Fuels and Chemicals

Raphael Katzen, Raphael Katzen, P.E., 9220 Bonita Beach Road, Suite 200, Bonita Springs, FL 34135

This presentation will provide a matrix of the various process steps which have been considered, some of which have been developed, to convert lignocellulosic biomass to fermentable sugars for production of ethanol, or other chemical products. The status of various pretreatments, and subsequent enzymatic saccharification and fermentation technologies will be presented, as well as product recovery and waste disposal systems. Current status of development, demonstration and industrial projects will also be indicated.

Thursday, 16 November 2006 - 12:50 PM

Flexible Biorefinery for Producing Value-Added Streams: Evaluation of the Cellulose Stream as a Source of Sugars and Pulp

Kiran L. Kadam, Richard Wingerson, Lawrence Brown, and Ed Lehrburger. PureVision Technology, 511 N. McKinley Ave., Fort Lupton, CO 80621

PureVision Technology, Inc. is developing a process for the fractionation of lignocellulosic biomass into three streams. This is achieved via two coupled reactors, one each for the two stages in a continuous process. Hemicellulose is hydrolyzed in the first stage, which also performs *in situ* solid/liquid (S/L) separation at operating temperatures, and yields a liquid stream

rich in hemicellulosic sugars. Lignin hydrolysis subsequently occurs in the second stage. The slurry obtained from this stage undergoes external S/L separation to yield the other two product streams: a lignin-rich liquid stream and a solid cellulose stream. Enzymatic hydrolysis of this relatively pure cellulose stream requires significantly lower enzyme loadings because of minimal enzyme deactivation from nonspecific binding to lignin. Also, at a given insoluble solids loading, higher cellulose content of the solids results in higher ethanol titer, which translates into significant energy savings during distillation. The cellulose produced is also low-enough in lignin to be used alternatively as market pulp. As corn stover and wheat straw are similar to hardwoods in fiber length, they can partially replace hardwood fiber in pulp blends. This approach potentially yields a higher value commodity and, unlike ethanol, does not require additional processing such as hydrolysis or fermentation. This paper will discuss process development efforts in realizing a flexible biorefinery that can be steered toward the sugar platform or the pulp & paper platform. Specifically, results on the evaluation of the cellulose streams from corn stover and wheat straw for the above two applications will be covered.

Thursday, 16 November 2006 - 1:10 PM

The Effects of AFEX Pretreatment on the Fermentability of Lignocellulosic Hydrolysates Using *Escherichia Coli* KO11

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Lignocellulosic bioethanol offers us several advantages in terms of economic development, energy security and environmental protection. Unfortunately, the complex nature of lignocellulosic plant material poses significant challenges to pretreatment, hydrolysis and downstream processing. In particular, the composition of biomass and pretreatment conditions dictate the products formed, including potential sugar degradation products. The presence of products such as furfural, hydroxycarboxylic acids and acetic acid strongly influence the fermentability of a hydrolysate. We are investigating the fermentability of hydrolysate from Ammonia Fiber Explosion (AFEX) treated corn stover at industrial relevant concentrations. The effects of various detoxification procedures such as overliming and adsorbent conditioning are evaluated. Furthermore, AFEX pretreatment is suspected to be a nutrient addition process via the residual ammonia on treated material. We are evaluating the effects of this residual ammonia on fermentation. The feasibility of simultaneous saccharification and co-fermentation with *Escherichia coli* KO11 using AFEX-treated corn stover and commercial hydrolytic enzymes is explored. To draw appropriate comparisons, hydrolysate from acid treated corn stover is analyzed concurrently with hydrolysates from AFEX treated stover. These studies and comparisons will help elucidate the effects pretreatment methods on hydrolysate fermentability and process economics.

Thursday, 16 November 2006 - 1:30 PM

Impact of Culture Nutrition on the Tolerance of Furan Inhibitors and the Conversion of High Xylose Concentrations to Ethanol by *Pichia Stipitis* Nrrl Y-7124

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Efficient fermentation processes to produce ethanol from both the hexose and pentose sugars available in low-cost lignocellulosic biomass are sought to support the expansion of the biofuels industry. Such an expansion is expected to strengthen our nation by lessening dependence on foreign sources of fuel, preserving our environment and national resources, and boosting our

rural economy. Stress tolerant microorganisms are needed that are able to consume both hexose and pentose sugars and also withstand, survive, and function in the presence of stress factors common to fermentations of lignocellulose hydrolysates, including various chemical fermentation inhibitors such as furfural, hydroxymethylfurfural (HMF), and ethanol. Furfural and HMF are key byproducts of the dilute acid pretreatment hydrolysis of lignocellulosic biomass, the most economical method of releasing hemicellulosic sugars for fermentation to ethanol biofuel. The availability of tolerant microbial catalysts would allow efficient fermentation of low-cost acid hydrolysates despite the presence of inhibitory byproducts. Our research has shown that natural strains of the yeasts *Saccharomyces cerevisiae* and *Pichia stipitis* can survive and adapt to the presence of furfural and HMF and that this survival is linked in part to a fully functioning pentose phosphate pathway, likely key in maintaining the cofactor balance needed for the *in situ* detoxification of furfural and HMF to their less toxic alcohols (furfuryl alcohol and 2,5-bis-hydroxymethylfuran, respectively). Data will be presented showing the impact of mineral and nitrogen source composition on the ability of *P. stipitis* to survive and detoxify furan inhibitors and to convert high xylose concentrations efficiently to ethanol. Implications of these findings in context of the current literature on biomass to ethanol conversion and stress tolerance will be discussed. Process-based strategies to produce a tolerant initial population and then to foster and sustain tolerance during growth and ethanol fermentation will be considered.

Thursday, 16 November 2006 - 2:00 PM

Ethanol Production from Xylose by Ethanol Resistant Derivatives of *Escherichia Coli* Fbr5 under Batch and Fed-Batch Conditions

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Residual agricultural biomass represents an untapped resource for renewable fuel production. Ethanol production from lignocellulosic biomass is not economically feasible, in part, due to limitations in biocatalyst performance. Obtaining a high ethanol yield from lignocellulosic biomass requires the use of a biocatalyst that rapidly produces ethanol with few byproducts, metabolizes all sugars produced by biomass treatment and resists toxins present in the feedstock and the fermentor.

Several ethanol resistant derivatives of the ethanologenic strain *Escherichia coli* FBR5 have been isolated. During pilot fermentor studies in a Luria broth medium containing 150 g/L xylose, strains ARL and ANE produced over 50 g/L of ethanol while FBR5 produces roughly 40 g/L of ethanol. Further fermentations were done with the goal of maximizing ethanol concentration. However, high concentrations of xylose (>175 g/L) were found to inhibit cell growth and ethanol production. Under fed-batch conditions where xylose concentrations were regulated at 100 g/L, ARL produced over 60 g/L ethanol. The fed-batch strategy combines the high ethanol yields and rapid ethanol production observed in batch fermentations with a product stream at a high ethanol concentration.

Thursday, 16 November 2006 - 2:20 PM

Bioethanol Production from Cellulosic Materials by Cell Surface Engineered Yeast Strains

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Display of novel enzymes on the yeast cell surface is very powerful method to develop the efficient whole cell biocatalysts, because the diffusion problem of substrate and product is circumvented. In addition, the displayed enzymes are regarded as a kind of self-immobilized

enzyme on the cell surfaces. In this study, we have developed the novel methods to display enzymes using cell wall anchoring proteins alpha-agglutinin. To show their applicability to the productions of biofuels and chemicals from biomass, the ethanol production from cellulosic materials was investigated by using yeast cells displaying cellulolytic enzymes. Due to the display of these enzymes, cellulosic materials were sequentially hydrolyzed to glucose on the yeast cell surface, immediately utilized and converted to ethanol by intracellular enzymes. The yield in terms of grams of ethanol produced per grams of carbohydrate utilized was over 0.45, which corresponds to over 89% of theoretical yield. These results demonstrate that a combination of cell surface displayed enzymes and intracellular metabolic system is a very effective approach to develop cells with novel catalytic and metabolic abilities for industrial applications.

Thursday, 16 November 2006 - 2:40 PM

Reaching High Substrate Loading in the Lignocellulose to Ethanol Process; Effects of Multiple Batches of Substrate Loading on Enzymatic Hydrolysis and Viscosity of Pretreated Barley Straw

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One of the aspects of creating an economically feasible lignocellulose to ethanol process is to secure a sufficiently high enough ethanol concentration for distillation. One prerequisite of doing so is to employ high dry matter loading of the substrate and high extent of cellulose hydrolysis. However, the high viscosity of most lignocellulosic substrates makes it difficult to operate with substrate loadings much higher than 10 % by weight of dry matter. The present study provides an evaluation of a fed-batch strategy, loading multiple batches of substrate to reach 15 % by weight of dry matter, during enzymatic hydrolysis at 50 °C, pH 5 of acid-steam exploded pretreated barley straw. The enzyme system Celluclast® (a cellulolytic enzyme preparation from *Trichoderma reesei*) and Novozym 188 (a β -glucosidase preparation from *Aspergillus niger*) was added either at the full dose for 15 % by weight of dry matter at the beginning of the hydrolytic reaction or in conjunction with the substrate during the fed-batch loading. Results regarding cellulose conversion, glucose yields, and viscosity changes during the hydrolysis are presented for several different sequential substrate loading and sequential substrate + enzyme loading regimes with the aim of providing insight into the interplay between substrate loading, viscosity and enzyme catalysed cellulose degradation of the barley straw material during the enzymatic hydrolysis reaction.

Catalytic Conversion of Renewable Resources to Synthesis Gases and Pyrolysis Oils (T4001)

Thursday, 16 November 2006 - 12:30 PM

Technoeconomic Comparison of Indirectly Heated and Directly Heated Gasification Processes for Making Mixed Alcohols Via Catalytic Upgrading of Synthesis Gas

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Processes to convert renewable lignocellulosic biomass materials such as corn stover, switch grass, or wood into transportation fuels are of significant interest today. Thermochemical routes using gasification and catalytic upgrading of the resulting synthesis gas are promising methods

for making liquid transportation fuels and chemicals from biomass. Two major types of high temperature gasification processes are often considered: indirectly heated gasifiers that generate process heat through the combustion of residual char externally to the gasifier vessel (eg. In another vessel), and high pressure, directly heated gasifiers that use oxygen to generate heat in the gasifier by partially oxidizing some of the biomass insitu. Each of these processes has tradeoffs in the capital equipment and operating costs requirements affecting the process economics. This paper will compare the technoeconomics of the indirectly heated and directly heated gasification processes for making mixed alcohols via catalytic upgrading of synthesis gas.

Thursday, 16 November 2006 - 12:50 PM

Gas Cleanup Technologies Suitable for Biomass Gasification to Liquid Fuels

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Nexant Inc., with support and funding from the US Department of Energy's National Renewable Energy Laboratory, recently completed work to identify commercial technologies that are suitable for synthesis gas cleanup for biomass gasification. Currently, there are various types of technologies available. Technologies selection for a specific system is generally determined by the composition of the syngas, which is influenced by the biomass feedstock and the operating conditions of the gasifier, the cleanup requirements for the intended use of the syngas, and economic considerations.

The cleanup requirements will vary for different syngas applications. For example, the cleanup required for syngas that will ultimately be fed to a reciprocating engine is much less than for syngas used in chemical synthesis. This study examined relevant technologies that could be required for syngas that will be used for Fischer-Tropsch (FT) liquids and alcohol synthesis.

Typical contaminants from biomass gasification include particulates, tars, alkali, nitrogen, and sulfur compounds. In most biomass feedstocks, the sulfur concentration is low; however, the sulfur impurities need to be removed from syngas that will be used for synthesis of alcohol and Fischer-Tropsch (FT) liquids. Additionally, some biomass feedstocks may contain halides or trace metals. Contaminants are undesirable since they can present emissions problems, damage downstream equipment, or deactivate catalysts. Gas cleanup technologies can be used to control the level of contaminants in the syngas. For example, technologies such as cyclone separators, barrier filters, and electrostatic precipitators are routinely used for solid particulate removal. Catalytic tar crackers are employed to destroy tars and nitrogen contaminants. Wet scrubbers are used to remove a number of contaminants such particulates, alkali, halides, soluble gases, and condensable liquids. Acid gas removal technologies encompass a large selection of processes including amine-based, physical solvent, liquid phase oxidation, and catalytic absorbent.

For this presentation, the discussion will focus on the operating size ranges and conditions, materials of construction, and cleanup parameters for technologies to remove particulates, tars, acid gas, ammonia, alkali, and halides from biomass derived syngas. Application of this analysis will be demonstrated in developing a cleanup configuration for low- and high-pressure gasifiers with a wood feed rate of 2,000 tonnes per day. The cleanup configuration will comprise of a combination of technologies that will achieve syngas specifications required for producing a variety of liquid fuels as part of a biomass refinery.

Thursday, 16 November 2006 - 1:10 PM

Upgrading Producer Gas from Biomass Gasification to Produce High Purity Hydrogen

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In the biorefinery concept, hydrogen is one commodity chemical that is very valuable for use either as an energy carrier for power generation or as a feedstock for producing other important chemicals such as ammonia. It is likely that the most efficient pathway to produce hydrogen from biomass is the thermo-chemical process path via biomass gasification followed by catalytic treatment of the cleaned producer gas to increase the hydrogen content followed by hydrogen purification/separation.

The traditional way to increase hydrogen content of the producer gas is by first passing the gas stream to a steam reformer at 800°C followed by a two-step water gas shift reactions (HT and LT shifts at 400 and 250°C, respectively). CO₂ is separated from hydrogen either by extraction or pressure swing absorption. The multistep process makes the process inefficient and costly.

At Iowa State University, research efforts have been made on improving the efficiency of producing hydrogen from biorenewable materials. Discussed will be results from tests conducted at the Biomass Energy Conversion Facility (BECON) in Nevada, Iowa which is operated by the Iowa Energy Center. A pilot scale fluidized bed reactor is used to produce the producer gas. The system is rated (2.8 MMBTU/h) thermal input, which corresponds to an average throughput of 180 kg/h (400 lb/h) of solid biomass fuel. The cleaned producer gas from this gasifier is upgraded for its hydrogen content by using core-in-shell catalyst/sorbent technology that has been developed at Iowa State University in the past three years. This technology utilizes a unique material called core-in-shell combined catalyst/sorbent pellets in which a CaO core is surrounded by a porous shell that supports a nickel catalyst. By using the pellets, the production of pure H₂ is reduced to a single step because simultaneous reaction rate improvement to produce hydrogen from the catalyst function and separation of H₂ and CO₂ via selective absorption of CO₂ by CaO can be achieved. Effects of operating conditions on the product stream compositions will be addressed.

Thursday, 16 November 2006 - 1:30 PM

Production of Clean Synthetic Gas from Biomass Using a Downdraft Gasifier

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Biomass is considered as a potential feedstock for sustainable energy production that can be converted to chemicals, fuels, electricity etc., either by thermochemical or biological processes. Gasification is one of the thermochemical methods of converting biomass to synthetic gas (CO and H₂), which could potentially be used to produce different chemicals such as acetic acid and ethanol via chemical or biological processes and/or generate electricity by using engines, turbines, fuel cells etc. However, the synthetic gas produced may contain different organic (Tars) and inorganic impurities, which have the potential to damage the process equipment used in

different conversion processes. Hence, the synthetic gas has to be cleaned to remove these impurities, and the extent to which the gas has to be cleaned is dictated by the end use application. The production of tars both in terms of quality and quantity depends on various factors such as the gasifier type, type of feedstock, moisture content of the feed, feed size, gasification conditions, atmospheric conditions etc. Therefore, additional work needs to be done that can correlate tar production in different types of gasifiers under varying operating conditions. This could help establish standard tolerance limits of tars for different end use applications. Active research is being carried out currently at Mississippi State University that involves the biological conversion of synthetic gas to ethanol and acetic acid. The presence of tars in the synthetic gas is expected to inhibit the growth of microorganisms. Hence, the feasibility of this process would entail minimal tar content in the synthetic gas being produced. The conversion of biomass to synthetic gas is being accomplished utilizing a downdraft gasifier. The effect of different feedstocks such as hard wood and soft wood on the production of tars is being evaluated. Also, the effect of different operating parameters on the production and quality of synthetic gas is being studied. Tar characterization will be done and the amount of tar produced during different gasification experiments will be measured, the results of which will be presented. These results will aid in the selection of a suitable method for the destruction/removal/reforming of the tars produced, which will be the future course of research.

Thursday, 16 November 2006 - 2:00 PM

Biomass Gasification with Nickel Oxide/Olivine Catalysts in Fluidized Bed Gasifier

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Tar removal from biomass gasification gas is a crucial problem in applying syngas from biomass for its downstream applications. Catalytic biomass gasification has given promising results for tar cracking. A few research groups have investigated the use of olivine for tar cracking. The presence of oxides of iron and magnesium in the mineral olivine give it the ability to crack higher hydrocarbons termed as tars. Olivine surely does have sustainable physical properties for the harsh conditions of a fluidized bed gasifier. Untreated olivine was previously compared by us with dolomite in cracking model tar compounds. Modifying the olivine by calcination at high temperatures showed very promising results towards tar cracking. Also tests related to attrition resistance showed that olivine is very capable of being the gasification catalyst as compared to dolomite. Nickel oxide is known in the literature as an effective catalyst for tar cracking and tar reforming. Therefore, the behavior of nickel oxide on olivine catalyst under reducing conditions with respect to tar cracking is studied.

The purpose of this study is to determine the conversion of a tar (naphthalene) using the nickel on olivine catalyst in a fluidized bed biomass gasifier and moreover to study the effect of olivine calcination on the conversion of tars.

In-situ removal of tar during biomass gasification is being performed in a bubbling fluidized bed biomass gasifier. Different forms of NiO/Olivine catalysts are used. These are: (i) nickel oxide on olivine, (ii) nickel oxide on calcined olivine, (iii) the calcination of catalyst mentioned under (i), and (iv) the calcination of catalyst mentioned under (ii).

The gasifying agent is air. The biomass feed rate is 1 kg/h. The temperature in the gasifier is maintained at 800 °C. Sand is used as the bed material along with the catalyst.

During the catalyst preparation the hardness of the nickel oxide on olivine catalyst was noticeable and it can be related to the attrition resistant property of olivine. The catalyst is characterized by means of XPS, XRD, SEM and EDX. XPS analysis has revealed that nickel is present at the olivine surface as Ni²⁺. Presence of iron oxide on the surface of the catalyst after impregnation of nickel and calcination of the catalyst is also seen.

The results of the activity for tar cracking using the catalysts, and the stability of the gasifier with respect to time are also discussed.

Thursday, 16 November 2006 - 2:20 PM

Production of Synthesis Gas and/or Hydrogen from Biomass Via Fast-Pyrolysis and Reforming Process

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Biomass materials, such as switchgrass and cornstovers, are very potential to be used as renewable resources for producing syngas or hydrogen which are used either for generating electricity or producing chemicals. The utilization of biomass, however, is limited by the cost of transporting. In addition to the location for collecting biomass which is generally far away from hydrogen/syngas production facilities, biomass has a low energy density thus it is expensive to transport.

In an effort to resolve this issue, we are developing a system for producing syngas or hydrogen from biorenewable material to be used for fueling existing power plants. In this system, biorenewable materials, such as cornstovers, are collected and preprocessed locally to yield energy-rich bio-oil and porous char via fast pyrolysis. The char can be injected back to the soil or used for producing heat. The bio-oil, which can be thought as densified biomass (density is 1280 kg/m³ compared to approximately 160 kg/m³ for original biomass), is transported by tanker trucks to a power generating facility where it is steam reformed to either produce synthesis gas or hydrogen which will be used as clean fuel for generating power. The potential benefits of this system include: 1). Efficient and economically profitable utilization of abundant biomass which is otherwise considered waste, 2) Less consumption of expensive fossil fuel and natural gas which potentially reduce the cost of power generating and furthermore reduces emission of CO₂.

To be discussed is the research work at Iowa State University in developing a process for producing bio-oil from biorenewable materials, such as cornstovers, that uses a 25kWth fast pyrolysis system which is equipped with a fractionating condenser system. The condenser system, developed at Iowa State University, yields bio-oil fractions containing very little lignin. Bio-oil reforming performance is improved if the lignin fraction is separated from the carbohydrate prior to reforming. The reformability of bio-oil to produce synthesis gas or hydrogen will be addressed. Effects of bio-oil composition and reaction conditions on the product yields will be discussed. Included in the discussion is the application of recently developed core-in-shell catalyst-sorbent material, which enables simultaneous hydrogen producing reactions and CO₂ by-product separation to produce highly pure H₂, for reforming bio-oil.

Thursday, 16 November 2006 - 2:40 PM

Stability Assessment of Wood and Bark Derived Bio-Fuels

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Heating value of bio-oils is reported to be half of conventional petroleum derived fuels. However, there are some engineering problems associated with these oils. Bio-oils are known to become unstable because of several self-catalyzed polymerization reactions. Polymerization reactions

become evident with increasing storage time. Consequently, these polymerization reactions release more water into the bio-oil with time. If the water levels in the bio-oils exceed 30% by volume the bio-oils start phase separating as well. Viscosity of the bio-oils has been known to increase significantly also as a result of aging. Higher viscosities of bio-oils can increase the pumping costs and can also cause deposit build-up on fuel injectors.

Bio-oil is known to be highly polar in nature due to the presence of many oxygenated compounds (10-25%). Bio-oils are also known to be very acidic in nature due to the presence of organic acids (5-12%). Because of this reason the bio-oils are also known to be very acidic which can cause corrosion problems. The above problems put together can limit the use of bio-oils as potential fuels. Hence, The primary focus of this study is to isolate the potential additives to stabilize the bio-oils and retain their homogeneity over extended storage time periods.

Pyrolysis experiments were carried out using an auger reactor at Mississippi State University by varying vapor residence times and pyrolysis temperatures. The feedstocks utilized were wood and bark derived from pine and oak. The reactor was operated in a semi-batch mode at a set auger speed of 8rpm. Reactor yields of greater than 60% were obtained. Potential additives from different groups of organic compounds will be selected for the prescreening studies. Matrix selection factors will include the bulk chemical costs, radical inhibition, hydrogen ion (H^+) donation, water inhibition, and solubilizing capabilities. Preliminary studies are underway for assessing the stability of bio-oils at a storage temperature of 80°C. A temperature of 80°C has been chosen to accelerate the testing of bio-oils. The overall objective of this study is to achieve the stability of bio-oils using different additives at different concentrations. Consequently, three additives with three concentrations (low, medium, and high) will be chosen to study the stability of bio-oils. By optimizing the additive concentrations of potential additives we will be able to present a cost-feasible solution to the bio-fuel stability problem.

Analytical tests will include the water content analysis of the bio-oils that will be measured periodically using Karl-Fisher titrator from Mettler Toledo®. Rheological analysis will also be performed using Brookfield® instrumentation. Heating values of bio-oils will be determined using a bomb calorimeter from Parr®. Flash point and cloud points will also be determined using Pensky-Martens® apparatus for the produced bio-oils. The results of this study will be presented at the meeting.

Life Cycle Analysis of Renewable Feedstock-Based Processes and Products (T4006)

Thursday, 16 November 2006 - 3:15 PM

Life Cycle Assessment of Integrated Biorefinery: Corn Grain, Corn Stover and Switchgrass

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Lignocellulosic biomass (e.g., crop residues, energy crops and etc.) is a potential raw material for lignocellulose-based ethanol production, while corn grain is currently the primary feedstock for ethanol production in the United States. Large scale technologies for lignocellulosic feedstock will likely be available in the near future.

An integrated biorefinery is defined as a biorefinery in which both lignocellulosic raw materials and starch raw materials are used to produce biobased products. One merit of integrated

biorefinery is that the starch based biorefining processes can utilize surplus energy from the lignocellulosic biorefinery process, in which fermentation residues and biogas from wastewater treatment are used as fuel sources to generate both electricity and steam. (These data are derived from our collaborates on the Role of Biomass in America's Energy Future project.)

This is a life cycle assessment study on ethanol production in an integrated biorefinery. The feedstock is corn grain as starch based biomass, and corn stover or switchgrass as lignocellulosic biomass. The system boundary includes biomass production, transportation of biomass to an integrated biorefinery, integrated biorefinery processes, transportation of ethanol to users, and ethanol fueled vehicle operation. Ethanol is used as a liquid fuel in a compact passenger vehicle in the form of E10 (a mixture of 10 % ethanol and 90 % gasoline by volume). The Ammonia fiber explosion process (AFEX) is used to pretreat corn stover and switchgrass, and a dry milling process is used as the starch based biorefinery. The allocation procedures for external functions are done by the system expansion approach. Thus, the system boundary is expanded to include the alternative product systems (e.g., gasoline fueled vehicle operation, etc.). The potential impact categories considered here are nonrenewable energy consumption, fossil fuel use (e.g., coal, crude oil and natural gas), climate change, photochemical smog, acidification, and eutrophication. Environmental impacts are estimated by characterization factors given by the United States Environmental Protection Agency (EPA-TRACI).

Thursday, 16 November 2006 - 3:35 PM

Considering Advanced Biorefineries in Context

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Mature processing technology scenarios for cellulosic biomass will be presented, including stand-alone production of power, Fischer-Tropsch (FT) fuels, and hydrogen, as well as co-production scenarios involving ethanol-power, ethanol-power-FT fuels, ethanol-hydrogen, ethanol-FT fuels-natural gas, and several of these products in conjunction with feed protein. Our results suggest that many mature processing technology scenarios will have overall efficiency (heating value of products/heating value of biomass) in excess of 70% and be economically competitive with conventional processes based on fossil resources at prices seen over recent years. These biorefining scenarios also result in significant greenhouse gas reductions and petroleum displacement, as will be presented.

When envisioning advanced biorefineries, it's also important to consider the field-to-fuel supply chain, strategic selection of feedstock, and retooling of agricultural practice to accommodate efficient production of both food and fuel. Optimizing the transition from the current corn ethanol industry to one centered around cellulosic feedstocks is also a vital concern. We will address each of these areas, building upon the above process analysis.

Thursday, 16 November 2006 - 3:55 PM

Life Cycle Analysis of Polyols from Soy Oil or Castor Oil

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Polyols for flexible foams are a class of materials currently made from petrochemical feedstocks, but which can be made largely from renewable resources such as soy oil or castor oil. A “cradle to gate” life cycle analysis was conducted for functionally equivalent polyols made from conventional feedstocks, soy oil and castor oil to understand the potential environmental benefits for using the renewable feedstocks and the key contributing factors to the environmental profiles of each material. Use of the renewable feedstocks offers significant advantages in reducing fossil resource use and greenhouse gas generation. The magnitude of the benefit depends critically on the assumptions made about farm inputs and outputs.

Thursday, 16 November 2006 - 4:15 PM

Optimal Biorefinery Resource Utilization by Combining Process and Economic Modeling

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The integrated biorefinery, which uses renewable feedstocks from the forest-based industries, has the opportunity to provide a strong, self-dependent, sustainable alternative for the production of bulk and fine chemicals from polymers, fiber composites and pharmaceuticals to energy, liquid fuels and hydrogen. With such a wide range of processing steps and possible products, it is obvious that identification of the optimum process structure can not be done based on heuristics or rules of thumb. Depending on market prices and trends, the optimum allocation of resources and production capacity may switch between the different products. Economic market analysis, predictive financial modeling, and optimization under uncertainty are tools that can be used to determine the sensitivity of a decision-making framework to market fluctuations. Thus there is a need for systematic, reliable methods capable of incorporating different levels of process detail in the decision making framework. In this work a mathematical optimization based framework is being developed, which enables the inclusion of profitability measures and other techno-economic metrics along with process insights and performance characteristics obtained from experimental and modeling studies. By utilizing process integration methods, the processing steps can be optimized to ensure efficient use of energy and materials resources while assuring an acceptable, minimal level of environmental impact through the use of EPA's WAR algorithm. A novel feature of the proposed framework is the decoupling of the complex models from the selection step, which enables adaptation to new developments within any of the processing steps and thus can incorporate novel innovative production processes in the decision-making framework. This decoupling enables more efficient solution of the production optimization/allocation problem as the non-linearities embedded in the process models have been removed.

Collaboration with key stakeholders in industry, academia and government has been established enabling access to proprietary process specifics and business models. In this way, experimental and theoretical efforts can supplement each other in a synergistic manner, by providing direction and data for continued work.

This contribution will illustrate the strategy for developing the decision making framework as well as highlighting the flexibility of the framework to utilize data from technological breakthroughs in the field of biorefining.

Thursday, 16 November 2006 - 4:45 PM

Impacts on Soil of Large-Scale Crop Residue Harvest for Biofuel Production

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Great enthusiasm exists among government agencies, private industry, and the general public for use of renewable feedstocks, such as crop residues and biomass crops, for production of ethanol and bio-based products. Proponents suggest that stover removal will provide growers with additional sources of income, expand the rural industrial base, and reduce reliance on increasingly scarce petroleum, all from material that is now considered “waste”. However, crop residues are not wasted if returned to the soil. Dynamics of organic matter decomposition give soil life and sustain its critical productive characteristics. Research has shown that residue removal reduces soil organic matter content, crop yield, and soil quality. In addition, residue removal leaves fields more susceptible to erosive losses of sediment and nutrients, with negative consequences for surface water bodies, including eutrophication and siltation. Failure to properly account for and predict the impact of residue removal on future crop yield, soil organic matter content, and water quality will have serious implications for the long-term sustainability of our food, feed, and fiber production systems. Promising research is underway to develop new farming systems that will permit substantial increases in biomass removal while sustaining soil and water resources, but the challenges are formidable.

Thursday, 16 November 2006 - 5:05 PM

Techno-Economic Analysis of Lignocellulose to Liquid Fuels Biorefinery Using Aspen Wood as Feedstock

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There has been an increasing interests in the conversion of lignocellulosic biomass to fuel grade ethanol in the recent years due to the need for minimizing oil imports, increasing oil prices and increasing global oil consumption and the need for alternative renewable energy and the requirement of minimizing greenhouse gas (GHG) emissions caused by the use of fossil fuel (Morrow 2006). At present, number of corn-to-ethanol plants have been commercially built and operating around the world, while no process for lignocellulosic biomass-to-ethanol, or cellulosic ethanol, has yet been commercially available because of existing technical, economic, and commercial barriers. However, cellulosic ethanol can be more effective and promising as an alternative renewable bio-fuel than corn ethanol in the long run because it could greatly reduce the net greenhouse gas (GHG) emissions as well as higher net fossil fuel displacement potential. With large-scale planting of fast-growing cellulosic energy crops such as hybrid poplar and switchgrass on different types of lands through plant breeding and improved crop management, the purchase cost of feed stocks could also be relatively lower (Kszos 2001). In this paper, a whole lignocellulosic biorefinery producing ethanol from Aspen wood (common hard wood species used in pulp and paper manufacture) is designed and modeled. The overall process efficiency and economic performance of the biorefinery to manufacture liquid fuels from lignocelluloses is studied. Environmental consideration is also taken into account. The biorefinery model can help us better understand the overall process and better predict the operating cost and environmental impacts and the overall viability of the biorefinery. Our result predicts that Aspen wood based lignocellulose to ethanol biorefinery is highly feasible and the economic and environmental performance compares favorably to today's corn-to-ethanol.

[References] William R. Morrow, W. Michael Griffin, and H. Scott Matthews. Modeling Switchgrass Derived Cellulosic Ethanol Distribution in the United States. *Environmental Science & Technology*, 40(9):2877-2886, 2006

Lynn Adams Kszos, Bioenergy from Switchgrass: Reducing Production Costs by Improving Yield And Optimizing Crop Management, <http://www.ornl.gov/~webworks/cppr/y2001/pres/114121.pdf> (May 14, 2006)

Thursday, 16 November 2006 - 5:25 PM

Life Cycle Assessment of Transportation Fuels Using Hybrid Models

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Alternative transportation fuels such as ethanol, Biodiesel, and hydrogen have become a subject of intense scientific scrutiny in light of dwindling fossil fuel reserves, increasing price and climate change. Ethanol and biodiesel have already been used as transportation fuels for sometime whereas hydrogen fuel is still in research and development phase. To evaluate the desirability and tradeoffs for using alternative fuels, a comprehensive life cycle assessment (LCA) is recommended. A number of process LCAs have been conducted for alternative transportation fuels. However, process-scale life analysis has certain limitations such as subjectivity involved in system boundary selection and incompleteness of the system [1] that often lead to conflicting conclusions [2,3]. This limitation is also relevant to other life cycle oriented approaches such as net energy analysis [3]. ISO has defined broad guidelines for cut-off criteria; however, they are difficult to meet due to lack of prior knowledge for inputs and processes. In process life cycle inventory, inputs from third tier and beyond are neglected introducing truncation errors. Another important unresolved challenge in LCA studies is that the underlying data are often thermodynamically inconsistent and may not even satisfy the laws of conservation.

To overcome the drawbacks, hybrid models have been introduced for LCA [1], and data reconciliation methods have been developed to enhance the quality of life cycle inventory data by imposing conservation laws [4]. There are three main hybrid models: tiered hybrid, input-output hybrid, and integrated hybrid. Hybrid models have been used for other products or economic sectors; however, application of an input-output hybrid model in life cycle analysis of transportation fuels is novel. Although subjectivity regarding system boundary selection still remains, it offers better resolution than a tiered hybrid model and the system is complete in terms of upstream input data requirements. We are working on the input-output hybrid model that combines a process system with input-output system and avoids double counting. It utilizes commodity and environmental flows data and process-based life cycle inventories (LCIs). Process level data will be collected from various sources including government organizations, trade/ industrial associations, and published literature. Economy scale data will be derived from the 1997 US economic input-output inventory. We will employ data rectification whenever possible to improve the data quality. A sensitivity analysis will also be conducted to identify the most influential processes or inputs.

We will present the results of hybrid analysis for gasoline, ethanol, and biodiesel in terms of energy consumption and environmental impacts, and offer a comparative perspective. Due to completeness of upstream requirements, conclusions obtained from a comparative study will be more reliable than those obtained from process LCAs. It is expected that the magnitude of energy consumption and environmental impacts are likely to be more than predicted by process LCAs. Our goal is to modify the hybrid model by incorporating ecological cumulative exergy [5] that captures contributions from ecology and, hence, better reflects the magnitude of sustainability of alternative fuels. The resulting thermodynamic input-output hybrid model will provide a new approach to address the issue of ecologically conscious product design and manufacturing. Indicators such as environmental loading ratio, yield ratio, impact per value

added, and sustainability index obtained from such a model can be used to evaluate the tradeoffs and appropriateness of transportation fuels.

References: [1] Suh S., Lenzen M., Treloar G.J., Hondo H., Horvath A., Huppes G., Jolliet O., Klann U., Krewitt W., Moriguchi Y., Munksgaard J., Norris G., 2004. System boundary selection in life-cycle inventories using hybrid approaches. *Environmental Science and Technology* 38(3) 657-664. [2] Kim S., Dale B., 2005. Environmental aspects of ethanol derived from no-tilled corn grain: nonrenewable energy consumption and greenhouse gas emissions. *Biomass and Bioenergy* 28, 475-48. [3] Pimentel D., 2003. Ethanol fuels: energy balance, economics, and environmental impacts are negative. *Natural Resources Research* 12(2), 127-134. [4] Yi, H.-S., Bakshi, B. R., Enhancing Life Cycle Inventories Via Reconciliation across Multiple Scales, AIChE 2005 Annual Meeting, Cincinnati, OH [5] Ukidwe N. U., Bakshi B. R., 2004, Thermodynamic accounting of ecosystem contribution to economic sectors with application to 1992 US economy. *Environmental Science and Technology* 38 (18): 4810-4827.

Separation of Processing Streams Derived from Renewable Feedstocks (T4003)

Thursday, 16 November 2006 - 3:15 PM

Biosep: a New Ethanol Recovery Technology for Small Scale Rural Production of Ethanol from Biomass

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Research activities on bioethanol have increased substantially as a result of the current concerns with energy security. Inexpensive biomass including forest residues, mill residues, agricultural residues, urban wood wastes and dedicated energy crops that exists in abundance across the entire United States could be harvested for ethanol production. However, efforts to exploit this resource have been limited due to the high cost of collecting and transporting distributed biomass to a central processing plant required by the current ethanol production technology of two-step distillation followed by molecular sieve drying.

MTR, together with the USEPA, is developing a new ethanol recovery technology called BioSep that combines a proven membrane technology (pervaporation) with an innovative condensation technology (dephlegmation). In simple pervaporation, a multicomponent liquid stream is passed across a selective membrane that preferentially permeates one or more of the components as vapor. Pervaporation is inherently energy-efficient because only the small fraction of the feed liquid that passes through the membrane must be vaporized. Alternatives such as distillation require vaporization of a much larger fraction of the feed to achieve the separation. A dephlegmation process consists of partial condensation with countercurrent flow of rising vapor and falling condensate. With the dephlegmator, better separation can be achieved and only vapor condensing at the top of the column must be cooled to the lowest temperature. Therefore, the BioSep process is cost-effective and energy efficient in recovering ethanol from biomass that will allow distributed and small-scale production of bioethanol across rural America.

The BioSep process includes two includes two membrane pervaporation steps, one upstream pervaporation step with ethanol permeable membrane is used to provide an ethanol enriched feed to the dephlegmator, and a second pervaporation dehydration step with water permeable membrane is used to treat the overhead ethanol product from the dephlegmator. In the latter step, the last 10 wt% of water in the alcohol vapor is removed to produce 99.5 wt% dry alcohols.

In this paper, the progress of this BioSep project will be reviewed with the focus on the discussion of the pervaporation membranes developed.

Thursday, 16 November 2006 - 3:35 PM

Concentration of Proteins from Switchgrass and Distiller's Grains Using Ultrafiltration during Biomass Refining

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Proteins can be a valuable co-product to ethanol within cellulosic biorefineries. These proteins are captured during a separate extraction step or from within the hydrolysate. However, protein extraction requires a large amount of solvent that must be removed in an energy intensive operation. In both cases, the proteins must be concentrated and purified before being sold as animal feed. Also, great care must be taken to insure that protein recovery does not significantly lower resulting ethanol yields. Ultrafiltration is an attractive method of concentration compared to salt or heat precipitation due to the ability to recycle the solvent and the lower energy requirement.

This research focuses on concentrating proteins from early cut Alamo switchgrass (*Panicum vergatum*) and distiller's dry grains and solubles (DDGS) released during cellulose hydrolysis and extracted as a separate process. We propose using a multi-stage simulated cross flow extraction to reduce solvent use while still maintaining protein yields during the extraction process. Transmembrane pressure, temperature, and solvent flow rate is varied within a tangential flow ultrafiltration system to determine its effects on protein recovery, concentration, and residence time. The concentrate is then analyzed for non-protein components to assess whether further purification is required. Finally, the remaining hydrolysate is fermented, and the kinetics and ethanol yield is compared to the protein-rich hydrolysate.

Thursday, 16 November 2006 - 3:55 PM

Nanofiltration & Separation of Hydrolyzates from Sugar Maple Wood

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We investigated the separation of hemicelluloses from sugar maple hydrolyzates in order to process them further by fermenting to bioethanol liquid fuels. The wood chips were pre-extracted using hot water according to a process developed at ESF. Papermaking pulps were prepared using traditional alkaline pulping processes conventional paper products may be manufactured downstream. The wood hydrolyzate leaches significant quantities of hemicelluloses along with a small amount of lignin and other extractives. The leachate was separated using nanofiltration membranes and acetic acid was obtained. Different methods for filtering the extracts and the properties of the permeates and concentrates were determined.

Thursday, 16 November 2006 - 4:15 PM

Cost Effective High Value-Added Chemical Extraction from Lignin with Gas Expanded Liquids

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We have developed a novel process to yield high value-added products from renewable resources using CO₂-expanded organic solvents (gas-expanded liquids). Modest pressures of carbon dioxide were added to a solution of lignin in an organic solvent. Dissolution of CO₂ into this mixture reduces the polarity and induces precipitation of high molecular weight lignin components along with high value added chemicals such as vanillin and syringaldehyde, that can be further extracted to provide profit for the pulp and paper industry. These results provide a preliminary concept for a new processing technique that promotes both sustainable technology and the importance of converting renewable biomass to valuable products.

Thursday, 16 November 2006 - 4:45 PM

Fractionation of Hot-Water Wood Extracts

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The wood extracts from hot-water extraction consist of monomeric and low molecular-weight oligomers of sugars (hexoses and pentoses), acetic acid, degraded lignin, and other low molecular-weight extractable substances. Hydrolysis of oligomers to monomeric sugars can be achieved by allowing more residence time for the wood extracts at high temperature under acidic conditions or could be achieved enzymatically. Separation of sugars and acetic acid is a key step in the biorefinery process. Several methods for the separation have been considered, including filtration, distillation, centrifugation, and chemical separation (i.e. chemical reactions that bond certain compounds to other molecules that allow them to be separated more easily). Membrane separation (or filtration) has been focuses in this study.

Thursday, 16 November 2006 - 5:05 PM

Solids Handling for Biorefinery Integration Using Process Engineering Simulators

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The world economy currently relies on oil as an energy source for fuels and petrol, and as the raw material source for almost any carbon-based commodity chemical. However, its soaring price, along with the new concerns about carbon dioxide and global warming, has triggered in recent years an unprecedented interest on renewable energy, which has been translated into an enormous effort invested in the development of new industrial biological processes. Biorefineries can be defined as a tightly integrated set of entwined biochemical and chemical processes that produce a portfolio of chemicals, fuels and energy from a renewable raw material. A general, simplified scheme of a biorefinery would consist of a pretreatment stage, a bioconversion stage and downstream processing (which can include many of the traditional unit operations).

The success of petrorefineries after the petroleum crisis in the late 1970's came from making the most of every drop of oil through process integration; in a parallel way, biorefineries will only become competitive by fractionating the very last drop of the 'barrel' of biomass using the same process integration tools. However, biorefineries will become even more complex than petrorefineries, as they will include pretreatment and bioconversion stages on top of the traditional chemical engineering unit operations. That implies that process integration for biorefineries will face inherited, as well as inherent, challenges.

Process engineering software packages are now major players in process integration, offering visual representation of the processes, and a full database of chemical compounds and unit operations. These characteristics offer invaluable insight into the studied processes. One of the

main challenges biorefinery integration will encounter is the inclusion of solids handling in the representation of processes: although 70% of the intermediate products and 60% of the final products handled by established process industries are solids (Charpentier 2005), either the associated models and flowsheets extremely simplify their behavior, or are plainly not included. This strategy clearly leaves out a whole range of improvements in the processes. In the case of biorefineries, almost all of the raw material will be solid, as well as many of the intermediate products. Thus, the right framework to deal with solids handling within process engineering packages is of utmost importance to underpin the development of competitive biorefineries.

Cereal biorefineries will play a key role in the new economic scenario: cereals offer large scale production, high energy density and preexisting infrastructures for handling and transportation. Among them, wheat, which has accompanied mankind in its evolution, will be one of the most important ones. In a cereal biorefinery, wheat, being composed of solid granular kernels, requires as first steps appropriate milling and separation into different fractions. The effectiveness of the fractionation at this stage of the process greatly affects the performance and efficiency of later stages. While milling and sifting are usually neglected in the simulation of industrial processes, they are highly complex and interacting operations, and have proved to be a real challenge for simulation.

This research is focused on the use of commercial process engineering software for solids simulation. Four different general, commercial, process engineering packages (Aspen Plus®, Hysys®, PRO/II® and Chemcad®) have been evaluated in order to assess their general adequacy for the implementation of solids operations, and the degree and flexibility of customization they support. The evaluated parameters encompass the definition of solid component to the limitations posed by the programs as a result of the introduction of solids in the flowsheet. As a result, some deficiencies and some directions for further improvement are pointed out. Finally, an example of the integration of solids handling in Hysys® is presented: a simplified sifting unit, and a roller milling unit for wheat are included in the process simulator. The model used in the roller mill is based on the concept of the breakage equation relating the particle size distribution resulting from roller milling of wheat to the input characteristics of the wheat and the design and operation of the roller mill (Campbell and Webb, 2001; Campbell et al., 2001). The work highlights the need to add population balance capabilities alongside the mass and energy balance facilities that currently form the basis of process simulators.

References

Campbell, G.M. and Webb, C., 2001, On predicting roller milling performance. I. The Breakage Equation, *Powder Technol*, 115: 234-242. Campbell, G.M., Bunn, P.J., Webb, C. and Hook, S.C.W., 2001, On predicting roller milling performance. II. The Breakage Function, *Powder Technol*, 115: 243-255. Charpentier, J.C., 2005, Four main objectives for the future of chemical and process engineering mainly concerned by the science and technologies of new materials production. *Chemical Engineering Journal* 107(1-3): 3.

Biological Conversions and Processes for Renewable Feedstocks II (T4008)

Friday, 17 November 2006 - 8:30 AM

Expression of Novel Enzymes for Biomass Conversion in *E.Coli*

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With in the next generation a major world energy source, conventional crude oil, will be exhausted. Sources of natural renewable energy are being explored. Ethanol derived from biomass is one such alternative to petroleum products. Ethanol from biomass will generate

economic development, provide environmental benefits and enhance national security. The Ammonia Fiber Explosion (AFEX) is a leading pretreatment process through which agricultural biomass could be pretreated followed by enzymatic hydrolysis to produce free sugars, followed by fermenting the sugars to ethanol using microbes. Significant cost reductions are still required to make biomass ethanol competitive with petroleum-derived fuels. Enzyme cost reduction for specific pretreatments is one particular cost area requiring effort.

Commercial enzymes available in the market are not tailor made for conversion of AFEX-treated biomass. These lack some important enzyme components and/or the relative ratios of enzymes are inadequate for complete cellulose and hemicellulose conversions. We report here the use of additional hydrolytic enzymes [eg, endoglucanase I (EGI), b-glucosidase, cellobiohydrolases I and II (CBH I & II), xylanase, xylobiase etc.] from different bacterial and fungal sources as well as non-hydrolytic enzymes like expansins along with commercial enzymes to enhance the conversion of AFEX-treated materials. These supplemental enzymes are expressed in *E. coli*. Our objective is more rapid biomass hydrolysis at high yields with lower total enzyme loadings to improve the economics of ethanol production.

Friday, 17 November 2006 - 8:50 AM

Enzymatic Processing of Corn Fibers for a Complete Recovery of Ferulic Acid and Fermentable Sugars

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Corn fibers from wet milling processes are a rich source for ferulic acid and fermentable sugars. Compared to other grain fibers, corn fibers are particularly recalcitrant, resisting enzymatic hydrolysis. Without pretreatment using harsh conditions, only a small percentage of ferulic acid and fermentable sugars could be released. Pretreatment not only represents extra steps in biorefinery but also renders the recovered sugars and ferulic acid unsuitable for some applications such as natural vanillin synthesis. The inhibitors generated from the pretreatment often lower the productivity and complicate the subsequent steps of bioprocessing. *Neosartorya spinosa* NRRL185 was discovered in our previous research as a microbe capable of producing and secreting useful cellulases and hemicellulases for processing various biomass feedstock. In this study, crude enzymes harvested at an appropriate time of cultivation were used to release ferulic acid and fermentable sugars from corn fibers. A complete recovery of ferulic acid and a complete hydrolysis of corn fiber polysaccharides were achieved without any pretreatment. Ferulic acid recovered from corn fiber was extracted with organic solvent and was then tested as a potential starting material for vanillin production. Using *Streptomyces setonii* ATCC391161, a known microbe capable of converting ferulic acid to vanillin, ferulic acid was converted to vanillin, indicating that corn fiber is a suitable source of ferulic acid in the synthesis of vanillin. The crude enzymes were also used to convert corn fiber and xylan-containing substrates to synthesize xylo-oligosaccharides. Xylo-oligosaccharides rich in 10-mers or higher were obtained. Fermentable sugars from corn fibers could be used for biofuels and other useful products. This work demonstrates the feasibility to build a biorefinery platform with multiple co-products from a single biomass feedstock.

Friday, 17 November 2006 - 9:10 AM

High-Value Lignin Co-Products through Pretreatment and Microbial Conditioning

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The conversion of lignocellulosic biomass continues to develop as a potential alternative source of transportation fuel. The major process steps involve pretreatment to degrade or disengage lignin, saccharification to depolymerize cellulose to sugars, and fermentation of sugars to ethanol. Recent, significant economic improvements in enzymatic saccharification have been made through DOE's support of projects by Novozymes and Genencor. This leaves pretreatment costs as a key obstacle to the lignocellulosic ethanol commercialization. Lignin is the most abundant biopolymer after cellulose. It inhibits enzymatic hydrolysis of cellulose, and process designs typically consign its recalcitrant, low-value forms to boilers. However, lignin, in appropriate molecular weight ranges, is a suitable component of phenolic resin plastics. The objective of this work is to apply microbial conditioning before and after pretreatment, to enhance ethanol yield and lignin extraction. The aim is to improve the performance observed with pretreatment, allowing reductions in severity and complexity to reduce costs and improve the economics for the biomass grower. In this work, Corn stover, switch grass and giant miscanthus were obtained, and inocula, such as bacteria from rumen, brewery waste, thermal springs, and wood-eating insect guts were screened and applied to the biomass before and after pretreatment. These included dilute acid pretreatment, expansion from high pressure and centrifugation, and Ammonia Fiber Explosion (AFEX). The conditioned biomass was subjected to simultaneous saccharification and fermentation (SSF) according to DOE-NREL protocol. Ethanol production for screening tests was estimated from carbon dioxide production, and results validated for select samples using HPLC. Residual lignin was subjected to mild acid washing and filtration. We have conducted prescreening and developed protocols using HPLC to determine solubilization of biomass components, and shifts in lignin molecular weight. As needed, IR techniques are used to evaluate changes in functional groups. As an applied component of our research, we have evaluated the residual lignin as an adhesive. Lignin has been incorporated into a soybean protein adhesive formulation and its effect on particleboard properties determined relative to the control particleboard.

Friday, 17 November 2006 - 9:30 AM

Genomics Enabled Optimization of E. Coli Succinate Production

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Traditional optimization of bacterial strains for biorefining applications is far from a simple task and involves a substantial understanding of the metabolic pathways involved. Population based genomics approaches offer the promise of more quickly identifying and manipulating the genetics behind production, however due to the large screening effort involved, these tools have been largely applied to selectable phenotypes. For example, we have developed a new technique, scalar analysis of library enrichments (SCALES), for identifying genes that may improve the productivity of engineered strains. We have applied this tool in several different contexts, including the production of different organic-acids in E. coli. To expand this approach, we initiated activities on the development of an antibiotic resistance reporter that responds to succinate concentrations. We

will report on the use of this reporter in combination with population-based genomics tools to select for succinate overproduction as well as identify the genetic elements involved in production optimization.

Friday, 17 November 2006 - 10:00 AM

Conversion of Glucose, Xylose, and Glycerol by *Rhodotorula Glutinis* into Triglycerides a Biodiesel Feedstock

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Rhodotorula glutinis is an oleaginous yeast that has the ability to produce up to 70% of its weight as oil in the form of triacylglycerol (TAG). The potential to use this oil as a feedstock of biodiesel production is considerable. The ulterior purpose is to use glycerol as a growth substrate for the yeast either solely or in combination with glucose or xylose. Glycerol is a byproduct of transesterification reaction of TAG. When TAG is reacted with an alcohol such as methanol in the presence of a catalyst, the ester bonds are broken and the fatty acids are methylated leaving the glycerol backbone as a by-product. The result is 90% fatty acid methyl esters (FAMES) and 10% glycerol. Biodiesel is a source of energy that is a mixture FAMES. Therefore, the generation of FAMES for the manufacturing of biodiesel produces considerable amounts of glycerol that, when recycled back into the production system, would provide an inexpensive carbon source for which to grow oleaginous yeast *R. glutinis*. This study is designed to determine the feasibility of the oleaginous yeast *R. glutinis* as a producer of FAMES since it accumulates TAG when grown on carbon substrates such as xylose, glucose, and glycerol. Preliminary results indicate that *R. glutinis* grown on glycerol and glucose as carbon substrates produce up to 31% dry cell weight (w/w) of TAG after 48 h. When grown on glycerol and xylose, the organism produced 17% TAG (w/w). From the results obtained, we can recommend that *R. glutinis* is a viable source of TAG for the production of biodiesel and that glycerol can be used in combination with glucose or xylose as a growth substrate to produce TAG. Future research will focus of the optimization of the conditions for yield TAG improvement.

Friday, 17 November 2006 - 10:20 AM

Biorefining Mixed Sugars Using High Densities of Growth-Arrested *Corynebacteria*

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Research and development of renewable energies has recently regained prominence given anticipated shortages of fossil-fuel-based energies and parallel rising prices of fossil-derived fuels and chemicals.

Particularly, the quantities of ethanol produced via biotechnological processes to displace petroleum as a transportation fuel are expected to dramatically increase in the coming years. At present, the bulk of the industrial ethanol production is ensured via the fermentation of easily accessible sugars, for example derived from corn starch, sugar cane or sugar beet. The yeast *Saccharomyces cerevisiae* is the primary organism to ensure these fermentations. However, the cost analysis of the existing production processes clearly demonstrates that their economic performances are tightly linked to the costs of fermentation raw materials. Furthermore, the flattening experience curve observed by industrial manufacturers suggests that radical innovation is needed to make bio-ethanol a competitive commodity compared to fossil fuels. As a result, it becomes increasingly clear that the global scale implementation of ethanol as a primary

transportation fuel will only become a reality once sugars can be extracted from abundant and easily accessible lignocellulosic biomass in a cost-effective manner. However, one of the current technological limitations of yeast-based processes is that they are significantly negatively impacted by the presence of various growth inhibitors that are typically generated at the pre-treatment step of the saccharification process of lignocellulosic materials.

We have previously validated the concept of decoupling the cell generation phase and the product production phase of fermentation processes, as a means to enable the use of conditions that are sub-optimal for cellular growth but optimal for product production. Moreover, we proposed a process that is characterized by a minimal number of manufacturing steps and that can be applied to anaerotolerant organisms, such as *Corynebacterium glutamicum*, or quorum sensing sensitive organisms such as *Escherichia coli*. This flexibility and simplicity in design represent important manufacturing advantages that combine with the proven robustness of selected industrial microorganisms to enable bioconversions characterized by favourable economics. The intrinsic robustness of the design we propose is a key feature for capturing synergies between various production processes, and thus making possible the optimum manufacturing integration within a biorefinery framework.

Furthermore, we have engineered the amino acid production workhorse *C. glutamicum* to produce ethanol via continuous or semi-continuous processes that operate at very high cellular densities and that do not require concomitant cellular growth¹⁾.

Notably, the strain/bioprocess couples we developed using these technologies exhibit two critical attributes: on the one hand a greatly reduced negative impact on yields of various growth-inhibitors that are typically present in saccharified mixtures of lignocellulosic biomass materials, and on the other hand the parallel utilisation of glucose and xylose. Moreover, essentially the same process can be applied to produce the organic acids lactate and succinate^{2,3)} at very high efficiencies.

This study was partially supported by a grant from New Energy and Industrial Technology Development Organization (NEDO).

1)M. Inui et al., J. Mol. Microbiol. Biotechnol. 8:243-254. 2004. 2)M. Inui et al., J. Mol. Microbiol. Biotechnol. 7:182-196. 2004. 3)S. Okino et al., Appl. Microbiol. Biotechnol. 68:475-480 2005.

Friday, 17 November 2006 - 10:40 AM

Development of Cereal-Based Biorefineries for the Production of Biodegradable Plastics and Platform Chemicals

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In the Satake Centre for Grain Process Engineering we are developing cereal-based biorefining strategies for the production of biofuels, biodegradable plastics and platform chemicals. Cereal grains are complex biological entities and we target the exploitation of all cereal components providing both value-added end-products and precursors for chemical synthesis. Hydrolysis of natural polymers (e.g. starch, protein) contained in cereals requires supply of a range of hydrolytic enzymes (e.g. amylase, protease), which are produced by fungal bioconversions. On-site production of these enzymes would result in the production of a high amount of fungal biomass. Fungal autolysis can be used to bioconvert this low-cost by-product into a nutrient-rich supplement (fungal extract) for microbial bioconversions. Mixing fungal extracts with cereal hydrolysates results in nutrient-complete microbial feedstocks. Optimising the exploitation of protein in cereal grains would enable the provision of optimum amounts of free amino acids and peptides to subsequent microbial bioconversions and the extraction of the remaining protein as a

value-added co-product with various current (food) and potential (biodegradable plastics) market outlets. The use of amino acids and peptides would enhance productivities improving significantly current fermentation practices that exploit only the starch component in cereal grains. In addition, the exploitation of all cereal components and low-cost by-product streams produced in a cereal-based biorefinery will result in waste minimisation and maximisation of carbon as well as other nutrient utilisation from the original cereal grain.

This work will present different feedstock formulation strategies based on the production of wheat hydrolysates and fungal extracts for economic microbial production of polyhydroxybutyrate and succinic acid.

Reactor Engineering for Biomass Feedstocks (T4004)

Friday, 17 November 2006 - 8:30 AM

Mixing and Scale-up of Stirred Tank Reactors Using Cfd Simulations

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Scaling up biochemical processes from laboratory scale (1-10 L) to pilot scale (100-1000 L) to industrial scale (10,000 – 1,000,000+ L) presents a significant engineering challenge because nearly every mixing factor changes. Typical scale-up techniques include maintaining one parameter constant such as 1) impeller tip speed, 2) Reynolds number, 3) mixing time, or 4) the ratio of power number to volume. However, all other factors change, raising questions about changes in performance with scale. Because impeller tip speed is often kept constant to avoid potential shear sensitivity effects on fermentative organisms, a computational fluid dynamic (CFD) model was applied to estimate the effect of this strategy on mixing performance, flow path, and power number differences during scale up. Laboratory, pilot, and industrial scale vessel configurations equipped with four, 90 degree baffles and one 45 degree pitched blade turbine (PBT) impeller were analyzed and compared to flow path data using laser doppler anemometry (LDA) and particle image velocimetry (PIV) at various Reynolds numbers where available in the literature. A CFD simulation will also be presented of an actual industrial scale fermentor described in the literature.

Friday, 17 November 2006 - 8:50 AM

Production of Sugars from Cellulose in Subcritical and Supercritical Water Using a Non-Isothermal Reactor

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Cellulose was reacted in subcritical and supercritical water in a non-isothermal tubular reactor. Feed entered the reactor at room temperature, and reactor exit temperatures were in the range of 200-400°C. The products include oligosaccharides, monosaccharides, and other small molecules. Results show that the pressure affects the monosaccharide yield and the ratio of fructose to glucose. As the pressure increased, the monosaccharide yield increased. The yield at the highest pressure of 7500 psig was about 60% at 280°C with a reactor residence time of less than 1 min. Low pressure increased the ratio of fructose to glucose. Results of ongoing reactor modeling using COMSOL Multiphysics™ finite element software will be presented and applied to the interpretation of experimental data.

Friday, 17 November 2006 - 9:10 AM

Hydrothermolysis of Agricultural Waste

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Some agricultural wastes such as wheat straw, bagasse and corncob were treated using a hot-compressed water-flow type reactor to obtain sugar solution as a feedstock for alcohol fermentation. Bagasse gave higher sugar yield than wheat straw, and the obtained sugar solutions were mainly composed of glucose, xylose, arabinose, xylobiose and cellobiose. On the other hand, corncob gave the highest sugar yield and included a lot of sucrose and fructose. The formation of furfural and HMF, which are known as inhibitors for alcohol fermentation, became remarkable when the temperature of hot water was over 260°C. The residue yield of each sample at a 260 °C-treatment was 25.9 wt% for wheat straw, 26.2 for bagasse, and 15.3 for corncob, respectively.

Friday, 17 November 2006 - 9:30 AM

Production of Biochemicals from Rice Husk Using a Membrane Reactor under Hydrothermal Condition

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Rice husk is one of the important biomass feedstocks which can be a raw material of chemicals products as well as the energy source. In this work we focused on furfural production from rice husk. It is known that furfural can be produced from pentoses that exist in rice husk; however, the undesired secondary decomposition of furfural thus obtained easily occurs to decrease the furfural yield because of its high reactivity. It is necessary to control such undesired side reactions. To solve such a problem, we have developed a membrane reactor system in which hydrothermal reaction and pervaporation occur simultaneously (reactive pervaporation) and shown its efficiency based on a series of experimental data using some model compounds and its mathematic analyses. In this presentation, the results of reactive pervaporation for an existing biomass, i.e., rice husk, are shown.

Friday, 17 November 2006 - 10:00 AM

Reactor Development for Partial-Oxidative and Catalytic Gasification of Biomass in Supercritical Water

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Supercritical water gasification is suitable for gasifying biomass with high moisture content. Biomass materials are easy to decompose in supercritical water. However char and tar are also produced by polymerization which proceeds simultaneously with decomposition. Char formation in supercritical water gasification cause a critical problem because it can trigger off reactor plugging. A reactors combination was proposed to prevent char plugging and to achieve high gasification efficiency at low temperature region (around 673 K) of supercritical water condition (Ind. Eng. Chem. Res. 2004, 43, 4097-4104). To improve this reactors system, we estimated char behavior in a reactor by computational fluid dynamic calculation. Gasification experiments were also conducted which showed high gasification efficiency.

Friday, 17 November 2006 - 10:20 AM

Ammonia Formation Rates in Biomass Pyrolysis

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Introduction For the development and design of advanced biomass conversion equipment, accurate experimental data of fundamental processes are highly important. Therefore, this paper aims to contribute to a better description of the chemical and physical processes occurring in biomass pyrolysis. The results of biomass pyrolysis experiments from the experimental set-ups at Eindhoven University of Technology, in which biomass is heated very fast (up to 1000 K/s) on a metal grid, are highlighted. Specific focus is on the product evolution rate of ammonia (NH_3), an important precursor for NO_x formation. The gas phase concentration of ammonia is followed on-line using single-frequency IR light, and also determined off-line by FT-IR based on the gas spectrum in the mid-infrared region.

Background Whatever conversion takes place in biomass conversion equipment, whether it is partial or complete oxidation, steam reforming, etc., it will always be preceded by, or at least influenced by biomass pyrolysis. Therefore, a lot of experimental effort and modelling has focused on this process. Many researchers have studied cellulose, which constitutes around 50% of woody biomass, as a model component. The well-known Broido-Shafizeh mechanism that describes the rate of weight loss of cellulose was developed in the 1970's [1,2]. Later work of Antal and Varhegyi [3,4,5] must also be noted. Many other papers on the weight loss rate due to biomass decomposition have appeared, for various feedstock and temperature regimes. These existing models give some information on the product species formed, but only in terms of product classes: gas, tar and char. For a pyrolysis model to be implemented in modern CFD process simulations, its output should be on a molecular level, i.e. give information about individual components. The development of such a model is a very difficult task, for several reasons: - The biomass sample must be heated very fast to minimize reactions already occurring in the warm-up phase. For TGA equipment with a low heating rate of 10-100 K/min, the error introduced by the weight loss during this phase is unacceptable. - An analysis method is required to measure the product formation rates of individual components almost instantaneously. - The amount of reactions occurring and reaction products formed is enormous. To circumvent the first problem, a so-called heated grid reactor can be used, a unique facility to measure the rate of pyrolysis and/or gasification reactions of very fine biomass and coal particles [6,7]. It can be used for the characterization of solid fuel samples at high heating rates and is described in more detail later. As an analysis method, rather than slow methods based on gas chromatography, and other methods where a gas sample must be taken and removed from the gas mixture, an in-situ spectroscopic technique is preferred. Therefore, we use a Tuneable Diode Laser (TDL) with fast frequency scanning properties to measure the temporal evolution of the Infra Red absorption at a specific frequency in the mid infrared region. By selecting the right frequency, the production rate of any component which absorbs infrared light can be determined, such as carbon monoxide [8] or in this case, ammonia. In conjunction to the TDL, we also use Fourier Transformed InfraRed (FT-IR) for two reasons. Firstly, due to the large number of products formed during the complex pyrolysis processes, care must be taken to avoid interference from other components. Secondly, while the TDL gives information about the relative rate of the concentrations of formed species, FT-IR can give more reliable information about the total amount formed.

Experimental The heated grid reactor consists of a metal wire mesh (stainless steel, platinum or other material) placed between two electrodes in a reactor chamber. The maximum operating temperature is given by the melting point of the metal. The reactor can be operated in pressurized conditions, or under vacuum, depending on the application. Gases can enter and leave the chamber from different ports located below the grid. Sintered porous material in the ports reduces the gas speed, to prevent the sample being blown away. The grid temperature is measured with a thin thermocouple (0.1 mm junction) placed on the mesh close to the sample. Optical windows are placed on the top and at both sides of the reactor (CaF_2), so that the

pyrolysis process can be investigated with a CCD camera (or any other alternative optical equipment). The evolved gases can be analyzed with a FTIR (Fourier Transform InfraRed spectrometer) and single-frequency IR. This is done in the mid infrared region, specifically for ammonia in the spectral range of 900-1200 cm⁻¹.

Results It was found that very little ammonia is produced from fresh wood, since wood typically contains < 1wt% of nitrogen. However for other fuels such as MDF it is substantial; apparently the glue in the MDF is a nitrogen source. N-rich model components have also been studied, notably urea and melamine. These components release nitrogen in the form of NH₃, HCN and HNCO. The production rates of these components are expressed in the form of first order kinetics. These kinetic data are vital for an accurate description of NO_x formation in biomass conversion equipment, and aim to contribute to the use of renewable fuels without creating harmful emissions to the environment.

References 1. A. Broido, Kinetics of solid phase cellulose pyrolysis, in: F. Shafizadeh, K.V. Sarkanen and D.A. Tillman (Eds.), Thermal uses and properties of carbohydrates and lignins, Academic Press, New York, 1976, chapter 19. 2. F. Shafizadeh, Pyrolytic Reactions and Products of Biomass, in R.P. Overend, T.A. Milne and L.K. Mudge (Eds.), Fundamentals of Biomass Thermochemical Conversion, Elsevier, London, 1985, pp. 183-217. 3. G. Várhegyi, M.J. Antal, T. Szekely and P. Szabo, Energy & Fuels, 3 (1989) 329-335. 4. G. Várhegyi, M.J. Antal, E. Jakab and P. Szabó, J. Anal. Appl. Pyrolysis, 42 (1997) 73-87. 5. M.J. Antal, Biomass Pyrolysis: a Review of the Literature. Part II – Lignocellulose pyrolysis, in K.W. Boer and J.A. Duffie (Eds.), Advances in Solar Energy, American Solar Energy Society, Boulder, CO, 1985, vol.2, pp. 175-255. 6. J.H.J. Moors, Pulverized char combustion and gasification at high temperatures and pressures, Ph.D. thesis, Eindhoven University of Technology, 1999. 7. J. Guo, Pyrolysis of wood powder and gasification of wood-derived char, Ph.D. thesis, Eindhoven University of Technology, 2004. 8. A. Toland, R.J.M. Bastiaans, A. Holten and L.P.H. de Goey, Kinetics of CO release from bark and medium density fibre board pyrolysis, submitted to Biomass and Bioenergy (2005).

Friday, 17 November 2006 - 10:40 AM

Optimization of Flash Carbonization(Tm) Conditions for Charcoal Production from Sunflower Shells

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Once again the rapidly escalating price of transportation fuels has engendered intense interest in the production of biodiesel and other liquid fuels from renewable biomass. Biodiesel is an expensive fuel because it is manufactured from vegetable oils. Fortunately the plants that produce vegetable oils often also produce copious lignocellulosic byproducts. For example, in addition to sunflower oil the sunflower plant produces shells, a flower, and a stem. It is often erroneously assumed that these lignocellulosic byproducts have no value. In a visionary paper Varhegyi et al. (Energy & Fuels, 1989, 3, 755-760) described the production of biocarbon (i.e. charcoal) from the sunflower stem. In this paper we detail the effects of process conditions (pressure, air-flow rate, and total air delivery) on the yields and properties of biocarbons that can be derived from the sunflower shell by use of the University of Hawaii's Flash Carbonization™ process. This process involves the ignition and control of a flash fire at elevated pressure (ca. 1 MPa) within a packed bed of biomass. The fire moves upward through the bed, against the downward flow of air, triggering the transformation of biomass into gas at elevated pressure, and charcoal with fixed-carbon yields that can reach the thermochemical equilibrium "limit" in less than 30 min of reaction time. Conditions that offer the highest fixed-carbon yield and greatest biomass throughput are identified. Sunflower shells are an ideal feedstock for biocarbon production by the Flash Carbonization™ process. Revenue from the sale of this charcoal can help to lower the price of biodiesel production and make biodiesel a more competitive transportation fuel.

Pretreatment of Lignocellulosic Biomass and Interactions with Other Processing Steps II (T4009)

Friday, 17 November 2006 - 12:30 PM

Adsorption and Desorption of Cellulase, Beta-Glucosidase, and Bsa Protein on Pretreated Corn Stover, Cellulose, and Lignin

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Addition of non catalytic proteins (e.g., BSA) and certain surfactants has been shown to enhance cellulose hydrolysis by enzymes or reduce the amount of enzyme required to realize a particular conversion. One plausible explanation is that the additives can reduce the nonproductive adsorption of enzyme on lignin. However, the interactions among substrate features, enzymes, and proteins are not clear, and experiments were conducted to better understand the mechanism by which these additives influence hydrolysis. Adsorption and desorption profiles were measured to better clarify the interaction of BSA, cellulase, and beta-glucosidase with cellulose, pretreated corn stover, and lignin prepared from corn stover. Adsorption of cellulase and beta-glucosidase on BSA-treated corn stover and lignin was also observed. This data indicated that both corn stover and lignin adsorb large amounts of all these proteins although in different relative amounts while cellulose only adsorbs cellulase significantly. BSA treatment was also shown to reduce adsorption of enzyme by corn stover and lignin.

Friday, 17 November 2006 - 12:50 PM

Improving Biomass Conversion by Better Fundamental Understanding of Pretreatments: the Case of Ammonia Fiber Explosion (AFEX)

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Ammonia Fiber Explosion (AFEX) is considered a leading biomass pretreatment process for cellulosic biomass. AFEX treats biomass with concentrated ammonia under pressure at temperatures up to about 100 °C. After a few minutes under these conditions, the pressure is rapidly released (the “explosion”). The ammonia evaporates and is recovered. The treated biomass is now much more easily converted by enzymes to sugars and thence to ethanol. In a recent comparative economic evaluation of advanced pretreatments by the National Renewable Energy Laboratory, AFEX performed better than all other pretreatments studied except for the dilute acid process. Improved understanding of the morphological changes and chemical compounds formed during AFEX may further improve the pretreatment performance.

In this presentation we give a broad outline of the morphological changes before and after AFEX process, using scanning electron micrograph (SEM) and laser confocal scanning (LCSM) imaging pictures. The chemical compounds released during the AFEX process are given by liquid chromatography followed by mass spectroscopy (LC-MS) and gas chromatography followed by mass spectroscopy (GC-MS). Supporting insights on lignin phenolics formed and their deposition on the biomass are obtained through the Prussian blue method and Electron Spectroscopy for Chemical Analysis (ESCA), respectively. The potentially inhibitory role of the chemical compounds formed during AEFX on subsequent enzymatic hydrolysis and fermentation will be discussed.

Friday, 17 November 2006 - 1:10 PM

A Novel Ionic Liquid Pretreatment Strategy to Achieve Enhanced Cellulose Saccharification Kinetics

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Biomass has the potential to be converted into value added products through a sugar platform. Sugar feedstock can also be converted to ethanol for fuel production. Techno-economic analysis conducted by NREL indicates that efficiency of the biomass saccharification step – hydrolysis of cellulose to glucose - is critically important in making the process cost-competitive. Cellulose hydrolysis in aqueous media suffers from slow reaction rates and low yields because cellulose is a water-insoluble crystalline biopolymer. To accomplish its hydrolysis, the hydrolyzing enzymes (cellulases) and water have to penetrate the crystalline fibrils. The tight packing arrangement of the fibrils not only excludes the enzymes but also water. Pretreatment methods which increase the surface area accessible to water and cellulases are vital to improving the hydrolysis kinetics and conversion of cellulose to glucose. We developed a novel technique wherein the cellulose is dissolved in an ionic liquid (IL) and is subsequently regenerated as an amorphous precipitate by rapidly quenching the solution with an anti-solvent. Hydrolysis kinetics of the regenerated cellulose were significantly enhanced as measured by initial rate of reducing sugar formation. With an appropriate selection of enzymes, initial rates were approximately an order of magnitude greater than those of untreated cellulose. Because of their extremely low volatility, ionic liquids are expected to have minimal environmental impact. A unique solvency characteristic of ILs which makes them ideal to work is that they are able to instantly reject all the dissolved cellulose in presence of anti-solvents such as water, methanol and ethanol. Once the cellulose is precipitated, the anti-solvent used for displacement can easily be stripped off the non-volatile IL via flash distillation and the IL recovered for subsequent reuse.

Friday, 17 November 2006 - 1:30 PM

Factors Affecting the Enzymatic Digestibility of Dilute Acid Pretreated Corn Stover

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A key barrier to the commercialization of fuels and chemicals produced from lignocellulosic biomass is the high cost and relative inefficiency of converting biomass into fermentable sugars. Dilute acid pretreatment is a promising technology for increasing the accessibility of cellulose to enzymatic hydrolysis. A better understanding of the interaction of enzymes with pretreated biomass is needed so that the rate and yields of sugars can be increased. Consequently, we continue to study the relationship between pretreatment conditions and the chemical and structural changes occurring in biomass during pretreatment. The purpose of this work was to uncover the factors that have the greatest influence in determining the enzymatic digestibility of the cellulose in dilute sulfuric acid pretreated corn stover. It has long been known that the removal of xylan greatly facilitates the enzymatic saccharification of the cellulose in biomass. It has been postulated that removal of lignin also increases digestibility. We have characterized a large set of dilute acid pretreated corn stover samples in which both xylan and lignin were removed to varying extents. All samples were treated at relatively high severities effecting >70% xylan removal. Additional modification of the samples to further decrease lignin content and/or change cellulose morphology was performed to examine how these affect cellulose digestibility. The crystallinity, particle size, porosity, cellulose degree of polymerization and cellulase binding of the samples was measured to determine the influence of these factors on the digestibility of

the samples. It appears from this work that a change in cellulose morphology has the greatest potential for affecting cellulose digestibility.

Friday, 17 November 2006 - 2:00 PM

Alternative Low-Cost Process for the Hydrolysis of Lignocellulosic Materials for Bioethanol Production

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The Energy Policy Act of 2005 (EPA2005) provides incentives for the production of up to 1 billion gallons of cellulosic ethanol by 2015. By 2012, 250 million gallons of bioethanol must be produced from qualified cellulosic materials. A solicitation of up to three integrated biorefinery demonstration projects was issued by U.S. Department of Energy on Feb. 22, 2006 for the demonstration of the production of bioethanol using lignocellulosic feedstocks with a total of 80 million dollars. An efficient and cost effective conversion technology is needed in order to convert lignocellulosic materials such as wood chips, corn stover and wheat straw to bioethanol or other commodity chemicals in a biorefinery. Many different conversion schemes have been proposed and tested in the laboratory and various scale piloting facilities for the conversion of biomass. These include concentration acid hydrolysis, dilute acid hydrolysis, and dilute acid pretreatment combined with enzymatic hydrolysis. Among these, the most desirable technology is the dilute acid/enzymatic hydrolysis process and it is pursued by several companies around the globe. TVA has studied and piloted the concentrated and dilute acid hydrolysis processes in the past 20+ years. Many testings have also been carried out for the dilute acid pretreatment and enzymatic hydrolysis process. It was found that a more efficient and cost effective technology is needed to propel the cellulosic ethanol industry to reach the 1 billion gallon goal. A new process combines the delignification and aqua hydrolysis technology was recently invented and developed at TVA. This innovative process initially removes some lignin by heating the biomass with a delignifying chemical at elevated temperature without biomass hydrolysis. The second stage completely hydrolyze the hemicellulose without any acid. The remaining cellulose can be hydrolyzed to glucose by separate acid hydrolysis or enzymatic hydrolysis. The new process doesn't require special alloy reactor and produces little degradation products. Higher value co-produce could be produced to improve the economics of the biorefinery. This presentation will describe such process and highlights its advantages over other biomass conversion processes.

Friday, 17 November 2006 - 2:20 PM

Understanding the Interactions between *T. reesei* Cel7a and the Plant Cell Wall Cellulose Substrate

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Understanding the complex interaction between the substrate chemistry and enzyme function is critical to improving enzymatic biomass conversion. Crystalline cellulose forms the core of carbohydrate microfibrils that provide structure and strength to plant cell walls. It has long been recognized that crystalline cellulose substrate is the most recalcitrant carbohydrate to enzymatic hydrolysis, making its conversion rate limiting in many processes. Carbohydrate binding modules (CBMs), which are a component of the *Trichoderma reesei* Cel7A cellobiohydrolase, may play an important role in the initial decrystallization of cellulose. We are evaluating the effect of cellulose crystallinity on *T. reesei* Cel7A action using pure cellulose samples of varying crystallinities (as measured by solid state NMR) and by site-directed mutagenesis of residues on the CBM. We have evaluated a set of 'disordered' or 'amorphous' celluloses generated from pure cellulose substrates (filter paper, Avicel, cotton, Sigma alpha cellulose and Sigmacell 50). Digestion studies with *T. reesei* Cel7A have confirmed that the new material is dramatically more

digestible, both in initial digestion rates and extent of digestibility. All four of the amorphous cellulose substrates appear, however, to have an upper limit of digestion between 70 to 80%. Whether the reason for this digestion limit is due to substrate or enzyme effects will be evaluated using cellobiohydrolase mutants with altered cellulose binding modules.

Friday, 17 November 2006 - 2:40 PM

Novel Cellulose- and Organic- Solvents-Based Lignocellulose Fractionation: an Update

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Effectively overcoming the recalcitrance of lignocellulosic materials is one of the largest technical obstacles to the production of chemicals and bioethanol from the most abundant renewable bioresource -- lignocellulose. A novel concentrated phosphoric acid/acetone lignocellulose fractionation for corn stover has been developed recently. This new technology has four distinctive features: modest reaction conditions (~50°C and atmospheric pressure); fractionation of lignocellulose into amorphous cellulose, hemicellulose sugars, lignin, and acetic acid; generation of highly reactive amorphous cellulose; and cost-effective reagent recycling. Here we will present the latest progress on this technology applicable to other lignocellulosic materials such as switchgrass, hybrid poplar (hardwood), and Douglas fir (softwood).

Chemical and Catalytic Conversions and Processes for Renewable Feedstocks (T4000)

Friday, 17 November 2006 - 3:15 PM

Transesterification of Poultry Lipids Using Mg-Al Hydrotalcite Derived Catalysts

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Currently, the United States with an average slaughter and processing of eight billion chickens each year ranks first in the world in poultry production and derived products. Concurrently with the production of meat, egg and animal fibers, vast amounts of by-products such as fat and soluble protein are generated representing approximately 40% of the weight of each slaughtered chicken. These by-products are mainly used to produce low value feedstuffs, underutilizing their energy content. The synthesis of biodiesel from poultry lipids provides a way to convert the by-product of a renewable resource to a very important value-added biofuel.

In this work, the use of heterogeneous base catalysts derived from Mg-Al hydrotalcite was investigated for the conversion of poultry lipid to biodiesel. This solid base showed high activity for triglyceride transesterification with methanol without signs of catalyst leaching. Catalytic performance was significantly affected by pretreatment and operating conditions. Calcination in N₂ was key in obtaining the highest catalyst activities. Also, methanol had to be contacted with the catalyst before reaction; otherwise, catalyst activity was seriously impaired. Rehydration of the calcined catalyst before reaction using wet nitrogen, however, decreased catalytic activity for the transesterification of poultry fat, in contrast to its positive impact on catalyst reported in condensation reactions¹. The catalyst underwent significant deactivation during the first reaction cycle probably due to deactivation of the strongest base sites. However, after the first reaction cycle, it was stable for subsequent cycles. Procedures for catalyst regeneration were also investigated and will be discussed.

Friday, 17 November 2006 - 3:35 PM

Preliminary Investigations of the Catalytic Deoxygenation of Fatty Acids

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Biobased sources of alkanes and alkenes are limited; such materials, however, would provide the most direct replacements of petroleum-based feedstocks. One possible route to alkanes and alkenes from readily available biomass is the decarboxylation of fatty acids. In this presentation, initial studies of the thermocatalytic conversion of oleic acid will be reported, specifically the decarboxylation of the acid to alkanes and alkenes. The reaction products formed in the presence of zinc oxide, alumina, and the zeolite ZSM-5 are compared those associated with thermal decomposition alone. At temperature below 250° C, thermal decomposition without catalysts shows only limited gaseous products characteristic of pyrolysis reactions. The reaction products formed in the presence of ZSM-5 are typical of catalytic cracking reactions. The products formed from ZnO suggest that two reactions proceed in parallel at these conditions. The presence of carbon dioxide is consistent with catalytic decarboxylation. The liquid phase products include significant production of zinc oleate via the fusion reaction. As the temperature is increased to 400°C, reactions over ZnO shift away from forming the metal soap to the production of hydrocarbons. The reaction of oleic acid over alumina at 400°C appears to involve reactions in series. Initially decarboxylation of the fatty acid occurs yielding heavier hydrocarbons. With longer reaction times, intermediate range (C8 – C10) hydrocarbons have been identified.

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The Effects of Temperature and Hydrogen on Glycerol Adsorption on Ruthenium Metal

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In efforts to understand the mechanism of aqueous hydrogenolysis of glycerol over noble metals, we seek to probe interactions between substrate molecules and the metal catalyst surface. Previous isotopic labeling work shows that substrate dehydrogenation is the first step in hydrogenolysis, although the exact mechanism of adsorption and is not known. This paper describes efforts to quantify the effects of temperature and adsorbed hydrogen on glycerol (GO) adsorption on ruthenium metal, by using a novel recirculating loop microreactor system. Glycerol adsorbs irreversible on a hydrogen free surface. In the presence of hydrogen GO does not adsorb. This suggests exclusion of glycerol from the surface by adsorbed hydrogen. Attempts to recover adsorbed glycerol species via washing with water and/or heating have not been successful. But hydrogen at elevated temperatures will remove adsorbed species in the form of methane. At 80 °C the addition of hydrogen stops the adsorption of GO and all the adsorbed carbon is converted to methane, while at 200 °C all adsorbed and solution species are converted to methane with a carbon recovery >90%. The total amount of carbon equivalents adsorbed does not vary at with increases in temperature but the GO conversion to other products increases with increase in temperature. The quantities of polyols adsorbed are significantly less, on a molar basis, than those obtained from gas-phase chemisorption of H₂ (3.2 $\mu\text{mol/g-Ru}$) and CO (5.8 $\mu\text{mol/g-Ru}$), suggesting multiple substrate-metal contact points.

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In-Situ X-Ray Absorption Spectroscopy of Supported Transition Metal Catalysts for Hydrogenolysis of Sorbitol and Oxidation of Glycerol

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Sorbitol and glycerol are listed as two of the Department of Energy's top 12 chemicals that will serve as key feedstocks in future biorefineries. This work applies heterogeneous catalysis to the aqueous phase hydrogenolysis of sorbitol and the aqueous phase oxidation of glycerol for the production of value-added chemicals. Heterogeneous catalysis operation in the aqueous phase can be complicated by metal particle instability, resulting in particle growth or leaching. Moreover, catalysis may occur on the solid catalyst surface or in the surrounding solution.

To evaluate the stability of Ru particles operating under aqueous conditions at 473 K a variety of catalysts (Ru/SiO₂, Ru/TiO₂, Ru/Al₂O₃, and Ru/C) were characterized in-situ with X-ray absorption spectroscopy (XAS). Treatment of the samples at 473 K with 40 bar H₂-saturated water resulted in significant particle growth for the Ru/SiO₂ and Ru/Al₂O₃ samples, while both the Ru/TiO₂ and Ru/C samples remained highly dispersed. Addition of a 0.4 M NaOH solution to the previous conditions resulted in continued Ru particle growth for the alumina sample while the carbon and titania supported samples remained stable. We then prepared a number of Ru-Pt/C bimetallic catalysts and characterized them with XAS. Results for the as-prepared samples revealed that for a Pt rich sample (11.1 wt% Pt, 3.2 wt% Ru) the Ru and Pt are well alloyed, while a 5.3 wt% Pt and 5.3 wt% Ru bimetallic catalyst had Ru segregated to the particle surface.

The hydrogenolysis of sorbitol (10 wt% sorbitol, 473 K, 40 bar H₂, CaO added to maintain pH = 11.9) has been performed over monometallic Ru (5 wt%) and Pt (3 wt%) catalysts. Following 5 h of reaction, the conversion of sorbitol over both catalysts was similar: 71% over Ru/C and 82% over Pt/C. The product selectivities, defined as the moles_{carbon in product} / moles_{carbon reacted in feed}, varied slightly between the two catalysts. The major products observed during the reaction were lactic acid, propylene glycol, ethylene glycol, methanol, glycerol, and methane. Interestingly, the hydrogenolysis of sorbitol over the Pt/C was observed at temperatures as low as 423 K whereas a minimum temperature of 473 K was necessary over the Ru/C catalyst. In the absence of base, the Ru/C catalyzed approximately 60% conversion of sorbitol to lower molecular weight C₄ and C₅ polyols along with carbon dioxide and methane, while over the Pt/C a low conversion of sorbitol was observed (<15%) with no gas phase products detected.

The aqueous phase oxidation of glycerol over carbon-supported Au catalysts (333 K, 1-10 atm O₂, 0.3 M glycerol, 0.6 M NaOH) has also been investigated. Initial rates are in good agreement with the published literature, however the observed selectivities to glyceric acid are poor for a wide range of Au particle sizes. To investigate the effect of a second metal on activity and selectivity, a Au on Pd bimetallic catalyst was prepared via a surface redox process. The XAS results showed that Au was coordinated to both Pd and Au. Reactivity studies suggest the bimetallic system is more stable than monometallic Pd. Additional kinetic studies are currently underway.

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Highly Selective Conversion of Glycerol to Propylene Glycol

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A highly selective process has been developed for converting glycerol to propylene glycol. The first commercial process using this technology is estimated to start production by October of 2006. This presentation is on the catalyst, selectivity, and reaction parameters for this process.

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A New Route to Improved Glucose Yields in Cellulose Hydrolysis

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Cellulose is the most abundant renewable carbon source available and can play a role in meeting our future energy needs if its reactivity can be improved. The crystal structure and hydrogen bonding in cellulose greatly limit access to β -1,4-glycosidic bonds by reactants and catalysts. Water is excluded almost completely from the crystalline regions in cellulose. This limitation makes cellulose hydrolysis much slower than starch. Cellulose decrystallization remains the bottleneck in cellulose conversion by chemical and biological process.

In our study of cellulose decrystallization using trifluoroacetic acid (TFA), an unusual inverse temperature-dependent swelling pathway was observed. Decreasing the TFA treatment temperature greatly accelerated the cellulose decrystallization process. It took only 100 minutes to completely decrystallize cellulose at 0 °C in TFA, a result not achieved for 48 hours at 25 °C in the same medium. Even though treatment at low temperatures eliminated the crystallinity, there were no observable morphology changes to cellulose's microfibrils in SEM images.

The majority of TFA used in cellulose decrystallization can be recycled via a vacuum process. The small remaining TFA, deep in the cellulose matrix, can act as a catalyst in dilute acid hydrolysis. This was realized by adding water to the cellulose sample to make a 0.5% TFA solution. The hydrolysis of treated cellulose was compared to that for untreated cellulose and starch. Treated cellulose showed a dramatic increase in glucose yield than the untreated material. The lower temperatures and shorter reaction times led to reduced production of degradation products such as HMF and levulinic acid. In addition, the total TFA amount required in the hydrolysis process was lower than that of H₂SO₄ in traditional dilute acid process.

Alternatively, the remaining TFA could be completely removed by water. The cellulose, after water wash, remained highly amorphous and active toward hydrolysis. Reactivity of regenerated cellulose was compared with untreated cellulose and corn starch under typical dilute H₂SO₄ (1% and 0.5%) hydrolysis conditions at different temperatures and reaction times in batch reactors. The reactivity of the regenerated cellulose was six times higher than that of untreated cellulose and only slightly lower than that of corn starch. The regenerated cellulose is also expected to be very reactive in enzyme hydrolysis process.