

78th Meeting of the Petroleum Environmental Research Forum
Philadelphia, Pennsylvania
17 November 2008: Board of Directors & Research Directors Meeting
18 – 19 November 2008: Fall Meeting

In Conjunction with the:
2008 American Institute of Chemical Engineers (AIChE) Annual Meeting
(<http://www.aiche.org/Conferences/AnnualMeeting/index.aspx>)
16-21 November 2008

Hosted by:

ExxonMobil

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Program

Monday, November 17, 2008

- 14.00 – 16.00: PERF Research Directors Meeting (Invitation only)
- 14.00 – 17.00: PERF Board of Directors Meeting (Invitation only)
- 19.00: PERF Board of Directors & Research Directors Dinner at the City Tavern
(Invitation only)

Tuesday, November 18, 2008

- 08.00: Registration
- 08.30: Welcome and objectives of the meeting by Todd Ririe, BP and PERF Chair
- 09.00: "The Environmental Impacts of Biofuel" - presented by Xiaomin Yang- BP
- 09.30: "Groundwater Impacts of Fuel Ethanol: Modeling Its Effect on Benzene Plume Attenuation and Elongation"- presented by Diego Gomez, Rice University
- 10.00: "Fungal Biotechnology Solutions to Problems in Cellulosic Next Generation Biofuels Production" - presented by Iva Jovanovic, Scientist with Pacific Northwest National Laboratory
- 10.30: "Environmental Laws and Regulations That May Impact Algae Production for Fuel Use" – presented by Rachel Lattimore, Esq., Arent Fox LLC
- 11.00: Lunch at Hilton Garden Inn
- 12.30: "Water and Soil Quality Implications Associated with Our Nation's Biofuels Mandate" – presented by Susan E. Powers, Clarkson University
- 13.00: "Indicators of Human Health Impacts from Ethanol and Gasoline Lifecycle Air Emissions" – presented by Amy Wormsley, Clarkson University

- 13.30: “Supercritical Fluid Technology for Sustainable Biofuel Production” - presented by Luc Van Ginneken, Flemish Institute for Technological Research (VITO), Belgium
- 14.00: "Environmental implications of four potential liquid biofuels in the soil" - presented by Dr. Ron Turco, Professor, Purdue University
- 14.30: Break
- 15.00: “Approaches for Quantifying the Sustainability of Bioenergy Feedstock Production Pathways” – presented by Dr. Peter Woodbury, Cornell University
- 15.30: “Carbonyl compound Emissions from Biodiesel Blends”- presented by Dr. Mingming Lu, Professor, University of Cincinnati
- 16.00: "Comparative productivity potential, environmental services and carbon, nitrogen, and water economies of candidate biofuel systems" - presented by Dr. Sylvie M. Brouder, Professor, Purdue University
- 17.00: Summary and close of meeting day
- 17.30 - 19.00: Reception at Tangerine Restaurant

Wednesday, November 19, 2008

- 08.30: "Implications of Biofuel Policy on Water Resources of the USA" - presented by Rosa Dominguez-Faus, Rice University
- 09.00: "Long-Term Impacts of Aquifer Contamination by Ethanol-amended Gasoline" - presented by Dr. Henry Corseui, Federal University of Santa Catarina, Brazil
- 09.30: Dr. Elaine Groom, Questor
- 10.00: “The Current State and Environmental Footprint of High-Yielding Non-Food Based Biomass Feedstock for Biofuel Production – from the Field to the Conversion Facility” – presented by Matthew McArdle - Mesa Reduction Engineering & Processing, Inc.
- 10.30: “Environmental Assessments for Ethanol Fuels as Part of the EPA FRS2 (Renewable Fuels Standard)” – presented by Bruce Bauman, API
- 11.00: Lunch
- 12.30 - 1400: Discussion Groups
- 14.00: Break
- 14.30 - 16.00: Discussion Groups Findings and Project Updates
- 16.00: Meeting Conclusion
- 16.00: Walking Tour of Philadelphia (potential)



78th Meeting of the Petroleum Environmental Research Forum (PERF)
hosted by ExxonMobil

Philadelphia (PA), November 17-19

Thematic Note

"The Environmental Impacts of Biofuel"- presented by Dr. Xiaomin Yang - BP America

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This presentation covers the potential soil and groundwater impacts associated with the production, storage, distribution and use of biofuels. A preliminary environmental quality assessment shows that the new generation biobutanol may be more environmental friendly than the ethanol fuel.

Since ethanol's environmental behavior is quite different from gasoline hydrocarbons, biofuel handling facilities are facing new environmental protection challenges imposed by various ethanol fuels. Those issues range from the design of ethanol storage tanks, to surface water collection and treatment, to emergency response procedure. In addition, ethanol could change the fate and transport of hydrocarbons in soil and water. For example, ethanol biodegradation consumed the subsurface electron acceptors which otherwise will be used for the biodegradation of petroleum biodegradations. So ethanol may elongate dissolved benzene plume, potentially doubling groundwater remediation cost and time. In addition, ethanol release can mobilize existing, stable petroleum hydrocarbon sources in the subsurface.

A life cycle fuel use process is used to assess the environmental quality of biofuels. The quality matrix includes the environmental fate and transport of biofuel molecule, its impacts on petroleum hydrocarbons, and release scenarios. The preliminary evaluation indicated that new generation biobutanol may not inherit the negative environment impacts that ethanol fuel has.

"Groundwater Impacts of Fuel Ethanol: Modeling Its Effect on Benzene Plume Attenuation and Elongation" - presented by Diego Gomez, Rice University

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A mathematical model was developed to evaluate the effect of the common fuel additive, ethanol, on benzene fate and transport in fuel-contaminated groundwater, and to discern the most influential benzene plume-elongation mechanisms. The model, developed as a module for the RT3D (Reactive Transport in 3-Dimensions) model, includes commonly considered fate and transport processes (advection, dispersion, adsorption, biodegradation and depletion of molecular oxygen during biodegradation) and substrate interactions previously not considered (e.g., a decrease in the specific benzene utilization rate due to metabolic flux dilution and/or catabolite repression) as well as microbial populations shifts. Benzene plume elongation predictions, based on literature model parameters, were on the order of 40% for a constant source of E10 gasoline (10% v/v ethanol), which compares favorably to field observations.

The model was also used to evaluate how the concentration of ethanol in reformulated gasoline affects the length and longevity of benzene plumes in fuel-contaminated groundwater. Simulations considered a decaying light non-aqueous phase liquid (LNAPL) source with a total mass of ~85 Kg and a seepage velocity of 9 cm/d, and corroborated previous laboratory, field and modeling studies showing benzene plume elongation due to the presence of ethanol. Benzene plume elongation reached a maximum of 59% for E20 (i.e., 20% ethanol content) relative to regular gasoline without ethanol. Elongation was due to accelerated depletion of dissolved oxygen during ethanol degradation, and to lower specific rate of benzene utilization caused by metabolic flux dilution and catabolite repression. The lifespan of benzene plumes was shorter for all ethanol blends compared to regular gasoline (e.g., 17 years for regular gasoline, 15 years for E10, 9 years for E50 and 3 years for E85), indicating greater natural attenuation potential for higher ethanol blends. This was attributed to a lower mass of benzene released for higher ethanol blends, and increased microbial activity associated with fortuitous growth of benzene degraders on ethanol. Whereas site-specific conditions will determine actual benzene plume length and longevity, these decaying-source simulations imply that high ethanol blends (e.g., E85) pose a lower risk of benzene reaching a receptor via groundwater migration than low ethanol blends such as E10.

"Fungal Biotechnology Solutions to Problems in Cellulosic Next Generation Biofuels Production" - presented by Iva Jovanovic, Scientist with Pacific Northwest National Laboratory

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The current state of the US fuel economy calls for a paradigm shift in fuel production. Production of ethanol and other “next generation” biofuels from lignocellulosic biomass represents a sustainable route to biofuels production. Currently, research in the area of cellulosic biofuels is focused on development of ethanol production processes from lignocellulose feedstocks such as corn stover, dried distillers’ grains (DDG), switchgrass, poplar and pine. Cellulose is the main structural polymer shared among these sources with hemicellulose and lignin content varying considerably. It has become imperative not only to understand but also control the biochemical processes around hydrolysis of lignocellulosic biomass.

Understanding the role of microbial enzymes in deconstruction of biomass is one of the primary interim goals in the overall biomass-to-fuel process development. Focusing specifically on how fungi degrade biomass through secretion of enzymes known as glycosyl hydrolases (GHs) will allow for fermentation technology to be better developed when considering ethanol production. The genomes of a variety of fungi contain up to 200+ GHs encoding genes thought to play roles in the hydrolysis of some or all of the components of lignocellulosic biomass. Our goal is to discover and utilize enzymes and organisms that best degrade complex biomass. In addition, we are performing research on non-traditional fungal ethanologens that are able to utilize both pentose and hexose sugars derived from hemicellulose and cellulose deconstruction.

Implications of Biofuel Policy on Water Resources of the USA" - presented by Rosa Dominguez-Faus, Rice University

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Developing a sustainable national biofuels program requires careful consideration of logistical concerns (e.g., suitable production and distribution infrastructure) and of unintended environmental impacts. An issue that has not been receiving the deserved degree of attention is that of the water and land resources demand to produce biofuels. Forecasting future demand of such natural resources and comparing them to available resources is a difficult task due to the many sources of uncertainty surrounding those matters. Water and land requirements of biofuels will depend on what feedstock is used as well as where the feedstock is grown. Additional temporal variability of climate plays a key role in forecasting the intensity of use of these resources as well as its availability. Changes in agricultural irrigation techniques, biotechnology advances such as improvement of crop yields, and conversion technology changes can alter the final value of overall land and water requirements. The high amount of variables playing a role in this analysis suggest that the proper method to make it is through the generation of possible future case scenarios but unfortunately these issues have not been addressed by many scientists. In this presentation we show a comparison of water requirements for different traditional feedstocks given current statistics, current state-of-the-art technology and current biofuel projections of the Energy Independence and Security Act (EISA) of 2007, as constructed by researchers at Rice University. This represents a baseline scenario. Ongoing research at Rice is constructing alternative scenarios, using an agricultural-climatic model combined with multiple potential technological, political and climatic changes.

“Water and Soil Quality Implications Associated With Our Nation’s Biofuels Mandate” – presented by Susan E. Powers, Clarkson University

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The harvest of corn stover or herbaceous crops as feedstocks for bioenergy purposes has been shown to have significant benefits from energy and climate change perspectives. There is a potential, however, to adversely impact water and soil quality, especially in Midwestern states where the biomass feedstock production would predominantly occur. The overall goal of this research is to provide a thorough and mechanistic understanding of the relationship between stover and/or herbaceous crop production management practices and resulting range of impacts on soil and water quality, with a focus on Eastern Iowa. The production of these bioenergy crops is compared to corn and corn-soybean rotations on eight different soils representative of the region. The APEX model, which predicts crop, water, nutrient, carbon and soil flows within an integrated agricultural and hydrological system, provides a means to quantify sustainability metrics and is used to generate sufficient data to provide a greater understanding of the particular variables that affect water and soil quality than previously possible. The sustainability metrics include total nutrient emissions to ground and surface water, total soil losses due to wind and water erosion, and cumulative soil carbon losses, all normalized to both acreage and the energy value of the potential biofuel production. As expected, the results clearly show the superiority of switchgrass from a soil and water quality perspective. They also show, however, that compared to corn-soybean rotations with conventional tillage, soil and water quality degradation can be reduced at the same time stover is collected under certain soil types and no-till agricultural practices. An analysis of variance identifies the most critical variables correlated to each of the sustainability metrics, thereby helping to identify the conditions that should be given the highest priority for sustainable bioenergy crop production.

Indicators of Human Health Impacts from Ethanol and Gasoline Lifecycle Air Emissions - presented by Amy Wormsley, Clarkson University

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Traditional lifecycle assessments have compared corn-based ethanol and unleaded gasoline for global warming, acidification, and eutrophication influences without adequately addressing the fuels' human toxicity impacts. This work quantifies indicators of human health impacts from ethanol and gasoline lifecycle air emissions. It also illustrates the shift in regional pollution associated with producing more ethanol as a gasoline substitute, as mandated by U.S., the Energy Independence and Security Act (EISA) of 2007. Emissions from increased corn growing and ethanol production will add to the health burden of people in the Midwest, but displace some of the petroleum impacts that people along the Gulf of Mexico currently endure.

Emission inventories from the Swiss Centre for Life Cycle Inventories' ecoinvent v2.0 database are multiplied by inhalation toxicity weights from the U.S. EPA's Risk-Screening Environmental Indicators (RSEI) computer-based screening tool to generate regional pollution profiles. During the production of corn-based ethanol, there are fewer emissions and lower human health impacts in both low and high population density areas than during the production of gasoline. There is, however, uncertainty in this analysis due to the inability to quantify all emissions based on the specific molecular species. Some of the emissions are aggregated and reported as "non-methane volatile organic compounds from unspecified origins." When these are excluded from production emissions inventories, corn-based ethanol's production emissions per vehicle mile create a higher human health impact than those of unleaded gasoline.

“Approaches for Quantifying the Sustainability of Bioenergy Feedstock Production Pathways”- presented Prof. Dr. Peter Woodbury, Cornell University

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There are multiple dimensions of sustainability, including soil, water, and air quality, greenhouse gas emissions, and energy inputs and outputs. Because many of these elements interact, they should be analyzed using an integrated approach. Because biomass will be produced and consumed in specific locations depending on local biophysical, infrastructure, economic, and social factors, such analysis should be spatially-explicit. Because the various benefits, costs, and trade-offs accrue in different places and at different times, analyses should be conducted at multiple spatial and temporal scales. I will discuss methods for quantifying sustainability with examples from ongoing collaborative research projects at different spatial scales.

Topic: Long-Term Impacts of aquifer contamination by ethanol-amended gasoline
– presented by Prof. Henry Corseui, Federal University of Santa Catarina, Brazil

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The main concerns in dealing with aquifer contamination by ethanol-amended gasoline are focused on the complex physical, chemical and biological interactions between gasoline constituents and ethanol, which may limit the selection of proper environmental restoration technologies. To evaluate the impact of ethanol in gasohol spills, studies are being performed by Petrobras in association with the Federal University of Santa Catarina in Florianópolis, SC, Brazil. This presentation shows results of long-term controlled release experiments (natural attenuation and bioremediation with nitrate), performed in a sandy aquifer with gasoline containing 24% ethanol since 1998. New natural attenuation studies with diesel and biodiesel mixtures (B20) as well as a risk assessment model that includes the effects of ethanol will also be presented.

“The Current State and Environmental Footprint of High-Yielding Non-Food Based Biomass Feedstock for Biofuel Production – from the Field to the Conversion Facility” – presented by Matthew McArdle – President of Mesa Reduction Engineering & Processing, Inc.

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One of the major challenges with biofuel conversion is the sustainable production of the feedstock used for producing the liquid fuels. Current first generation ethanol production utilizing corn has received significant attention on its perceived negative influence on food prices and the environment impacts from its production. Dedicated energy crops that are non-invasive, high-yielding, and non-food sources like switchgrass, sorghum, and woody crops will permit second generation biofuels to be produced in a much more environmentally sound process. The field to facility life cycle analytical methodology developed by Mesa is a way to calculate the total costs of producing biomass feedstock for liquid fuel conversion. The presentation will focus on the development of aggregation systems capable of assessing the overall impacts of second generation biomass feedstock which will be critical to the successful implementation of any biofuel program.

“Supercritical Fluid Technology for Sustainable Biofuel Production” – presented by
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The methyl esters of vegetable oil – or biodiesel – are very similar to conventional (fossil) diesel fuel, and can be used as a blend in any conventional diesel engine without any modification. The base-catalyzed or acid-catalyzed transesterification of the triglycerides in vegetable oil with a simple alcohol – such as methanol – to form glycerol and the fatty acid methyl esters (FAMES) has been the preferred method for a long time. However, a relatively long reaction time is needed when using either an acidic (1-45 h) or basic (1-8 h) catalyst to form the esters. In addition, removal of both the catalyst and the saponified products (which are formed due to a side reaction of the triglycerides with the catalyst) after the reaction is needed to obtain purified biodiesel. This downstream-processing step, however, consumes a lot of process water.

To avoid the problems associated with the conventional production method, VITO investigated the production of biodiesel in high temperature pressurized methanol (HTPM) without using a homogeneous catalyst. In this process, pure biodiesel can be obtained without the need for elaborate downstream processing. The purpose of the first part of this presentation is to give an overview of the production of biodiesel using the HTPM process. The advantages and disadvantages are addressed. The paper also addresses our latest efforts, in which VITO – together with three industrial partners – has set up a consortium that is responsible for the international marketing, production and exploitation of the new biodiesel technology.

In the second part of the talk, the opportunities that supercritical fluids can offer to treat lignocellulosic feedstocks for bioethanol production will be addressed.

"Environmental implications of four potential liquid biofuels in the soil" - presented by Dr. Ron Turco, Professor, Purdue University

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The nascent state of the biofuels industry calls for an important early assessment of potential environmental impacts of the alcohol components. The impact of biofuels on soil processes must be understood to allow the development of data in support of an unbiased discussion concerning the possible environmental consequences of the materials. It is most important that these data be developed before any negative situations have occurred. In this initial study, two soils (Drummer and Tracy with high and low organic matter, respectively) were treated with the ^{14}C -liquid biofuel candidates, methanol, ethanol, propanol, and butanol. An applied concentration range from 100 to 10% alcohol was generated by diluting the alcohol with a stock mixture of benzene, toluene, ethylbenzene, and xylene in a 1:1:1:1 ratio. Following the application, the soil water content was held at an ideal level for microbial activity. We followed the degradation of the alcohol by trapping of ^{14}C -alcohol that was volatilized, $^{14}\text{C-CO}_2$ a result of degradation and conducting an analysis of the soil ^{14}C residual levels, allowing a mass balance to be developed. Overall, the majority of the alcohols applied to the soil were either degraded by soil microorganisms or volatilized, as little of the alcohols remained in the soil at experiment's termination. The primary loss of alcohol for all concentrations of methanol, ethanol, and propanol was through biodegradation. Less than 10% of methanol and ethanol was volatilized; in contrast approximately 30% of propanol was volatilized. Methanol and ethanol in the soil is rapidly degraded in 10-20 days. In contrast, at concentrations greater than 10% most of the butanol was volatilized while little of it remained long-enough in the soil to be biodegraded. The exception to this is the 10% butanol treatments where most of the butanol applied was converted to $^{14}\text{C-CO}_2$. The ramifications and limitations of these findings are also discussed.

"Comparative productivity potential, environmental services and carbon, nitrogen, and water economies of candidate biofuel systems" - presented by Dr. Sylvie M.

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Long-term sustainable biofuels production with the concomitant protection and improvement of air, soil and water resources requires a concerted effort by the scientific community to gain knowledge regarding the comparative production potentials and environmental impacts of biofuel cropping systems. U.S. agriculture has extensive experience with intensive maize production and much recent discussion on energy from plants has focused on simply repurposing the existing farming systems towards ethanol instead of or in addition to animal feed. Both the grain and the stover can be used in energy production but removing the majority of the aboveground biomass from a farm field may negatively impact air, soil, and water quality. Alternative annuals, herbaceous perennials including novel species such as *Miscanthus* imported from Europe and low-input native systems may offer key advantages over maize production. Farmers can use existing farm equipment and these systems are expected to require far fewer energy and financial inputs than maize. However, at present, research on N and C cycling in these candidate biomass systems is fragmented and incomplete, a critical barrier to profitable, sustainable, and environmentally benign on-farm implementation of the U.S. biofuel agenda. Likewise, understanding crop water balance and optimizing water use efficiency will be essential to renewable biofuel success as water is expected to be the single, most limiting factor that transcends the multiple agro-ecozones in which U.S. biofuel production will be pursued. Accompanying this field experimentation will be the creation of a model repository and cyberinfrastructure that provide for curation of a wide variety of data such that archived data can be preserved, retrieved, understood, and accurately repurposed in a user environment that facilitates data mining, integration, and synthesis of disparate datasets. Project results will provide critical baseline knowledge regarding the relevant production and environmental merits of candidate biofuel systems, knowledge also necessary for valid, model-based food and fuel projections and development of informed public policy.