Tulane University – CPERC/DOE Research Proposal

Tulane is submitting two projects that are complimentary. The first involves initial studies into the economic production of butanol from sugar mill wastes (and other biomass sources). The second project compares the production and distribution costs and CO_2 emissions for multiple alternate fuels (including butanol) as well as a reference model for traditional fossil based transportation fuels.

Butanol: Production from Sugar Mill Waste Products

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The Tulane CPERC team proposes a research project on the economic production of butanol from sugar mill waste products. The project follows two parallel paths:

1. Utilization of sugar mill wastes to produce butanol via a variety of microbial pathways.
2. Process design and pilot scale experiments for the purification of butanol [from the products of item (1)] into a fuels grade product.

Tulane researchers will collaborate with other CPERC partners from Nicholls State University and the Audubon Sugar Institute, especially regarding the fermentation studies. Only item (1) will be addressed in this first year of funding

Introduction

Butanol production from fermentation has been practiced commercially for over a century. While, historically, it ranks second only to ethanol fermentation by yeast in its production scale, the commercial manufacture of butanol via fermentation has almost been completely replaced by petrochemical routes. The earliest known microbial route to butanol was described and implemented by Weitzman (1915).

Butanol is primarily used as an industrial solvent. However, its energy content per gallon is closer to gasoline than ethanol (see Table 1), making it a more attractive biofuel replacement. In addition, the purification of butanol from a fermentation broth comprised primarily of water can be achieved with significantly less energy than its ethanol counterpart. Hence, the potential exists for a cost-competitive biofuel without federal subsidies. Furthermore, butanol does not readily attract water (as does ethanol), which further adds to it attractiveness – especially in humid climates.

Table 1: Energy Content

Fuel	Content (Btu/gallon)
Unleaded Gasoline	114,000
Butanol	105,000
Ethanol	84,000

Alcohols including butanol, isopropanol and ethanol accumulate as end products of a bacterial fermentation pathway called the butyric-butylic fermentation (BBF) which uses substrates such as the hexose sugars glucose and fructose, or 5 carbon sugars such as xylose (present in plants!) which can be converted in the cell to yields a variety of alcohols and other valuable end products that represent a potential multibillion dollar industry for Louisiana and the United States (Somerville, 2006).

Butanol has been recently recognized as a commercially viable biofuel. In June 2006, British Petroleum and Dupont announced a partnership to manufacture this material in the UK from sugar (*BP and DuPont Announce Partnership to Develop Advanced Biofuels* 2006. These companies are working with British Sugar to convert the country's first ethanol fermentation facility and are examining the possibility of constructing larger facilities in the UK to expand globally. With the sugar industry being a major component of the state's economy, it is imperative that Louisiana universities explore the possibility of developing a similar path from sugar and its waste by-products. Ultimately, this path would lead to the development of an energy efficient biobutanol process from cheaper cellulosic sources.

Even with all of butanol's potential as a biofuel, substantial technical challenges remain with regard to commercial implementation. For instance, seamless integration of biobutanol production into an existing sugar mill or ethanol plant will require several process engineering considerations. Some questions requiring such expertise would be:

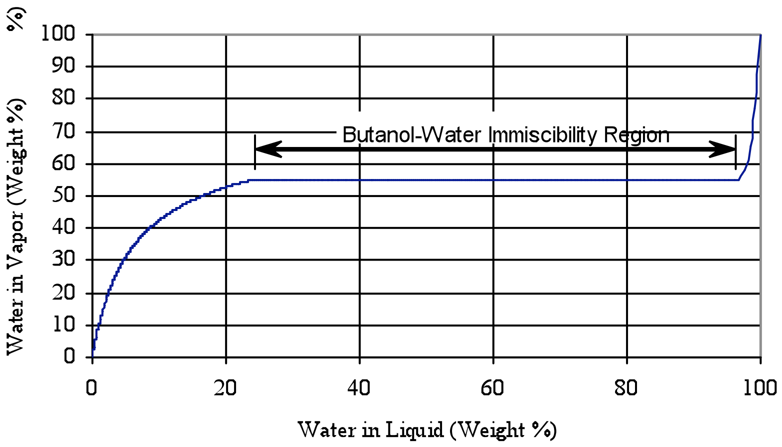
1) Which equipment can be selected for use in both sugar and ethanol/butanol production?

2) How should new equipment be incorporated to minimize the impact on current sugar production practices?

3) Which purification option will provide maximum energy efficiency with minimum environmental impact?

Butanol is more easily purified from an aqueous stream than ethanol because of its immiscibility under certain conditions. Both alcohols form azeotropes with water (Figures 1 and 2). For completely miscible systems (*i.e.* ethanol-water), the azeotrope provides a substantial barrier to further purification. Significant economic capital and energy are required for such separations. Azeotropic butanol-water compositions, however, are immiscible for a wide range of conditions. For instance, butanol-water mixtures at 95°F whose compositions fall within 24-97 weight% water (Figure 1) separate into two liquid phases; a butanol-rich phase (76 weight% butanol) and a water-rich phase (97 weight% water). This behavior allows purification options that circumvent the azeotrope.

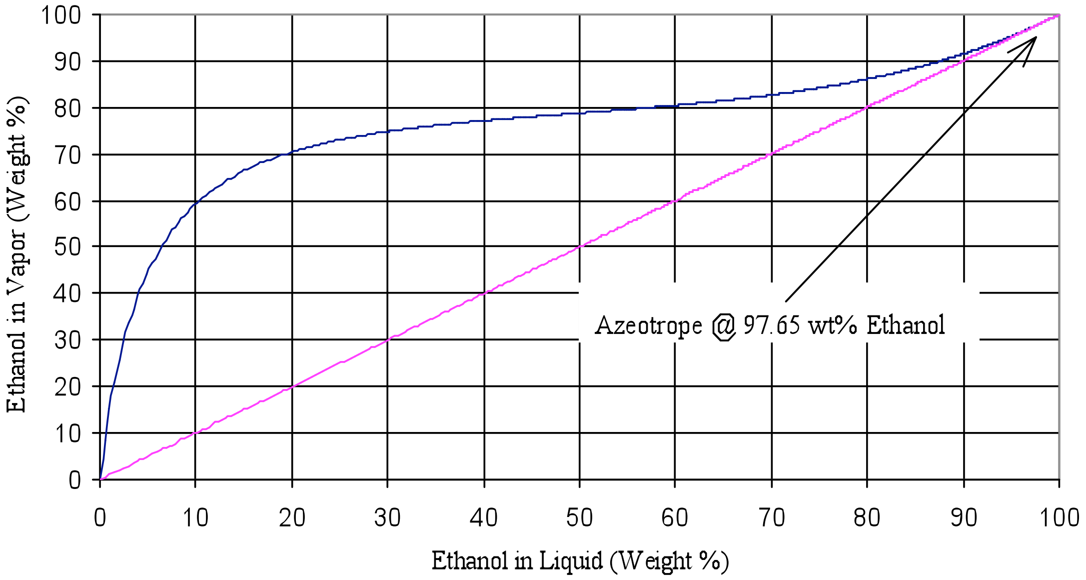
Figure 1: Butanol-Water Phase Equilibrium @ 95°F



The presence of specific species would eliminate this advantage. Most butanol fermentation processes also produce acetone and ethanol. Either of these in significant amounts removes the immiscibility region and requires additional equipment to achieve the desired purification. For this reason, we believe a multi-disciplinary approach will be the quickest path to development of a commercially viable process. Individuals with fermentation expertise (*e.g.* biology and biotechnology) should work closely with process engineering experts to identify and remove the obstacles to obtaining the most energy-efficient option.

Fermentation processes generate significant aqueous waste streams after the desired component has been separated. Current technology for biobutanol production is no exception. The most efficient fermentation process for butanol (U. S. Patent 5753474, 1996) claims to generate a concentrated aqueous butanol stream of only 8-15 weight%. This process is also described in Ramey & Yang, 2004. Any economically viable process must incorporate energy-efficient steps to purify the aqueous streams for recycle to the fermentation step.

Figure 2: Ethanol-Water Phase Equilibrium @ 95°F



A successful process for producing butanol from sugar mill wastes will have a significant and profound economic and technological impact on Louisiana's sugar industry. Sugar production from cane occurs for only a few months following harvest. Utilizing each production facility to manufacture biobutanol the remainder of the year would employ more individuals and increase the profitability of this sector of the state's economy.

The Proposed Effort

We propose an incremental approach to development of a commercially viable process from (eventually) cellulosic material. The process for the manufacture of fuel-grade butanol from sugar mill waste material is comprised of two steps: 1) biological production of a butanol/water mixture; and 2) purification and separation of butanol from the reaction mass.

Three major steps or phases are envisioned. In each phase, parallel efforts dealing with both the bioproduction of butanol and the process design/development will be performed.

Phase I (12 months):

Fermentation efforts will focus on identifying yeast strains that maximize butanol production from sugar mill waste while minimizing creation of other species. Laboratory fermentation studies will be performed to determine the optimum conditions (*e.g.* waste particle size, temperature, pH, etc.) for each strain. High-throughput screening techniques will be applied to rapidly obtain this data on multiple strains.

Process design efforts during the initial phase involves a study of numerous butanol purification schemes. Each purification option's sensitivity to butanol and fermentation by-product (*e.g.* ethanol, acetone, etc.) concentration will be studied. Each scheme will be investigated based on capital investment, energy-efficiency, and environmental impact. Much of this effort has already begun. Detailed process simulations for four purification alternatives have been developed for a 2 wt% butanol-in-water feed composition. Sensitivity and optimization studies for these process options must be completed. Computer simulations for other alternatives must be developed.

The fermentation and simulation efforts will affect each other in a cyclical fashion during this phase. The laboratory fermentation results will be incorporated into the detailed simulations for each purification alternative. Additional process simulation work will be performed to guide future laboratory studies to the overall process optimum.

At the conclusion of Phase I, our laboratory and process simulation studies will have identified the optimal process for Phase II. Other researchers at the business school will also have completed a commercial/economic analysis of the overall market for alcohol based fuels and will have made a preliminary estimate of the potential for penetration of that market by Butanol. We emphasize again that only Phase I will be performed during the first year of funding. Phases II and III are dependent on successful funding efforts for future years.

Phase II (12 months):
This phase includes scaling up the optimal process developed from Phase I. Fermentation vessels on the order of 10-20 liters will be employed during this phase. The purification section will be scaled to match the butanol production rate from fermentation. Once operational, we will use this small pilot-plant to confirm our laboratory findings. Overall material balances will be obtained and additional optimization will be performed. All pilot-scale operation data will be used to determine capital investment requirements and rates-of-return for incorporating the optimal biobutanol process into a typical Louisiana sugar mill.

Fermentation studies during Phase II will focus on screening a number of biological organisms for production of butanol from cellulose. This study will begin with naturally occurring organisms that are known to digest cellulosic material (*e.g.* bacteria from bovine gut and termites, fungus from rotting trees, etc.). It is unlikely that these organisms' metabolic pathways will produce significant quantities of butanol without genetic modification. Hence, pathways for organisms that have already been mapped will be analyzed to determine whether genetic modifications would increase their likelihood of producing feed for another butanol-producing organism (*i.e.* glucose or butyric acid) or butanol directly from cellulose.

As new biological candidates are identified during Phase II, their results will be incorporated into simulations of the optimal process to determine their impact. Additional studies on the pilot-scale may be warranted if the feed composition to the purification section is expected to change significantly when the cellulose-digesting organisms replace their glucose-digesting counterparts.

At the conclusion of this second phase, we will have determined the following:

1. Economics for incorporating the optimal glucose-to-butanol process into a typical Louisiana sugar mill or ethanol plant. These results will be transmitted to the Tulane business school researchers analyzing the economic aspects of this proposal.
2. Reliable operating conditions for the optimal glucose-to-butanol process.
3. Several biological candidates for producing butanol from cellulose.

Phase III (12 months):
During this third phase, we intend to partner with a sugar mill to commercialize the piloted process. Negotiations for this phase will take place at the very beginning of the project. During this phase, the proposed commercial process will contain those organisms which have been piloted from Phase I. We have identified the Audubon Sugar Institute as a partner to assist us in finding a candidate. We will work closely with the candidate to transfer the technology and will provide process assistance during start-up. A further increase in scale will occur at this phase. Hence, some additional pilot-scale studies may be required to convince our sugar mill partners of the reliability of our claims.

During this phase, we will select the best cellulose-digesting candidate for scale-up. This organism will be studied on the pilot-scale to identify those process modifications necessary to obtain results similar to those observed during the Phase II laboratory studies. The incremental economic impact of replacing the glucose-digesting organism with this candidate will be determined from material balances on the pilot plant. At the conclusion of Phase III, we will work with our sugar mill partner to incorporate the new biological organism into the commercial biobutanol process.

Throughout each phase, our findings will be disseminated in technical publications and at technical conferences. To increase our chances of completing Phase III, we will also present at conferences attended by potential commercial partners.

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The Impact of Carbon Emissions Policy and Transportation Costs on Alternative Transportation Fuel Supply Chain Economics

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Introduction
As nations search for methods to reduce green house gas emissions, there is a renewed focus on alternate fuels, such as ethanol, bio-diesel, and butanol. Although several of these fuels have a long history of production, they have not been widely adopted in the absence of significant government mandates or subsidies. For an alternate transportation fuel to displace conventional oil derivatives such as gasoline and diesel, there must be a reasonable probability that the fuel can become competitive in total costs, including production, distribution, and consumption. To date, no alternative fuels have passed this test in the United States. However, one cost that has long been absent in energy prices is the cost of environmental emissions. Quantifying the exact cost of any emission is likely to remain impossible, but incorporating some non-zero cost has the potential to significantly change the economics of the transportation fuel industry. The move to institute markets for carbon dioxide emissions makes it possible that some previously omitted costs will be included in future energy prices in the U.S. as has been true in European markets for several years. A key issue, however, is the timeline in which such markets are implemented and the resulting CO_2 prices. Given the regulatory uncertainty, it is difficult to justify major capital investments to reduce CO_2 until a clearer picture of costs and benefits emerges.

Phase 1 (2008)

Our initial plan is to develop a relatively high level aggregate planning model. In order to understand the impact that carbon markets might have on alternate fuel adoption, we will compare the production and distribution costs and CO_2 emissions for multiple alternate fuels as well as a reference model for traditional fossil based transportation fuel. The model will be calibrated using cost estimates provided by the Louisiana Clean Power Energy Research Consortium (CPERC). The data inputs and scenarios include:

- Initial alternate fuel production cost and potential production learning rates
- Initial alternate fuel distribution costs and cost trajectories
- Carbon dioxide emissions from alternate fuel production and consumption
- Conventional fuel price trajectories
- Carbon prices under multiple market scenarios
- Regulatory timing and intensity

Although land use is not expected to be the explicit focus of our analysis, we note that recent studies have emphasized that the case for bio-fuel carbon-dioxide emission reductions is dependent upon land use markets and policies. As the science about land use improves, we will incorporate these costs into the analysis.

Phase 2 (2009+)

As the economic data inputs improve over time, it will be possible to develop more detailed models that incorporate finer grained data about spatial characteristics of production and demand and have more accurate economic data as inputs. In addition, it will be possible to more accurately model the impact of regulatory delay on the decisions of market participants in order to develop a clearer picture of technology adoption under different regulatory regimes.

Phase 3 (2009+)

The effects of regulatory uncertainty surrounding carbon dioxide policy are felt in many industries beyond transportation. Power generation is a key area where there will be significant investment over the next twenty years in order to replace aging generation infrastructure. Due to their varied carbon emissions characteristics, the technologies that will be adopted are highly dependent upon carbon policy. In an analysis that parallels the phase 1 and 2 transportation fuel study, we will model the aggregate cost of electricity under multiple scenarios of (1) continued "wait and see" what carbon legislation will pass, (2) continued investment in natural gas combined cycle capacity, (3) aggressive investment in efficiency improvements, (4) aggressive investment in alternate fuels and generation technology, including wind, solar, and biofuels, (5) investment in coal, (6) investment in nuclear energy, and combinations of these options.

The results of these analyses will be useful to policy makers as they consider which technologies (if any) can most benefit from subsidies and mandates. Further, we expect to benefit firms that are subject to regulation and are planning to invest in renewable energy resources by helping to guide their technology selection and provide a framework to assess technology and CO_2 market risks.

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