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Ashley Haub

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Production of Biobutanol from Biomass Using Novel Membrane Reactor:
a P3 Experience by Ashley Haub

An Undergraduate Honors College Thesis

in the

Ralph E. Martin Department of Chemical Engineering
College of Engineering
University of Arkansas
Fayetteville, AR

by

Ashley R. Haub

April 2009

My contribution to this project:

As a member of the biobutanol design team, I have been involved with this project through all of its phases, including research, technical design, laboratory experimentation, and presentation of results at the National Sustainability Design Expo in Washington, D.C. When investigating potential feedstocks for our process, I was responsible for researching the use of forestry waste and chicken litter. This involved both literature research as well as contact with local experts in these individual fields. I also participated in designing a laboratory-scale process that would produce butanol from food waste via a fermentation process. This required determining which steps were required for the process, designing the equipment, and assembling the apparatus for experimentation. For the laboratory experimentation phase, I assisted in pre-treating the food waste and mixing media for growing a stable bacteria culture. After the laboratory experiments were completed, I was heavily involved in writing both the technical report detailing the results of the project as well as the proposal for the next phase of the project. I worked alongside the team coordinator to proofread and edit the final report draft. At the sustainability expo, I was one of the speakers chosen to present our project to the judges. For detailed information regarding this project, please see the attached team report in the Appendix.

Appendix

Team Project Report:

I. EXECUTIVE SUMMARY

Date of Project Report: March 23, 2009

EPA Agreement Number: SU83392701

Project Title: Production of Biobutanol from Biomass Using Novel Membrane Reactor

Faculty Advisers: Hestekin, Jamie; Thoma, Greg; Clausen, Ed

Department and Institution: Ralph E. Martin Department of Chemical Engineering, University of Arkansas

Student Team Members: Benbrook, Stephen; Boyd, Robert; Draehn, Ellen; Haub, Ashley; Heeb, Rhett; Thibodeaux, Natalie; White, Kris

Project Period: August 2008 through May 2009

Project Amount: \$10,000

Description and Objective of Research

Developing renewable energy resources is one of the main challenges facing the world today. Our energy sources must become more renewable, more efficient, and safer for the environment. With the use of automobiles, the world has been able to make long distances seem shorter, but those automobiles have recently come under scrutiny due to sustainability and emission issues. The predominant current fuel source, gasoline, is from a limited resource – fossil fuels – which is in high demand. Most of the world's supply is purchased from a limited number of sources. The high demand has caused depletion of oil wells and mass outflow of capital which threaten the continued operation of automobiles. Currently, the United States imports 5 billion barrels of oil per year, creating a pressing need to find a viable, sustainable alternative.

Past research efforts have made significant progress on electric and ethanol-based solutions; however, butanol is another sustainable alternative. First generation biofuel research has focused mainly on ethanol. Recently, biobutanol has become an attractive alternative to ethanol as a fuel oxygenate due to its low vapor pressure, high energy density, and ability to be blended with gasoline at the refinery which saves the trouble of transporting ethanol and gasoline separately to the fueling stations. Butanol's higher energy density increases a vehicle's fuel efficiency in comparison to ethanol. The high miscibility of butanol and gasoline gives greater flexibility in mixture composition. In addition, modern gasoline automobile engines can use butanol without any engine modifications. Biobutanol does not require automakers to compromise on performance to meet environmental regulations. Older automobiles also benefit from butanol being less corrosive than ethanol since it will not corrode rubber seals.

The purpose of Phase I was to investigate a method for producing biobutanol on a large scale from a waste feed stock using a novel fermentation and membrane separation method. The accepted method for biobutanol production is based on a fermentation process that produces acetone, butanol, and ethanol utilizing *Clostridium beijerinckii* in a bioreactor. The product solvents are also accompanied by water in the process and require several separations to produce a pure butanol product.

Producing biobutanol from a waste product on a large scale is a novel idea. Because of this, there is very little research available in this area. Previous fermentation research has primarily focused on the production of ethanol or biobutanol using cellulosic or agricultural feed stocks. The Phase I research team, Team **R**azorbacks **E**ngineering **F**uel **S**olutions for **E**veryone (Team REFUSE), sought to design a fermentation process that would produce butanol from food waste. Team REFUSE cultivated a partnership with Chartwells, the campus food service provider for the University of Arkansas, for the acquisition of food waste. They used the samples provided to run tests on food waste composition and determine the viability of using the food waste in an ABE fermentation process.

Summary of Findings (Outputs/Outcomes)

Food Waste Composition

Team REFUSE first performed sugar and starch assays on food waste from an on-campus cafeteria to determine its composition. The testing of the Chartwells food waste indicated the waste had approximately 10% sugar and 25-30% starch content, which is sufficient for use in fermentation.

Fermentation

The fermentor used in the laboratory-scale was a two-liter Bioflow II reactor from New Brunswick Scientific. Bacterial cultures are difficult to maintain and do not initially adjust well to change. To minimize cell loss, inoculation of the reactor was accomplished in three steps. First the fermentor was run on a batch basis with media as a feed stock. When the cells were actively growing and producing product, the reactor was switched from a batch to continuous process. When the bacteria growth was stabilized in the continuous process, the growth medium was exchanged for food waste.

The team chose to use *Clostridium beijerinckii*, a bacterium that produces butanol, as the best bacterium to process food waste. Due to the difficulty in growing the *C. beijerinckii* culture, experimentation was performed with *C. tyrobutyricum* because it was readily available. *C. tyrobutyricum* is a close relative of *C. beijerinckii* that produces butyric acid instead of butanol and is often used in a two-step fermentation process to produce butanol. This culture successfully produced butyric acid from food waste, and from these results it is reasonable to postulate that experimentation with *C. beijerinckii* will also process food waste. At the time of this report's submission, a healthy *C. beijerinckii* culture had been obtained and experimentation is ongoing.

Pervaporation

Pervaporation combines permeation and evaporation with good energy efficiency. This technology is based on the different diffusion rates of specific components through the membrane. The feed flows across the inlet side of a hydrophobic membrane, and a portion of this stream is pulled through the membrane in vapor form. A vacuum is applied on the opposite side of the membrane to increase mass transfer. The permeate vapor is then condensed and

collected. The portion of the feed that does not diffuse through the membrane, the retentate, consists mostly of water and is recycled and disposed.

To obtain a purified butanol product, Team REFUSE built a custom pervaporation system with a PDMS (polydimethylsiloxane) membrane to evaluate the separation of butanol from water. Several condenser solutions were tested including chilled brine, liquid nitrogen, and dry ice in ethylene glycol. The best results were obtained from the dry ice in ethylene glycol at -15°C . The chilled brine solution failed to condense most of the permeate while the liquid nitrogen froze the condensate, plugging the vacuum. The permeate and feed concentrations were obtained using gas chromatography. Based on these test results, membrane separation has potential for larger-scale implementation.

Life Cycle Assessment

In Phase I of this project Team REFUSE illustrated through a life cycle assessment (LCA) the environmental advantages of producing butanol. In America, transportation fuels account for 34% of greenhouse gas emissions; therefore, it was assumed for this assessment that the function of fuel is to move a vehicle. The basis for the assessment was the energy content of 1 kg of butanol, 33.3 MJ/kg.

The LCA compared butanol to gasoline and ethanol using the SimaPro software program and Recipe Endpoint (H). Gasoline emits 2.17 kg of CO_2 more than the production method of biobutanol. When compared to corn ethanol, the process for producing biobutanol produces less CO_2 by a margin of 1.05 kg of CO_2 per kg butanol. The LCA confirms that biobutanol is more sustainable than both gasoline and ethanol.

Conclusions

Phase I proved the feasibility of using a fermentation reaction as the primary step in production of biobutanol from food waste. Currently, carbohydrates, including sugars, starches, and even cellulose, can be used as the raw feed to produce alcohol-based fuels via microbial fermentations. Food waste contains an adequate amount (approximately 40%) of these raw materials in a form easily utilized by the bacteria, as proven by the team's food waste analysis.

Phase I made substantial progress towards demonstrating the production of biobutanol from food waste. First, the team was successful in producing butyric acid from food waste using the bacteria culture *C. tyrobutyricum*, which is closely related to *C. beijerinckii*. Experimentation with *C. beijerinckii* is ongoing. Pervaporation experiments were also successful.

Based on Phase I research, biobutanol production via food waste is has potential to be a sustainable alternative fuel technology. Experimentation on the fermentor residence time and pervaporator operating conditions could increase the yield and profitability of the process. Based on the life cycle analysis performed in Phase I, it is clear that the separation of butanol from the fermentor effluent is a critical step in improving the sustainability of the production process. Therefore more research is required to improve this technology. Phase II proposes to do this by building a pilot-scale plant and gathering experimental data.

Proposed Phase II Objectives and Strategies

Research on a larger scale is necessary to the development of a full-scale design of a continuous, economically viable butanol fermentation process from food waste. To achieve this goal a pilot-scale model has been designed that incorporates and builds upon the methods proven successful in Phase I.

In Phase II, senior chemical engineering design students will build and operate a pilot scale model that will process 150 pounds per day of food waste from one of the cafeterias at the University of Arkansas to approximately 190 mL per day of biobutanol. Building and operating this unit will allow the Phase II team to experiment with several operating variables that affect yield and process efficiency. One of the questions raised by the experimental results in Phase I was the potential benefit of the conversion of starches to butanol. In Phase II Team REFUSE will determine the relationship between residence time and starch conversion. Although a longer residence time will allow more of the starches to be converted to butanol, at a certain point the bacteria will actually begin to decrease butanol production due to a lack of sugars.

Experimentation in Phase II will determine the optimal balance between residence time and starch conversion.

Experimentation is also needed to increase the effectiveness of the pervaporation system. Altering the vacuum pressure and feed temperature of the pervaporator unit will affect the flux through the membrane. Increasing vacuum on the membrane or increasing the temperature of the liquid through the membrane will increase the flux. When using a hydrophobic membrane, increasing the component flux will increase the butanol concentration in the permeate stream.

The experimentation period will last for one month and the results of the process optimization will assist the team in designing a full-scale facility that could be implemented on a university campus. Approximately 1 million pounds of food waste are disposed of each day by American universities which could potentially be turned into 8 million gallons of butanol per year.

Processing all of a university's food waste will make the institution more sustainable and will offset a portion of the fuel costs for the university vehicles.

Supplemental Keywords

Biobutanol, pervaporation, *Clostridium beijerinckii*, fermentation, ABE fermentation, food waste, alternative fuel source, alternative fuel, sustainability

II. BODY OF REPORT

A. Summary of Phase I Results

1. Background and Problem Definition

Developing renewable energy resources is one of the main challenges facing the world today. Our energy sources must become more renewable, more efficient, and safer for the environment. With the use of automobiles, the world has been able to make long distances seem shorter, but those automobiles have recently come under scrutiny due to sustainability and emission issues. The predominant current fuel source, gasoline, is from a limited resource – fossil fuels – which is in high demand. Most of the world's supply is purchased from a limited number of sources. The high demand has caused depletion of oil wells and mass outflow of capital which threaten the continued operation of automobiles. Currently, the United States imports 5 billion barrels of oil per year¹, creating a pressing need to find a viable, sustainable alternative.

Past research efforts have made significant progress on electric and ethanol-based solutions; however, butanol is another sustainable alternative. First generation biofuel research has focused mainly on bioethanol². Recently, biobutanol has become an attractive alternative to ethanol as a fuel oxygenate due to its low vapor pressure, high energy density, and ability to be blended with gasoline at the refinery which saves the trouble of transporting ethanol and gasoline separately to the fueling stations. Butanol's higher energy density increases a vehicle's fuel efficiency in comparison to ethanol. The high miscibility of butanol and gasoline gives greater flexibility in mixture composition. In addition, modern gasoline automobile engines can use butanol without any engine modifications². Biobutanol does not require automakers to compromise on performance to meet environmental regulations. Older automobiles also benefit from butanol being less corrosive than ethanol since it will not corrode rubber seals³.

2. Purpose, Objectives, Scope

The purpose of Phase I was to develop technology for producing biobutanol from a waste product. Butanol is made commercially from butane, which is obtained from fossil fuels. Producing butanol by fermentation is a sustainable alternative. Fermentation also allows more flexibility in the feed stock, with appropriate adjustments to pretreatment.

Producing biobutanol from a waste product on a large scale is a novel idea. Research has mainly been conducted using cellulosic or agricultural feed stocks⁴. Biobutanol fermentation requires a feed stock that contains or can be converted to simple sugars and starches. Team REFUSE evaluated the feasibility of using agricultural waste, forestry waste, chicken litter, and consumer waste products as potential feed stocks. Forestry waste products such as fallen tree limbs and sawdust were rejected as a possible feed stock due to the difficulty of converting the cellulose into the simple sugars required for the fermentation. Agricultural wastes including corn stover, wheat straw, and soy straw were rejected because of the difficulty in collection and transportation as well as the need for cellulose conversion to sugars (30-40% cellulose)^{5,6}. Although chicken litter can be obtained for approximately \$8/ton⁷, there would still be the difficulty of processing the cellulose (about 35% cellulose⁸). Food waste was chosen from the myriad consumer wastes for several reasons. First, it is readily available in significant quantities from a variety of sources such as restaurants, grocery stores, hospitals, and cafeterias. It is

estimated that the largest 500 universities across the United States dispose of approximately one million pounds of food waste every day. Team REFUSE performed laboratory tests to determine that food waste (from the University of Arkansas food service, assumed typical) contains approximately 10% simple sugars (by weight) and 25-30% starches that are suitable for fermentation. Finally, the only acquisition cost associated with food waste are the minimal collection and transportation cost.

Once the feedstock was chosen, a bench-scale model was designed and built to test the fermentation using food waste. The team considered two methods of separating butanol from the fermentation reactor broth. The first was distillation. The difficulties of using distillation with this process related to the high water content in the product stream and the multiple component interactions between water, acetone, and butanol. The high water content requires a large energy input to heat the water, which is in great excess compared to butanol. In addition, when the butanol composition of a butanol-water mixture is between 2% and 35%, two distinct liquid phases will form⁹. Based on a simulation performed by the team, separation of the crude fermentation product would require a total of three separate distillation columns. Because of this, pervaporation is a more attractive purification method. Pervaporation is not affected by azeotropes and eliminates the need to vaporize all of the water in the product stream.

3. Data, Findings, Outputs/Outcomes

Life Cycle Assessment

In Phase I of this project Team REFUSE illustrated through a life cycle assessment (LCA) the environmental advantages of producing butanol. In America, transportation fuels account for 34% of greenhouse gas emissions¹⁰; therefore, it was assumed for this assessment that the function of fuel is to move a vehicle. The basis for the assessment was the energy content of 1 kg of butanol, 33.3 MJ/kg. The distances the food waste and the final product will be transported were assumed to be one mile or less for a university-scale plant implemented near the campus.

Unlike most feed stocks, food waste is considered a waste stream, and for the purpose of the LCA, has no initial carbon burden. The most significant contributor to both the required energy and emissions was the separations step of the process. It accounts for 0.511 kg of CO₂ per kg of butanol produced and is the largest contributor by almost a factor of ten. These figures are based on a worst-case scenario for energy input. With further refinements in pervaporation technology, it would be possible to dramatically decrease the energy inputs. To achieve this goal, the most significant step would be to replace the refrigeration cycle with cooling water.

The LCA compared butanol to gasoline and ethanol using the SimaPro software program and Recipe Endpoint (H). Gasoline emits 2.17 kg of CO₂ more than the production method of biobutanol. When compared to corn ethanol, the process for producing biobutanol produces less CO₂ by a margin of 1.05 kg of CO₂ per kg butanol. The LCA confirms that biobutanol is more

sustainable than both gasoline and ethanol. Other impact categories of the LCA comparisons are given in Figure 1 below.

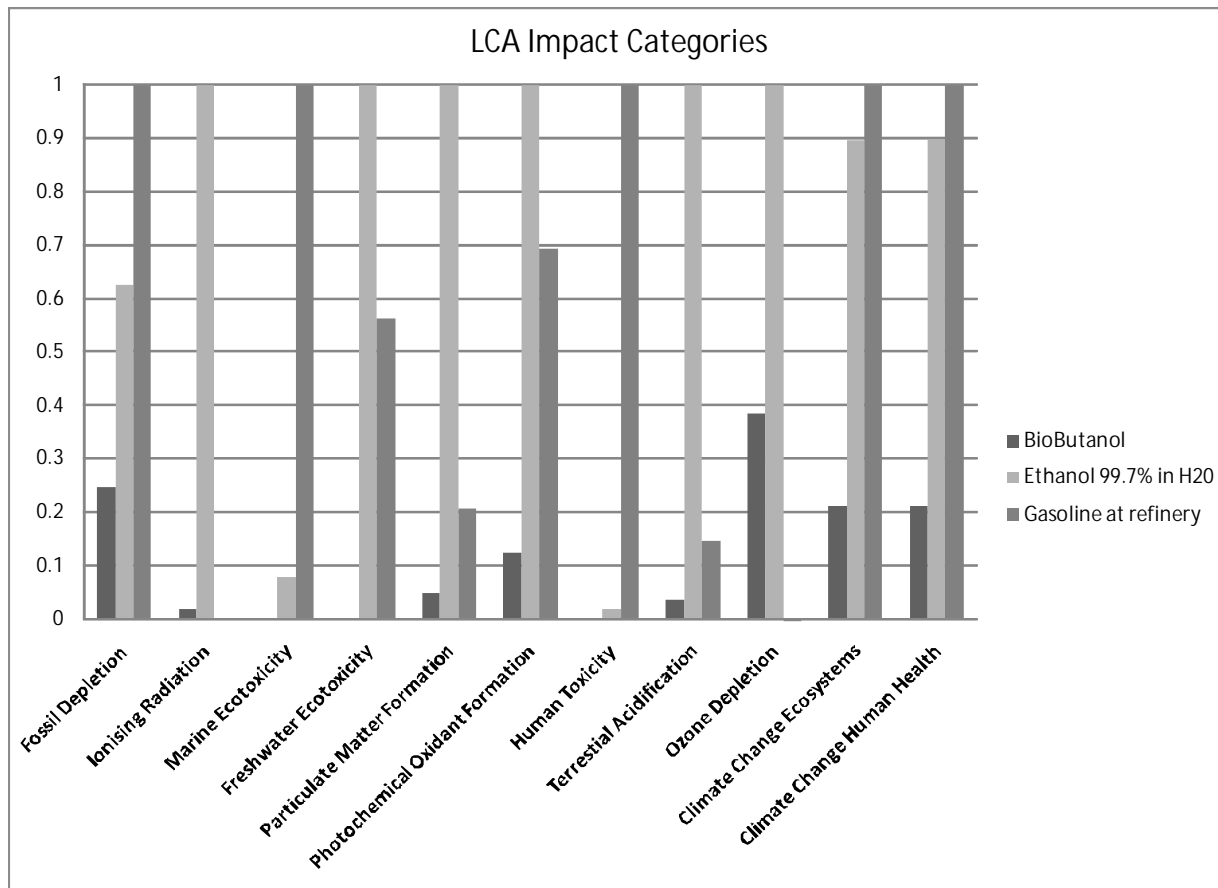


Figure 1. Comparison of biobutanol to ethanol and gasoline using different impact categories.

Fermentation

The acetone-butanol-ethanol (ABE) fermentation process was implemented in 1916 to produce acetone via the Weizmann organism¹¹. Weizmann patented the process for producing acetone from starch using the bacterium *Clostridium acetobutylicum* in 1919. In a typical process, *C. acetobutylicum* first produces butyric, propanoic, and acetic acids. The fermentation continues through a solventogenesis stage which produces butanol, acetone, and ethanol¹¹. The butanol, acetone, and ethanol are produced in a 6:3:1 volume ratio¹². One of the problems with butanol production by way of ABE fermentation is that too high of a butanol concentration inhibits the process. *C. acetobutylicum* cannot survive at a butanol concentration above 7%, thus to obtain higher butanol concentrations, modifications have been made both to the bacterium and the ABE process.

Before fermentation experimentation could be started, the team researched which butanol-producing bacterium would be used. Butanol fermentation research focuses on two main species, *Clostridium acetobutylicum* and *Clostridium beijerinckii*. The key difference between these strains is found in their carbohydrate metabolism processes. *C. beijerinckii* is able to

process a variety of carbohydrates found in food waste; *C. acetobutylicum* is more limited. Therefore, *C. beijerinckii* was chosen as a more effective bacterium for this process¹³.

The fermentor used in the laboratory-scale was a two-liter Bioflow II reactor from New Brunswick Scientific. Bacterial cultures are difficult to maintain and do not initially adjust well to change. To minimize cell loss, inoculation of the reactor was accomplished in three steps. First the fermentor was run on a batch basis with media as a feed stock. When the cells were actively growing and producing product, the reactor was switched from a batch to continuous process. When the bacteria growth was stabilized in the continuous process, the growth medium was exchanged for food waste.

Due to the difficulty of growing the *C. beijerinckii* culture, experimentation was performed using *C. tyrobutyricum*, a close relative of *C. beijerinckii* that produces butyric acid instead of directly producing butanol. Healthy *C. tyrobutyricum* seed cultures were readily available; therefore, research could begin immediately using this bacterium while the team continued to work on growing a large *C. beijerinckii* seed culture. The fermentor effluent was analyzed by high-performance liquid chromatography (HPLC) and the results are shown in Table 1. *C. tyrobutyricum* successfully produced butyric acid from food waste.

Table 1. Butyric Acid production in fermentor over time.

Time (h)	Butyric Acid Concentration (g/L)
0	0
5	3.88
24	20

We are continuing to work on establishing a *C. beijerinckii* culture, and expect to have results from fermentation using this microorganism at the competition in April.

Pervaporation

Experimentation of the separation of solvent products was performed through a pervaporation apparatus using a PDMS (polydimethylsiloxane) membrane. This technology has advantages over traditional distillation for this process because of its ability to successfully separate an azeotropic mixture^{14,15}. Pervaporation is also an ideal choice to extract the low butanol concentration typically found in fermentor effluents^{15,16}. The high water-to-butanol ratio in the fermentor effluent also requires a substantial amount of heat duty in a traditional distillation column in order to vaporize all of the water. In contrast, the pervaporation feed only has to be heated, not vaporized. Furthermore, a relatively small amount of butanol must be condensed on the permeate side. This, coupled with butanol's low heat of vaporization, requires less heat duty to accomplish the separation.

Pervaporation combines permeation and evaporation with good energy efficiency. This technology is based on the different diffusion rates of specific components through the

membrane. The feed flows across the inlet side of a hydrophobic membrane, and a portion of this stream is pulled through the membrane in vapor form. A vacuum is applied on the opposite side of the membrane to increase mass transfer. The permeate vapor is then condensed and collected. The portion of the feed that does not diffuse through the membrane, the retentate, consists mostly of water and is recycled and disposed^{15,16}.

In Phase I, one-liter feed solutions containing varying amounts of butanol ranging from 10 g/L to 50 g/L were prepared to test the pervaporation system. This range of concentrations was chosen based on expectations of ABE fermentor effluent compositions. The bench-scale apparatus operated in a batch mode in which the feed was re-circulated through a heated 1-liter flask at 55°C. The pervaporator unit was sized for a 2-liter fermentor unit and was built by the department machinist. A diagram of the unit is given in Figure 2. The feed was pumped into the pervaporation housing and across the membrane. Butanol selectively diffused through the membrane and condensed on the permeate side. The condenser consisted of a glass cold finger immersed in a cooling liquid. When the circulated batch run was completed, the condensate was collected and analyzed.

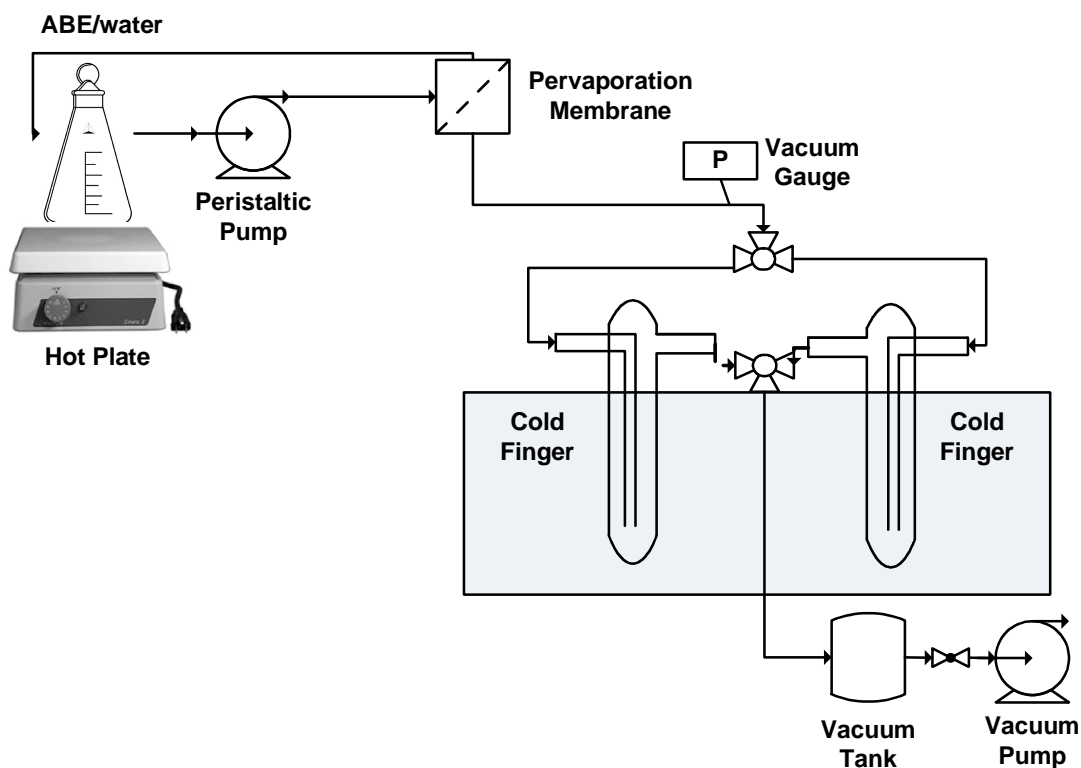


Figure 2. Pervaporation experimental apparatus schematic.

Several condenser solutions were tested including chilled brine, liquid nitrogen, and dry ice (CO₂) in ethylene glycol. The best results were obtained from the dry ice in ethylene glycol at -15°C. The chilled brine solution failed to condense most of the permeate while the liquid nitrogen froze the condensate, plugging the vacuum. The permeate and feed concentrations were

obtained using gas chromatography. Experimental butanol fluxes from these tests are shown in Table 2.

Table 2: Butanol flux relative to feed concentration condensed in Dry Ice and Ethylene Glycol

Run	BuOH Concentration in Feed (g/L)	BuOH Flux (g/m ² hr)
1	9.3	11.4
2	20.0	15.7
3	26.82	58.9
4	49.62	85.4

Pilot Scale Design

After the pervaporation and fermentation experiments were performed, it was concluded from the results that food waste is a suitable feed stock for producing biobutanol. The next step was to design a pilot-scale plant that would produce fuel grade biobutanol using the food waste from the University of Arkansas cafeterias. The pilot-scale unit is designed to process 150 pounds of food waste per day and demonstrate production of a 95% butanol product by pervaporation. The detailed design and operation for the pilot scale is discussed in section B.1 of this document.

4. Discussion, Conclusions, Recommendations

Increasing the efficacy with which renewable fuels can be manufactured is a major step to decreasing the amount of fossil fuels imported and consumed in the United States. Biofuels manufactured from biomass, especially waste, are one viable way in which this can be accomplished. Butanol has several benefits that make it a more desirable fuel than ethanol as mentioned above.

Phase I proved the feasibility of using a fermentation reaction as the primary step in production of biobutanol from food waste. Currently, carbohydrates, including sugars, starches, and even cellulose, can be used as the raw feed to produce alcohol-based fuels via microbial fermentations. Food waste contains an adequate amount (approximately 40%) of these raw materials in a form easily utilized by the bacteria, as proven by the team's food waste analysis.

Phase I made substantial progress towards demonstrating the production of biobutanol from food waste. First, the team was successful in producing butyric acid from food waste using the bacteria culture *C. tyrobutyricum*, which is closely related to *C. beijerinckii*. Experimentation with *C. beijerinckii* is ongoing. Pervaporation experiments were also successful.

Based on Phase I research, biobutanol production via food waste is has potential to be a sustainable alternative fuel technology. Experimentation on the fermentor residence time and

pervaporator operating conditions could increase the yield and profitability of the process. Based on the life cycle analysis performed in Phase I, it is clear that the separation of butanol from the fermentor effluent is a critical step in improving the sustainability of the production process. Therefore more research is required to improve this technology. Phase II proposes to do this by building a pilot-scale plant and gathering experimental data.

Phase I was successful in laying the groundwork for partnerships with several different organizations on the University of Arkansas campus. The most important partnership established was with Chartwells, the campus dining service. They were eager to provide food waste statistics as well as samples for the laboratory experiments. Other individuals at the University have also been helpful with the research process. Dr. Ya-Jane Wang from the Food Sciences department assisted in performing sugar and starch assays to determine the food waste composition. Graduate students in the Chemical Engineering department have assisted the Phase I team in fermentor operation and troubleshooting. Several letters of continued support are attached at the end of this document.

This project branches out to many areas, including chemistry, engineering, biochemistry, microbiology, and food sciences. As a result of this project, Team REFUSE gained valuable experience in all of these areas. The entire experience served to strengthen each individual team member's engineering skills, which will be invaluable to them as they prepare to enter the workforce. These skills include applying engineering design concepts as well as laboratory experimentation and data analysis. Finally, the group environment fostered the development of interpersonal communication skills and teamwork.

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B. Proposal for Phase II

1. P3 Phase II Project Description

Relationship of Challenge to Sustainability (People, Prosperity, and the Planet)

People

The proposal for a second phase of this project focuses on further developing the technology to convert food waste to fuel grade butanol. The conversion of food waste into transportation fuel has several societal benefits. According to the Energy Information Administration, the United States currently imports 5 billion barrels of oil per year. The production of fuel from locally available waste materials could reduce society's dependence on imported fossil fuels. If fuel was produced domestically, all of the economic benefits would supplement local economies as opposed to foreign economies. Biobutanol plants partnered with university cafeterias could be used as a testbed to develop the technology necessary to produce butanol on an industrial scale. Furthermore, university-scale biobutanol plants could be utilized as an important educational tool for students and would help universities become more sustainable. Currently the largest 500 universities dispose of one million pounds of food waste per day. Using conversion ratios from Phase I, this could potentially amount to 1.5 million gallons of butanol per year.

Prosperity

The most significant short-term cost for the implementation of fermentation-produced butanol is the research required to make it a competitive alternate fuel. Specifically, further research is required in the areas of fermentor operating conditions and butanol separation, as well as pretreatment and types of feedstock. Data from pilot scale studies on the University of Arkansas campus will allow an economic analysis to be performed for a full-scale plant, which would process approximately 1 ton of food waste per day at the UA. Phase II of this project is an important intermediate step in the progression towards profitable industrial production of biobutanol.

Planet

Production of butanol from food waste utilizes a waste feed stock to produce an environmentally friendly fuel alternative. The current trend is to produce biofuels from crop-based feed stocks, primarily corn and soybeans. This requires extensive resources such as water, fertilizer, land, and energy for growth, harvest, and transportation. Most importantly, using crops to produce fuel competes with human consumption. In contrast, food waste only requires the energy involved in collection, transportation, and transformation to butanol. The Life Cycle Assessment in Phase I proved the cradle-to-grave assessment of food waste to butanol was favorable over other alternate fuels.

Converting food waste to biobutanol benefits the environment by reducing carbon emissions. Because of the large quantities of fossil fuels used today, sequestered carbon continues to be rapidly reintroduced into the environment. It is clear that reducing consumption of non-renewable resources like fossil fuels will be one of many critical steps on the path towards achieving sustainable consumption. By using a waste stream as a feedstock for fuel production,

less fossil carbon will be reintroduced into the carbon cycle. Furthermore, had the food waste been allowed to decompose naturally, it would have released methane into the atmosphere. Methane has a global warming potential that is 25 times greater than carbon dioxide. In contrast, when a biofuel is combusted, carbon will be released in the form of carbon dioxide, which is less harmful to the environment than methane. Thus, making butanol from food waste not only reduces the *amount* of carbon emissions but also decreases the harmful environmental effects of these emissions.

Challenge Definition and Relationship to Phase I

In Phase I, Team REFUSE proved that food waste could be successfully converted to butyric acid via the bacteria *Clostridium tyrobutyricum*. Research on a larger scale is necessary to the development of a full-scale design of a continuous, economically viable butanol fermentation process from food waste. To achieve this goal a pilot-scale model has been designed that incorporates and builds upon the methods proven successful in Phase I.

The pretreatment process in Phase I was a batch method in which each step was performed manually. Phase II will also utilize a batch method, however, the pretreatment will be entirely mechanized. The fermentation in Phase I was achieved in a Bioflow II reactor from New Brunswick Scientific. In Phase II a custom fermentor will be built that models the Bioflow II reactor on a larger scale. It incorporates agitation as well as pH and temperature control. The main difference between the Phase I and II models is in the pervaporation unit. In Phase II a portion of the reactor effluent will be purified by pervaporation; however, the final product will be a nearly pure organic mixture of butanol, ethanol and acetone (~95%). This will be accomplished by two pervaporation systems in series. Once this purity is achieved, distillation to remove the remaining water is feasible.

A new team of senior chemical engineering students will build and operate the pilot scale unit with guidance from faculty advisers. In Phase II, the students will be able to gather data and optimize the process. The first area of focus will be on increasing yield. This will require an optimization between the residence time in the fermentor and the conversion of sugars and starches to butanol. The students will also determine the most favorable operating conditions for the pervaporation system using a factorial experimental design to determine the optimum membrane flux. The variables affecting the flux include temperature, flow rate, and vacuum pressure. Using the data collected from Phase II, the students will design a full-scale plant that could be implemented on any university campus.

Innovation and Technical Merit

The idea of recycling waste to produce a useful product is not new, especially with sustainability being on the forefront of national attention; nor is the idea of using agricultural products to make fuel. However, using a *waste* material as a feed stock to produce biobutanol has not been

researched. This proposal is based on the premise that it is possible to produce biobutanol from food waste. A process flow diagram of the Phase II pilot plant is shown in Figure 3.

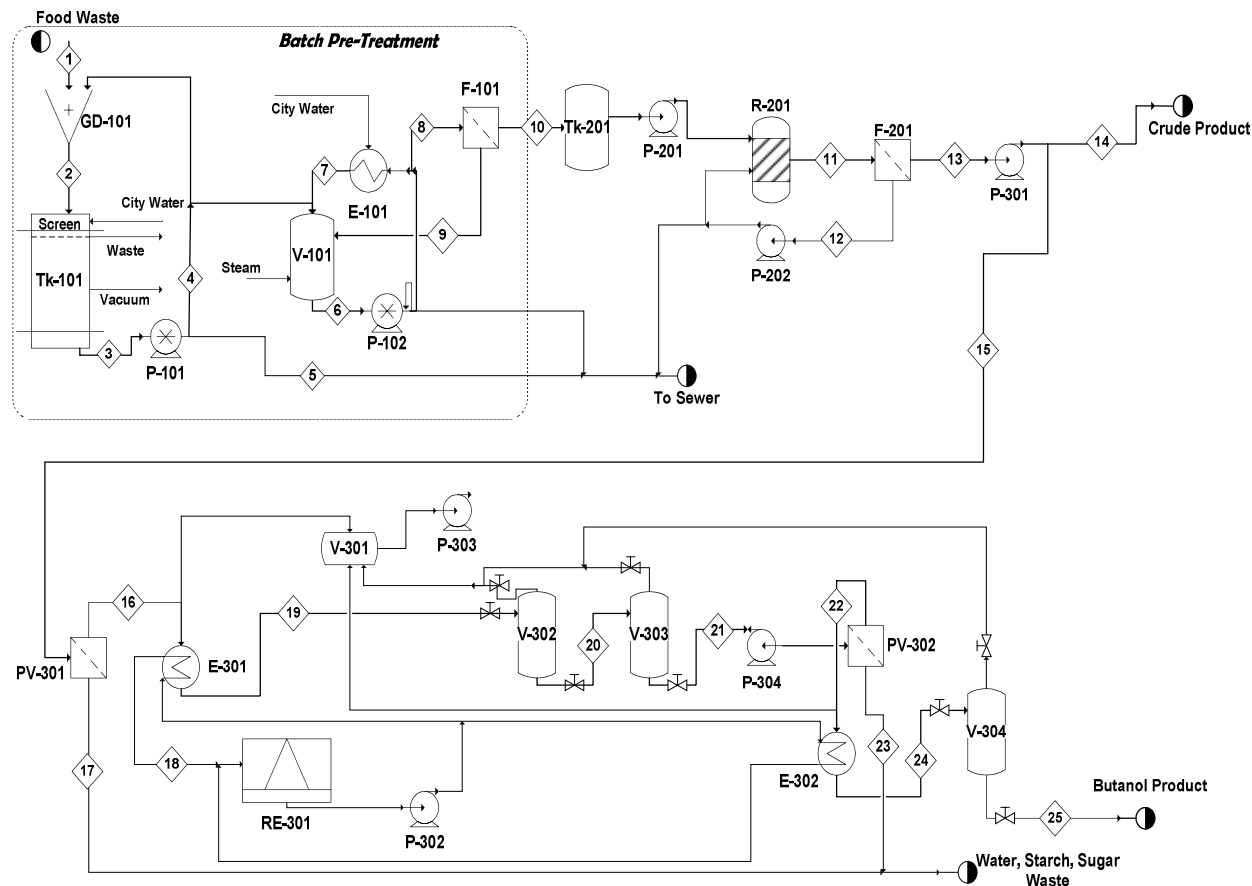


Figure 3. Pilot Scale Process Flow Diagram

Overview of Process

This process is designed to convert 150 pounds per day of food waste from one of the cafeterias at the University of Arkansas to approximately 190 mL per day of biobutanol. Each day a representative sample of food waste will be collected and transported to the Engineering Research Center (ERC) about five miles south of the main campus. Phase II will be implemented during the fall semester 2009 by a team of Chemical Engineering Senior Design students. The student team will construct a Phase II pilot-scale facility, gather experimental data, and design a facility to convert all University of Arkansas food waste to biobutanol. The entire cost of the project including the pilot plant unit and operating expenses will be \$74,164. A breakdown of expenses can be found in the attached budget justification sheet.

Process Description

After each meal cafeteria employees will separate food waste from non-food items and collect random samples of the waste in six 5-gallon HDPE pails. Once a day the six pails will be

transported via truck to the ERC. At the ERC, each waste pail will be discharged into the garbage disposal (GD-101 in Figure 2).

The garbage disposal has a water/food-waste slurry circulating at 12 gpm through the garbage disposal to a screen located horizontally across the vacuum filter receiver (Tk-101). The purpose of the screen is to filter the large solids from the circulating slurry. A vacuum is applied beneath the screen to assist the drainage of the slurry through the cake on the screen. The circulation pump (p-101) is a positive displacement type which is required to handle the particulates and the moderate viscosity of the slurry. Three 30-gallon batches will be processed per day. After each batch is processed, the filtered solids will be scraped from the screen and sent to the sewer.

The food waste slurry (stream 4) is then sent to the sterilizer (v-101) to kill any pathogens present and to provide sufficient temperature and residence time to gelatinize the starches and complete the extraction of sugars. The sterilizer is a 14.7 psig rated, 50 gallon, stainless steel pressure vessel. Each 30-gallon batch is heated to 120 °C by injecting 25 pounds of 50 psig steam. The batch is held at 120 °C for 20 minutes. After sterilization, gelatinization, and extraction are complete the sterilized batch is pumped by the sterilizer discharge pump (P-102) at 12 gpm to the sterilizer cooler (E-101) and through the re-circulating loop (stream 7) back to the sterilizer. The sterilizer cooler consists of 75 feet of ½" OD copper tubing coiled into fifty 6" diameter coils. The coil of tubing will be about 50" long and this coil will be fitted into an 8" diameter by 60" long PVC pipe. Cooling water at about 3 gpm will be passed through the shell-side of the coil-in-pipe heat exchanger. After the slurry is cooled to 30 °C, the slurry will be re-circulated through the membrane ultrafilter (F-101) to remove all solids from the fermentor feed. The permeate stream (stream 10) from the fermentor Feed Filter is discharged to the fermentor feed tank (Tk-201). The filtration cycle is stopped when the permeate flow drops to 10% of its original value. At this time the slurry remaining in the sterilizer vessel will be sent to the sewer.

The fermentor feed tank and fermentor (R-201) must be sterilized with a bleach/water mixture prior to operation. The bleach must be re-circulated several times through the system before being drained. After the bleach is drained, the system must be purged with deionized water. The sterilization step is critical for removing all potential bacterial contaminants from the process.

The fermentor will be fed from the fermentor feed tank at a maximum feed rate of 3 gallons per hour by a peristaltic feed pump (P-201). The fermentor will be an agitated 55-gallon HDPE tank. The agitator shaft will be sealed by means of an inexpensive water seal. The maximum residence time for this vessel is 24 hours. The bacteria *Clostridium beijerinckii* will process the food waste and produce acetone, butanol, and ethanol in a 3:6:1 volume ratio, respectively. The fermentor effluent (stream 11) will be sent through the cell filter (F-201) to recover the bacteria cells and recycle them back to the fermentor (stream 12).

The permeate stream (stream 13) leaving the cell filter will be split into two separate streams. Approximately one-ninth (1 L/h) of this stream will be fed to the first pervaporation system (stream 15), and the remainder (stream 14) will be sampled and properly disposed. Both pervaporator units will be constructed from stainless steel and will use PDMS

(polydimethylsiloxane) membranes. The first pervaporator (PV-301) will have a surface area of 0.5 m² and the second will have a 0.3 m² area. The retentate stream (stream 17), which contains excess water and any remaining sugars and starches, will be sent to the sewer. The permeate from the first stage (stream 16) will be approximately 50 % butanol by mass. This vapor stream will be sent to the first pervaporator condenser (E-301), which operates at 50 mmHg absolute. The permeate stream is condensed using a -10 °C brine-water mixture, which is circulated through the annulus side of a double-pipe condenser (stream 18). The condensed permeate will be collected in the eight-quart permeate receiver (V-302). Once per day, the Permeate Receiver will be emptied into the feed tank (V-303) for the second pervaporator (PV-302). Prior to emptying the receiver, the second-pervaporator feed tank will be placed under vacuum via proper adjustment of the valves in the system.

The condensate from the first stage (stream 21) will be fed to the second stage pervaporator. The permeate vapor exiting the second pervaporator consists of a mixture that is 95 % butanol or greater (stream 22). As with the first pervaporator, the retentate is sent to the sewer (stream 23). The second condenser (E-302) and vacuum system is identical to the first stage condenser system. The condensed butanol product will be sampled and collected in an eight-quart vacuum receiver (V-304).

Measurable Results (Outputs/Outcomes), Evaluation Method, and Demonstration Strategy

The primary goal of Phase II is to demonstrate the production of biobutanol from food waste on a pilot scale and evaluate the economic feasibility of this process. One of the questions raised by the experimental results in Phase I was the potential benefit of the conversion of starches to butanol. In Phase II Team REFUSE will determine the relationship between residence time and starch conversion. Although a longer residence time will allow more of the starches to be converted to butanol, at a certain point the bacteria will actually begin to decrease butanol production due to a lack of sugars. Experimentation in Phase II will determine the optimal balance between residence time and starch conversion.

Experimentation is also needed to increase the effectiveness of the pervaporation system. Altering the vacuum pressure and feed temperature of the pervaporator unit will affect the flux through the membrane. Increasing vacuum on the membrane or increasing the temperature of the liquid through the membrane will increase the flux. When using a hydrophobic membrane increasing the component flux will increase the butanol concentration in the permeate stream.

For Phase II there is a need to determine the composition of sugars, starches, and butanol at several different stages in the process. Samples will be taken before the sterilization process and after the fermentor feed filter to monitor any change in sugar concentration. Another sample will be taken after fermentation to measure the composition of the crude product. An additional sample will be taken from the pervaporator retentate to measure any unreacted sugars and starches. Finally a sample will be taken of the purified butanol product. The Food Science department will be contracted to perform starch and sugar assays.

In Phase I of this project several corporate and community partnerships were explored. A strong partnership has been developed with the university food service provider, Chartwells. Chartwells has promised to continue this partnership throughout Phase II by providing the team with food waste samples. This partnership with Chartwells has also allowed us to establish a preliminary partnership with the University of Arkansas. The University currently has a strong interest in promoting sustainability on campus. Phase II will continue to build on these relationships established in Phase I as well as establish new relationships within the University. The University of Arkansas Sustainability Council has an ongoing mission of reducing the environmental impact of the University. The students will be required to develop a university information and involvement plan that will explain this project's contribution to sustainable energy. In addition to this plan, the students will be required to prepare a detailed analysis of the regulatory environment in which the project will be implemented. This analysis will include a determination of all waste products and an analysis of acceptable disposal methods for these wastes. The development of the university involvement plan and environmental analysis will ensure that all parties involved are informed about and approve of the implementation of this project in their community. If the project is a success, Team REFUSE will seek to publish the findings from Phase II.

Integration of P3 Concepts as an Educational Tool

Phase I was an effective educational tool because it required the design team to utilize a wide variety of skills including but not limited to engineering, economical, and biochemical understanding of the process. In addition, the students performed a cradle to grave LCA for the production of butanol from food waste. With the international emphasis on sustainability, LCA is becoming an increasingly common tool. Exposing students to systems scale environmental assessments provides them a valuable perspective as they enter industry. The task given to the students in Phase I was to choose a sustainable and economical feed stock for butanol production and to perform bench-scale tests of the fermentation and separation of the butanol product from the fermentation broth.

Phase II of this project will continue to enrich the educational experience of students involved in the project. For this phase, the design team will scale up the bench scale system evaluated in Phase I into an operational pilot plant. The students will collect data and optimize the process to maximize its efficiency. The student team will perform this work as a requirement for their senior capstone design course. The detailed design, construction, and operation of this plant will give the students invaluable experience in applying their academic knowledge to a real-world situation. The pilot plant built and the research performed in Phase II has great potential to extend beyond the capstone design course requirements. This project would be well-suited for individual students, both undergraduate and graduate, to continue research. Plans are already in place for graduate students to continue research in the production of biobutanol from food waste after the pilot unit is built.

Phase II addresses the interests of a university campus in becoming more sustainable in an innovative and creative manner. The University of Arkansas currently disposes of approximately seven tons of food waste each week. This waste is sent directly to the sewer. The approach of producing biobutanol from food waste is a new way of partnering with a university campus to reduce waste and produce a valuable product.

If Phase II is successful, a full-scale process will be designed that can be implemented on any university campus. The team will propose this design to the University of Arkansas Sustainability Council as a working model of a sustainable method to dispose of food waste, targeting an increased awareness of the availability and creative utilization of renewable resources. Using food waste from the University cafeterias as a feedstock for the biobutanol plant will demonstrate both the creative application of a renewable resource as well as the reduction of waste output. All of these aspects will combine to create a rich educational experience for the Phase II team and to increase the awareness of environmental sustainability to all University of Arkansas students.

2. Project Schedule

Task 1: Review Phase I Work

The Team REFUSE students will review the work completed by the Phase I team and make any changes to the design they deem necessary.

Task 2: Grow Clostridium Culture

Due to the difficulty of growing *C. beijerinckii* bacteria culture, growth of this culture will begin immediately.

Task 3: Purchase Pilot Plant Components

Students will purchase all of the components for the pilot plant using the process flow diagram and the itemized budget proposed by the Phase I team.

Task 4: Construction of Pilot Plant Unit

Students will construct a pilot plant at the Engineering Research Center (ERC) with faculty guidance.

Task 5: Start-up

Students will test all processes in the plant for proper functionality.

Task 6: Plan for waste food collection

Students will work with their individual schedules and Chartwells schedules to set up a plan for waste collection.

Task 7: Test Full Scale

Students will work for four weeks to test the pilot plant on a continuous daily basis. One week with regular media, and then three weeks with food waste.

Task 8: Economic Analysis

The team will continue to evaluate the economical viability utilizing the information from the pilot plant.

Task 9: Report Results

The experimental results of Phase II will be documented. These findings as well as a university scale model of a biobutanol production facility will be presented to the University of Arkansas Sustainability Council. If applicable, the students will work towards publication of their results.

ID	Task Name	Sep 2009					Oct 2009					Nov 2009				Dec 2009		
		8/23	8/30	9/6	9/13	9/20	9/27	10/4	10/11	10/18	10/25	11/1	11/8	11/15	11/22	11/29	12/6	
1	Review	[Blue bar]																
2	Culture Growing	[Blue bar]																
3	Purchase	[Blue bar]																
4	Construction	[Blue bar]																
5	Startup	[Blue bar]																
6	Collection	[Blue bar]																
7	Test	[Blue bar]																
8	Economics	[Blue bar]																
9	Report	[Blue bar]																

Figure 4. One year Project Schedule

3. Partnerships

The most significant partnership developed in Phase I was with Chartwells. Team REFUSE approached Chartwells with a request to collect food waste from one of the campus cafeterias for use in the Phase I bench-scale research. They were eager to work with the team and supply samples of food waste as well as statistical data. They have also written a letter of support regarding Phase II. In Phase II, Chartwells would provide approximately 150 pounds of food per day from one of the cafeterias to be used in the pilot plant. This partnership is the first step in working with the University of Arkansas to promote waste reduction and sustainability on campus. If successful, Team REFUSE will design a model for an operation that could be implemented on any University campus.

Team REFUSE will also be working closely with the Ralph E. Martin Department of Chemical Engineering here at the University of Arkansas to continue researching biobutanol from food waste. The department has written a letter of support for Phase II pledging to allow Team REFUSE access to laboratory space in the Engineering Research Center. This space will be used to house the Phase II pilot-scale model. The department has also given their full support to using Phase II as credit for the honors section of the senior capstone design course (CHEG 4443). The department is fully committed to utilizing this project as an educational tool for its chemical engineering students.

III. SUPPORTING LETTERS



3202 Bell Engineering Center • Fayetteville, Arkansas 72701-1201 • (479) 575-4951 • (479) 575-7926 (FAX)

College of Engineering
Ralph E. Martin Department of Chemical Engineering

10 March 2009

Selection Committee
EPA P3 Competition

RE: Letter of support for P3 Competition team REFUSE

I am pleased to write this letter of support for our P3 Competition team working on project REFUSE which explores the conversion of food waste into biobutanol. This team, led by Dr. Jamie Hestekin as faculty mentor and design instructor, has conducted their P3 project as part of the Honors section of their capstone design experience (CHEG 4443). The project has been an excellent educational experience for the students, particularly the challenge of designing and conducting lab experiments in support of their project.

As a department, we have consistently worked to incorporate real world applications in our students' course work. In the past, we have participated in the WERC Environmental Design competition held at New Mexico State University in Las Cruces, NM. The WERC competition was also a great opportunity for our students, and our teams have been very successful in past competitions. In a similar fashion to this year's P3 competition, the WERC competition was used as the design project in CHEG 4443. Our institutional commitment to having students involved in such competitions has been ongoing for several years, and I believe the commitment of the faculty has been critical to keeping students energized throughout the process.

Project REFUSE will have continued support from the department if it proceeds to Phase II. The pilot scale model the students have proposed will require lab space, and we are committed to making that space available in our Engineering Research Center (ERC). We have plans to continue using this P3 project as a teaching tool, particularly in the senior level design classes in fall 2009 where students will facilitate the construction of this facility and work to collect data for economic analysis. We are excited to be involved in this competition and look forward to continued involvement of students in developing technologies to meet the needs of tomorrow.

Best regards,



Thomas O. Spicer, PhD, PE
Professor and Head
Ralph E. Martin Leadership Chair in Chemical Engineering

Morgan Stout
435 N. Garland
ARKU 209
Fayetteville, AR 72701
March 10, 2009

To Whom It May Concern,

I was very pleased to hear about the P-3 proposal from the team at the University of Arkansas on converting the waste food from our dining halls to butanol through Project REFUSE. Chartwells is the dining service company for the University of Arkansas and provides dining services for the more than 16,000 students, through three dining halls and many other food service providers on campus.

Chartwells is an organization that is devoted to sustainability and has made many efforts to improve dining facilities with that thought in mind. Our parent company, Compass group, emphasizes sustainability through their Compass 360° program. Compass group strives to lead the foodservice industry in saving our resources for our world and our customers. Compass Groups 360° program is based on the four tenants of Nutrition and Wellness, Sustainability, Compass in the Community, and Corporate Governance and Ethics. We believe that if we all work together we can make a difference for *everyone, everyday, and everywhere*. As a company we will continue to find ways to improve our carbon footprint and continue those efforts in all of our facilities.

The University of Arkansas also demands high levels of sustainability in all aspects on campus. The core mission of the University is to be a nationally competitive, student-centered research university serving Arkansas and the world. The University is committed to reducing environmental impacts and neutralizing its carbon footprint. The University is working to educate students, faculty, and staff and the citizens of Arkansas about proper environmental stewardship. The University of Arkansas Sustainability Council has been formed based on seven pillars: Academic and Research; Energy; Water Resources; Food, Agriculture, and Forestry; Land Use and Development; Pollution Prevention and Waste Minimization; and Social and Community.

Preliminary Estimates indicate that the three dining halls on campus provide over 7 tons of production and post-consumer waste food. University Dining Services has taken measures to reduce this number through removal of trays from dining halls, but a solution to handle this waste is still very desirable. Chartwells is committed to providing 300 lbs of waste daily for every working day during the fall 2009 semester as Project REFUSE requires it for their research. We sincerely hope that their research will yield solutions that help everyone as we work together for a more sustainable world.

We will provide our **full support** to this project and continue to pursue sustainability efforts in all of our operations.

Sincerely,



Morgan Stout
Director of Operations
Chartwells/University of Arkansas



UNIVERSITY of ARKANSAS

1871

SUSTAINABILITY COUNCIL

To: US EPA P3 selection team

From: Nicholas R. Brown ^{PhD}
Executive Assistant for Sustainability

Re: support for University of Arkansas Team REFUSE

Date: 12 March 2009

I am pleased to give my recommendation to the project presented by the University of Arkansas Team REFUSE to the 2009 EPA P3 Competition.

Team REFUSE has worked hard during their collegiate careers to succeed in a challenging and demanding academic program, and their diligence has extended to their efforts for this competition. They have a strong desire to incorporate sustainability into the world of professional engineering. They've collaborated with the UA Sustainability Council and other organizations across campus to bring us all a step closer to a renewable and sustainable fuel source.

The University of Arkansas looks forward to the findings of this team, and hopes to incorporate their successful results into our continuing research programs.

IV. BUDGET AND BUDGET JUSTIFICATION

Personnel

No costs supported under this solicitation.

Fringe Benefits

No costs supported under this solicitation.

Travel

The students taking part in the construction and operation of this pilot facility will be traveling to Oklahoma City to attend and present their findings at the 2-day GROW Oklahoma Biofuels Conference. This will cost about \$3,590 which was calculated for a 7 member team and one advisor spending 2 nights in 5 hotel rooms at \$150/night. Added to this was \$1,176 in meals for the team for 3 days as well as \$114 for a rental van and \$800 in registration fees.

Equipment

\$16,150 is allocated to major pieces of equipment. Included in this amount is \$2,755 for a 560 gallon, conical-bottom tank for holding the feed to the fermentor. \$2,500 is allotted for construction of a one-half square meter pervaporator unit to be built in the Chemical Engineering shop. A refrigeration unit will be purchased for \$3,900 for cooling the fluid used in condensing the vapor from the pervaporators. A data acquisition system costing \$3,995 will be used to gather temperature, pressure, and pH data from the system and send them to a central computer for recording. An optical density measurement system will also be purchased for \$3,000 to monitor cell growth in fermentor. Also included is 10% of the major equipment cost for any pricing contingencies making the total \$17,765.

Supplies

The majority of the money in the proposal, \$31,267, is allocated for supplies. Major contributions to the total for supplies include a 2-hp industrial garbage disposal, two stainless steel vessels, twelve membrane ultrafilters, a pH pump control system, and a computer for data analysis. Other minor supplies include pumps and piping. Again 10% was added for any pricing contingencies, making the total for supplies \$34,397.

Contractual

No contractual costs are needed as part of this solicitation.

Indirect Costs

The indirect costs will be 42% of the total direct costs. This is per our University policy.