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The Production of Biobutanol from Biomass Via a Hybrid Biological/Chemical Process

The Production of Biobutanol from Biomass Via a Hybrid Biological/Chemical Process

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Chemical Engineering

by

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Abstract

Biobutanol use as a fuel began in the late 19th century. Problems remain in economic viability. A review of the state of the art and need for technical advances is presented.

The technical potential of producing biofuel from a naturally occurring macroalgae was studied. The algae grow in Jamaica Bay, New York City, in contaminated water. The process consisted of mechanical harvesting, drying, grinding, and acid hydrolysis to form an algal sugar solution. Clostridium beijerinckii and C. saccharoperbutylacetonicum were used in an acetone butanol ethanol (ABE) fermentation to make butanol. Fermentation was followed by distillation Butanol concentrations during fermentation reached 4 g/L. The recovery of reducing sugars in the media was 0.29 g butanol/g sugar. Feedstock with greater than 7 g/L butyric acid caused death of the butanol-producing bacteria.

The kinetics of the production of 1-octadecanol from octadecanoic acid was investigated in a liquid-phase trickle-bed reactor by hydrogenation. The primary reactions occurring in the reactor were the desired conversion of octadecanoic acid to 1-octadecanol and the subsequent undesired conversion of 1-octadecanol to octadecane. A series-parallel kinetics model first order in acid and zero order in hydrogen was developed to predict these two reactions. The activation energies of the reactions were 63.7.8 and 45.6 kJ/mole, respectively. The conversion of octadecanoic acid and the selectivity to the desired product as functions of temperature, space velocity, and inlet octadecanoic acid concentration were then estimated. The model predicts maximum productivity of 1-octadecanol at higher temperatures and short residence times. Parametric plots show productivity to be $\geq$0.48 g 1-octadecanol/g octadecanoic acid at 566 ^{o}F and a 0.1 h residence time.

The model from the 1-octadecanoic acid study was fitted to several sets of data for the hydrogenation of butyric acid to butanol in the temperature regime of 300-400 ^{o}F and pressures of 700-1000 psig. The model failed to accurately predict the final concentrations of 1-butanol and butane. Reasons for this are suggested and future work to fix this problem is presented and discussed.

Acknowledgments

I would like to thank the Ralph E. Martin Department of Chemical Engineering for the opportunity to participate in this degree program. Special thanks go to Dr. Tom Spicer, Dr. Buddy Babcock, and Dr. Ed Clausen for their support, encouragement, and occasional prodding.

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Special thanks also go to my graduate research committee, who all played important roles in the progress of my research efforts. Dr. Mike Ackerson, Dr. Bob Beitle, Dr. Jamie Hestekin, Dr. Christa Hestekin, and Dr. Mark Arnold formed an awesome team and kept me on track throughout my studies.

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All of my fellow graduate students have been great to work with, but certain of them have become close friends as well as fellow students. Dr. Jianjun Du and Dr. Keerthi Srinivas helped me get into the routine of being a student. Dr. Alice Jernigan worked with me on research, edited many of my papers, manuscripts, collaborated on classwork, fed me, offered a shoulder to cry on from time to time, and helped to keep me sane. She will be a friend for life. Dr. Lauren Merriman also edited my writing, collaborated with me on research, and became a life-long friend. Alex Lopez began his graduate school career as my mentee, but quickly became a collaborator, confidant, advisor, and friend. Dr. Ellen Brune and her husband Stuart have been enthusiastic cheerleaders and great support. Dr. McKinsie Fruchtl has been a collaborator, friend, and cheerleader.

The University of Arkansas is a highly student-focused institution, and there have been several people in administrative roles that have gone out of their way to help me complete my scholastic journey. Dr. Collis Geren and Dr. Todd Shields provided me with encouragement and extra financial support. Dr. Patricia Koski and Dr. Susanne McCray offered encouragment, advice, and guidance.

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Table of Contents

List of Published Papers

Chapter 2 – Published as a chapter in the book Applied Microbial Engineering

Hestekin JA, Lopez AM, Clausen EC, Potts TM, Biobutanol: an important biofuel and bio-product. Appl Microb Eng 2013:450-87. doi:10.1201/b15250-18

Chapter 3 – Article Published in Environmental Progress and Sustainable Energy

Potts T, Du J, Paul M, May P, Beitle R, Hestekin J. The production of butanol from Jamaica bay macro algae. Environ Prog Sustainable Energy 2012;31(1):29-36

Chapter 4 – Article Published in the Journal of the American Oil Chemist's Society

Potts TM, Durant K, Hestekin J, Beitle R, Ackerson M (2014) Catalytic Production of 1-Octadecanol from Octadecanoic Acid by Hydrotreating in a Plug Flow Reactor. J Am Oil Chem Soc 91: 1643-1650. DOI 10.1007/s11746-014-2501-7

Chapter 1

Introduction

This dissertation has as its focus the production of fuel-grade 1-butanol from biomass waste products. The work began as a study of the fermentation of algal sugars obtained from the algae *Ulva lactuca* and expanded to the development of a broader methodology to produce 1-butanol from a variety of sugar solutions via a novel hybrid biological-chemical process. The first step of the hybrid process is the production of butyric acid from sugar solutions, and was not a part of this dissertation. The second step of this process is the liquid phase catalytic hydrogenation of butyric acid to 1-butanol and is reported in Chapters 4 and 5 of this dissertation. The kinetic model developed for the hydrogenation of butyric acid, reported in Chapter 4, provides a tool for the design of a process that will produce low cost 1-butanol for use as a biofuel and solvent, as reported in Chapter 5. The dissertation is presented in the format of published papers, with each manuscript comprising one chapter. The four manuscripts are Chapters 2-5 of this dissertation.

The paper presented in Chapter 2 was generated as a review of the status and importance of biobutanol as a biofuel and solvent. In this paper, the history of biologically generated butanol (biobutanol) is described. The industrial uses of biobutanol, both as a fuel and as a solvent, are discussed. The current market size for biobutanol is estimated, as is its' potential for use as a fuel or fuel additive. Biobutanol is compared to petroleum based gasoline and bioethanol, and the advantages and disadvantages of each are enumerated. Three biobutanol production schemes, isobutanol production, 1-butanol production via a one step process, and 1-butanol production via a two-step process, are discussed and compared. The two-step process consists of fermenting sugars to butyric acid in one biological reactor with a bacterial strain, such as *C. tyrobutyricum*,

to generate butyric acid and a second biological reactor with a different bacterial strain, such as *C. beijerincki*, to ferment the butyric acid to 1-butanol. The recovery of biobutanol from fermentation broth is discussed. Economic discussions of the cost of production of biobutanol for the three production schemes are presented.

Chapter 3 was generated as a summary of research done at the University of Arkansas on the conversion of algal sugars from Ulva lactuca to biobutanol as a biofuel and solvent. This paper describes work that was partially funded by the City of New York, the Mack-Blackwell Rural Transportation Center, and Statoil. The paper begins with an estimate of the amount of algal sugars available from Jamaica Bay on a yearly basis. A method of drying the algae prior to grinding developed in our laboratories is described. The release of algal sugars by acid hydrolysis with sulfuric acid on a laboratory and pilot scale was studied at several acid concentrations, solids loadings, and hydrolysis times. The algal sugar solutions were fermented to 1-butanol with three different bacterial strains in incubation bottles and a stirred reactor with continuous feed and product recovery. A scale-up of the fermentation method was performed with one bacterial strain, *Clostridium saccharoperbutylacetonicum*. Details of this scale-up exercise are presented and discussed. The feasibility of the two stage, two bacteria fermentation presented in Chapter 2 was tested and it was determined that with the bacterial strains investigated, the two step process was not viable due to the poisoning of the bacteria by the butyric acid.

The paper presented as Chapter 4 was generated as a summary of research done at the University of Arkansas on the catalytic hydrogenation of 1-octadecanoic acid to 1-octadecanol. This chemical was chosen as a safe and convenient surrogate to develop a model of the kinetics of the two step, series-parallel reaction to provide a tool for the analysis of the kinetics of the

hydrogenation of organic acids to the analogous alcohol. A Hougan-Watson model for the kinetics of the two step, series-parallel reaction set was developed. This model consists of 4 coupled differential rate equations with two rate constants, one for each reaction. The model assumes that the only reactions taking place in the reactor are the hydrogenation of the acid to the desired alcohol and the subsequent undesired hydrogenation of the alcohol to the corresponding alkane. Experimental samples of the products of the hydrogenation reactions were generated in a pilot scale liquid phase hydrogenation reactor. These samples were analyzed with gas chromatography. The rate constants of the model were determined by least squares fit comparing the experimental values of the concentrations of the reactants and products to those predicted from the model. The functional relationship between temperature and the rate constants, assumed to be Arrhenius functionality, was determined by empirical plot of ln(k) versus 1/T for both rate constants and from this plot, the Arrhenius constants were determined. The Arrhenius constants were then coupled with the rate equations to compare the experimental product concentrations to those estimated by the model.

Chapter 5 consists of a paper describing the application of the model developed in Chapter 4 to the conversion of butyric acid to 1-butanol for use as a biofuel and solvent. The model developed in Chapter 4 was used to determine the Arrhenius rate constants for the liquid phase catalytic hydrogenation of butyric acid to butanol, using a set of samples obtained from a small-scale hydrogenation reactor operated at varying pressures, temperatures, and space velocities. Comparisons between the experimental and modeled values of the product concentrations were made. These comparisons indicate that the model predicts the final concentrations of 1-butanol and butane poorly. Reasons for this are suggested, and further work designed to improve the predictions are presented and discussed. A mechanism for estimating the

maximum production of 1-butanol per mole of butyric acid in the feed was developed. This optimization mechanism was used to estimate productivities at several reactor operating conditions.

Chapter 6 of this dissertation summarizes the work described in Chapters 2-5, and presents several possible extensions of this work.

Chapter Two

Biobutanol: An Important Biofuel and Bio-Product

Potts TM, Hestekin JA, Lopez AM, Clausen EC
Appl Microb Eng 2013:450-87. doi:10.1201/b15250-18

Abstract

Biobutanol as a fuel has been around since the late 19th century. Since its inception many technologies have improved its technical and economic viability including genetic modification of organisms, separation advancement, and new feedstocks for production. However, 100 years later, problems still remain in economic viability caused by need for new organisms and advanced separations. This chapter will discuss the important advances as well as looking at what still needs to be done in order to realize biobutanol as a large scale fuel replacement strategy.

History of Biobutanol

Butanol production via bacterial fermentation has taken place for over 100 years. In 1862, Pasteur first recorded the production of butanol by a microorganism he called *Vibrion butyrique*. In 1905, Schardinger isolated a bacterium that produced acetone, butanol, and ethanol. Within 5 years, a British company, Strange and Graham Ltd, began research on the biological production of solvents for the manufacture of synthetic rubber. One of the Strange and Graham employees, Chaim Weizmann, left the company and while at Manchester University isolated a new bacterium, *Clostridium acetobutylicum*, which produced quantities of acetone, butanol, and ethanol in the ratio of 3:6:1 from potato starch. He was awarded a patent on this process in 1915 (Weizmann 1915).

During the course of World War I, British supplies of acetone were depredated by Axis naval and aerial forces. The Weizmann process was selected for production of acetone, and several plants were constructed in Britain, Canada, and the US for the conversion of corn mash and liquor to acetone. The conclusion of World War I left very large inventories of the byproduct butanol. These stockpiles were used by DuPont as feedstock for the production of butyl acetate, a solvent for nitrocellulose acetate lacquer. Existing acetone plants were converted to butanol production to support this solvent production.

Fermentation production of butanol proliferated and feedstock shifted from corn liquor to molasses, which supported greater solvent productivity in the 1930's. Many new microorganisms were found (and patented) during this time. At the height of World War II, acetone was once again in short supply, and many new production facilities were implemented worldwide for acetone production via fermentation of molasses, corn mash, and other feedstocks (Kopke and Duerre 2011). After the war, advances in petrochemical technology and cheap oil yielded processes that greatly lowered the cost of manufacturing of acetone and butanol, and fermentation of these solvents could no longer compete economically. Few fermentation facilities survived and by 1970, the ABE industry in the US was nearly ended (Ni and Sun 2009). Foreign facilities lasted another 20 years, and the last large scale ABE plant in China was closed in 2004. With the increased worldwide demands for crude oil and the increase in price, interest in ABE fermentation has renewed in recent years (Koepke and Duerre 2011). China has resumed ABE production in 11 plants, one of which is a 30,000 ton/year facility in Jilin China, operated by Cathay Industrial Biotech (Ni and Sun 2009). In the US, Gevo is operating a 10 million gallon/year of iso-butanol facility at Luverne, MN. The Gevo butanol is being sold to Sasol for solvent applications.

Butanol Uses and Markets

Currently, butanol is produced from petroleum derivatives to be used as a solvent and chemical intermediate for many important products (Ezeji et al. 2007). As a solvent, butanol is used in the production of paints, dyes, and chemical stabilizers. In the chemical industry, butanol is used in the production of various plastics and polymers such as safety glass, hydraulic fluid, and detergents (Mariano et al. 2012). The worldwide chemical market for butanol is approximately 950 million gallons produced mainly by Dow Chemical Company, DuPont, BASF, and Oxea Group (Yuan and Hui-feng 2012). In Brazil butanol is produced internally by the company Elekeiroz and in China 50% of the butanol consumed is imported with the remainder produced by ABE plants operated by small solvent companies (Mariano et al. 2012). The worldwide demand for butanol is expected to increase by 3.2% per year with concentrated demand in North America, Europe, and Asia (Green 2011). Costs for producing butanol from fossil fuels are at $3.30/gal with wholesale at $3.80/gal (Ramey and Yang 2004).

Many companies are looking at producing butanol as a biofuel. This would allow greater production of renewable bioenergy in the automotive market and present an opportunity for butanol to enter the energy sector with specialty fuels such as jet fuel. However, the main issue keeping biobutanol from becoming a large scale commercial success as a fuel is that it must compete with existing biofuels such as ethanol. Current estimates for the cost of producing fuel grade biobutanol lie between $3.50-$4.00/gallon while bioethanol is currently produced at $2.50 (Ramey and Yang 2004). On an energy basis (using LHV) the cost comparison results in butanol outputting 25.6-29.2 MJ/$ while ethanol provides 32.3 MJ/$ (Weast 1978). The main reasons for the higher price of butanol are the low yields from fermentation due to the high toxicity of butanol and costly separations involved in removing water and other non-desirables in fuel grade

butanol (Tashiro et al. 2005). When the cost of producing butanol approaches $2.50/gallon, the butanol market can expand into the fuel additive market and compete for the greater than 22 billion gallon market currently monopolized by ethanol. Figure 1 shows the current market of butanol, mainly as a solvent and additive, and also demonstrates the potential if butanol becomes an additive or ideally a drop-in fuel. As shown in the figure, the current market is a small sliver of the potential market if the price was reduced.

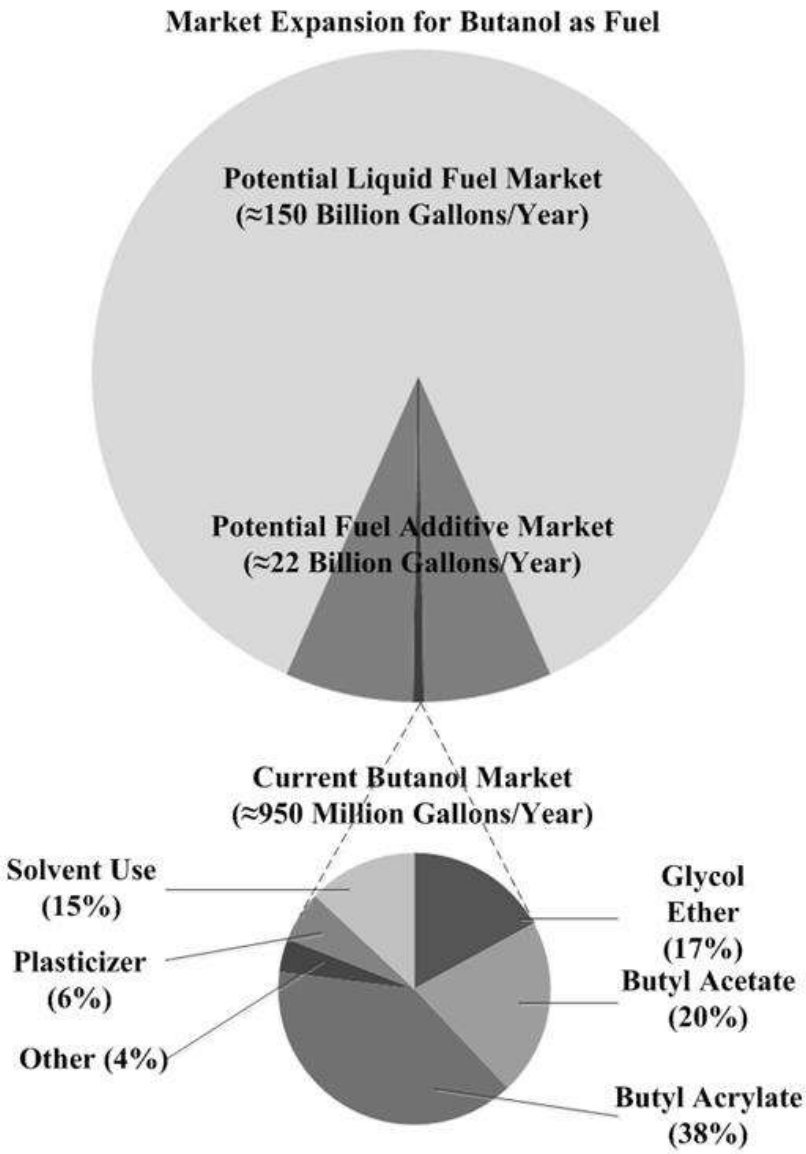

Figure 1. Current Butanol market and expansion potential to fuel additive and direct fuel competitor.

In order for butanol to have the greatest impact in the liquid fuel industry both it must become a drop-in fuel. This would require that butanol could be produced cost competitively with liquid petroleum on a MJ/$ basis. Today gasoline is produced with an energy output of 35.9MJ/$. However cheap gasoline at $2/gallon has an energy output of 59.9 MJ/$ setting the target even higher for a potential drop in fuel. When butanol approaches this value, the market

for butanol production can expand out of the fuel additive market and begin to alleviate the 135 billion gallons of gasoline currently being consumed in the Unites States annually. Implementation of renewable butanol as a pure energy fuel would require little or no automotive redesign (Szulczyk 2010). Further, most of the transportation and delivery methods for the fuel industry would remain the same, limiting the time required for complete conversion of U.S. infrastructure for butanol fuel.

In order to facilitate the penetration of butanol into vehicular use, many researchers are looking at developing new production techniques using wild and genetically engineered bacteria in order to boost butanol yield and bacterial tolerance to butanol (Rosgaard et al. 2012). Companies such as Silicon Valley based Cobalt and Brazil's Green Biologics are currently designing and running pilot-scale butanol facilities to develop the technologies needed for large scale butanol production (Herndon 2012, Nielsen 2012). In China companies such as Ji-An Biochemical, Guiping Jinyuan, and Jilin Cathy have ramped up production of butanol from ABE

methods to meet the high demand for butanol in the solvent market (Ni and Sun 2009). BP and DuPont are also developing a butanol production facility through a company named Butamax™ Advance Biofuels with expected production in 2014 (Martin 2012). Gevo has a similar biobutanol making process and plans to retrofit existing ethanol plants for butanol production as early as 2014 (Lane 2012).

Advantages of Butanol as a Fuel or a Fuel Additive

The US is now consuming approximately 360 million gallons of gasoline per year (DOE/EIA-0383 2012). This number is expected to decrease slightly, as higher prices at the fuel pump lead to less driving and thus smaller demand. However, the demand for vehicular fuels in developing countries is expected to increase and off-set lower consumptions in the US. The higher fuel prices translate to high prices for goods and services dependent on transportation. Thus, the European Union issued the biofuels directive, officially 2003/30/EC, which set the goal of replacing 5.75% of all transport fossil fuels (gasoline and diesel) with biofuels by 2010. Some years later, the US congress passed the Energy Independence and Security Act of 2007, which among other regulations and goals, expands the national renewable fuels standard to 9 billion gallons in 2008, with a phased increase to 36 billion gallons by 2022.

A by-product of using fossil fuels is carbon dioxide, a greenhouse gas. Rise of average global temperatures has been linked to increasing carbon dioxide concentration in the atmosphere. Approximately one fourth of human generated carbon dioxide emissions are from use of fossil derived vehicular fuels for cars and light trucks (Jaffe et al. 2011). Thus, replacement of fossil derived fuel with a (nearly) carbon dioxide-neutral fuel such as butanol could have major implications to the environment and world economy.

The proven oil reserves available to the world as of 2011 were estimated at 1350 billion barrels, with just over 200 billion barrels in North America (Jaffe et al. 2011). In addition to these proven reserves, there are estimates that there are an additional unconventional, mostly in oil shale and shale oil, 1300 billion available in North America and 2129 billion barrels available worldwide. At the current rate of consumption, and using Jaffe's numbers, the US and Canada could supply their own demands for about 24 years with proven reserves and about 178 years with the proven and unconventional, technically recoverable reserves. For the world as a whole, proven supplies would meet current demand for about 43 years while the proven plus unconventional would meet current demand for about 112 years. Of course, these numbers are based on several admittedly flawed assumptions: the demand will not change; there will be no shift in energy consumption from fossil fuels to other forms of energy from nuclear, coal, natural gas, wind power, solar power, or alternative fuels from biomass. It is highly probable that demand for oil in highly industrialized countries with stable populations will continue to decrease slightly, but that demand in developing countries will increase at rates commensurate with availability and price. It is also probable that as oil production shifts from easy to attain proven resources to more difficult to process unconventional reserves that oil prices will rise sharply and demand will be reduced. Higher oil prices will make the transition to the use of electric energy for many applications currently met with oil more attractive, but will drive cost of living higher and lower living standards for the bulk of the world's population. It is also highly probable that because of the very large consumption numbers, no single alternative energy source can supplant the use of oil, and each potential source will play an important role in niche markets. However, with proven oil reserves being >40 years with unconventional sources, it is

likely that in order to have biobutanol as a large scale fuel replacement that the economics and the environmental implications must be verified and improved.

Current biofuels production efforts focus primarily on bioethanol and biodiesel, with other potential fuels, such as biobutanol, poised on the wings to become major players if certain technological advances can be realized. Table 1 lists certain fuel properties of ethanol and butanol. As can be seen from the table, 1-butanol exhibits some characteristics that make it a good candidate for vehicular fuel or fuel additive when compared to ethanol. Butanol has a higher energy density with an LHV (Lower Heating Value) of 99,800 btu/gal as contrasted to ethanol at 76,000 btu/gal. Ramey found in his test of a 1992 Buick driven across the country on B100 (100% butanol) that the gas mileage was 8% better (based on volume of butanol used) than on gasoline (Szulczyk, 2010). Edmunds tested several 2007, flex-fuel Chevrolet Tahoes operated on both E85 (85% ethanol, 15% gasoline) and gasoline and found that the gas mileage was 26% less when operated on E85 (Edmunds 2007). Additionally, the Ramey Buick's engine had no modifications whereas the Edmunds Tahoe required an engine specifically designed to run on either gasoline or E85. This is another advantage for butanol as contrasted to ethanol: butanol will run in most vehicles without engine modifications, whereas ethanol at concentrations higher than 10% requires extensive modifications. This is because butanol is much less corrosive than is ethanol. Ethanol has high miscibility with water and will absorb moisture from the air. If the water content of the ethanol/gasoline mixture becomes too high, the fuel will phase separate with a water/ethanol layer in the bottom of the tank. This layer will render the vehicle inoperable. To return the vehicle to service, the tank must be drained, cleaned, and thoroughly dried. Butanol has much less miscibility and is not hygroscopic and thus does not present this problem. As can also be seen in Table 1, the Reed vapor pressure of butanol is much

lower than that for ethanol or gasoline. This gives some advantages to butanol but also some disadvantages. The lower vapor pressure means that butanol vapor emissions from fuel tanks, storage facilities, etc. are much less than corresponding emissions from ethanol or gasoline. Additionally, the lower vapor pressure and higher flash point of butanol means it is somewhat less of a fire hazard when spilled than is ethanol, although when blended with gasoline, this is a moot point. One disadvantage of the lower vapor pressure of butanol is that the low temperature starting capabilities of the vehicle is less than with higher vapor pressure fuels. Again, when in a gasoline blend, this is a moot point due to the very high vapor pressure of gasoline. A second disadvantage of butanol as contrasted with ethanol is that the butanol octane number is lower, about the same as winter gasoline. Ethanol, with a much higher octane number, can serve as an anti-ping additive or octane booster in gasoline. On the other hand, butanol, with its lower octane number, can be blended with diesel as well as gasoline. Butanol/diesel blends have been found to increase diesel mileage, reduce emissions of hydrocarbons and non-hydrocarbon pollutants, and enhance cold starting properties of diesel engines. (Altun et al. 2011, Dogan 2011, C. Chen et al. 2011, Yao et al. 2010) Still to be determined is whether butanol added to diesel fuel will adversely affect engine lifetime. Both ethanol and butanol are oxygenates, with butanol at 21.6% and ethanol at 34.7%. EPA requirements for oxygenates in fuels favor the use of ethanol for its higher oxygen content. Butanol is somewhat more toxic to many forms of life (including humans) than is ethanol, which may favor the continuing use of ethanol instead of switching to butanol (Szulczyk 2010). However, butanol is much less toxic than many compounds commonly found in gasoline and from a purely technical viewpoint; the advantage to ethanol is minimal.

However, the primary reason that butanol has not become a major biofuel is that it costs much more to produce than does ethanol. To supplant ethanol as a biofuel, the manufacturing

cost will need to be reduced by half. This topic is discussed in greater detail elsewhere in this paper.

Table 1. Properties of Various Fuels.

Property	**Butanol**	**Ethanol**	**Gasoline**	**No. 2 Diesel**	**Jet Fuel**	**Hydrogen, liquid**
Chemical Formula	C4H9OH	C2H5OH	C4-C12	C3-C25	C5-C12	H2
Molecular Weight	74.1	46.1	100–105	≈200	~140	2.0
Wt % Carbon	64.8	52.2	85–88	84–87	~84	0.0
Wt % Hydrogen	27.0	13.1	12–15	33–16	~16	100.0
Wt %Oxygen	21.6	34.7	0.0	0.0	0.0	0.0
Specific gravity, 60° F	0.8	0.8	0.72–0.78	0.81–0.89	0.8	0.1
Density, lb/gal @ 60° F	6.8	6.6	6.0–6.5	6.7–7.4	6.8	0.6
Boiling temperature, °F	244.0	172.0	80–437	370–650	349.0	-423.0
Reid vapor pressure, psi	0.3	2.3	8–15	0.2	0.4	na
Heat of vaporization, btu/lb	256	396	150	100	150	198
Research octane no.	96	108	90–100	na	na	na
LHV Energy Density, btu/gal	99,800	76,000	115,000	130,500	135,000	30,000
Freezing point, °F	-130.0	-173.2	-40	-40–30	-54	na
Viscosity @ 60° F, Cp	3.0	1.19	0.37–0.44	2.6–4.1	2	na
Flash point, closed cup, °F	84	55	-45	165	100	na
Autoignition temperature, °F	650	793	495	≈600	410	1058
LFL, wt%	1.4	4.3	1.4	1.0	0.6	4.0
HFL, wt%	11.2	19.0	7.6	6.0	5.0	75.0
Specific heat, Btu/lb °F	0.55	0.57	0.48	0.43	0.51	0.002

Production of Butanol Biofuels

There are three different schemes for the production of butanol that will be talked about in this paper. Isobutanol, 1-butanol production via a one step process, and 1-butanol production via a two-step process. All three of these schemes will be discussed in the paper below and the advantages\disadvantges of using isobutanol over 1-butanol will also be discussed.

Isobutanol Production

An additional form of butanol currently being researched for biofuel production is isobutanol. Isobutanol differs from 1-butanol in a variety of ways. Some key differences are presented in Table 2 and the molecular structures of the two molecules are given in figure 2. The main benefit

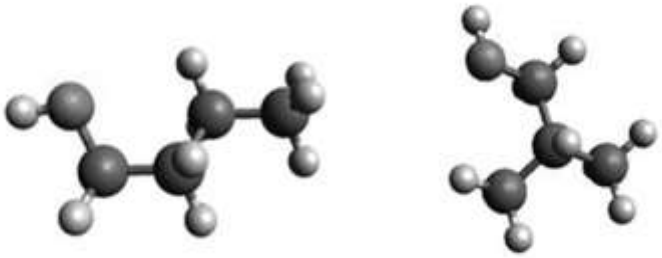

Figure 2. Molecular representations of (left) 1-butanol and (right) isobutanol. Generated from Avogadro modeling software.

of isobutanol over 1-butanol is that the octane number is much higher, resulting in greater fuel efficiency. Isobutanol has also been shown to reduce stress corrosion cracking in engines and has lower hygroscopicity than bioethanol (Gevo 2012). Currently isobutanol is synthesized using syngas. However, this method is expensive due to high temperature and catalysts requirements, so economical and renewable methods for isobutanol are attractive (Li et al. 2011a). Renewable isobutanol can be produced from a variety of bacterial fermentation methods. Many are specifically designed bacteria genetically modified to resist isobutanol poisoning and maximize productivity (Atsumi et al. 2010). A few processes focus on the development of isobutanol from non-fermentative pathways, eliminating the need for a source feedstock. The main approaches of each production pathway will be discussed below.

Table 2. Property comparison between N-Butanol and Isobutanol (Glassner 2009)

	Isobutanol	N-Butanol

Octane Number	98-102	87
Oxygen Content (%)	21.6	22
Reid Vapor Pressure (psi)	4-5	0.33
Energy Content (MJ/kg)	32.6	33.4
Viscosity (cP)	3.95	3.00
Cost ($/gal)	3.75-4.25	3.50-4.00
Density	802	810

Isobutanol is produced in bacteria following a specific enzymatic process within the bacterial glucose consumption pathway. Glucose or a similar sugar is consumed via the glycolysis pathway to produce pyruvate. Then pyruvate is catalyzed by a series of enzymes and reaction intermediates to form isobutanol. Figure 3 outlines this reaction pathway. Understanding

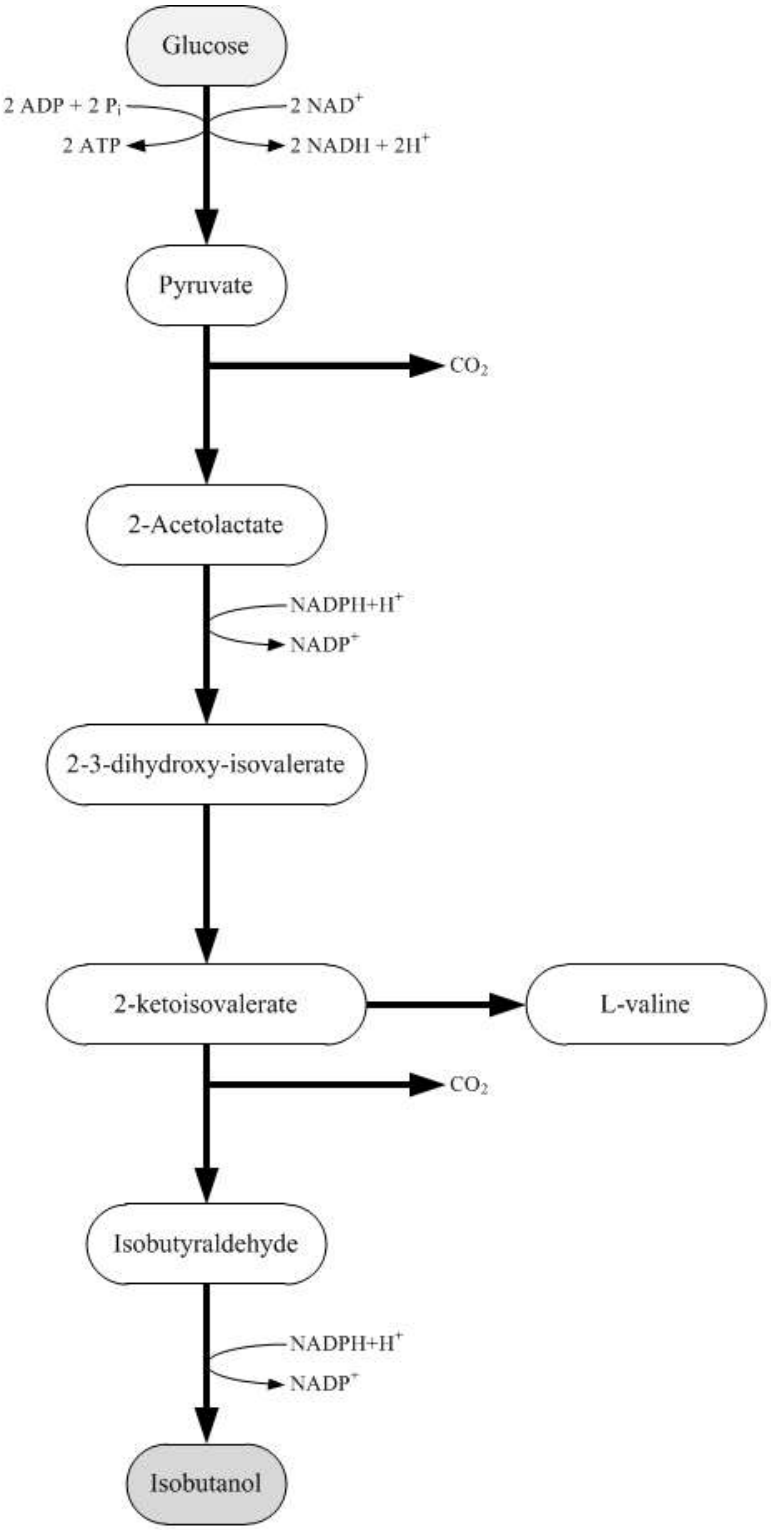

Figure 3. Isobutanol Enzymatic Pathway (Atsumi et al. 2010, Lu et al. 2012)

this pathway has allowed researchers to improve the activity of enzymes that lead to isobutanol formation while inhibit additional enzymes in bacteria that result in unwanted products.

The isobutanol fermentation began in the mid 2000's following interest in bioethanol and other biofuels. Since then a large number of bacteria have been identified naturally and designed for isobutanol production. Currently the main producers of isobutanol are *E. Coli*, *Bacillus subtilis*, and *Corynebacterium glutamicum* (Blombach and Eikmanns 2011). However, each of these bacterial strains has their limitations with the main issue being that most fermentation systems are intolerant of isobutanol, dying off when concentrations of isobutanol exceed 8 g/L (Atsumi et al. 2010). To combat this issue, many researchers have begun to identify methods to extract the isobutanol as it is produced or improve bacterial tolerance to isobutanol. A successful method would involve utilizing of both mitigation regimes.

Escherichia. coli (*E. coli*) has been studied over the past decade for isobutanol production. Research has been focused on using the 2-keto acid-based pathway for isobutanol production from glucose (Smith and Liao 2011). Many key enzymes have been isolated via protein purification and verified using SDS-PAGE in order to conduct *in vitro* studies. Some enzymes and genes of study include aldehyde reductase and alcohol dehydrogenase (Atsumi et al. 2009). Another method developed to improve isobutanol production in *E. coli* involves *in situ* product removal (gas sparging). Isobutanol produced by engineered *E. coli* is constantly stripped out of the fermentation system with air and is subsequently condensed and absorbed in chilled water. This method allows the bacteria to continue to produce isobutanol without the issue of product inhibition. With *in situ* product removal, isobutanol productivity reached 50 g/L in 72 hours with an isobutanol yield of 0.29 g isobutanol/g sugar (Baez et al. 2011). This corresponds to 68% of the theoretical maximum yield. Other efforts in *E. coli* isobutanol production involve using elementary mode (EM) analysis to determine the theoretical maximum production of isobutanol and 1-butanol in *E. coli* (Trinh 2012). This method seeks to analyze current work

done on engineering *E. coli.* in order to determine the ideal mechanisms for anaerobic biobutanol production. Using EM analysis, a significant understanding of the metabolic pathways that *E. coli* employs was obtained and applied for strain optimization for biofuel production (Trinh et al. 2011).

Bacillus subtilis is another promising isobutanol producing bacteria. *Bacillus subtilis* possesses a much higher isobutanol tolerance than that of *E. coil* and *C. glutamicum* (Jia et al. 2012). However, its production capabilities are much less. The highest reported yield of isobutanol from *B. subtilis* is approximately 0.08 g isobutanol/g sugar (19% theoretical yield). Main issues associated with *B. subtilits* lie in the overproduction of acetate and lactate (Li et al. 2011a). Significant work needs to be done to direct the carbon flux to isobutanol production and improve isobutanol yields.

Corynebacterium glutamicum has been researched as a candidate for isobutanol production. Major advantages of using *C. glutamicum* is that it is more robust compared to *E. Coli*. However, many side products are formed with *C. glutamicum* fermentation. A significant genetic modification procedure is required for extractable concentrations of isobutanol. Current research progress shows isobutanol concentrations at approximately 4.0 g/L in 96 hrs. This results in a theoretical yield of 19% (Smith and Cho 2010). Other researchers have been able to improve upon this to reach a theoretical yield of 77% by allowing cell growth under aerobic conditions and then depriving the bacteria of oxygen to boost isobutanol production (Blombach et al. 2011). Final isobutanol concentrations also showed promise with >10g/L as a final concentration and a maximum productivity of approximately 0.9g/Lh (Blombach et al. 2011).

Saccharomyces cerevisiae (brewer's yeast) has also been studied for isobutanol production potential. The idea behind using *S. cerevisiae* is that the metabolic pathways for

ethanol production can be deleted and the pathways leading to isobutanol production can be overexpressed. Current results are still in the initial phase with concentrations <1g/L being produced and yields less than 1% (Lee et al. 2012, X. Chen et al. 2011) Significant work is still needed to direct the carbon flux toward isobutanol production and match productivities gained by other bacteria.

Recent interesting approaches for isobutanol production include photosynetic pathways. Li et al. (2012) report a method for producing isobutanol in a fermentation system that relies solely on carbon dioxide and energy generated from man-made photovoltaic cells (solar panels). This method is best described as a type of pseudo-photosynthesis that can have a higher efficiency than current fuel biological systems. However, this report only lists biofuel concentrations of 1.4 g/L after 100 hours of bacterial activity. The bacteria, *Ralpha Eutropha*, were also reported to have a low contamination tolerance, implying that expensive sterilization procedures will need to be in place for sufficient large scale production (Li et al. 2012). Other research with *Ralpha Eutropha* show that the maximum yield is approsimately 78% with concentrations of 4.5 g/L. (Atsumi et al. 2008, Lu et al. 2012) Atsumi et al have begun looking at producing biofuels from cyanobacteria. Currently they are focusing on the production of 1-butanol, isopropene, and isobutanol using *S. elongates* and *Synechocystis sp.* (Atsumi et al. 2008, Machado and Atsumi 2012). The results show that fuel production is possible, but much more research is needed to match the current yields of other biofuel production methods. A summary of the maximum isobutanol yields obtained is given in table 3. Much work has been accomplished in this field. However, the main issue with isobutanol production is the low yields from fermentation. Additionally, high costs for genetic modification and maintenance of bacterial strain purity puts a significant financial strain on the process. In order for isobutanol

production to reach large scale implementation, these issues must fully be addressed. As such, current 1-butanol production technology possesses a significant advantage for industrial implementation and will become a major player in second generation biofuel production.

Table 3. Summary of Fermentation Bacteria and Maximum Yields

Microorganism	Maximum Isobutanol Yield g isobutanol/g sugar	Study
Escherichia Coli	0.42	Bastian et al. 2011
Bacillum subtilis	0.08	Li et al. 2011a
Saccharomyces cerevisiae	0.006	Kondo et al. 2012
Corynebacterium glutamicum	0.32	Blombach et al. 2011
Ralph eutropha	0.33	Atsumi et al. 2008

Classical ABE Process

Butanol has been explored as a transportation fuel for many years, dating back to the First World War. A representative fermentation of 6C sugars with *C. acetobutylicum* can produce acetone, butanol and ethanol in the ratio of 3:6:1 acetone:butanol:ethanol. This fermentation has become known as ABE fermentation. Since that time, other bacteria have been employed for ABE fermentation with slightly different product distributions, nutrient requirements, and carbon source preference. Several bacterial strains developed from *C. acetobutylicum*, including *C. Beijerinckii*, *C. butyricum*, and *C. Saccharoperbutylacetonicum*, have been found to be productive with glucose, arabinose, and xylose (Chin 1991, Ounine 1983). During batch processing, ABE solvents are generated in two distinct time-based phases. After a stable cell mass has been achieved, the bacteria will typically produce organic acids such as lactic acid, acetic acid, and butyric acid. This is the first phase of production and is characterized by a drop of pH from about 6.5 to less than 4.5, due to the formation of the organic acids. The first phase is termed the acidogenesis phase. The acidogenesis phase is also characterized by the evolution of gases, predominantly hydrogen. During the second metabolic phase, termed the solventogenesis

phase, the bacteria will employ additional pathways, which convert the organic acids to the corresponding solvents. This phase is characterized by a gradual rise in pH as the acids are consumed and by increased carbon dioxide evolution. The transition from acidogensis to solventogenesis is probably driven by a predominance of the non-disassociated form of the organic acids, which readily traverse the cell membrane (Awang 1988). The metabolism process for *C. acetobutylicum* is shown in figure 4. This metabolic scheme was developed in the mid-

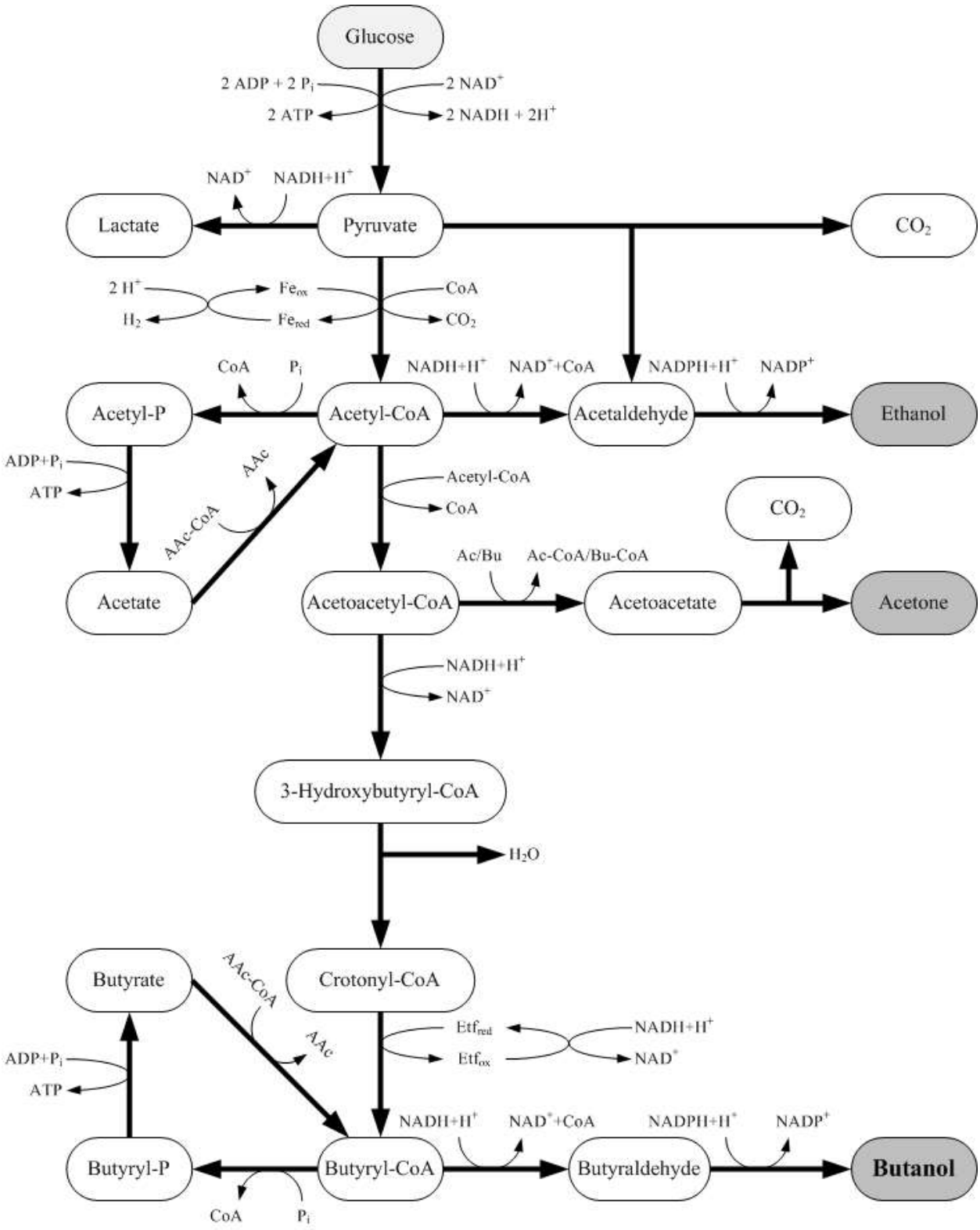

Figure 4. Metabolic Pathway to Solvents with *Clostridium Acetobutylicum*.

1970s by Doelle and Stanier, and has undergone some refinement over the years (Doelle 1975,

Stanier et al. 1976). During batch fermentation processes, it was found that the initial glucose concentration needed to be above 60 g/L to ensure enough glucose remained during the second phase to support solvent production (Monot et al. 1982). Glucose limited broths are restricted to acid production. Limited organic nitrogen availability during the solventogenesis phase leads to greater butanol productivity (Monot and Engasser 1983, Andersch et al. 1982). Organic nitrogen present during the first phase of fermentation promotes cell growth and acid generation. As the pH drops, the utilization of the organic nitrogen is inhibited and solventogenesis is enhanced. On the other hand, the presence of inorganic nitrogen appears to reduce cell growth, acid generation, and solvent production. In a like manner, sulfate and phosphate limitation enhances solventogensis (Bahl and Gottscalk 1984). Higher levels of sulfate and phosphate shift production from hydrogen to lactic acid and limit solvent productivity and butanol selectivity. When hydrogen partial pressures were maintained at 3 to 5 atmospheres, butanol production increased by 18% (Yerushalmi, et al., 1985). During solventogensis, hydrogen production ceases as the excess reducing agent is used for solvent production (Awang 1988).

Cultures of the various clostridial strains used for ABE fermentation undergo time-dependent degeneration with respect to solvent production. Strain degredation of *C. acetobutylicum* can be mitigated by limiting phosphate (Ezeji et al. 2005a). *C. beijerinckii* benefits from the addition of dilute acetate (Chen and Blaschek 1999). Several bacterial strains have been used for the ABE fermentation of 1-butanol. Table 4 lists several strains, and the carbohydrate feedstocks used by several researchers.

Table 4. Examples of ABE fermentation

Feedstock	Bacterial strain	Reference
Algal biomass	*Pasteurianum* *Saccharoperbutylacetonicum*	Nakas et al. 1983 Potts et al. 2012
Apple Pomace	*Acetobutylicum, butyricum*	Voget et al. 1985a

Cassava	*Saccharoperbutylacetonicum*	Thang et al. 2010
Cheese Whey	*Acetobutylicum* Unspecified	Maddox et al. 1993 Stoeberl 2011
Corn	*Acetobutylicum* *Beijerinckii* *Acetobutylicum* *Acetobutylicum*	Chiao and Sun 2007 Ezeji et al. 2005b Killeffer 1927 Weizmann 1915
Jerusalem artichokes	*Acetobutylicum*	Marchal et al. 1985
Molasses	*Beijerinckii* Various *Acetobutylicum*	Ezeji et al. 2005b D.T. Jones 2001 Dong 2011
Potatoes	*Beijerinckii, acetobutylicum* *Acetobutylicum* *Acetobutylicum* *Acetobutylicum* *Saccharoperbutylacetonicum* *Acetobutylicum*	Gutierrez et al. 1998 Grobben et al. 1993 Weizmann 1915 Fernbach and Strange 1911 Al-Shorgani et al. 2011 Dong, 2011
Sweet potatoes	*Acetobutylicum* *Beijerinckii*	Chiao and Sun 2007 Ezeji et al. 2005b
Sago	*Saccharoperbutylacetonicum*	Al-Shorgani et al. 2012
Argi-hydrolysate	*Acetobutylicum* *Beijerinckii*	Dong 2011 Qusheri 2008
Food Waste	*Acetobutylicum*	Patakova et al. 2009
Sorghum bagasse	*Acetobutylicum*	Zhang 2011
Rice Bran	*Saccharoperbutylacetonicum*	Al-Shorgani 2012

In addition to naturally occurring, selected, strains, much research is ongoing with genetic modifications of bacterial strains. These efforts are focused on increasing the tolerance to butanol (Thormann et al. 2002, Allcock et al. 1981), increasing the selectivity to butanol compared to acetone or ethanol (Green et al. 1996, Tummala 2003), alleviate the pronounced two phase metabolic cycle (Young et al. 1989, Papoutsakis et al. 1993, Blaschek et al. 1995), and increase resistance to attack by phages (Jones et al. 2000).

Some of the difficulties in achieving high butanol productivity can be engineered away by designs of fermentation, *in situ* removal of inhibitory products, and increasing the effective specific cell mass in the reactor. Lost productivity in batch fermentation due to start up, shut down, and batch preparation can be minimized by operating continuous reactors. In continuous fermentation systems where production is coupled to cell growth, the productivity of a continuous stirred tank fermenter increases with feed rate until it reaches a maximum value. As the feed rate is further increased, the productivity decreases abruptly as cells are washed out of the reactor because cell generation is less than cell loss in the outlet stream from the reactor. There are two generally accepted methods for increasing productivity beyond this maximum, cell immobilization and cell recycle. Cell immobilization is a technique for retaining cells inside the reactor through attachment to a surface (Hu and Dodge 1985), entrapment within porous matrices (Cheetham et al. 1979), and containment behind a barrier or self-aggregation (Karel et al. 1985). Cell recycle is a technique for separating the cells from the product stream by centrifugation, filtration or settling in a conical tank, followed by returning the cells back to the reactor (Shuler and Kargi 2002). Of these two methods, cell immobilization is generally restricted to the laboratory because of significant fouling. In assessing cell recycle technologies, centrifugation to remove cells can be cost prohibitive, and simple settling with or without the addition of flocculating agents requires large tanks because of the similarity in densities between cells and the fermentation broth. Many improvements have been made in axial flow filtration, which have helped to reduce the cost of commercial application of these systems. Cell recycle on a two liter reactor allowed eight weeks of continuous fermentation with *C. Beijerinckii* when coupled with in-situ removal of product (Potts et al. 2012). Membrane fouling, a common problem with cell recycle reactors was kept in check with an automated, time-based backflush

system. Cell immobilization in packed bed reactors has been studied by several, with bonechar, clay brick particles, and polymeric substrates (Qureshi et al. 1995, Qureshi et al. 2005, Napoli 2011). When coupled with one of several butanol removal techniques, described in the butanol separation section of this chapter, operation of continuous reactors for ABE production is a viable technical process.

Typical yields for ABE fermentation are in the range of 0.15-0.25 g of butanol per gram of glucose with productivities of 15.8 g/Lh (Qureshi 2001), 9.5 g/Lh (Ramey 1998), 6.5-15.8 g/Lh (Qureshi 2008), 6.7 g/Lh (Ezeji 2007), 0.2 g/Lh (Golueke 1957), 0.2 g/Lh (Jesse 2002). Unfortunately, both yield and productivity are limited by the presence of butanol in the broth, which is inhibitory to the fermentation. Some researchers report increasing yields substantially by employing in-situ removal of the butanol during fermentation. In-situ removal of the butanol can be coupled with cell recycle for additional gains, and in some cases, with carefully defined medium, individuals have reported achieving yields close to the theoretical or stoichiometric yield of 38% fermentation of glucose to solvent (Ramey 1998, Qureshi 2000). The many techniques used for in-situ removal of the butanol are discussed elsewhere in this paper. It may be noted that those who report very high butanol productivities typically operate small reactors at highly optimized conditions. Operations in pilot plant and industrial scale reactors do not achieve these high levels, but 18-22 g/L is apparently the norm when high sugar substrates are fed to the bacteria (Ni and Sun 2009).

While much progress has been made in the enhancement of the economics of ABE processing, the difficulties of the cost of feedstock materials and the energy cost of separation of the butanol from the large mass of water inherent in the fermentation process. It appears to us that the efforts toward establishing low cost lignocellulose for other biofuels, such as bioethanol,

are applicable to the biobutanol process as well. On the basis of feedstock costs, biobutanol looks like a very attractive replacement for bioethanol, due to several advantages butanol has as a vehicular fuel. The cost of butanol isolation and purification, thus, remains the most troublesome impediment for the replacement of ethanol with butanol. If some technical improvement can be made to ABE processing to relieve the purification costs, the future of biobutanol looks rosy, if the purification costs remain high, the future of biobutanol looks bleak. Separations will be discussed later in this book chapter.

Two Step Process

An interesting approach to improving the ABE fermentation was presented by Ramey (1998), who described a continuous process for producing butanol from sugars by using two different strains of bacteria. In this approach, *C. tyrobutyricum* (or other similar strains) is used to produce butyric acid from sugars and *C. acetobutylicum* (or other similar strains) is used to produce butanol from the butyric acid. These two steps are usually accomplished in two separate fermenters. Butyric acid from the first fermenter can be added to the second fermenter without concentration (Ramey 1998, Bahl 1992) or by separation of the butyric acid from the broth of the first fermenter followed by addition to the second fermenter (Du et al. 2012). Comparable yields of butyric acid from glucose were obtained in using either *C. tyrobutyricum* or *C. thermobutyricum* (Weigel et al. 1989, Wu and Yang 2003). Liu et al. (2006) developed *C. tyrobutyricum* mutants which gave higher butyrate yields (>0.4 g/g) and concentrations (43 g/L). In producing butanol from sugars by either the direct or indirect fermentation routes, Ramey (1998) noted that 38% of the carbohydrate was converted to butanol by the indirect route using *C. tyrobutyricum* and *C. acetobutylicum*, while only 25% of the carbohydrate was converted to

butanol using the direct route with *C. acetobutylicum* alone. Furthermore, Ramey (1998) noted that the butanol productivity increased by 78% when using the indirect fermentation route.

C. tyrobutyricum converts both glucose and xylose to butyric, acetic and lactic acids. Elevated pH (>6.3) is favorable for the production of butyric acid, and lower pH (<5.7) is more favorable for the production of acetic and lactic acids (Zhu and Yang 2004). Higher total acid yields are attained at reduced pH, but higher butyrate selectivities and concentrations are attained at increased pH. Table 5 shows a summary of acid production from glucose by *C. tyrobutyricum* as obtained by Wu and Yang (2003) and Du et al. (2012). As expected, immobilized cell systems outperformed free cell systems, and extractive fermentation systems outperformed both the free cell and immobilized cell systems because the solvent removes the inhibitory product butyrate. However, acid extraction can only occur at lower pH levels since most solvents extract products only in the free acid form, and many solvent systems are not particularly selective. In the work by Du (2012), the separation is done at a neutral pH with high selectivity and productivity of butyric acid.

Table 5. Comparison of Fermentation Results from Free Cell, Immobilized Cell and Extractive Fermentations Using *C. tyrobutyricum* ATCC 25755 (Wu and Yang 2003, Du et al. 2012)

	Free Cells (pH 6.0)	Immobilized Cells (pH 6.0)	Immobilized Cells (pH 5.5)	Extractive Fermentation (pH 5.5)	EDI Separation (pH 6.3)
OD_{max}	5.8	11.5	8.2	8.1	14.5
Butyrate concentration (gl^{-1})	16.3	43.4	20.4	301	>150
Butyrate yield (gg^{-1})	0.34	0.42	0.38	0.45	.45
Acetate yield (gg^{-1})	0.120	0.095	0.115	0.111	N/A
Butyrate productivity ($gl^{-1}h^{-1}$)	0.193	6.77	5.11	7.37	
Product selectivity	0.74	0.81	0.77	0.80	.92
Product purity				0.91	

By feeding a mixture of glucose and butyric acid (from *C. tyrobutyricum*), *C. acetobutylicum* can remain in the solvent producing stage and produce higher yields and concentrations of butanol than when feeding sugars to *C. acetobutylicum*. Huang et al. (2004) fed a mixture of glucose and butyrate to a fibrous bed bioreactor containing *C. acetobutylicum* ATCC 55025 at 35°C and pH 3.5-5.5. An optimal butanol productivity of 4.6 g/Lh and a butanol yield of 0.42 g/g were obtained at a dilution rate of 0.9 h^{-1} and a pH of 4.3 with 54 g/L glucose and 3.6 g/L butyric acid in the feed stream. The concentration of butanol was 5.1 g/L on average, and the conversions of glucose and butyric acid were 19% and 31%, respectively. The optimum solvent (ABE) yield was 0.53 g/g, under the same process conditions. By contrast, the optimum single step (conventional) ABE fermentation has an optimum butanol yield of 0.25 g/g and a productivity of 4.5 g/Lh.

As described in the ABE process section, the product concentration in the two fermenters can be increased with cell recycle or immobilization. Concentrations of butyric acid in the first fermenter and of butanol in the second fermenter are limited by product inhibition. Product inhibition can be minimized by in-situ removal of the butyric acid from the fermenter and in-situ removal of butanol from the second reactor. The techniques used for these separations are discussed in the section on separation and purification. Once butyrate is concentrated, it must then be converted into butanol via reaction or a second fermentation step (Green and Crow 2009).

Separations and Purification

In-situ product removal is designed to increase the yield and productivity of a fermentation process by (Freeman et al. 1993):

1. Minimizing the effects of product inhibition on the producing cell, thus allowing for continuous expression at the maximum production level;

2. Minimizing product losses resulting from cross-interaction with the producing cell, environmental conditions or uncontrolled removal from the system (e.g. by evaporation); or

3. Reducing the number of subsequent downstream processing steps.

The product yield is set by overall stoichiometry, the production of cells and cell maintenance. However, in fermentation systems that produce multiple liquid phase products, selective *in-situ* removal of one of the products may cause the fermentation system to overproduce that product, and thereby increase the yield of that product relative to the other products in the product matrix. This phenomenon is illustrated in the following examples. Wu and Yang (2003), in fermenting glucose to butyric and acetic acids using *C. tyrobutyricum* with and without *in-situ* removal of products by solvent extraction, utilized an amine-based solvent system that preferentially (but not totally) extracted butyric acid over acetic acid. Without product removal, their fed-batch system gave a butyric acid yield of 0.34 g/g and an acetic acid yield of 0.12 g/g, for a product selectivity of 0.74. With product extraction, the overall butyric acid yield was 0.45 g/g and the acetic acid yield was 0.11g/g, for a product selectivity of 0.80. Thus, the fermentation system produced more butyric acid than acetic acid as the butyric acid was preferentially removed by extraction.

Similarly, Grobben et al. (2003), in fermenting potato wastes to acetone, butanol and ethanol using *C. acetobutylicum* with and without *in-situ* removal of products by perstraction, utilized a solvent system that preferentially removed butanol (K=3.5) over acetone (K=0.65) and

ethanol (K=0.2). Without product removal, their fed-batch system steadied at 12 g/L of butanol, 4 g/L of acetone and just under 1 g/L of ethanol. With product removal, the butanol concentration (both extracted and in the fermenter) reached 39 g/L and the acetone concentration reached 11.5 g/L. In both of these fermentation systems, the preferentially extracted product (butyric acid in the *C. tyrobutyricum* system and butanol in the *C. acetobutylicum* system) was preferentially produced over the lesser extracted product. If a separation system could be developed that removed only butanol (or butyric acid), perhaps only minimal amounts of acetone and ethanol (or acetic acid) would be produced and nearly all of the sugar substrate would be diverted to the preferred product.

In-situ Butyric Acid Separation for Two Step Production of Butanol

The two most common technologies proposed for separating organic acids from water are liquid-liquid extraction (Mamade et al. 2006, Matsumato et al. 2004, Zigova and Sturdik 2000, Ramey 1998) and electrodialysis (Wang et al. 2006, Hestekin et al. 2002, Nghiem et al. 2001, Huang et al. 2007 Lee 2005). Although liquid-liquid extraction works well, the acid typically has to be protonated for efficient extraction. The pKa of butyric acid is 4.82 and this low pKa requires lowering the pH of the solution from optimal fermentation range (near neutral) in order to remove the organic acids.

Electrodialysis (ED) has a significant advantage with pH flexibility—the removal of products from fermentation broth can occur at a pH that enables the formation of products in their ionized form, a condition that is more desirable for fermentation processes. Huang et al. (2007) published a review on ED techniques, costs and production capacities, showing that ED has been effectively used in concentrating amino acids, lactic acid, citric acid, formic acids, and butyric acid. However, ED is not typically selective for one organic acid over another. In

contrast, electrodeionization (EDI) may be selective for particular organic acids because this technology combines selectivity in the membrane with selectivity of the ion exchange resins. Thus, EDI is more effective for *in-situ* product recovery from fermentation broths than ED (Datta et al. 2002).

EDI has been used for concentration of organic acids. Specifically, Widiasa et al. *(*2004) concentrated citric acid from 2,000 to 60,000 ppm. Arora et al. (2007) and Lin et al. (2004) separated organic acids from fermentation broths with initial concentrations below 1 g/L to final concentrations of less than 1 mg/L. Unfortunately, neither of these studies addressed selective organic acid separation. Interestingly, Semmens and Gregory (1974) demonstrated that ion exchange beads become more selective for organic acids as chain length increases. Takahsashi et al. (2003) reported that the selectivity of organic acids with anion exchange membranes could be described by the nature of the ion exchange selectivity but, as the length of the chain increases, hydrophobic interactions increase and thus the selectivity of the membrane starts to increase for that acid.

In-situ Butanol Separation

There are many techniques that have been used for the separation of butanol from aqueous streams including liquid-liquid extraction (Ezeji et al. 2007), distillation (Skouras and Skogestad 2004), and gas stripping (Ezeji et al. 2004). However, when separation is used in conjunction with a fermentation process, preservation of substrate, organisms and medium components must be considered in applying any separation technique. Liquid-liquid extraction using organic solvents, although quite useful in performing the separation, often results in the contamination of the recycled fermentation medium by ppt or ppm levels of the solvent which can result in the inhibition of the fermentation or even cell death. Distillation, although highly

effective in recovering a number of fermentation products, can thermally degrade sugar substrates or other medium components or produce thermal by-products. In addition, azeotropes can develop during distillation, which limit the separation. For these reasons, the most commonly proposed method for selective extractions of butanol from fermentation broths is pervaporation (Ezeji et al. 2007, Liu et al. 2005, Vane 2005, Yeom et al. 2000, Jitesh et al. 2000, Liu et al. 2005, Thongsukmak and Sirkar 2007, Olsson et al. 2001, Qureshi et al. 1999, Park and Geng 1996).

Distillation

For butanol, the most common form of separation is multi-step distillation. Butanol obtained from fermentation is fed to a distillation unit at a concentration between 1-3 weight percent, which is much lower than found in ethanol systems where typical concentrations range between 9-13 weights percent (Pfromm 2010). The distillation unit generates a distillate where the concentration of butanol is at the azeotropic point of 55.5 weight percent. Then the partially pure butanol allowed to phase-separate in a decanter into butanol and water rich phases. Next, the butanol rich phase is fed into a second distillation unit to bring it up to purity while the water rich phase is fed back to the first distillation unit. A schematic of this procedure is given in figure 5.

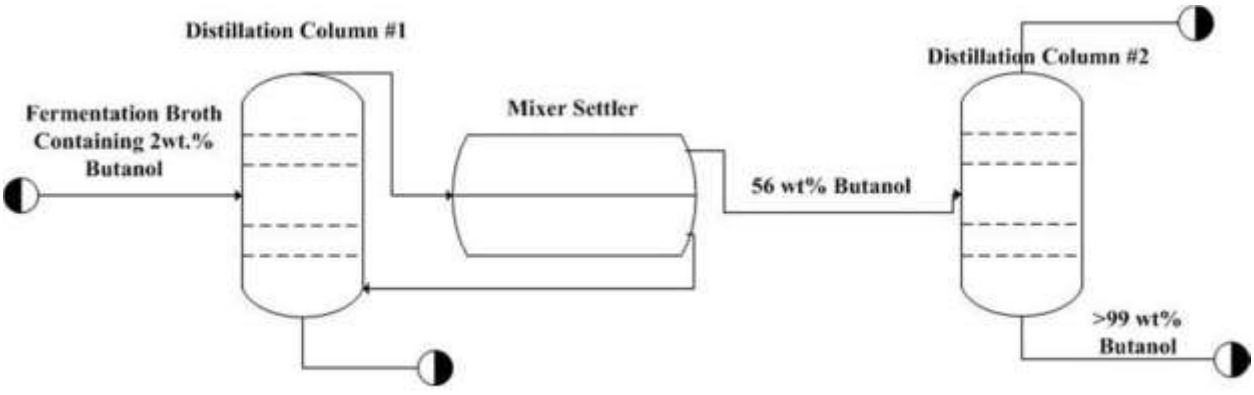

Figure 5. Process flow diagram of current butanol distillation technology.

Membrane Separation

Another method that shows promise in butanol purification is membrane separations (Garcia et al. 2011). Membranes can be used within the fermentation system to continuously draw out product while keeping the bacterial environment stable, effectively maximizing productivity without dealing with bacterial tolerance. Membranes can also be used to effectively separate out butanol without extracting out acetone and ethanol side products. This would encourage bacterial to break down these side products into butanol, further improving yields. Membrane extraction (perstaction) is another effective method for butanol purification. This is similar to general membrane extraction except the use of a chemical potential gradient is applied instead of a pressure driving force. An extractive solvent is placed on one side of the membrane system and fermentation broth is flowed past the membrane. Butanol's affinity for the solvent allows it to move through the membrane into the solvent. This allows for fast and efficient production separation for fermentation systems. Studies using membrane based extraction techniques have proven to reduce product inhibition while boosting glucose consumption and overall productivity (Tanaka et al. 2012, Jeon and Lee 1989).

Pervaporation

Another membrane separation for biobutanol production is pervaporation. Fermentation broth is flowed past a membrane with a vacuum imposed on the other side. Volatile components are pulled through the membrane and vaporized by the low pressure on the vacuum side of the membrane. The products are then condensed and collected. A schematic of this process is shown in figure 6. Figure 6 also shows a significant advantage of pervaporation that it can separate outside the vapor-liquid equilibrium of butanol water allowing for much higher selectivity's to be obtained. Many studies have been conducted in order to model pervaporation technology for

butanol recovery (Li et al. 2011b, El-Zanati et al. 2006, Wijmans and Baker 1995). Other studies focused on membrane materials such as zeolites (Bowen et al. 2002, Bowen et al. 2003, Pera-Titus et al. 2006), polymeric resins (Nielsen and Prather 2008), mix matrix membranes (Wang et

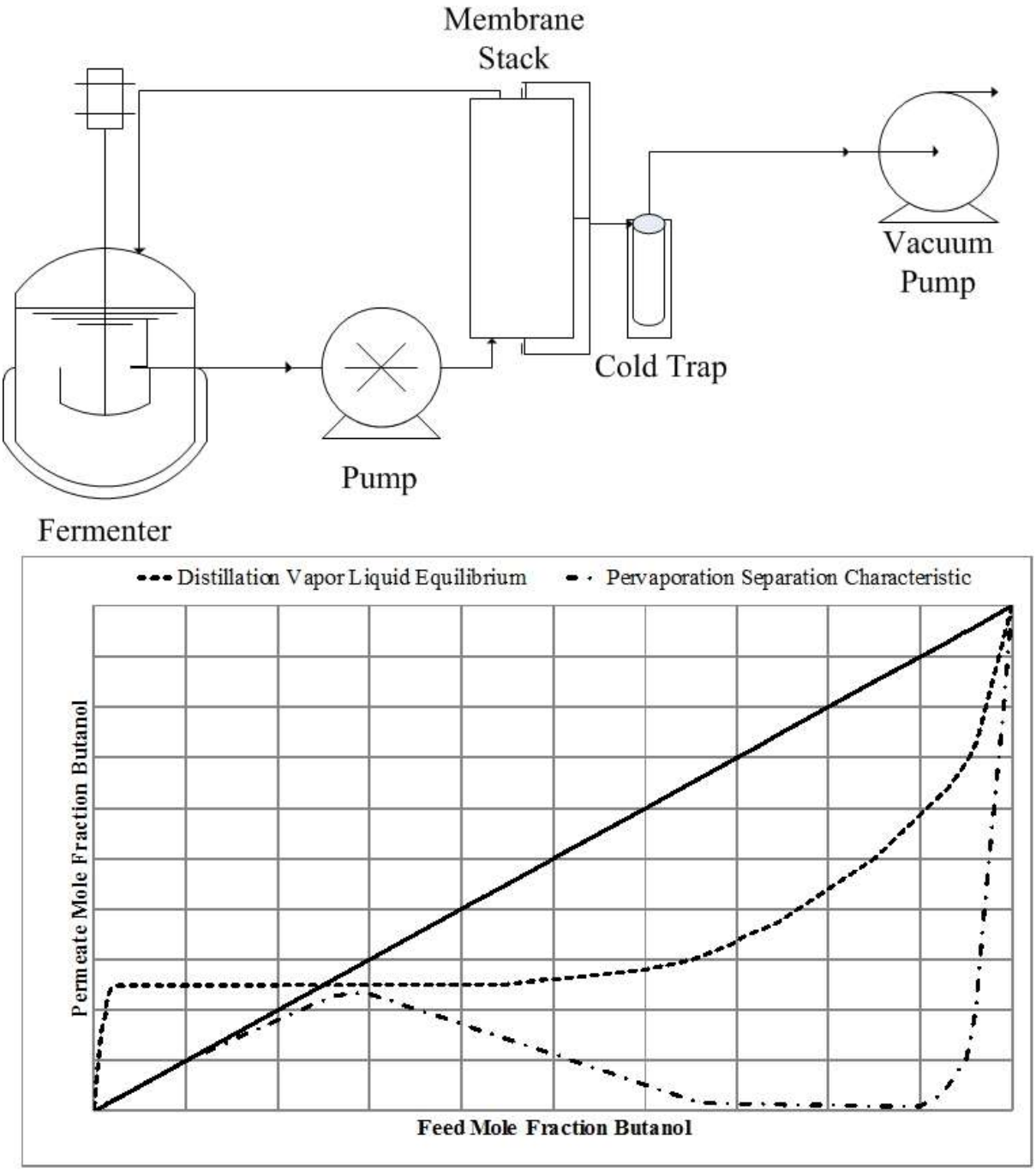

Figure 6. (Top) Process Schematic for Butanol Pervaporation. (Bottom) Comparison of Pervaporation and Distillation Separation Characteristics.

al. 2009), and silica based membranes (Hickey and Slater 1991, Fouad and Feng 2009). Some studies focused on studying the effects of fouling and concentration polarization in order to reduce these adverse effects (Qureshi and Blaschek 1999, Fouad and Feng 2008). Consensus of results implies that pervaporation is a very suitable butanol separation technique and is capable of moving butanol fermentation away from batch schemes into continuous processes. Pervaporation systems involving butanol can be operated at low temperatures while still performing selective separation of butanol, and can be employed on both laboratory and commercial scales (Vane 2005). In most of these pervaporation applications, butanol is the most selective component because it is the most hydrophobic component and has the highest solubility in the membrane (Olsson et al. 2001). As an example, Liu et al. (2005) used polydimethylsiloxane based membranes on a quaternary mixture of acetone (1.57%), ethanol (0.9%) and butanol (1.11%) in water and found selectivities to water of 2.4, 3.8, and 9.6, respectively. When the concentration of butanol was increased relative to ethanol and acetone, the selectivity of butanol to the other components also increased. When more selective membranes such as a liquid pervaporation membrane (Thongsukmak and Sirkar 2007) or a silicalite/silicone membrane (Qureshi et al. 1999) were used, butanol selectivities ranging from 40-100 were obtained. Park and Geng (1996) showed that increasing the pervaporation membrane area in a fed-batch butanol production system yielded higher glucose consumption rates and higher production rates.

Gas Sparging

This process involves bubbling an inert gas (typically nitrogen or CO_2) through the fermentation broth. Volatile components in the fermentation broth (butanol) are stripped from solution and into the vapor phase where it is carried out of the fermentation system. The vapor is

then condensed and collected as product. Results from gas sparging implementation show that high flowrates of inert gas can maximize product recovery (Ezeji et al. 2007). However, inhibitory effects were increased, resulting in lower glucose consumption rates (Park et al. 1991).

Liquid-liquid extraction (LLE)

In LLE a third component is added to a binary mixture in order to create a second liquid phase, one which has a high concentration of product and one with a high concentration of the original solvent. Common practices involve adding an organic solvent to an aqueous solution in order to extract out an organic product. The second phase is then processed through another separation step (which is generally simple and cheap) in order to obtain pure product. Recently ionic liquids have been studies for use in LLE of butanol fermentation systems. Their chemical versatility makes them ideal solvents for butanol extraction (Fadeev and Meagher 2001). Eleven ionic liquids were studied for butanol selectivity and extraction efficiency. Results showed that butanol selectivity can exceed 100 with good extraction efficiencies ranging between 60-80% (Ha et al. 2010). Other studies have focused on using hexane (Gomis et al. 2012), other alcohols (Takriff et al. 2008), surfactants (Dhamole et al. 2012), and biodiesel as an extractant (Adhami et al. 2009).

A summary of butanol separation techniques is provided in table 6. Each technique has their advantages and limitations, but each can be an effective method for separation with the proper process in place. As research continues, each method will become more cost effective and efficient in preferentially separating butanol from other unwanted fermentation products.

Table 6. Summary of Butanol Separation Methods

Separation Method	Key Advantages	Major Limitations	Approximate Cost ($)
Distillation	Fast, efficient, low capital cost	High energy and operating cost	$$$$
Membrane	Selectivity and Low	Time intensive and	$$$$

Separations/Filtration	energy requirements	high capital costs	
Perstaction	Selectivity and simple process	Fouling, slow, high capital cost	$$$
Pervaporation	Selectivity	Fouling, Slow, high capital & operating costs	$$$
Electrodialysis	Very high selectivity	High capital cost, slow	$$$
LLE	Inexpensive	Not well suited for continuous processing	$$
Gas Sparging	Inexpensive	Low selectivity, high processing cost (compressed gas)	$$

Biofuel Production Case Studies

In order to create a fair industrial perspective of current biofuel technology, case studies were developed for butanol and ethanol production. Each case study focused on the capital and operating costs of producing 10 million gallons of biofuel per year. This was done with a combination of literature, scaling using well known chemical engineering practices, and simulation (when necessary). Figure 7 shows the major steps in producing ethanol and butanol

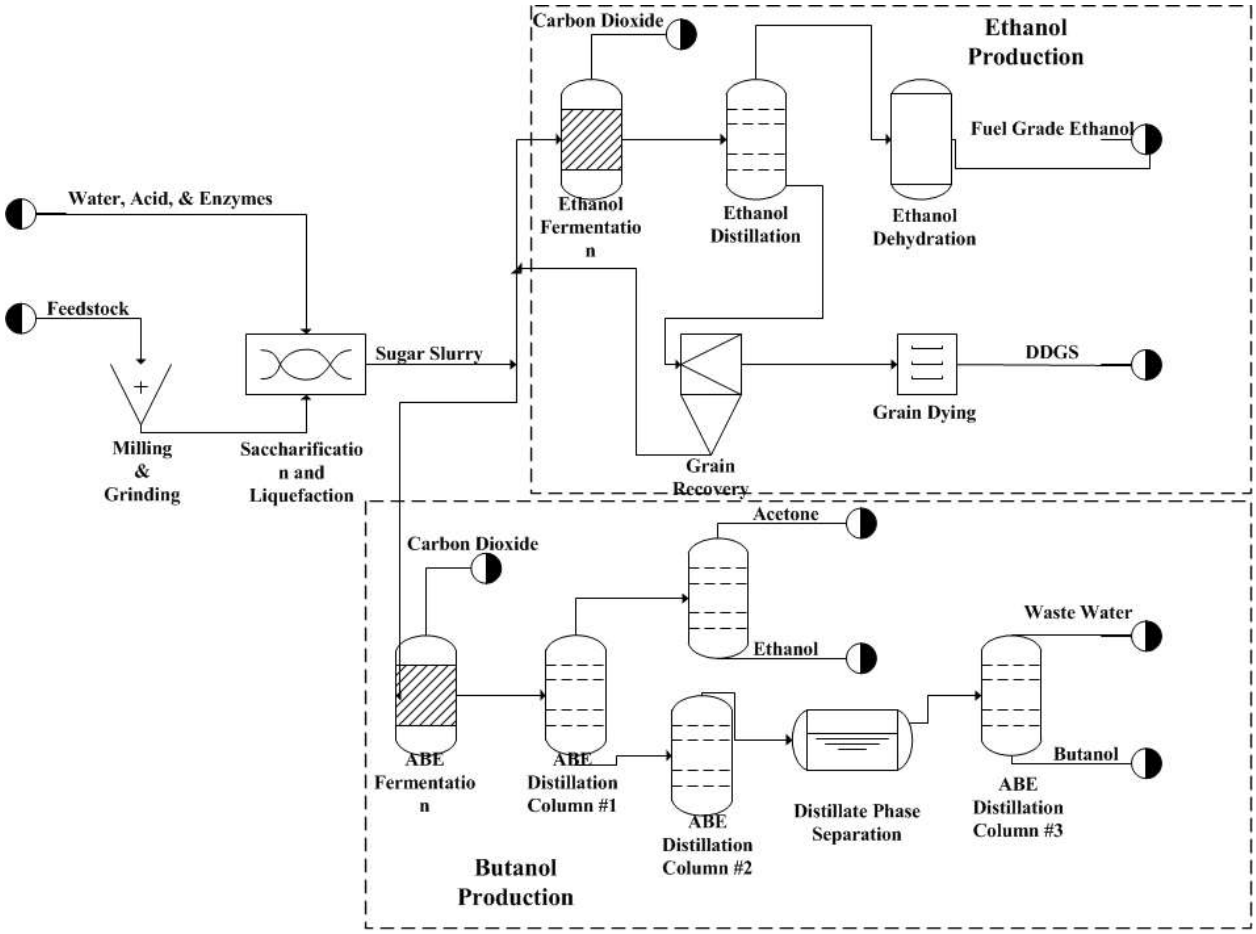

Figure 7. Comparison of Ethanol and Butanol Current Production Methods.

respectively. As shown, the front end of both processes are the same with significant differences upon production of sugars. Commentary on the major limitations and potential for each biofuel is also presented.

Bioethanol Case Study

Bioethanol is currently the largest biofuel being producing globally. With feedstocks and technology readily available, production of ethanol has steadily increased over the past decade. For this case study, costs reported are higher than estimates for larger scale plants on a per gallon basis. This is due to lower economies of scale values than what is expected for full scale production facilities. The major costs are broken down in six main areas: raw materials, milling, saccharification, fermentation, distillation, and dehydration. Utilities, additional products, and

depreciation are all considered. For ethanol biofuels, the main raw material cost is the feedstock, corn. In a 10 million gallon plant, approximately 3.6 million bushels of corn are needed since the productivity of corn ethanol production is 2.8 gallons per bushel (Wu 2007). The price of corn is at approximately $7.38 dollars per bushel, resulting in a feedstock cost of $26.3 million per year (www.quotecorn.com). This high cost makes producing solely ethanol from corn a non-profitable endeavor. However, dried distillers grain with solubles (DDGS) is also produced in corn ethanol plants, improving the economics of the process and making plants feasible. About 18 pounds of DDGS is produced per bushel of corn, resulting in approximately 30,000 metric tons of DDGS produced. Additional raw materials required include bacteria, enzymes, and chemicals for saccharification and fermentation. Total cost for these materials are approximately $27.5 million per year (Whims 2002).

The next costs to consider are costs from milling and saccharification of corn to extract the fermentable sugars. There are two options for this process, dry milling and wet milling. In most ethanol plants, dry milling is used due to the lower capital costs (Whims 2002). Wet milling only becomes profitable for large ethanol production facilities (> 50 million gallons ethanol produce per year). The costs of corn milling are approximately $2.56 million in capital. Saccharification and liquefaction costs mainly include requirements for enzymes, acids, and water for the breakdown of corn kernels and extraction of sugars. Sulfuric acid is commonly used with an amylase based enzyme (Kwiatkowski et al. 2006). Costs for saccharification are $4.01 million.

The next step is the fermentation of sugars. Yeast is the most commonly used microorganism for this process. Fermentation occurs in batches and generally takes 45 hours per batch (Pfromm et al. 2010). Capital costs for fermentation are $7.92 million. Separation of the

products is the final step in production. These costs are divided into distillation and dehydration of ethanol and purification of solids into DDGS. These costs are approximately $6.04 million and $13.44 million respectively. Costs for DDGS processing is high due to the centrifugation and drying steps required in removing water from the DDGS (Kwiatkowski et al. 2006). From this information, total capital and operating costs were obtained. All values were obtained by various case studies of ethanol economics and time correct to meet today's price expectations. Tables 7 and 8 show the estimated capital and operating costs associated with the 10 million gallon facility.

Table 7. Estimated capital costs for 10 million gallon ethanol production facility.

Plant Section	Capital Costs (US$ million)
Milling	2.56
Saccharification	4.01
Fermentation	7.92
Ethanol Purification	6.04
Byproduct Processing	13.44
Support Systems	1.28
Total	35.25

.

Table 8. Estimated Operating costs for 10 million gallon ethanol production facility

Category	Cost (US$ million)
Raw Materials	27.5
Fuel Costs	1.83
Electricity	1.68
Labor and Maintenance	1.63
Administrative and Other	0.93
Total	33.57

Economic feasibility can be determined by examination of cash flows expected from this facility. The current price of ethanol and DDGS is approximately $2.50/gallon and $350/MT respectively. From these prices the expected revenue from a 10 million gallon ethanol facility is approximately 35.5 million dollars (nasdaq.com, grains.org). The revenue generated from this

production facility would be insufficient for the investment required. In order for this process to become economically feasible, the process would need to have sufficient scale-up such that economies of scale allow revenue to overtake the increase in capital and operating costs. This has been demonstrated in larger ethanol production facilities. Another possibility is the use of government subsidies in the form of tax credits to mitigate costs and allow the plant to be profitable. Historically small scale facilities were subsidized by tax credits to allow proper scale-up so that plants could become self-sustaining once it reached set productivity levels. With the loss of ethanol subsidies, small scale facilities are no longer economically viable. Current large scale facilities operate at profit. However, as next generation biofuels continue to develop, ethanol production will level off and newer fuels like butanol will see a major boost in production.

Biobutanol Case Study

The similar costs for the butanol estimates, found in tables 9 and 10, were gleaned from several sources and recalculated as needed to match the 10 million gallons per year butanol production rate (Durre 2007, Gapes 2000, Qureshi 2012, Zhu and Yang 2010). The raw materials cost were estimated by assuming $100/ton for wheat straw and $7.38/bushel for the corn (www.quotecorn.com 2012). The productivity of wheat straw to butanol was assumed to be 147 kg of butanol from 751 kg of wheat straw (Qureshi 2012). The productivity of corn starch to butanol was assumed to be 2.5 bushels of corn to one gallon of butanol (Ramey 2004). Capital equipment costs for milling and saccharification were assumed to be similar, regardless of feedstock. Capital costs for purification were calculated using standard estimating techniques, as were the operating costs for fuels, labor and maintenance, and administrative and other. For a plant 5 times larger, Zhu estimates the cost per gallon for butanol from corn starch at

$2.56/gallon and from wheat straw at $2.15/gallon. These numbers are consistent with those of Table 8 and 9 **if you do not have to amortize capital**.

Table 9. Estimated capital costs for 10 million gallon butanol production facility.

Plant Section	Capital Costs (US$ million) Corn Starch	Capital Costs (US$ million) Wheat Straw
Milling	3.91	2.86
Saccharification	6.12	4.49
Fermentation	14.56	19.87
Butanol Purification	4.00	4.00
Byproduct Processing	13.44	18.34
Support Systems	1.28	1.28
Total	43.32	50.84

Table 10. Estimated Operating costs for 10 million gallon butanol production facility

Category	Cost (US$ million) Corn Starch	Cost (US$ million) Wheat Straw
Raw Materials	29.50	15.80
Utility Costs	2.20	2.20
Labor and Maintenance	1.32	1.32
Administrative and Other	0.98	0.98
Total	34.00	20.30

Comparing the relative costs of ethanol production to butanol production a few conclusions can be made. First, neither process is economical for fuel production at this scale without government subsidies or a major price increase. Second, when comparing the capital costs of the two processes, butanol is much higher due to the much larger fermenters required because of low yield organisms. Thus, the continued research in high yield organisms is justified. However, it should be noted that separations research can lead to lower fermenter sizes as well. In the operating costs, surprisingly, there doesn't seem to be much difference in butanol or ethanol production. This has been reported else ware (Zhu et al. 2009).

Conclusions

- Figure 8 shows a spike in the amount of butanol related scientific literature in the last 5 years. This demonstrates that it is clearly being research as a biofuel as well as a solvent.
- Research is taking place on isobutanol production, one step 1-butanol production, and two step 1-butanol production. At present, one step 1-butanol production is the only process that is large scale commercialized.

- Costs of butanol remain high because of low organism productivity and difficulty of operation.

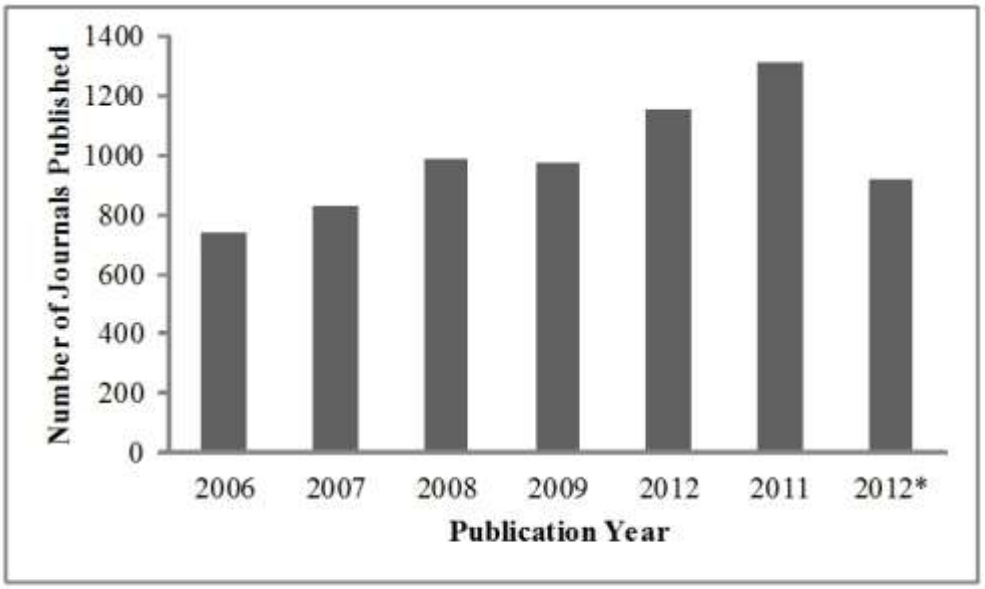

Figure 8. Butanol Journal Publications by Year. Data Obtained from Web of Science. *As of November 2012.

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Chapter 3

The Production of Butanol from Jamaica Bay Macro Algae

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Abstract

This study ascertained the technical potential of producing biofuel from a naturally occurring macroalgae. The algae examined grow in Jamaica Bay, New York City, on water containing nitrates, phosphates, and carbon dioxide that comes from the atmosphere. The process consisted of manual and mechanical harvesting, drying, grinding, and subjecting the algal matter to acid hydrolysis to extract carbohydrates to form an algal sugar solution. Fermentation of that solution to butanol was performed with butanol ultimately removed by distillation. An average of 15.2 g/L of reducing sugars was extracted in the hydrolysate showing that macroalgae (*Ulva lactuca)* have significant usable carbohydrates after hydrolysis. It was found necessary to remove the excess solids from the hydrolysate prior to fermentation, as the productivity fell by 75% if this was not done. With the bacterial strains (*Clostridium beijerinckii* and *C. saccharoperbutylacetonicum*) and the algal sugar solutions used, an acetone butanol ethanol (ABE) fermentation was used to make butanol. The butanol concentration in the fermentation broth reached about 4 g/L, which is close to the theoretical value for the sugar concentration obtained, and compares well (when adjusted for sugar concentration in the media) with values reported in the literature for other systems. The recovery of reducing sugars in the media during the pilot study was 0.29 g butanol/g sugar.

Keywords: biofuels, butanol, algae, fermentation, ABE

Introduction

The objective of this study was to ascertain the technical potential of producing biobutanol from algae that naturally grows in nutrient contaminated rivers, lakes, and bays. Of major concern is the removal of excess dissolved nitrates and phosphates [1-7], carbon dioxide [8-25] and heavy metals [26-30]. This study also compared butanol production from the classic acetone-buanol-ethanol (ABE) fermentation and the two step fermentation process. *Ulva lactuca*, a species of green macroalgae, has both a high growth rate and high carbohydrate content and was used because it is highly desirable to remove it from Jamaica Bay in New York City. Macroalgae grows in tropical to polar waters with different strains dominating in differing climatic regions [2].

Although earlier studies suggested that *U. lactuca* was not an economically attractive bio-energy crop, there is a renewed interest in the use of this and other algal species when nitrogen and phosphorous remediation is paired with biofuel production [2,8,9,13,14,22,31-34]. Much research has been done on the conversion of lipids from various algal species into biodiesel by a variety of methods: however, the high carbohydrate contents of *U. Lactuca* and other macroalgae indicates that a more cost effective strategy might be to ferment the carbohydrates from these algal species to either ethanol or butanol [32]. The latter biofuel, i.e. butanol, has the potential to augment or even replace ethanol as a gasoline additive due to several advantages that include low vapor pressure (emission reduction), high energy density (enhanced miles per gallon), and blending options (increased concentration) [33,35-38]. For this reason, a butanol case study was chosen for development with New York City Department of Environmental Protection. Butanol has been explored as a transportation fuel for many years, even back as early as the First World War. A representative fermentation of sugars with *C. acetobutylicum* can produce acetone,

butanol and ethanol in the ratio of 3:6:1 acetone:butanol:ethanol. This fermentation has become known as ABE fermentation as eluded to earlier [39]. Since that time, other bacteria have been employed for ABE fermentation with slightly different product distributions, nutrient requirements, and carbon source preference.

During batch processing, ABE solvents are generated in two distinct time-based phases. After cell mass has been generated, bacteria will typically produce organic acids such as lactic acid, acetic acid, and butyric acid. In the metabolism process, the bacteria will employ additional pathways which convert the organic acids to the corresponding solvents. The first of these phases is referred to as the acidogenesis phase, and the second phase is referred to as the solventogenesis phase. Metabolism makes a transition from acidogenesis to solventogenesis typically with a change in the pH of the fermentation broth. Typical yields for ABE fermentation are in the range of 0.15-0.25 g of butanol per gram of sugar with productivities of 0.5 grams/hour^{-}/liter [37-38, 40-47]. Unfortunately, both yield and productivity are limited by the formation of butanol, which is inhibitory to the fermentation. Some researchers report increasing yields substantially by employing in-situ removal of the butanol during fermentation [41,42,44,46-50]. In-situ removal of the butanol can be coupled with cell recycle for additional gains, and in some cases, with carefully defined medium, individuals have reported achieving yields close to the theoretical or stoichiometric yield of 38% fermentation of glucose to solvent [38,51].

In contrast to the ABE process, Ramey proposed accomplishing the fermentation in two steps to improve yield [38,52,53]. In the two-step process, the sugars in the fermentation broth are first converted to butyric acid by a bacterium such as *C. tryobutyricum* operating in its acidogenesis phase. The resultant butyric acid is collected and fed to a second fermentation

reactor charged with a solventogenesis bacterium such as *C. beijerinckii*, which converts the butyric acid to butanol.

Both the ABE and the two-step process have been studied for the conversion of starches, such as from corn stover, or glucose to butanol, but to the best of our knowledge this is the first study comparing one and two-step fermentation of algal sugars to butanol. Germane to this effort is the assessment of the potential of *U. lactuca* harvested from Jamaica Bay, a coastal estuary in New York City, for nitrogen and phosphorous removal coupled with its use as a raw material for biofuel. A 2009 study was conducted under New York City's Department of Environmental Protection (NYCDEP) Jamaica Bay Ecosystem Pilot Project series, during which a survey of 46 shoreline sites around Jamaica Bay was conducted [54]. Data collected included the presence and level of *Ulva* accumulation in the shallow waters of coves, inlets, basins and beaches. While the survey was not comprehensive, it did visit known sites of past accumulation that were accessible for algae harvesting. We report on the harvest and use of Ulva from Jamaica Bay, and show that butanol may be produced from this material. The outcomes of this study should provide a basis for determining the potential for macroalgae to be used in fuel grade butanol production.

Methods

Harvest, drying, and pretreatment via hydrolysis.

NYCDEP has a fleet of garbage and floatable debris, skimmer boats at its disposal. A photograph of a skimmer boat loaded with macroalgae is shown in **Figure 1**.

Figure 1 Approximately 2.0 m3 of Ulva Biomass Collected by Skimmer in 1.5 hours (Photograph by Peter May)

Along with manual shoreline harvests, two skimmer boats and one barge were made available for the New York City Department of Environmental Protection Ulva harvest effort. It is assumed that a skimmer boat had approximately 8.0 m^3 algae storage of capacity before needing to offload its Ulva harvest [55]. This boat capacity, when combined with that of the barge, provided a total of 24 m^3 of algae storage.

Harvested *U. lactuca* was received at the University of Arkansas – Fayetteville in sealable 19.0 liter plastic buckets. Based on observations from early acid hydrolysis studies, the procedure chosen for algae pretreatment was to air dry the biomass, dry grind, and then hydrolyze with dilute acid. Algae was removed by hand from the buckets and scattered onto expanded metal racks in a greenhouse. The biomass was left undisturbed for 3-5 days, then collected and bagged. Several lots of received algae were tested daily for moisture content by gravimetric analysis of the moisture loss during a 6 hour 120 ^oC oven treatment. Air dried alga was ground by several methods. All size reduction steps were done after a visual inspection of the alga lots and removal of foreign items, such as plastic, shells, rocks and pebbles, etc.

After drying and grinding, the algal samples were subjected to acid hydrolysis by placing 100 grams of algal powder per liter of liquid into a digestion vessel. The appropriate amount of sulfuric acid was added to the digestion vessel, which was placed in a steam autoclave and steam heated for the designated time. The autoclave operated at approximately 125 ^oC. A set of studies on the carbohydrate extraction were performed: extraction times of 10, 15, 30, 60, 70, and 120 minutes with 1.0% sulfuric acid; and concentrations of sulfuric acid at 0.5%, 1.0%, 2.0%, and 5.0% (by weight) for 70 minutes. After hydrolysis the pH was adjusted to a value deemed suitable for fermentation (approximately 4.5-5). The media to be fermented was then steam sterilized for 30 minutes at 125 ^oC.

Benchtop ABE fermentation.

The solution of extracted carbohydrates was subjected to a classical ABE fermentation with known butanol producing bacteria. Based on literature results, *Clostridium beijerinckii, ATTC 35702* was selected for study in reactor schemes of the one-step (traditional ABE) process and the two-step process [38]. *C. beijerinckii, ATTC 55025* and *C. saccharoperbutylicum, ATTC 27021* were also used. Cultures grown in the 2.0 liter reactor (1.8 liter working volume) in a media of 6.5 g/L peptone (or tryptone), 3.5 g/L yeast extract, and 20 g/L glucose tested the applicability of the *C. beijerinckii* for the one-step process. A schematic of the reactor is given as **Figure 2**.

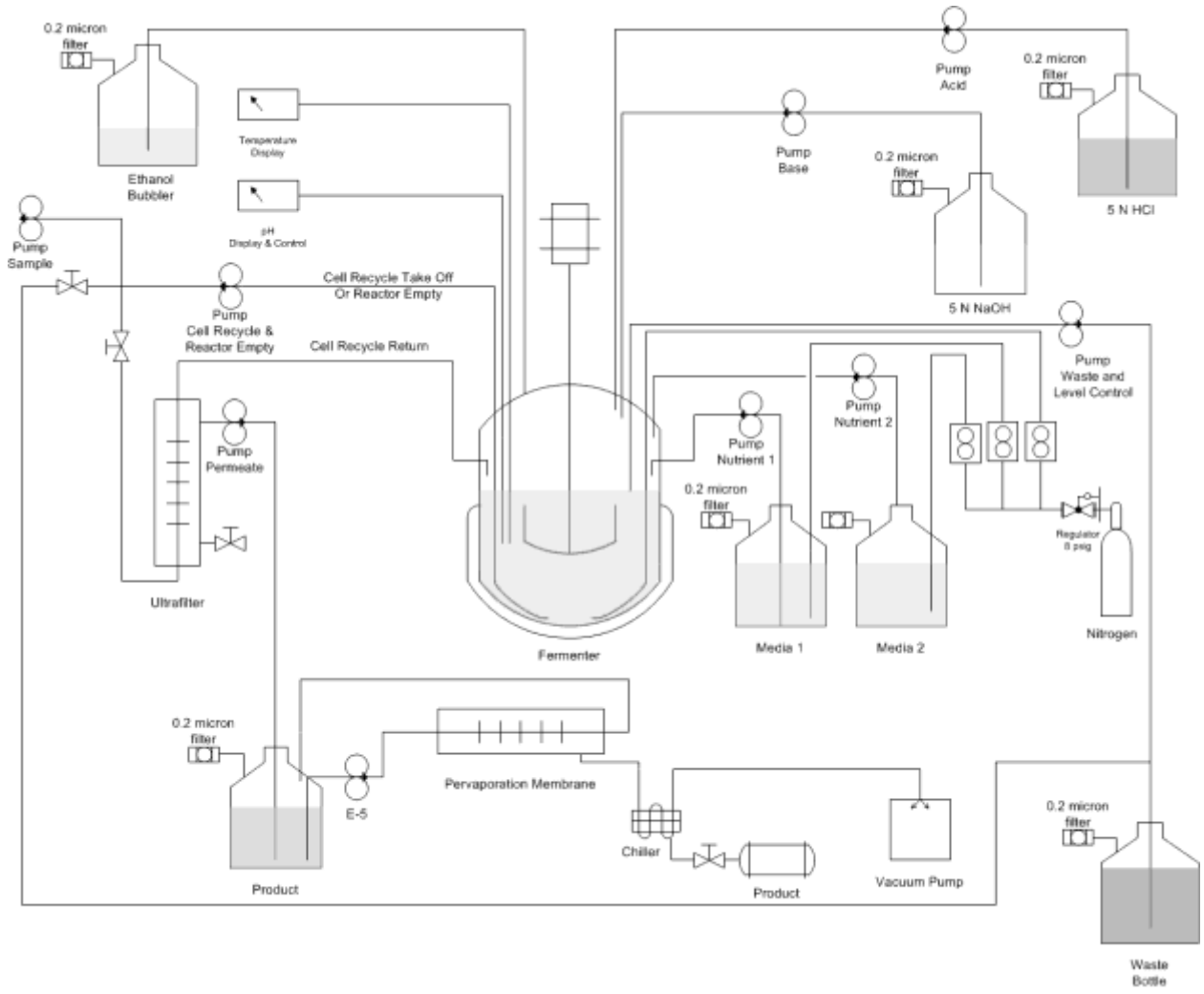

Figure 2: Schematic of Bench Scale Fermentation Reactor

Media was fed to the reactor at approximately 1.5 liters/day. To allow for cell recycle, reactor effluent was passed through a hollow fiber membrane at an approximate rate of 2.5 liters/minute and the permeate take-off was adjusted to approximately 1.35 liters/day. A cell purge of about 0.15 liters/day kept the reactor level constant. Samples were removed daily and were analyzed by HPLC for glucose and butanol content, by spectrophotometer for optical density at 600 nm, and by GC for organic acid and solvent content. The optical density values were converted to

dry cell mass with a predetermined relationship between optical density and dry cell mass determined with an Ohaus drying scale.

Larger scale ABE for butanol production

For the purpose of a proof-of-concept demonstration, one liter of fuel grade butanol was made from *U. lactuca*. The ABE process was scaled to 20 liter batch size by equipping ten 20-liter carboys for fermentation. Two kilograms of dried and ground alga were placed in a carboy. The carboy was filled to 20 liters with 1% sulfuric acid and the alga was hydrolyzed at 125 ^{o}C for 70 minutes. For comparison, some of the carboys were filtered and centrifuged to remove the solid material, while other lots were fermented without solids removal. The pH of each 20 liter lot was adjusted to 4.5 with 10 N sodium hydroxide and sterilized for 30 minutes at 125 ^{o}C. When cooled, the resultant algal sugar medium was sparged for approximately 10 minutes with nitrogen. The lot was then inoculated with *C. saccharoperbutylacetonicum* and incubated for 3-5 days at 37 ^{o}C with intermittent agitation. Butanol was recovered from the fermentation broth by a heterogeneous azeotropic distillation. The azeotrope is broken in the decanter, where phase separation takes place due to the limited solubility of butanol in water. The distillation was done in two steps using the same column/ condenser/ decanter setup.

Benchtop two-step fermentation

To compare the one-step process to the two-step process, sixteen bottles of butyric acid and TYG media of various concentrations were prepared as two sample sets. Set 1 contained 3.3 g/L glucose, 1.1 g/L tryptone and 0.6 g/L of yeast extract. Set 2 contained 15.6 g/L glucose, 5.1 g/L tryptone, and 2.7 g/L yeast extract. All components were measured into the culture bottle with a Mettler-Toledo top-loading balance. Butyric acid was added to the bottle in a range of values. The pH of each bottle was adjusted to 4.8 with 10 N sodium hydroxide, and sterilized at

125 ^{o}C for 15 minutes. When cooled, each bottle was sparged with nitrogen for 2 minutes, and then 2 milliliters of sterile 1.5% sodium sulfide was added as an oxygen scavenger. Each bottle was inoculated with 10 milliliters of a culture of *C. saccharoperbutylacetonicum* grown in 6.5/3.5/20 g/L of TYG media. The bottles were incubated in the lab at room temperature, approximately 21 ^{o}C, for five days. Samples were drawn from the bottles with sterile hypodermic syringes and subjected to butanol analyses in a Waters Breeze HPLC system.

Analysis

Analyses of glucose in the fermentation broth were done by two methods. A Waters Breeze system was fitted with a Shodex SPO810 column. The solvent was a very dilute (0.5 millimolar) sulfuric acid operating isocratically at a flow rate of 1.0 milliliter/minute. This column was selected to measure the solvents from the fermentation broth but it was discovered early in the research that interferences with the organic acids limited its utility to measure acetone and ethanol. A second method was used to measure invert sugars in the hydrolysate and fermentation, namely a spectrophotometric method that employs 3,5 DNS (3,5-dinitrosalicylic acid).

GC analysis of the hydrolysate and fermentation broth was also used to determine organic acids and solvents. The column chosen (Supelco Inc., Bellefonte, PA) was glass (2 m x 2 mm) packed with 80/120 Carbopack BAW/6.6% Carbowax 20M. The oven temperature was programmed from 125 °C to 195 °C at a rate of 10 °C/min after an initial holding time of 7 minutes. A final holding time of 11 minutes allowed sufficient time for the butyric acid to elute. The injector and detector temperatures were both set at 250 °C. Helium was the carrier gas set at a flow rate of 30 milliliter/min.

Results

Harvest

Harvesting of Ulva (Macro) algae is a difficult step because it is not uniform and only grows in certain places in a waterway. However, in areas with large accumulation algal growth is significant enough to make harvesting it for fuel production and nitrogen (N) and phosphorous (P) clean-up feasible. From the 2009 a survey of 46 shoreline sites around Jamaica Bay, it was found that of the 46 sites surveyed 39 sites had Ulva accumulations [54]. Of the sites, 8 were considered heavy in accumulation (160,000 kg/season), 18 were considered moderate in accumulation (20,000 kg/season), and 13 were considered minor in accumulation (not significant enough to harvest). At seven sites, there was no visible accumulation of macroalgae. Only one minor site was considered inaccessible by boat for skimming. A pilot harvest conducted on September 10^{th} 2010 in the Paedergat Basin of Jamaica Bay provided approximately 2.0 m^3 of skimmed and drained *Ulva* in a 1.5 hour time period. These algae were sent to John Miller at Western Michigan for analysis and it was found that the sample was 85% water weight upon harvesting. Further, it was found that the dry sample contained 3.71 wt% nitrogen and 0.184 wt% phosphorous. Given that the bay is approximately 2.85×10^{11} liters, a removal of even heavy accumulation with 2 skimmer boats (160,000 kg/season) would result in less than 0.1 mg/L reduction of nitrogen throughout the bay. Thus, the skimmer boats would help reduce the overall amount of the unsightly macroalgae but would not significantly change the environment of the bay, and algae to fuel would be sustainable from season to season. If more boats were employed the amount of algae harvested could increase, but would still remain relatively low by fuel standards (discussion later). New York City already employs several skimmer boats to clean-up garbage from the bay and so dedicating 2 skimmer boats to algae harvesting is not unreasonable.

The addition of more skimmer boats would depend largely on the level of nitrogen reduction desired as well as co-products (ie, butanol) productivity.

Drying

Hydrolysis of starches to carbohydrates is an important step in ultimate fuel production. However, in order to hydrolyze the inside of algae cells the cell wall must be compromised. Preliminary work (data not shown) indicated that grinding and acid hydrolysis performed poorly on wet alga most likely indicating that the cell walls remained intact. In contrast, air dried alga, after size reduction, yielded suitably sized particles which lead to higher carbohydrate release. It was determined that when layered on the expanded metal screen tables to a depth of about 3 inches, all of the algae dried at about the same rate. A 3 inch layer of algae on the ground dried evenly throughout its thickness but required 4-6 days to reach the target 65% dry weight. If the layer was thicker than 3 inches, the inner algae dried much slower than the top or bottom of the layer.

Samples of Jamaica Bay *Ulva* were subjected to greenhouse drying. **Figure 3**

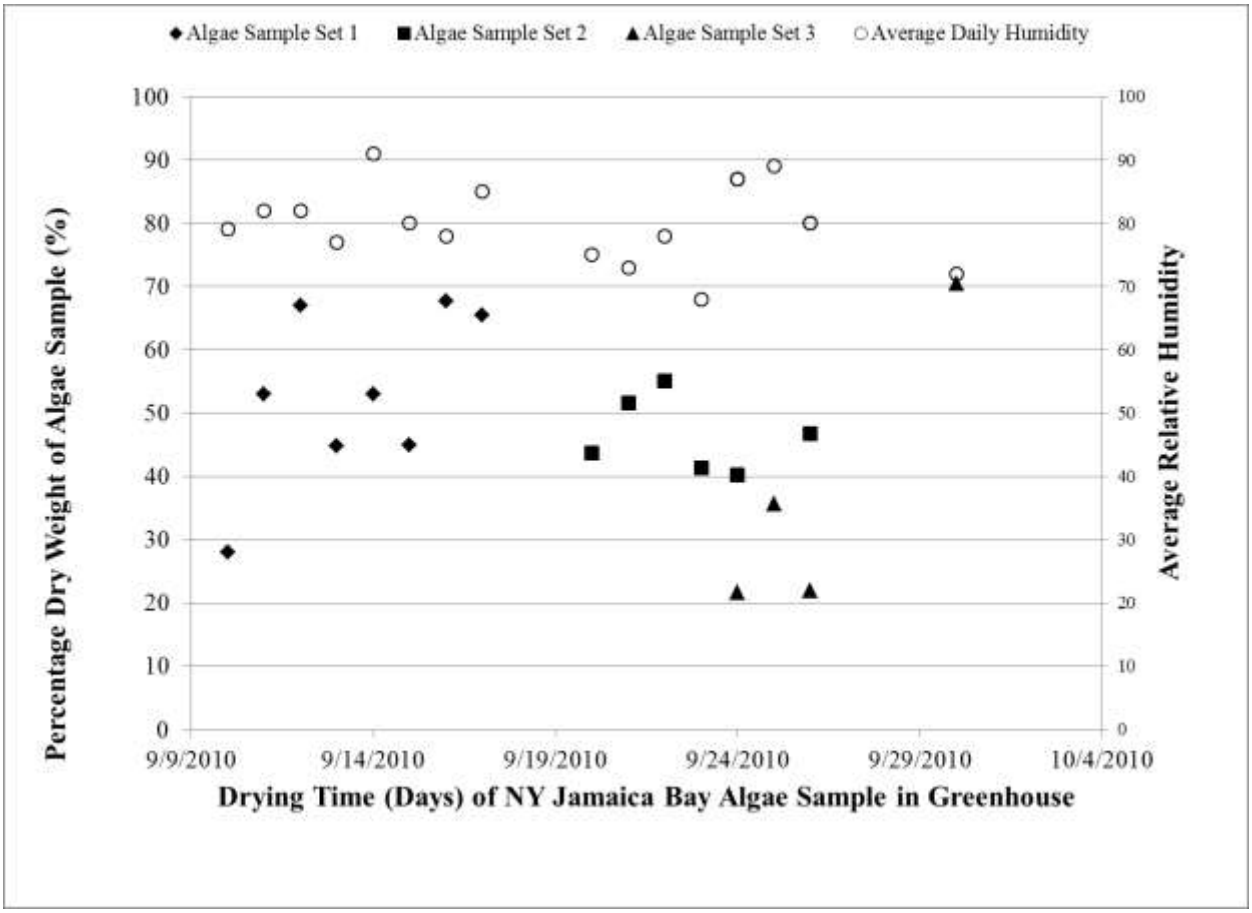

Figure 3: Dry Weight of Algae Samples and Relative Humidity as a Function of Time in Greenhouse

shows the percentage dry weight of the samples as a function of time and shows the average relative humidity as reported for the Fayetteville weather station for the same time periods. Samples 1 and 3 reached the target 65% dry weight within 3-5 days, but sample 2 remained wetter (<60% dry weight) for the 4 day duration of its drying study. This data loosely tracks with humidity and temperature, which ranged from 75F (in the middle of sample set 2) to 90 F (at the end of sample set 3). However, the inconsistency of the air drying data probably suggests that, while air drying is possible, it is difficult with varying weather patterns. However, a long

term study on the drying would help determine optimum conditions. Using these drying data, if the amount of algae collected from the New York site is expected to be 160,000 kg/year per site (24,000 dry kg/year), the density of wet algae is 1000 kg/m^3, the drying layer is 3 inches, there is an 8 month drying season, and the drying cycle is 4 days; approximately 35 m^2, or less than 0.01 acre, will be required to support the drying operation for recovery of algae from 2 skimmer boat harvesters. Since this land area is practical, drying on land without the aid of other heat sources is reasonable. Heat, squeegee, and other methods of drying could be examined but would add to the overall costs of this process.

Hydrolysis

Hydrolysis is necessary to convert starches to fermentable sugars. Because little was known on the effects of acid hydrolysis on macroalgae, a study was performed on the impact of different hydrolysis conditions on the recovery of fermentable sugars. The results of the acid hydrolysis experiments are shown in **Figure 4** and **Figure 5**. **Figure 4**

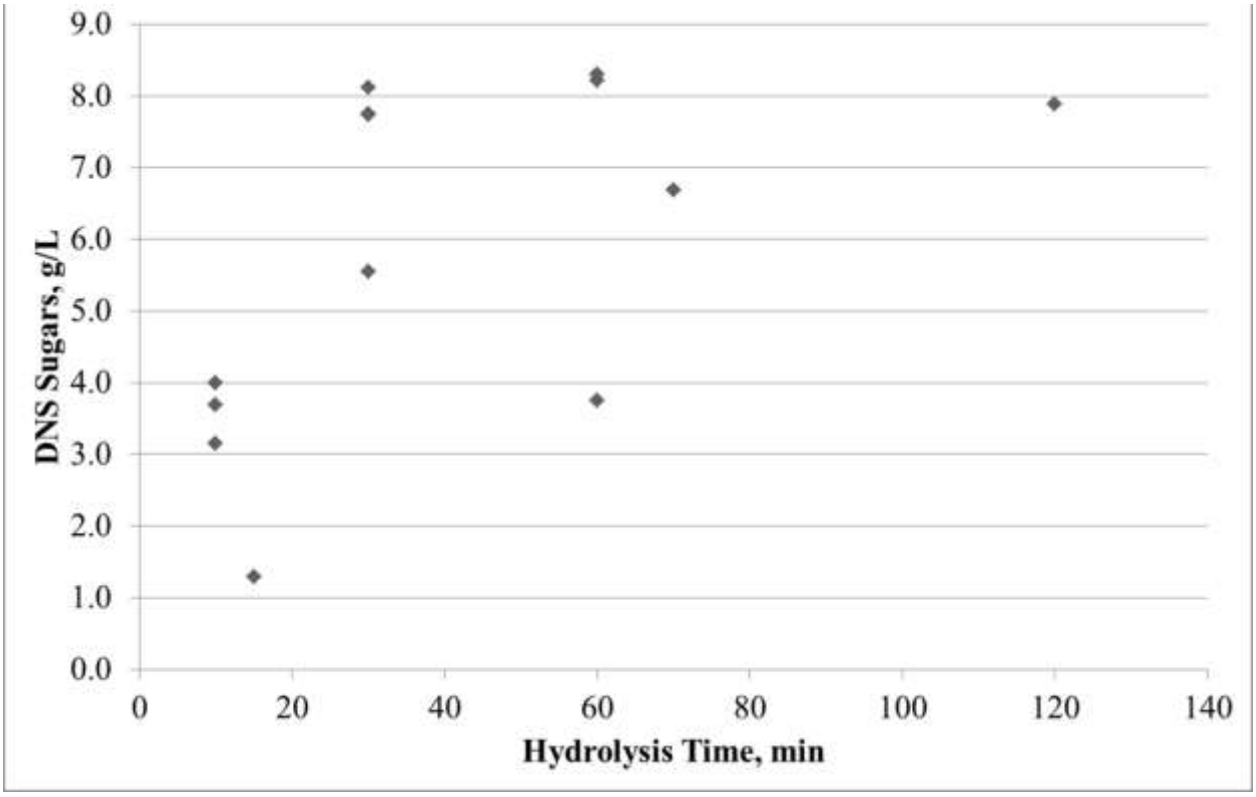

Figure 4: Acid Hydrolysis: Carbohydrate Concentration by DNS as a Function of Extraction Time

shows the concentration of reducing sugars in the hydrolysate as measured by DNS assay when 1% by weight sulfuric acid was used. This study shows that hydrolysis times greater than 30 minutes do not appear to increase sugars release significantly. Reducing sugars in *U. lactuca* obtained at 70 minutes of hydrolysis with 1% sulfuric acid varied from 6 to 18 grams per liter of glucose equivalent. The average of six batches was 15.2±1.9 g per liter. However, it is

important to point out that this assay measures only reducing sugars and so that some sugars measured may not be fermentable while others that are potentially fermentable may not be measured.

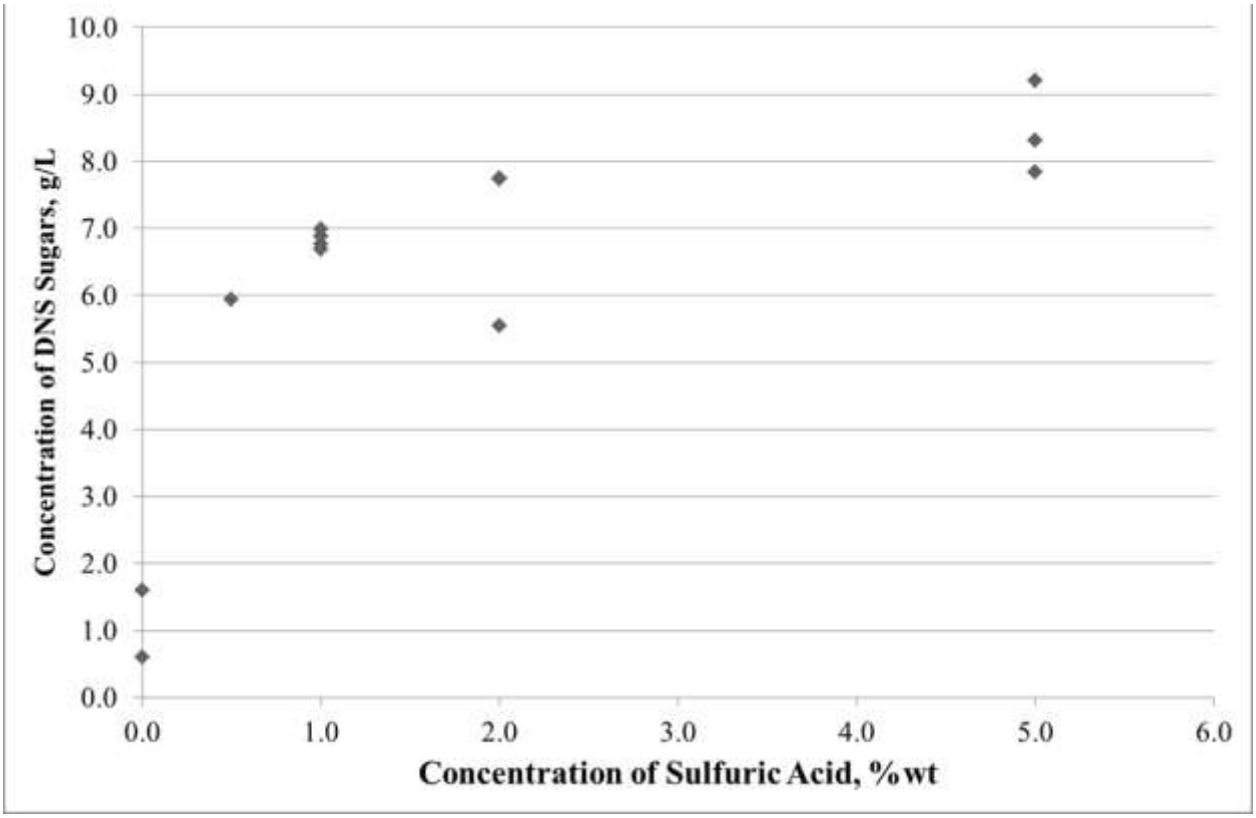

Figure 5: Acid Hydrolysis: Carbohydrate Concentration by DNS as a Function of Sulfuric Acid Concentration

Figure 5 shows the concentration of reducing sugars obtained when subjected to varying concentrations of sulfuric acid for a period of 30 minutes at 125 ^{o}C. These data suggest that acid concentrations greater than 2% do not add significantly to the amount of reducing sugars obtained. For reasons of economics, it is desirable to obtain the highest concentration of reducing sugars possible consistent with the use of the minimum amount of acid and hydrolysis time. Combined, **Figures 4** and **5** suggest processing with 2% by weight sulfuric acid for a

hydrolysis time of 30 minutes. Solids loading for these studies were 100 mg of dry algae per 1 liter of acid since a more concentrated solution resulted in a paste that was difficult to process.

Benchtop fermentation

Two fermentation methods can be used for making butanol; a one-step process (ABE) or a two-step fermentation through butyric acid as an intermediate. Both of these methods were explored when using algae as a feedstock. The first method, or the ABE fermentation, has been used for many years. The results of one-step continuous fermentation with cell recycle on TYG media with *C. beijerinckii* are shown as **Figure 6**.

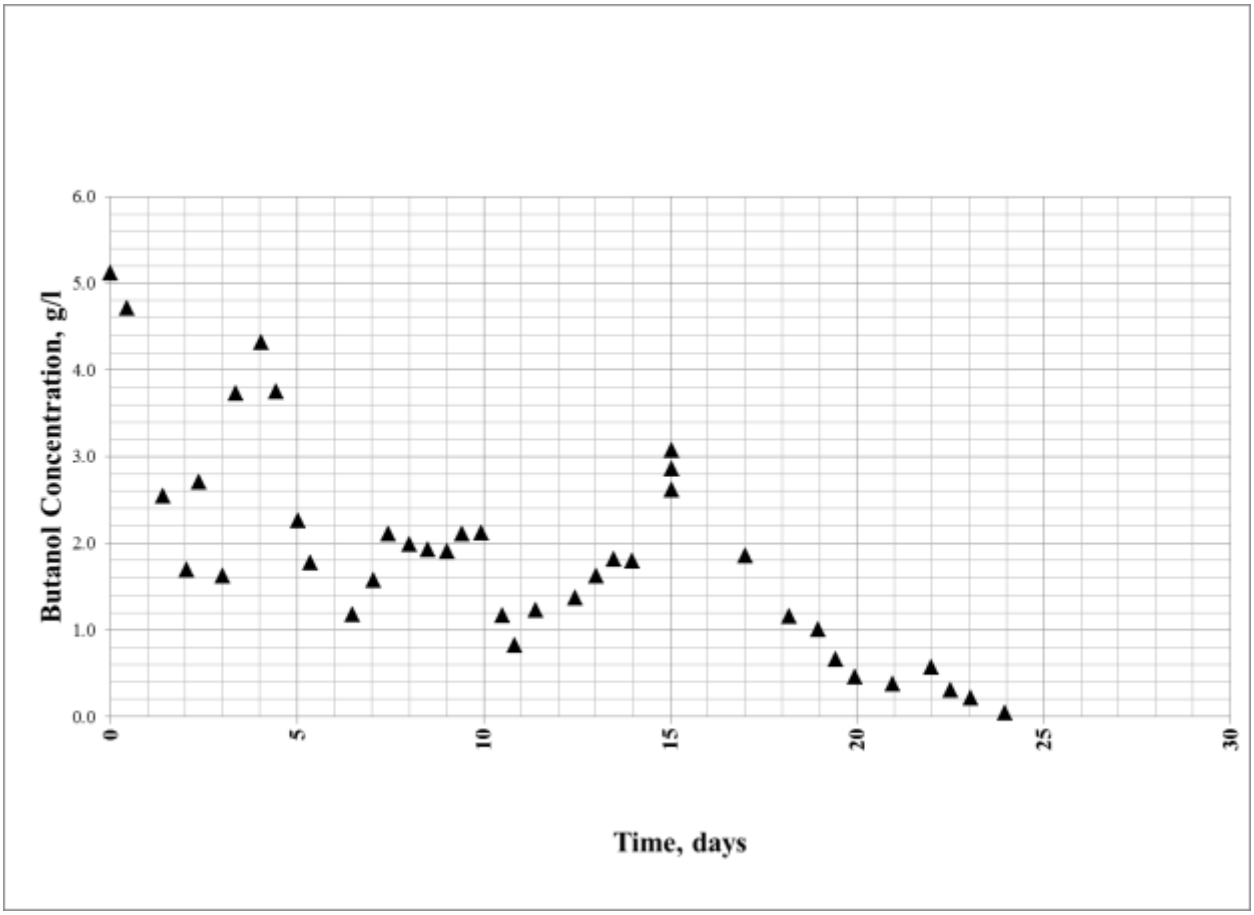

Figure 6: *C. Beijerinckii* Fermentation with PYG at 6.5:3.5:20 g/L

This figure tracks the quantities of the organic acids and solvents leaving the reactor during a three-week period. Values for butanol indicate that the *C. beijerinckii* has high utility for the conversion of glucose to butanol. A strategy was implemented to make the butanol concentration higher to give lower solvent recovery costs. The medium feed rate was kept at a slow rate and the resultant productivity was also low (<5 g/Lday). Productivities of 12 g/Lday were reported in the literature for this system, but these were at higher glucose feeds than are feasible from an algae hydrolysis [49]. A strain of *C. saccharoperbutylacetonicum* was obtained for similar testing. A continuous fermentation run with cell recycle in a 2.0 liter continuous reactor with PYG medium was made. The results of the run are given as **Figure 7**.

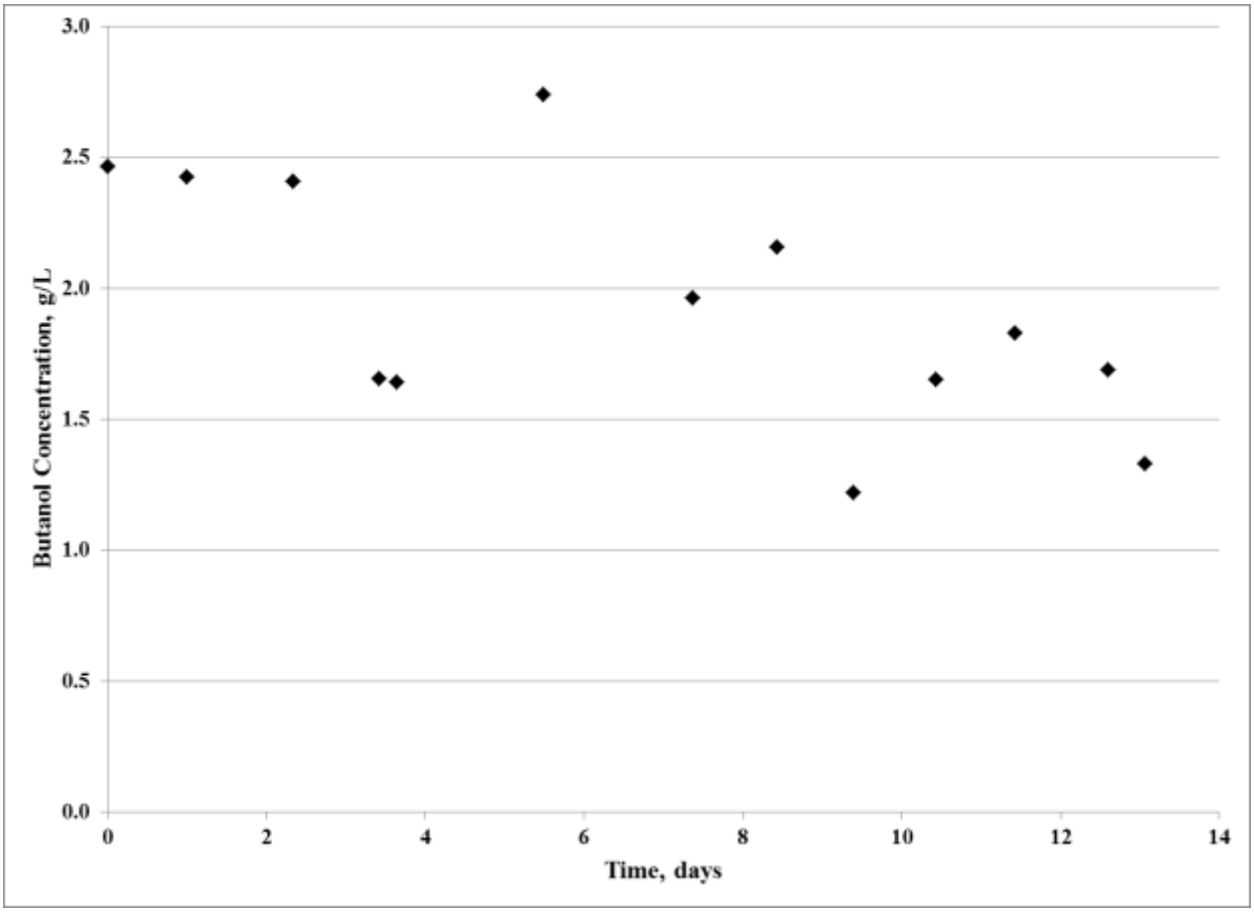

Figure 7: *C. Saccharoperbutylacetonicum* Fermentation with PYG at 6.5:3.5:20 g/L

The butanol concentrations during the course of this fermentation run are similar than those obtained from the *C. beijerinckii*. It should be noted from both of these figures that the overall butanol concentration is slowly decreasing over time. This is because of known toxicity of butanol to cell growth and thus it suggested to us that a batch process, which allows for a significantly higher amount of fresh cell growth, may be more feasible for producing butanol from algae sugars over a long period of time. It was observed during the course of the fermentation run that the *C. saccharoperbutylacetonicum* appeared to be more tolerant to air exposure than *C. beijerinckii.* Thus, since this process was being designed to operate in small scale in the field, *C. saccharoperbutylacetonicum* was chosen as the primary organism for algal sugar solutions because the risk of accidental air exposure exists.

C. saccharoperbutylacetonicum was then used to ferment algal sugar solutions, filtered and non-filtered. It should be noted that the algal solutions were made directly from the hydrolysate **with no addition of salts, yeast, or other growth augmenters**. In a large scale operation, fermentation without medium addition would drastically reduce the costs. After 8 days, the butanol concentrations in all of the samples appeared to reach their maxima (determined by the lack of gas evolution). Data suggests that the presence of solid algal matter in the fermentation broth is inhibitory to the production of biobutanol from *Ulva lactuca* feedstocks, perhaps due to competitive fermentation. Algal samples with solids reached a concentration of 1.0 ±0.2 g/L, while samples without filtering reached a concentration of 4.0±0.2 g/L. Thus, in processing of *Ulva* algae for butanol production all samples should be filtered.

Using a two-step process to make butanol was also explored. The two-step process has the potential advantage of higher yields of butanol but has not been explored with algae as a feedstock. Unfortunately, data indicate that the two-step process offers no advantages with the

bacterial strains tested when algae was used as a starting feedstock. This conclusion was based on the examination of two sets of culture bottles with differing amounts of TYG and butyric acid, as summarized in **Figure 8**.

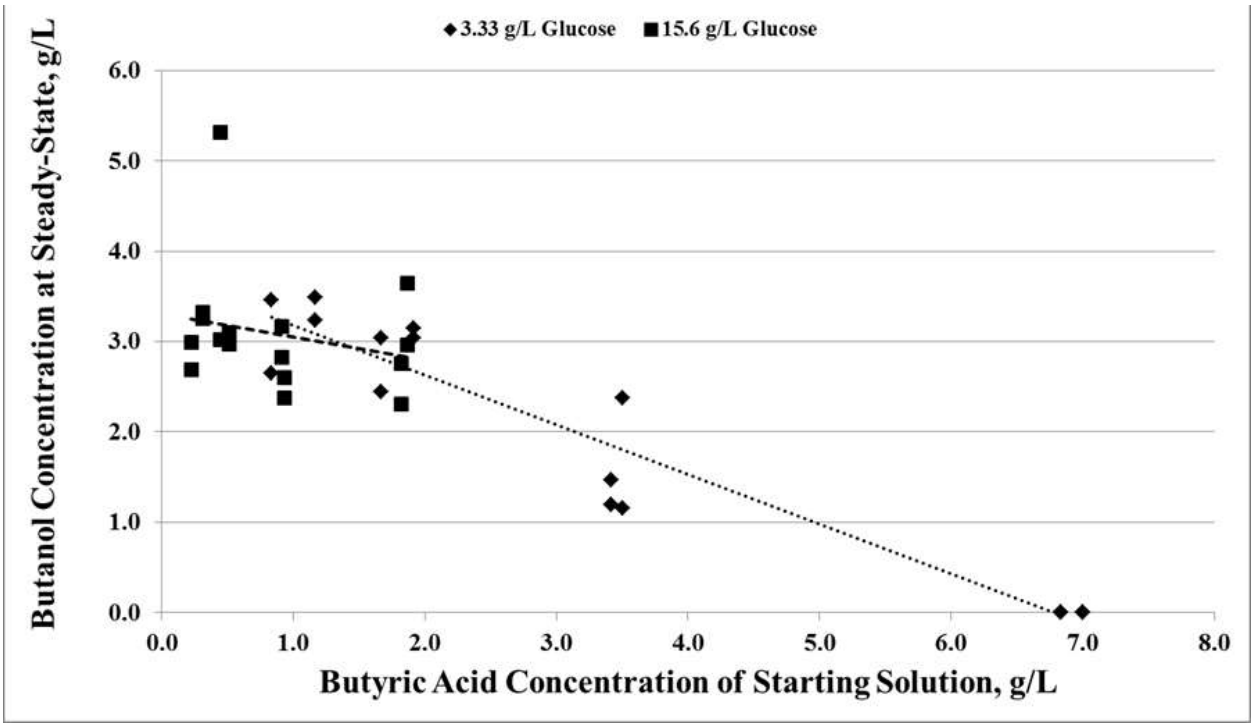

Figure 8: Use of *C. Saccharoperbutylacetonicum* for the Second Step of the 2-Step Process

As **Figure 8** shows, the final butanol concentration is inversely related to the concentration of the butyric acid in the starting solution. This was true for both pure sugar and algae samples. Where the butyric acid concentrations in the two sets were about the same, the final concentrations of butanol were also about the same. This indicates that the final concentrations achieved in both sets were independent of the amount of glucose fed to the bacteria, but were limited by the amount of butyric acid present. The butanol concentrations were fairly constant at about 3 g/L until the butyric acid concentration reached 2 g/L, at which the butanol production decreased. At the highest butyric acid concentration, 7.0 g/L, no butanol

was detected in the culture bottles. All 16 bottles exhibited some increase of turbidity, with the greatest increase occurring in the lower (less than 3 g/L butyric acid). The *C. beijerinckii* would not grow nor produce butanol in media where the butyric acid concentrations were above about 0.5 g/L and in solutions where the butyric acid concentrations were less than about 3 g/L. Similarly, the *C. saccharoperbutylacetonicum* produced butanol in concentrations nearly identical to those produced in batch mode one-step process reactors. Any potential productivity increases obtained from a first step reaction, such as butyric acid optimization in fermentation with *C. tyrobutyricum*, appear to be negated by inhibition brought about by higher butyric acid levels. It is possible that other *Clostridium* organisms, sugar concentrations, etc. will be more tolerant and will better utilize butyric acid but this technology was not seen as appropriate for large scale algae to butanol production at this time.

Pilot Scale Study

The primary purpose of this work was to perform a case study on Jamaica Bay *Ulva* algae and the appropriateness of producing fuel grade butanol from these algae. The large scale conversion of algae to butanol could clean-up the bay as well as providing fuel grade butanol for use in New York City. The first part of this study was to look at a larger scale production of butanol. Approximately 204 liters of acid hydrolyzed media was fermented, with about 1.14 liters of biobutanol recovered via heterogeneous azeotropic distillation. The first distillation step provided approximately 2.5 liters of butanol-rich top phase in the decanter. This collected liquid was subjected to a second distillation which yielded the final product of 1.14 liters. As the 204 liters of media contained an average of 15.2 grams per liter of sugar equivalent, the total media contained approximately 3100 grams of sugar equivalent. In the 204 liters of acid hydrolyzed media, 20.4 kg of dry algae was used giving an overall yield of sugars per algae of 15.2%. Since

the specific gravity of the biobutanol at room temperature is 0.81, 920 grams of biobutanol were formed from the 3100 grams of sugar equivalent, for a yield of about 29% grams biobutanol per gram of sugar equivalent. This number compares favorably with the theoretical number for total solvents from fermentation from glucose, which is 38%, but is higher than the expected butanol value of 23% (assuming a solvent ratio of 3:6:1 acetone:butanol:ethanol). The yield is consistent than the 29-30% reported by Ounine et al for the conversion of pentoses to butanol by *Clostridium acetobutylicum*. Ounine et al suggested that with 5 carbon sugars the ratio is closer to 2:7:1 for acetone:butanol:ethanol [55]. Since HPLC data indicates a sugar composition 27% glucose (6 carbon sugar), 57% arabinose (5 carbon sugar), and 16% xylose (5 carbon sugar), the yield found in the pilot study is not unreasonable.

As a design basis, it was assumed that dry *Ulva* is available at a scale of 24,000 dry kg per year (the value found from harvesting heavy accumulation sites with 2 skimmer boats in a season). This value is based on observation of the bay and values reported by Bruhn [2]. Under these circumstances and based on results obtained during the course of this work, a combination of solar drying, grinding, and acid hydrolysis, produces a carbohydrate stream containing approximately 4,200 kg of fermentable material. The carbohydrate stream could, in principle, be used for a variety of biofuels which include butanol (the focus of this study), ethanol, acetone, or an acid equivalent of the final biofuel. Batch fermentation via the traditional ABE with *C. saccharoperbutylacetonicum* would yield approximately 290 g butanol per kilogram carbohydrates, a mixture of C5 and C6 sugars. Using the butanol yield of 290 g, the theoretical maximum solvent production of 380 g, and a 3:1 ratio of acetone to ethanol as constraints, a biofuel plant producing 3,300 gallon per year butanol as the primary product is predicted from the two skimmer boat harvest. Obviously, this is a low quantity of fuel that would not be

economical to produce and sell in a traditional sense. However, the benefits of bay clean-up combined with fuel generation for powering NYCDEP fleet vehicles may make this project attractive. Another option would be to take the algae and remove it from the bay, dry as shown, and use as a low grade fertilizer. As this project continues, all options should be considered. Further, if harvesting methods can be improved and\or more boats deployed, it is possible that at some point macroalgae from Jamaica Bay will be a sustainable feedstock for butanol. Brune [2] found the volume of the bay was estimated at $2.8x10^{11}$ liters and the rolling average of nitrogen in the bay to be 0.5 mg/L. Using a design basis of lowering the bay concentration 0.1 mg/L on a yearly basis (3.71% nitrogen), it is found that the bay could support up to 415,000 gallons/year of butanol production. This suggests that the possibility of a full scale plant exists.

Conclusions

This work demonstrates that butanol may be made on a pilot scale from algal sugars. Sufficient carbohydrates can be recovered with a 1% acid hydrolysis at 125 ^{o}C for 30 minutes, with an average concentration of 15.2 g/L of reducing sugars in the fermentation feedstock. It was found necessary to remove the solids from the hydrolysate prior to fermentation, as the productivity fell by 75% if this was not done. With the bacterial strains (*C. beijerinckii* and *C. saccharoperbutylacetonicum*) and the algal sugar solutions used, the two step fermentation process offers no apparent advantage over the classic one-step ABE process with algal sugars.

The butanol concentration in the fermentation broth reaches about 4 g/L, which is close to the theoretical value, and compares well (when adjusted for sugar concentration in the media) with values reported in the literature for other systems. Complete fermentation on the basis of grams of sugar to grams of butanol is more nearly reached when the media is stripped of the butanol, either as an intermediate step or continuous in-situ removal, followed by an additional

round of ABE fermentation. The recovery of grams of butanol from grams of reducing sugars in the media during the pilot study was 29%, a value higher than expected.

Acknowledgments

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Chapter 4

Catalytic Production of 1-Octadecanol from Octadecanoic Acid Using Plug Flow Reactor Hydrotreating

Potts TM, Durant K, Hestekin J, Beitle R, Ackerson M (2014)
J Am Oil Chem Soc 91: 1643-1650. DOI 10.1007/s11746-014-2501-7

Abstract

1-octadecanol (stearic alcohol) has uses ranging from lubricants to perfumes. The production of 1-octadecanol from octadecanoic acid (stearic acid) was investigated in a liquid-phase trickle-bed reactor by hydrogenating octadecanoic acid using a Ni/Co/Mo sulfide catalyst. The primary reactions occurring in the reactor were the desired conversion of octadecanoic acid to 1-octadecanol and the subsequent undesired conversion of 1-octadecanol to octadecane. A model was developed to predict these two reactions. The model found to be most useful for this system was a series-parallel reaction first order in octadecanoic acid and 1-octadecanol and pseudo-zero order in hydrogen for both reactions. The activation energies of the first and second reactions were 63.7.8 and 45.6 kJ/mole, respectively. From these values, the conversion of octadecanoic acid and the selectivity to the desired product as functions of temperature, space velocity, and inlet octadecanoic acid concentration were estimated. The model predicts the maximum productivity of 1-octadecanol occurs at higher temperatures with short residence times. Parametric plots show productivity to be ≥0.48 g 1-octadecanol/g octadecanoic acid at 566 ^{o}F and a 0.1 h residence time.

Keywords: octadecanoic acid, 1-octadecanol, hydrogenation, kinetics

Introduction

Low cost synthesis of vegetable oil source alcohols, especially for hexadecanol (cetyl alcohol) and octadecanol (stearyl alcohol), is becoming increasingly important commercially. Much has been reported in the literature on the hydrotreating of the fatty acids, but there are few reports on measuring the kinetic constants for these reactions(1-2). Octadecanoic acid has been studied to a lesser extent than other fatty acids, and the present study is intended to elucidate the kinetics of the hydrogenation of octadecanoic acid while considering the undesired conversion of 1-octadecanol to octadecane.

Adkins (3) first reported the catalytic hydrogenation of vegetable oils using a copper chromite catalyst. Others performed catalytic hydrogenation of acids to alcohols, usually at high temperature and pressure (4-6). Copper chromite catalysts in various forms have been used to produce of alcohols from vegetable and other crop oils (7-8). Because of the limitations of low surface area, low activity, and water stripping inherent in the use of copper chromite catalysts, studies turned to the use of noble metals (9) and multi-component metallic catalysts, especially Ru based catalysts (10-12). We know of no other studies using Ni/Co/Mo catalysts for the conversion of octadecanoic acid to 1-octadecanol.

Ackerson and Byars (13-14) devised a variation of catalytic hydrogenation for the treatment of petrochemicals and other waste products and this process was applicable to 1-octadecanol synthesis. In their process, the solute (octadecanoic acid) was pressurized with hydrogen in the saturated liquid state to minimize equipment size and operating cost. The process, known as IsoTherming®, differs from conventional hydroprocessing in that all of the hydrogen required for the reaction is delivered solvated in the liquid inert diluent to transport the reactants through the catalyst bed. Delivery of the hydrogen solvated in the liquid diluent avoids the need for a large hydrogen recycle system. Solvation is achieved by adding an inert diluent to

the feed and dissolving the required amount of hydrogen into that feed. The reactant mixture then enters the reactor in the liquid state. The amount of inert diluent is determined by the solubility of hydrogen in the inert and the total amount of hydrogen required. The purpose of the liquid recycle is to carry the unreacted hydrogen back to the reactor and to act as a heat sink to remove the heat of reaction and limit the temperature rise through the bed allowing for a more isothermal operation. The reactor used in the present study did not employ recycle, but instead was operated in trickle-bed mode, which is one pass through the reactor. In this case, the reactor behaved as a plug flow reactor.

The hydrogenation of octadecanoic acid progresses in two reactions, shown as reactions 1 and 2.

$$R - COOH + 2H_2 \rightarrow R - CH_2OH + H_2O \qquad (1)$$

$$R - CH_2OH + H_2 \rightarrow R - CH_3 + H_2O \qquad (2)$$

The first of these reactions is the hydrogenation of the octadecanoic acid to 1-octadecanol, and the second reaction is the hydrogenation of 1-octadecanol to octadecane. For producing 1-octadecanol, the first reaction is desired whereas the second reaction is not. A determination of kinetic parameters that describe equations (1) and (2) was sought to develop a simple model for the IsoTherming® process as a function of parameters typically adjusted for optimal conditions (temperature, pressure, feed). Such a modeling effort forms the basis of a sensitivity analysis to predict productivity (mol alcohol formed / mol acid fed).

Experimental Procedures

Experimental determinations of the rate constants and hydrogen reaction order were performed in a series of hydrogenation reactions of octadecanoic acid. A schematic of the

reactor, a pilot-scale IsoTherming® catalytic hydrogenation reactor used for the study is shown in **Figure 1**. The catalyst selected was nickel-cobalt-molybdenum mixture on trilobal

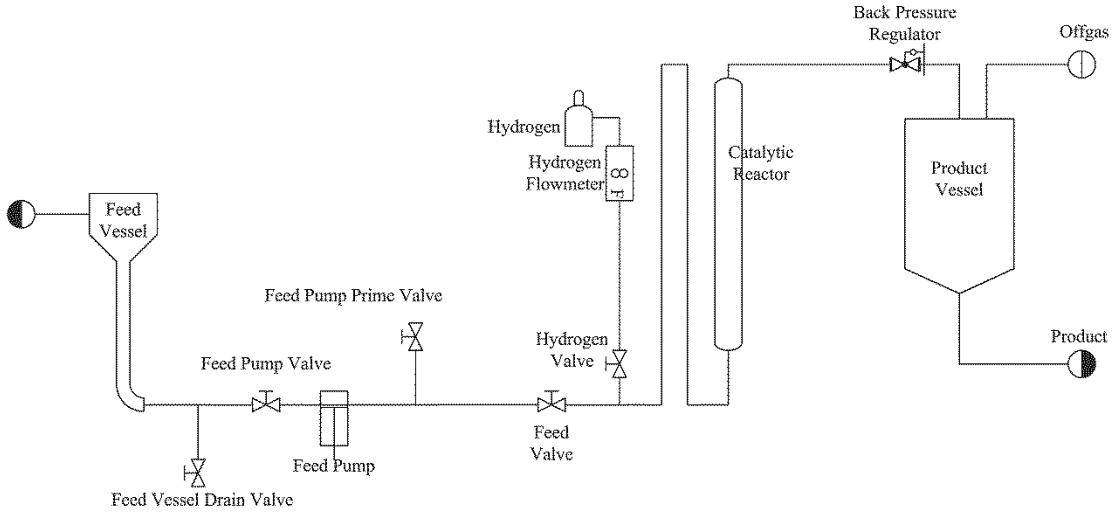

Figure 1: Reactor Schematic

aluminum oxide. The reactor was a 5/8" 316 stainless-steel tube with stainless-steel screen end caps. The lower end was filled with a short layer of small glass balls to hold the catalyst in place. 90 mLs of packing was slowly added with vibration and tamping. The catalyst was then topped with a second layer of glass balls. The reactor was installed in the system, and once leak tight, the catalyst was activated by sulfiding with 10% butanethiol in light paraffin solvent over a period of approximately 8 h.

It was necessary to solvate the octadecanoic acid in warm diluent so that it could be pumped into the system. The diluent chosen was a mixed light-paraffin solvent. The feed stream consisted of the octadecanoic acid and light-paraffin solvent mixture at 5 wt% octadecanoic acid. The reactor temperature was varied from 120 to 232 ^{o}C, while the space velocity, the reciprocal of the residence time of the feed in the reactor, was varied between 0.5 and 2.0 h^{-1}. The hydrogen flow rate was varied so that it was approximately eight times (by mole ratio) that of the octadecanoic acid. This was done so that hydrogen would not be the limiting reactant. Sampling

was done after temperatures and pressures reached steady state and approximately two system volumes (about 200 mLs) of feed solution had passed through the system. Samples were approximately 100 mLs in size. Once started, the system was operated continuously until all samples were completed.

Analysis of the feed material and each of the various collected product samples was done on an HP5890 gas chromatograph (GC). The GC was equipped with a 30 m HP-1 capillary column (Agilent Technologies, Santa Clara, CA, USA). Detection of the sample was achieved with a flame ionization detector. Data acquisition and reduction was done with the Agilent ChemStation software installed on a personal computer.

Reactions 1 and 2 were used in a plug flow reactor model to determine the concentrations of octadecanoic acid, C_A, hydrogen, C_B, 1-octadecanol, C_C, and octadecane, C_D. Various kinetic models were tested to represent each reaction. The coupled differential equations for the rate of concentration changes for this system are shown as Eqs. 3-6:

$$\frac{dC_A}{dt} = -\frac{k_1 C_A C_B^n}{denominator} \tag{3}$$

$$\frac{dC_B}{dt} = -\frac{k_1 C_A C_B^n}{denominator} - \frac{k_2 C_C C_B^n}{denominator} \tag{4}$$

$$\frac{dC_C}{dt} = \frac{k_1 C_A C_B^n}{denominator} - \frac{k_2 C_C C_B^n}{denominator} \tag{5}$$

$$\frac{dC_D}{dt} = -\frac{k_1 C_C C_B^n}{denominator} \tag{6}$$

where t was the time that the reactant spent in the reactor, k_i were the two rate constants, n was the reaction order with respect to hydrogen. Equations (3) – (6) include the provision for chemisorption, with the denominators capable of representing adsorption of all species:

$$\text{denominator} = 1 + \sum K_i C_i \quad (7)$$

Note that this representation of the system assumes reactions on the surface of the catalyst govern the conversion of acid to alcohol and alkane, respectively. Alternate forms would include external or internal mass transfer limitations, or a combination thereof, owing to the possibility of boundary layer formation or diffusional limitations about or within a catalyst particle, respectively.

The reactions were assumed first order with respect to octadecanoic acid and to 1-octadecanol as suggested by Patterson (15). The Arrhenius equation was used to to examine temperature effects:

$$k_i = a_i e^{-\frac{E_i}{RT}} \quad (8)$$

where ai were the frequency factors for the two reactions, Ei were the activation energies, R was the ideal gas constant and T was the absolute temperature.

A MatLab® (The MathWorks, Inc., Natick, MA, USA) program was written to determine the rate constants from the system of differential equations that minimized a least squares criteria (lsq):

$$\text{lsq} = \sum (C_{i,\text{reactor exit}} - C_{i,\text{predicted}})^2 \quad (9)$$

where the reactor exit concentrations are compared to those values predicted from the model. To perform this least square minimization, 17 sets of conditions (all at 2000 psig) were integrated from t=0 to t=tau, defined as the residence time in the reactor.

Finally, the values of k_i, a_i, and E_i generated from the first MatLab® routing were used as input for a sensitivity analysis to investigate the space defined by tau, temperature, and pressure, in all 44 sets of conditions. In the above treatment, the value of the hydrogen concentration in diluent was required. In the absence of direct measurement capability, the hydrogen concentrations were estimated with an Aspen (AspenTech, Burlington, MA, USA) simulation. This simulation was tested for validity by comparing results from the simulation to experimental values reported by those determined by Park (16). Good agreement with these values was obtained using a multicomponent flash calculation with Peng Robinson thermodynamics. The Aspen simulation molar fractions of hydrogen in alkane agreed with the experimental values within 10%. Based on this finding, we assumed that the Aspen simulation could be used to generate the hydrogen molar fractions at the experimental conditions.

Results and Discussion

All octadecanoic acid was converted to 1-octadecane when the temperature was above 177 ^{o}C at the space velocities used, and those data points were deemed not useful for the modeling. Temperatures in the range of (300-450^{o} F) and were examined at three pressures (700, 1400 and 2000 psi). The values tested for the reaction order for hydrogen, n, were -1/2, 0, 1, 2, and ½, with provision for chemisorption by inclusion of a denominator typical of a Hougan-Watson expression. Testing all of the permutations of (3) – (6), i.e. different n, inclusion or absence of a denominator, led to a "best fit" of first order in all species (acid, alcohol, and hydrogen). **Figures 2 and 3** are Arrhenius plots that indicate the fit used to

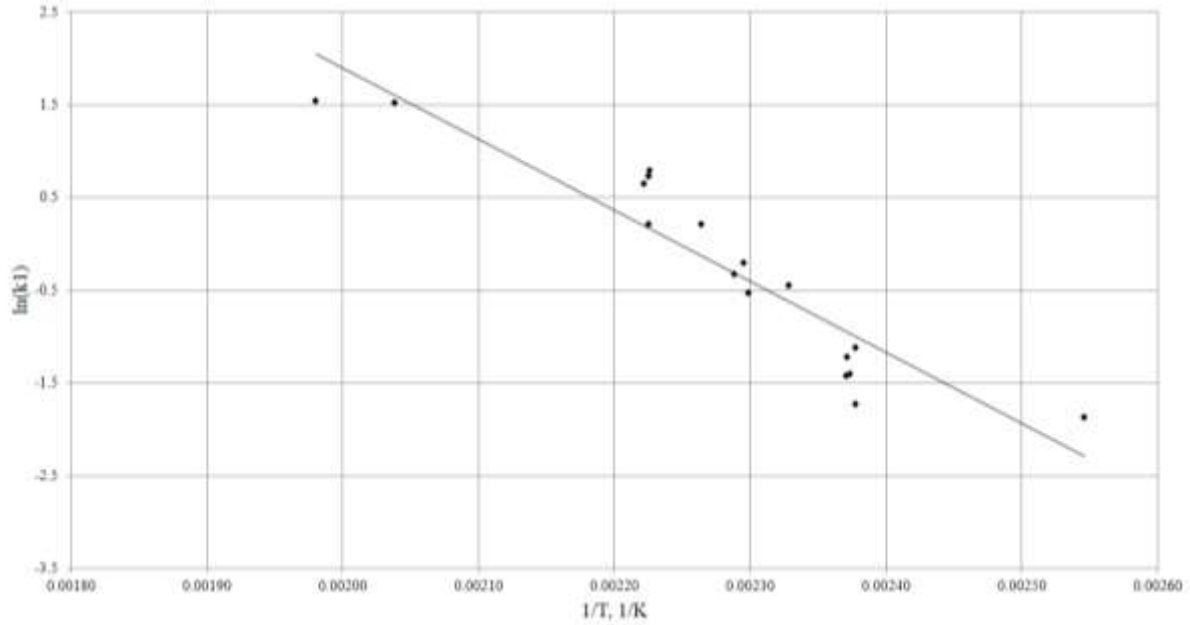

Figure 2: Plot of ln(k1) versus 1/Temperature

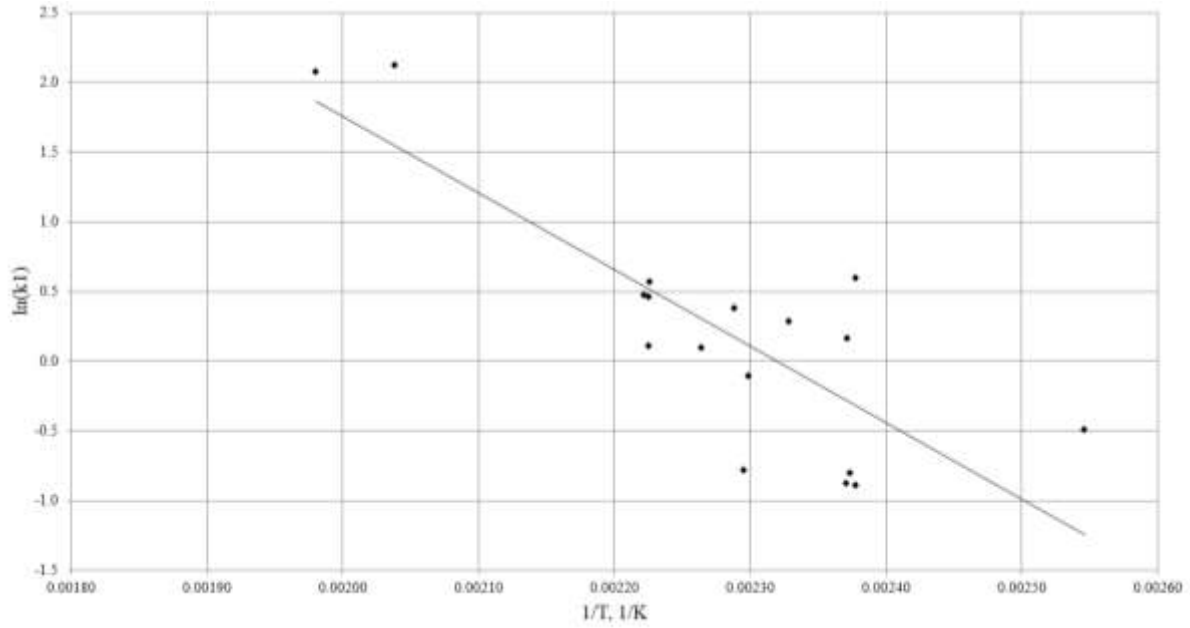

Figure 3: Plot of ln(k2) versus 1/Temperature

calculate E_i for each reaction, with the activation energies for the two reactions given in **Table 1**. The activation energy of the first reaction was very comparable to those obtained by

Table 1: Arrhenius Constants for the Hydrogenation of octadecanoic Acid

	Frequency Factor, s^{-1}	Energy of Activation, kJ/mol
Reaction 1 (dehydration of octadecanoic acid)	3.20×10^{7}	63.7
Reaction 2 (dehydration of 1-octadecanol)	3.81×10^{5}	45.6

Chen et al. (18) for lactic acid (56.6 kJ/mole) and propionic acid (67.1 kJ/mole). Chen and coworkers did not consider the second reaction, however, we found that the second reaction happens to a significant degree and must be considered.

Figures 4 – 7 were used as figures of merit to indicate the effectiveness of the model to describe various effluent concentrations of acid, alcohol, alkane, respectively. In the

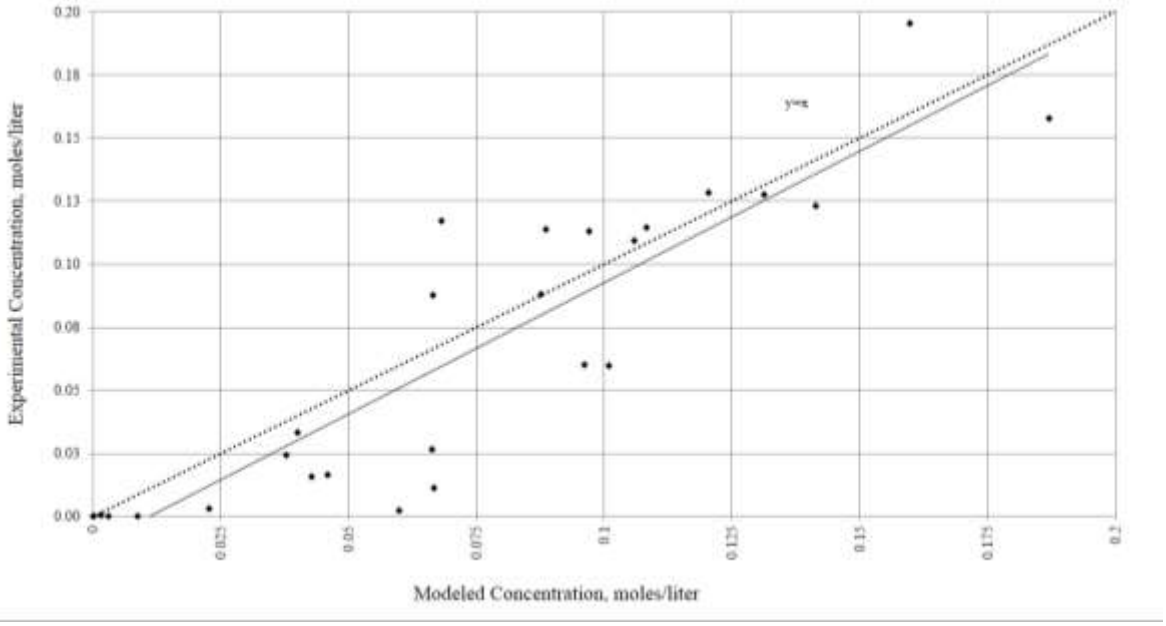

Figure 4: Comparison of experimental versus predicted final concentrations of octadecanoic acid

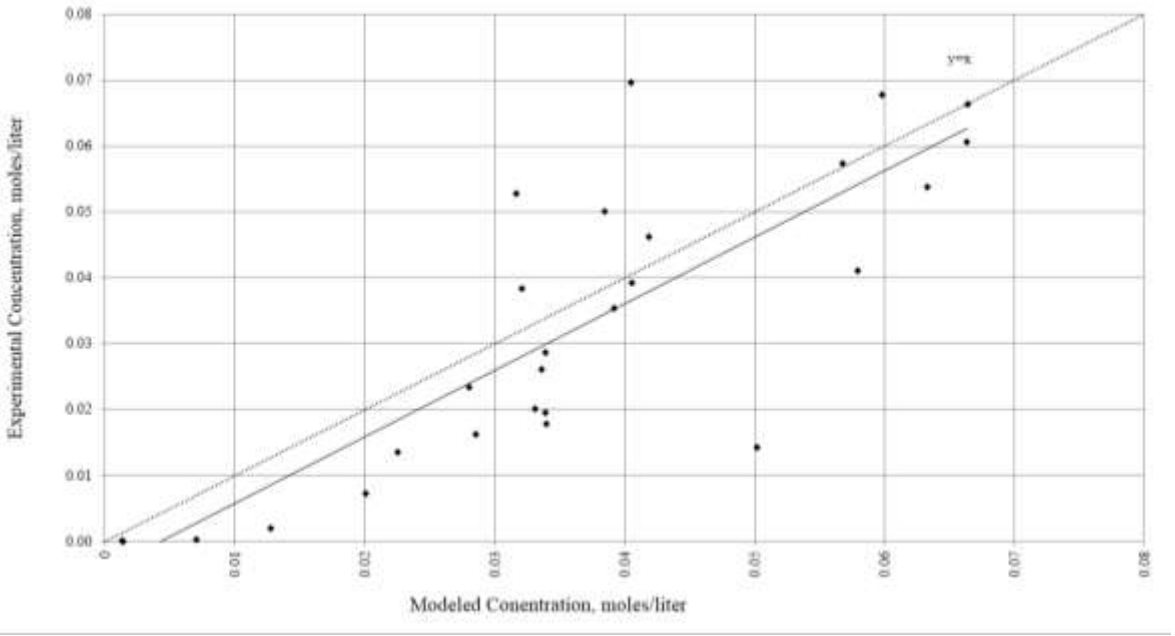

Figure 5: Comparison of experimental versus predicted final concentrations of 1-octadecanol

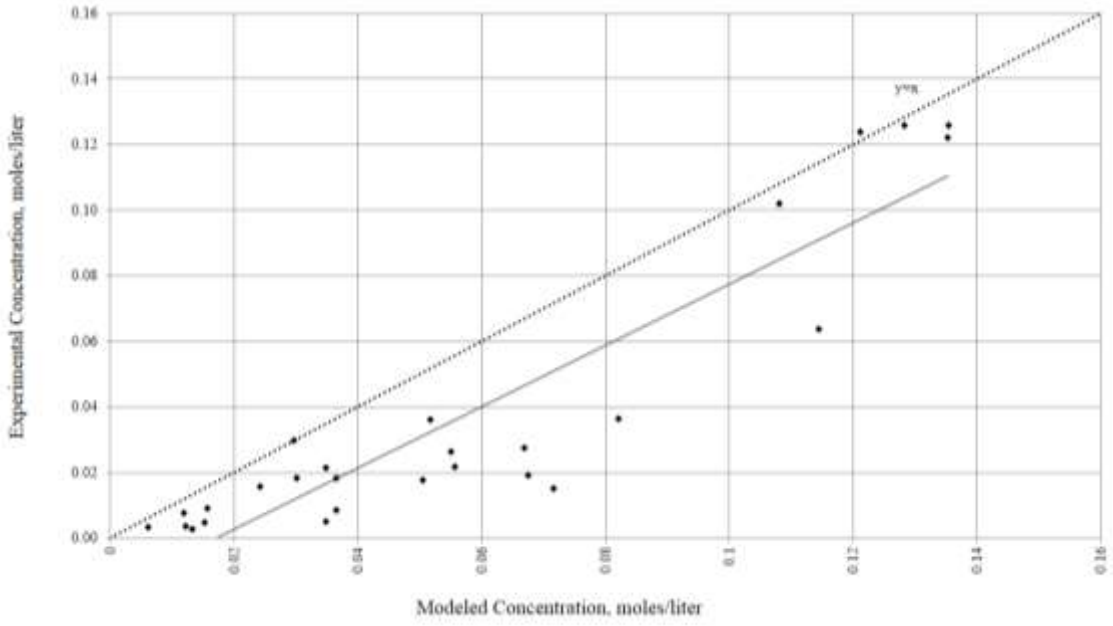

Figure 6: Comparison of experimental versus predicted final concentrations of octadecane

figures, perfect agreement between model and experiment would be indicated by a direct variation (y=cx) with c equal to unity. Good agreement for all three species were observed by comparing the line y=x with Experimental vs. Modeled values. The figures have slopes equal to

1.01 (acid), 1.01 (alcohol), and, 0.93 (alkane), which are close to the desired value of 1.0. In its present form, the model over predicts the three major species of interest; this is likely to have occurred because other byproducts could have been formed but were not accounted for in the model. Nevertheless, good agreement between experimental and calculated values allowed for a sensitivity analysis to be performed.

It is interesting to note that Patterson (15) reported a pseudo-zero order dependency for the hydrogenation of fats and oils, which, upon quick examination, would conflict with this study. Since the value of n (hydrogen order) determined to be the best fit of the data was n=1, and the IsoTherming® process is designed to run with excess hydrogen as evident by the presence of gas phase throughout the reactor, one could present k_i as the product of the rate constant and liquid phase hydrogen concentration. For the case of IsoTherming®, rate constants that are pseudo-zero order for hydrogen are easily obtained from our data and the Aspen simulation (data not shown). Hydrogen concentration independence was further tested by estimating the Biot number for a catalyst particle. The Biot number is defined by:

$$Bi = \frac{X_L \bar{k}_c}{D_{TA}^e} \tag{9}$$

where

B_i is the dimensionless Biot number

X_L is the characteristic length, [m]

D_{TA}^e is the mass diffusivity, [Pa m^2/s]

$\overline{k_c}$ is the mass diffusivity, [m/s], as given Eq. 10:

$$\bar{k}_c = \frac{\dot{n}_A}{A \Delta C_A} \tag{10}$$

In Equation (10),

$\dot{n}_A$ is the mass transfer rate, [moles/s]

A is the effective mass transfer area, [m^2]

ΔC_A is the concentration difference driving the diffusion, [moles/m3]

Measurement of the catalyst particles determined that they were, on average, 0.52 mm by 2.02 mm long and with a mass of 0.0043 g so that

X_L= 2.5x10^{-4} m (the radius of one catalyst particle)

A = 3.17x10^{-6} m^2 (the surface area of one catalyst particle)

D_{TA}^{e}= 3.11 Pa m^2/s (tabulated value from Wicks et al. (17)

As a limiting (maximum) case, one flow rate of hydrogen going into the reactor was 3.54x10^{-5} mole/s and there was 66.7 g of catalyst in the reactor, so the molar feed rate associated with one particle was $\dot{n}_A$ = 2.36x10^{-9} mole/s. For our reactor, ΔC_A =600 mole/m^3, the maximum change in concentration of the hydrogen in the reactor assuming that all acid was converted to alkane. Thus, the mass diffusivity was 1.24x10^{-6} m/s and the Biot number was 0.001375. Since this number is very small, we expect the hydrogen concentration to be essentially constant in the liquid phase. This low value indicated that the maximum possible consumption of hydrogen within a catalyst particle was greatly exceeded by the hydrogen available in the liquid phase for the reaction. One possible concern with the above calculation was the use of the particle radius as the characteristic length. Since it was beyond the scope of this work to define the boundary layer associated with mass transport to the catalyst, geometric considerations for the maximum thickness of such a layer to be on the order of the catalyst particle size. We expect the actual boundary layer to be much smaller because of the superficial velocity of the liquid through the reaction, with the mass transfer coefficient calculable with a variety of correlations.

The above argument supporting the fact that hydrogen, treated either as a first order or pseudo-zero order component, manifests itself as an excess reactant permits one to strongly examine the kinetic expression describing IsoTherming® with respect to the acid feed concentration. Based on the Biot number calculations and Arrhenius dependency of the data, it is likely that the Axens catalyst was operated under conditions that were not diffusion limited since no break in the slopes of Figures 2 and 3 were observed. The values of k_i determined by the model are the observed reaction rate constant, the product of the intrinsic value times and the interparticle effectiveness factor ($k_{intrinsic}*\eta$). In the absence of catalyst physical property data, the effectiveness factor cannot be calculated based. Nevertheless, the k_i values can be used to examine the sensitivity of the system to various combination s of temperature, pressure and feed combinations since the value of η for a first order reaction is independent of external concentration.

The 1-octadecanol is the desired product and maximization of this product can be studied with parametric plots based on the developed model. One such parametric plot is shown in **Figure 7**. The trends shown in **Figure 7** indicate that better productivity was achieved at higher temperatures with higher space velocities, i.e. shorter residence times in

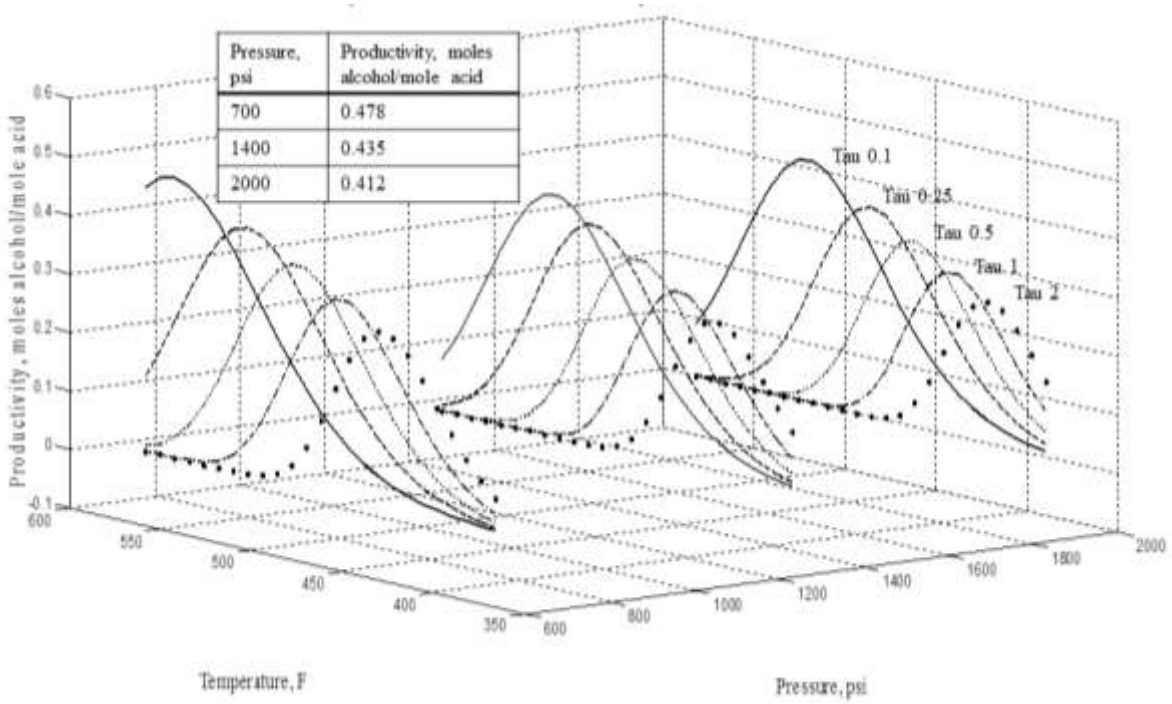

Figure 7: Predicted productivity of 1-octadecanol per gram of octadecanoic acid at varying temperatures and space velocities

the reactor. Although our experimental work found complete conversion to the undesired product octadecane at temperatures above 177 ^{o}C, this was at relatively long residence times. The trend analysis presented in Figure 7 predicts that optimum productivity in this reactor for 1-octadecanol would occur at 566 ^{o}F with a residence time of 0.1 hs. Further investigations will explore the data space around this set of conditions to confirm that the model developed can predict conditions of high productivity. Minor modifications to the hardware will enable these investigations. Thus, we have shown that by understanding the reaction kinetics of both reactions one can achieve high productivity without having to change catalysts.

Conclusions

1-Octadecanol was made in a liquid-phase trickle-bed catalytic reactor by the catalytic hydrogenation of octadecanoic acid. A model of the parallel-series reactions was generated and correlated to experimental values of hydrogenation conducted in a plug flow reactor at pressures

of 700, 1400 and 2000 psig (13.8 MPa) hydrogen and at varying temperatures and space velocities. The model most useful for this system was found to be a series-parallel reaction first order in octadecanoic acid and pseudo-zero order in hydrogen. The Arrhenius frequency factors and the activation energies for both reactions have been estimated. The activation energy of the first reaction was 63.7 kJ/mole and the activation energy of the second reaction was 45.6 kJ/mole. From these values, the conversion of octadecanoic acid and the selectivity to the desired product as functions of temperature, space velocity, reactor pressure, and inlet octadecanoic acid concentration were presented. The model predicts maximum productivity of 1-octadecanol per mass of octadecanoic acid occurs at higher temperatures with short residence times.

Acknowledgements

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Chapter 5

A Biological Fermentation of Biomass to Butyric Acid Followed by Catalytic Hydrogenation of the Butyric Acid to 1-Butanol

Abstract

A Langmuir-Hinshelwood-Hougen-Watson (LHHW) differential rate model with the assumption that effects of adsorption/desorption were small is developed for the kinetics of the hydrogenation of butyric acid to 1-butanol. The hydrogenation reactions modeled are the series-parallel reactions of the butyric acid hydrogenated to 1-butanol followed by subsequent hydrogenation of the 1-butanol to butane. Experimental sample sets of the hydrogenation reactions were obtained in a liquid phase trickle-bed plug flow reactor. Concentrations of the reactants (excepting hydrogen) and products were determined by gas chromatography. The hydrogen concentration was assumed to be saturation concentration as calculated by ChemCad (Chemstations, Houston, TX) at the conditions of temperature and pressure for each data set. The model was fitted to several sets of data in the temperature regime of 300-400 F and pressures of 700-1000 psig by adjusting the reaction rate constants to a least squares minimum deviation between the modeled and experimental values. The fit between the modeled and experimental values was not good. A perusal of the mass balances (Table 2) indicates that the balance is good when the conversion of butyric acid is small, but carbon is apparently lost with higher conversions of butyric acid. Failure of the carbon molar balance can be explained several ways and future work with the potential of closing the molar balance and allowing for proper estimation of rate constants is discussed.

Introduction

Butanol, in two isomeric configurations, has several attractive properties with regard to its use as an automotive fuel. Like ethanol, butanol is an oxygenated fuel additive. Compared to ethanol, butanol has higher energy content, 36.5 MJ/kg versus 26.8 MJ/kg. Butanol is less volatile, with a vapor pressure at 70 F of 0.63 psi versus 2.25 psi for ethanol (Potts, 2010). Butanol is less corrosive than ethanol, and can be pipeline transported. The lower corrosivity also allows much higher blends with gasoline for vehicular use, whereas higher concentrations of ethanol in gasoline can damage conventional engines and their ancillary systems. Current processes for the production of butanol, especially from biomass, are expensive compared to those for ethanol when compared on a basis of moles produced. However, when compared on the basis of lower heating value (LHV), a process based on the science described in this paper becomes much more attractive (**Table 1**).

Table 1: Estimated Lower Heating Values per gram of sugar feedstock for various processes

Process	LHV, KJ per gram of sugar consumed
Cellulosic Bioethanol (Sedlak and Ho, 2004)	10.2
Classical ABE (Quershi, 2008)	8.3
This process (Potts, 2011 & Du, 2011)	12.3

The world market for 1-butanol in 2012 was 850 million gallons (Yang, 2010). Very little of this is currently used for fuel applications, but is rather used as a solvent or as a reactant to make higher value chemicals (Hernandez, 2001, Gu, 2010).

Most of the 1-butanol produced world-wide is produced in a two-step synthesis. The first step is the hydroformylation of propylene to butanal (also known as butyl aldehyde or butyraldehyde) (Love, 1979).

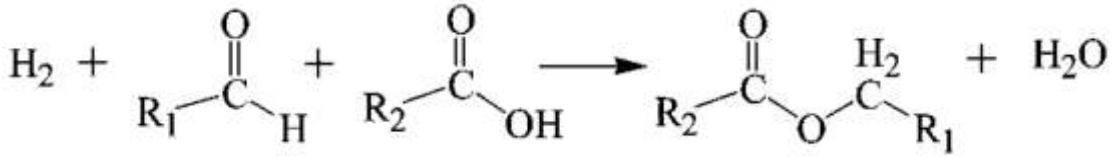
(1) $CH_3CH = CH_2 + CO + H_2 \xrightarrow{catalyst} CH_3CH_2CH_2CHO$

The second step is the catalytic hydrogenation of the butanal to 1-butanol (Unruh, 1999).

(2) $CH_3(CH_2)_2CHO + H_2 \xrightarrow[catalyst]{} CH_3(CH_2)_2CH_2OH$

A major problem with the industrial process is the tendency for the butyric acid and butanal to react to form the butyl-butyl ester (Tang, 2008).

(3)



A second issue is the relatively high cost of performing two high temperature catalytic hydrogenation reactions in sequence.

The conversion of biomass, especially waste biomass, to butanol may hold the promise of low cost fuels and solvents. A review of the history and current status of the production of bio-butanol may be found in Hestekin et al. (Hestekin, 2013). The production of butanol by the ABE (acetone-butanol-ethanol) fermentation process is hampered by the low titer of the fermentation and the high cost of removal of the butanol from the very large amounts of accompanying water (Hestekin, 2013).

Electrodialysis and electrodeionization (EDI) have been shown to remove butyric acid from fermentation broths with high efficiency and low cost (Du, 2012). The availability of highly concentrated, low cost butyric acid allows the consideration of a novel hybrid biological process combined with a traditional chemical process for the conversion of biomass to butanol (Potts,

2011). The first step of this hybrid process is the fermentation of biowaste to butyric acid, using Clostridium tyrobutyricum, as described by Du (Du, 2012). The butyric acid will ionize slightly and the butyrate ion can be continuously removed from the fermentation broth with high efficiency by membranes employing electrodialysis or electrodeionization. The EDI process yields concentrated butyric acid and the remaining water can be removed by molecular sieves, or since the azeotrope is broken by the EDI, by distillation.

With concentrated butyric acid available, it should become economically feasible to convert the butyric acid to 1-butanol by catalytic hydrogenation. This paper reports the study of this hydrogenation reaction. Adkins reported the hydrogenation of various vegetable oils over a copper chromite catalyst (Adkins, 1931). Since that time, a plethora of researchers have investigated a multitude of hydrogenation reactions. In particular, carboxylic acids have been reported to have been catalytically hydrogenated to corresponding alcohols. (Richardson, 1945, Willemart, 1948, Hoffmann, 1955, Aly, 2001, Nakaoka, 2003, Manyar, 2010, Potts, 2014). Because the rather large exotherm of these hydrogenation reactions, it has proved advantageous to perform the hydrogenation in the liquid phase (Tahara, 1997). Ackerson and Byars developed a plug flow reactor operating at high pressure and moderate temperatures for the conversion of a variety of waste fats to valuable saturated products (Ackerson, 1998, Ackerson, 2005). Singh and Vannice reviewed the kinetics of the liquid phase hydrogenation reactions (Singh, 2001). Potts and co-workers used an Ackerson reactor to study the kinetics of the liquid phase hydrogenation of 1-octadecanoic acid to 1-octadecanol (Potts, 2014). Of particular interest in the 1-octadecanoic paper was the study of the series-parallel reaction wherein the acid reacts with hydrogen to make the alcohol and the alcohol reacts with more hydrogen to make the alkane. A model of the differential rate equations was assembled, and the rate constants for both reactions were

estimated. The model developed for the 1-octadecanoic acid work is applied to the hydrogenation of butanoic acid (butyric acid) in this paper.

One measure of the performance of a reactor wherein a series parallel reaction is conducted is the selectivity. Several similar definitions of selectivity can be used; here we define selectivity as the moles of the desired product divided by the total moles of product mixture. Augustine reviews concepts of selectivity in hydrogenation reactions (Augustine, 1997). In general, higher temperatures lead to lower selectivity. Usually, but not always, higher hydrogen pressures lead to lower selectivity. Thus, to maximize selectivity, it is generally prudent to operate the reactor at low temperatures and pressures. The selection of the pressure is a trade-off, if the pressure is too low, mass transport of the hydrogen to the catalyst can become limiting. Type I selectivity is when two simultaneous reactions are occurring with a reactant mixture of multiple reactants. Type 2 selectivity is defined when two parallel reactions are taking place from the same reactants. Type 3 selectivity is when multiple product species are formed in sequential steps. The hydrogenation of carboxylic acids exhibits Type 3 selectivity. In systems where Type 3 selectivity is seen, the selectivity can often be increased by lowering the hydrogen availability. Less active catalysts will also promote greater selectivity, as will using a catalyst whose active sites are predominately on the surface of the catalyst particle, i.e. low porosity and/or surface area. Selectivity can be affected by the solvent, especially the polarity, in Type 3 selectivity reactions. Concentration of the reactants in the solvent can also play a major role in determining selectivity, with lower concentration feeds generally giving greater selectivity. The reactions studied here exhibit chemeoselectivity, in that the carboxylic acid hydrogenates much differently than does the hydroxyl group of the alcohol.

Selectivity can be a misleading criterion for reaction design, as maximum selectivity can be achieved when the conversion of the butyric acid is minimized. The usual purpose of reaction design is to maximize the amount of desired product from the reactant stream. Stated in another way, the usual purpose of reaction design is to maximize both selectivity and conversion of the feed simultaneously. Levenspiel provides a critereon for such design (Levenspiel, 1999). The approach of Levenspiel maximizes the concentration of the desired product in the product stream by considering both selectivity and conversion of the feed. This approach is discussed further in the experimental procedures section of this paper.

Experimental Procedures

Two reactor systems were used for this study. The first reactor used was in the pilot plant of Process Dynamics. The second hydrogenation reactor used for this research was originally built by a team of undergraduate chemical engineering students for the 2013 International Environmental Design Contest, sponsored by the WERC consortium and The University of New Mexico. Their system, designated as “the Bell reactor”, was rebuilt and modified to support this research. A schematic of the Bell system is shown as **Figure 1**. A description of the Bell system follows.

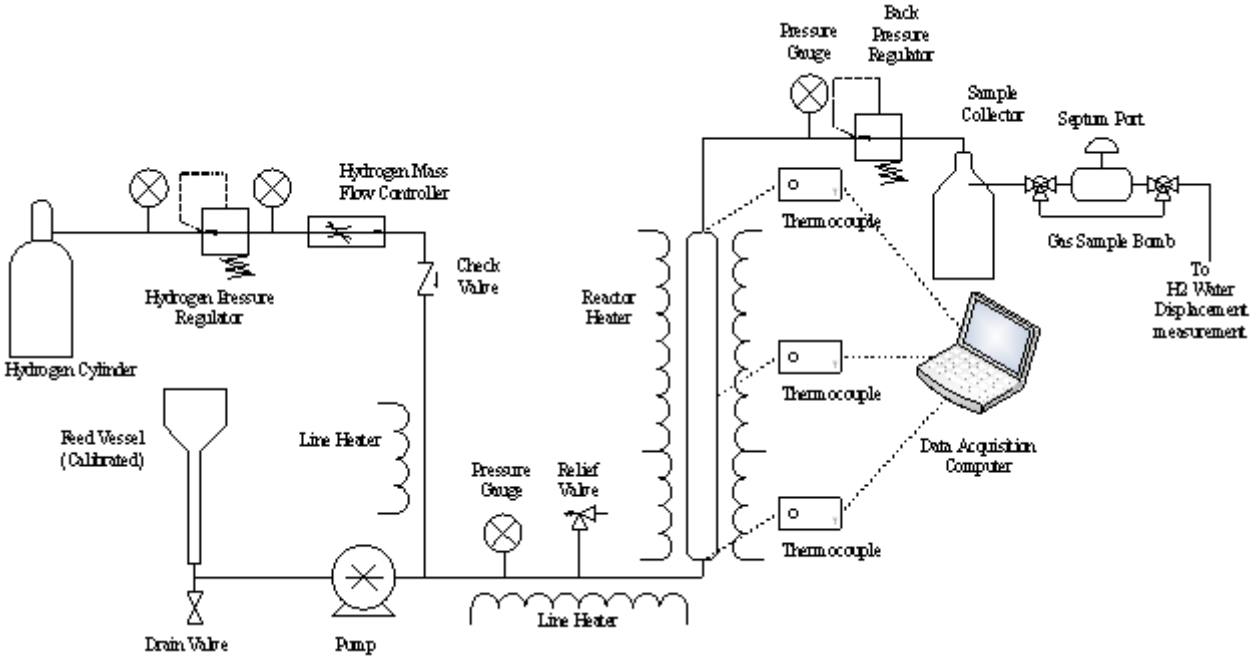


Figure 1: Schematic of Catalytic Hydrotreater

The hydrogen mass flowmeter (MFC) was a Brooks (Hatfield, PA) Model 5850. The instrument was factory calibrated for carbon dioxide, but was used for hydrogen service in this application. A new calibration curve was generated by measuring the hydrogen flow at various MFC settings using water displacement over a measured time. During runs, the MFC reading was recorded and translated to a hydrogen flow rate using the calibration curve. The Swagelok (Solon, OH) check valve, model SS-CHS4-1, protected the MFC by preventing high pressure liquid from back-flowing into the MFC. The feed vessel was a glass 250 ml buret with a funnel-shaped addition welded to its top. The drain valve was a Swagelok ball valve, model SS-SKPS4. The pump was a Waters (Milford, MA) model 501. The transfer lines and reactor were heated with Briskheat (Columbus, OH) BWH heating tapes. The lines and reactor were insulated by wrapping with silica cloth tape and over-wrapping the silica tape with fiberglass insulation. The voltages through the heating tapes were controlled by ISE (Cleveland, OH) Variac voltage

regulators. Temperatures were monitored with shop-built J-type thermocouples connected to an Omega (Stamford, CT) OM-USB-TEMP temperature data acquisition module. The signals generated by the data acquisition were sent via USB cable to a laptop computer equipped with the Omega Tracer-DAQ Pro software. Temperature control was accomplished by manual adjustment of the Variac voltage regulators. The transfer lines were heated with one set of heating tapes and monitored with one thermocouple, the reactor was heated with two tapes and control was effected by two Variacs and two thermocouples. Pressure gauges were Bourdon Tube type and the supplier for these was unknown. The model 26-1763-24-283 back pressure regulator was from Tescom (McKinney, TX). The low pressure exhaust of the back pressure regulator was ¼" stainless steel tubing, and this tube was fitted with a rubber stopper drilled to fit the tube. The liquid sample collectors were glass 250 ml side arm flasks from VWR. The rubber stopper affixed to the back pressure regulator was sized to fit these sample collectors. A larger, 1000 ml side arm flask replaced the sample collectors during those time periods during the hydrogenation runs when no sample was collected. The gas sample bomb was shop built and consisted of a short 2" NPT nipple in stainless steel, two 2" NPT elbows, two 2" x 1/4" NPT bushings, and two ¼" NPT by ¼" Swagelok SS-SKPS4 valves. The gas sample bomb was connected to the side arm of the liquid sample container with 3/16" I.D. silicone tubing. The water displacement hydrogen volume measurement system is shown in **Figure 2**.

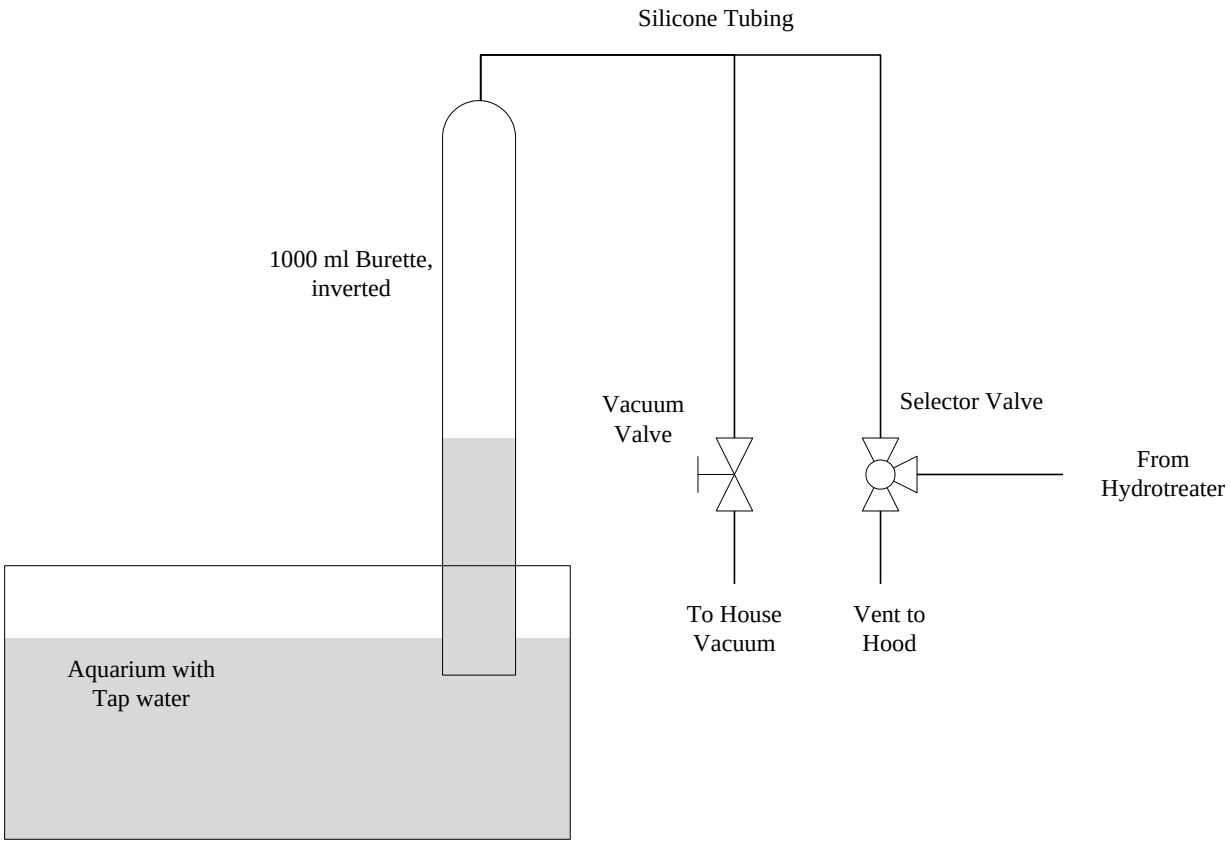


Figure 2: Water Displacement Hydrogen Volume Measurement System

The water container of this system consisted of a 5 gallon aquarium tank. Gas displacement was done in a 1 liter burette held in an inverted configuration in the aquarium. The burette was held in position with a ring stand and attached burette clamp. The valve arrangement for the measurement system was two Swagelok ball valves, one a model SS-SKPS4 block valve and the other a SS-44S4 three way valve. All connections were made with 3/16" I.D. silicone tubing.

The catalyst selected for this work was Axens (Rueil-Malmaison, France) HT438, a Ni/Cr/Mo catalyst on trilobal aluminum oxide pellets. This catalyst was selected because there were quantities of it available at no cost. The inert carrier selected for use was charcoal starter, refined light kerosene. Charcoal starter was readily available at low cost from a variety of local

big box stores. Due to the volumes of inert used during this study, the commonly used laboratory solvents would have been cost prohibitive.

The reactor was constructed from ¾" O.D. stainless steel tubing. The overall length of the reactor was 24". The tubing was washed and rinsed with acetone prior to packing with catalyst. A ¾" stainless steel nut was used to swage a two piece stainless ferrule set on each end of the reactor tube. The larger opening of the bottom ¾" x ¼" reducing coupler was fitted with a disk of fine mesh stainless steel screen and was attached to the reactor tube. The reactor tube was filled to 2 inches with 3 mm glass beads and vibrated both longitudinally and laterally. 67.4 grams of Axens HT438 catalyst was added in small aliquots with longitudinal and lateral vibration to reduce the possibility of voids and packing bridges. The length of the packing bed was measured at 18.5 inches. The volume of the resultant catalyst bed was just under 60 mls. A top cover of 3.5 inches of 3 mm glass beds was added to the reactor. The larger opening of the top ¾" x ¼" reducing union was fitted with second disk of fine mesh stainless steel screen and the union was attached to the upper end of the reactor, sealing the reactor bed. This fitting culminated with a ¼" stainless tube to which was attached a ¼" compression fitting tee. The vertical leg of this tee was fitted with a 1/8" swaged into position so that its working end was just above the screen disk capping the upper end of the reactor bed. The horizontal leg of the tee was used to attach the liquid feed line. This assembly was leak tested by connecting the lower end to the hydrogen pressure source and capping the upper end. The hydrogen pressure was slowly raised to 850 psig. All fittings were soaked with soapy water and inspected for bubbles. When no bubbles appeared, the hydrogen source valve was closed and the pressurized system was left for 4 hours. Leak integrity was confirmed when the pressure dropped less than 5 psig on the Bourdon tube pressure gauge. The hydrogen was slowly vented from the reactor, and the cap and

hydrogen source line were disconnected. The reactor tube was placed in the reactor shell, and the annulus between the shell and reactor was filled with dry sand to act as a heat transfer medium. The reactor shell was constructed of 2.5" stainless steel pipe with a shop-built end plate drilled and machined to allow the insertion of the lower reactor thermocouple. The shell also had been drilled in the midpoint of its length for the insertion of a thermocouple. Prior to the addition of the sand, this midpoint thermocouple was positioned so that it was touching the outer wall of the reactor tube. After the addition of the sand, the reactor was then plumbed into the hydrotreater system.

The hydrogen flow was started at 50 sccm with the back pressure regulator completely open. The Variacs were adjusted so that the temperatures as measured by the four thermocouples were about 250 F and the system was left to dry for 2 hours. The catalyst was then sulfided with 10% butanethiol in charcoal starter as prescribed by the vendor of the catalyst, Axens.

The Process Dynamics reactor was similar to the Bell system described above, but the catalyst bed length was slightly longer, the data acquisition system was more extensive, and the PD system was operable at much higher pressures and flow rates. The Bell system was limited to 1000 psig operation, whereas the PD system could be operated easily to 2500 psig. Also, the Bell system employed the Waters 501 HPLC pump with a maximum usable flow rate of about 3.5 ml/min and the PD system employed pumps from Eldex (Napa, CA) that deliver much higher flow rates. The Bell unit was limited to 130 sccm of hydrogen and the PD system with larger orifice MFCs was capable of several standard liters per minute.

The experimental matrix for this study was generated by variances in pressure, temperature, and space velocity of the reactants through the catalyst bed. Temperatures were varied from 250 F to 390 F, the pressures were varied from about 600 psig to 2250 psig, and the

space velocity was varied from 0.33 to 0.67 hr^{-1}. For the Process Dynamics, one sample consisting of approximately 100 grams of was collected for each condition of temperature, pressure, and reactor space velocity. For the Bell study, three samples of approximately 100 grams were collected at each condition of temperature, pressure, and reactor space velocity.

Analysis of the samples was done on a Shimadzu 2014 gas chromatograph equipped with a Phenomenex ZB-FFAP capillary column with dimensions 30 m x 0.32 mm x 0.25 um. The FID detector was at 300 C and the injection port was at 300 C. For the liquid samples, injections were made with a Shimadzu AOC-20i autoinjector. Injection size was 3 ul at a 10:1 split. The temperature profile used for the liquid samples was 35 C for 3 minutes, ramp at 15 C/min to 200 C, and 200 C for 3 minutes. Triplicate injections were made of all liquid samples. External standards of ACS grade butanol and butyric acid solvated in charcoal starter fluid were used to generate calibration curves for each chemical, which were then used to quantify the chromatograms. The butane peak and butyric acid peak in the sample chromatograms were baseline separated from the multiple charcoal starter peaks and base line integration (manual) was used to ascertain peak areas. The butanol peak co-eluted with a broad, diffuse peak of the charcoal starter fluid. The butanol peak area was determined by tangent-skim integration (manual). Gas samples were extracted from the gas sample bomb with a Hamilton (Reno, NV) 250 ul gas tight syringe. 50 ul of the sample was immediately manually injected into the Shimadzu GC. The split ratio for the gas samples was 10:1, and the column temperature was isothermal at 35 C. Analysis time was 4 minutes. The butane calibration curve was generated by manual injections of differing volumes of butane gas at room temperature and pressure with a Hamilton 250 ul gas tight syringe. This calibration curve was used for both the gas samples, and with appropriate unit conversion, for the liquid samples.

The hydrogen concentration in the liquid inert carrier was estimated with ChemCad (Chem Stations, Houston, TX). A ChemCad version 6.4.2. model consisting of two input streams, a flash vaporizer, and three output streams was generated. Two components, hydrogen and decane, were added to the model. Peng-Robinson with regular SRK-PR BIPs was selected as the thermodynamics package. Phases selected were vapor/liquid/liquid/solid. The Peng-Robinson global enthalpy model was selected with ideal gas heat capacity from the DIPPR tables. The liquid mixing density was calculated from the weighted mole percent. The vapor density model used was the ChemStations method. The first input stream was selected as hydrogen and the second input stream was selected as normal decane. Normal decane was selected as a surrogate for the charcoal starter used in the reaction studies. For each sample collected, the flow rate of hydrogen was set to that of the hydrogen MFC, the flow rate of decane was set to the flow rate of the sample as calculated from the time of the sample collection and the mass of sample collected. The temperature of the flash vaporizer was set to the averages of the temperatures recorded for the upper two thermocouples for the time of sample collection. The pressure was set to the averages of the pressures recorded from the two pressure gauges. The model was executed and in all cases, all of both components were split between the vapor phase and the first liquid phase. The molar fractions of the liquid phase were converted to a hydrogen concentration in moles/L and this was assumed to be the saturation hydrogen solubility in the charcoal starter fluid.

The generation of the hydrogen concentration assumed that the model was adequate to determine real world values. This assumption was tested by using the model to calculate values at conditions described by Park, and the calculated values were compared to the experimentally determined hydrogen concentrations as measured by Park (Park, 1995). Park et al. measured the

saturation hydrogen concentration in several paraffinic hydrocarbons, including decane, at temperatures in the range of 125 F to 305 F and pressures up to 2500 psig.

It was assumed that the consumption of hydrogen during the reaction was small compared to the hydrogen available for reaction, and that the hydrogen concentration in the reactor remained constant throughout the reaction. This assumption was tested by calculating the reduction of hydrogen from the molar concentrations of the products at the end of the reactor and the stoichiometry of the two reactions. Thus, for each mole of butanol produced, the hydrogen was reduced by two moles, and for each mole of butane produced, the hydrogen was reduced by three moles. The final hydrogen available was determined by subtracting the hydrogen consumed from the initial hydrogen available. The final hydrogen available was then compared to the saturation concentration. A final hydrogen amount that was larger than the saturation concentration validated the assumption of non-variant hydrogen concentration.

The hydrogenation of butyric acid proceeds in two steps, given as equations 4 and 5:

(4) $C_3H_7COOH + 2H_2 \rightarrow C_4H_9OH + H_2O$

(5) $C_4H_9OH + H_2 \rightarrow C_4H_{10} + H_2O$

The first reaction gives the desired product, 1-butanol, whereas the second reaction consumes the butanol produced in the first reaction to make butane. This reaction mechanism is typically called a series-parallel reaction network (Hill, 1977). Ideal reactor conditions will maximize the production of butanol and at the same time, minimize the production of butane. To design a reactor for the hydrogenation of butyric acid to butanol, it is therefore necessary to develop a model that will predict the reaction products of both the butanol and butane. The model chosen for this study is a set of 4 differential rate equations, where the equations are given as equations 6, 7, 8, and 9. This set of differential equations is similar to those used in the 1-octadecanoic acid

paper with the assumption that adsorption/desorption of the species onto catalyst active sites are not rate determining steps.

(6) $\frac{dC_A}{dt} = -k_1 C_A C_H$

(7) $\frac{dC_H}{dt} = -k_1 C_A C_H - k_2 C_O C_H$

(8) $\frac{dC_O}{dt} = k_1 C_A C_H - k_2 C_O C_H$

(9) $\frac{dC_B}{dt} = k_2 C_O C_H$

In these rate equations, k_1 is the rate constant for reaction 1, k_2 is the rate constant for reaction 2, C_A is the concentration of butyric acid at time t, C_H is the concentration of hydrogen at time t, C_O is the concentration of butanol at time t, and C_B is the concentration of butane at time t. When the assumption was made that the hydrogen concentration was the saturation concentration at the existing conditions of pressure and temperature, and that the hydrogen in the inert carrier liquid was replenished faster than its consumption in the two reactions, Equation 7 becomes

(7b) $\frac{dC_H}{dt} = 0$

The validity of these assumptions is discussed in detail in the results and conclusion section of this paper.

The reactor system as built did not conveniently allow for the determination of the concentration of the reactants and products as a function of time. Analytical data consisted of the concentrations of butyric acid, butanol, and butane at the entrance of the reactor and at the exit of the reactor. To estimate the values of k_1 and k_2, a MatLab (Math Works, Natick, Mass) program was written that repetitively integrated over the residence time the 4 differential equations from the starting concentrations while adjusting the values of k_1 and k_2 to give values of the concentrations at the end of the reactor. This iterative process was optimized on the sum of the

least squares differences between the integrated values of the concentrations of butyric acid, butanol, and butane and the actual concentrations. This iterative process was performed on each analytical data point. The resultant table of k_1 and k_2 values were used to generate a plot of $\ln(k_1)$ versus 1/T and a plot of $\ln(k_2)$ versus 1/T. From these plots, the frequency factor and activation energy for the two reactions were obtained from the Arrhenius equation, Eq. 10.

(10) $$k = ae^{-\frac{E_A}{RT}}$$

In equation 10, k is the reaction rate constant, a is the frequency factor, E_A is the activation energy, R is the gas constant, and T is the absolute temperature.

Once the Arrhenius constants were known, it was possible to use the 4 rate equations to calculate modeled values for each experimental condition used. A second MatLab program was written to use the Arrhenius constants and the temperature to calculate the values of k_1 and k_2, then integrate over the known residence time the four rate equations to determine the modeled final concentrations of butyric acid, butanol, and butane. From this set of data, a plot of the modeled values versus the experimental values for each of the three species was generated. Following the method of Levenspiel, expressions for the productivity, here defined as the concentration of butanol produced per starting concentration of butyric acid, may be developed (Levenspiel, 1999). Dividing equation 8 by equation 6 gives

(11) $$\frac{dC_o}{dC_A} = -1 + \frac{k_2}{k_1}\frac{C_o}{C_A}$$

Separation of variables in this time-independent equation gives

(12) $$\frac{dC_o}{-1+\frac{k_2}{k_1}C_o} = \frac{dC_A}{C_A}$$

Integrating the left side from the initial concentration of butanol, 0, to the final value of butanol, C_o, and the right side from the initial concentration of butyric acid, C_{A0}, to the final value of butyric acid, $C_{A,}$, yields

(13a) $\frac{C_o}{C_{A0}} = \frac{1}{1-\frac{k_2}{k_1}}\left[\left(\frac{C_A}{C_{A0}}\right)^{\frac{k_2}{k_1}} - \frac{C_A}{C_{A0}}\right]$ for $\frac{k_2}{k_1} \neq 1$

(13b) $\frac{C_o}{C_{A0}} = \frac{C_A}{C_{A0}} \ln \frac{C_{A0}}{C_A}$ for $\frac{k_2}{k_1} = 1$

Equation 13 has a maximum for the productivity of butanol, $C_{o,max}$ at

(14a) $\frac{C_{o,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}}$ for $\frac{k_2}{k_1} \neq 1$

(14b) $\frac{C_{o,max}}{C_{A0}} = 0.368$ for $\frac{k_2}{k_1} = 1$

Results and Discussion

Table 1: Analytical Statistics

hr		psig		F		Butane		Butanol		Butyric	Std Dev
Avg Tau	Std Dev	Avg P	Std Dev	Avg T	Std Dev	Avg Wt%	Std Dev	Avg Wt%	Std Dev	Avg Wt%	Std Dev
0.482	0.015	692.5	18.1	327.4	0.9	0.628%	0.014%	0.234%	0.021%	3.67%	0.07%
0.503	0.031	711.1	1.6	349.9	0.6	1.089%	0.040%	0.348%	0.016%	3.34%	0.02%
0.473	0.003	716.7	3.1	295.5	0.6	0.205%	0.012%	0.186%	0.026%	3.26%	0.12%
0.478	0.006	715.1	1.2	324.6	0.3	0.452%	0.027%	0.352%	0.034%	3.60%	0.08%
0.488	0.006	716.1	5.5	347.4	1.5	0.793%	0.032%	0.572%	0.038%	3.46%	0.06%
0.247	0.001	726.4	1.1	308.5	0.8	0.091%	0.005%	0.156%	0.028%	4.61%	0.19%
0.244	0.001	725.4	1.6	348.0	1.0	0.390%	0.025%	0.416%	0.038%	4.08%	0.02%
0.243	0.001	722.2	7.9	327.6	1.5	0.163%	0.018%	0.309%	0.021%	4.31%	0.10%
0.246	0.002	720.0	-	382.3	2.0	1.154%	0.128%	0.619%	0.051%	3.14%	0.58%
0.244	0.002	721.3	3.9	349.1	0.9	0.347%	0.032%	0.465%	0.040%	4.13%	0.20%
0.253	0.003	935.0	-	334.3	0.4	0.103%	0.010%	0.227%	0.020%	4.26%	0.28%
0.239	0.003	964.2	2.3	315.6	0.9	0.041%	0.005%	0.130%	0.011%	4.77%	0.22%
0.241	0.004	949.0	3.8	350.0	0.2	0.149%	0.006%	0.338%	0.014%	4.62%	0.08%
0.245	0.000	983.3	2.5	369.6	0.2	0.270%	0.016%	0.509%	0.024%	3.73%	0.09%
0.321	0.002	811.1	1.7	338.0	0.2	0.054%	0.004%	0.193%	0.014%	4.15%	0.03%
0.321	0.003	818.3	2.5	359.0	-	0.109%	0.020%	0.344%	0.020%	3.84%	0.04%
0.349	0.002	823.3	2.5	392.1	0.4	0.390%	0.019%	0.504%	0.024%	2.52%	0.29%
0.685	0.008	806.7	12.3	392.1	0.2	0.621%	0.074%	0.683%	0.037%	1.84%	0.62%
0.679	0.015	821.1	1.7	313.4	0.8	0.058%	0.003%	0.256%	0.036%	3.76%	0.31%
0.326	0.001	824.2	3.3	323.0	0.9	0.048%	0.003%	0.167%	0.013%	5.11%	0.05%
0.332	0.008	804.7	51.1	342.8	1.5	0.093%	0.008%	0.311%	0.026%	4.91%	0.05%
0.318	0.002	821.7	2.5	353.5	0.8	0.108%	0.007%	0.361%	0.011%	4.10%	0.41%
0.629	0.006	817.8	5.5	350.0	-	0.192%	0.005%	0.587%	0.015%	3.90%	0.03%
0.634	0.006	826.4	3.3	372.1	3.2	0.366%	0.022%	0.742%	0.028%	3.06%	0.17%

Table 1 summarizes the analytical results from the gas chromatographic analyses. Each line in **Table 1** represents nine analytical data points, three duplicate injections of each of three approximately identical reactor conditions. The three reactor conditions samples were taken consecutively from the reactor with no changes of temperature, pressure, or residence time. However, because the reactor conditions were not perfectly stable, there were some variations in pressure, temperature, and residence time. The liquid feed pump proved to be very stable and reproducible and variance of the residence time of the reactants in the reactor proved to be quite small. The temperature was less stable, but still shows relatively small standard deviations from the averages of the three sample collections. The pressures as read from the mechanical pressure gauges show much more variation than the other two variables, but the standard deviations are still well below 10% of the average values. **Table 1** indicates that the weight-based concentrations of butane, butanol, and butyric acid are very reproducible for each condition of the reactor.

Table 2 summarizes the carbon molar balance as defined by equations 1 and 2. The lines of **Table 2** correspond to the same sets of nine analytical data points as described in the description of **Table 1**. The carbon molar balance was defined as the number of moles of carbon in the analytical sample of the samples taken from the end of the reactor relative to the number of moles of carbon in the analytical sample of the feedstock going into the reactor. The average value of the carbon molar balance for the various reactor conditions were generally in the 95-105%, with the range of values from 74% to 117%. The four lowest carbon balances ranged from 74% to 79%, and it is interesting that all four of these values were at the extremes of temperatures used for the reactor conditions. These four data sets were not used in the development of the model or in its testing.

Table 2: Carbon Molar Balance

hr		psig		F		Carbon Molar Balance	
Avg Tau	**Std Dev**	**Avg P**	**Std Dev**	**Avg T**	**Std Dev**	**Avg**	**Std Dev**
0.482	0.015	692.5	18.1	327.4	0.9	103%	2%
0.503	0.031	711.1	1.6	349.9	0.6	113%	1%
0.473	0.003	716.7	3.1	295.5	0.6	79%	3%
0.478	0.006	715.1	1.2	324.6	0.3	98%	2%
0.488	0.006	716.1	5.5	347.4	1.5	111%	3%
0.247	0.001	726.4	1.1	308.5	0.8	105%	4%
0.244	0.001	725.4	1.6	348.0	1.0	109%	2%
0.243	0.001	722.2	7.9	327.6	1.5	104%	2%
0.246	0.002	720.0	-	382.3	2.0	117%	14%
0.244	0.002	721.3	3.9	349.1	0.9	110%	6%
0.253	0.003	935.0	-	334.3	0.4	99%	7%
0.239	0.003	964.2	2.3	315.6	0.9	106%	5%
0.241	0.004	949.0	3.8	350.0	0.2	111%	2%
0.245	0.000	983.3	2.5	369.6	0.2	99%	3%
0.321	0.002	811.1	1.7	338.0	0.2	94%	1%
0.321	0.003	818.3	2.5	359.0	-	93%	1%
0.349	0.002	823.3	2.5	392.1	0.4	77%	7%
0.685	0.008	806.7	12.3	392.1	0.2	74%	10%
0.679	0.015	821.1	1.7	313.4	0.8	78%	5%
0.326	0.001	824.2	3.3	323.0	0.9	102%	1%
0.332	0.008	804.7	51.1	342.8	1.5	103%	1%
0.318	0.002	821.7	2.5	353.5	0.8	88%	8%
0.629	0.006	817.8	5.5	350.0	-	91%	1%
0.634	0.006	826.4	3.3	372.1	3.2	83%	2%

One of the assumptions of the model was that the hydrogen dissolved in the inert carrier was replenished from the hydrogen excess as fast as it was consumed in the reactions, so that the hydrogen concentration remained constant. Because we could not measure the hydrogen concentration with our analytical instrumentation, we could not test this assumption directly, but an indirect measure was available. The saturation concentration of hydrogen in the carrier was estimated from ChemCad. The hydrogen consumption during the reaction was estimated from the stoichiometry of reactions 1 and 2 and the extent of the reaction as determined by the analysis of the exit stream from the reactor. The initial hydrogen available for the reaction was determined from the mass flow controller and the flow rate of the carrier into the reactor. The

final hydrogen availability was assumed to be the initial hydrogen minus the hydrogen consumed. If the final hydrogen availability was above the saturation concentration, it was assumed that the hydrogen concentration remained constant for that particular set of reactor conditions. **Table 3** summarizes these calculations. In all but one case, the final hydrogen availability was greater than the saturation pressure of the hydrogen in the carrier, and so constant hydrogen concentration was assumed. This data set, at 824 psig pressure and 323 F, was not used for the model development or testing.

Table 3: Hydrogen Balance Estimates

hr		**psig**		**F**		**Excess H2**	
Avg Tau	**Std Dev**	**Avg P**	**Std Dev**	**Avg T**	**Std Dev**	**Avg**	**Std Dev**
0.482	0.015	692.5	18.1	327.4	0.9	81%	12%
0.503	0.031	711.1	1.6	349.9	0.6	68%	12%
0.473	0.003	716.7	3.1	295.5	0.6	86%	3%
0.478	0.006	715.1	1.2	324.6	0.3	74%	3%
0.488	0.006	716.1	5.5	347.4	1.5	60%	4%
0.247	0.001	726.4	1.1	308.5	0.8	94%	1%
0.244	0.001	725.4	1.6	348.0	1.0	69%	1%
0.243	0.001	722.2	7.9	327.6	1.5	81%	1%
0.246	0.002	720.0	-	382.3	2.0	45%	3%
0.244	0.002	721.3	3.9	349.1	0.9	69%	2%
0.253	0.003	935.0	-	334.3	0.4	43%	2%
0.239	0.003	964.2	2.3	315.6	0.9	37%	1%
0.241	0.004	949.0	3.8	350.0	0.2	28%	3%
0.245	0.000	983.3	2.5	369.6	0.2	17%	1%
0.321	0.002	811.1	1.7	338.0	0.2	75%	1%
0.321	0.003	818.3	2.5	359.0	-	63%	2%
0.349	0.002	823.3	2.5	392.1	0.4	61%	1%
0.685	0.008	806.7	12.3	392.1	0.2	232%	11%
0.679	0.015	821.1	1.7	313.4	0.8	89%	5%
0.326	0.001	824.2	3.3	323.0	0.9	-5%	0%
0.332	0.008	804.7	51.1	342.8	1.5	63%	15%
0.318	0.002	821.7	2.5	353.5	0.8	49%	1%
0.629	0.006	817.8	5.5	350.0	-	47%	3%
0.634	0.006	826.4	3.3	372.1	3.2	35%	2%

The molar concentration of butyric acid in the reactor product stream subtracted from that of the reactor feed stream divided by the butyric acid molar concentration of the reactor feed stream was defined as the conversion. Thus, a conversion of 0% indicates that no reaction occurred, and a conversion of 100% indicated that the product stream contained no butyric acid, i.e., all of the acid was consumed in the reaction. The conversions of the various reactor conditions are summarized in **Table 4**. Again, each line of **Table 4** represents nine analytical samples, three each of three reactor product samples all at approximately the same conditions. The conversions were rather low, ranging from -2% to 62%. The -2% represents a theoretical implausibility, that the butyric acid in the product stream was greater than that of the feed stream. This anomaly was probably due no reaction taking place and evaporation of a small amount of the inert carrier from the analytical sample. For the purpose of developing and testing the model, all data sets with conversions below 10% were not considered.

Table 4: Conversions of Butyric Acid

hr		psig		F		Butyric Conversion	
Avg Tau	Std Dev	Avg P	Std Dev	Avg T	Std Dev	Avg	Std Dev
0.482	0.015	692.5	18.1	327.4	0.9	23%	1%
0.503	0.031	711.1	1.6	349.9	0.6	30%	0%
0.473	0.003	716.7	3.1	295.5	0.6	32%	3%
0.478	0.006	715.1	1.2	324.6	0.3	24%	2%
0.488	0.006	716.1	5.5	347.4	1.5	27%	1%
0.247	0.001	726.4	1.1	308.5	0.8	2%	4%
0.244	0.001	725.4	1.6	348.0	1.0	14%	0%
0.243	0.001	722.2	7.9	327.6	1.5	8%	2%
0.246	0.002	720.0	-	382.3	2.0	34%	13%
0.244	0.002	721.3	3.9	349.1	0.9	13%	4%
0.253	0.003	935.0	-	334.3	0.4	10%	6%
0.239	0.003	964.2	2.3	315.6	0.9	-2%	5%
0.241	0.004	949.0	3.8	350.0	0.2	2%	2%
0.245	0.000	983.3	2.5	369.6	0.2	21%	2%
0.321	0.002	811.1	1.7	338.0	0.2	12%	1%
0.321	0.003	818.3	2.5	359.0	-	19%	1%
0.349	0.002	823.3	2.5	392.1	0.4	47%	6%
0.685	0.008	806.7	12.3	392.1	0.2	62%	13%
0.679	0.015	821.1	1.7	313.4	0.8	29%	6%
0.326	0.001	824.2	3.3	323.0	0.9	3%	1%
0.332	0.008	804.7	51.1	342.8	1.5	7%	1%
0.318	0.002	821.7	2.5	353.5	0.8	23%	8%
0.629	0.006	817.8	5.5	350.0	-	27%	1%
0.634	0.006	826.4	3.3	372.1	3.2	43%	3%

The relatively poor fit between the experimental and modeled concentrations of the butanol and butane has several possible explanations, based on the failure of the carbon molar balances at higher conversions of butyric acid. It is possible that products are lost from the sample during collection and preparation for GC analysis. The butanol is volatile and butanol vapors will be swept from the sample collection vessel by the flowing hydrogen from the reactor. The butane is even more volatile, so one would expect the sample loss phenomenon to be worse for the butane than for the butanol. The butane, in particular, is dispersed between the liquid sample and the flowing gas stream, as evidenced by the analysis of the sample liquid and by analysis of the sweep gas as captured by the gas sample bomb. When the conversion rate of

butyric acid is low, nearly all of the butane detected was solvated in the liquid sample, but when the conversion rate reached 25% of the butyric acid, the amounts of butane in the liquid sample and in the sweep gas were about the same. The final amounts of butane reported in Table 1 consisted of the sum of the amounts in the sweep gas and those in the liquid samples. Future studies in this reactor system should include a study of the gas chromatography. An improved method for analytical recovery of the butanol and butane should be developed.

Another explanation for lower than predicted values of butanol and butane could be that other reactions are taking place. The condensation polymerization of butyric acid with butanol to form the ester butyl butyrate is well known, and takes place in the temperature regime considered in this study (Ju, 2011). They reported very low reaction rates at room pressure and found that the activation energy was in the range of 40-70 kJ/mole. A similar esterification reaction occurs between butanal and butanol (Tang, 2008). The butanal could be formed from the partial hydrogenation of the butyric acid (Yokoyama, 1992). Yet another reaction leading to lower than expected quantities of butane could be the catalytic reforming of the butane to shorter chain alkanes or alkenes and hydrogen. Butane can be steam reformed, with the water present as an impurity in the feed (butyric acid is very difficult to dehydrate completely) or as the product of reactions 1 and 2. Bhatta and coworkers found that reforming of the butane to lower hydrocarbons and hydrogen can occur at as low as 225 C, although not to stochiometeric quantities (Bhatta, 1969). The occurrence of other reactions should be studied with the improved gas chromatography protocols. Analytical standards of the possible reaction products should be procured, and calibration curves established for each. Analysis of the catalytic hydrogenation products should include testing the product samples for these potential products. These suggestions are discussed in greater detail in Chapter 6 of this dissertation.

Conclusion

A model for the kinetics of the hydrogenation of butyric acid to 1-butanol has been developed. The model chosen was a Langmuir-Hinshelwood-Hougen-Watson (LHHW) differential rate model with the assumption that effects of adsorption/desorption were small so that the denominator of the rate equation was one. Experimental sample sets were obtained in a liquid phase trickle-bed plug flow reactor. Concentrations of the reactants (excepting hydrogen) and products were determined by gas chromatography. The hydrogen concentration was assumed to be saturation concentration as calculated by ChemCad (Chemstations, Houston, TX) at the conditions of temperature and pressure for each data set. The model was fitted to several sets of data in the temperature regime of 300-400 F and pressures of 700-1000 psig by adjusting the reaction rate constants to a least squares minimum deviation between the modeled and experimental values. These calculations indicate that there was a poor fit between the modeled and experimental values. We suggest that the poor fit is due to ineffective analytical methodology or that other reactions were taking place. Future studies that may provide better fit are suggested and discussed.

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Chapter 6

Conclusion

The papers presented in this dissertation chronicle a study of the production of 1-butanol from bio-mass. The research thrust was originally the conversion of algae to 1-butanol by bacterial fermentation, but as the study progressed, the focus shifted to a more generalized production scheme, culminating in a hybrid bacterial/catalytic hydrogenation process that may find use in the production of third generation bio-fuels. Following a brief introduction of the scope of the dissertation in Chapter 1, Chapter 2 discusses the classical methods of the production of bio-butanol from the work of Weizmann (Weizmann, 1915) to current acetone-butanol-ethanol production facilities in Brazil and China (Mariano, 2012). Chapter 2 has been published as a book chapter (Hestekin, 2013). Chapter 3 describes the fermentation study conducted in our laboratories. The study consisted of the fermentation of algal sugars to 1-butanol by several bacterial species, including *Clostridium acetobutylicum*, *Clostridium beijerinckii*, and *Clostridium saccharoperbutylacetonicum*. The two reactor, two bacteria production mode was proposed by Ramey in 1998 (Ramey, 1998). This proposed process was studied and found untenable with the continuous flow fermentation reactor and the three bacterial strains considered. The results of the fermentation study were published, and Chapter 3 is that publication (Potts, 2012). The hybrid biological/chemical process was selected for further research. The chemical process step of the hybrid production scheme is the catalytic hydrogenation of butyric acid to butanol (Potts, 2011). The hydrogenation is a two-step, parallel-series pair of reactions with the butyric acid converted to butanol in the first step and the butanol converted to butane in the second step. Butanol is the desired product, whereas butane is unwanted. The reaction kinetics of the hydrogenation reactions were studied in a pilot plant high

pressure, moderate temperature plug flow reactor operated in a trickle bed mode. The reaction model was developed using 1-octadecanoic acid as a surrogate for the noxious butyric acid. The manuscript reporting this study was accepted for publication by the Journal of the American Oil Chemists Society. The manuscript is presented in this dissertation as Chapter 4 (Potts, 2014). The surrogate work was followed up with a study of the reaction kinetics of butyric acid. A manuscript of the study results has been prepared but has not yet been submitted for publication. The manuscript of the butyric acid work is presented as Chapter 5. Collectively, Chapters 2-5 present a novel approach to the production of fuel-grade bio-butanol with the promise of being economically competitive with butanol produced from propylene, the major production method.

Future Work

The results described in this dissertation suggest several further research opportunities. Of especial interest are new studies related to the hydrogenation kinetics studies as described in Chapter 4 and Chapter 5. The next section describes some of these opportunities, with suggested hypotheses, methods, and potential pitfalls.

Future Work Suggestions

1. Study the kinetics of the hydrogenation of butanol

Hypothesis to be tested

The kinetics of the hydrogenation of butanol to butane can be modeled with a Langmuir-Hinshelwood-Hougen-Watson (LHHW) differential rate model. (Davis and Davis, 2003)

Methodology

A matrix of hydrogenation experiments should be run in the range of 320-400F, 800-1600 psig, and 1-4 hr-1. The compositions of the resultant products will be subjected to

the Potts/Beitle/Durant model and the k value of the reaction determined for each data point. The collected set of k values will then be fit by least squares to the Arrhenius equation to generate a pre-exponential value and an activation energy value.

Major difficulties to be overcome

- The analysis of butanol and butane mixtures in kerosene is quite difficult.
- There may be other reactions taking place. (See suggestion 3.)

2. Develop a model to estimate hydrogenation of butyric acid/acetic acid mixture

2a. Determine the kinetic constants for acetic acid

Hypothesis to be tested

The kinetics of the hydrogenation of acetic acid to methanol and the subsequent hydrogenation of methanol to methane can be modeled after a LHHW differential rate model. (Potts, 2014)

Methodology

A matrix of hydrogenation experiments for acetic acid and methanol should be run in the range of 320-400F, 800-1600 psig, and 1-4 hr-1. The compositions of the resultant products will be subjected to the Potts/Beitle/Durant model and the k values of the two reactions determined for each data point. The collected set of k values will then be fit by least squares to the Arrhenius equation to generate pre-exponential values and activation energy values for each reaction.

Major difficulties to be overcome

- The analysis of methanol and methane in a background of kerosene is quite difficult.

- There may be other reactions taking place.

2b. Modify existing model for butyric to include the competitive acetic acid reactions

Hypothesis to be tested

The kinetics of the hydrogenation reactions of a feedstock comprised of both butyric acid and acetic acid can be modeled by the network of four chemical reactions as studied in chapter 5 of this dissertation and the results of future work item 2a, using a LHHW model with 8 differential rate equations. (Potts, 2014)

Methodology

A matrix of hydrogenation experiments for butyric acid, butanol, acetic acid and methanol should be run in a range of temperatures, pressures, and space velocities based on the results of previous work and the work of 2a. The compositions of the resultant products will be subjected to an expanded Potts/Beitle/Durant model and the k values of the four reactions determined for each data point. The collected set of k values will then be fit by least squares to the Arrhenius equation to generate pre-exponential values and activation energy values for each reaction.

Major difficulties to be overcome

- With eight differential equations in the model, the number of experimental conditions should be large.
- The analysis of the products will be challenging.

3. Study side reactions of hydrogenation of butanol

3a. Polymerization of butyric acid with butanol or butanal

Hypothesis to be tested

During the hydrogenation of butyric acid, some measureable quantity of polymer may be formed from in a two-step process, the hydrogenation of the butyric acid to butanal, followed by the condensation polymerization of butanal to C8 hydrocarbons. (Ju, 2011, Yokoyama, 1992, Tang, 2008)

Methodology

Standards of the polymeric compounds that might be expected (butyl butylaldehyde and possibly others) will be obtained. GC analysis of the procured standards will be performed. The resulting GC traces will be compared to those of products from the hydrogenation of butyric acid. Presence of measurable amounts of polymeric compounds will prove the hypothesis. Absence of any polymeric compounds in the hydrogenation samples will suggest that the hypothesis is not valid.

Major difficulties to be overcome

- Careful thought will be necessary to select the proper polymeric compounds for the study.
- Fresh hydrogenation samples may be required.

3b. Butane will undergo catalytic reforming to lighter paraffinic carbon compounds and hydrogen

Hypothesis to be tested

During the hydrogenation of butyric acid, some measureable quantity of butane will be catalytically reformed, producing lower molecular weight alkanes, carbon, and hydrogen (Bhatta, 1969). The quantity of the butane cracked can be modeled, and the model can be

incorporated into the model developed in chapter 5 of this dissertation to more closely predict the composition of the hydrogenation product stream.

Methodology

The gas injection manifold for the hydrotreater could be modified by installing another mass flow controller to the system. The added MFC would be used to inject a known amount of butane into the inert carrier. The mixture would be pumped through the reactor. The effluent gas and liquid streams would be analyzed for butane by gas chromatography, and the total butane determined would be the sum of that in the gas and in the liquid. The first set of experiments would be done with no butyric acid in the feed; the second set of experiments would incorporate 5 wt% butyric acid in the inert feed.

Major difficulties to be overcome

- At the low temperatures of the hydrogenation reactors used for this study, the conversion of butane may be very low.
- It will be necessary to develop the capability for fast, accurate gas analyses.
- If extensive butane conversion takes place, the catalyst may be deactivated by carbon formation.

4. Study the impact of CO2 expanded solvents on hydrogenation of butyric acid

Hypothesis to be tested

Using an equimolar mixture of hydrogen and carbon dioxide as the hydrogenation gas will cause a quantifiable change in the production of butanol from the hydrogenation of butyric acid. (Lopez-Castillo, 2008) The productivity of butanol will be changed because of the solubility of the hydrogen in the carrier will be different when carbon dioxide is

present. Changes of hydrogen solubility can be predicted based on three component solubility theory. The model developed in Chapter 5 of this dissertation can be used to predict the production of butanol and butane by incorporating the change in hydrogen solubility.

Methodology

A chemical process simulator, such as Aspen or ChemCad, would be used to model the solubility of hydrogen in the carbon dioxide/inert carrier. Experimental confirmation could be performed by using the method of Lopez-Castillo, 2008. Confirmation of the effect of the changed hydrogen solubility on the hydrogenation reactions could be achieved by equipping an existing hydrotreater with a high pressure pump procured to deliver both subcritical and supercritical CO2.

Major difficulties to be overcome

- The equipment modifications for the experimental work will be costly.
- A dedicated gas chromatograph with gas sampling, liquid sampling, and detection adequate for the gases and liquids used for the experimental study will be required.
- Operation of the integrated system will require a great deal of skill.

5. Estimate the maximum and optimum concentration of butyric acid in the feedstock

Hypothesis to be tested

The temperature rise of the reactant mixture due to the exothermic heat of reaction can be modeled based on the amount of butyric acid in the feedstock. This model can be combined with the model developed in Chapter 5 of this dissertation to predict the

production of butanol and butane from the butyric acid as a function of the concentration of the butyric acid in the feed.

Methodology

The temperature rise in the reactor due to the exothermic hydrogenation reaction will be modeled in ChemCad or Aspen. Trends for temperature rise will be generated on a basis of reactor temperature, pressure, space velocity, and concentration of butyric acid in the feed stream. Excess hydrogen will be assumed. No recycle will be assumed. The Potts/Beitle/Durant model for butanol and butane production will be modified so that the integration will include effect of the temperature rise on the k values of the reactions.

Major difficulties to be overcome

- This may be an iterative process, especially if the temperature rises are relatively large.
- The project will be computer intensive.

6. Study the order of the reactions of the hydrogenation of butyric acid and of butanol

Hypothesis to be tested

The method of initial rates can be used to determine the reaction order of hydrogen during the hydrogenation of butyric acid, and during the hydrogenation of butanol (Hill, 2003).

Methodology

A new hydrogenation reactor will be constructed, loaded with a short bed of the chosen catalyst. Temperature and pressure will be selected to consume about 50% of the butyric acid for a relatively long space time, perhaps 30 minutes. A space time that will cause

about 10% conversion of the butyric acid will be selected for the experimental set, which will consist of varying the concentration of butyric acid in the feedstock. A second experimental set will consist of a fixed butyric acid concentration and varying hydrogen concentrations (differing pressures). The method of Initial Rate Measurements as described by Hill will be used to determine the order of the butyric acid hydrogenation reaction (Hill, 1997). The first experimental set will determine the order with respect to butyric acid, the second will determine the order with respect to hydrogen. Two additional experimental sets using butanol as the feed instead of butyric acid will determine the orders with respect to butanol and hydrogen for the hydrogenation of butanol.

Major difficulties to be overcome

For accurate determinations, it may be necessary to develop analytical methods for determining the hydrogen concentrations.

7. Ascertain the sensitivity of the Axens HT438 catalyst to water in the feedstock

Hypothesis to be tested

The Axens HT-438 catalyst will tolerate small quantities of water in the hydrogenation feed stock, but if the water content rises above some measurable amount, the catalyst will be adversely affected (Coleman, John, Personal communication, 2012).

Methodology

A reactor will be assembled with a known amount of Axens HT-438 catalyst. Feed stocks will be prepared with several different water contents. The reactor will be operated with a temperature and pressure at some values chosen on the basis on a predicted optimum

productivity. The product stream will be periodically analyzed for nickel, chromium, and molybdenum. Metal content versus time plots will be generated, and trend analyses performed on these plots.

Major difficulties to be overcome

- A fast, low cost method of analysis of the product stream for the three target metals will be required.
- Determination of operating conditions and acceptable catalyst losses will be somewhat subjective.

8. Study the solvent effects of the hydrogenation of butyric acid

Hypothesis to be tested

The use of a polar solvent instead of the non-polar kerosene will change the selectivity of the hydrogenation products, butanol and butane (Mukherjee and Vannice, 2001).

Methodology

The process described in Chapter 5 of this dissertation will be replicated substituting an aprotic polar solvent, such as propylene carbonate, for the kerosene. The process will be replicated a second time with a protic polar solvent, such as nitromethane.

Major difficulties to be overcome

- Safe handling of the nitromethane will be of great importance
- The polar solvents may degrade the Axens catalyst
- The reaction conditions used for the study may lead to solvent/hydrogen reactions involving saturation of the double bonds or hydration reactions removing the oxygen from the solvent molecule.

9. Design Study

Hypothesis to be tested

The results of chapters 4 and 5 may be used to design a production facility, one which will accept relatively pure butyric acid as a feedstock and produce 1-butanol as the preferred product. From the facility design, capital costs for the facility and its operating costs may be estimated.

Methodology

Standard engineering practices as suggested by Peters, Timmerhaus, and West will be followed. (Peters, Timmerhaus, and West, 2002)

Major difficulties to be overcome

For very large processing units, estimates for capital and operating costs may not be readily available from real systems.

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Appendix 1: MatLab™ Code

```
% Opt2.m
% MatLab to call the procedures for
% Determining the k values for catalytic hydrogenation
% of Stearic Acid
% Copyright Robert Beitle and Tom Potts
% Fall 2011
% Optimization for multiple points (complete data set)
% First order in alcohol and first order in hydrogen

% set convenient format
format('compact');
format('long');
% Define starting k value, which is the rate constant for the reactions
   k(1)=1;
   k(2)=1;

% Set the number of data points to run
   n=16;

% Define the vector of initial and final values
   Intval=zeros(n,9);
% intval(1) is the residence time of the reactants in the reactor, so the
% integration below will be over the range [0, tau]
% Initial concentrations
%   2=stearic acid
%   3=hydrogen
%   4=stearyl alcohol
%   5=stearane
% Final concentrations
%   6=stearic acid
%   7=hydrogen
%   8=stearyl alcohol
%   9=stearane
Intval = [
];


% set up a vector for the calculated k values
   kf=zeros(n,2);
```

```
for i=1:n
% Call the optimization through fminsearch, returns k value that most
% generates the final value of the product concentration which most closely
% matches the experimental value of the product concentration
   k(1)=1;
   k(2)=1;
   kf(i,:) = fminsearch(@(u) mbanana(u, Intval(i,:)), k);
end

disp(kf)


function lsqdiff=mbanana(k, intvals)
% Optimization function
% Set up initial and final concentration values
% Integrate from zero to tau and define the optimization function
% Catalytic hydrogenation of Stearyl Alcohol
% Tom Potts
% Fall 2011

% Temperature 313
% Sample 120801HT2A

% tau is the residence time of the reactants in the reactor, so the
% integration below will be over the range [0, tau]
   tau = intvals(1) ;

% Define your initial concentrations here
%   1=stearic acid
%   2=hydrogen
%   3=stearyl alcohol
%   4=stearane
   Czero(1)=intvals(2);
   Czero(2)=intvals(3);
   Czero(3)=intvals(4);
   Czero(4)=intvals(5);
```

```
% Define your final concentrations here
%   1=stearic acid
%   2=hydrogen
%   3=stearyl alcohol
%   4=stearane
    Cfinactual=zeros(4,1);
    Cfinactual(1)=intvals(6);
    Cfinactual(2)=intvals(7);
    Cfinactual(3)=intvals(8);
    Cfinactual(4)=intvals(9);

 % Now call the diff eqns concatinating the k vector with the inital
 % conditions, this piggy backs the kvector to pass it to the reactions
[X,T]=ode45(@rxns2, [0 tau], Czero, [], k);
% Find end of reactor concentrations calculated by the integration
% mn is the matrix of the calculated concentrations at the various times
% through the reactor. We want the last values of the matrix, these are
% the final concentrations from the reactor
%   1=stearic acid
%   2=hydrogen
%   3=stearyl alcohol
%   4=stearane
    mn=size(T);
    C1=T(mn(1),1);
    C2=T(mn(1),2);
    C3=T(mn(1),3);
    C4=T(mn(1),4);

% Define lsqdiff as objective function
%   1=stearyl alcohol
%   2=hydrogen
%   3=stearane
% Note: for this calculation set, the hydrogen concentration is assumed
% constant, so there is no hydrogen term for the lsqdiff
    lsqdiff=(C1-Cfinactual(1))^2+(C3-Cfinactual(3))^2+(C4-Cfinactual(4))^2;
```

```
function dC=rxns2(t,C,k)
% the coupled rate reactions functions
% Hydrogenation of stearyl alcohol
% First order in alcohol,first order in hydrogen
% Tom Potts
% Fall 2012

%   1=k1, the rate constant for reaction 1
%   2=k2, the rate constant for reaction 2
   k1=k(1);
   k2=k(2);

% set up vector for the return values
   dC=zeros(4,1);

% rate equations defined here
%   1=stearic acid
%   3=stearyl alcohol
%   2=hydrogen (assumed constant for this calculation set)
%   4=stearane

   dC(1)= - k1*C(1)*C(2)^0.5;
   dC(2)= 0;
   dC(3)= + k1*C(1)*C(2)^0.5-k2*C(3)*C(2)^0.5;
   dC(4)=k2*C(3)*C(2)^0.5;
```