Techniques for Evaluating and Guiding Development of Renewable Chemical Technologies for Sustainable Products

By

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Dedication

This dissertation is dedicated to my mother, Radha Gunukula, my twin brother, Santhosh Gunukula, and my younger brother, Venkat Gunukula.

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Abstract

The bulk chemical industry has long been dominated by products made from the petroleum feedstock. Increasing concerns over the volatility of petroleum feedstock prices and the environmental impact of petroleum extraction and processing have driven interest in bulk chemical production from sugars. Innovation in bio-catalytic and chemical catalytic technologies is enabling researchers to develop efficient conversion technologies for the production of biorenewable chemicals from sugars. In a resource constrained world, it is critical to develop these new biorenewable chemical technologies in a sustainable manner. This study addressed some of the problems related to the sustainability assessment of new biorenewable chemical technologies. A new approach was introduced by combining the methods of feasible space, techno-economic analysis, and life cycle assessment to evaluate and guide the development of new biorenewable chemical technologies. Generalities in the area of biorenewable chemical production were found from the analysis of multiple biorenewable chemical processes. The risk analysis has shown that economic and market risks to biorenewable chemical investments can be reduced and profitability of investments can be increased with platform technologies. Comparative economic analysis of multiple biobased adipic acid routes has shown that the significant weakness of purely chemical route to a target biorenewable chemical can be overcome by producing an intermediate chemical form sugars using a biocatalyst and then converting this biological intermediate to the target biorenewable chemical using a chemical catalyst.

CHAPTER 1

General Introduction

The bulk chemical industry has long been dominated by products made from petroleum feedstocks such as coal, natural gas, and crude oil. The petroleum feedstock reserves are finite and depleting rapidly. The extraction and processing of petroleum feedstock have been causing detrimental impacts to ecosystems, soils, and ground water [1-3]. The volatility of petroleum feedstock prices increases economic risk to investments for the production of bulk chemicals from petroleum feedstock. Increasing concerns over the volatility of petroleum feedstock prices and the environmental impact of petroleum extraction and processing have driven interest in bulk chemical production from a large variety of plant-derived feedstocks such as carbohydrates, triglycerides, glycerol, and lignin [4-8]. The effect on food prices and environmental impacts such as eutrophication are, however, concerns with the production of chemicals from a plant derived feedstock [9].

One can create a route to produce a value added biorenewable chemical from plant-derived feedstocks solely using a chemical-catalytic conversion pathway, as well as wholly bio-catalytic conversion pathway, and also by integrating bio-catalytic and chemical-catalytic technologies. The catalytic conversion of plant-derived feedstocks to biorenewable chemicals has been the subject of intense research. Various homogeneous and heterogeneous catalysts were proposed for the production of bio-commodity chemicals from carbohydrates, triglycerides, fatty acids, glycerol, and lignin [10-14]. Conversion of highly functionalized sugar into a value added organic chemical using a metal catalyst can achieve high rates of production. However, such conversion may reduce selectivity of a chemical reaction and lower the activity and stability of the metal catalyst. For example, the high turnover frequency of metal catalysts were achieved for

the oxidation of glucose to glucaric acid using Pt/C catalyst and the conversion of fructose to ethylene glycol using Ru catalyst [15,16]. However, the ethylene glycol and glucaric acid yields of only 60.0% were achieved using these catalysts [15, 16]. Low selectivity and stability might hinder the development of an economically viable route solely through chemical catalysis [17]. One way to overcome such issues with metal catalysts is by reducing the functionality of the chemical catalytic substrate. The functionality of a substrate can be reduced using a biocatalyst.

A common approach to reduce the functionally of biomass-derived sugar into a value added biorenewable chemical is to use microbial metabolism. The development of highly specialized biological processes has become commonplace as developments in the biological sciences have made it much easier to modify microbial metabolism to create efficient industrial biocatalysts. Recently, *Escherichia coli* are engineered to produce fatty acids, alkanes, 1,4-butanediol, fatty alcohols, and waxes from carbohydrates [18-20]. One of the advantages of microbial production is that it can convert highly functionalized sugar into a single biorenewable chemical with high specificity, however, with low volumetric productivity. Often, microbial strains like *E.Coli* can't sustain to high fermentation titers of a biorenewable chemical. Low volumetric productivities and fermentation titers may create a barrier to achieve economic viability for a specific biorenewable chemical route.

The significant weaknesses of both chemical catalysis and bio-catalysis can be overcome by deriving an intermediate chemical from highly functionalized sugars via microbial technology and then converting this mono or bi functionalized biological intermediate to a specific-target biorenewable chemical using chemical catalysis through decarbonylation, hydrogenation, hydrogenolysis, oxidation, cycloaddition or dehydration. The National Science Foundation (NSF)-funded Engineering Research Center for Biorenewable Chemicals (CBiRC) is developing

technologies to facilitate the transformation of the chemical industry from the petroleum feedstock to bio-based feedstock through the coupling of bio-catalysis and chemical-catalysis. The philosophical basis of CBiRC arises from two concepts; a) "*efficient conversion processes for producing chemicals from biobased feedstocks will tend to be based on a synergistic combination of biocatalysis and chemical catalysis; and b) transforming the chemical industry from petrochemicals to biorenewable chemicals will require a generalized framework that can produce a range of chemicals using a common technology*" [21].

The CBiRC research team is currently focused on diversifying the chemical production through manipulation of fatty acid/polyketide metabolic platform with subsequent chemical catalyst conversion. Researchers in CBiRC are developing three technologies for the conversion of glucose into a range of commodity chemicals: the carboxylic acid, the pyrone, and the bi-functional technologies. The carboxylic acid technology involves microbial-based production of short-to-medium chain fatty acids that can further converted through chemical catalysis into a range of commodity chemicals [22, 23]. For example, a representative process is hydrogenation of fatty acids to fatty alcohols. The pyrone technology involves the production of pyrones via bio-catalysis followed by ring opening or aromatization using chemical catalysis to produce a range of chemicals such as sorbic acid and benzoic acid [24, 25]. The bi-functional technology involves biological production of bi-functional intermediates such as 6-hydroxy hexenoic acid and 1,6-hexanediol that are subsequently upgraded to yield α, ω-functionalized molecules such as adipic acid and dodecanoic acid via chemical catalysts [26, 27].

This research presents methods and techniques for evaluating CBiRC type new biorenewable chemical technologies. In Chapter 2, a feasible space method was extended by combining it with techno-economic analysis (TEA) and life cycle analysis (LCA) to determine

economic and environmental viability of a biorenewable chemical production process. Feasible space method was used to analyze multiple biorenewable chemical processes in chapter 3 to determine the generalities in the area of bio-commodity chemicals. In chapter 4, various risks associated with the investments for the production of biorenewable chemicals using the CBiRC type technologies and single-product technologies were evaluated. Multiple routes to adipic acid were evaluated in chapter 5 to identify general rules regarding the choice of handoff chemical in systems of coupled biological and chemical catalysts.

A fundamental question for the CBiRC researchers who are developing renewable chemical routes is how to predict its commercial and environmental feasibility during process development and how to identify and understand the nature of the key barriers to commercial feasibility for a potential chemical route. It is not enough to identify technical barriers, but to understand how an improvement (or decline) in one process area affects performance in another. That is, to understand the trade-offs among the many processes that make up the biorenewable production process. In chapter 2, feasible space method was combined with techno-economic analysis (TEA) and life cycle assessment (LCA) methods to determine economic and environmental viability of a process for the production of biorenewable chemical. Combining these methods allows the trade-offs among key process parameters to be quantified. These trade-offs can be used to set performance targets that will ensure the commercial and environmental feasibility of the full production process for the development teams.

The TEA and LCA methods can be used to assess economic and environmental viability of chemical and fuel production processes, respectively [28, 29]. The TEA and LCA are well established methods, which when used to assess new biorenewable chemical processes, ensures that target prices, energy consumption, and greenhouse gas (GHG) emissions can be achieved

[28, 29]. The development of a detailed process model consisting of major unit processes is necessary to assess economic and environmental viability of a process for the production of biorenewable chemical using TEA and LCA methods. The production cost can be used as an economic performance metric, and energy consumption and GHG emissions can be used as environmental performance metrics. The material and energy balances of the detailed process model are needed to estimate production cost, energy consumption, and GHG emissions of the biorenewable chemical production process. These balances can be estimated by writing out mass and heat balance equations of each unit process and solving these equations using methods such as Gaussian elimination. The calculation of equilibrium constants and heat of reactions from thermodynamic data are necessary to solve system of mass and heat balance equations. A time-consuming search is required to find this data of equilibrium constants and heat of reactions. The simulation software ASPEN Plus® and SuperPro designer® does estimate material and energy balances instantly. The results of simulation are also used to size and cost process equipment. The process equipment cost is used to estimate the capital cost of production plant.

ASPEN Plus® was used for simulation of distillation type processes and catalytic reactions. ASPEN Plus is the accepted industry standard process simulation software that provides sophisticated models of vapor-liquid equilibrium separations and chemical reactions which will allow to more accurately simulating distillation and catalytic reactions. The RadFrac method was used to perform the simulation of distillation columns. The ASPEN Plus® shell and tube model was utilized to determine the areas of the condenser, reboiler, and heat exchanger columns. SuperPro Designer® was used for simulation of seed and product fermentation, vacuum filtration, and countercurrent solvent extraction using rotating disc contactor column, because

this software provides necessary models of these processes that are not available in ASPEN Plus®.

The feasible space method was demonstrated in chapter 2 by analyzing the production of capric acid process. The aim of the chapter 3 work was to find out the results of analysis of capric acid production are generalizable to other bio-commodity chemical production processes. The economic and environmental performances of a range of bio-commodity chemical production processes were determined in hopes of finding general trends in the area of bio-commodity chemical production. The anaerobic production processes of adipic acid, succinic acid, 3-hydroxy propionic acid, 1, 3- propanediol, isobutanol and aerobic production process of 1, 3- propanediol have chosen for the analysis of multiple biorenewable chemical processes using the feasible space method.

Significant research is ongoing throughout the world that is aimed at developing single-product technologies that target a single biorenewable chemical [30-32]. Unfortunately, this approach is slow and costly as it requires all the investment in time and money for one chemical at a time. Moreover, investing capital for producing renewable chemicals via technologies that yield a single-product is less profitable because this technology must live with the risks of a specific chemical production. Having the ability to yield a suite of products with the same technology, the CBiRC technology may provide commercial advantage to the renewable chemical producers by reducing risks and by increasing the profitability of an investment relative to the single-product technologies. In chapter 4, it has been quantified how CBiRC technology impacts the risks to the irreversible investment for the renewable chemical production relative to the single-product technology.

The mean and variance of NPV distribution can be used to represent profitability and risk to biorenewable chemical investments, respectively. Mean reverting process was used to generate sample paths for each economic variable of single-product and platform technologies. The Monte Carlo simulation then randomly drew values from each sample path of economic variable to generate a unique set of market prices and costs from which NPV was computed. The entire distribution of all draws (10,000) resulted in a NPV distribution for investment in a single-product technology as well as the platform technology.

Since it is possible to produce a specific-target biorenewable chemical from numerous biologically derived intermediate chemicals via chemical catalysis, a fundamental question for the integration of bio-catalysis and chemical catalysis is which intermediate chemical should be derived from the sugar via bio-catalysis before it is handed off to the chemical catalyst platform. One of the disadvantages of integration of bio-catalysis and chemical catalysis technology is an increase in number of process steps relative to a purely bio-catalytic or chemical catalytic route. This increase in the number of process steps may increase the production costs of a chemical. That means it is not always feasible to produce a value-added chemical from the integration of bio-catalysis and chemical catalysis. Before determining the hand-off chemical, it is therefore important to screen the possible multiple routes to the target value added chemical at the earliest stages of development to see should value added chemical be yielded from sugar through coupling of bio-catalysis and chemical catalysis is economically viable over purely biological or purely chemical catalysis. In chapter 5, purely biological, purely chemical, and two integrated biological and chemical routes to adipic acid were evaluated to determine for inherent advantages of one pathway relative to the others. It is expected to identify the most promising

pathway to adipic acid and “hand-off” point. It may be able to deduce some general rules regarding the choice of pathway in systems of coupled biological and chemical catalysts.

I have analyzed economic viability of multiple biorenewable chemical routes in chapters 2, 3, 4, and 5. The TEA method was used to assess economic viability of biorenewable chemical routes. The important economic variables in the TEA model are the prices of glucose, electricity, and natural gas. A variation in the prices of glucose, electricity, and natural gas was found in the literature [33-37]. The prices of sugar, electricity, and natural gas were found to be in the range of 0.19-0.65 ($/kg), 0.05-0.12 ($/kWh), and 1.92-12.69 ($/MMBtu) respectively [33-37]. The values of 0.30 ($/kg), 0.07 ($/kWh), and 3.35 ($/MMBtu) represent the average prices of sugar, electricity, and natural gas, respectively. The average prices were estimated using the historical price data from 2007 to 2015 [35-37]. These average price values were used while performing economic analysis of biorenewable chemical routes.

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CHAPTER 2

Evaluating and Guiding the Development of Sustainable Biorenewable Chemicals with Feasible Space Analysis

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ABSTRACT

The economic and environmental performance of a biorenewable chemical process was analyzed by defining the feasible design space in terms of process parameters. This approach can be used to evaluate the feasibility of chemical processes for a range of process parameter values. Defining the feasible spaces of a process under development provides valuable information about the feasibility of the process and the trade-offs in performance among unit processes. The results of feasible space analysis can be used to set performance targets for the process development and to avoid unfruitful development costs. A process for the synthesis of saturated fatty acid from glucose using a biocatalyst was analyzed using the feasible space approach. Bio-catalyst yields of ≥ 0.25 gg^{-1}, titers of ≥ 40 gl^{-1}, and volumetric productivity of 2 $gL^{-1}h^{-1}$ are found to result in cost, greenhouse gas emissions, and energy consumption as good as or better than conventional coconut oil derived fatty acid process.

Key words: Biocatalysis, Biomass conversion, Process development, Feasible space, Fatty acid, Sustainability

Introduction

There is growing interest in biorenewable chemicals because of their perceived economic and environmental benefits [1]. It is expected that production from renewable, plant-derived sugars should, in the long-run, allow a low cost of production relative to conventional petrochemicals. Environmental benefits are also expected through the use of biorenewable feedstock, particularly in terms of carbon footprint. Unfortunately, none of these benefits are certain and recent biorenewable chemical investments have included some high-profile disappointments [2]. To avoid such disappointments, the economic potential and environmental sustainability of a new chemical production process should be determined before large irreversible investments are made in full process development and scale-up.

The techno-economic analysis and life cycle assessment are often used to assess the economic and environmental performances of new chemical processes [3,4]. One process realization or a single combination of process parameters (yield, selectivity, etc.) is usually evaluated when assessing the potential of a new chemical process [4]. If such analyses indicate that a process is not economically viable and environmentally sustainable, the further development may be stopped. The economic and environmental viability of a new chemical process, however, still may be achieved by further improvement of the process. It is, therefore, necessary to assess a new chemical processes for a range of combinations of process parameters to avoid missing investment opportunities for the production of chemicals. Such assessment enables to determine combinations of process parameters that would give economically and environmentally feasible chemical production process. Determining such feasible combinations of process parameters will allow development teams to focus on improving process parameters that, on the basis of the current state of technology, are not in the feasible range.

A new biomass conversion technology (biological, chemical, and thermos-chemical) has to pass through multiple stages of process development (laboratory-, pilot-, and demonstration-scale) before it is implemented at commercial scale. Often transition from early research to commercialization transition takes 10 years or more and requires large capital investment [5]. Reducing technology development time will enable faster access to markets. Technology development can be accelerated by coordinating efforts between multiple development teams working on different process technologies such as catalytic conversion and separations. In this example, the economic performance of a new chemical process might be improved by developing a separation process that can be used to easily recover and recycle unconverted raw material given that it is difficult to improve the catalyst conversion. Technology development efforts tend to have an asymptotic return on investment, such that economic benefit per dollar invested in improving process performance grows smaller. Determining process parameters that are likely to be most fruitful to pursue improvement can allow companies that produce biorenewable chemicals to avoid unfruitful investments in technology development.

Several semi-quantitative methods have been proposed that integrate economic and environmental indicators to provide a generic ‘feasibility score’ that is useful as a way to sift through many novel biorenewable chemical routes early in the development process [6]. None of these methods, however, provide the quantitative information about the fruitful investments and the consequences of process trade-offs. Understanding these consequences allows the setting of meaningful performance targets and the coordinating of development goals for the further development of a process for the production of a new chemical. . We addressed the shortcomings of existing approaches by combining feasible space, TEA and LCA methods to quantitatively assess the economic and environmental viability of a new biorenewable chemical production for

a range of combinations of process parameters. In addition, combining these methods enables to determine trade-offs among the process parameters and to optimize technology development resources of time and money.

The feasible space method maps the trade-offs in process parameters into production performance metrics, such as production cost of a process. Such a mapping defines a "space" of process parameters that will result in a commercially viable process for chemical production. The feasible space method has been used to optimize cost performance of existing production processes. The feasible space method is, however, never utilized to optimize environmental performance of new and existing chemical production processes. For example, Joseph et al. (2006) has proposed a framework based on the feasible space method to optimize a chromatography column for the separation of biopharmaceuticals at large-scale [7]. This framework is used to select optimal design parameters, such as diameter, and operating conditions, such as flow rate, that minimize the operating cost of the chromatography column. In addition to cost considerations, a new and existing chemical processes must meet environmental objectives, as there is growing concern over the increasing greenhouse gas (GHG) concentrations in the atmosphere [8]. Since the energy sector is one of the major sources of GHG emissions, it is also essential to develop energy efficient chemical processes.

The minimum selling price (MSP) can be used as an economic performance metric, and energy consumption and GHG emissions can be used as environmental performance metrics [9]. The MSP of a biorenewable chemical that is synthesized using a biocatalyst, for example, is driven by the costs of feedstock, fermentor, and separations [10]. Feedstock cost is dominated by the yield of chemical per unit of feedstock and the price of feedstock [11]. The separation cost is driven by product titer [12]. The production rates influence the capital and operating costs of the

fermentor [13]. Similar to the MSP, the GHG emissions and the energy consumption of a biocatalytic process are largely influenced by productivities, titers, and yields. The feedstock production might cause the largest life cycle environmental impact in the biorenewable chemical production system. The yield determines the amount of feedstock required for making chemical and thus the feedstock contribution to the overall energy consumption and GHG emissions of the biorenewable production system. The energy requirement of the fermentation process depends on the agitator power (kW) which, in turn, depends on production rates. The fermentation titer impacts the energy demand and GHG emissions of downstream processes.

In the current work, the production of fatty acid from glucose using a biocatalyst was used as a model system to demonstrate the assessment of a new biorenewable chemical process by combining the methods of feasible space, TEA, and LCA. Fatty acids are platform molecule that can be transformed into a range of industrial chemicals, such as fatty alcohols [14], α-olefins [15], ethyl esters [16], and alkanes [17]. Global consumption of fatty acids is increasing at a rate of 3% annually [18]. Currently, fatty acids are primarily made from natural oils, such as coconut oil [18]. The hydrolysis of these natural oils results in a mixture of fatty acids that is further fractionated into pure fatty acids. The environmental impact of conventional fatty acid production is high, as the fractionation process consumes large amounts of fossil energy [19]. The new market opportunities for fatty acids and negative environmental impacts of conventional process have driven interest towards developing efficient biocatalysts to synthesize fatty acids from sugars [20]. Producing fatty acids in a microorganism would allow tailoring properties, such as chain length and functionality, which can add special value by addressing the needs of various industries such as the detergent industry [21].

In this work, we used capric acid as a model fatty acid to evaluate the economic and environmental performance of fatty acid production by combining the methods of feasible space, TEA, and LCA. A process flow diagram (PFD) for the synthesis of capric acid was developed. The PFD was modeled to determine material and energy balances for the capric acid production process for various combinations of yield, titer, and productivity. These balances were used to estimate MSP, energy use, and GHG emissions of the capric acid production process. The assessment of glucose based capric acid production process by combining methods of feasible space, TEA, and LCA enables to gain valuable process insights that can be used to evaluate and guide the development of a new biocatalyst for the production of capric acid. This assessment indicated that glucose based capric acid production process has a potential to compete with the conventional technology in terms of economic and environmental performance. The biocatalyst development team must achieve fermentation yields of > 0.25 g g^{-1} and titer of > 40 g l^{-1} to meet the performance of the conventional technology in terms of cost, energy use, and GHG emissions.

Process Description and Modeling

Process flow diagram description

We created a PFD of the process for the capric acid production from glucose (Figure 1). The annual plant capacity of 40,000 metric tons of glucose conversion and the plant life of 20 years are assumed. The PFD has three major sections: seed fermentation, product fermentation, and separation/purification, which are described in detail in the following subsections.

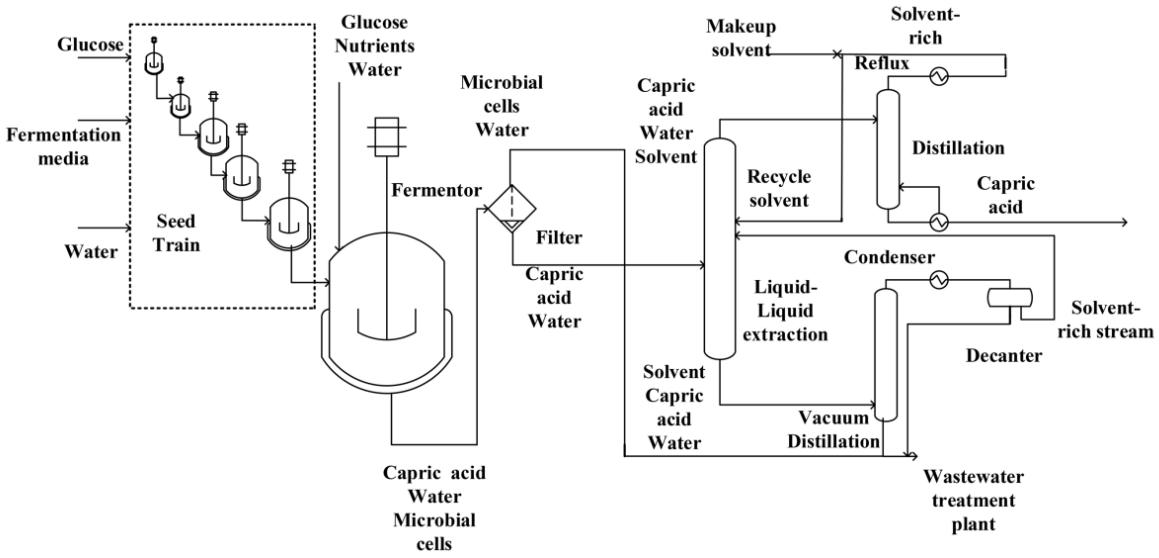

Figure 1 Proposed process flow diagram for the production of capric acid from glucose

Seed fermentation section

A strain of *Escherichia coli* can be used to synthesize capric acid from glucose [20]. This strain is cultivated under microaerobic conditions on Luria Bertani (LB) medium in a seed fermentation train consisting of a series of fermentors [22]. The first fermentor in the seed fermentation train with a volume of 10 L is inoculated with an *E. coli* cell culture grown in a small laboratory scale fermentor with a volume of 1 L. After *E. coli* cells were grown to a particular density, the cell broth was transferred to the next reactor in the seed fermentation train, and so on. After attaining required cell density for the inoculation of the production fermentors, the *E. coli* cell broth from the final seed reactor was sent to the production fermentor.

SuperPro Designer® was used to simulate the seed fermentation train. The material and energy balances and the volumes of seed fermentors were estimated from these simulations. The growth of *E. coli* in the seed fermentation train was modeled using conventional Monod kinetics. A value of 0.4 h^{-1} was used for the maximum specific growth rate. The yield coefficient of

biomass from glucose was taken as 0.5 (g dcw) (g glucose)$^{-1}$. The seed reactors were assumed to be operating in batch mode with a turnaround time 6-hours [23].

Product fermentation section

The microbial inoculum from the final fermentor of the seed fermentation train was fed to the production fermentor. The production fermentor was operated in fed-batch mode by feeding glucose. In the production fermentor, microbial cells synthesize capric acid from glucose and secrete capric acid into the fermentation broth. The production of capric acid was carried under microaerobic conditions at 37 ^{o}C. A base was added to the fermentor to maintain a pH of 5 as the production of capric acid would otherwise cause a decrease in pH.

The production fermentor was modeled using SuperPro Designer® to estimate its volume. Capric acid was assumed to be a growth-associated product, with the specific rate of capric acid production being directly proportional to the specific growth rate [24]. The values for maximum specific growth rate, biomass yield, and capric acid yield were taken as 0.1 h^{-1}, 0.05 (g dcw) (g glucose)$^{-1}$, and 0.38 g (g glucose)$^{-1}$, respectively.

Separation and purification section

The fermentation broth containing capric acid, water, nutrients, and other impurities is sent to a rotary vacuum filter. The filter removes microbial cells and other solids from the fermentation broth [12]. The retentate of microfiltration, containing microbial cells and other solids, was discharged as a waste stream. The flow rates of retentate and filtrate and filter membrane area were estimated using cake dryness and filtration time data.

The capric acid can be extracted from the clarified fermentation broth by solvation with hexane. The reader is referred to the Appendix A about details on the solvent selection criteria and solvent extraction process modeling. SuperPro Designer® Version 9.0 was used for the

simulation of the solvent extraction column. The volumetric flow rates of the raffinate and extract phases of the column, the diameter of a column, and the number of stages were estimated from the simulation.

The extract phase, containing hexane, capric acid, and a very small amount of water, was sent to a distillation column. Distillation was utilized to recover the hexane. The hexane and water mixture was collected as a condensate at the top of the distillation column. This mixture was recycled to the solvent extraction column. The capric acid was recovered from the reboiler at the bottom of the distillation column. ASPEN Plus was used to simulate the distillation column because it provides sophisticated models (such as RadFrac) that can be used to model distillation columns rigorously.

The small amount of hexane, dissolved in the continuous phase of the solvent extraction column, can be recovered using an evaporation column followed by a centrifuge. The top vapor stream of the evaporation column containing water and hexane was sent to a condenser. The evaporator, condenser, and centrifuge processes were modeled using the ASPEN Plus. The parameters for the evaporation column were determined using vapor-liquid equilibrium data of hexane-water mixtures. The non-random two-liquid model was used to generate such equilibrium data. The shell and tube model in ASPEN Plus was chosen to model the condenser.

Estimation of microbial capric acid MSP

The built-in cost models in the SuperPro Designer simulation were used to estimate the equipment costs of the seed and production fermentors, the vacuum filter, and the solvent extraction column. The cost of the distillation column was estimated on the basis of the type of tray, the number of trays, and the tower diameter [25]. A cost correlation between purchase-cost and the outside surface area of the tubes was used to calculate the costs of the condenser, the

reboiler, and other heat transfer equipment [26]. The purchase cost of the centrifuge was estimated using an empirical equation based on the diameter [26]. The equipment costs were updated to US $2015 prices using chemical engineering plant cost indices. The ratio factors based on delivered equipment cost were used to estimate the fixed-capital investment for the capric acid production plant [25].

The required quantities of raw materials and utilities were calculated using the simulated material and energy balances. The prices of glucose, hexane, natural gas, and electricity were assumed as 0.30 \$ kg^{-1}, 0.40 \$ kg^{-1}, 3.35 \$ $MMBtu^{-1}$, and 0.07 \$ kWh^{-1}, respectively. The long term mean or average prices of electricity and natural gas were used in the calculation. These average values were estimated from the ten year data of electricity and natural prices in the U.S. The hexane price was obtained from the SuperPro Designer® software pure component database. The price of glucose was obtained from a personal communication with the managers of corn wet milling plants in the Midwest region of the United States. A correlation between the plant capacity and the operating labor was used to determine labor charges [25]. The costs associated with maintenance and operating overheads were assumed as 8% and 23% of total purchased equipment cost and labor cost, respectively [26]. Wastewater treatment was assumed to take place in an external facility for a fee of \$0.22 per kg of organic removed [26]. The calculations for the depreciation of capital investment were carried out using the Modified Accelerated Cost Recovery Systems (MACRS) method [26]. The general expenses were calculated as 10 % of total revenues generated from the sales of capric acid [26]. An economic model was built using the estimated capital and operating costs. The discounted cash flow analysis method was used to estimate the MSP of capric acid [9]. A discount rate of 10% was chosen for this analysis [9]. The

MSP of capric acid was calculated for various combinations of titers, yields, and volumetric productivities.

Estimation of GHG emissions and energy consumption

The GHG emissions and energy consumption of the process for the production of capric acid from glucose were estimated using the Life Cycle Analysis (LCA) approach. The functional unit was defined as 1 kg of capric acid made from corn. The system boundaries include cultivation of corn, conversion of corn to glucose through the corn wet milling process, and the microbial synthesis of capric acid from glucose.

The CO_2 emissions associated with corn grain production and corn wet milling process to convert corn into glucose were obtained from Akiyama et al. (2003) as 0.15 kg/kg-glucose and 0.35 kg/kg-glucose, respectively. The value of CO_2 absorbed by corn plants from the air was accounted as 1.47 kg/kg-glucose [27]. This value was estimated from the stoichiometry of glucose formation by corn plants from water and CO_2 [27] . It requires a total of 7.5 MJ to make 1 kg of glucose from corn, which includes the energy requirements for corn planting, cultivating, harvesting, and wet milling [27]. The mass ratio allocation method was used to allocate process flows among the products of the corn wet milling process [27]. The electricity and steam requirements, which were estimated from the simulation of the process, are utilized to determine the energy consumption and GHG emissions associated with the production of capric acid from glucose. The lifecycle energy for producing 1MJ of electricity and steam from natural gas in the USA and corresponding GHG emissions were found in the Ecoinvent database [28].

Estimation of selling price, GHG emissions, and energy consumption of coconut-oil-derived capric acid

A mixture of capric acid, octanoic acid, palmitic acid, and lauric acid and glycerol is formed when coconut oil is hydrolyzed [29]. The by-product glycerol is separated from the mixture of fatty acids using a distillation column [29]. The fatty acid mixture is then fractionated into capric, octanoic, palmitic acid, and lauric acids using fractional distillation column [29]. We did not perform economic analysis of the conventional process for capric acid production, as the market price of capric acid is available from ICIS chemicals [30].

The environmental performance metrics of conventional production were estimated using the LCA approach. The functional unit was defined as 1 kg of capric acid made from coconut oil. The system boundaries include cultivation of coconuts, production of oil from coconuts, and the synthesis of capric acid from coconut oil. The life cycle inventories for processes of cultivation of coconuts and extraction of oil from coconuts were found in the Ecoinvent database [28]. The material and energy balance data for hydrolysis, distillation, and fractionation processes were obtained from Gervajio (2005). The overall energy consumption and GHG emissions of the conventional process were allocated among capric, octanoic, palmitic, and lauric acids based on their concentration in the fatty acid mixture.

Results and Discussion

Since it is difficult to graph and visualize the four or more dimensional performance surfaces that represent the effect of three or more variable process parameters on a performance metric, a three-dimensional representation is used. Based upon feedback from the Center for Biorenewable Chemicals (CBiRC) Scientific Advisory Board, a rule-of-thumb volumetric productivity target for a bulk chemical via microbial synthesis is 1-3 $gL^{-1}h^{-1}$. The results of

economic analysis indicate that volumetric productivities greater than 2 $gL^{-1}h^{-1}$ have a small effect on the cost of capric acid production. For a given yield and titer, the production cost of making capric acid is reduced only by 5% when the volumetric productivity is increased from 2 $gL^{-1}h^{-1}$ to 3 $gL^{-1}h^{-1}$. The economic and environmental performance metrics of capric acid production are, therefore, estimated for a wide range of titers and yields and the constant volumetric productivity of 2 $gL^{-1}h^{-1}$. The lower and upper bounds for yield and titer are assumed to be 10 and 100% of the maximum yield of capric acid and 10 and 200 gl^{-1}, respectively. The maximum yield of capric acid from glucose under growing conditions ($\mu = 0.04\ h^{-1}$) is calculated as 0.38 (g capric acid) $(g\ glucose)^{-1}$ by incorporating stoichiometry with mass and redox balances.

Energy, GHG, and cost performance surfaces

Performance surfaces for energy, GHG, and cost are generated by mapping energy consumption, GHG emissions, and MSP of capric acid production to the corresponding titers and yields, respectively (Figure 2a, 2b, and 2c). For a given titer, MSP, energy consumption, and GHG emissions of capric acid production process are inversely related to yields (Figure 2a, 2b, and 2c). In addition, the performance energy, GHG, and cost surfaces of capric acid production have a similar shape (Figure 2a, 2b, and 2c). This indicates that the MSP, energy consumption, and GHG emissions of capric acid production are highly correlated. In other words, replacing corn with another feedstock, in an effort to reduce the total energy consumption of the process for capric acid production, will also increase or decrease the production cost.

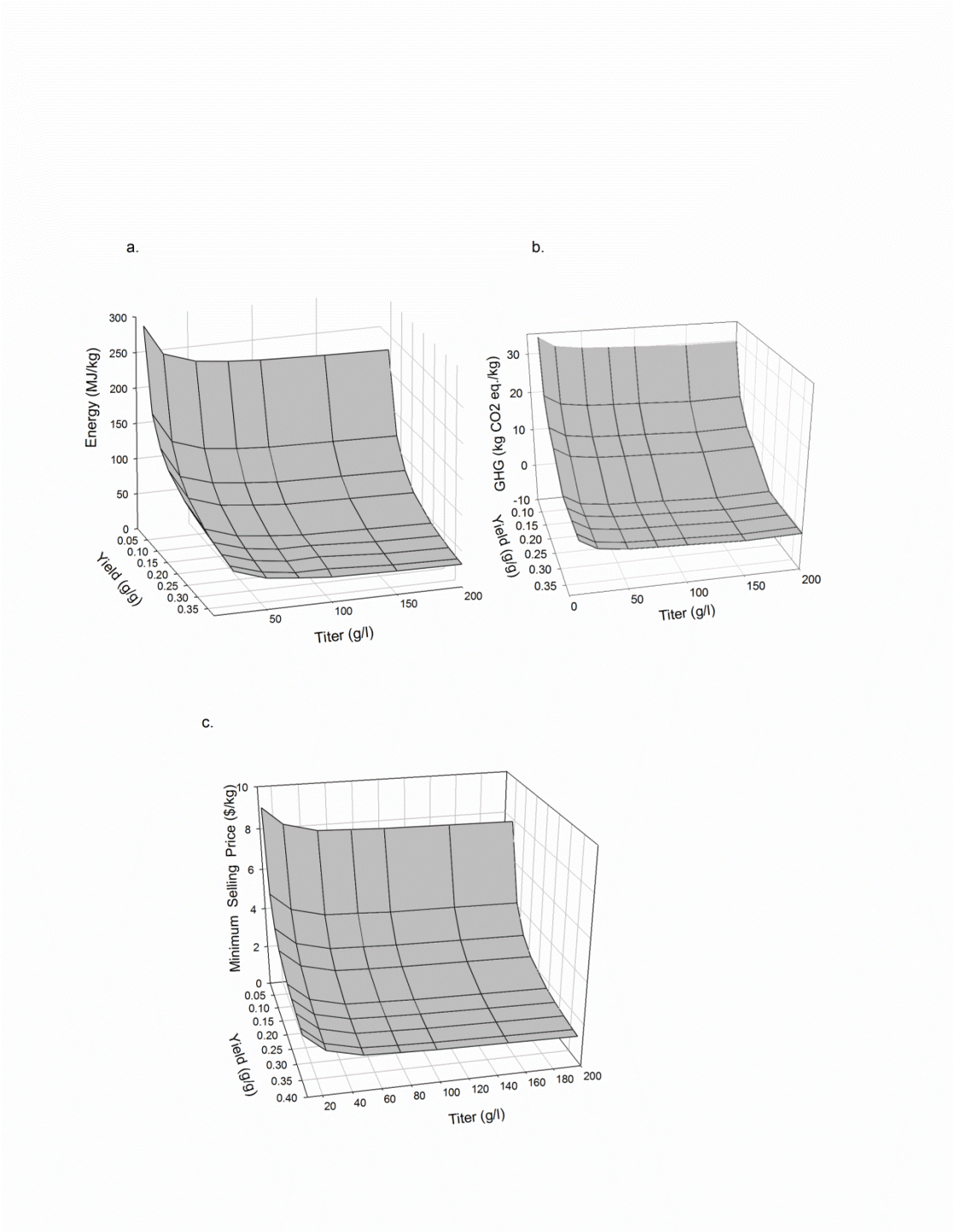

Figure 2 Performance surfaces of process for the production of capric acid from glucose
(a) Energy performance surface (b) GHG performance surface (c) Cost performance surface

A percentage change in the value of yield will have higher impact on performance metrics of capric acid production than the same percentage change in the value of titer. For example,

there is a nearly 500% increase in the total energy consumption, as the capric acid fermentation yield drops from 0.38 gg^{-1} to 0.04 gg^{-1} for a given titer (Figure 2a). On the other hand, for a given yield, there is only a 100% increase in energy consumption when the titer falls from 200 $gl^{-1}$to 20 gl^{-1} (Figure 2a). This is because any change in the value of the fermentation yield will have an effect on the entire upstream of the capric acid production chain, including corn agriculture, glucose production from corn, and the fermentation processes.

When titers are low and yields are high, the variation in titer affects the energy consumption, GHG emissions, and MSP of the capric acid production process more than yield does (Table 1). The energy consumption of the separation and purification processes dominates the overall energy consumption of capric acid production process for low titers because of the high energy requirement to evaporate the large amount of water that is associated with low titers. Such a high energy requirement is the reason for the high production cost and high GHG emissions of capric acid production for low titers.

Table 1
Dominant process sections of capric acid production

	Region 1[a]	Region 2[b]	Region 3[c]	Region 4[d]
Feedstock (Glucose) production				
Seed fermentation				
Product fermentation				
Separation and purification				

The performance surface is used to identify process sections that dominate the overall performance of capric acid production. In order to find dominant process components, we divide the performance surface into four regions.

[a] Region 1 represents high titers (>100 gl^{-1}) and high yields (>0.32 gg^{-1}) region of performance surface;

[b] Region 2 represents the high titers (>100 gl^{-1}) and low yields (<0.16 $gg^{-1}$and >0.04 gg^{-1}) region of performance surface;

[c]Region 3 represents the low titers (<30 $gl^{-1}$and > 10 gl^{-1}) and high yields (>0.32 gg^{-1}) region of performance surface, and

[d]Region 4 represents the low titers (<30 $gl^{-1}$and > 10 gl^{-1}) and low yields (<0.16 $gg^{-1}$and >0.04 gg^{-1}) region of performance surface.

A green box indicates the dominant process section in a particular region of energy performance surface

A blue box indicates the dominant process section in a particular region of GHG emissions performance surface

A yellow box indicates the dominant process section in a particular region of cost performance surface

Energy, GHG, and cost feasible spaces

The cradle-to-gate energy consumption of coconut-oil-derived capric acid production process is estimated as 49 MJ/kg, which is used to determine the constraint energy plane seen in Figure 3a. The space between the energy performance surface and the constraint energy plane is referred to as the energy feasible space (Figure 3a). We refer to the curve resulting from the intersection of the performance surface and the constraint plane as the feasible energy curve (Figure 3a). For combinations of yield, titer, and volumetric productivity within the energy feasible space, the glucose-based capric acid production consumes an amount of energy that is less than or equal to that consumed in conventional capric acid production. This is because the use of a biocatalyst that can synthesize capric acid with a high selectivity avoids the requirement

for the highly energy intensive fractionation process that is used in the conventional process. In addition, the energy required to make glucose is less than that of coconut oil (data is not shown).

The GHG space is created by determining the GHG constraint plane (Figure 3b). The cradle-to-gate GHG emissions of conventional capric acid production are estimated as 0.51 (kg CO_2 eq.) (kg capric acid)$^{-1}$. The CO_2 uptake by coconut trees and GHG emissions of coconut oil production process were taken as 0.0097 (kg) (kg capric acid)$^{-1}$and 0.23 (kg CO_2 eq.) (kg capric acid)$^{-1}$ for the calculation of the GHG emissions of the conventional process. These values were obtained from the Ecoinvent data base. The GHG emissions of process for the production of capric acid from coconut oil were estimated as 0.29 (kg CO_2 eq.) (kg capric acid)$^{-1}$. This GHG emissions value is estimated using the process energy requirement of capric acid production from coconut oil. The GHG emissions of glucose-based capric acid production process are found to be negative for some combinations of process parameters (Figure 3b). These negative emissions occur because the cradle-to-gate GHG emissions associated with capric acid production are less than the fixation of CO_2 into glucose by the growing corn plants. When capric acid is converted into products like fuel, the carbon stored in the capric acid is emitted as CO_2 during combustion. In such a case, the GHG emissions of capric acid production process must be estimated without considering the value of CO_2 fixation as glucose.

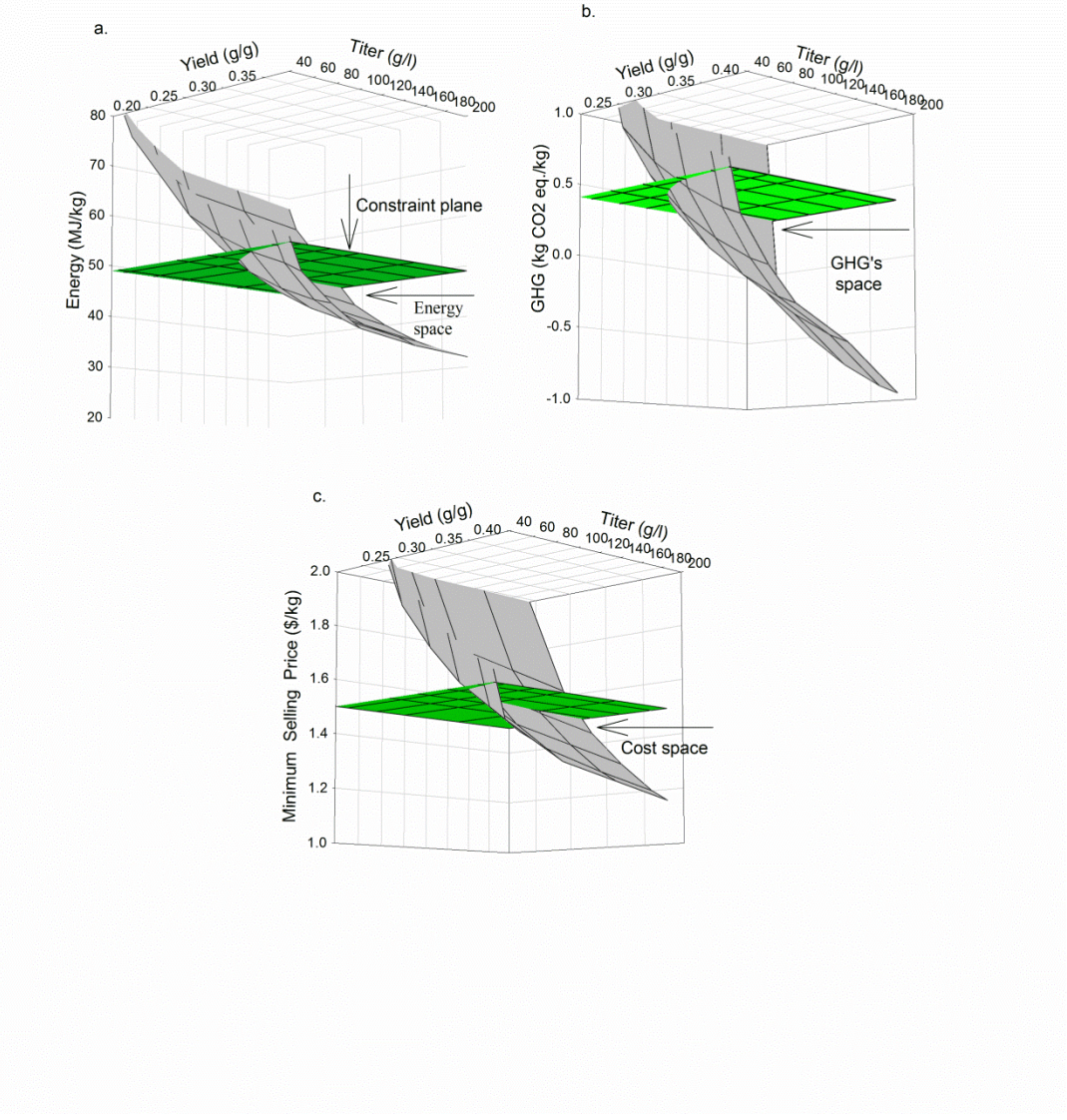

Figure 3 Three-dimensional feasible space of process for the production of capric acid
(a) Energy feasible space (b) GHG feasible space (c) Cost feasible space

The market price of capric acid is 1.50 $/kg [30], which is used to determine the cost constraint plane (Figure 3c). The space between the cost performance surface and the constraint cost plane is referred as the cost feasible space (Figure 3c). The MSP of glucose-based capric

acid production is estimated for a range of process parameters following discounted cash flow analysis. A summary of capital and operating costs of the capric acid production plant is presented in Tables 2 and 3. The total capital investment and operating expenses for synthesizing capric acid vary with combinations of process parameters. The estimates in Tables 2 and 3 represent the capital and operating costs of synthesizing capric acid from glucose using a biocatalyst that enables a titer of 75 gl^{-1}, a yield of 0.36 gg^{-1}, and a volumetric productivity of 2 $gL^{-1}h^{-1}$. We will show subsequently for this yield, titer, and productivity, the microbial production system has a lower production cost than that of the conventional capric acid production process.

The risk to the capital investment associated with producing a biorenewable chemical is high when the market prices of the raw materials and the product are volatile [32]. In general, investors expect high return on investment (i.e. high profits) when there is a high investment risk. The cost feasible space shows obtainable profits with the production of capric acid using a biocatalyst for a wide range of process parameters (Figure 3c). For a given investment risk, the cost feasible space can be utilized to determine titer, yield, and productivities that are necessary to generate expected return on investment for the production of capric acid at a commercial scale. For example, if investors are expecting a profit of $0.30 per kg capric acid when there is a high investment risk, it is necessary to develop a biocatalyst that produces capric acid at a yield of 0.38 gg^{-1}, a titer of 200 gl^{-1}, and a volumetric productivity of 2 $gL^{-1}h^{-1}$ (Figure 3c).

Table 2
Components of total capital investment for capric acid production

	Million USD 2015
Total equipment purchase cost (TEP)	7.0
Installation cost (39% of TEP)	2.7
Instrumentation (43% of TEP)	3.0
Piping (31% of TEP)	2.1
Electrical (10% of TEP)	0.7
Buildings (15% of TEP)	1.05
Yard improvements (12% of TEP)	0.84
Service facilities (55 % of TEP)	3.8
Total direct plant costs (TDC)	21.4
Indirect costs	
Engineering & Supervision (32% of TEP)	2.24
Home office & Construction (34% of TEP)	2.38
Contingency (15% of TEP)	1.05
Legal expenses (4% of TEP)	0.28
Contractors fee (19% of TEP)	1.33
Total indirect capital costs (TIC)	7.28
Working capital (5% of TDC+TIC)	1.43
Solvent cost	0.031
Total capital investment [a]	30.1

[a] This estimated capital investment is for synthesizing capric acid via microbial technology that has achieved fermentation yields of 0.36 gg^{-1}, volumetric productivity of 2 $gL^{-1}h^{-1}$, and fermentation titer of 75 gl^{-1}

Table 3
Operating expenses for capric acid production from glucose

	Million USD/year
Glucose	10.7
Media	0.9
Utilities	1.7
Waste disposal	0.25
Fixed costs[a]	2.9

[a] Fixed costs include labor wages, property taxes, insurance, operating overhead, and depreciation

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The feasible cost space can be used to guide the choice of a viable target molecule from the set of possible products that can be made from capric acid. For example, capric acid can be converted into 1-decanol [29] via hydrogenation and 1-nonene [2] via decarbonylation. The average market prices of 1-decanol is 2.20 $/kg and of 1-nonene is 1.50 $/kg [30]. The cost feasible space shows that a production cost of at least $1.20 is necessary to synthesize one kg of capric acid from glucose (Figure 3c). The feedstock (capric acid) contributions to the overall cost of 1-decanol and 1-decene production are $1.20 and $1.64, respectively. The feedstock cost contribution is estimated using practical yields that are based on conversion of capric acid. The margins left for energy and other operating costs of 1-decanol and 1-decene production are $1.00 and -$0.14, respectively, after subtracting the feedstock cost from the market prices of 1-decanol and 1-decene. Such a simple analysis indicates that the development of a technology for converting capric acid into 1-decanol is clearly a promising option.

As shown in Figure 3a, 3b, and 3c, the GHG feasible space is larger than those for energy and cost. In other words, there are more combinations of yield, titer, and productivity for which capric acid production meets the GHG constraint than there are combinations that meet the

energy and cost constraints. However, capric acid production is said to be economically and environmentally viable for a combination of process parameters only when the production meets all three constraints. In order to determine process parameters that meet all three constraints, we define the two dimensional (2D) feasible space of capric acid production using energy, GHG, and cost feasible curves, the maximum biosynthesis pathway yield, the maximum assumed titer, and the fixed volumetric productivity.

2D-feasible space of microbial capric acid process

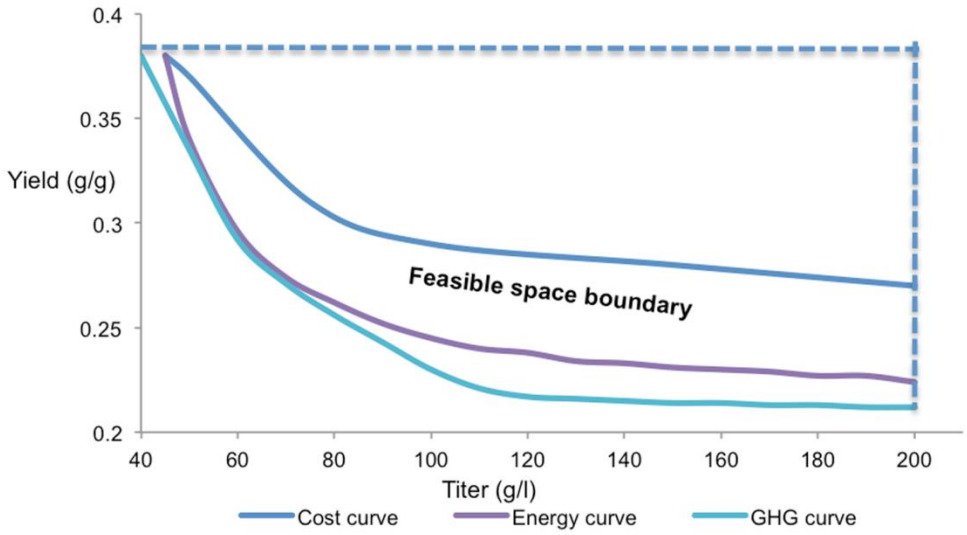

Figure 4 Two-dimensional feasible space for the production of capric acid from glucose bounded by titer, yield, and the cost curves for a constant volumetric productivity (2 $gL^{-1}h^{-1}$)

The feasible space in Figure 4 can be used by a research and development team that is developing biocatalysts for synthesizing capric acid from glucose to find out whether the biocatalytic technology has attained the required economic feasibility and environmental sustainability. For example, the *E. coli* strain developed by the CBiRC research team currently exhibits a yield of 0.27 gg^{-1}, a volumetric productivity of 0.8 $gL^{-1}h^{-1}$, and a titer of 15 gl^{-1}. The CBiRC research team has not yet achieved a process for the production of capric acid that is environmentally and economically feasible, as this combination of process performance

parameters is not present in the feasible space of capric acid production (Figure 4). The economic and environmental viability of a capric acid production process requires further improvement of the biocatalyst. The feasible space of capric acid production can be used to set performance targets for further improvement of the biocatalyst.

The trade-offs between yields and titers shown in Figure 4 are used to set performance targets for the development team. The economic and environmental viability of capric acid production can be achieved through many different routes. For example, one route is to push the capric acid yields to from 0.27 gg^{-1} to 0.38 gg^{-1}, the volumetric productivity from 0.8 $gL^{-1}h^{-1}$ to 2 $gL^{-1}h^{-1}$, and the titer from 15 gl^{-1} to 45 gl^{-1} (Figure 4). Another route is to achieve titers of greater than 200 $gl^{-1}$and a volumetric productivity of 2 $gL^{-1}h^{-1}$, while maintaining a yield of 0.27 gg^{-1} (Figure 4).

The performance targets will be determined by identifying the best route from all possible routes. The best route can be identified by comparing, among the possible routes, the development time and costs that are necessary to achieve an economically and environmentally viable process for capric acid production via each possible route. The research and management teams can qualitatively estimate such development times and costs for each route. The technological barriers and uncertainties that thwart attempts to improve fermentation yields, titers, and volumetric productivities will impact the amount of time and money necessary for achieving the performance targets. The resources necessary to push the performance level of a biocatalyst will be high in the presence of technological barriers. Further research is necessary to develop a method or a framework that can be used to quantify the amount of time and cost required to push the currently attainable yields, titers, and productivities in order to meet the performance targets.

In addition to the trade-offs, the feasible space in Figure 4 shows that there is a small effect of increase in capric acid titers of >100 gl^{-1} on the MSP, GHG emissions, and energy consumption of the process. Hence, the financial resources must be directed to improving biocatalyst yields or production rates after the development team has managed to achieve titers of >100 gl^{-1} (Figure 4). The results of feasible space analysis, therefore, can be utilized to optimize the resources of time and money required for the development of the biocatalyst for capric acid production.

The fermentation metrics of at least 0.27 gg^{-1} yield and 45 gl^{-1} titer are desirable for commercial relevance (Figure 4). With the advancement of capric acid production from laboratory- to pilot- and then to commercial scale, there is a possibility of performance loss, due to technical risks [33]. For example, in the case of aerobic fermentations, difficulties in maintaining the desired dissolved oxygen concentration in a commercial-scale fermentor could reduce the performance levels of a microbial strain to values below those obtained in the laboratory-scale fermentor. If such technical risks make it impossible to achieve biocatalyst yields of $\geq$ 0.27 gg^{-1} or titers of $\geq$ 45 gl^{-1}, the development of a biocatalyst becomes unviable. In such a situation, it is highly desirable to stop further development of the strain. There is no existing methodology in the literature for quantifying such performance losses during the scale-up of a process for the production of biorenewable chemical. Experts in bio manufacturing, however, can estimate such performance losses qualitatively from their experience of technology de-risking.

Figure 4 shows that the feasible GHG and energy curves of capric acid production are below the feasible cost curve. This indicates that capric acid production is environmentally sustainable if it achieves economic viability, but the opposite may not be true. Since the cost of

the feedstock (glucose) dominates the overall production cost (Figure A1), it may be possible to shift the feasible cost curve to below the energy and GHG curves by developing a biocatalyst that can synthesize capric acid from an inexpensive feedstock.

Variation of the feasible space boundary in Figure 4 can be caused by the price volatility of glucose, natural gas, electricity, solvent, and capric acid [32]. Such a variation can be used to indicate the financial risk associated with the investment for producing biorenewable chemicals: there will be a low financial risk for producing capric acid if the variation of the feasible space boundary of capric acid production is low. The variation of the feasible space boundary can be quantified using a procedure based on Monte-Carlo simulation [34].

Sensitivity analysis

The feasible space in Figure 4 shows how different values of titer and yield impact MSP, GHG emissions and the energy consumption of capric acid production. The feasible space analysis cannot show the impact that changes in a certain process assumption will have on the performance metrics of capric acid production. Thus, a sensitivity analysis is performed to identify process parameters that are key drivers of performance metrics of capric acid production. The fermentation yield of 0.36 gg^{-1}, volumetric productivity of 2 $gL^{-1}h^{-1}$, and the fermentation titer of 75 gl^{-1} are selected to perform the sensitivity analysis. The results of this analysis are also applicable to all feasible combinations of yields, titers, and volumetric productivities because we used the same assumptions when estimating the performance metrics of capric acid production for a range of process parameters.

The variation of MSP is measured for a ±10 % change in the prices of glucose, natural gas, and electricity, in the plant capacity, in the wastewater treatment cost, in the media cost, and in the fermentation turnaround time (Figure A2). The results of the sensitivity analysis show that

the MSP of capric acid is most sensitive to the glucose price. A 10% increase in the glucose price results in a 5% increase in the MSP of capric acid (Figure A2). Similarly, the sensitivity estimates for the plant capacity, the wastewater treatment cost, and the natural gas price are 3%, 1%, and 0.5%, respectively (Figure A2).

A variation in the values of CO_2 intake from air by corn plants is found when compared to the data of the Weidema et al. (2013) and Akiyama et al. (2003). The GHG emissions of steam and electricity generation vary with the type of fuel used for their production. Thus, the sensitivity of GHG emissions associated with capric acid production is measured both for a ± 10% change in the GHG emissions associated with the production of utilities and for a ± 10% change in CO_2 intake (Figure A3). A change in the value of CO_2 intake causes the most variation in the GHG emissions associated with capric acid production.

The sensitivity of overall energy consumption of capric acid production is measured for a ± 10% change in the energy requirement values of seed and production fermentation, and of the extraction, distillation, evaporation and glucose production processes. The process energy requirements of the fermentation and purification processes are considered in the analysis to determine the effect of uncertainties associated with the results of the ASPEN Plus and SuperPro Designer® process simulations. The energy required to make glucose from corn is the major parameter affecting the overall energy consumption (Fig A5). An 8% increase in the value of overall energy consumption results from a 10% increase in the value of the energy requirement of glucose production (Figure A4).

Discussion

The existing methods in literature can be used to qualitatively assess new biorenewable chemical technologies. These methods consider a single process realization to determine

economic feasibility and environmental sustainability of a new biorenewable chemical production process. The potential investment opportunities may be missed with the use of single process realization approach. Combining feasible space, TEA, and LCA methods enables to quantitatively determine economic viability and environmental sustainability of a new biorenewable chemical production process for a range of process parameters. Combining feasible space, TEA, and LCA methods, therefore, provides an alternative to the qualitative and single-process realization approaches for evaluating routes for the production of biorenewable chemicals.

Combining feasible space, TEA, and LCA methods enables to gain process insights for a new biorenewable chemical production. Such insights can be used to guide the development of new biorenewable chemical production process. The nonexistent of a feasible space for a new biorenewable chemical production process indicates that this process cannot compete with the conventional process. In such cases the further development of the new biorenewable chemical production process must be stopped to avoid potential losses to capital investments. The analysis of a new technology by combining feasible space TEA and LCA methods, therefore, avoids potential losses to biorenewable chemical investments. The feasible space of a biorenewable chemical production process shows trade-offs among process parameters that can be used to set performance targets to technology development teams. The feasible space of a chemical process enables to determine values of process parameters for which the investments for further improvement of a new biorenewable chemical process will result in insignificant economic and environmental benefits. The feasible space of a new process for the production of biorenewable chemical is, therefore, used to optimize new technology development resources of time and money.

The feasible space of a biorenewable chemical route can be defined in four steps. The first step is to create a PFD for the production of the chemical. The second step consists of modeling the PFD to estimate performance metrics (MSP, energy consumption, and GHG emissions) of the production system for a wide range of process parameters. Performance surfaces for cost, energy, and GHG are generated by plotting a performance metric on the z-axis and corresponding process parameters on the x-and y-axes. The third step is to estimate the production cost, the energy consumption, and the GHG emissions of the competing route. The performance metrics of the competing route are then used to determine constraint cost, energy, and GHG planes. The intersections of performance surfaces for cost, energy, and GHG and constraint cost, energy, and GHG planes are used to produce the feasible cost, energy, and GHG curves, respectively. When such feasible curves are plotted, the area inside the boundaries defines the feasible space for the biorenewable chemical route in step 4.

The assessment of a new biorenewable chemical production process by combining methods of feasible space, TEA, and LCA is demonstrated by evaluating economic potential and environmental sustainability of capric acid production process from glucose using a biocatalyst. The process insights that are gained from the feasible space of capric acid process are used to evaluate and guide the development of a biocatalyst for the production of capric acid from glucose. The existence of a feasible space for the capric acid production process indicates that this biocatalytic technology has potential to compete with the conventional technology in terms of cost, GHG, and energy consumption. The feasible space of capric acid process has shown that a biocatalyst development team must achieve fermentation yields of at least 0.27 g/g and titers of at least 45 g/l for economic and environmental viability. The feasible space of capric acid

process indicates that increasing titer beyond 100 g/l will have negligible impact on production cost, energy consumption, and GHG emissions of the capric acid production process.

The investments for the development of alternative technologies for the efficient conversion of plant derived feedstock to chemicals are limited. Therefore, the investments for the development of economically unfeasible and environmentally unsustainable technologies must be avoided. The extension of feasible space method by combining with TEA and LCA methods enables to identify potential technologies for the production biorenewable chemicals. The development of potential biorenewable chemical technologies will allow transforming the chemical industry from petrochemicals to biorenewable chemicals.

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CHAPTER 3

Sustainability Analysis of Multiple Bio-commodity Chemical Processes

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ABSTRACT

The minimum selling price (MSP), specific energy consumption, and greenhouse (GHG) emissions resulting from biobased production of adipic acid, succinic acid, 1,3-propanediol, 3-hydroxy propionic acid, and isobutanol were estimated for various combinations of titer, yield, and volumetric productivity. The MSP, energy consumption, and GHG emissions of anaerobic bio-commodity chemical processes were found to be nearly the same for a given titer, yield, and productivity. The estimated MSP of bio-commodity chemicals produced via aerobic respiration was found to be nearly 30% higher than those of produced through anaerobic fermentation respiration. Bio-catalyst yields of ≥ 0.32 g/g and titers of ≥ 45 g/l were found to result in cost, GHG emissions, and energy consumption as good or better than conventional petrochemical production processes. The economic and environmental benefits of improving titer beyond 150 g/l and volumetric productivity beyond 2 g/l/h were found to be low for the production of bio-commodity chemicals using a biocatalyst. The comparative economic analysis indicates that provision of feedstock is the dominant cost in commercially viable bio-commodity chemical production systems.

Keywords: Adipic acid, Succinic acid, 1,3-Propanediol, 3-Hydroxy propionic acid, Isobutanol, Bio-commodity chemicals, Biocatalyst

Introduction

Fuels and chemicals are conventionally made from crude oil, coal, and natural gas [1]. The reserves of fossil feedstocks are finite and will be depleted in the coming years [1]. The GHG emissions resulting from the production of fuels and chemicals using petroleum feedstock can cause global warming [2]. The depletion of fossil resources and growing concern over the climate change impacts are shifting the world focus from fossil based chemical and fuel production to biobased production [3]. One way to convert agricultural and forestry materials into sustainable products is using biocatalysts [4]. Advances in the synthetic biology and metabolic engineering have made it possible to modify microbial metabolism to develop efficient industrial biocatalysts that are used to make chemicals and fuels from plant-derived carbohydrates. In general, development of a biocatalyst will take between 10 and 15 years, and requires large capital investments [4]. To avoid unfruitful investments, it is necessary to determine the economic feasibility of biocatalyst development for producing chemicals or fuels from carbohydrates. To have a lower environmental impact, the GHG emissions and energy consumption of a bio-commodity chemical production process must be lower than that of conventional counterpart.

In previous work, we introduced the feasible space method for analyzing and guiding the development of biocatalysts for the conversion of carbohydrates to bio-commodity chemicals [5]. We demonstrated the feasible space method by determining the economic feasibility and environmental sustainability of capric acid production process for various combinations of titer, yield, and productivity [5]. The aim of this work is to determine if the results of analysis of capric acid production are generalizable to other bio-commodity chemical production processes. We determined the economic and environmental performances of a range of bio-commodity

chemical production processes that were chosen to be representative of a wide range of such production processes in hopes of finding general trends in the area of bio-commodity chemical production. The process variables of nature of fermentation (aerobic/anaerobic), the type of separation processes for the extraction of a product from the culture media, and the availability of data for the process simulations were considered while selecting the multiple bio-commodity chemical production processes. The production of succinic acid, adipic acid, isobutanol, 1, 3-propanediol, and 3-hydroxy propionic acid (3-HPA) from corn derived sugar using biocatalysts were chosen for the analysis of multiple bio-commodity chemical routes using the feasible space method.

The GHG emissions, energy consumption, and production cost of multiple bio-commodity chemical routes are found to be similar for a given combination of titer, yield, and productivity. These performance metrics of bio-commodity chemical production is, however, found to vary with the type of fermentation. The general cost, energy, and GHG contour plots are created for the aerobic and anaerobic production of bio-commodity chemicals. These contour plots can be used to screen new bio-commodity chemical routes during early stages of biocatalyst technology development. We found following generalities in the area of bio-commodity chemical production. The titer greater than 125 g/l and volumetric productivities greater than 2 g/l/h are found to have a low effect on the economic and environmental performance of the bio-commodity chemical production. If the production cost of a bio-commodity chemical production is lower than that of its conventional counterpart, we find that the GHG emissions and energy consumption of the bio-commodity chemical process are also lower than those of the competing process. These generalities can be used as general rules of thumb in the development of biocatalysts for the bio-commodity chemical production.

Methodology

Criteria for the selection of chemicals

The criteria for the selection of a range of biorenewable commodity chemical processes were determined by considering the process characteristics that influence the economics of bio-commodity chemical production. The major process steps in the production of a bio-commodity chemical using a biocatalyst are feedstock production, fermentation, and separation and purification [29-30]. The process economics of a bio-commodity chemical production are, therefore, driven by the costs of sugar (feedstock), media, fermentor, and separations. The feedstock cost is related to the yield [6]. The amount of base or acid necessary to maintain pH of the fermentation process is one of the factors affecting the cost of fermentation media. The addition of acid/base to a fermentation media can be minimized by developing a biocatalyst that is tolerant to a wide range of pH values [7]. The fermentor cost is a function of volumetric productivity and the type of fermentation process (aerobic/anaerobic) [8]. The volumetric productivity is in turn depends on the product formation kinetics (growth associated /non-growth associated/mixed mode) and the mode of fermentation process (batch/fed-batch/continuous) [9]. The biorenewable commodity chemical production processes are generally fall into the category of fed-batch and mixed-growth systems [9].

The separations cost is driven by titer, nature of product accumulation (intracellular/extracellular), and the type and number of unit processes used for the extraction of a product [10]. In general, the first step in the downstream processing of extracellular chemical production involves separation of microbial cells from the culture media [9]. The exception to this generality is seen in the cases of isobutanol and ethanol production [11, 12]. After the primary step, adsorption, distillation, or solvent extraction can be used to extract a product from

the clarified culture media [9]. The low capacity and troublesome solids handling of adsorption process made this process not suitable for the extraction of a product from the clarified culture media [13]. In the third step, various purification processes such as crystallization or adsorption (Ion-exchange) are used to purify the product. The capital and operating costs of separation and purification processes are directly related to the volume of feed from which the product is extracted [9]. The second step of the downstream processing is, therefore, dominates the total downstream costs.

The intracellular chemical production additionally requires two steps after separating the cellular material from the culture media. The first additional step involves lysing microbial cells to extract the product, and the second step consists of removing cell debris [9]. The homogenization process is used for lysing microbial cells, and the membrane filtration processes are used to remove the cell debris [9]. The additional capital operational costs due to the requirement of homogenization process followed by ultrafiltration and nanofiltration processes could make intracellular production economically unattractive for commodity chemical production. The lack of data on type and concentration of cellular material has prevented us testing this hypothesis. We, therefore, selected multiple bio-commodity chemical processes that meet the following criteria of process characteristics: Aerobic/Anaerobic, fed-batch, mixed-growth kinetics, extracellular product formation, high/low pH resistant bio catalyst, and distillation/solvent processes for the extraction of a product from the clarified culture media (Table 1).

Table 1
Model molecules for analyzing multiple microbial pathways using the feasible space approach

Bio-commodity chemical	Resistance to pH	Type of separation	Type of cultivation
Succinic acid	High	Distillation	Anaerobic
Adipic acid	Low	Distillation	Anaerobic
Isobutanol	High	Distillation	Anaerobic
1,3 Propanediol	High	LLE	Anaerobic
1,3 Propanediol	High	LLE	Aerobic
3-HPA	Low	LLE	Anaerobic

We created process flow diagrams (PFD) for the production of bio-commodity chemicals listed in the Table 1. The PFDs include production of glucose from corn through dry-mill process, bio-commodity chemical fermentation, separation and purification of bio-commodity chemical, and the production of dried distillers grains with solubles (DDGS). The glucose was assumed to be derived from corn, as it is produced abundantly in the United States. The annual plant capacity of 150,000 MT of corn conversion to bio-commodity chemical was assumed. The cost advantages due to plant size were cease to exist for bio-commodity chemical production plant capacity of greater than 150,000 MT of corn conversion (Data is not shown).

Production of Isobutanol

The recombinant microorganisms developed by Feldman et al., (2011), can produce isobutanol from a carbon source under anaerobic conditions [14]. Isobutanol can be extracted during the isobutanol fermentation using the vacuum stripping technique [11]. After fermentation, the culture media and the stripped isobutanol-water mixture were sent to a distillation column to extract isobutanol (Figure B1). The decanter followed by evaporation processes were used for further purification of isobutanol. The operating conditions and modeling parameters of isobutanol production were obtained from Tao et. al [11].

Production of Adipic acid

Adipic acid can be made from glucose using the anaerobic reverse β-oxidation pathway in *E. coli* [15]. Ammonium Hydroxide was added continuously to the fermentor to maintain pH because the adipic acid product tends to lower pH of the culture media. The microbial cells were removed from the culture media using a rotary vacuum filter (Figure B2). Distilling the clarified culture media containing adipic acid and monoammonium adipate results in a liquid bottoms that include adipic acid and 30 wt% of water [16] (Figure B2). The distillation was carried out under super atmospheric pressure and a temperature of 170 ^{0}C to remove ammonia and necessary water. The distillation bottoms were cooled to 30 ^{0}C using a heat exchanger before the adipic acid-water mixture is transferred to a crystallization column [16]. The adipic acid crystals were separated from the slurry using the filtration process (Figure B2). A dryer was used to remove moisture from the wet crystals (Figure B2).

Production of Succinic acid

The yeast strains were genetically modified to make succinic acid from a carbon source under low pH and anaerobic conditions [17]. The processes for extracting and purifying succinic acid from the culture media are similar to that of adipic acid except the vacuum distillation is carried under vacuum for the succinic acid separation[18] (Figure B2).

Production of 3-HPA

The 3-HPA can be made from glucose using the β-alanine pathway in *Saccharomyces cerevisiae* under anaerobic conditions [19]. After cell clarification, solvent extraction process was used to extract 3-HPA from the clarified culture media (Figure B3). Methyl isobutyl ketone (MIBK) can be used as an organic solvent [20]. The extractant phase of solvent extraction column containing MIBK and 3-HPA was transferred to a distillation column to recover MIBK

solvent and to purify 3-HPA (Figure B3). The dissolved MIBK in the raffinate phase can be extracted using another extraction column. The organic solvent heptane was selected to dissolve the MIBK. The MIBK-heptane mixture was separated into pure MIBK and heptane using a distillation column (Figure B3). The necessary liquid-liquid equilibrium data and vapor-liquid equilibrium data were generated using the local composition models UNIQUAC and NRTL, respectively.

Production of 1,3-propanediol

The biological processes for the production of 1, 3-propanediol from glucose were developed [21]. The 1, 3-propanediol fermentation can be carried out under aerobic/anaerobic conditions [21, 22]. The processes for the recovery of 1, 3-propanediol from the culture media are similar to that of 3-HPA except the type of organic solvent used for the extraction of 1, 3-propanediol from the clarified culture media (Figure B3). In the case of 1, 3-propanediol, the clarified culture media was contacted with the solvent extractant 1-hexanol [23].

Process modeling

SuperPro and ASPEN Plus simulation software were used to model each chemical production process. The equipment used in the production of each bio-commodity chemical was sized using the SuperPro and ASPEN Plus simulation software. The on-site equipment cost was estimated using purchase-cost charts [24, 25]. The total capital investment of chemical production was estimated using a method based on delivered cost of process equipment [24,25]. The material and energy balances of each chemical production process were obtained from the process simulations. The material balance was used to calculate the required quantity of raw materials, and the energy balance was utilized to determine steam and electricity requirements. The raw material and utility prices used in this analysis are listed in Table 2. The costs of

operations (labor-related), maintenance, operating overhead, and depreciation, and general expenses were calculated following standard procedure. The discounted cash flow analysis (DCA) method was used to compute the bio-commodity chemical MSP. The discount rate of 10% was assumed in the DCA [26].

The life cycle analysis (LCA) approach was used to estimate cradle-to-gate energy consumption and GHG emissions of bio-commodity chemical production processes. The LCA system boundary covers all activities from corn production up to the production of bio-commodity chemical. The life cycle GHG emissions and energy consumption of steam and electricity production were obtained from the Ecoinvent database [27]. The economic allocation approach was used to partition energy consumption and GHG emissions of bio-commodity chemical production process among the product and co-product DDGS [28].

Table 2
Economic assumptions

Corn cost ($/bushel)	3.50
Electricity price ($/kWh)	0.07
Natural gas price ($/MMBtu)	3.35
Internal rate of return	10.0%
Equity percent of total investment	100.0%
Number of working days	350

The MSP, energy consumption, and GHG emissions of bio-commodity chemical production processes were determined for various combinations of yield, titer, and volumetric productivity. The performance contour plot for cost was created by mapping bio-commodity chemical MSP to the corresponding yield, titer, and volumetric productivity. Similarly, performance contour plots for energy and GHG were created. The energy consumption and GHG emissions of petroleum based adipic acid, succinic acid, isobutanol, 3-HPA, and 1, 3-propanediol production processes were obtained from the literature [29-30]. The market prices of these

chemicals were obtained from ICIS chemicals. The performance metrics of conventional processes and performance contour plots were used to determine feasible curves of cost, energy, and GHG. The feasible space of each bio-commodity chemical production process was defined by graphing the feasible curves of cost, energy, and GHG along with yield, titer, and productivity constraints. The maximum attainable yield, titer, and production rates were used to determine yield, titer, and productivity constraints, respectively.

Results and Discussion

The MSP of adipic acid, succinic acid, 1,3-propanediol, 3-HPA, and isobutanol were calculated for various combinations of yield, titer, and productivity. The contour plots that represent the relationship between bio-commodity chemical MSP, yield, titer and productivity for bio-commodity chemical processes were created (Figure B4, Figure B5, and Figure B6). These figures shown a percentage change in the value of yield will have higher impact on the bio-commodity chemical MSP than that of titer and productivity. For example, there is a nearly 1000% increase in the bio-commodity chemical MSP, as the fermentation yield drops from 1 g/g to 0.1 g/g for a given titer and productivity. On the other hand, for a given yield there is only a 200% increase in MSP when titer falls from 200 g/l to 10 g/l. This is because any change in the value of fermentation yield will have an effect on the entire upstream of bio-commodity chemical production process including corn agriculture, glucose production from corn, and the fermentation processes.

The MSP of bio-commodity chemicals, except those produced aerobically, is found to be nearly constant for a given titer, yield, and productivity. The estimated MSP of 3-HPA, for example, produced under anaerobic fermentation is $1.13 for the yield of 0.6 g/g, productivity of 2 g/l/h, and titer of 50 g/l (Figure B5). For this combination of process parameters, the estimated

MSP of aerobically produced 1, 3-propanediol is $1.66. Such an increase in MSP is due to the requirement of high capital and operating costs for the aerobic cultivation as compared to anaerobic processes. The current avaliable agitator size limits the aerobic fermentor volume to 4000 kiloliters [8]. The cost advantages due to the economies of scale are, therefore, minimized, which increases the capital cost of aerobic cultivation. The compressor energy requirements and the energy losses in gassing systems increase the operating costs of aerobic cultivation processes [8].

The addition of acid/base to maintain neutral pH in the production fermentor is found to have negligible impact on the production cost of bio-commodity chemicals. For example, an ammonia base is added to the fermentor during the adipic acid fermentation to maintain the pH around 7. The addition of such base is not necessary for the succinic acid fermentation as the genetically modified yeast strain can make succinic acid under low pH conditions. The production costs of adipic and succinic acids for a given combination of yield, titer, and productivity, however, are found to be nearly same (Figure B5). The salts formed due to the addition of acid/base will be ended up with the DDGS. In this analysis, we assumed that the presence of salts do not affect the market price of DDGS.

For a given titer, the downstream processing costs of bio-commodity chemical processes are nearly same yet number and type of separation processes are different. For example, the distillation and solvent extraction processes are used to extract isobutanol and 3-HPA from the culture media using the distillation and solvent extraction processes, respectively. Moreover, the total number of required unit processes for the purification of isobutanol is low compared to the purification of 3-HPA. The MSP of isobutanol and 3-HPA are, however, found to be nearly the same for a given titer, yield, and productivity.

Since the MSP of a bio-commodity chemical varies with the titer, yield, productivity, and the type of fermentation, we generated general cost contour plots in terms of yield, titer, and productivity for the aerobic and anaerobic production of bio-commodity chemicals (Fig 1). The data of MSP of 3-HPA is used to generate cost contour plot for the anaerobic process, and the data of MSP of 1,3-propanediol that is produced via aerobic cultivation is used to generate general cost contour plots for the aerobic process.

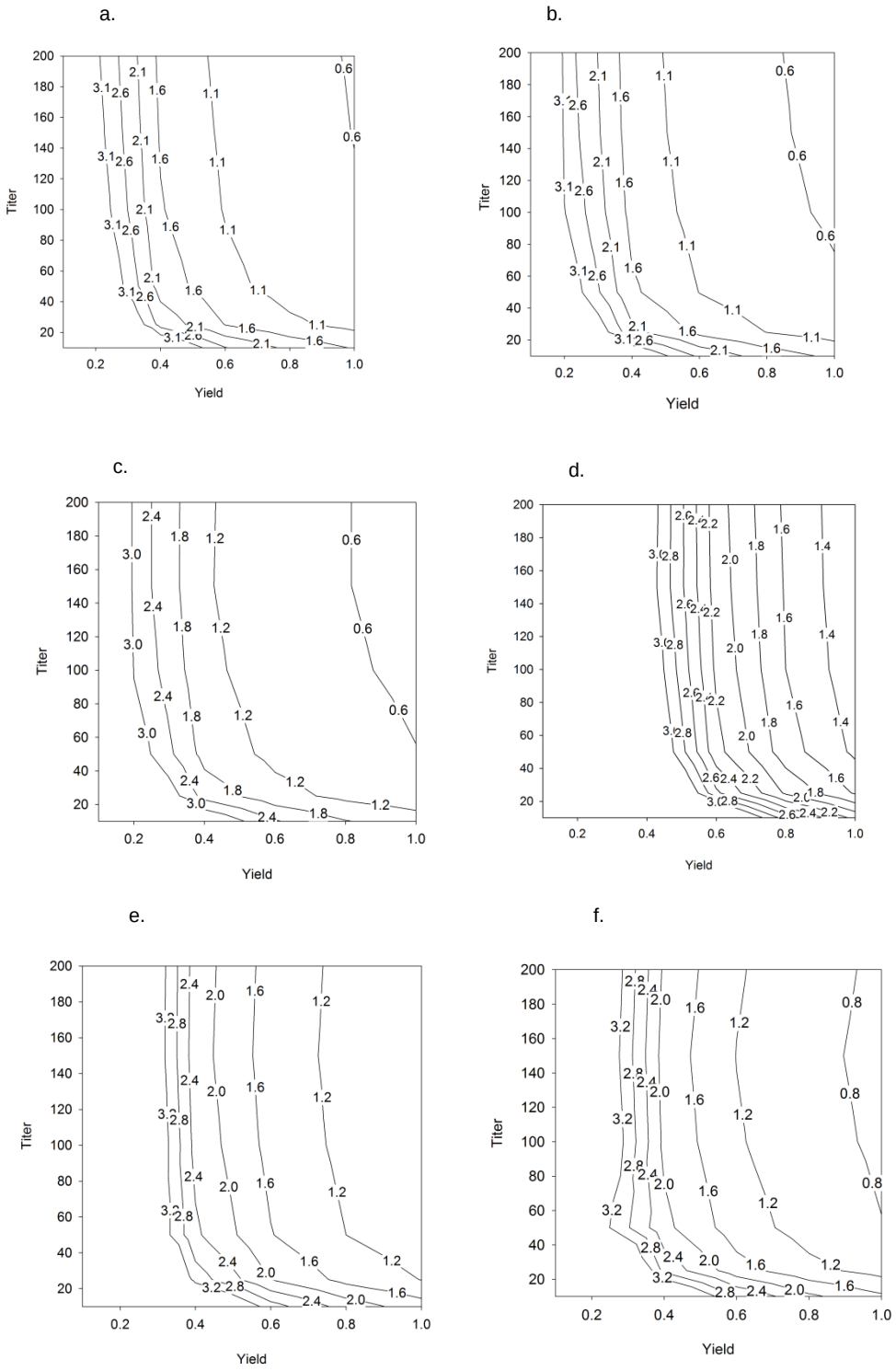

Figure 1 General cost contour plots for anaerobic production of bio-commodity chemical with a productivity of a) 1g/l/h, b) 2 g/l/h, c) 3 g/l/h; for aerobic production of biocommodity chemical with a productivity of d) 1g/l/h, e) 2 g/l/h, f) 3 g/l/h. Contour lines represent minimum selling price ($/kg) of bio-commodity chemical

Comparison of general cost contour plots of anaerobic process indicates that volumetric productivities greater than 2 g/l/h have a small effect on the MSP of bio-commodity chemical (Fig 1). For a given yield and titer, the MSP of making a bio-commodity chemical is reduced only by nearly 3.5% when the volumetric productivity is increased from 2 g/l/h to 3 g/l/h (Fig 1). The similar comparison shows 16% decrease in MSP for the aerobic based bio-commodity chemical routes (Figure 1). Similar to the volumetric productivity, there is a non-linear relationship exists between the bio-commodity chemical MSP and the product titers. The economic benefits of improving fermentation titer beyond 150 g/l are found to be low for both aerobic and anaerobic bio-commodity chemical production processes. For a given yield and productivity, the bio-commodity chemical MSP is reduced only by 2% when the titer is increased from 150 g/l to 200 g/l (Fig 1). Thus, investments for pushing microorganism titers beyond such optimal values of productivity and titer must be avoided.

The general contour plots can be used for the early screening of processes for the production of bio-commodity chemicals using biocatalysts. For example, glucaric acid can be made from glucose using *E. coli* under anaerobic conditions. The theoretical yield and production rates of glucaric acid are estimated as 0.3 g/g and 2 g/l/h, respectively, from the stoichiometric calculations[15]. The current market price of glucaric acid is $1.50 per kg. The MSP of glucaric acid is $2.00 for these theoretical values and the titer of 200 g/l. Thus, developing a technology for the production of glucaric acid appears economically unfeasible.

Performance cost targets can be set for the biocatalyst development team using the general contour plots of cost. For example, the average market price of adipic acid is 1.50 ($/kg.). For this target price, the contour plot in Figure1 shows various economically viable combinations of yield, titer, and volumetric productivity for making the adipic acid from glucose

using a biocatalyst. The yield, titer, and volumetric productivity targets for the technology development team can be determined by selecting one viable combination. This selection can be done by comparing development time and costs that are necessary to develop a biocatalyst that exhibits each viable combination of process parameters. The management and research teams together can qualitatively compute such development time and costs [5].

The salts formed due to the addition of acid/base during and after fermentation process will be separated out with the DDGS. In this analysis, we assumed that the presence of salts do not affect the market price of DDGS. The presence of salts and residual amounts of bio-commodity chemicals, however, may impact the DDGS price. The DDGS price of $160 per metric ton is assumed. To determine the impact of change in DDGS price on the bio-commodity chemical MSP, we computed the MSP for the following DDGS prices: $120, $80, $40, $0 per metric ton. The bio-commodity chemical MSP is increased by 2.5%, 5.7%, 8.2%, and 12.2% for these DDGS prices.

The energy and GHG contour plots were created for the bio-commodity chemical processes using the values of estimated energy use and GHG emissions of bio-commodity chemical production processes, respectively (Figure B7 and Figure B8). The energy, GHG, and cost contour plots of bio-commodity chemical production processes have resulted in a similar shape (Figure B1, Figure B7 and Figure B8). This indicates that the MSP, energy consumption, and GHG emissions of bio-commodity chemical processes are highly correlated. In other words, replacing corn with another feedstock, in an effort to reduce the total energy consumption of the process for bio-commodity chemical production, will also increase or decrease the production cost.

The comparison of GHG and energy contour plots indicates that the energy consumption and GHG emissions of bio-commodity chemical production processes, except the bio-commodity chemical that is made using aerobic cultivation, are found to be nearly same for a given combination of titer, yield, and productivity. In addition, the decrease in the energy consumption and GHG emissions of anaerobic processes are found to be very low (≈ 0) when the volumetric productivity is increased from 1 g/l/h to 2 g/l/h. The decrease in the energy consumption and GHG emissions of aerobic process is, however, around 4% and 0.4%, respectively, when the productivity is increased from 1 g/l/h to 2 g/l/h for a given titer and yield. Similar to the bio-commodity chemical MSP, the general counter plots of GHG and energy are generated for the processes of bio-commodity chemical production (Figure 2). Similar to the MSP contour plots, the general GHG and energy contour plots shown in Figure2 can be used to screen early stage bio-commodity chemical processes in terms of environmental performance and to set environmental performance targets.

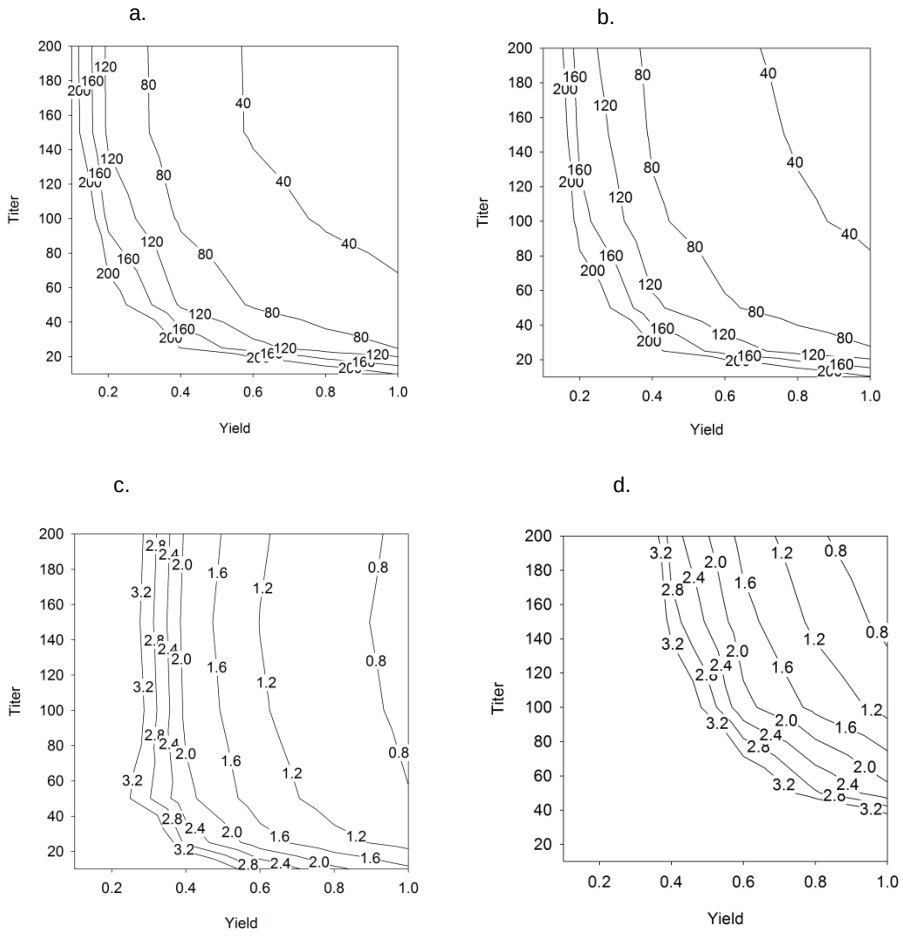

Figure 2 General Energy and GHG contour plots. a) Energy use (MJ/kg) plot for the anaerobic production of bio-commodity chemical b) and for aerobic production of bio-commodity chemical; c) GHG (kg CO_2 eq./kg) plot for the anaerobic production of bio-commodity chemical d) and for aerobic production of bio-commodity chemical

Conventionally, adipic acid, succinic acid, isobutanol, 1,3-propanediol, and 3-HPA can be derived from a petroleum feedstock [29, 30]. The average market prices ($/kg) of adipic acid, succinic acid, isobutanol, 1,3-propanediol, and 3-HPA are 1.6, 1.6, 1.20, 1.7, and 1.3 respectively, which are obtained from ICIS chemicals. The cradle-to-gate energy consumption of producing adipic acid, succinic acid, isobutanol, 1,3-propanediol, and 3-HPA from a petroleum feedstock are 124, 110, 60, 150, and 120 respectively [29, 30]. The cradle-to-gate GHG

emissions (kg CO_2 eq./kg) of conventional adipic acid, succinic acid, isobutanol, 1,3-propanediol, and 3-HPA processes are 9, 12, 3, 12, and 7 respectively [29, 30]. These market prices, energy consumption, and GHG emission values were used to determine feasible cost, energy, and GHG curves using the general contour plots of cost, energy, and GHG respectively [5]. For example, the theoretical production rate of adipic acid synthesis under anaerobic conditions is estimated as 2 g/l/h from the in silico flux analysis/stoichiometric modeling [15]. For this productivity, the contour line of 1.50 in Figure1b represents the feasible MSP curve. Similarly feasible energy and GHG curves are determined using general energy and GHG contour plots, respectively.

The 2D feasible space of adipic acid, succinic acid, isobutanol, 1,3-propanediol, and 3-HPA were defined by graphing feasible curves along with yield, titer, and productivity constraints (Figure 3). The stoichiometric yields of bio-commodity chemicals were used to determine the yield constraints. The maximum stoichiometric yields of adipic acid, succinic acid, isobutanol, 1,3-propanediol, and 3-HPA are 0.52 g/g, 0.6 g/g, 0.42 g/g, 0.45 g/g, and 0.4 g/g respectively. The titer of 200 g/l and productivity of 2 g/l/h were assumed as titer and volumetric productivity constraints, respectively. The graphing of feasible curves and constraints did not result in a feasible space for the production of 1,3-propanediol via aerobic cultivation. This is because the requirement of high capital and operating costs for the aerobic cultivation process.

The comparison of feasible spaces of processes for the production of bio-commodity chemicals shows that a biocatalyst must exhibit titers of at least 45 g/l (Figure 3). Similarly, biocatalyst development team must achieve bio-commodity chemical yields of at least 0.34 g/g. If the toxicity of a bio-commodity chemical to biocatalyst limits the concentration of a chemical in the fermentation systems to lower than 45 g/l, the additional investments to increase the yield

and product rates of the biocatalyst will become unviable (Figure 3). In such cases, the investments must be diverted to develop an alternate biocatalyst to make the bio-commodity chemical.

The results of this analysis indicate that MSP curve is limiting among MSP, energy, and GHG curves (Figure 3). It means that economic viability of a bio-commodity chemical route is uncertain, when the GHG emissions and energy consumption of bio-commodity chemical production process are lower than that of conventional counterparts.

Feedstock is the dominant cost in any commercially viable bio-commodity chemical production system. To test this hypothesis, the MSP of biorenewable chemicals are segmented into individual cost components. The fermentation yield of 0.4 g/g, volumetric productivity of 2 g /L/h, and the fermentation titer of 100 g/l are selected to test this hypothesis. The results of this analysis are also applicable to all feasible combinations of yields, titers, and volumetric productivities because we used the same assumptions when estimating the performance metrics of capric acid production for a range of process parameters. It has been found from this analysis that the feedstock cost dominates by >45% of MSP of bio-commodity chemicals.

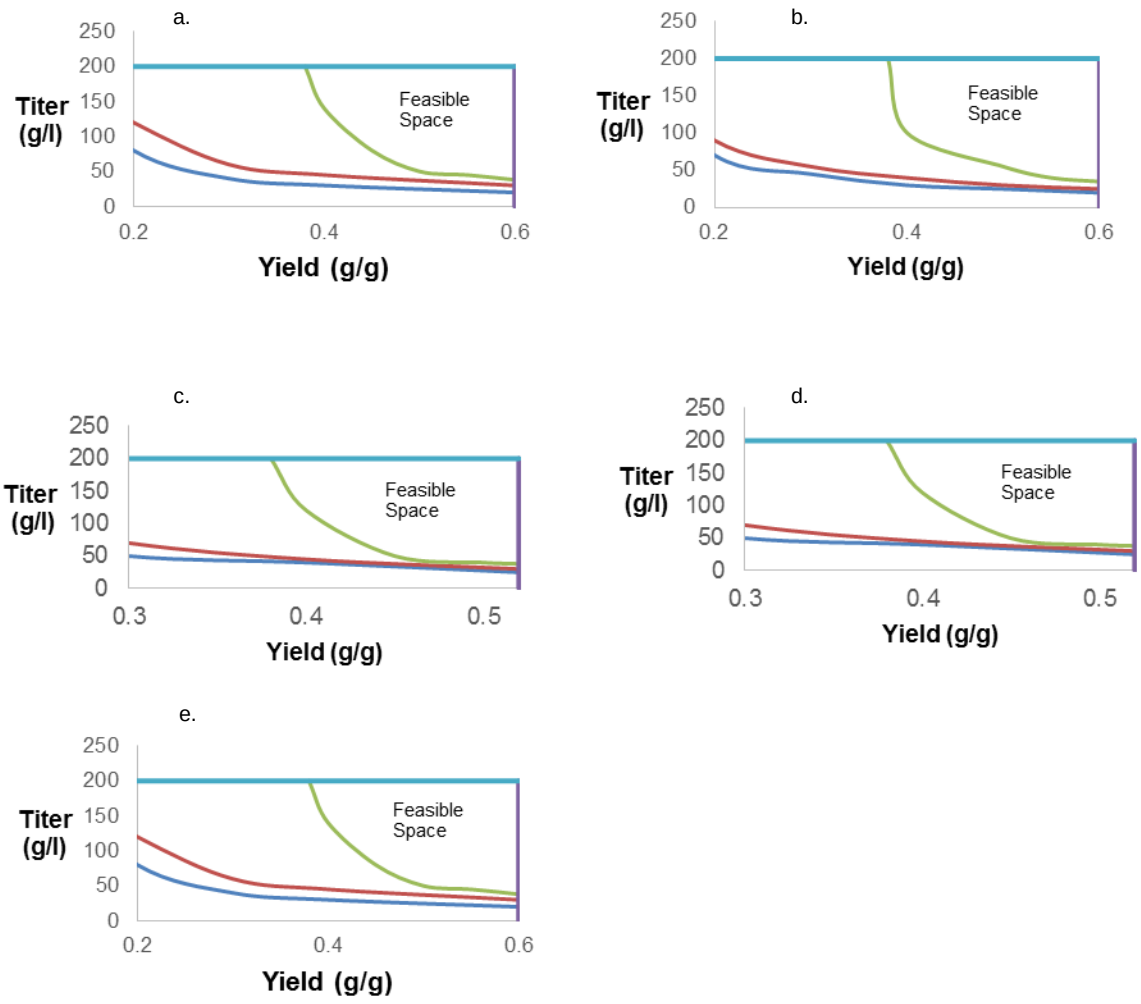

Figure 3 Feasible space of processes for the production of a) 3-HPA, b) 1,3- Propanediol, c) Adipic acid, d) Succinic acid, e)Isobutanol. Green curve represents the feasible cost curve, Red curve represents the feasible energy curve, and the Blue curve represents the feasible GHG curve

Conclusion

The MSP, energy consumption, and GHG emissions of six bio-commodity chemical production processes are estimated for various combinations of titer, yield, and volumetric productivity. The comparison of results shows that economic and environmental performances of bio-commodity chemical processes are mainly dependent on the titer, yield, productivity, and the type of fermentation. The addition of acid/base to maintain neutral pH in the production fermentor is found to have negligible impact on the production cost of bio-commodity chemicals. It has been found from the analysis that for a given titer, the downstream processing costs of analyzed bio-commodity chemical processes are nearly same yet the number and type of the separation processes are different.

The fermentation yields of at least 0.32 g/g and titers at least 45 g/l are required to achieve a process for the production of a bio-commodity chemical that is environmentally and economically feasible. It is found that investments for improving titer beyond 150 g/l and volumetric productivity beyond 2 g/l/h will result in minimal economic and environmental benefits for the production of bio-commodity chemicals using a biocatalyst. The comparative economic analysis indicates that the cost of the feedstock dominates the MSP of bio-commodity chemical that is made using a biocatalyst.

Acknowledgements

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CHAPTER 4

Risk advantages of platform technologies for biorenewable chemical production

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Abstract

Recent investments in bio-based chemical development are financing the construction of commercial production facilities, often designed to produce a single biorenewable chemical. Investments in technologies targeting a single biorenewable chemical are subject to significant technological and market risks. Platform technologies that can convert biomass into a range of related biorenewable chemicals can reduce these risks significantly. Researchers are now developing platform technologies that combine bio-and chemical-catalysis, such as a process of converting glucose into fatty alcohols of specific carbon chain length. The financial risk and profitability of investments in platform technology producing fatty alcohol of different chain length were analyzed. A techno-economic model to evaluate single- and platform technologies was developed. A platform technology that can produce two products: 1-decanol and a blend of dodecanol and 1-tetradecanol reduces financial risk of investment by 23% and increases profitability by 55% compared to production via single-product technologies. This financial advantage of two-product technology is eliminated as the cost of switching between products rises above $4 MM for a 14 metric-ton/yr plant. Investments in technologies that can produce a larger number of products provide higher returns lower risk. Other less quantifiable risk advantages of platform technologies that nonetheless important are also discussed.

Key words: Platform technology, biorefinery, biorenewable chemical, financial risk, biocatalysis, chemical catalysis

Introduction

Most industrial chemicals used as materials, plastics, surfactants and solvents are currently derived from petroleum feedstock. Depleting non-renewable petroleum feedstock and environmental considerations have been drastically changing the prospects for renewable biomass as a raw material for industrial chemicals [1]. In order to transform the petroleum-based chemical industry to a bio-based chemical industry, a substantial amount of research is ongoing throughout the world targeting one biorenewable chemical at a time. For example, Burk et al., (2013) describe a biological process for converting sugars into 1, 4-butanediol [2]; bio-isoprene can be synthesized by genetically modifying microbial cells to overexpress levels of an isoprene synthase polypeptide and a mevalonate kinase polypeptide [3]; and biobased chemical company Rennovia, Inc. is commercializing a catalytic process for the production of adipic acid from carbohydrates [4].

Unfortunately, this approach of developing single-product technologies is slow and costly, as it requires all the investment in time and money for one chemical. Moreover, investing capital for producing biorenewable chemicals via technologies that yield a single-product magnifies a variety of the technological and market risks that characterize the highly competitive chemicals industry. Volatility in prices of feedstock, energy, and the market demand for chemicals are just a few of the sources of market and financial risk of investment in the biorenewable chemical business [5]. Since biorenewable chemicals can either structurally or functionally replace existing petrochemicals, renewable chemicals compete for market share with existing petrochemical products. Thus, there is a risk of reduction in market price as supply is increased by new market entry and a risk of aggressive price reduction by incumbent petrochemical companies, whose capital investments are already partially or fully depreciated.

During the scale-up of pioneer renewable chemical technologies, there is risk of process failure due to technical barriers, characterized as technology risks [6]. Furthermore, lack of economies-of-scale may create a barrier to market entry for low profit margin biorenewable chemicals synthesized via single-product technologies.

The various risks to the investments in the biorenewable chemical business may be reduced by producing biorenewable chemicals via platform technologies. We define a technology as a platform technology when it meets following criteria: 1) it enables the synthesis of multiple chemicals; 2) the technological investments made in the synthesis of each chemical are at least partially used in the research and development of one or more other chemicals; 3) the production of each chemical in the platform uses at least 60% of the same plant equipment as the other products in the platform - in other words, it should enable the plant to make multiple chemicals by slightly modifying existing production equipment; and, 4) the products made using the chemicals platform can be sold in different market segments. The platform concept fits into one class of biorefinery identified by Sadhukhan et al., (2014) in which a portfolio of products are derived from a single biomass feedstock using flexible conversion processes [7]. Thus, the development of platform technologies can expedite the development of a biorefinery that operates similarly to an oil refinery.

The recent development of a reverse β-oxidation pathway in *E.coli* as reported by Cintolesi et al., (2014), for example, facilitates the synthesis of a range of di-carboxylic acids with varying carbon chain length from glucose [8]. This technology is considered a platform technology for the following reasons: Of these di-carboxylic acids, medium chain di-acids such as adipic acid can address the needs of the nylon industry [9], and the long chain di-acids such as octadecanedioic acid have applications in polyamide, polyurethanes, lubricants and adhesive

industries [10]. Since the mechanism with which the reverse β-oxidation pathway in *E.coli* that makes medium and long chain di-acids is similar, the technological advancements made in the development of bio-catalytic technology to synthesize medium chain di-acids are applicable to the synthesis of long chain di-acids. Although separation and purification processes are somewhat different for medium and long-chain di-acids, the production of these di-acids will utilize a substantial portion of the same equipment including the seed and product fermentors.

Platform technologies for biorenewable chemical production can be developed using purely biological, purely chemical, integration of biological and chemical processes, or thermochemical processes. The above mentioned reverse β-oxidation pathway in *E.coli* to synthesize various di-acids is considered as an example of a purely biological method. Similarly, synthesis gas from the thermochemical conversion of biomass can be used to synthesize a range of products, including paraffins and olefins using the Fisher-Tropsch process [11] and methanol using Cu/Zn/Al catalyst [12].

One example of a purely chemical approach is the oxidation of glucose over a platinum catalyst which yields glucaric acid [13]. This glucaric acid subsequently undergoes selective dehydration to lactones or selective esterification to polyglucaric esters [14]. Another example is the catalytic dehydration of fructose to 5-hydroxymethylfurfural [15], which can be further transformed catalytically into various bio-fuels and bulk chemicals [16]. As an example of an integrated approach, triacetic acid lactone is produced biologically from sugars through overexpression of 2-pyrone synthase in Saccharomyces cerevisiae [17] and this biological intermediate is catalytically upgraded to sorbic acid, hexenoic acid, and γ-caprolactone [18].

The concept of a platform technology is somewhat related to, but different from platform chemicals, as described by Werpy and Peterson (2004), who identified the most promising building block chemicals that can be derived from biomass. Among the building block chemicals identified by Werpy and Peterson (2004), most of chemicals can be produced via microbial technology, and subsequently upgraded to yield a diverse portfolio of biorenewable chemicals using a chemical catalyst [19].

The NSF engineering research Center for Biorenewable Chemicals (CBiRC) is currently developing three platform technologies by integrating bio- and chemical- catalysis (The Center for Biorenewable Chemicals, 2008). One of these three technologies is the carboxylic acid platform technology [20]. In this platform, microbial strains such as *E.coli* are engineered to synthesize various carbon chain lengths of fatty acids from glucose via the fatty acid biosynthesis pathway [21], and these fatty acids are subsequently upgraded to yield fatty alcohols of different carbon chain length using a chemical catalyst [22] (Figure1). The medium- and long-chain fatty alcohols are used in perfume, fragrances, cosmetics, pharmaceutical, and surfactant and lubricant industries [23].

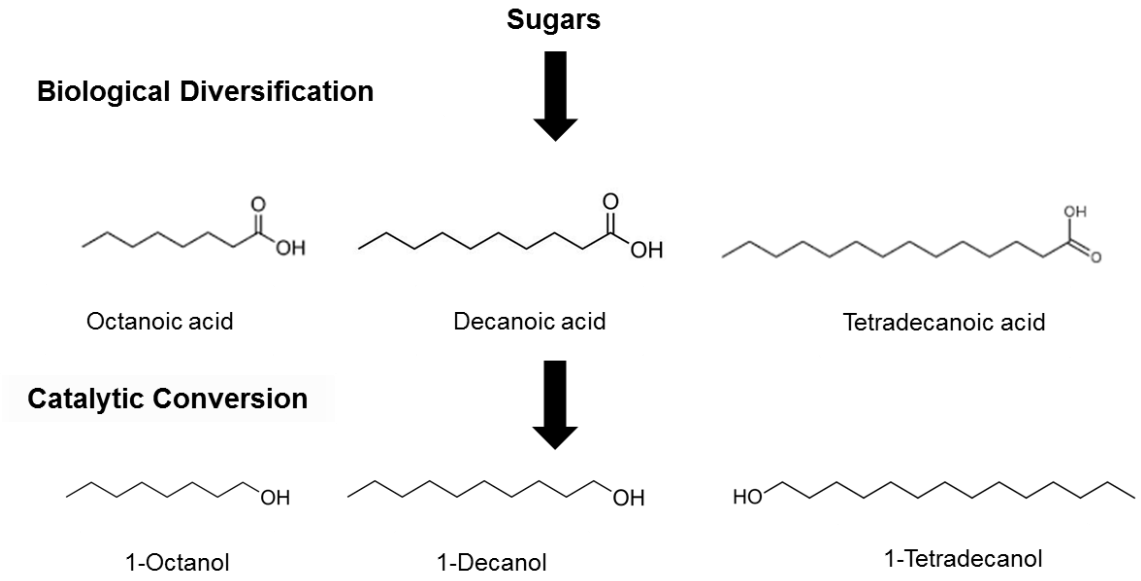


Figure 1 The carboxylic acid platform technology : Production of a wide array of fatty alcohols by coupling of biological and chemical catalysis

In this paper we analyze and compare the risks of investment in technologies for producing fatty alcohols of different chain length via both single-product and platform technologies. We quantitatively analyze financial risk and the profitability of investment, and qualitatively evaluate other risks of investments in developing single and platform technologies. Financial risk is quantified by assuming all the risk due to variation in prices is captured in the standard deviation of the probability density function of net present value (NPV) of irreversible capital investment[1] in biorenewable chemical production [24, 25]. The expected values of the probability density function of NPV are used as an indicator to measure the profitability of an irreversible investment: as the expected NPV increases, provided it is positive, the profitability

[1] The capital invested in a chemical plant cannot be fully recovered when the plant is retired or retrofitted, thus investment in a chemical plant is characterized as an irreversible investment (Dixit and Pindyck, 1994)

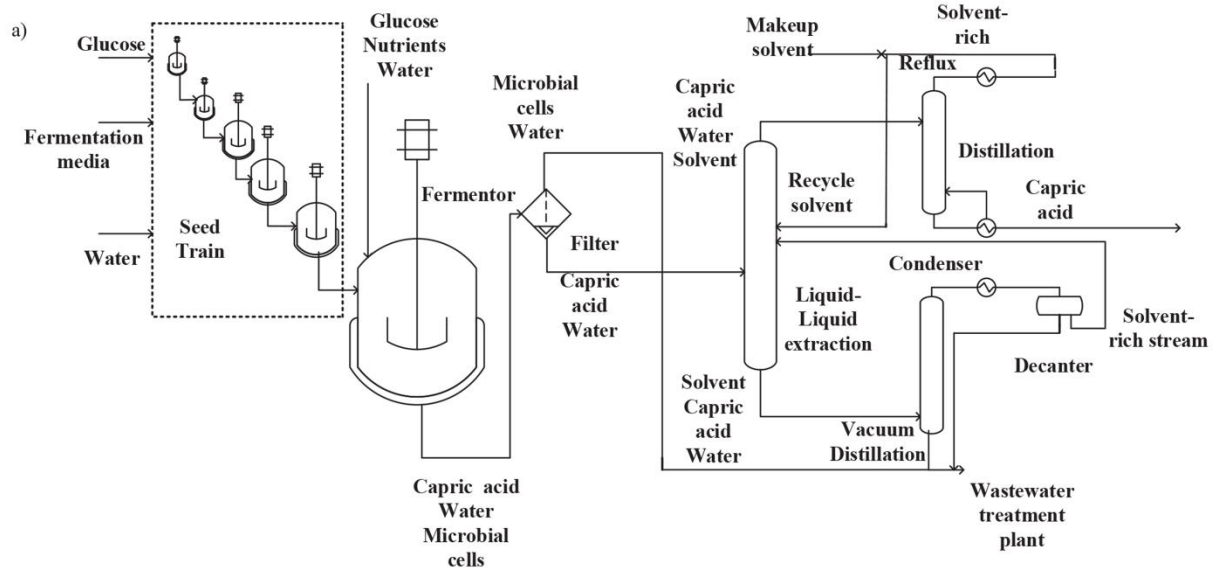
of an irreversible investment will increase [24]. Technology risk is quantified by estimating the likelihood of process failures that occur during scaling-up a novel bio-renewable chemical technology. Such an estimation of process failures requires a very large amount of process performance data from commercialized renewable chemical technologies [6]. Unfortunately, at this point in time these data for biorenewable chemical technologies are limited, because the biorenewable chemical industry is still in its infancy. It is also very difficult to predict risks of scientific breakthroughs and competitive market behavior. Thus, we qualitatively analyze these other risks and advantages of platform technologies that are currently impossible to quantify.

We quantify financial risk and profitability of investment by simulating single-product and platform technologies for producing fatty alcohols of different chain length using process simulation software. We create a techno-economic model by estimating capital and operating costs using simulated material and energy balances. The prices of feedstock, energy and products are modeled as a mean-reverting process. A switching rule based on cost of switching between products is developed and used in the economic model to represent profit-seeking plant operation. A Monte Carlo simulation is performed to predict the probability distribution of NPV of investment in fatty alcohol production. Comparison of the expected value and standard deviation of distributions NPV for technologies that can reach one or more products has shown that the carboxylic acid platform technology can reduce the financial risk and increase the profitability of investment. The influences of product carbon chain length and switching cost on the risks of investment in platform technologies are investigated. Finally, we qualitatively evaluate other risk impacts of platform technologies.

Methodology

Description of fatty alcohol production process

The process flow diagram for fatty alcohol production from glucose is shown in Figure 2. The annual plant capacity and plant life are taken to be 40,000 metric tonnes of glucose conversion and 20 years, respectively. The process flow diagram is similar for both the single-product and platform technologies for fatty alcohol production. However, in the platform technology the versatility of the fatty acid biosynthesis pathway makes it possible to produce fatty acids with varying carbon chain lengths. The versatility of this pathway is achieved by introducing a unique acyl-ACP thioesterase gene into a microorganism for the synthesis of a specific chain length of fatty acid. For instance, expressing class I acyl-ACP thioesterase genes into a microorganism can terminate fatty acid chain elongation and produce the myristic acid (C14:0), whereas expressing class III acyl-ACP thioesterase genes into a microorganism enables the synthesis of octanoic acid (C8:0) [26]. In this production process, the biologically produced fatty acid then undergoes hydrogenolysis over a copper chromite catalyst to yield a fatty alcohol [22].



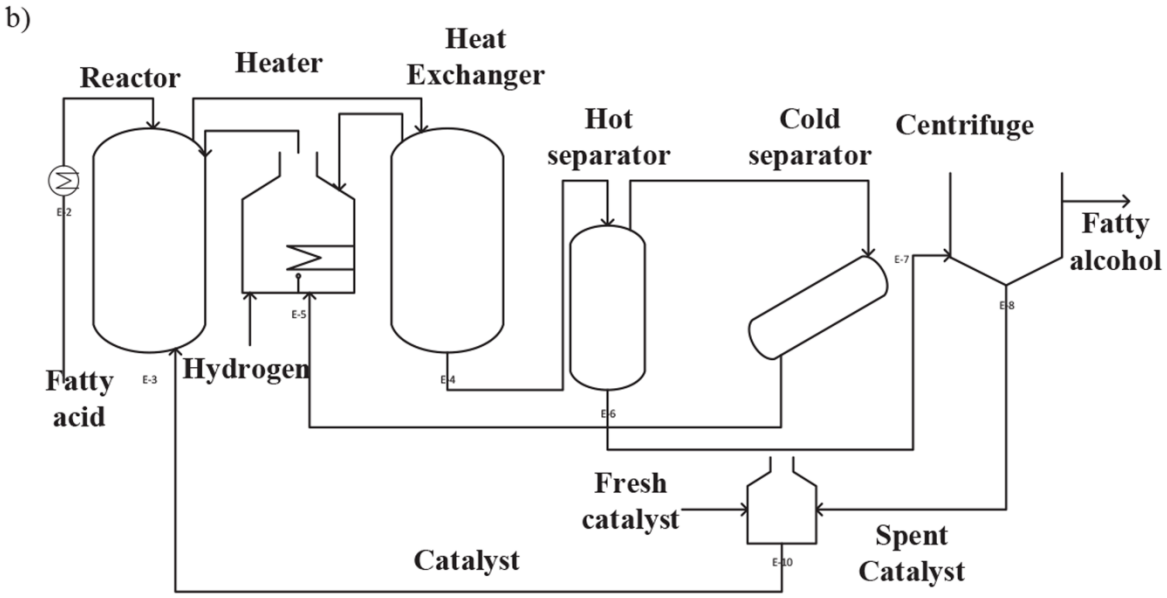


Figure 2 Process flow diagram a) Fatty acid production (adapted from Gunukula and Anex, unpublished work) b) Fatty alcohol production (adapted from Gervajio, 2012)

The fatty alcohol production process starts with adding preserved genetically modified *E.coli* seed culture to the first bioreactor in the seed fermentation train which consists of series of bioreactors that increase incrementally in size by a factor of 10 [27]. Once the *E.coli* cells are grown to a fixed concentration, the entire cell culture is transferred into the subsequent bioreactor in the seed train. This process is repeated until the cell count and concentration required for the fatty acid production process is achieved in the final bioreactor of seed train. Glucose and other nutrients are added at each stage as necessary for *E.coli* growth.

The *E. coli* cells from the final bioreactor in the seed train are sent to the aerobic production fermentor, operating at 37^0 C in fed-batch mode, to synthesize fatty acid from glucose under M9 minimal media. During product fermentation, CO_2 is evolved as a gas and fatty acid is produced as an extracellular product. The separation of *E.coli* cells from the fermentation broth containing fatty acid, *E.coli* cells and other impurities is achieved using a rotary vacuum filter.

Fatty acid from the clarified fermentation broth is extracted using solvent extraction column with the aid of the extracting agent hexane [28]. The extractant phase of the solvent extraction process containing hexane and fatty acid is separated into pure fatty acid and hexane using distillation. Vacuum distillation and decantation processes are used to recover solvent present in the raffinate phase of solvent extraction process.

The purified fatty acid undergoes a high pressure hydrogenation reaction to fatty alcohol over a bimetallic catalyst in a catalytic reactor. After high pressure hydrogenation process, the mixture of hydrogen, fatty alcohol, and catalyst slurry from the catalytic reactor is sent to the two-stage cooling/expansion system to recover unreacted hydrogen that is later mixed with the make-up hydrogen before recycled to the hydrogenation reactor. Using a basket centrifugal separator, the fatty alcohol/catalyst slurry stream is separated into a fatty alcohol stream with some traces of solids and a catalyst slurry stream. The catalyst slurry is recycled to the catalytic reactor, and the solid traces in the fatty alcohol stream are removed by the filter [22].

Process simulation

SuperPro Designer®, (2014) was used for simulation of seed and product fermentation, vacuum filtration, and countercurrent solvent extraction using rotating disc contactor column, because this software provides necessary models of these processes that are not available in ASPEN Plus®, (2014). The biomass growth in the seed train was modeled by Monod kinetics with a maximum specific growth rate of 0.4 hr^{-1} and a biomass yield of 0.4 g (dcw)/g glucose. For the modeling of production fermentor it was assumed that there is no biomass growth, and the product yield is 0.34 g fatty acid/g glucose. The information on operating conditions and other modeling parameters that are required for the simulation of the seed and product fermentors were obtained from personal communication with the CBiRC development team

(Table C1). SuperPro Designer® process simulation software was used to simulate the seed and product fermentors for the fatty acid production.

The necessary area of the rotary vacuum filter to remove *E.coli* cells from the fermentation broth and number of stages, diameter and height of the solvent extraction column were estimated using the SuperPro Designer® process simulation software. The needed design parameters for the solvent extraction column simulation were determined as described in our unpublished work (Table C2).

ASPEN Plus® was used for simulation of the overall process, excluding fermentation, filtration, and solvent extraction processes, because it is the accepted industry standard process simulation software that provides sophisticated models of vapor-liquid equilibrium separations and chemical reactions which allowed us to more accurately simulate distillation and catalytic reactions. The simulated extractant and raffinate material flows of solvent extraction process were imported into ASPEN Plus® software, which were used as inlet streams to distillation columns. The RadFrac method was used to perform the simulation of distillation columns. Distillation column simulation defined the required number of trays and column diameter for the particular separation. The ASPEN Plus® shell and tube model was utilized to determine the areas of the condenser, reboiler, and heat exchanger columns in the fatty alcohol process.

For the design of catalytic reactor, we selected an operating temperature of 553 K and 30 MPa which yield nearly 100 % conversion of fatty acid with 95% selectivity to fatty alcohol [22]. We could not obtain kinetic data related to the high pressure hydrogenolysis of saturated fatty acid so the catalytic reactor was modeled using the ASPEN Plus® stoichiometric reactor model. The two-stage cooling/expansion, and centrifugal separator processes were also modeled

using the ASPEN Plus® process simulation software. Required design parameters and operating conditions for these processes were determined using standard engineering methods [29]. In this work we did not model any wastewater treatment processes and utility production. Instead, utilities were assumed to be purchased from an external facility and wastewater was assumed to be treated by an external facility for a fixed price.

Economic model and key assumptions

An Excel VBA (Visual Basic for Applications) economic model was developed using discounted cash flow analysis (DCF) to determine the distribution for the NPV of an investment for both single-product and platform technologies. The simulated material and energy balances data were imported into Excel spreadsheet from SuperPro Designer® and ASPEN Plus® models. The amount of raw materials, natural gas, cooling water, and electricity required for the fatty alcohol production were determined using material and energy balance data. The operating labor-related charges were estimated using a correlation between operating labor and plant capacity as described by Peters et al. (1991). The maintenance wages and benefits (MW&B) were assumed to be 4.5% of total direct plant cost. The maintenance overhead and other maintenance related costs were calculated as 135% of MW&B [29]. The operating overhead and property taxes were assumed to be 23% and 2% of labor cost and total direct plant cost, respectively [29]. Annual plant depreciation was computed using the Modified Accelerated Cost Recovery Systems (MARCS) method [30]. Total general expenses were estimated as 10% of total revenues generated from fatty alcohols [30].

Equipment costs of seed and product fermenters, vacuum filter, and solvent extraction column were calculated using a built-in cost model in the SuperPro Designer® simulation software. Distillation column purchase cost was estimated based on the number of trays and

diameter [30]. The cost of the catalytic reactor was computed using a design equation from Peters et al. (1991) based on the reactor type and volume. The condenser, reboiler, and other heat transfer equipment purchase costs were estimated using a cost correlation method based on heat transfer area [29]. An empirical equation based on bowl diameter presented in the Seider et al., (2010) was utilized to calculate the purchase cost of basket centrifuge. The equipment costs were indexed to US $2014 prices using chemical engineering plant cost indices (Chemical Engineering Plant Cost Index (CEPCI), 2015).

The fixed-capital investment for a fatty alcohol production plant was estimated using ratio factors based on the equipment purchase cost quoted in Peters et al. (1991, pp. 182). The prices for glucose, nutrients, solvents, utilities, catalyst and product were obtained from market data. Future cash flows were projected over the plant life using incurred operating costs and sales of a fatty alcohol. After deducting taxes, at the rate of 39% on the gross profit provided it is positive, from gross profit gave us net profit for each operating day. These net profits were discounted to the year 2014 at the fixed internal rate of return of 10%. NPV of an investment was calculated by subtracting the total investment cost from the summation of all discounted net profits over the plant life.

Variables in the economic model that cause uncertainty in fatty alcohol sales, operating costs, and ultimately NPV of an investment are the price of feedstock (i.e., glucose), price of product (i.e., fatty alcohol), price of hydrogen, price of catalyst (i.e., copper-chromite), price of electricity, and the price of natural gas. We assume that although input prices move up and down in the short run, they revert to the marginal cost of production in the long run [31]. Therefore, in the DCF analysis, price dynamics were modelled as stochastic mean-reverting processes [31]. The following mean-reverting process equation was used to model economic variables:

$$x_t = x_{t-1} + \eta(\bar{x} - x)\mathrm{dt} + \sigma\epsilon_t\sqrt{\mathrm{dt}} \qquad (1)$$

Here, η is the speed of reversion; x_t is the commodity price at time t; $\bar{x}$ is the long-run marginal price of the commodity or long term mean; σ the variance parameter; $x_t - x_{t-1}$ is the change in price over any time interval dt; and ϵ_t is a random number with zero mean and unit standard deviation. Mean-reverting process parameters for the respective economic variables were estimated from historical time series data. We obtained historical glucose price data from the United States Department of Agriculture, (2014); fatty alcohol price data from ICIS chemical pricing, (2014); hydrogen, natural gas, and electricity price data from the United States Energy Information Administration, (2014); copper and chromium data from United States Geological Survey, (2014). Sample paths were generated for each economic variable over the plant life by calculating a trajectory for x_t with a time interval (dt) of one day using Mean-Reverting process equation.

The Monte Carlo simulation then randomly drew values from each trajectory of economic variable to generate a unique set of market prices and costs from which NPV was computed. The entire distribution of all draws (10,000) resulted in a NPV distribution for investment in a single-product technology as well as the platform technology.

Switching cost

In principle, with a platform technology a chemical company could switch products many times, but in practice this is unlikely. Whenever a chemical company switches its production from one product to another, it incurs the cost of process conversion (X_{sw}). We break this cost into one-time and recurring switching costs. When a change in technology, taken as an example for one-time switching cost, requires different separation equipment, chemical companies will have to invest only on one occasion to purchase this equipment. Once the firm has switched, they

own the equipment. While in other cases, for example replacing an expensive noble metal catalyst with another in order to switch the production, an investment is necessary for each switching because chemical firms generally lease an expensive metal catalyst. Thus there is a cost associated with each switch between products that is characterized as recurring switching cost.

Since switching the production from one chemical to another requires additional investment (switching cost), a chemical firm will switch production only when the economic return generated from switching production is greater than the switching cost. Following this logic, a switching rule based on switching cost was developed to determine the possibility of switching among different products with platform technologies at any future time. The development of switching rule is explained in detail in the Appendix B.

We used this switching rule in the aforementioned Excel VBA model to determine the probability distribution of NPV of an investment for the carboxylic acid platform technology. At each time period t (t =0, 0.25 yr, 0.5 yr, … 20 yrs.), the developed Excel VBA model compares the net profit from the current product production with the net profit from the alternative product production, and if the net profit from current product production is less than that of the alternative product production, then the decision to switch to an alternative product will be made based on the switching rule. When the decision to be made is switch to an alternative product at any future time t, the switching cost is discounted to the current time, t=0, at a rate of return (r) of 10% and added to the total capital investment.

Results and discussion

Quantitative analysis of platform technology

In this section, we quantify and compare the financial risk and profitability of an irreversible investment for the production of fatty alcohol via single-product and carboxylic acid platform technologies. We assume single product technologies produce blend of 1-dodecanol and 1-tetradecanol or 1-decanol from glucose, and the 2- product carboxylic acid platform technology can convert glucose into a blend of 1-dodecanol and 1-tetradecanol and has a flexibility to switch to 1-decanol with the switching cost of ≈ 0. The switching cost is assumed to be zero because the production of one fatty alcohol to another fatty alcohol using the carboxylic acid platform technology is simply achieved by changing the bio-catalyst.

Both single and 2- product platform technologies are modeled using process simulation software to estimate steady state flow rates of products and raw materials. The capital expenses for the production of fatty alcohols via single and 2- product platform technologies are estimated using standard methods (Table 1). Future price trajectories of each stochastic variable (glucose, fatty alcohol, natural gas, electricity, copper chromite catalyst, hydrogen prices) are generated over the plant life of 20 years following mean revering processes. Parameters required for the mean reverting process are determined through linear regression using historic time series data (Table 2). With this information, an Excel VBA based-model was developed to determine NPV of an investment. Monte Carlo simulation is then performed to derive a distribution for the NPV of an investment for a fatty alcohol production via single and 2- product platform technologies.

Table 1
Total capital cost estimation for fatty alcohol production Process

	USD (in millions)
Total Equipment purchase cost (TEP)	9.2
Installed cost (32% of TEP)	2.9
Instrumentation (43% of TEP)	3.9
Piping (31% of TEP)	2.8
Electrical (10% of TEP)	0.9
Buildings (15% of TEP)	1.38
Yard Improvements (12% of TEP)	1.1
Service facilities (55% of TEP)	5.0
Total Direct plant cost (TDC)	**27.18**
Engineering and supervision (32% of TEP)	2.9
Construction Expenses (34% of TEP)	3.1
Legal Expenses (4% of TEP)	0.36
Contractor's fee (19 % of TEP)	1.17
Contingency (35% of TEP)	3.2
Total indirect capital cost (TIC)	**10.8**
Working capital (10% of TIC)	1.08
Solvent cost	0.04
Catalyst cost	0.2
Total capital cost	**39.7**

The resulting probability density functions of NPV are graphed in Figure 3. Deriving the NPV distribution of an investment in a project that employs a single-product technology to convert glucose into blend of 1-dodecanol and 1-tetradecanol, an expected value of $12 million and standard deviation of $25 million are estimated. The average value and the standard deviation of NPV distribution are found to be $ 20 million and $26 million respectively for the investment in single-product technology that can produce 1-decanol from glucose (Figure 3). If the investment is made in the 2- product platform technology that has a flexibility to switch to an alternative fatty alcohol, the project mean and standard deviation of NPV distribution are calculated as $ 31 million and $20 million, respectively (Figure 3). The difference between two

mean NPVs, that is, $ 31 million - $ 12 million and $ 31 million - $ 20 million determine the increase in profitability of an investment by 2- product platform technology compared to single-product technologies. Comparing standard deviation of NPV distribution of investment for 2-product platform technology, that is, $ 20 million with that of single-product technology, that is, $ 25 million and $ 26 million shows that financial risk due to volatilities in prices of product, feedstock, energy, and catalyst is reduced by the 2- product platform technology.

This reduction in financial risk and increase in profitability of investment with the 2-product platform technology will be explained as follows. For example, Figure 4 shows the five-year forecasted net profits that are generated from the blend of 1-dodecanol and 1-tetradecanol and 1-decanol production via single-product technologies. If a technology only makes one product (either blend of 1-dodecanol and 1-tetradecanol or 1-decanol), a chemical firm must live with the up and down swings of these net profits that are caused due to volatilities in market prices of product, feedstock, energy, and catalyst. However, suppose the chemical firm has the platform technology to produce multiple products. If the net-profits of an alternative product become more attractive, the chemical firm can consider switching. The expectation to switching is that market prices of product, feedstock, energy, and catalyst will revert toward their long-term means, that the net-profit difference may not justify the cost of switching production. This ability to switch between products with platform technologies reduces the impact of market volatility and increases value of the investment.

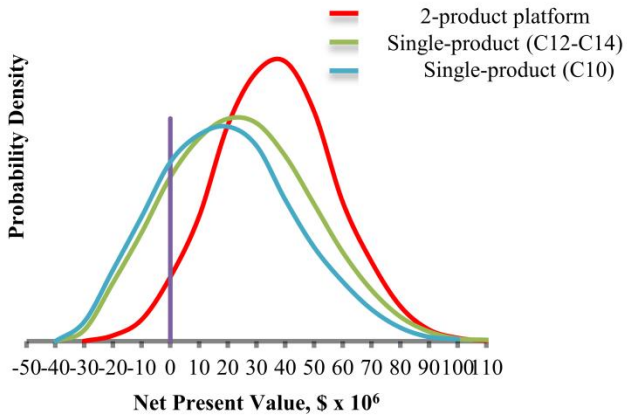


Figure 3 NPV distributions for 2-product platform technology making 1-Decanol & Blend of dodecanol and 1-tetradecanol and single product technology making either 1-Decanol or Blend of dodecanol and1-tetradecanol

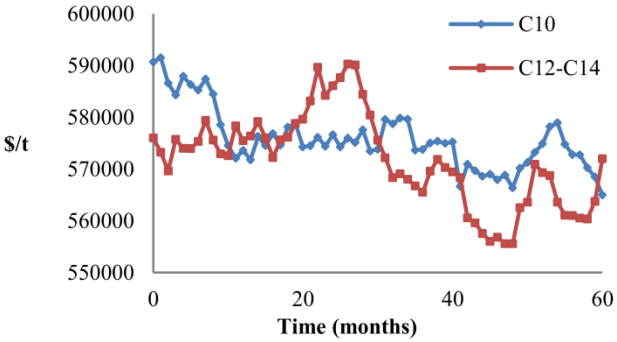


Figure 4 Five year forecast of net profits of 1-Decanol (C10) & Blend of dodecanol and1-tetradecanol (C12-C14)

Impact of multiple products

In this section, we analyze how the increase in the number of products in the "product suit" of platform technology impacts the financial risk and profitability of investment. The product suit of single-product technologies contain only one product, and the product suites of two, three, and four product platform technologies contain two, three, and four products respectively.

The financial risk and profitability of investment for making 1-octanol, 1-decanol, blend of 1-dodecanol and 1-tetradecanol, and 1-hexadecanol via single-product technologies are determined by deriving probability density function of net present value (Table 3). The prices of 1-octanol and 1-hexadecanol are modeled using mean reversion process, and required mean reversion parameters are estimated from their respective historical data (Table 2). The estimated operating costs of 1-octanol production are slightly higher than the 1-decanol production, and of 1-hexadecanol production are slightly lower than the 1-decanol production. The results summarized in Table 3 show that as the profitability of investment for the fatty alcohol production via single-product technologies increases the financial risk to investment also increases. Among the four fatty alcohols analyzed in this work, the investment for the production of 1-octanol has high profitability and financial risk, and for the production of 1-hexadecanol has low profitability and low financial risk (Table 3). This high profitability is due to the high long term mean price of 1-octanol compared to other fatty alcohols, and the high financial risk is a result of high volatility or variability in the price of 1-octanol (Table 2).

Table 2
Mean reverting parameters of economic variables

Economic Variable	Long-run mean	Variance parameter	Reversion Speed (day^{-1})
Glucose	0.30 ($/kg)	0.004	0.15
Natural gas	3.35 ($/MMBtu)	0.014	0.018
Electricity	0.07 ($/kWh)	0.001	0.18
Hydrogen	2.5 ($/kg)	0.014	0.01
Copper chromite	8.5 ($/kg)	0.023	0.18
1-Octanol	2.2 ($/kg)	68.25	0.15
1-Decanol	2.0 ($/kg)	9.14	0.0033
Blend of dodecanol and 1-tetradecanol	1.9 ($/kg)	12.21	0.0017
1-Hexadecanol	1.6 ($/kg)	7.83	0.015

Table 3
Results for impact of increase in number of products in the product suit

Product suit of Technology	Profitability	Risk
Single-product technology		
1-Octanol	$29 MM	$31 MM
1-Decanol	$20 MM	$26 MM
Blend of dodecanol and 1-tetradecanol	$12 MM	$25 MM
1-Hexadecanol	-$01 MM	$12 MM
Two-product technology		
1-Octanol & 1-decanol	$38 MM	$22 MM
1-Octanol & Blend of dodecanol and1-tetradecanol	$37 MM	$21 MM
1-Octanol & 1-hexadecanol	$29 MM	$31 MM
1-Decanol & Blend of dodecanol and1-tetradecanol	$31 MM	$20 MM
1-Decanol & 1-hexadecanol	$20 MM	$26 MM
Blend of dodecanol and 1-tetradecanol &1-Hexadecanol	$12 MM	$25 MM
Three-product technology		
1-Octanol,1-decanol& Blend of dodecanol and1-tetradecanol	$45 MM	$16 MM

In order to compare the economic value of investment for synthesis of fatty alcohols using 2-product platform technologies with that of single-product technologies, NPV of investment for all possible product suites of 2-product platform technologies with four fatty alcohols are estimated (Table 3). It is found from results that the profitability of investment increases and financial risk of investment decreases with 2-product platform technologies compared to single-product technologies (Table 3). However, the economic value generated from 2-product platform technologies with a product suit of 1-hexadecanol and 1-octanol, 1-decanol, or blend of 1-dodecanol and 1-tetradecanol is similar to that of single-product technologies making 1-octanol, 1-decanol, and blend of 1-dodecanol and 1-tetradecanol, respectively. This exception is because net revenues generated from 1-hexadecanol production over the simulated time period is always less than that of other fatty alcohols, and thus it is not attractive to consider switching to 1-hexadecanol production with a 2-product platform

technology. Thus, the addition of low value product such as 1-hexadecanol to the product suit of platform technology will not improve the economic value of investment for the synthesis of biorenewable chemicals using platform technologies.

Since the product suit of 2-product platform technology having 1-hexadecanol will not add any value to the investment, we analyze product suit of 3-product platform comprising only 1-octanol, 1-decanol, and blend of 1-dodecanol and 1-tetradecanol. The probability distribution of NPV of an opportunity of investment for the fatty alcohol production via 3-product platform technology is calculated to determine financial risk and profitability of investment (Table 3). The results in Table3 show that the 3-product platform technology increases profitability of investment to $45 million, which is higher than that of single- and 2-product technologies, and decreases the financial risk to $16 million, which is lower than that of single- and 2-product technologies (Table 3). Thus, profitability of investment increases and financial risk of investment for the biorenewable chemical production via platform technologies decreases as the number of products in the product suit of platform technology increases. However, the extent of this impact on the economic value with the increase in number of products in the product suit of platform technology will depend upon the type of product in the product suit. For instance, as shown above the addition of low value product such as 1-hexadecanol to the product suit of platform technology can't improve the economic value of investment.

Sensitivity to switching cost

The production of fatty alcohols is a somewhat unique case. In general, there is a cost associated with platform technologies for switching from one product to another. In order to see how switching cost influences the economic advantages provided by platform technologies,

profitability of investment for the synthesis of fatty alcohols via 2-product platform technology is computed for increasing one- time and recurring switching costs.

The profitability of investment for the 2-product platform technology allowing access to two markets 1-decanol and blend of 1-dodecanol and 1-tetradecanol for increasing recurring switching costs is estimated by exercising the economic model nested with Monte Carlo simulation (Figure 5). As shown in Figure5, the profitability of investment decreases with increasing recurring switching cost. Similar behavior in profitability is observed with increasing one-time switching cost (data is not shown). This decrease in profitability is primarily because the 2- product platform technology will allow its production to switch less and less as the switching cost increases.

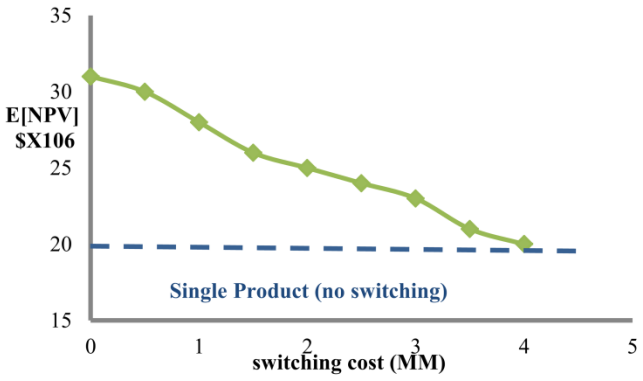


Figure 5 Effect of recurring switching cost on the expected NPV of 2-product platform technology making 1-Decanol & Blend of dodecanol and1-tetradecanol

For the recurring switching cost of $4MM (Figure5) and one-time switching cost of $6MM, the profitability of investment for making fatty alcohols via 2-product platform technology converges to the value provided by single-product technology. Hence, the economic advantage provided by the 2-product platform technology allowing access to two markets (1-decanol and blend of 1-dodecanol and 1-tetradecanol) vanishes when the switching cost is

greater than $4MM in the case of frequent investment and greater than $6MM in the case of one-time investment.

One reason for the different maximum values for one-time and recurring switching costs is the dependence of profitability of investment on discount rates. While exercising the economic model nested with Monte Carlo simulation, switching cost is added to the total capital investment in the case of one-time investment and in the case of frequent investment, switching cost at the time of switching is discounted to the year of 2014 at the fixed internal rate of return of 10%, and then added to the capital investment. The application of discount rates that are less than or greater than 10% will result in maximum values of recurring switching costs that are less than or greater than $4MM. In conclusion, the switching cost limits the commercial advantage provided by the platform technologies irrespective of the nature of switching cost. In the following section, we will qualitatively state other advantages of platform technologies for biorenewable chemical production.

Qualitative risk analysis of the platform technology

We have so far considered market risk due to variation in the prices seen in the market. Another dimension of market risk results from depression of the market equilibrium or long-term mean price of a chemical as new producers enter into the market. This reduction in equilibrium market price is dependent on the price elasticity of supply and demand of a chemical. Such price depression will decrease the current equilibrium price of a chemical and set a new equilibrium price [32]. If the equilibrium price is highly sensitive to market supply and demand, there is more risk to the investment, particularly to the ‘single-product’ technology. For instance, the market price of ethane in the US fell nearly by 50 percent since 2005 as its production has increased from 700,000 barrels per day in 2005 to 1,000,000 barrels per day in 2013, as a result of the

shale gas revolution [33]. If a technology only made ethane, there would be a high risk of incurring financial losses to a company if profit margins were low, as is often the case for commodity chemicals. An advantage of a platform technology is that if the market for one target product collapses, such as ethane in this example, the investment is not lost because production can shift to another chemical with a relatively small additional capital investment.

Another source of risk to the investment in the biorenewable chemical business is associated with scaling-up a new technology. When an incipient technology is scaled up from laboratory- to pilot-, to commercial scale, there is a risk of short fall in technology performance due to insurmountable technological barriers that are not identified at the research and development stage [6]. If a single-product technology experiences such insurmountable technical barriers, complete losses of capital and technical investments are likely. However, these losses are significantly reduced in the case of platform technologies. If development of a particular technology, the synthesis of fatty alcohols from fatty acid for example, fails to meet process performance targets during scale up, perhaps the chemical catalyst cannot achieve necessary levels of selectivity under production conditions, much of the technology of the carboxylic acid platform can simply be repurposed to target a different molecule within the platform, such as n-alkanes [34]. Thus, the investments made in developing and commercializing the fermentation technology for fatty acid production from biomass and the separation of fatty acids from fermentation media are saved and redirected into another product line.

Platform technologies also provide an opportunity to deliver multiple commodity chemicals to the market with one facility thus reducing production cost. Werpy and Peterson, (2004) have identified the most promising building block chemicals that can be derived from glucose. In addition, they identified a diverse portfolio of chemicals that can be subsequently

produced from these building block chemicals. Most of the chemicals identified by Werpy and Peterson, (2004) are commodity chemicals with relatively small markets; much smaller than ethanol, for example. This small market size limits the feasible capacity of a production facility if designed to produce only a single-product. The high production cost due to the diseconomies of scale may create a barrier for market entry for commodity chemicals, which generally have low profit margins. Having the ability to produce multiple products using the same equipment, platform technology makes it possible to capture the economies-of-scale possible from a large biorefinery– without over supplying any individual product market.

Investments in platform technologies for producing high-profit margin specialty chemicals may over time lead to the production of commodity chemicals. In general, it requires large capital investment to construct high capacity plants for producing conventional commodity chemicals. The requirement of such high capital investments will create a barrier entering into the commodity chemical business. One strategy to overcome this barrier is to make a higher value chemical via platform technology. If production and marketing of the first, higher-value products is successful, technologies can be refined and de-risked. As technology risks decrease, it may be possible for firms to take on more market risk. Firms will have both technological and financial capacity to increase plant capacity as necessary to produce larger volume commodity chemicals from biomass. For example, when investments made by a company in the microbial production of specialty chemicals such as azelaic acid via reverse β oxidation [8] are profitable; then there is an opportunity to expand plant capacity in order to make a commodity chemical such as adipic acid.

The inherent functionality of biomass also creates an opportunity for making novel chemicals with unique and improved properties. Such novel products can functionally replace

existing petro-chemicals or create new opportunities in the chemicals markets. The risk to the capital investments for the synthesis of novel biorenewable chemicals via single-product technologies is high as markets for these products are not yet developed and there is high uncertainty associated with their market potential [14]. These risks can be reduced by making novel products via platform technologies as technical and capital investments of platform technologies can be spread over replacement, functional replacement, and novel chemical products. Moreover, with platform technologies a company can adjust production volumes of making drop-in and novel chemicals according to their market growth potentials.

Conclusions

There are several different types of risks associated with the production of biorenewable chemicals. These risks reduce the profitability of capital investments in single-product technologies and are a deterrent to investments in biomass conversion technologies. In this work, we have shown quantitatively how platform technologies can reduce financial risks and increase the value of investments in biorenewable chemical production relative to single-product technologies. Platform technologies that produce a large range of different chemicals generate higher returns with lower risk. The benefits of platform technologies are reduced as the cost of switching between products increases. Platform technologies also reduce the risk of introducing novel and low-market volume products to the market.

Biorenewable chemical companies may benefit from developing platform technologies, particularly if they already have appropriate technical and marketing expertise. However, bringing a product into a new market can be more expensive than developing the product and often requires specialized technical skills as well. Thus capturing the benefit of making multiple

products from a single technology platform may significantly increase the total investment required and reduce the appeal of platform technologies, particularly to smaller firms.

Firms that already operate facilities such as biofuel plants or biorefineries built around corn wet or dry mills are likely to find it easiest to incorporate platform technologies to produce a range of chemical and fuel products for the obvious reasons that these plants have some of the requisite infrastructure and these firms have diverse technical talents. The exact type of technology platform that makes the most sense for any firm, however, will depend on that firm's endowment of technical and physical resources. Further research is required to define how characteristics of a technology platform such as number of products, range of product markets, variability of market prices, correlation between market prices, and nature of separation processes benefit the unique circumstance of a particular firm.

In general, the advantages of a multi-product approach improve the prospects for developing biorefineries built around or incorporating platform technologies. Easing access to capital through development of risk reducing platform technologies can stimulate the growth of the biorenewable fuel and chemical industries. Targeting biobased chemical platform technologies in research and development funding may therefore accelerate the growth of a biobased economy.

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CHAPTER 5

Comparative Economic Analysis of Bio-based Routes to Adipic Acid

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ABSTRACT

Techno-economic studies of four processes for production of adipic acid from glucose are performed to determine the economic potential of each route. We analyzed the purely biological, reverse β-oxidation in *E. coli*; purely chemical, oxidation of glucose via chemical catalysis yielding glucaric acid that further undergoes catalytic hydrodeoxygenation to adipic acid; and biological production of 6-hydroxyhexanoic acid or 1, 6-hexanediol, which are subsequently converted chemically to adipic acid using a metal catalyst. The adipic acid production capacity of 80,000 metric ton/year is assumed. The estimated total capital investments are $ 157 MM, $ 81 MM, $166 MM, and $177 MM for the adipic acid production via purely biological, chemical, and two integrated routes, respectively. The catalyst costs are estimated as $40 MM, $36 MM, and $37 MM for the purely chemical and two integrated routes to adipic acid respectively. The estimated adipic acid minimum selling price (MSP)s are $1.36/kg, $1.56/kg, $1.48/kg, and $1.61/kg for the adipic acid production via purely biological, purely chemical, and two integrated routes, respectively. The co-product revenue and the use of unpurified sugars improve the economics of adipic acid production using purely biological and two integrated routes to adipic acid. The pH dependence of a chemical catalytic reaction can impact the adipic acid MSP. The catalyst yields, turnover frequency, and catalyst life must be greater than 40% of theoretical, 0.01 s^{-1}, and 100 h to achieve economic viability of a process for the production of adipic acid using purely chemical and integrated routes to adipic acid.

Keywords: Techno-economic analysis, Adipic acid, Chemical catalyst, Biocatalyst, Reverse β-oxidation

Introduction

Adipic acid is a commodity chemical and can be used majorly in the production of nylon as a monomer [1]. It has also found applications in a wide range of industries including, but not limited to, energy, food, and pharmaceutical. The projected adipic acid global demand in 2017 is more than 2.7 billion kilograms [1]. The adipic acid is primarily made from the catalytic oxidation of a mixture of petroleum feedstock cyclohexanol and cyclohexanone [1]. Risks to the use of petroleum feedstock include limited availability, disruptions to the imports, and the price volatility [2]. In addition to these risks, there are concerns over the environmental impacts of conventional adipic acid production as the oxidation of cyclohexanol and cyclohexanone emits the greenhouse gas nitrous oxide [1]. It is expected that the functional replacement of petro-based adipic acid with the glucose derived adipic acid can lower such risks and environmental impacts.

Glucose can be converted into adipic acid solely using a chemical-catalytic technology, as well as wholly bio-catalytic technology, and also by integrating bio-catalytic and chemical-catalytic technologies. The purely chemical catalytic route to adipic acid involves the oxidation of glucose via chemical catalysis yielding glucaric acid [3] that further undergoes catalytic hydrodeoxygenation to adipic acid [4]. The reverse β-oxidation pathway in *E.coli* can be utilized for the synthesis of adipic acid from glucose [5]. The integrated biological and chemical catalysis approach includes reverse β-oxidation production of 6-hydroxyhexanoic acid and 1, 6-hexanediol[5], which are subsequently converted to adipic acid using a metal catalyst [6].

The development of glucose conversion technologies for the production of adipic acid is at the research and development stage. It is necessary to determine the economic potential of early stage technologies to avoid the investment losses [7]. The performance targets for the

technology development can be set by understanding how process structure and key process parameters influence the production cost of adipic acid. In addition, eliminating major bottlenecks in the process helps us to successfully implement biobased adipic acid technologies at commercial scale. In this work, we performed the economic and modeling analysis to determine the economic viability of synthesizing adipic acid from glucose via four possible routes, to identify major bottlenecks, and to find out the impact of key process parameters on the overall economics of adipic acid production. In addition, economic analysis enables us to determine advantages and disadvantages of one pathway relative to the others

The process flow diagram (PFD)s for four bio based adipic acid routes were created. The adipic acid processes were modeled using ASPEN Plus® version 8.6 and SuperPro Designer® version 9.0 simulation software. The simulation results were used to estimate capital and operating costs of adipic acid production. The discounted cash flow analysis was used to estimate minimum selling price (MSP) of adipic acid [8]. The comparative economic analysis has shown that adipic acid production using purely biological route is more promising. Low catalyst selectivities to glucaric acid hinder the development of an economically viable route to adipic acid solely through chemical catalysis. The low fermentation yield makes the production of adipic acid via 1, 6-hexanediol economically unfeasible. It is economically viable to make adipic acid via 6-hydroxyhexanoic acid. This route, however, looks less promising compared to the purely biological route because of the increase in the number of process steps.

Process Description and Modeling

Purely biological route to adipic acid

A PFD was developed for the purely biological adipic acid route. (Figure 1). The PFD include production of glucose from corn through dry-mill process, adipic acid fermentation,

separation and purification of adipic acid, and the production of dried distillers grains with solubles (DDGS). The production of glucose and DDGS were modeled using the SuperPro Designer® simulation software. The necessary modeling parameters for the production of glucose from corn and DDGS drying processes were obtained from Kwiatkowski et al., 2006 [9]. Adipic acid can be produced from glucose via an anaerobic reverse β-oxidation pathway in *E.coli* [5]. The product and seed fermentors were modeled using the SuperPro Designer® simulation software. The reactions, product yields, product rates, operating conditions, and modeling parameter values of seed and product fermentations can be found in the supplementary materials (Table S1, S2, and S3). The fermentation yields and product rates were obtained from the in silico flux analysis/stoichiometric modeling [5]. An ammonium base was added during fermentation to maintain pH in the range of 5-7 [10].

Microfiltration was used to remove *E.coli* cells from the fermentation broth [10]. The remaining solids from the microfiltration permeate were separated via centrifugation [10]. The clarified fermentation broth containing water, adipic acid, diammonium adipate, and other impurities was sent to a distillation column, which is operated at a temperature of 300^0 C and a pressure of 25 atm [10]. Such high distillation temperatures are necessary to remove ammonia and to form pure adipic acid from diammonium adipate [10]. The distillation liquid bottom that includes pure adipic acid, 20 wt% water, and other impurities was cooled down to 60^0C. The distillation column was modeled using the ASEPEN Plus® simulation software. The ultrafiltration process was used to remove protein impurities from the cooled distillation liquid bottoms [11]. The adipic acid was extracted from the ultrafiltration filtrate using the crystallization column [10]. The solubility of adipic acid in water as a function of temperature was obtained from the Fruchey et al., 2014, which was used to model the crystallization column

[12]. The slurry of adipic acid crystals was filtered and the wet crystals were dried using the rotary vacuum drier. Most processing conditions for membrane filtration processes were assumed for the modeling purpose.

Purely chemical route to adipic acid

A PFD for the process of chemical catalytic conversion of glucose to adipic acid was developed (Figure 2). The presence of impurities in the sugar stream, that is produced using corn dry milling process, may poison the metal catalyst. The use of pure glucose stream was, therefore, assumed as a raw material for the process of adipic acid production using the purely chemical route. Pure sugar can be made from corn using commercialized and matured corn wet milling process. We obtained price of sugar as 0.30 ($/kg) from a personal communication with the managers of corn wet milling plants in the Midwest region of USA.

The production of adipic acid was modeled using the ASPEN Plus®. Glucose is oxidized to glucaric acid using platinum-carbon (Pt/C) catalyst in a continuous-stirred tank reactor (CSTR) [13]. The pH and temperature of the oxidation reaction were maintained between 8-11 and 45- 65^0C, respectively [13]. The glucose oxidation results in the formation of glucaric acid along with by-products glycolic acid, glyceric acid, erythronic acid, oxalic acid, and tartaric acid [13].Similar to the purely biological route to adipic acid, yields and rates that are estimated under ideal conditions were used for the modeling of purely chemical route to adipic acid. The steady state condition and no transport limitation of reactants and products in a reactor represent ideal conditions for chemical catalytic reactions [15]. The 100% conversion of glucose and 55% selectivity to glucaric acid were assumed for the modeling purpose [13]. The rate data for the modeling of glucose oxidation reaction were obtained from the Dirkx et. al (1977) and Dijkgraaf et. al (1987) [14].

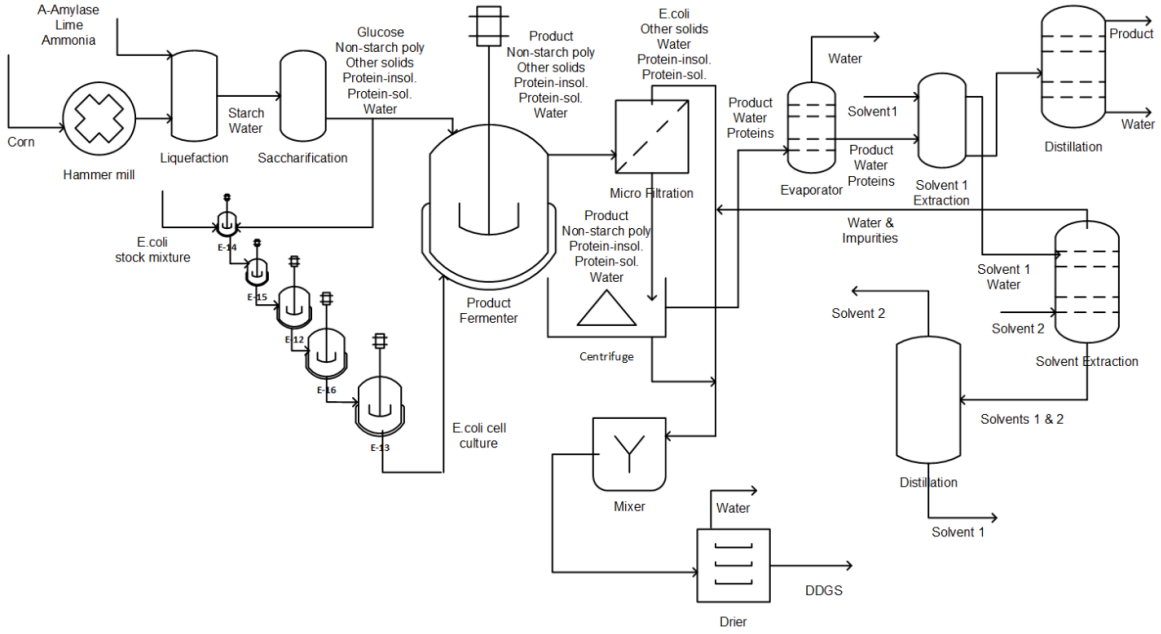

Figure 1 Simplified process flow diagram of purely biological route to adipic acid production

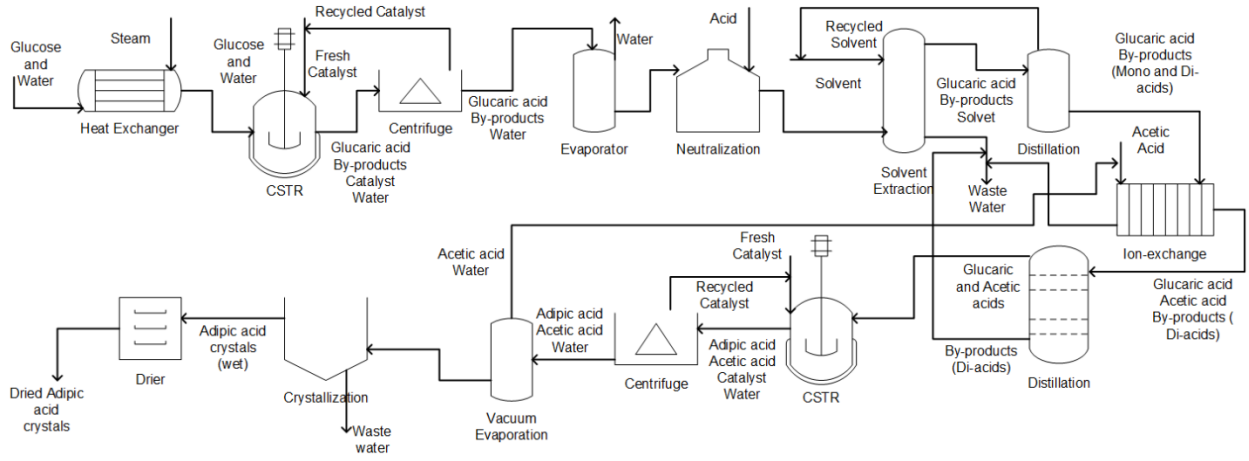

Figure 2 Simplified process flow diagram of purely chemical route to adipic acid production

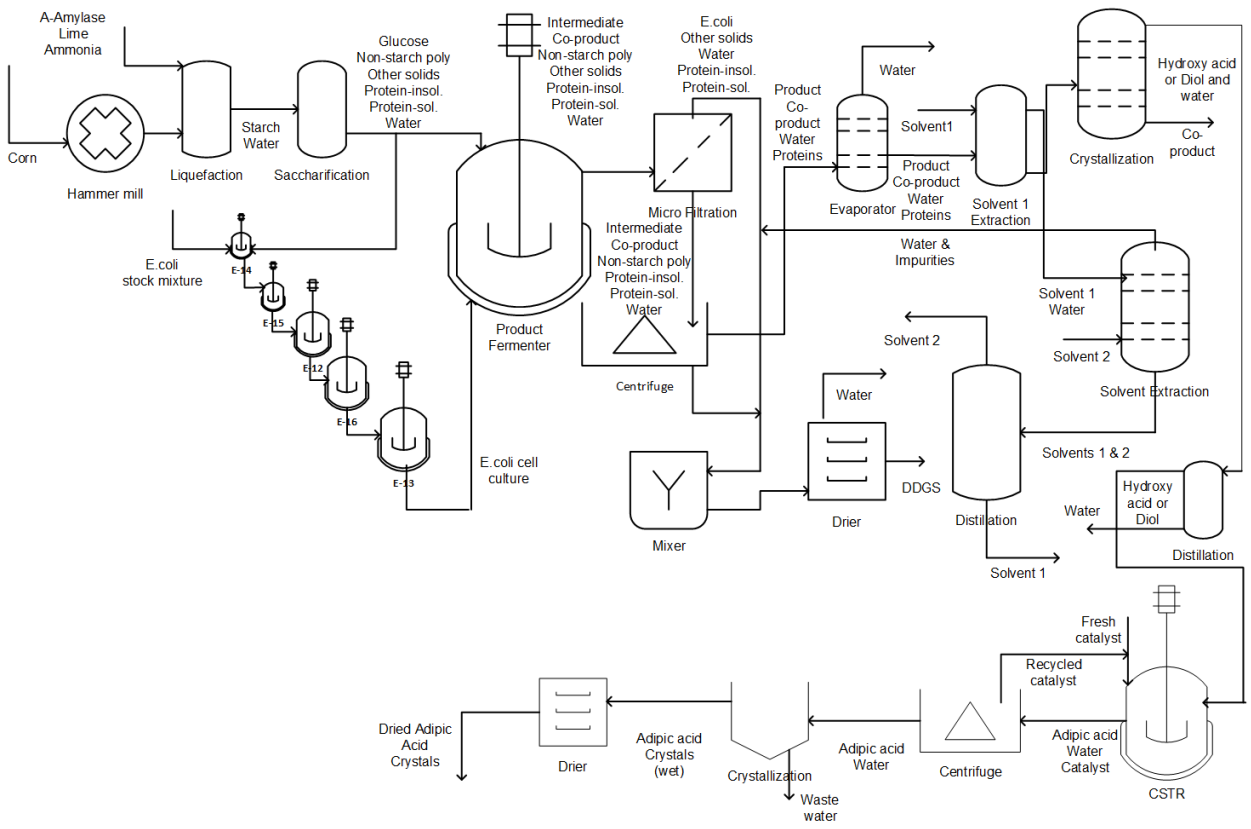

Figure 3 Simplified process flow diagram of adipic acid production via 6-hydroxyhexanoic acid 1,6-hexanediol routes

The product stream from the CSTR was sent to a centrifuge to recover Pt/C catalyst particles. The evaporation and neutralization processes were then used to remove water and to lower the pH of product stream to 5, respectively. Hydrochloric acid was used for the neutralization purpose. After the neutralization process, the mixture of by-products and glucaric acid were extracted into organic solvent heptane [14]. The solvent was separated and recovered using a distillation column. The extracted mixture of mono and dicarboxylic acids was further separated into mono and dicarboxylic acids using an ion-exchange column [16]. The glucaric acid was separated from the di-carboxylic acid mixture using a distillation column. We modeled

liquid-vapor equilibria and liquid-liquid equilibria using the Non-Random Two-Liquid (NRTL), UNIversal QUAsi Chemical (UIQUAC) models, respectively.

The glucaric acid is hydrodeoxygenated to adipic acid using a platinum-rhodium (Pt-Rh) bimetallic catalyst in a CSTR reactor [4]. This hydrodeoxygenation reaction is conducted in presence of acetic acid[4]. The operating conditions for this reaction were obtained from Boussie et al., 2010. The 100% conversion of glucaric acid and 89% selectivity to adipic acid were assumed for the modeling purpose [4]. A surrogate reaction was used to model the kinetics of hydrogenation reaction as the rate data for glucaric acid hydrogenation was not found in literature [17-19]. The acetic acid was recovered using the vacuum evaporation column. The adipic acid was purified using the crystallization column [12].

Adipic acid production via 6-hydroxyhexanoic acid and 1, 6-hexanediol

The PFDs were created for the production of adipic acid via 1, 6-hexanediol and 6-hydroxyhexanoic acid (Figure 3). Biocatalysts can make a product from unpurified sugars. Glucose made from corn via dry-grind process was, therefore, assumed as a feedstock for the production of adipic acid via integrated routes. Similar to the purely biological route to adipic acid, DDGS is one of the co-products of adipic acid production via two integrated routes to adipic acid. Glycolate and 4-aminobytyric acid were other the co-products products of 6-hydroxyhexanoic acid and 1, 6-hexanediol production respectively (Table S1)

The operating conditions for the 1, 6-hexanediol and 6-hydroxyhexanoic acid fermentations can be found in the supplementary materials (Table S2). Similar to the purely biological adipic acid route, fermentation broths containing 1, 6-hexanediol and 6-hydroxyhexanoic acid were clarified using the microfiltration process. The solvent extraction technique was used to recover 1, 6-hexanediol and 6-hydroxyhexanoic acid from the clarified

fermentation broth. The solvents 1-hexanol and hexane solvents were employed for the extraction of 1, 6-hexanediol and 6-hydroxyhexanoic acid, respectively [20, 21]. The distillation column was used to recover solvents and purify 1, 6-hexanediol and 6-hydroxyhexanoic acid. The NRTL and UNIQUAC models were used to generate liquid-vapor equilibria and liquid-liquid equilibria data, respectively. Similar to the purely biological route, the fermentor, solvent extraction column, and microfiltration process were modeled using SuperPro Designer® simulation software and the distillation column was modeling using ASPEN Plus®.

1, 6-hexanediol and 6-hydroxyhexanoic acid were oxidized to adipic acid using PtBi bimetallic catalyst in a CSTR reactor [22]. The CSTR reactor was modeled using ASPEN Plus®. The operating conditions for CSTR catalytic reactor, catalytic conversions and selectivities, and necessary rate data for the modeling kinetics of 1, 6-hexanediol and 6-hydroxyhexanoic acid oxidation reaction were obtained from the personal communication with the Center for Biorenewable Chemicals (CBiRC) research team. A yield of adipic acid (98%) has taken for the modeling purpose. The normal distillation process was used to remove water from the product mixture of catalytic reactor. The distillation liquid bottom containing 20 wt% water, adipic acid, and other impurities is cooled to room temperature using a condenser, before it is sent to crystallization column. The wet adipic acid crystals were dried using a dryer. The distillation and condenser columns were simulated using ASPEN Plus®. The crystallization column and dryer were modeled using SuperPro Designer® simulation software.

Adipic acid MSP estimation

We assumed adipic acid plant capacity of 80,000 MT/yr and plant life of 20 years in all cases. The equipment cost used in glucose production from corn and the capital and operating costs of the dryer used for DDGS processing were taken from Kwiatkowski et al[9]. The

equipment costs were adjusted to a required size using the six-tenths rule. A built in economic cost model in SuperPro Designer® simulation software was used to estimate the equipment costs of seed and product fermentors, membrane filtration processes, solvent extraction column and the crystallization column. The equipment costs for distillation columns were calculated on the basis of number and type of trays[23]. The purchase costs of evaporators, reboilers, and condensers were estimated using the cost correlation equations presented in Seider et al, 2010[24]. Purchase costs for catalytic reactors (CSTR) were estimated using cost curves in Peters et al, 1991[23]. Catalyst cost was estimated as the sum of precious metal cost and $11/kg of catalyst support and manufacturing. It is assumed that the catalyst manufacturer will be able to recover 95% of the metals in the spent catalyst. Total fixed-capital investment for adipic acid production was estimated using the ratio factors based on purchase costs of equipment[22].

The simulated energy balances were used to determine the steam and electricity requirements of adipic acid production. The quantities of raw materials were determined using the simulated material balances. The prices of raw materials and utilities used in this analysis can be found in the supplementary materials (Table S4). The wastewater was assumed to be treated at an external facility for a fixed price of $0.22 per kg organic removed[24]. The labor requirements (employee-hours/day/processing step) were calculated using the correlation between operating labor and the plant capacity[23]. The maintenance wages and benefits (MW&B) were assumed to be 4.5% of total direct plant cost[24]. The maintenance overhead and other maintenance related costs were calculated as 135% of MW&B[24]. The operating overhead and property taxes were assumed to be 23% and 2% of labor cost and total direct plant cost, respectively[24]. Annual plant depreciation was computed using the Modified Accelerated Cost Recovery Systems (MARCS) method[23]. Total general expenses were estimated as 10% of total revenues generated from fatty

alcohols[24]. The income tax was assumed as 35%. The minimum acid selling price (MSP) is computed using discounted cash flow analysis. The MSP is the minimum price that the adipic acid must sell for in order to generate a net present value of zero for 10% internal rate-of-return[25].

Results and Discussion

Purely biological route to adipic acid

The estimated total capital investment for the adipic acid production plant and adipic acid MSP are $157 MM and $1.36 per kg, respectively. Compare to other biobased adipic acid routes, the MSP of adipic acid that is made via purely biological route is found to be low (Figure 4). This is mainly because the number of chemical transformations required to make adipic acid via purely biological route are less and highest possible yields for the adipic acid production in comparison to purely chemical and two other integrated routes to adipic acid. The adipic acid MSP is majorly dominated by feedstock and separation costs (Figure 4). The feedstock and separation costs account nearly 38% and 40%, respectively, to the overall MSP of adipic acid. The sum of energy costs of evaporating water and removing ammonia from ammonium adipate using super atmospheric distillation column, and the membrane costs for the separation of protein impurities dominate the separation costs of adipic acid process.

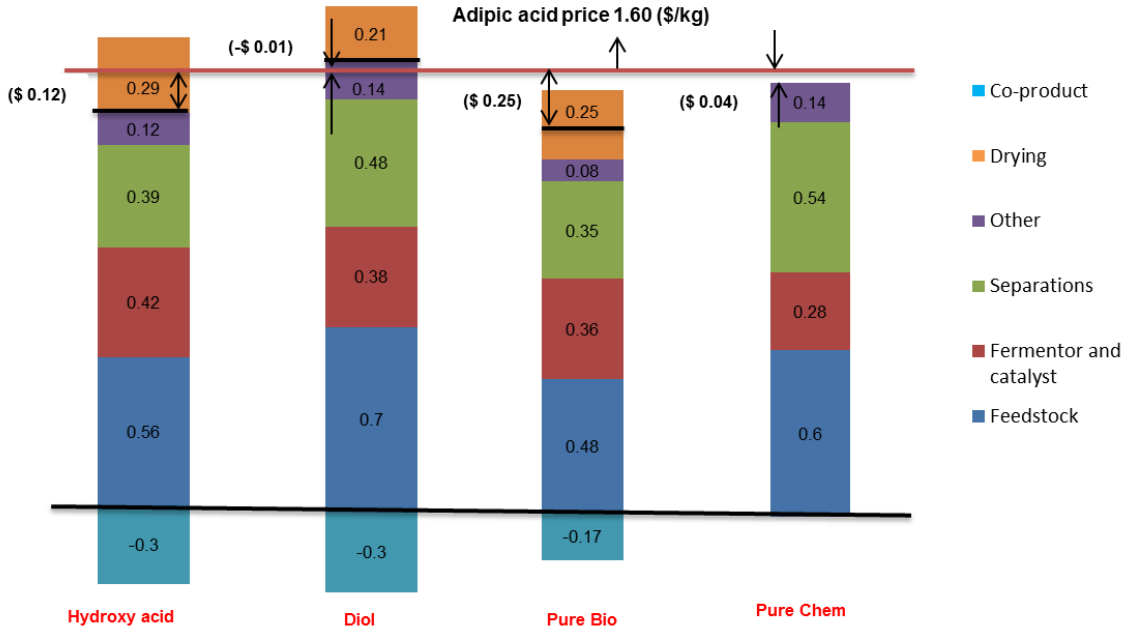

Figure 4**.** Cost analysis of multiple routes to adipic acid. Values in parentheses represent the margins after subtracting the adipic acid minimum selling price from the market price. The light blue, red, green, yellow, and blue bars indicate the feedstock cost, fermentor and catalyst, separations, drying, and co-product contributions to the minimum selling price of adipic acid, respectively

We assumed the fermentation titer of 50 g/l for the base case design. The adipic acid MSP is calculated for a range of titers to determine the impact of fermentation titer (Figure 5a). It is found that there is non-linear or curvilinear relationship exists between fermentation titer and the adipic acid MSP (Figure 5a). The economic benefits of pushing adipic acid titer beyond 125 g/l are found be low (Figure 5a). The adipic acid MSP is decreased only by 5.4% when the adipic acid titer is increased to 200 g/l from 125 g/l (Figure 5a). If the adipic acid toxicity for a microbial strain limits achieving fermentation titers of greater than 25 g/l, it is economically unfeasible to synthesize adipic acid via purely biological route (Figure 5a). In such cases,

microbial strain can be used to covert glucose to an intermediate like 6-hydroxyhexanoic acid that is further upgraded to yield adipic acid using a chemical catalyst.

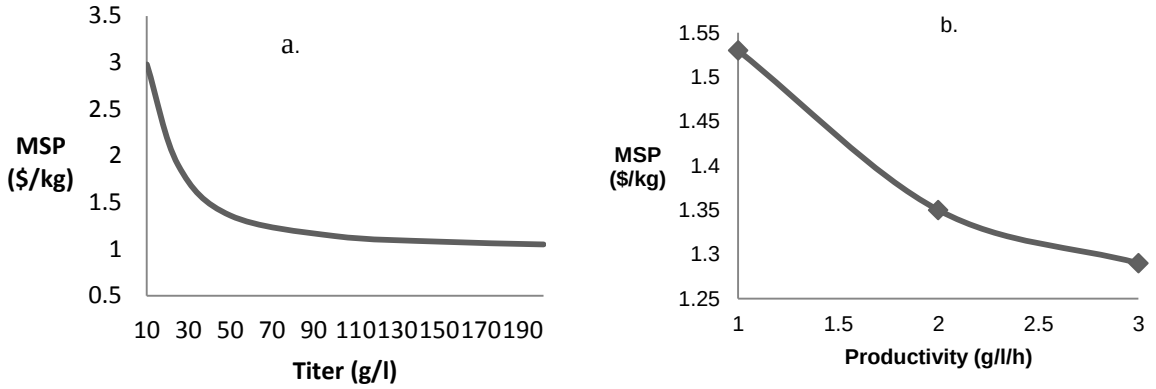

Figure 5 Effect of change in titer and productivity on the process economics of adipic acid production via purely biological route. (a) Titer vs. adipic acid MSP (b) Productivity vs. adipic acid MSP

The specific productivity of *E. coli* for the synthesis of adipic acid via reverse β-oxidation pathway is 1.41 g/g (CDW/h)[5]. For this specific productivity, various volumetric productivities (g/L/h.) can be attained by varying initial biomass concentration (g/l) in the production fermentor. The volumetric productivity of 2 g/l/h was used for the base case design. The adipic acid MSP is calculated for a range of volumetric productivities to determine the impact of volumetric productivity (Figure 5b). It has been found from the analysis that volumetric productivities greater than 2 g/l/h have a low effect on the adipic acid MSP. The adipic acid MSP is reduced only by 5% when the volumetric productivity is increased from 2 g/l/h to 3 g/l/h (Figure 5b).

Purely chemical route to adipic acid

The estimated capital cost for the production of adipic acid plant is $81 MM. The calculated total costs of metal catalysts are $36 MM. The estimated MSP of adipic acid that is made via purely chemical route is $1.56 per kg.

The pH dependency of the glucose oxidation reaction, which is catalyzed by the Pt/C catalyst, significantly increases the cost of adipic acid production. Since the formation of glucaric acid and other by-products lower the pH of the reaction mixture in CSTR, a base (e.g. KOH) is added to maintain the pH of glucose oxidation reaction in the range of 8-11. A strong acid is (e.g. HCL) added to the product mixture of oxidation reaction to lower its pH to 5 before it is sent to a solvent extraction column. Lowering the pH of the product mixture can increase the distribution coefficient of glucaric acid[20]. The inorganic salts formed after the addition of strong acid will be disposed as waste. The estimated total costs of acid, base, and salt disposal are around $0.07 per kg of adipic acid, which is nearly 5% of the total production cost of adipic acid.

The separations cost of purely chemical route is high compared all other routes because of low catalyst selectivities resulted in the by-product formation. The oxidation of glucose using Pt/C catalyst results in a lower selectivity to glucaric acid. The low Pt/C catalyst selectivity results in a by-product formation. The physical and chemical properties of these by-products are very similar to that of glucaric acid, which makes separations more expensive and complicated (Figure2 and Fig 4). Achieving high catalyst selectivity greatly improves the overall economics of adipic acid production process. The estimated adipic acid MSP is $1.36 for the complete conversion of glucose and 100% catalyst selectivity to the glucaric acid.

The problem with low catalyst selectivity could be overcome by carrying out chemical catalytic reactions under low conversions[26]. To determine the impact of catalytic conversion on

the economics of purely chemical route, the adipic acid MSP is estimated for a range of catalytic conversions with 100% selectivity to the glucaric acid (Figure 6a). The decrease in catalyst conversion of glucose to 40% from 100% will increase the adipic acid MSP by nearly 40%. The estimated adipic acid MSP is $1.65 for the 40% conversion of glucose and 100% catalyst selectivity for the glucaric acid, which is higher than the market price of adipic acid. Moreover, results show that there is a rapid increase in the production cost when catalyst conversion falls below 40% (Figure 6a). It is, therefore, economically unviable to make adipic acid via purely chemical route for low catalytic conversion of glucose values. The increase in adipic acid MSP with low conversions is attributed to the recycling unconverted glucose to the catalytic reactor.

The intrinsic kinetic parameters of glucose oxidation and glucaric acid hydrodeoxygenation reactions were used while estimating the adipic acid MSP. The diffusion limitation of reactants could lower the TOF of oxidation and hydrodeoxygenation reactions when catalytic reactors are scaled-up[15]. The adipic acid MSP is estimated for a range of values of turnover frequency (TOF) of glucose oxidation and glucaric acid hydrodeoxygenation reactions to determine the impact of reaction kinetics on the economics of adipic acid production. The results show a non-linear increase in the adipic acid MSP when the TOF of catalytic reactions fall below 10^{-2} s^{-1}(Figure 6b and Figure 6c). This is mainly because the catalyst cost is increased to nearly 400 million USD when the TOF of metal catalyst is on the order of 10^{-3} s^{-1}. It is economically unfeasible to synthesize adipic acid via purely chemical route if the TOF of metal catalysts are lower than the order of 10^{-2} s^{-1} (Figure 6b and Figure 6c). The TOF of oxidation and hydrodeoxygenation catalysts, therefore, must be in the range of 1 s^{-1} to 0.01 $s^{-1}$for commercial relevance (Figure 6b and Figure 6c). The reactions with higher values of turnover frequencies (> 10^{1} or more) can be influenced by transport limitations[15].

We assumed there is no loss of oxidation catalyst activity due to deactivation for the base case design. The Pt/C catalyst used for the glucose oxidation, however, can be deactivated by the dissolution of oxygen atoms into the platinum lattice[14]. The catalyst activity data published by Dijkgraaf et. al. (1988), shows that the presence of oxygen deactivates Pt/C catalyst rapidly[14]. The loss of catalyst activity is determined as about 20% after 3 hours[14]. The deactivated Pt/C catalyst can be regenerated using a reducing agent[14]. The complete regeneration of Pt/C catalyst might take long time (2 to 3h) [14]. Multiple catalytic reactors are, therefore, necessary for the continuous production of adipic acid. The addition of an extra catalytic oxidation reactor to the adipic acid production will increase the previously estimated adipic acid MSP to $1.60 from $1.56 per kg.

It has not been mentioned in the literature about the hydrodeoxygenation catalyst stability and reuse. The catalytic conversion of a molecule with the carboxyl group might result in the catalyst deactivation due to coking[26]. The deposited coke on the catalyst can be removed using the process called oxidative regeneration[27]. The adipic acid MSP is calculated for a range of values of catalyst life to determine the impact of catalyst deactivation on the economics of purely chemical route to adipic acid. In this analysis, we assumed that there is a loss of 5% noble metal and 100% catalyst support for every regeneration cycle. The regeneration cost of coked catalyst was calculated as the sum of the costs of energy requirement for coke combustion, 5% noble metal catalyst and catalyst support. There is a non-linear relationship exists between the adipic acid MSP and the catalyst life (Figure 6d). The economic benefits of improving catalyst life beyond 100 h are found to be low (Figure 6d). The metal catalyst life of at least 100 h is required to achieve the economic viability of synthesizing adipic acid via purely chemical route

(Figure 6d). This is mainly because the regeneration cost is increased to more than 10 million USD from 1 million when the metal catalyst life is decreased from 200 h to 100 h.

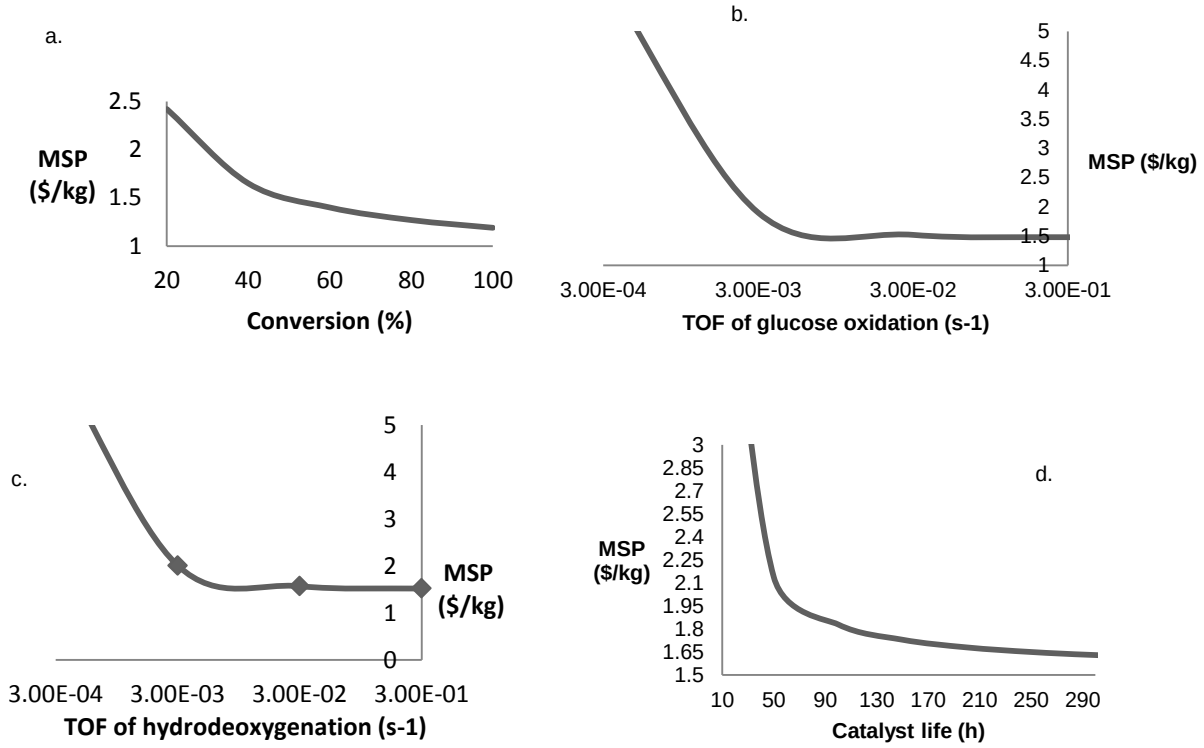

Figure 6 Sensitivity to minimum selling price of adipic acid that is made via purely chemical route. (a) Catalytic conversion vs. adipic acid MSP (b) TOF of glucose oxidation vs. MSP of adipic acid (c) TOF of hydrodeoxygenation reaction vs. MSP of adipic acid (d) Catalyst life vs. MSP of adipic acid

Adipic acid production via 6-hydroxyhexanoic acid

The estimated total capital cost of adipic acid production plant and the catalyst costs are $166 MM and $36 MM, respectively. The estimated adipic acid MSP is $1.48. The production of 6-hydroxyhexanoic acid from glucose via reverse β oxidation in *E. coli* results in a co-product glycolic acid. The co-products DDGS and glycolic acid were assumed to be sold at the prices of $0.16 and $0.80 per kg, respectively.

The synthesis of adipic acid via 6-hydroxyhexanoic acid requires higher capital investments compared to the purely biological route to adipic acid. Such a high capital

investments are mainly because of increase in process steps with the integrated biological and chemical catalysis approach. This increase in number of process makes the production of adipic acid via 6-hydroxyhexanoic acid less promising as compared to the purely biological route. When compared to the purely chemical route to adipic acid, the feedstock contribution to the adipic acid MSP can be lowered by 12.5% by producing adipic acid via 6-hydroxyhexanoic acid. Such a decrease in feedstock contribution is mainly because having the biocatalysis upfront enables the use of impure and inexpensive sugars. In addition, the low selectivities of the catalytic oxidation of glucose can be avoided with this integrated biological and chemical route as the *E. coli* can synthesize intermediate 6-hydroxyhexenoic acid from glucose with a high selectivity.

The TOF of 6-hydroxyhexanoic acid oxidation reaction is 0.022 s^{-1}. The low solubility of oxygen in water might affect oxygen diffusion rates in a catalyst particle, when the catalytic reactor is scaled up. The oxygen diffusion limitation could lower the TOF of 6-hydroxyhexanoic acid reaction. If such diffusion limitations reduce the TOF to 0.0022 s-1, the adipic acid MSP is increased to $1.64, which is greater than the target adipic acid price. If the TOF of this oxidation reaction is improved to 2 s^{-1}, the adipic acid MSP will be reduced to $1.45. Similar to the purely chemical route to adipic acid, the TOF of PtBi catalyst that is used for the oxidation of 6-hydroxyhexanoic acid must be in the range of 1 s^{-1} to 0.01 s^{-1} for commercial relevance.

There may be the possibility of deactivation of PtBi catalyst due to coking during the oxidation of biological intermediate 6-hydroxyhexanoic acid. Similar to the purely chemical route to adipic acid, it has been found that the metal catalyst life of at least 100 h is required to achieve the economic viability of producing adipic acid from glucose via 6-hydroxyhexanoic acid.

Adipic acid production via 1, 6-hexanediol

The estimated capital cost for the production of adipic acid is $177 MM. The calculated total cost of metal catalyst is $37 MM. The synthesis of 1, 6-hexanediol from glucose via reverse β oxidation in *E. coli* results in a co-product amino-butyric acid. The co-products DDGS and amino-butyric acid from the adipic acid production were assumed to be sold at the prices of $0.16 and $0.80, respectively. The estimated MSP of adipic acid that is produced via 1, 6-hexanediol is $1.61 per kg, which is higher than the market price of adipic acid MSP (Figure4).

The feedstock contribution to the MSP of adipic acid that is made via 1, 6-hexanediol is nearly $0.70 (Figure4). The low fermentation yields of 1, 6-hexanediol is the main reason for the high feedstock cost contribution. The high metabolic energy requirement for the synthesis of 1,6-hexanediol via reverse β-oxidation pathway in *E. coli* strain limits the 1, 6-hexanediol yield to 0.30 g/g-glucose[5]. Such a low fermentation yield makes it economically unfeasible to make adipic acid via 1, 6-hexanediol.

The revenue generated from the DDGS sale is a vital part of the economics of the adipic acid production using purely biological and two integrated biological and chemical routes. (Figure4). Retrofitting existing corn grind ethanol production facility to produce adipic acid using purely biological route and integrated biological and chemical route is, therefore, an economically viable option. In addition to the co-product value, there are other benefits such as low feedstock supply chain risk and the optimized feedstock supply logistics with the ethanol plant retrofitting. The contamination of DDGS with the adipic acid, however, may affect the DDGS price as the presence of adipic acid might have feed palatability and animal health impacts.

Sensitivity analysis

Uncertainty in the prices of corn, natural gas, and electricity, waste water treatment costs, and the estimation of total capital investment can impact the adipic acid MSP. Sensitivity analysis was performed to determine the impact of these major economic assumptions on the adipic acid MSP. The sensitivity to adipic acid MSP was estimated for a +/- 20% change in the values of economic assumptions. For the purely biological route to adipic acid, the corn price and the capital investment have the dominant impact on the adipic acid MSP. When the corn price is increased from $3.50 to $4.2 per bushel, the increase in adipic acid MSP of 7 % is observed. The adipic acid MSP is increased by 5% when the total capital investment is increased from $157 MM to $188 MM. The natural gas price, wastewater treatment cost, and electricity price showed moderate impact on the adipic acid MSP. (Figure S1).

The MSP of adipic acid that is made via purely chemical route is most sensitive to glucose price. An 8% increase in the value of adipic acid MSP is observed for a 20% increase in the value of glucose price. The catalyst cost and total capital investment showed moderate impact on the adipic acid MSP. The sensitivity to the adipic acid MSP is estimated as 2.7% and 2.5% for the total capital investment and natural gas price, respectively. The impact of waste water treatment cost and electricity price on adipic acid MSP is not significant (Figure S2)

For the process of adipic acid production via 6-hydroxyhexanoic acid, the corn price showed major impact on adipic acid MSP. When the corn price is increased from $3.50 to $4.2 per bushel, the increase in adipic acid MSP of 6.6 % is observed. The adipic acid MSP is moderately sensitive to the total capital investment, natural gas price, catalyst cost, and the co-product glycolic acid price. The sensitivity estimates for the total capital investment, natural gas price, co-product glycolic acid price, and catalyst cost are 5%, 3%, 2.5%, and 2% respectively.

The wastewater treatment cost and electricity price showed no impact on the adipic acid MSP (Figure S3).

Similar to other biobased routes to adipic acid, the feedstock price causes the most variation in the MSP of adipic acid produced via 1, 6-hexanediol. When the corn price is increased to $4.2 per bushel, the adipic acid MSP increases by 8%. The total capital investment and co-product amino butyric acid price showed moderate impact on adipic acid MSP. When the total capital investment was reduced to $142 MM, a 6% decrease in adipic acid MSP is observed. Adipic acid MSP is increased by 3% when amino butyric acid price is increased from $0.80 to $0.96 per kg. Similar to other biobased routes to adipic acid, the impact of waste water treatment cost and electricity price on adipic acid MSP is not significant (Figure S4)

Conclusions

The comparison of economic analysis of four biobased adipic acid routes indicate that the purely biological route is the most promising to convert glucose into adipic acid because of high biocatalyst selectivity to adipic acid and the required number of chemical transformations are less than that of other routes to adipic acid. The results of economic analysis indicate that a biocatalyst must exhibit adipic acid titers of at least 25 g/l and volumetric productivities of greater than 1 g/l/h to achieve economic viability of adipic acid production via the purely biological route. The production of adipic acid via 1, 6-hexanediol is found to be least promising adipic acid route among analyzed biobased routes to adipic acid, which is mainly due to the low fermentation yields of 1, 6-hexanediol.

Low catalyst selectivity and pH dependence of the glucose oxidation reaction may hinder the development of an economically viable route solely through purely chemical route. The significant weaknesses of the purely chemical route to adipic acid can be overcome by deriving

6-hydroxyhexenoic acid from glucose using a biocatalyst and then oxidizing this biological intermediate to adipic acid using a metal catalyst. High biocatalyst selectivity to 6-hydroxyhexenoic acid and a high tolerance of a biocatalyst to a wide range of pH values allow us to overcoming the weakness of a purely chemical route to adipic acid. The increase in number of process steps in comparison to a purely biological route to adipic acid makes the production of adipic acid via 6-hydroxyhexanoic acid less promising as compared to the purely biological route.

We found that the TOF of metal catalysts that are used in the production of adipic acid via purely chemical route and integrated biological and chemical routes must be in the range of 0.01 s^{-1} to 1 s^{-1}. Achieving a metal catalyst life of at least 100 h is required when there is a possibility of a metal catalyst deactivation due to coking. The Catalyst yield of at least 40% theoretical is necessary to achieve economic viability for producing adipic acid via purely chemical route. Further research is required to find out the results of analysis of adipic acid production are generalizable to other purely chemical and integrated biological chemical routes to bio commodity chemicals.

The use of unpurified sugars and the co-product DDGS revenue can add economic value to the production of adipic acid using purely biological route and integrated biological and chemical routes. Thus co-locating bio commodity chemical production facilities adjacent to existing corn dry grind ethanol production plants can provide cost benefits to chemical producers. However, further research is necessary to determine adverse impacts (if any) to both corn grind ethanol and bio commodity chemical facilities from such co-location arrangements.

Acknowledgements

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CHAPTER 6

General Conclusions

New technologies for the conversion of plant-derived feedstock to biorenewable chemicals must transition through multiple stages of process development before they are implemented, commercially. Assessing the economic potential of plant-derived feedstock conversion technologies is necessary in order to select the most promising targets and to identify technology development bottlenecks that should be the focus of development effort. In addition to economic potential, environmental viability of a process should be assessed to guide development of a more sustainable chemical industry. In chapter 2 of this thesis, the feasible space, techno-economic analysis (TEA), and life cycle assessment (LCA) methods were combined to quantitatively assess the economic and environmental viability of a new biorenewable chemical production for a range of combinations of process parameters. The feasible space of a process for the production of biorenewable chemical is particularly useful when multiple sub-processes are developed in parallel. The trade-offs among the sub-processes identified by the feasible space can guide coordination of efforts among the development teams. This coordination will reduce development cost and time for the development of a new biorenewable chemical route.

The production of capric acid from glucose using a biocatalyst was used as a model system to demonstrate the assessment of a new biorenewable chemical process using the feasible space, TEA, and LCA methods. This assessment indicated that the proposed glucose-based capric acid production process likely to be economically and environmentally competitive with the conventional production process. The analysis predicts that the biocatalyst development team must achieve fermentation yields of > 0.27 g g^{-1} and product titer of > 45 g l^{-1} to meet the

performance of the conventional technology in terms of cost, energy use, and GHG emissions. Further research is required to determine the effect of uncertainty of economic parameters such as prices of glucose and natural gas on the feasible space of a biorenewable chemical.

In chapter 3, the feasible space method was used to analyze economic and environmental performance of the following bio-commodity chemical systems: 1. anaerobic production of 3-hydroxy propionic acid, 2. 1,3-propanediol, 3. succinic acid, 4. adipic acid, 5. isobutanol, and, 6. aerobic production of 1,3-propanediol. The analysis of multiple bio-commodity chemical systems indicate that the minimum selling price (MSP), energy consumption, and greenhouse gas (GHG) emissions of bio-commodity chemical systems are dependent on the yield, titer, productivity, and the type of fermentation (aerobic/anaerobic). The general contour plots of MSP, energy, and GHG that represent the effect of titer, yield, and productivity on cost, energy use, and GHG emissions of bio-commodity chemical systems were, therefore, created for aerobic and anaerobic fermentation processes. Such general contour plots can be used to determine the economic and environmental viability of early stage biocatalytic technologies.

The analysis of multiple bio-commodity chemical systems has shown that the separation and purification costs of bio-commodity chemical production are mainly dependent on the product titer. The impact of pH dependency of a fermentation process on a bio-commodity chemical MSP is negligible. The fermentation yields of at least 0.32 g/g and titers of at least 45 g/l are required to achieve a process for the production of a bio-commodity chemical that is environmentally and economically feasible. The investments for improving titer beyond 150 g/l and volumetric productivity beyond 2 g/l/h are found to result in minimal economic and environmental benefits for the production of bio-commodity chemicals using a biocatalyst. Similar to biocatalytic technologies, the analysis of multiple chemical catalytic and

thermo-chemical technologies using the feasible space method could result in general contour plots for chemical catalytic and thermo-chemical based bio-commodity chemical processes. Further research is required to find the existence of general trends in the area of bio-commodity chemical production using chemical catalytic and thermo-chemical technologies.

There are many types of risks associated with biorenewable chemical production. These risks reduce the profitability of capital investments for biorenewable chemical production and deter investments in developing and commercializing biorenewable chemical technologies. In chapter 4, it was shown that the platform concept to synthesize biorenewable chemicals can reduce market risks and increase the value of investments in biorenewable chemical production relative to single-product technologies. The economic risk analysis has shown that the number of products made and cost of switching between products influence the economic advantage of platform technologies for biorenewable chemical production. It has also been shown that platform technologies provide an opportunity to deliver multiple commodity chemicals to the market by reducing production cost of each chemical. The production of biorenewable chemicals via platform technologies reduces the risk of introducing novel and low-market volume products into the market. The technology risks of commercializing early stage platform technologies were not accounted for this work. Future work is necessary to introduce a novel method that is used to quantify technology risks.

In chapter 5, following multiple routes to adipic acid from glucose were evaluated: i) purely biological, reverse β-oxidation in *E.coli*; ii) purely chemical, oxidation of glucose via chemical catalysis yielding glucaric acid that further undergoes catalytic hydrodeoxygenation to adipic acid; and iii and iv) biological production of 6-hydroxyhexanoic acid or 1, 6-hexanediol via reverse β oxidation, which are subsequently converted chemically to adipic acid using a

metal catalyst. The results show that by-product revenue improves the economics of the purely biological and two integrated routes to adipic acid. One of the major by-products here is DDGS. Thus, incorporating purely biological and integrated bio-and chemical-catalytic technologies into existing ethanol production plants can improve the economics of biorenewable chemical production.

Compared to other routes, the purely biological route to adipic acid looks more promising since fewer chemical transformations are required to make adipic acid from glucose using a bio-catalyst. One of the disadvantages with the purely chemical catalytic approach is the low catalyst selectivity to intermediate glucaric acid. A range of by-products are formed when glucose is oxidized using the Pt/C catalyst due to low Pt/C selectivity to glucaric acid. The physical and chemical properties of these by-products are similar to that of glucaric acid, which makes separations more expensive and complicated. The problem of low selectivities can be overcome by producing adipic acid via 6-hydroxyhexanoic acid as the high biocatalyst selectivity to 6-hydroxyhexenoic acid minimizes the by-product formation. The increase in number of process steps compared to the purely biological route to adipic acid makes glucose-1, 6-hexanediol-adipic acid route less promising. The glucose-1, 6-hexanediol- adipic acid route is not economically viable as the microbial yield of 1, 6-hexanediol production is very low. Further research is necessary to deduce general rules regarding the choice of a handoff chemical in systems of coupled biological and chemical catalysts by evaluating multiple biorenewable chemical systems.

This research has shown that the production of chemicals from plant-derived feedstock can lower the GHG emissions and energy consumption relative to conventional petroleum feedstock. The other environmental benefits are also expected through the use of plant-derived

sugars, particularly in terms of water effluents and solid wastes. Further research is necessary to quantify these benefits. It is evident from this research that it is economically feasible to produce bio-commodity chemicals with a market price of greater than 1.50 ($/kg). However, volatility of chemical prices and low profit margins may hinder investments for commercializing new bio-commodity chemical technologies. Co-locating bio-commodity chemical production plants adjacent to corn grind ethanol facilities can increase profit margins by reducing the production cost. However, the negative impacts to both corn grind ethanol and bio-commodity chemical facilities from such co-location arrangements must be determined. With the current advancement in bio and chemical catalytic technologies, the production of bio specialty chemicals using these technologies is clearly an economically viable option. Targeting bio specialty chemical technologies in research and development funding may therefore accelerate the growth of a biobased economy.

This research has quantitatively shown that the production of chemicals from biobased feedstocks through coupling of biological and chemical catalysis can overcome the significant weakness of both chemical catalysis and bio-catalysis. It has also shown that production of a range of chemicals using a common technology can reduce various economic risks, which will ease access to the capital investments for the production of biorenewable chemicals. Such an increase of capital investments can help transforming chemical industry from petrochemicals to biorenewable chemicals.

APPENDIX A

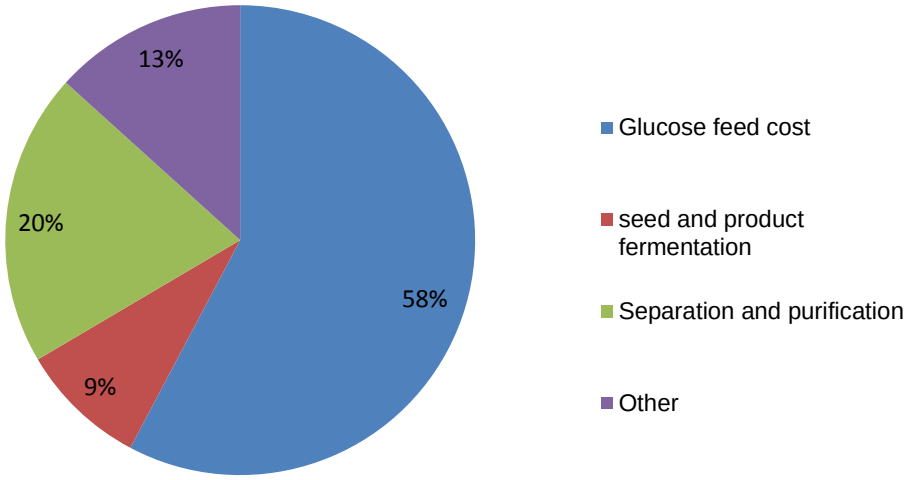

Figure A1 Major cost contributors to the MSP of capric acid that is synthesized from glucose using a biocatalyst

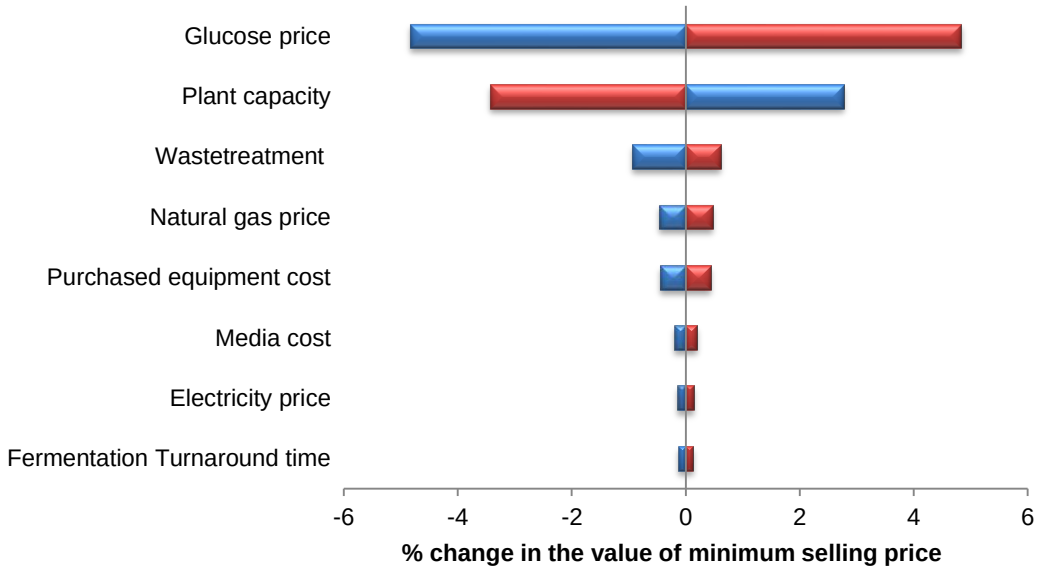

Figure A2 Sensitivity of MSP of capric acid that is synthesized from glucose using a biocatalyst to various economic variables.

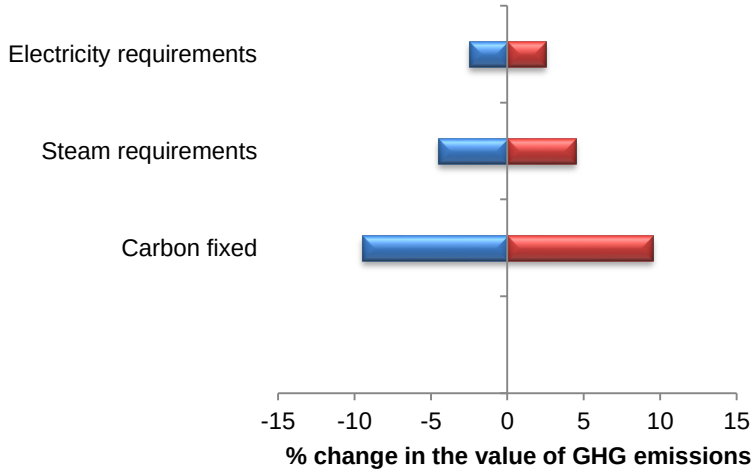

Figure A3 Sensitivity of total GHG emissions of a process for the production of capric acid from glucose for a +/- 10% change in the values of GHG emissions of steam production, electricity production, and carbon fixed as a glucose by corn plants when they are growing.

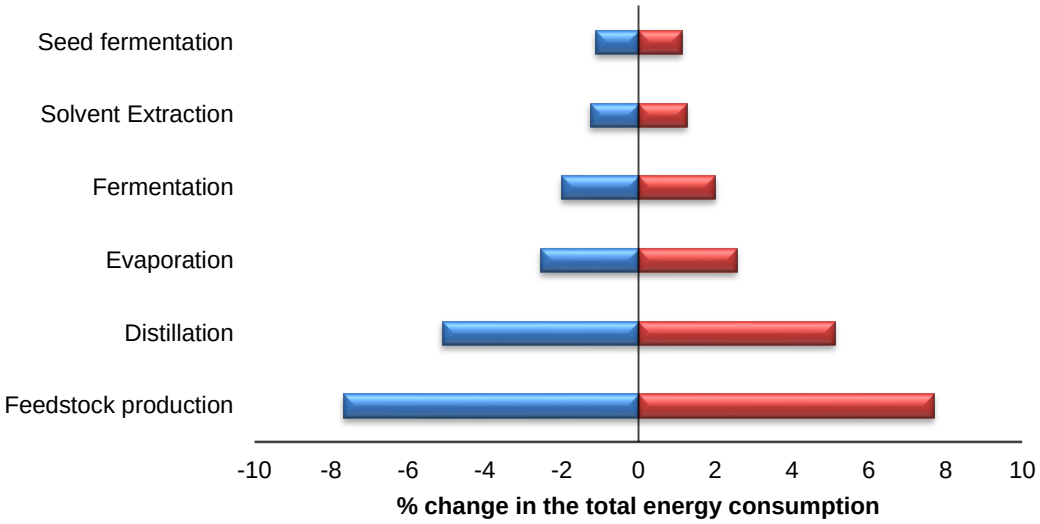

Figure A4 Sensitivity of total energy consumption of a process for the production of capric acid from glucose to energy consumption of individual unit processes

Modeling solvent extraction process

Selection of a solvent

A suitable solvent for the extraction of capric acid from the clarified fermentation broth is selected using the following solvent selection criteria. A most suitable solvent for the extraction of capric acid must have high partition coefficient, no or minimal solubility in water, high volatility relative to that capric acid, lower boiling point than water, and moderate interfacial tension [1]. We screened nearly two hundred industrial solvents and found that chloroform, hexane, heptane, benzene, 1-octanol, and 1-decanol are most suitable organic solvents for the extraction of capric acid from the clarified fermentation broth. These organic solvents are found to have similar partition coefficients. As a result, all the solvents are comparable with regard to selectivity for the capric acid and the required solvent to feed ratio. Therefore, the economic performance of the solvent extraction process greatly relies on the total energy requirement of a process, which is in turn depends on the enthalpy of vaporization of a solvent and the solubility of water in the solvent [1]. The use of chloroform and hexane as extraction agents requires lower energy for the extraction of capric acid compared to other solvents because of its low enthalpy of vaporization and low water solubility in chloroform and hexane. However, large scale capric acid extraction using chloroform as a solvent is prohibited by health and environmental risks. Therefore, we selected hexane as the most suitable solvent for the extraction of capric acid from a clarified fermentation broth.

Selection of processing equipment

The solvent extraction can be done on the industrial scale using various processing equipment. The Rotating Disc Contactor (RDC) is selected as the solvent extraction process equipment because of its high capacity and mass transfer efficiency [2].

Estimation of partition coefficient

The partition coefficient of capric acid between hexane and water is estimated by generating ternary plot for capric acid-water-hexane mixture using the Non-random two-liquid model (NRTL).

Estimation of continuous and dispersed phase velocities

1. Since the density of hexane is lower than the density of the water and capric acid feed mixture (or clarified fermentation broth), the hexane is assumed as dispersed phase and water and capric acid feed mixture is assumed as continuous phase.
2. For the solvent extraction process, there exists a tradeoff between number of stages and solvent to feed ratio. Therefore, trial and error method is used to determine the optimal solvent to feed ratio, on weight basis, for the capric acid separation. The ratio of dispersed phase volumetric rate (V_D) (m3/hr) to continuous phase volumetric rate (V_C) (m3/hr) is then calculated using the densities of continuous and dispersed phases and the optimal solvent to feed ratio.
3. For a given (V_d/V_c), the holdup of dispersed phase at flooding (h_f) is obtained from the solvent extraction handbook [2].
4. The characteristic velocity (u_o) is estimated for well-designed and commercial RDC columns using the value of dimensionless group ($u_0\mu_C\rho_C/\sigma\Delta\rho$) of 0.01 [2]. Here σ is an interfacial tension between hexane and capric acid-water phase, μ_C is the viscosity of the continuous phase and ρ_C is the density of the continuous phase, and $\Delta\rho$ is the difference between the continuous and dispersed phases.

5. The sum of continuous and dispersed phase velocities at the flooding $(U_D + U_C)_f$ is obtained for a given ratio of volumetric velocities (V_d/V_c) and characteristic velocity from the Seader et al. (2010) [1].
6. The sum of continuous and dispersed phase velocities at the 50% of flooding $(U_D + U_C)_{50\%}$, which is equal to $(U_D + U_C)_f /2$, is used for the design of RDC column [1].

Procedure for estimating geometry of a RDC column

1. The area of a RDC column is calculated from the ratio of volumetric flow rate of continuous or dispersed phase (V_D or V_C) to their respective phase velocities (U_D or U_C).
2. After finding the column diameter (D) from area, the rotor disk diameter(R), compartment height (H), and the stator opening diameter(S) of RDC column are calculated from the standard ratios given in the handbook of solvent extraction [2].
3. The slip velocity (V_s) is calculated using the Equation (A1).

$$U_{cf} = \frac{Vs \exp(-hf)}{\frac{\alpha}{hf}+1/(1-hf)} \qquad \text{(A1)}$$

Where α is the ratio of phase velocities and U_{cf} is the velocity of the continuous phase at flooding.

4. For a given slip velocity, the specific power input group(N^3R^5/HD^2) of a RDC column is obtained from slip velocity vs. specific power input group curves that are presented in the handbook of solvent extraction [2].
5. The rotor speed (N) is then calculated using the values of specific power input group, rotor disk diameter, column diameter, and the compartment height.

6. Normally, disperser hole diameter (D_h) ranges between 1.3 mm to 6.4 mm [3]. Small hole diameters are avoided in the treatment of fermentation broth applications where the potential for plugging is a concern. Therefore, the disperser hole diameter of 6.4 mm is assumed for the RDC column design.

Procedure for estimating drop size (d_{32}) in a RDC column

1. The drop size of a dispersed phase in a RDC column is predicted using the Equation (A2) [4].

$$d_{32} = 0.705\left(\frac{\sigma}{g\Delta\rho}\right)\frac{D_h^{0.8}}{N^{0.185}}\frac{\left({}^{V_c}/_{V_d}\right)^{0.15}}{(V_c+V_d)^{0.1}} \quad \text{(A2)}$$

Where g is the acceleration due to gravity.

Procedure for estimating mass transfer coefficients in a RDC column

1. The interfacial surface area per unit volume of a two-phase mixture (a) is calculated using Equation (A3) [1].

$$a = \frac{6h_f}{d_{32}} \quad \text{(A3)}$$

2. The overall mass transfer coefficient (K_{OD}) based on the dispersed phase is estimated using Equation (A4) [1]. The dispersed and continuous phase mass transfer coefficients (k_D and k_C) are determined using empirical equations presented in the Seader et al. (2010) [1].

$$\frac{1}{K_{OD}} = \frac{1}{k_D} + \frac{1}{mk_c} \quad \text{(A4)}$$

Where m is equal to the partition coefficient

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APPENDIX B

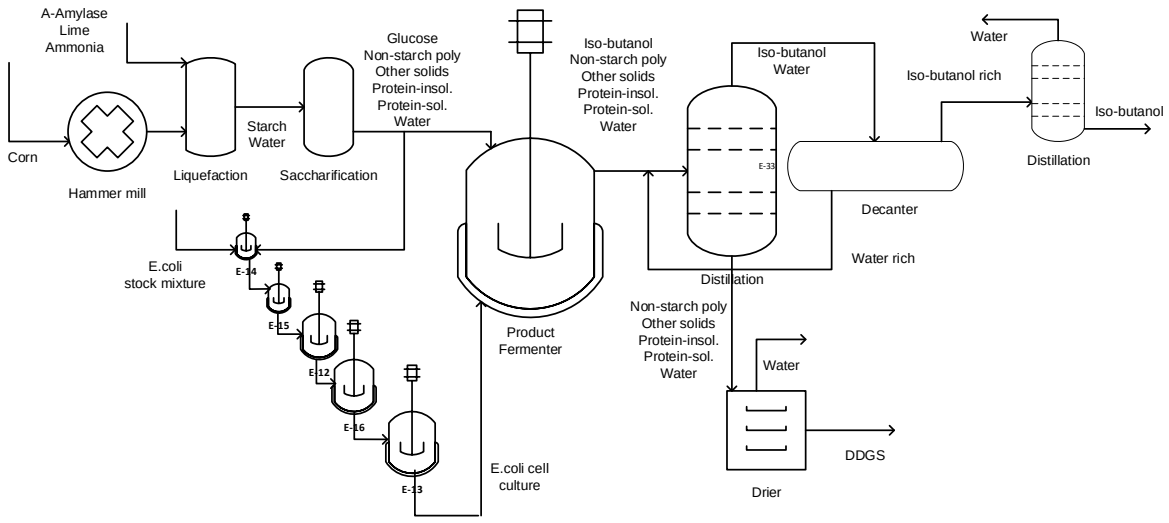

Figure B1 Process flow diagram for the production of Isobutanol

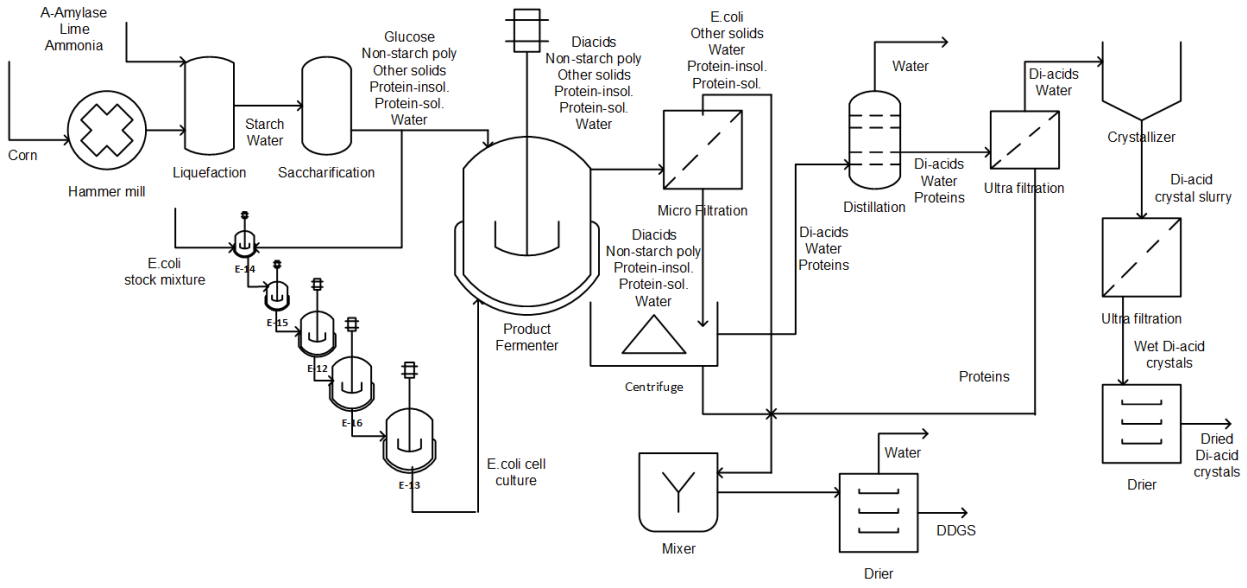

Figure B2 Simplified process flow diagram for the production of Diacids

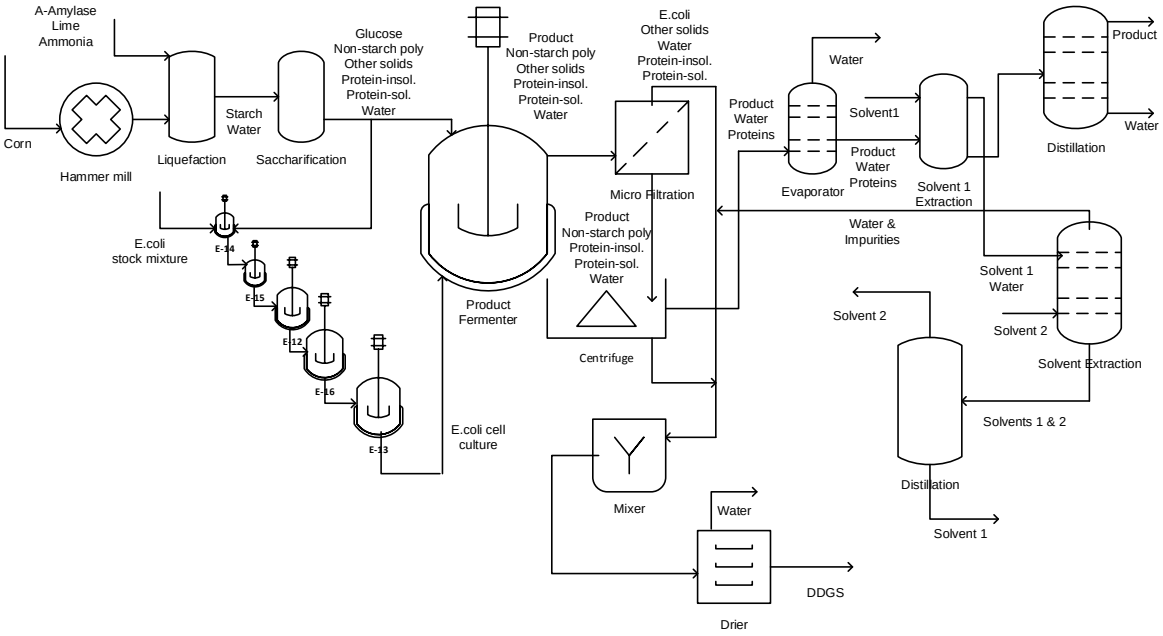

Figure B3 Simplified process flow diagram for the production of 3-Hydroxy propionic acid and 1,3- Propanediol

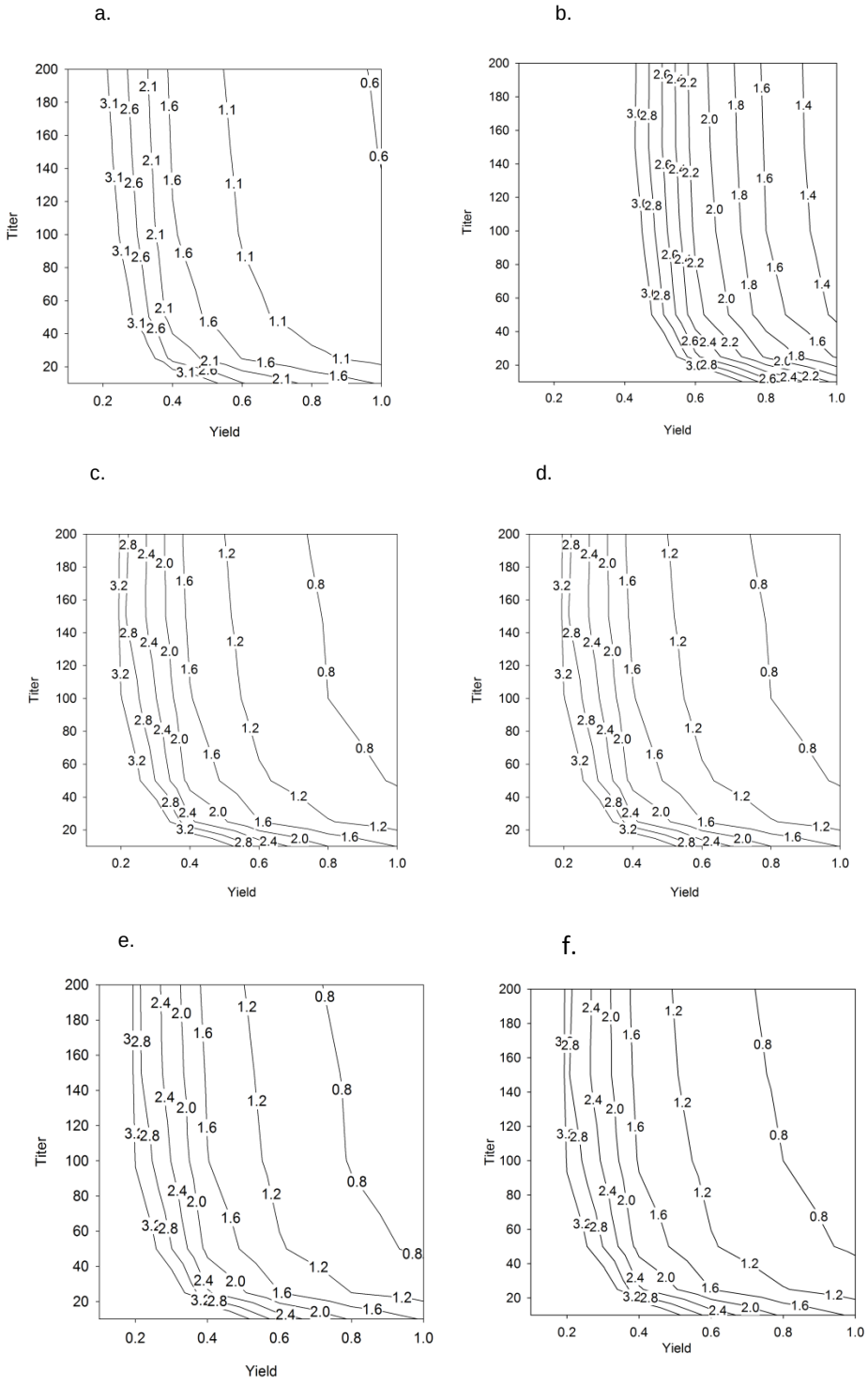

Figure B4 Cost contour plots in terms of titer, yield, and productivity of 1 g/l/h for the production of a) 3-HPA b) 1,3-propanediol (aerobic cultivation) c) adipic acid d) succinic acid e) 1,3- propanediol (an aerobic fermentation) f) Isobutanol

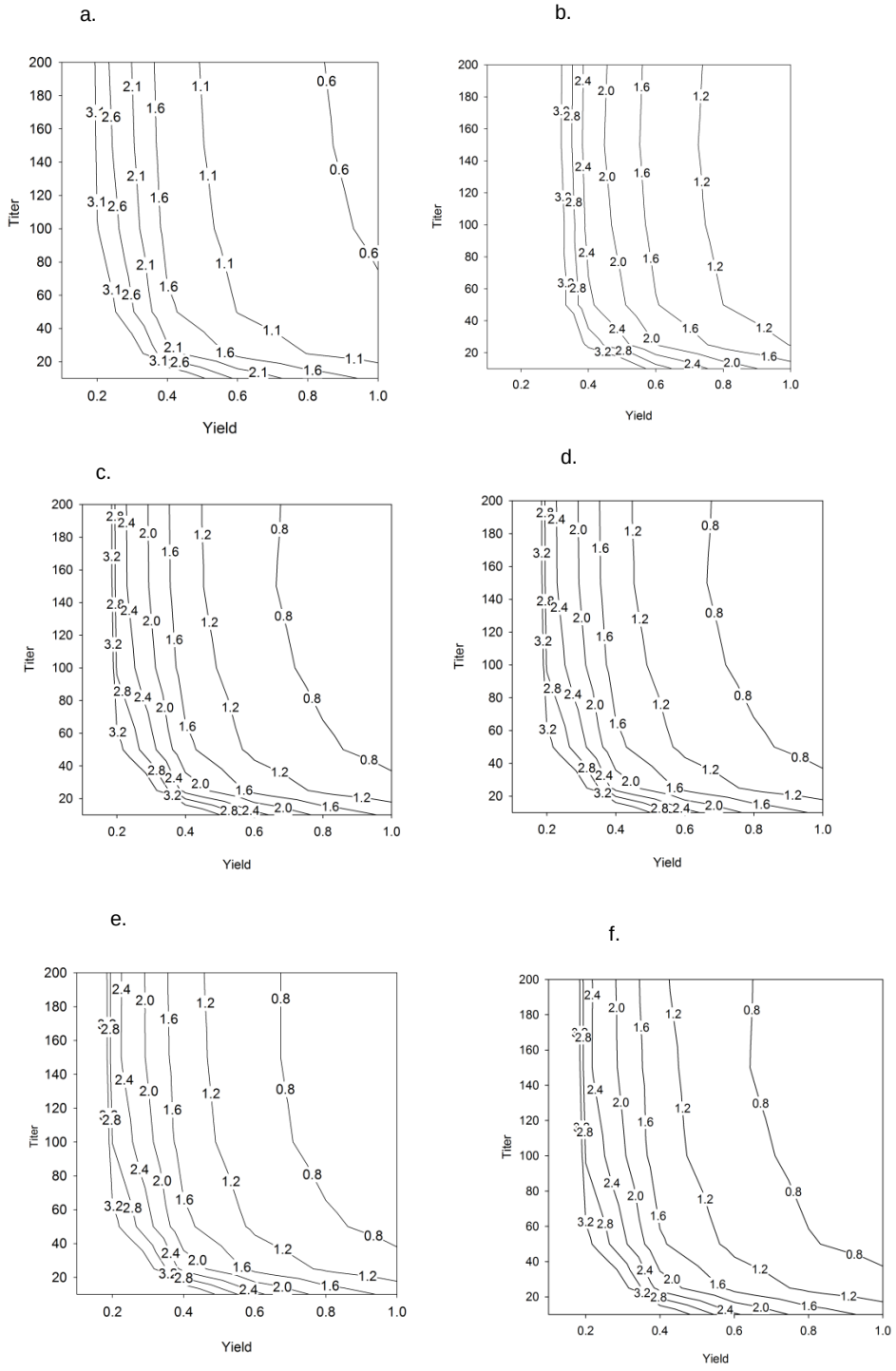

Figure B5 Cost contour plots in terms of titer, yield, and productivity of 2 g/l/h for the production of a) 3-HPA b) 1,3-propanediol (aerobic cultivation) c) adipic acid d) succinic acid e) 1,3-propanediol (anaerobic fermentation) f) Isobutanol

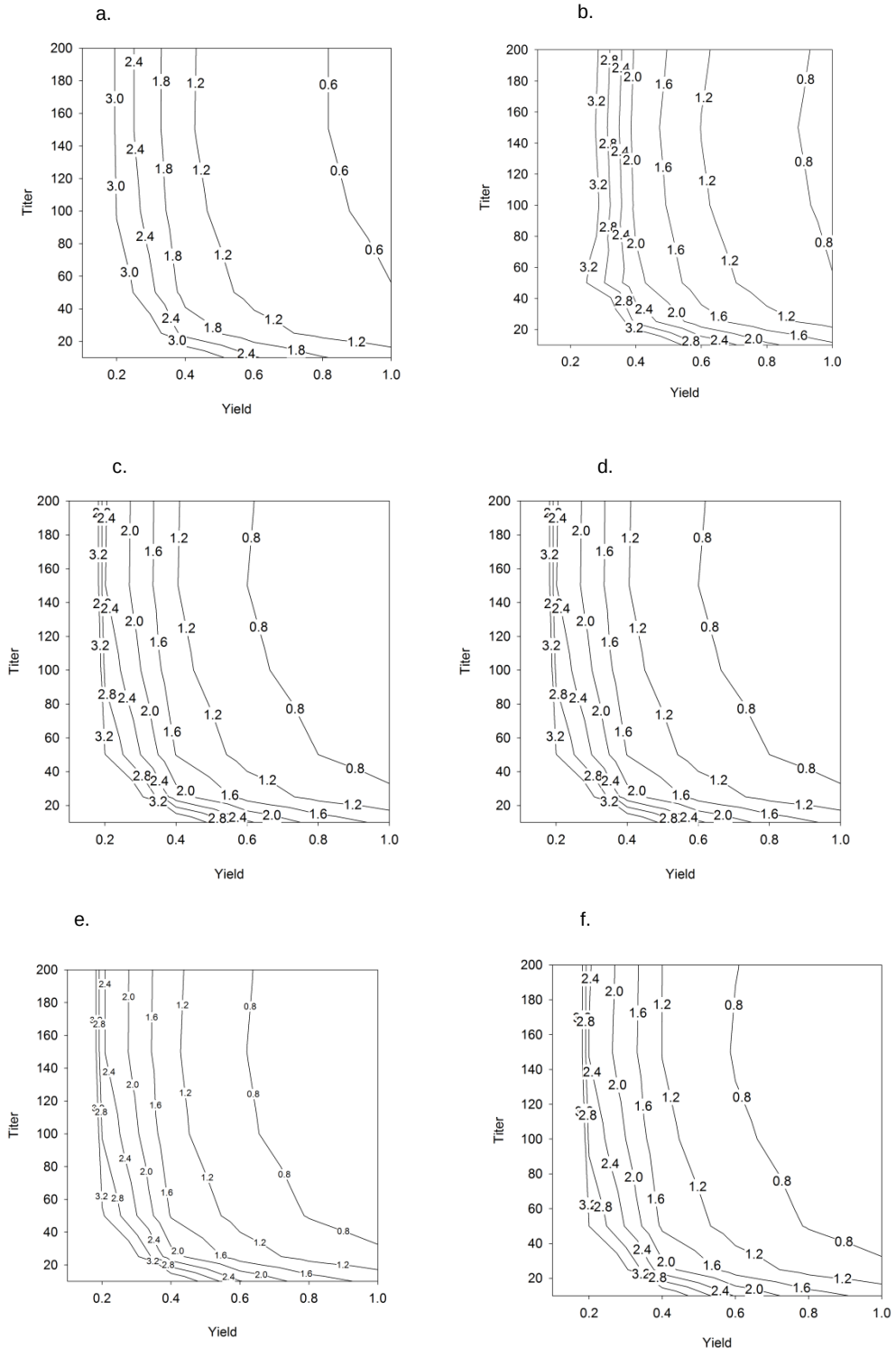

Figure B6 Cost contour plots in terms of titer, yield, and productivity of 3 g/l/h for the production of a) 3-HPA b) 1,3-propanediol (aerobic cultivation) c) adipic acid d) succinic acid e) 1,3-propanediol (an aerobic fermentation) f) Isobutanol

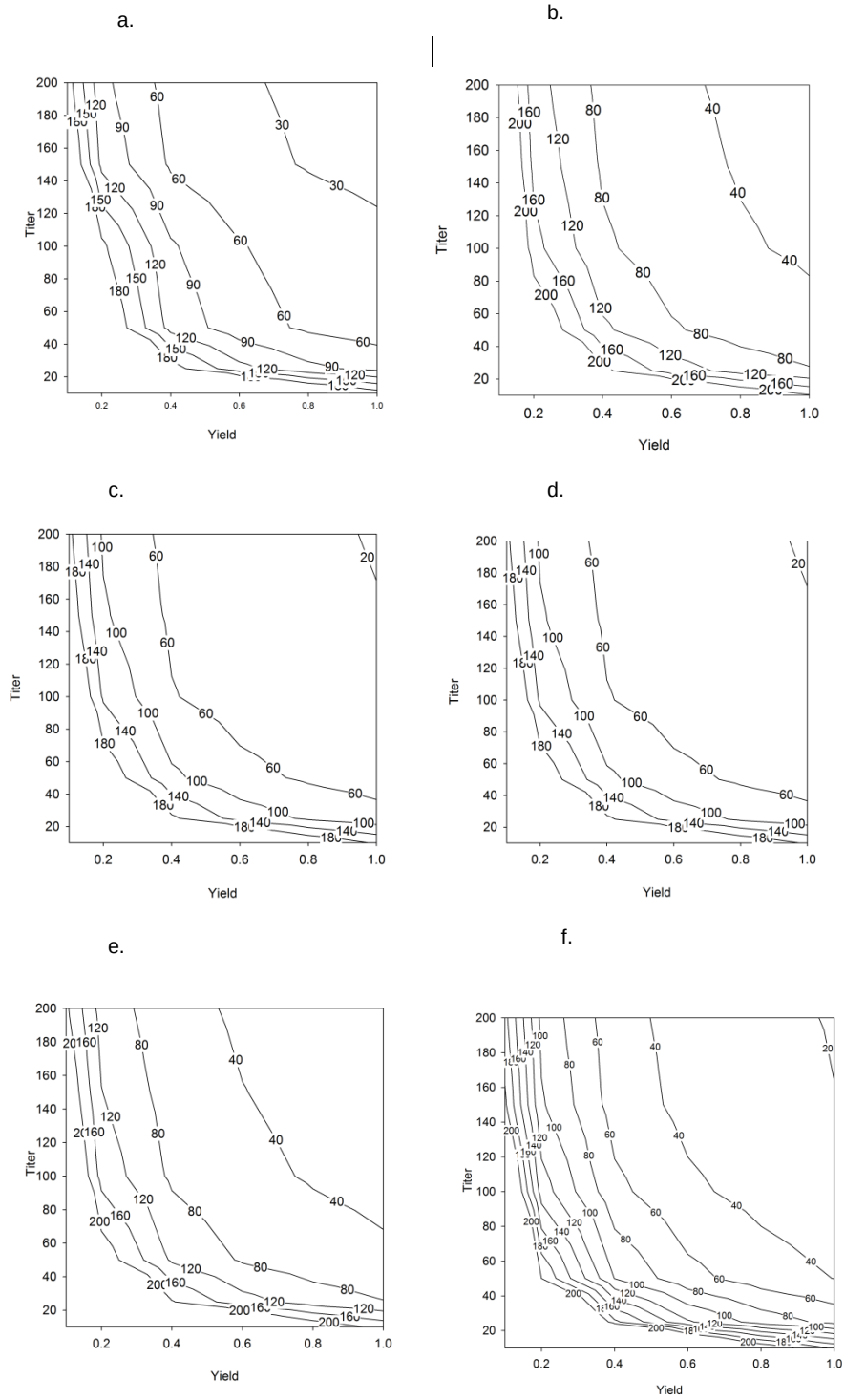

Figure B7 Energy contour plots in terms of titer, yield, and productivity for the production of a) 3-HPA b) 1,3-propanediol (aerobic cultivation) c) adipic acid d) succinic acid e) 1,3- propanediol (an aerobic fermentation) f) Isobutanol

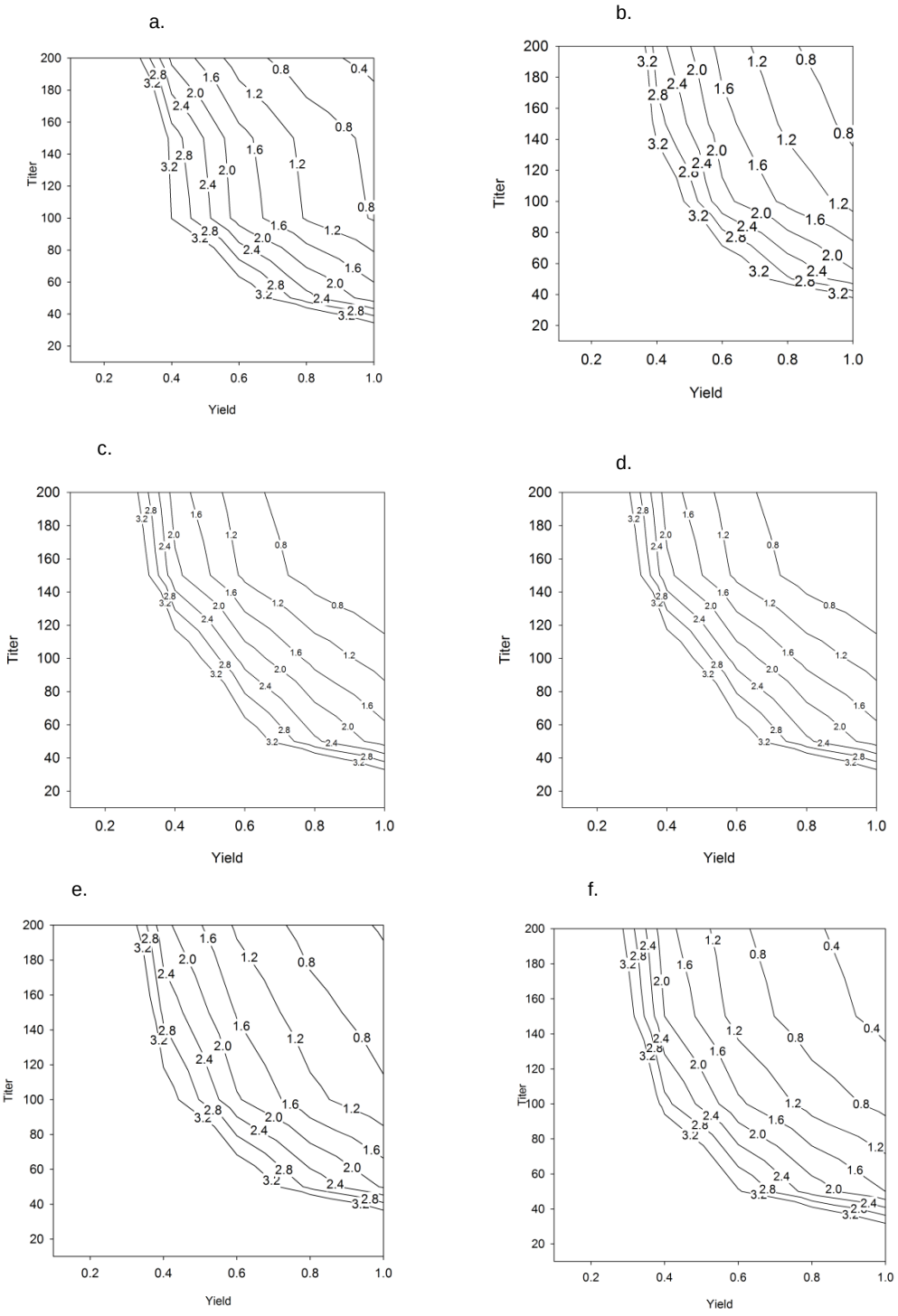

Figure B8 GHG contour plots in terms of titer, yield, and productivity for the production of a) 3-HPA b) 1,3- propanediol (aerobic cultivation) c) adipic acid d) succinic acid e) 1,3- propanediol (anaerobic fermentation) f) Isobutanol

APPENDIX C

Table C1

Yield and kinetic parameters for fatty acid production

Parameter	Seed fermentor	Product fermentor
E.coli yield (dcw g/g glucose)	0.4	0
Max specific growth rate (hr^{-1})	0.4	0
Product yield (g FA/g glucose)	0	0.32
Titer (g FA/l)	0	75
Productivity (g FA/l/hr)	0	2
Media	Defined	M9
Temperature (^oC)	37	37

Table C2

Estimated design parameters for solvent extraction process using rotating disc contactor column

Parameter	Value
Solvent to feed ratio	1.4
Holdup at flooding	0.38
Characteristic velocity (m/sec)	0.15
Slip velocity (m/sec)	0.14
Rotor disc diameter (m)	1.39
Stator diameter (m)	1.62
Impeller rotation speed (rpm)	30.0
Distributor hole diameter (mm)	6.40
Diameter of a bubble (mm)	0.41
Interfacial surface area per unit volume (m^2/m^3)	1738
Dispersion phase mass transfer coefficient (m/sec)	$8.6x10^{-3}$
Continuous phase mass transfer coefficient (m/sec)	$1.4x10^{-4}$
Overall mass transfer coefficient (K_{OD}) (m/sec)	$6.12x10^{-5}$

Switching rule

A chemical company can produce two chemicals, product A and product B, using a platform technology is expected to last for 20 years. Let's assume that the company is currently producing product A, and it can switch to product B at any time t, where $0 \leq t \leq T$; T denotes plant life, and is taken to be 240 months in this example case. We proposed the switching rule as follows: when the net profit from product B production is greater than that of product A production at time t, company can switch to product B if the expected pay off, that is, the present

value of the difference in expected net profit between product B and product A from t to t+h (where h = 0, 3, 6,…, 240-t months) is greater than the switching cost. Here, we assume chemical firms sign quarterly contracts for their production, thus, the decision whether to switch production from one product to another will take place every three months.

The company will switch to product B, from product A, at time t when:

$$(Net\ profit\ of\ product\ B\ production)_t > (Net\ profit\ of\ product\ A\ production)_t \quad \text{(C1)}$$

And

$$X_{sw} > \sum_t^{t+h} \left(\frac{[\mathrm{E}_{Net\ profit,B}]_{t+h}}{(1+r)^{t+h}} - \frac{[\mathrm{E}_{Net\ profit,A}]_{t+h}}{(1+r)^{t+h}} \right) \quad \text{(C2)}$$

$$E\ [Net\ profit\ of\ B\ ]_{t+h} = E\ [sales\ from\ B]_{t+h} - E\ [operating\ expenses\ of\ B]_{t+h} \quad \text{(C3)}$$

$$E\ [Net\ profit\ of\ A\ ]_{t+h} = E\ [sales\ from\ A]_{t+h} - E\ [operating\ expenses\ of\ A]_{t+h} \quad \text{(C4)}$$

Here, we assume that the price of a product follows mean reverting process. If the price of a product at time t is x_0 and long-run marginal price of a product is $\bar{x}$ then its expected that the price at a future time t+h is given by Dixit and Pindyck, 1994

$$E(x_{t+h}) = (\bar{x} + (x_0 - \bar{x})exp^{-\eta t+h}) \quad \text{(C5)}$$

$E\ [sales]_{t+h}$ = ($\bar{x} + (x_0 - \bar{x})exp^{-\eta t+h}$) x three-month production of a chemical (kg) (C6)

Similar to product price, the prices of glucose, natural gas, electricity, hydrogen, and the catalyst are modeled using mean reversion process, which are used in estimating expected value of operating expenses.

$E\ [operating\ expenses\ ]_{t+h}$ = Three-month production of a chemical (kg) x [(fixed operating costs per kg of product) + $(E\ (G_{t+h}) \times Y_{B/G})$ +$(\ E\ (N_{t+h}) \times Y_{\frac{B}{N}})$ + $(E\ (E_{t+h}) \times Y_{\frac{B}{E}})$ + $(\ E\ (H_{t+h})e^{-\eta t} \times Y_{\frac{B}{H}})$ + $(\ E\ (C_{t+h})e^{-\eta t} \times Y_{\frac{B}{C}})$] (C7)

Where $Y_{B/G}$ is product yield (kg product/kg glucose); $Y_{B/N}$ is natural gas requirement (MMBtu/kg product); $Y_{B/E}$ is electricity requirement (kWh/ kg product); $Y_{B/H}$ is hydrogen requirement (kg/kg product); and $Y_{B/C}$ is catalyst requirement (kg/kg product)

Expected values at any future time for glucose $E(G_{t+h})$, natural gas $E(N_{t+h})$, electricity $E(E_t + h)$, hydrogen $E(H_{t+h})$, and catalyst prices $E(C_{t+h})$ are modelled as below provided they follow mean reverting process:

$$E\ (G_{t+h}) = \bar{G} + (G_0 - \bar{G})exp^{-\eta t+h} \quad \text{(C8)}$$

$$E\ (N_{t+h}) = \bar{N} + (N_0 - \bar{N})exp^{-\eta t+h} \quad \text{(C9)}$$

$$E\ (E_{t+h}) = \bar{E} + (E_0 - \bar{E})exp^{-\eta t+h} \quad \text{(C10)}$$

$$E\ (H_{t+h}) = \bar{H} + (H_0 - \bar{H})exp^{-\eta t+h} \quad \text{(C11)}$$

$$E\ (C_{t+h}) = \bar{C} + (C_0 - \bar{C})exp^{-\eta t+h} \quad \text{(C12)}$$

Where $\bar{G}$,$\bar{N}$, $\bar{E}$, $\bar{H}$, $\bar{C}$ are the long-run marginal prices of the glucose, natural gas, electricity, hydrogen, and catalyst price, respectively, and G_0, N_0, E_0, H_0, C_0 are the prices of the glucose, natural gas, electricity, hydrogen, and catalyst price, respectively at time t.

APPENDIX D

Table D1. Fermentation Reactions

Reaction [a,b]	**Product**
2 ADP + 2 Pi + 3/2 $C_6H_{12}O_6 \rightarrow$ 2 H_2 + $C_6H_{10}O_4$ + $C_2H_4O_3$ + CO_2 + 2ATP	Adipic acid
8/3 ADP + 8/3 Pi + 3/2 $C_6H_{12}O_6 \rightarrow$ 2 H_2 + 1/3 H_2O + $C_6H_{12}O_3$ + 1/3 $C_2H_4O_3$ + 7/3 CO_2 + 8/3 ATP	6-hydroxyhexanoic acid
1/2 NH_3 + 4 ADP + 2 Pi + 2 $C_6H_{12}O_6 \rightarrow$ 5/2 H_2 + $C_6H_{14}O_2$ + 1/2 $C_4H_9NO_2$ + 4 CO_2 + 3ATP + H_2O + AMP	1,6-hexanediol

[a] For convenience, formate is assumed to be all converted to CO_2 and H_2

[b] The stoichiometry is calculated based on the *in silico* assessment results by Cintolesi *et al*[1]

Table D2. The operating conditions and modeling parameter values of seed fermentation

Inoculum level in the final seed fermentor	10 vol % of production vessel size
Batch time	24 h
Fermentor turnaround time	12 h
Number of trains	2
Number of fermentor stages	5
Corn steep liquor (CSL) loading	0.50 wt %
Diammonium phosphate (DAP) loading	0.67 g/L
E. coli yield (dcw g/g glucose)	0.5
Max specific Growth rate (hr^{-1})	0.4

Table D3. The operating conditions and modeling parameter values of product fermentation

Temperature	37°C
Specific productivity	1.41[a] (g adipic acid/g CDW/hr)
	1.22[a] (g 6-hydroxyhexanoic acid/g CDW/hr)
	0.79[a] (g 1,6- hexanediol/ g CDW/hr)
Product yield	0.52[a] (g adipic acid/g glucose)
	0.45[a] (g 6-hydroxyhexanoic acid/ g glucose)
	0.30[a] (g 1,6- hexanediol/ g glucose)
E. coli yield (dcw g/g glucose)	0.04[a] (purely biological route to adipic acid)
	0.077[a] (6-hydroxyhexanoic acid route)
	0.070[a] (1,6-hexanediol route)
Max specific Growth rate (hr^{-1})	0.10[a] (purely biological route to adipic acid)
	0.22[a] (g 6-hydroxyhexanoic acid/ g glucose)
	0.19 [a] (g 1,6- hexanediol/ g glucose)
Inoculum level	10 vol %
Corn steep liquor (CSL) level	0.25[b] wt %
Diammonium phosphate (DAP) level	0.33[b] g/L

[a] The values are obtained from the Cintolesi *et al.*

[b] The values are obtained from the Tao *et al.*

Table D4

Economic assumptions

Corn cost ($/bushel)	3.50
Electricity price ($/kWh)	0.07
Natural gas price ($/MMBtu)	3.35
Internal rate of return	10.0%
Equity percent of total investment	100.0%
Number of working days	350

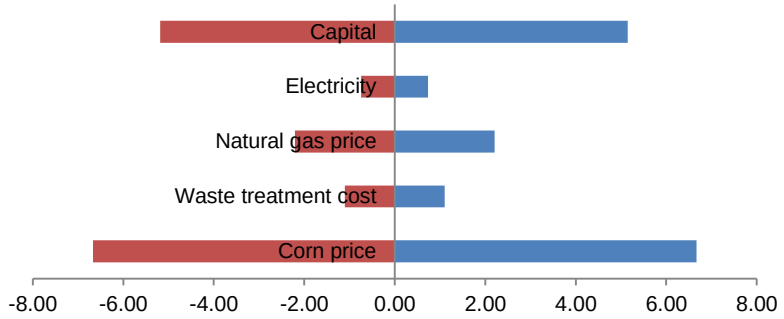

Figure D1 Sensitivity of minimum selling price of adipic acid synthesized via purely biological route to various economic variables.

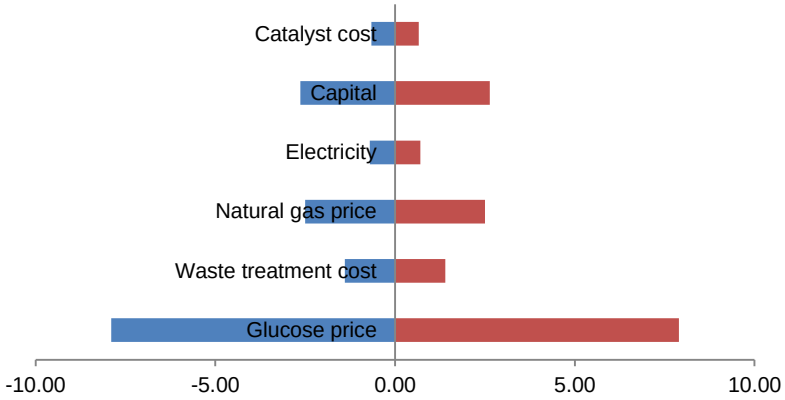

Figure D2 Sensitivity of minimum selling price of adipic acid synthesized via purely chemical route to various economic variables.

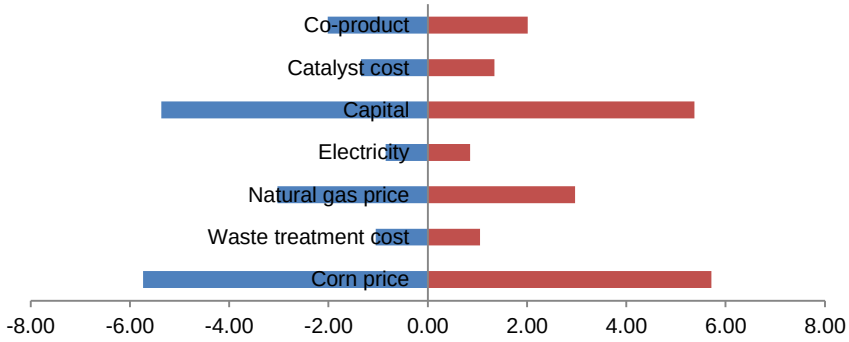

Figure D3 Sensitivity of minimum selling price of adipic acid synthesized via hydroxy acid route to various economic variables.

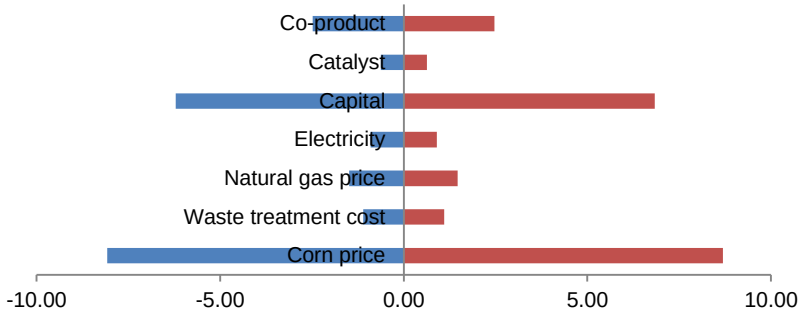

Figure D4 Sensitivity of minimum selling price of adipic acid synthesized via diol route to various economic variables.