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Technoeconomic analysis of fermentative-catalytic biorefineries: model improvement and rules of thumb

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Technoeconomic analysis of fermentative-catalytic biorefineries: Model improvement and rules of thumb

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ABSTRACT

The NSF Engineering Research Center for Biorenewable Chemicals (CBiRC) has as its primary mission the transformation of the US chemical industry from one that relies primarily on fossil carbon (i.e., petroleum derivatives) to one that uses biorenewable carbon (i.e., photosynthetically derived carbon – typically sugar) as a primary feedstock. The work reported in this thesis, at its core, aimed to provide CBiRC with better tools to predict the costs and lifecycle impacts of proposed pathways to new biorenewable chemicals. The CBiRC LCA team[1] has developed and/or used multiple tools to assess the economic viability – or more specifically, the estimated minimum selling price (e.g., cost of production) – for several biorenewable chemicals. The CBiRC LCA team[2] has developed and/or used multiple tools to assess the economic viability – or more specifically, the estimated minimum selling price (e.g., cost of production) – for several biorenewable chemicals. Specifically, they have developed proof-of-concept technoeconomic analyses (TEAs) based on approximately six key parameter estimates. They have also conducted detailed TEAs on later-stage processes using commercially available software such as Aspen™ and SuperPro®. The Raman group also developed a model that is more complex than the proof-of-concept TEA, but simpler than SuperPro-based models, initially referred to as BioPET (Biorenewables Process Evaluation Tool).

[1] The CBiRC LCA team is led by Robert P. Anex, Professor at University of Wisconsin. Professor D. Raj Raman is the other faculty member of the LCA team, and is also advisor to the author of this thesis.
[2] The CBiRC LCA team is led by Robert P. Anex, Professor at University of Wisconsin. Professor D. Raj Raman is the other faculty member of the LCA team, and is also the graduate advisor to the author of this thesis.

This thesis begins in chapter 2 with a reorganizing and expansion of BioPET. The improved and expanded version was given the new moniker of ESTEA (Early Stage Techno**e**conomic Analysis). Specific improvements made in the transition of BioPET to ESTEA included the following: (1) clarifying data flow and overall spreadsheet organization, (2) revising labor costs (3) accounting for solvent costs (4) accounting for consumption of organic material (5) adding additional hydrolysis unit operations (6) adding a greenhouse gas emission estimation block and (7) providing new macro-based graphs and analyses. The latter part of chapter 2 describes validation activities related to ESTEA. ESTEA was run with process parameters appropriate to the production of Ethanol, Succinic Acid and Adipic Acid. The resulting MESP values were compared with estimates from more detailed process models in SuperPro (Intelligen Inc., Scotch Plains, NJ), BioPET using results from a previous Masters student in the Raman group, Joshua T. Claypool (Claypool and Raman, 2013), and literature values.

In chapter 3, we use ESTEA as a framework for examining the impact of key process parameters on estimated unit cost of product. Specifically, computer code was written to allow exploration of a large parameter-cost-space, and the results were analyzed to develop simple generalizations, or "rules-of-thumb" regarding the relationship between key process parameters and MESP. Computer code (written in Microsoft VBA within Excel) enabled the systematic manipulation of key inputs while recording the impact on the minimum estimate selling process (MESP) predicted by ESTEA. This provided insight into the influence of process parameters on overall cost. Finally, CHAPTER 4 summarizes the key findings from this work.

CHAPTER 1. GENERAL INTRODUCTION

Thesis organization

This thesis contains a general introduction (chapter 1), two research articles (chapters 2 and 3), and general conclusions (chapter 4). The general introduction includes objective of this thesis, a description of the thesis organization, and details of the author's role in every chapter.

The thesis has its papers written as per the ASABE style guide for technical publications. The work was initially divided into three papers, and draft versions of these papers are available as meeting papers from ASABE International Meeting, 2014 (Viswanathan et al., 2014a; Viswanathan et al., 2014b, Viswanathan and Raman, 2014). However, major revisions were made to all of these meeting papers in the production of this thesis, and the work has been restructured into two papers, which will be submitted for publication to Chemical Engineering Research and Design (chapter 2) and Journal of Cleaner Production (chapter 3).

The primary author, with support and assistance of co-authors, conducted the research and composed the articles presented in this thesis. The major professor provided detailed editing of each of the manuscripts. Additional details regarding the primary author's role in each of the three papers is provided below, immediately after the detailed description of each chapter.

The first paper (chapter 2) describes a major reorganization and enhancement of an existing spreadsheet-based cost-analysis tool for industrial chemical production processes using biorenewable carbon. The existing model was entitled BioPET (Biorenewables

Process Evaluation Tool), and was developed by a previous Masters student in the Raman group, Joshua T. Claypool (Claypool and Raman, 2013). In this thesis, we have named the modified and improved model "ESTEA", which stands for Early Stage Technoeconomic Analysis. To create ESTEA, we modified the overall data flow and spreadsheet organization to make them easier for users to understand. We replaced existing primitive mass balance calculations by a full-fledged component balance, which explain flow of major components including product, water, solvents, and wastes through the process model. We enhanced ESTEA by allowing up to two hydrolysis process steps with acid/base addition based on ratio of aqueous flow. Labor cost calculations were revised, with operating labor cost calculations modified to provide labor cost for every unit process, and non-operating labor included as a percent of operating labor, based on literature. In addition, ESTEA users can add solvents (three options) to any unit operation of downstream processing, and can select the solvent recovery fraction, which is critical to accurate costing. We added a greenhouse gas block to allow users to estimate the emissions associated with the production of the chemical in question. This block included an accounting for the greenhouse gas associated with feedstock production, based on published values of GHG emissions from four different potential feedstocks. Additionally, we wrote VBA code to automate several common analyses, and to produce automatically several graphs of interest, such as a radar plot showing how fermentation costs vary with three key parameters. We added the capability to include secondary and tertiary separation unit operations as well as hydrolysis unit process, to facilitate more complex separation techniques. We also permitted users to specify multiple secondary feedstocks (such as solvents) which are then included in the overall cost calculations. Chapter 2 describes these

changes in detail. The primary author revised the model and wrote the first draft of this chapter. The spreadsheet and macros were developed by the primary author with the guidance of the major professor. As mentioned previously, Joshua T. Claypool developed BioPET, which became the base model for developing ESTEA. Malcolm Squire (at the time, an undergraduate at the University of Minnesota participating in another NSF-sponsored REU program co-directed by Dr. Raman, and jointly mentored by Joshua Claypool and the primary author) also contributed to development of ESTEA. Squire created a life cycle inventory focused on greenhouse emission values for different feedstocks, and developed a preliminary model of overall greenhouse gas emissions that implemented in BioPET and subsequently improved upon and included in ESTEA. Then second part of chapter 2 includes validation ESTEA by modelling ethanol, succinic acid and adipic acid process in ESTEA. To validate the ESTEA results, we reworked the existing process models in BioPET and in SuperPro to its closest approximation. We show that the cost estimations from ESTEA were similar to those from literature, and they require far fewer inputs to achieve. The greatest deviation by line item are in the areas of feedstock and downstream processing, and we explain the reasons for these deviations. The primary author conducted all of the modelling, and wrote the first draft of this chapter.

The second paper (chapter 3 seeks to make simple generalizations regarding relationships between key process parameters and cost of the product. We modeled a process for producing a hypothetical chemical from sugars (feedstock) based on fermentation followed by separation, catalytic conversion in the presence of a solvent to a desired product and finally purifying it. We examined the cost over a wide range of possible process parameters. Unsurprisingly, certain combinations of key parameters – e.g., process

yields, solvent recovery – are interrelated. We discuss these interrelationships to provide insight into the generalized cost structures of biorenewable chemicals. We also looked at seven separate "base case" scenarios – ranging from an extremely low-cost one-step-process based compound, to a high-cost multi-step compound, and for each case conducted a comprehensive sensitivity analysis. This effort is then translated into a series of key "rules of thumb" for biorenewable chemical production, illustrating ranges of key parameters needed to achieve certain cost goals. The primary author conducted all of the modelling, and wrote the first draft of this chapter.

Chapter 4 is a comprehensive summary of this work including general and specific discussion in previous chapters.

Literature review

Factors favoring bio-based chemicals

In the early 21st century, interest in bio-based chemicals grew out of increased concern regarding depleting crude oil resources, the attendant increases in oil prices, increasing concern regarding the environmental impacts of oil exploration and extraction, and interest in finding markets for surpluses of plant-based carbon (e.g., maize grain). Increased domestic oil production coupled with expanding bio-based fuels decreased US crude oil imports from 60% to 40% of consumption from 2005 to 2012. Reports from the US DOE indicate that more than 30% of US petroleum consumption can be supplied by bio-based resources (Bioenergy Technologies Office, 2013). Similarly, fossil-derived chemicals (including plastics) can potentially be replaced as bio-based chemicals (Philip, 2014) – in

fact, bio-based chemicals are a much easier target from a carbon-mass standpoint (Nikolau et al. 2008). Bio-based products are expected to account for nearly USD 500 billion per year by 2025, and globally, the chemical industry is expected to grow at 2 trillion USD per year (USDA, 2008). Examples of anticipated growth in the biobased sector include BASF's 1,3 Propanediol plant in Loudon Tennessee, BioAmber's bio-succinic acid plant in Ontario, Canada (Philip, 2014) and Succinity GmbH's (BASF and Corbion Purac joint venture) bio-succinic acid plant in Montmelo, Spain. Bio-based resource are generally regarded as being more sustainable (Hatti-Kaul et al. 2007), and can contribute to domestic job growth – an estimated 20,000 new jobs could result by 2025 due to this industry, thus helping stem the loss of chemical industry jobs that the US saw through the latter half of the 20th century (Erickson, 2014). In the shorter term, the USDA estimates that the number of jobs associated with the production, supply chain, support and maintenance, and logistics of bio-based chemicals amounts to ~3500 by 2017. USDA also believes that a dramatic increase in production of C_2 chemicals, followed by C_3, C_4 and specialty oils could drive short-term job growth to 19,400 (USDA, 2014). Nexant, while serving as a consultant to the USDA, shows bio-based chemicals as market competitive with petro based products (USDA, 2014) (Bioenergy Technologies Office, 2013).

Commercializing a bio-based chemical is influenced by factors such as cost and availability of feedstock, capital investments, the overall process efficiency as reflected in process parameters such as reaction rates, separation efficiencies, heat requirements, and similar (USDA 2014) (United States International Trade Commission, 2011). These parameter values associated with each of the factors are crucial in determining the overall financial viability of the full-scale plant, but at early stages of process development, limited

knowledge of detailed process parameters make it extremely challenging to develop process models using advanced and complex software. . In such status quo, a simpler model that need only a few process parameters can predict the progress of process certainly, though their results are not as accurate as full-fledged software models, they can provide an insight of process development at their primitive years. (Bunger, 2012).

Scaling up and government support

Here at the beginning of the 21st century, bio-based processes are still in the developmental stage; to scale up, they require essential financial support in the form of investments, feedstock supply and downstream processing (Biotechnology Industry Organization, 2012). Industry leaders believe that because of the large feedstock requirement, new technologies will be market competitive only if feedstock is priced at 25-30 cents per kg (Biotechnology Industry Organization). The growth and development of bio-based industries benefit from government supports through grants, loans, tax incentives and programs such as procurement policies, small scale industry investment programs and research funding (Biobased Chemicals and Products, 2000). To this end, multiple governmental programs exist in the US, such as Farm Security and Rural Investment Act, and the U.S. Farm Bills which provide loans and funds for development of biomass research (Golden and Handfield, 2014). To have a sustained impact, bio-based chemicals must ultimately be competitive with petro-based products. Regulatory action by the US government can encourage this sector (Philip et al., 2013). For example, the April 2012 National Economy Blueprint, aimed to “lay out strategic objectives that will help

realize the full potential of the U.S. bioeconomy and to highlight early achievements toward those objectives" (National Bioeconomy Blueprint, 2012). The Federal Bioeconomy strategic objectives were to intensify and extend research and development, thrust lab to market transformation by reducing barriers, develop bioeconomy workforce and cultivate partnerships between organizations (Obama, 2009).

Technoeconomic analysis at CBiRC

Real-world process development involves years of work during which the process is painstakingly evolved from lab bench scale to full scale, sometimes characterized by the technology readiness level (TRL) metric developed by NASA (Mankins, 1995). Refining ideas proposed by the Michigan Biotechnology Institute (MBI), Peter Keeling modified the TRL formalism to make it specific to the biorenewable chemical industry, as shown in Figure 1. Based on his experience and on conversations with member companies of CBiRC, Keeling included estimates of the cost of advancing between TRLs, which are also included in Figure 1.

To perform a technoeconomic analyses using software such as SuperPro Designer or Aspen Economic Analyzer, large amounts of technical information related to the process are required. At early stages of process development, many of these required process parameters are unknown. Hence, to perform technoeconomic analyses at this early stage of process developments, the CBiRC LCA team developed a simple 'Proof of Concept TEA' (TRL 3) (Figure 1 and Figure 2), while Claypool and Raman developed a more sophisticated (but still simple compared to full process models) Microsoft excel-based tool, BioPET (TRL

4). As the technology is scaled up in CBiRC, the technoeconomic analyses transitions to higher and more complex models and simulations such as SuperPro Designer and Aspen Economic Analyzer (TRLs 5 and 6). As shown in Figure 1, there are significant investments needed to advance from one TRL to the next. For this reason, realistic estimates of the eventual commercial viability of a particular process are highly desirable early in the development cycle.

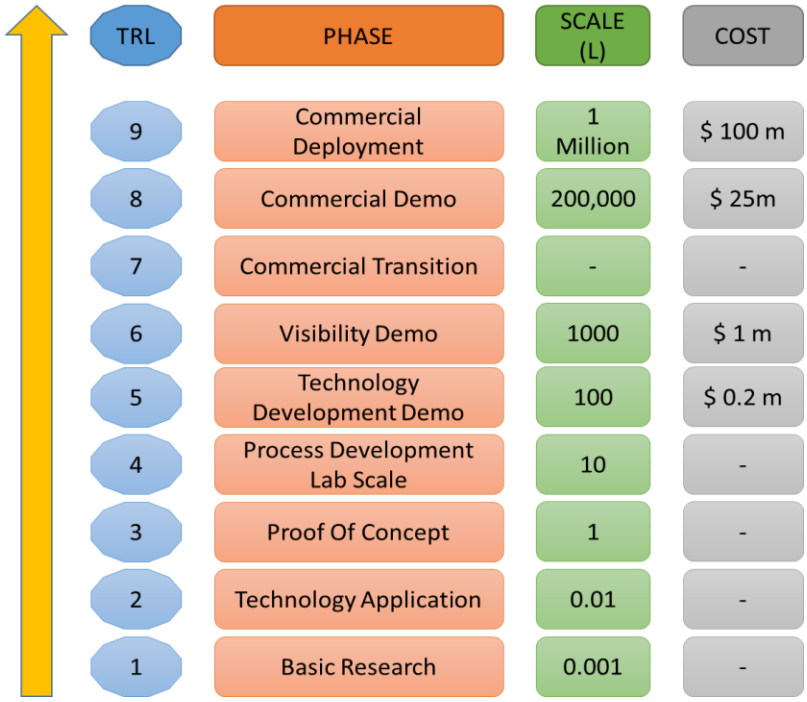

Figure 1 Technology Readiness Levels as applied to the biochemical industry, by Keeling (personal communication 2014), including phase, scale, and approximate capital costs associated.

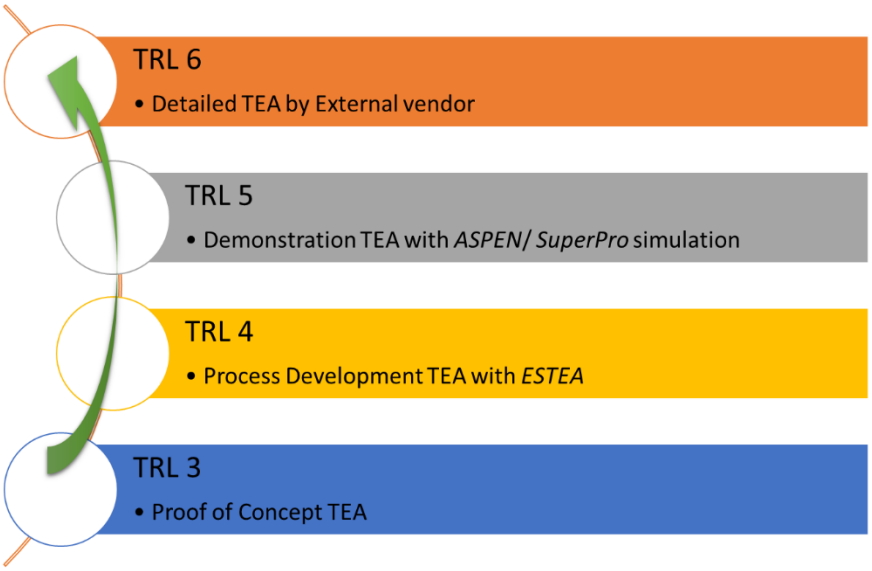

Figure 2 Levels of TEA associated / appropriate to TRL

The development of BioPET was motivated by a desire for a simple modeling tool requiring just a few key parameters for each unit operation, but allowing some capability to explore how the process costs would vary with parameter values to enable the identification of process pinch-points (Claypool and Raman, 2013). The implementation of BioPET was as an Excel-based cost estimation tool for industrial chemical production processes using biorenewable carbon (i.e., sugar) as feedstock. The model was targeted at early stages in process development, at which time many key parameter values are either unknown or only known with a very low degree of certainty. The primary objectives while developing BioPET were ease of use, clarity, and minimum process input requirements. The first iteration of the tool met those requirements, but based on user experiences with the tool, there were significant opportunities to improve it.

Other investigators (e.g., Piotrowski et al., 2014, Turton et al., 2012) have developed simplified models for early-stage TEA of chemical processing. Furthermore, commercial software is also available for process modelling (e.g., SuperPro Designer). The scope and nature of several of these models is summarized in Table 1.

As is evident in Table 1, even though all these models are aimed at simplified TEA, their approaches and scope vary greatly. Models such as nTEE (Piotrowski et al., 2014) and CAPCOST (Turton et al., 2012) focus on providing estimates of capital and operating costs. Specifically, nTEE (new nova methodology for techno-economic evaluation), conducts technoeconomic evaluations based upon material and energy flow data. Using mass and energy flow data, nTEE computes capital and operating expenditures (CAPEX and OPEX, respectively), and estimates the project internal rate of return (IRR, defined as the discount rate at which the net present value of all cash flows is zero) (Piotrowski et al., 2014). Similarly, CAPCOST (Capital Cost Estimation Software) is an MS Excel-based cost estimation tool that allows users to select equipment from a detailed list of options, specifying a list of input parameters including dimensions, material of construction, operating conditions and other accessories; a list of raw materials used in the process can also be specified. The CAPCOST model estimates CAPEX (capital expenditures, which are the purchase cost) for each piece of equipment, as well as OPEX (operating expenditures including utilities and raw material costs). CAPCOST also allows for a cash flow analysis and for Monte Carlo simulation. The CAPCOST model uses a combination of cell formulae and VBA coding to achieve its functionality.

Going beyond the mass/energy based CAPEX and OPEX estimates of nTEE and CAPCOST, other organizations have attempted to provide models that allow more detailed process design, to the level of specific unit operations. Examples of these more specific models include SuperPro Process Designer (which is included in Table 1 as a point of reference), Aspen HYSYS, and CHEMCAD. However, all three of these require significant detailed process information to perform a TEA; such information is more likely to be available at TRL 4 or 5 than at TRL 3.

A specific capability desired for the CBiRC LCA/TEA effort that led to BioPET was to have a simple modeling tool appropriate to the level of knowledge typical for TRL 4. This implies that only a few key parameters be established for each unit operation. This reduced set of key parameters, along with some assumptions, would allow sizing the process and exploring how the process costs would vary with parameter values. In so doing, the model would enable the identification of process pinch-points (Claypool and Raman, 2013). As is evident from Table1, no single existing model provided these capabilities. BioPET was an Excel-based cost estimation tool for industrial chemical production processes using biorenewable carbon (i.e., sugar) as feedstock. BioPET was targeted at early stages in process development, at which time many key parameter values are either unknown or only known with a very low degree of certainty. The primary objectives while developing BioPET were ease of use, clarity, and minimum process input requirements. The first iteration of the tool met those requirements, but based on user experiences with the tool, there were significant opportunities to improve it.

Table 1 Comparison of Models/Tools available for sizing and costing processes, including their area of application, scope and handling complexity. Fer – Fermentation, Sep – Separation/Purification, Cat – Catalysis, Cap – Capital cost, Op – Operating cost

Model/ Tool Name	Scope Sizing			Scope Costing		Implementation	Approx. no. of inputs per Unit Op	Levels of TRL	Comments
	Fer.	Cat.	Sep.	Cap.	Op.				
nTEE	-	-	-	●	●	A set of formulas based on literature	NA	3	Perform simple cost estimation based on capital and operating costs
CAPCOST	-	-	-	●	●	Microsoft Excel	5 - 10	4	Based on Brief information from user, it calculates cap, utility and raw materials costs
SuperPro	●	●	●	●	●	Stand-alone model, unknown language	6 - 10	5	More complex simulation for process modeling (sizing and costing
BioPET	●	●	●	●	●	Microsoft Excel	3	4	CBiRC LCA/TEA effort, developing a process-cost estimation model for early stages of process development
ESTEA	●	●	●	●	●	Microsoft Excel	3	4	Refined and modified version of BioPET

ESTEA vs SuperPro

To clarify the differences between modeling in ESTEA and SuperPro, the process inputs required from user for a single unit operation (namely fermentation) are presented here. Figure 3 is a screenshot from SuperPro's fermentation process input. The user has to provide process-specific information such as stoichiometric reaction(s) producing the product of interest, extent of reaction and reaction limiting components, residence time, and stream flows. Operating conditions such as temperature, pressure, heat transfer agents, power consumption, and aeration supply to fermenter are also required. Emissions, if any, are to be specified as are their respective percentages. Details regarding process vessels are also to be provided. Figure 4 is a screenshot from the GUI page of ESTEA, showing fermentation inputs. These are limited to *titer, productivity, and yield.*

Figure 5 is a screenshot of the ESTEA Fermentation page, illustrating the methodology of costing and sizing fermentation process. Multiple other values that are required by more advanced modeling programs are estimated (i.e., calculated) within ESTEA based upon a combination of known parameters and literature data. For example, rather than a user sizing the fermentation reactor, ESTEA uses the total annual productivity and number of operating days to estimate the mass flow of product. That mass flow (kg/h) is then used, along with estimates of stage yields, to compute the required mass flow of intermediate product from the fermenter. Combining knowledge of the fermenter product mass flow with fermenter productivity (one of the key inputs that is required for fermentation), the fermentation capacity is readily determined. The fermentation input (titer, productivity, yield) parameters, parameters from other unit processes/operations, and process assumptions serve as the overall input for sizing and costing fermentation

process. Unlike more sophisticated process models, ESTEA assumes a reasonable estimation (e.g., streams and their flows). The user can also modify these process assumptions.

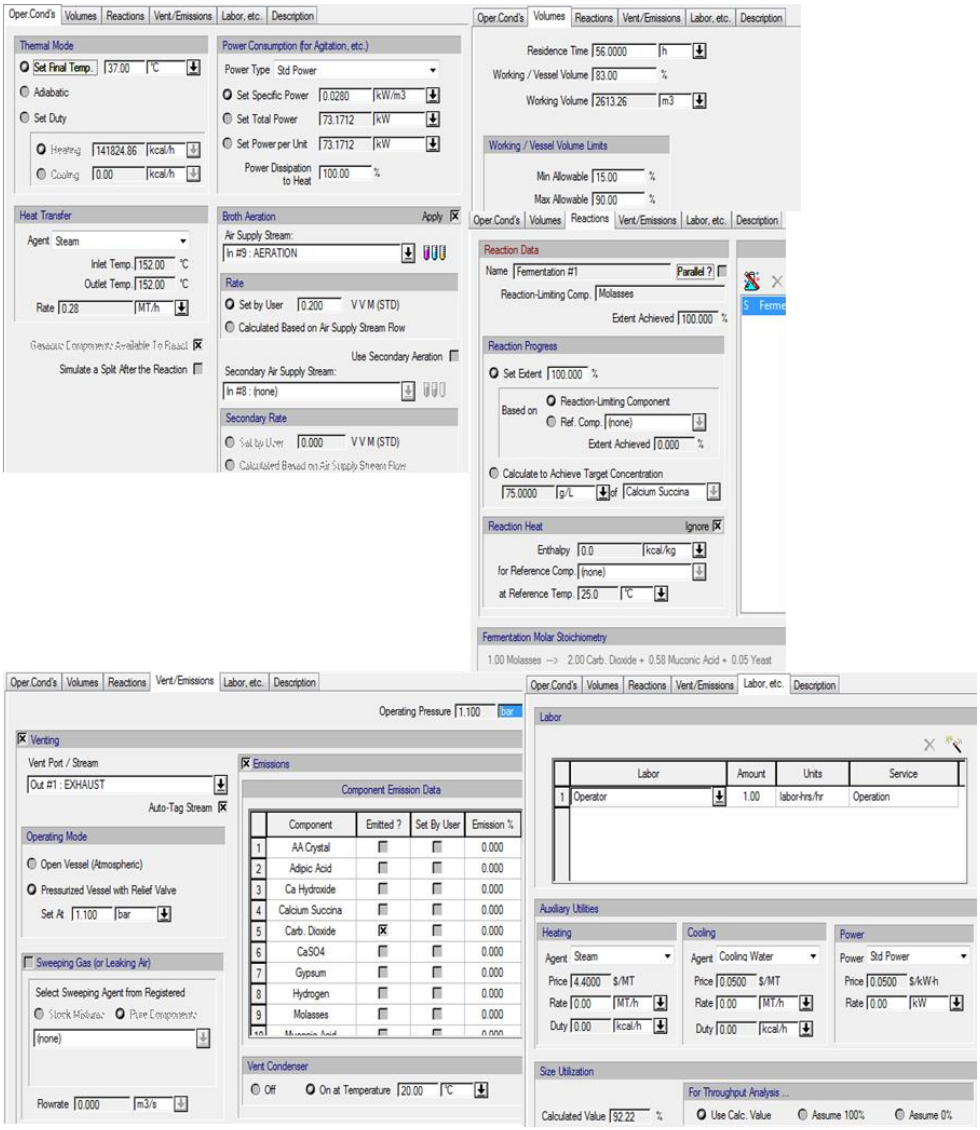

Figure 3 SuperPro process input tab for fermentation operation, showing key process parameters required from user

Fermentation [F]	Extra-Cellular Product
Productivity (g/L/h)	2.0
Titer (g/L)	40
Yield (kg/kg)	47%

Figure 4 Screenshot: ESTEA's GUI showing fermentation input slot including parameters – titer, productivity, and yield

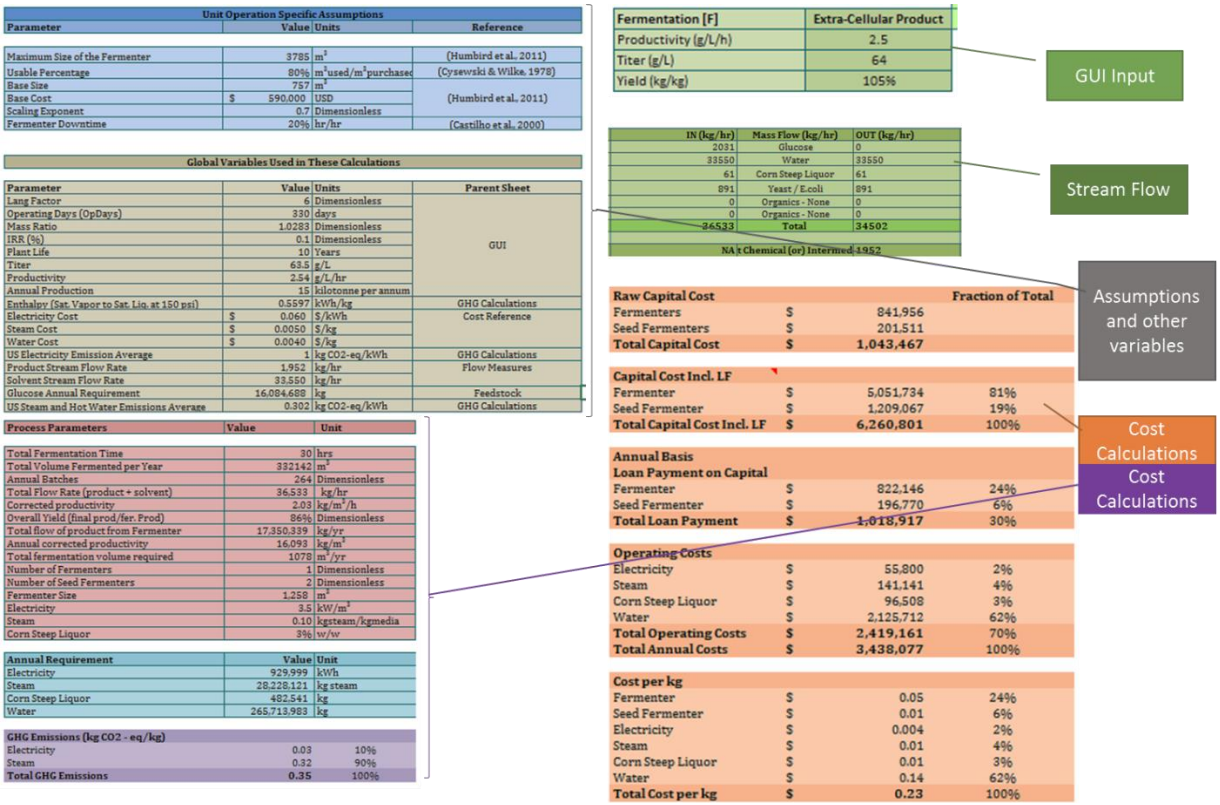

Figure 5 Screenshot: ESTEA showing segments of process input required, assumptions used for calculation, stream flow data, sizing and costing calculations

Strengths and weaknesses of BioPET

BioPET's major strength was its simplicity and ease of use. When processes are at early stages of, the process parameters estimated at lab scale or bench scale are insufficient to construct full-fledged models in process design software (e.g., SuperPro). BioPET filled this space of constructing a preliminary process design, sizing it and predicting the costs related using a reduced set of parameters.

Although BioPET generated significant interest with the CBiRC researchers and industry members, multiple weaknesses were also identified by these groups. Some of them included: Inconsistent data flow throughout the model – the organization of model was such that sizing and cost calculations were cluttered across multiple sheets, which makes it difficult for the user to follow. BioPET could only handle simple processes with fewer unit operations, it was not suitable for some slightly more complex processes of interest to CBiRC researchers and industry members. Numerical values which are either constants, unit conversions, assumed parameters were undeclared.

Rules of thumb on scaling and progressing

There are existing rules of thumb on scaling and designing processes. Some of them include design concepts, sizing guidelines for process vessel and piping, instrumentation design, heuristics, designing with simulation softwares, rules of thumb on physical and thermal properties, trouble shooting, and process economics and many other providing information and solutions that process engineering need (Woods, 2007; Hall, 2012). Because of ESTEA's implementation as an MS-Excel tool, it is relatively easy to use VBA

code to automate the exploration of the parameter space in ESTEA. We leveraged this capability to correlate process parameters with MESP. Process yields, plant size and fermentation parameters such as titer, productivity were analyzed to predict relationship with product cost calculated in ESTEA. These results were distilled into a handful of cost-relevant rules as presented in chapter 3.

Overall goals of this work

The objective of this work was to address issues in BioPET. The reorganized BioPET has, revised the orientation and flow of information throughout the model and was renamed ESTEA. The scope of ESTEA is broader than that of BioPET through the incorporation of secondary and tertiary separations, hydrolysis unit process block, accounting for solvents and water addition through process stages, more sophisticated labor cost calculations, and a GHG emissions calculation block. We have also strengthened the reliability of ESTEA by eliminating hard coding errors, and we validated ESTEA's sizing and costing calculations through models comparison with commercial software and BioPET, we also validated GHG emissions calculations with literature. Finally we have added several new charts and analyses capabilities through VBA scripts and have used ESTEA to develop several rules of thumb for designing fermentative – catalytic biobased process models.

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CHAPTER 2. DEVELOPING AND VALIDATING AN EARLY-STAGE COST ANALYSIS AND LIFECYCLE GREENHOUSE-GAS EMISSION ESTIMATION TOOL FOR BIORENEWABLE PROCESSING

A paper to be submitted to *Chemical Engineering Research and Design Journal*

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Introduction

Models that incorporates process and economic information are invaluable in research and project implementation. These models serve as precise tools of common language for both technical and financial fields. Biorenewables Process Evaluation Tool (BioPET) is MS Excel based Technoeconomic Analysis (TEA) model that uses minimal data inputs for process evaluation. BioPET targets the gap between preliminary cost evaluation (Peters et al., 2003) and detailed cost evaluation as in advanced process models such as SuperPro Designer, by performing early stage cost estimation for process models which are one step advanced from preliminary cost estimations but which still do not have the detailed process information required by full process model software tools (Raman and Claypool, 2013).

The goal of this work was to advance BioPET to ESTEA (**E**arly **S**tage **T**echno**e**conomic **A**nalysis), newly developed tool and validate it. We revised the overall data flow and structured spreadsheets to make them easier for users to understand. We developed component balances to replace existing mass balance calculations. We added two hydrolysis process steps with acid/base addition. Labor cost calculations were also thoroughly modified to calculate operating labor cost for every unit process and overall non-operating labor costs as percent of operating labor, based on literature. We also allowed users to estimate solvent requirement (three options) for downstream processes. Water removal per process can also be regulated by the user. We added a greenhouse gas block to allow users to estimate the emissions associated with the production of the chemical in question. This block included an accounting for the greenhouse gas associated with feedstock production. To accommodate more complex process schemes, secondary and tertiary separation units were added. Furthermore, each tab for a unit operation now has a formula block listing all formulae used in sizing and costing processes. Hard coding error detector was included in the model to facilitate identification of any undefined numerical errors in the formulae. In addition, we developed additional display capability such as, tornado plots to represent the sensitivity of key results to major input parameters, and radar plots to illustrate the impact of fermentation parameters on fermentation cost. Given the broad changes made, we undertook validation of ESTEA. Cost and GHG emission estimations were validated. GHG emissions estimation results were validated with BREW project. ESTEA's cost estimation results were compared with that of BioPET, SuperPro and literature values.

Materials and methods

Introduction to BioPET and discussion of issues needing to be addressed

BioPET provides a single tab (entitled GUI) within the spreadsheet which serves as the primary user interface by allowing the user to enter process information and to see key summarized results. Carbon flows through the process from fermentation through separation of fermented product, catalytic conversion, and ending with purification of the desired product. The processes/steps can be toggled on and off. To make the estimation process simple, only streams consisting primary product and solvent are considered. The user inputs in GUI are used for sizing of unit operations. Intermediate computations are done on a calculation specific sheets. 'Plant Costs" is one such sheet where cost calculations related to sizing and costing these unit operations are performed. "Summary Tables" contain information about flow measurements of streams and mass fraction of product entering unit processes. Cost in $ per kg for all utilities used are provided in the "Cost Indices" data sheet. The "GUI" tab displays key inputs and final results of the BioPET model, most importantly the Minimum Estimated Selling Price (MESP) of the compound in question, along with graphical representations of cost distribution (Raman and Claypool, 2013).

BioPET was subjected to thorough examination through user trial. Based on their feedback, we worked on improving and modifying BioPET. Particular concerns addressed included:

1. Inconsistent flow of information - calculations related to sizing and costing a unit operation was distributed across several sheets. This makes challenging to follow calculations in BioPET
2. BioPET uses undefined numerical values in the form of unit conversions, constants, and assumed values as hard coding errors in formulae. But these values are not addressed anywhere, which raises the questions on using those values
3. Cost of feedstock, electricity, water were outdated
4. Labor costing was very primitive. Labor cost estimations were based on a fraction of overall capital costs, instead of process-based labor calculations
5. BioPET was unable to handle some processes of relevance to the intended user base (CBiRC researchers and industry members). For instance, processes with more than one separation method or processes that utilizes solvents that heavily impact cost calculations could not be modeled

Key changes to ESTEA

Structural modifications – data flow

ESTEA has revised BioPET's information flow. The GUI page still serves as the input space for user to provide process information, as well as the page where critical final results are presented. However, each unit process sheet names are represented in GUI for clarity. The unit operation pages contain sizing and cost calculations of all operations selected in GUI page. Furthermore, the unit operations are arranged in the order as in GUI.

An active unit operation in every page has a red indicator to its left, which helps in identification. Calculations for unit operations are categorized as 'Unit operations specific assumptions', which include assumed parameters specific to that unit operation with their units and references, 'Global variables used in these calculations', comprising of parameters used in sizing which are derived from other process or other sheets, followed by main sizing calculation, utility annual requirement, information on greenhouse gas emission estimations for steam, electricity or feedstock processing is provided under GHG emissions. Cost calculations for unit operations run parallel to sizing calculations. Cost estimations include the following five stages: In Stage I, literature-based equations are used to estimating raw capital cost of equipment used in the process. In Stage II, a Lang factor is applied to the capital cost. Stage III amortizes capital cost to an annual basis using user-provided interest rate and project duration. Stage IV, includes costing utilities required to operate processes. It comprises steam, electricity, extractant (Extraction unit process), adsorbent and column regenerant (Adsorption), separating agent (Crystallization). Stage V consolidates all the capital costs and operating costs to come up with cost contribution by that unit operation per kg of final product. The formula section, running across the stages contain essential formulas and steps used by ESTEA for that unit operation. Formulas, which are used to perform sizing calculations are provided in here for the user to understand better the background of sizing numbers.

Other sheets in ESTEA:

- BioPET's 'Flow measures' included product, solvent, unreacted product and unreacted solvent flows across unit processes. ESTEA has modified Flow Measures

greatly into a well-defined component balance. The newly replaced component balance sheet has a brief discussion on stream flowrates and their compositions IN and OUT of every unit operation.

- Cost reference, has three major sections: A utility cost assumptions that include cost assumptions of all utilities such as electricity, water and process specific raw materials such as feedstock or catalyst. The second section comprises Labor cost assumptions and calculations. The third section consolidates all active unit operation's capital cost estimations, operating costs, labor, and calculations on other costs such as maintenance and repair, operating supplies, patents and royalties, general expenses and plant overhead. With total annual costs normalized by annual production rate, the *Minimum Estimated Selling Price (MESP)* is calculated. It is MESP that is then reported as the primary "result" of the model in the GUI.
- The GHG Calculations sheet contain an inventory of GHG based process assumptions and computes total GHG emission results from active unit operations. The sheet includes average GHG emissions, range of average fossil energy use and sugar content of different feedstock.
- Hypo is a newly added feature in ESTEA, which involves sensitivity analysis of selected parameters of unit processes (Viswanathan et. al., 2014). A variety of charts generated by this analysis tool provide an overview of how MESP value changes over a variety of different scenarios and processes values.
- Tornado, Fer. Analysis, and Graphing sheets serve as data sources for Tornado plot, Radar plot and MESP vs productivity, Titer, yield charts respectively. These data sources contain parametric values generated by VBA code that run multiple

scenarios on the model. Plots are automatically generated using these values. In the later part of this thesis, we discuss these plots in detail.

- Unit Conversion sheet is the outcome of a particular issue addressed in BioPET. This sheet is an inventory of constants and unit conversion numerical values used by the model. Every numerical value used in the model is given a specific name (e.g., Working hours per day = 24, named as *wrk.hrs*). These values are then referenced by their names within cell formulae, reducing hardcoding errors (Rawat et al., 2011).

Table 1 includes a list of all sheets in ESTEA, and their significance. Data flow in ESTEA can be divided into four segments: *Inputs, Process Calculations, Results and Analyses Data, Consolidated Results (Figure 1).* Users provide input via GUI, from which flow measurements are calculated for every unit process. Process calculations are performed in the order of feedstock, fermentation, separation, catalysis and finally purification. Process calculation sheets are named based on their function and order (e.g., Primary separation, Secondary separation). Results and Data analyses segment include extracted cost and GHG calculation results from all unit processes sheets and other VBA based models such as *Fermentation Analyses, Tornado Plotting*. The final results are then consolidated and reported in GUI, while 'Key Output' holds additional charts and diagrams.

Table 2 Flow of data in ESTEA

Sheet Name	GUI Reference (If any)	Significance
GUI	NA	User input and calculated MESP and GHG emissions
Output	NA	Key Charts developed based on input parametric values
F & Cent	Fermentation (F)	Fermentation and Centrifugation sizing and costing
S - I	Separation I (S – I)	Separation I sizing and costing
S – II	Separation II (S – II)	Separation II sizing and costing
H – I	Hydrolysis I (H – I)	Hydrolysis I sizing and costing
S – III	Separation II (S – III)	Separation III sizing and costing
C – I	Catalysis I (C – I)	Catalysis I sizing and costing
C – II	Catalysis II (C – II)	Catalysis II sizing and costing
C – III	Catalysis II (C – II)	Catalysis II sizing and costing
H – II	Hydrolysis II (H – II)	Hydrolysis II sizing and costing
P – I	Purification I (P – I)	Purification I sizing and costing
P – II	Purification II (P – II)	Purification II sizing and costing
Comp. Bal.	NA	Stream flowrates and composition
Cost Ref.	NA	Inventory – Utilities and raw materials costs, consolidated cost calculations from active unit process sheets, Labor cost calculations
GHG Cals	NA	Inventory – GHG related assumptions, consolidated GHG calculations
Unit Conv	NA	Inventory – constants, assumed parameters, unit conversions
Hypo	NA	Model Analysis (Viswanathan et al., 2014)
Tornado	NA	Tornado Chart calculations
Productivity **Titer** **Yield**	NA	Charts predicting the relationship between fermentation parameters and MESP
HCER	NA	Hard Coding Error results

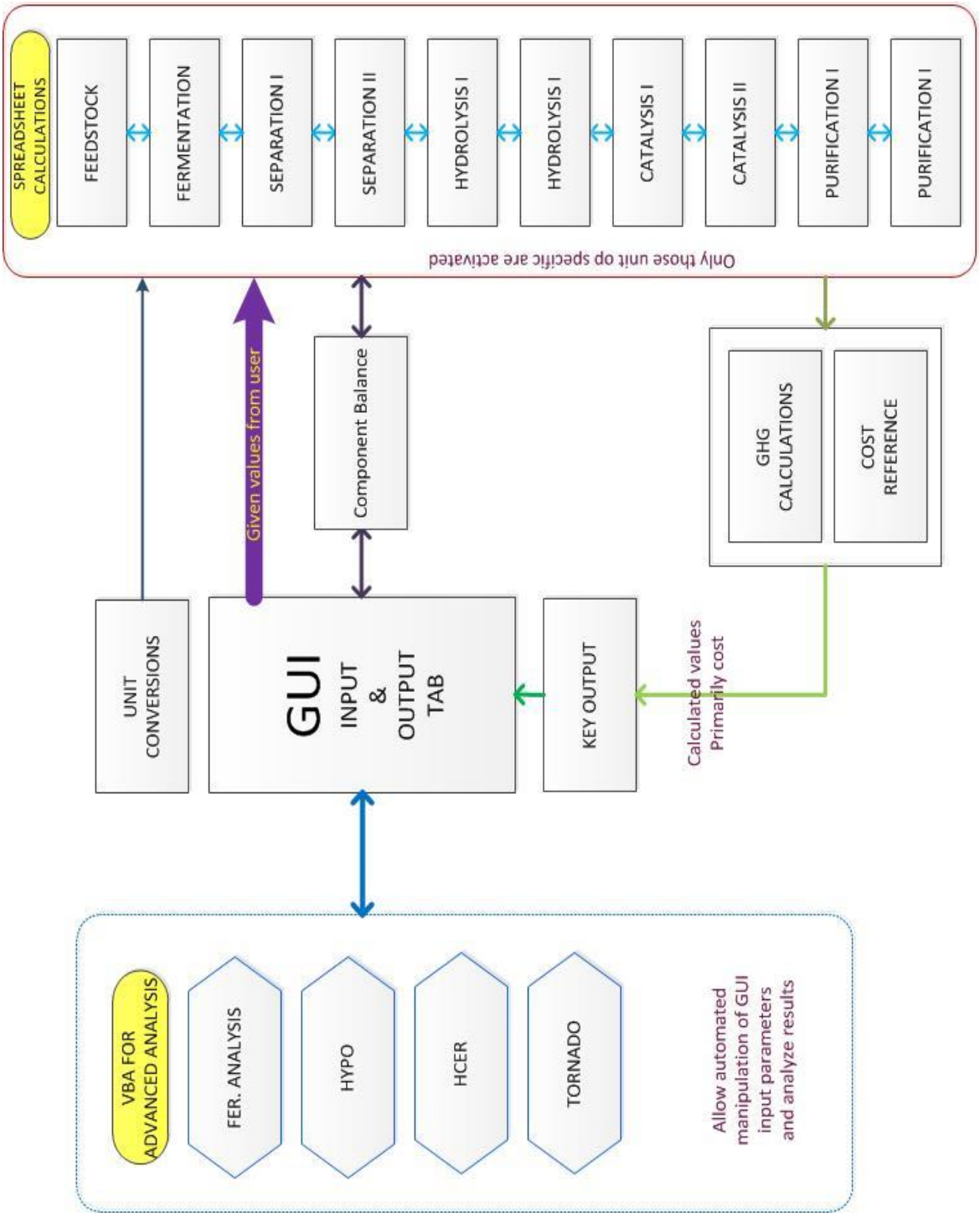

Figure 6 Flow of Data in ESTEA

Catalysis calculation changes

Reactor volume is one of the parameters estimated in designing catalysis process. Equation (1) was employed by BioPET. But was dimensionally inconsistent. In ESTEA, bed volume is replaced by space velocity (hr^{-1}) which is inverse of residence time (hr) as shown in equation 2.

$$\frac{ktonnes}{[Operating\ hours]*[Bed\ Volume]*Solvent\ Density*Mass\ fraction*Process\ efficiency*\%usable\ reactor} \quad (1)$$

$$\frac{ktonnes}{(Operating\ hrs)*(Space\ velocity*\ Solvent\ Density*Mass\ fr.*\ Process\ efficiency*\%usable\ reactor} \quad (2)$$

A new catalytic process uses a 3-train catalytic reactor configuration with one on-stream reactor, one regeneration and one standby. BioPET modeled single catalytic reactor and bed. ESTEA will account for two more reactors and catalyst bed (regeneration and standby). BioPET did not account for the initial purchase cost of noble metal catalyst and assumed 99% recovery and returned to the manufacturer at the end of plant life. ESTEA has modified the cost calculation such that the initial purchase cost of catalyst and periodic catalyst replacement costs are accounted in the techno-economic analysis. Its value at the end of plant life is discounted to present year basis.

Labor calculation modifications

BioPET calculated labor cost as a percentage of total capital investment. A factor of 10% was assumed for feedstock handling, downstream at 5% per unit process. In ESTEA labor cost has been broken down into three divisions: *Operating labor*, *Supervision, and*

Direct salary overhead. Operating labor costs are calculated based workers per unit per shift for every unit operation (Peters et al., 2003). Supervision costs are considered as 52% of operating labor, direct salary overhead at 40% of operating and supervision costs (Towler and Sinnott, 2008). Labor charges are assumed at $26/hr but it is flexible and the user can change vary it. Total number of shifts per day is 3, so that every individual works for 8 hours a day. Table 2 illustrates operators/unit/shift used in labor costing. Equation 3 – 5 below summarize the direct labor cost calculations. In ESTEA, operating labor per unit operation is estimated, allowing users to understand the distribution of labor costs effects throughout the plant

$$Operators\ per\ day\ =\ Operators/shift\ *\ No.of\ shifts*\ No.of\ units \quad (3)$$

$$Operating\ Labor/yr\ =\ Labor\ charge(\$/hr)*wroking\ hours*Operating\ days \quad (4)$$

$$Annual\ Labor\ cost = Operating\ labor/yr\ +\ Supervision/yr\ +\ Direct\ salary\ overhead/yr \quad (5)$$

Input – Operators/Unit/Shift for Unit processes

Table 3 Input – Operators/Unit/Shift for Unit processes

Process/Unit	Operators/unit/Shift
Raw Materials Handling	3
Fermentation	0.5
Centrifugation	0.2
Separation I	0.2
Hydrolysis I	0.5
Catalysis I	0.5
Purification I	0.25

Addition of LCA

To evaluate the processing of biomass feedstock into commodity or bulk chemicals on the basis of sustainability and environmental feasibility, an add-on was built into ESTEA to perform a coarse life cycle assessment alongside the techno-economic evaluation. To develop the simultaneous LCA add-on, a life cycle inventory was created and includes greenhouse gas (GHG) emissions from the production of four different biomass feedstocks – corn grain, corn stover, sugarcane, and switchgrass. Emissions from feedstock transportation were ignored for simplicity.

The location of feedstock production, however, was taken into account based upon current or likely geographic locations for commercial-scale production of the crops. Corn grain emissions reflect estimates from seven states in the upper Midwest United States Corn Belt. Corn stover and switchgrass emissions reflect estimates in the upper Midwest US Corn Belt, as well as southern Ontario, Canada. Sugarcane emissions reflect estimates in Brazil. The average of published literature GHG emission values was taken for each feedstock and used in the development of ESTEA LCA. Type of feedstock, their average GHG emissions, method of allocation and plant growth locations used in ESTEA are provided in Table 3.

Table 4 Greenhouse gas emissions values for four feedstocks used, including allocation strategies used in analyses, references, and locations

Feedstock Type	GHG Emissions ($g CO_2$-eq / kg feed)			Allocation Strategy	Comments
	Low	High	Average		
Corn Grain (US Midwest)	171.7	825.0	271.6	Displacement method (for ethanol co-products), System expansion method	Reflects estimates in seven states across upper Midwest United States (Corn Belt).
Corn Stover (US Midwest and Southern Ontario)	-40.0	96.2	70.3	Displacement method (for ethanol co-products), System expansion method, Mass method	Reflects estimates in seven states across upper Midwest United States (Corn Belt) and southern Ontario province of Canada.
Sugarcane (Brazil)	36.3	39.9	38.4	Energy method	Reflects estimates in Brazil.
Switchgrass (US Midwest and Southern Ontario)	110.3	145.2	127.7	Displacement method (for ethanol co-products)	Reflects estimates in upper Midwest United States (Corn Belt) and southern Ontario province of Canada.

Feedstock emissions averages were then converted into units of grams CO_2-equivalents per kilogram of product, rather than per kilogram of feed. This was integrated into ESTEA's GHG Calculations sheet using the annual glucose requirement and annual production defined for a given process. However, since ESTEA works with annual fermentable sugar requirement, often glucose, conversion rates were necessary to obtain the average yield of fermentable sugars from cellulose and hemicellulose. A 60% glucose yield from cellulose and a 90% fermentable sugar yield from hemicellulose by acid

hydrolysis were used (Wyman et. al., 2005). The compositions of the feedstocks (percent starch in corn grain, percent cellulose and hemicellulose in lignocellulosic biomasses) was also needed. Corn grain contains 72% starch (McGraw-Hill, 2008), corn stover contains 49% cellulose and 26% hemicellulose (Kaliyan and Morey, 2009), sugarcane contains 42% cellulose and 29% hemicellulose (Kim and Day, 2010), and switchgrass contains 44% cellulose and 29% hemicellulose (Kaliyan and Morey, 2009). These compositions, along with the conversion yields stated earlier, were used to obtain the feedstock greenhouse gas emissions per kilogram of product.

To obtain GHG emissions for the processing of the feedstock into the end product, steam and electricity estimates were used. The United States national average GHG emissions for electricity and steam/hot water were used to calculate the emissions produced by the electricity- and steam-use per process step. Once the GHG emissions from the process electricity and steam-use were calculated, they were combined with the feedstock GHG emissions to find the total GHG emissions for any process defined in ESTEA. The results are presented to the user both in a numerical total and also in a column graph dividing the GHG emissions up by process step (feedstock, fermentation, separation/purification, and catalysis) and using colors to show emissions from feedstock, electricity, or steam.

New unit processes, solvents, water, organics

To extend the capacity and capability of the model in handling complex processes, several new unit processes we added to the model. ESTEA has been equipped with

hydrolysis process sizing and cost estimations (*Hydrolysis I and II)*. Hydrolysis accompanies a basic reactor and centrifugation process design to enable mixing of Acid/Base stream with incoming product stream, followed by removal of product and solvent. Reactor and centrifugation sizing assumptions are from already existing centrifugation and catalysis operation. User can choose Acid/Base to hydrolyze, ESTEA provides choice of sodium hydroxide, potassium hydroxide, potassium chloride, sodium chloride, nitric acid, hydrochloric acid as the options to choose. Solvent flowrates are determined as a fraction of aqueous flow into the unit operation. Reactor sizing reactor is based on residence time per cycle of product, solvent and aqueous flow into the system. Centrifugation following hydrolysis to remove solids from the hydrolysis process outflow stream.

To accommodate more complex processes where the product needs more than one separation step, ESTEA has an addition of secondary and tertiary separation process that can be toggled on if necessary. These secondary and tertiary separation units includes four modes of separation, identical to those available in Separation I. Sizing and costing calculations for these unit operations is same as for separation I process.

ESTEA provides opportunity to include solvents, additional water in downstream processing and organics presence in fermentation broth. The user can make use of maximum three options of solvents and water addition. Figure 2 shows the GUI template for solvent, water and organics section. Flowrates of solvents and water are based on fraction of aqueous phase flow provided by the user. User have the flexibility to specify the solvent feed and recovery stage, percent solvent recovered. Users must to be cautious that solvent/water recovery stage is either its own feed stage or after feed stage, but not before

feed stage, as ESTEA is not capable of performing back flow. Presence of organic or inorganic waste matter in fermented broth has been accounted in ESTEA. A maximum of two options can be chosen. Enabling it will calculate 1% of product flowing out (kg/hr) of fermentation broth as organics. It is assumed that these wastes are removed by Separation I/II. Figure 2 is a screenshot of a section of ESTEA's GUI indicating solvents, water and organic/inorganic wastes process inputs.

Solvent I	Hexanol
Solvent: Aqueous Ratio	1
Solvent Density (kg/m^3)	866
Solvent Price ($/kg)	$ 0.98
% Solvent Recovered	90%
Hexanol Feed Stage	Separation2
Hexanol Recovery Stage	Separation2
Organic/Inorganic Waste I	Name
Status	Yes
Recovery Stage	Separation1
Process Water A IN	A
Status	No
Water A : Aqueous Ratio	1
Feed Stage	Separation1
Recovery Stage	Separation1

Figure 7 GUI section of newly added Solvents, Water Addition, and Organics

Hard-coding error minimization

One-third to one-half of spreadsheet models contain errors, this leads to inaccurate results (Galletta et al., 1997). Powell et al., sampled 50 spreadsheets from various organizations and sources. His auditing results concluded 43.5% of cells were Hard-coding errors. Vertika Rawat, a prior Raman group Masters student, developed VBA based coding to detect hard-coding errors in Excel spreadsheets (Rawat et al., 2011). We employed Rawat's Hard-coding error detector VBA program in ESTEA. The program was run through every unit process sizing and costing spreadsheets. The cell error rate in ESTEA was 1%. In total of 1920 cell values checked, cells with hard coding errors were 25. Formulas with errors were then reviewed. The errors were due to either unity, powers of 10 and one particular error was due to accounting for regeneration and standby reactors in catalysis. The existing HCE were considered non-offending and were not modified.

Other changes

The following are other minor changes made to the model.

- Numerical values assumed for calculations in BioPET were following different unit system (e.g., kWh, mmBtu). In order to maintain consistency among units used, we generalized all units in SI system
- Flow of extractant, separating agents, solvents, Acids/base into a unit operation are based on aqueous flowrate. We have accounted for "Percent Water Removal" in downstream processing stages to regulate aqueous composition
- There is always 2% of water and 1% of product lost at every unit process

Validation approach

ESTEA's validation can be subdivided into two segments. The first segment include validation of the cost estimation part of ETSEA by modeling processes in ESTEA and comparing the results with BioPET, SuperPro, and literature. The second segment involved validating the GHG estimator via comparison to literature (ref BREW).

Validation – cost estimation

The second segment of validation included testing models developed in ESTEA with BioPET, SuperPro and literature. BioPET was previously validated using process models of Adipic acid, Ethanol, Styrene and Succinic acid (Claypool and Raman, 2013). During that effort, BioPET results were compared with those from SuperPro models of the same process. Following a similar approach, we validated ESTEA's results on those process models with BioPET, SuperPro, as well as with literature values. Process models were constructed in ESTEA for Ethanol, Adipic acid, Succinic Acid and Styrene. These models were reworked in SuperPro and BioPET. The parametric values used for construction of these models are from Claypool and Raman, 2013. The following Tables (Tables 4,5, and6) representing process parametric values used for sizing and costing in BioPET and ESTEA are the adopted ones from Claypool and Raman, 2013.

Table 5 BioPET and ESTEA Inputs – Ethanol

Input Variable	Value
Annual Production	40 MGY (119.1 KTA)
Operating Days	330 days
Internal Rate of Return	10%
Plant Operating Life	10 years
Mass Ratio	1
Fermentation	
Productivity	2 g/L/hr
Titer	100 g/L
Yield	0.51 g/g
Separation	Distillation
Relative Volatility	10
Purity	0.5
Yield	99.9%
Catalysis A -> C	N/A
Primary Purification	Distillation
Relative Volatility	10
Purity	0.95
Yield	99.9%
Secondary Purification	N/A

Table 6 BioPET and ESTEA Inputs – Succinic Acid

Input Variable	Value
Annual Production	15 KTA
Operating Days	330 days
Internal Rate of Return	10%
Plant Operating Life	10 years
Mass Ratio	1
Fermentation	
Productivity	2.54 g/L/hr
Titer	63.5 g/L
Yield	1.049 g/g
Separation	N/A
Catalysis	N/A
Primary Purification	Crystallization

Table 6 continued

Mass Separation	1 kg $_{agent}$/kg$_{product}$
Purity	0.5
Yield	99%
Secondary Purification	Crystallization
Mass Separation	1 kg $_{agent}$/kg$_{product}$
Purity	0.95
Yield	99.9%

Table 7 BioPET and ESTEA Inputs – Adipic Acid

Input Variable	**Value**
Annual Production	15 KTA
Operating Days	330 days
Internal Rate of Return	10%
Plant Operating Life	10 years
Mass Ratio	1.0283
Fermentation	
Productivity	2 g/L/hr
Titer	40 g/L
Yield	.47 g/g
Separation	N/A
Catalysis A	Hydrogenation / Platinum
Selectivity	99%
Conversion	90%
Catalyst Life	5-years
Primary Purification	Crystallization
Purity	0.5
Yield	99.9%

Validation results (SuperPro – ESTEA – BioPET - literature)

Validation of ESTEA was performed by comparing feedstock, fermentation, downstream and other costs between the models. The drivers for estimated cost

differences were analyzed. Market price from literature for the three cases (Ethanol, Succinic acid, Adipic acid) were then compared with MESP values from BioPET and ESTEA. Assuming literature values as the line of mark, BioPET, ESTEA and SuperPro's MESPs were compared to analyze their percent deviation from literature values. Figure 3 was the representation of ESTEA's ethanol model results, indicating cost distribution among factors such as labor, feedstock, fermentation, downstream, others. Downstream includes product separation, catalytic conversion and product purification. Others include costs related to maintenance, plant overhead, general expenses, patents and royalties. Cost distribution for succinic acid is shown in Figure 4 and adipic acid model in Figure5.

Effect of downstream processing can be clearly explained by comparing the following figures. From Figure 3 only 3% of the total cost of ethanol production was from downstream processing, the major cost was from feedstock consumption (70%). The ethanol process employs a relatively simple separation method, no catalytic conversion is required. In the cases of succinic acid and adipic acid, significant downstream processing is required involving cost consuming crystallization methods. Crystallization require additional separating agents, thus increasing operating costs. Catalytic conversion requirements increase adipic acid costs. Together, these result in downstream processing cost for succinic acid at 43% and adipic acid – 27% of production cost. Furthermore, the dependence of Labor on number of unit operations used can be observed distinctly. Varying labor cost distribution can be seen between ethanol and the other two chemicals, where downstream processing is heavier in the latter, reflecting higher labor requirements. Model comparison between ESTEA and BioPET, in terms of estimated cost factors was performed (Figure 6). Significant difference were noted in feedstock calculations. Labor

cost modifications have an impact, but those impacts are relatively small compared to feedstock costs. Maintenance and other costs are indirectly affected by production costs and hence there exist a difference in their cost calculation.

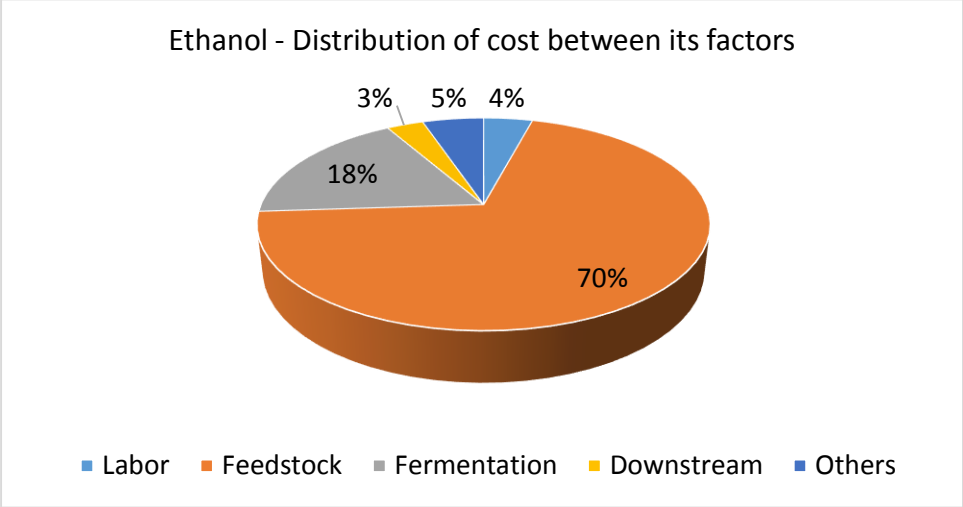

Figure 8 Case- I: Ethanol – ESTEA's cost distribution including capital and operating cost between its factors of labor, feedstock, fermentation, downstream and others

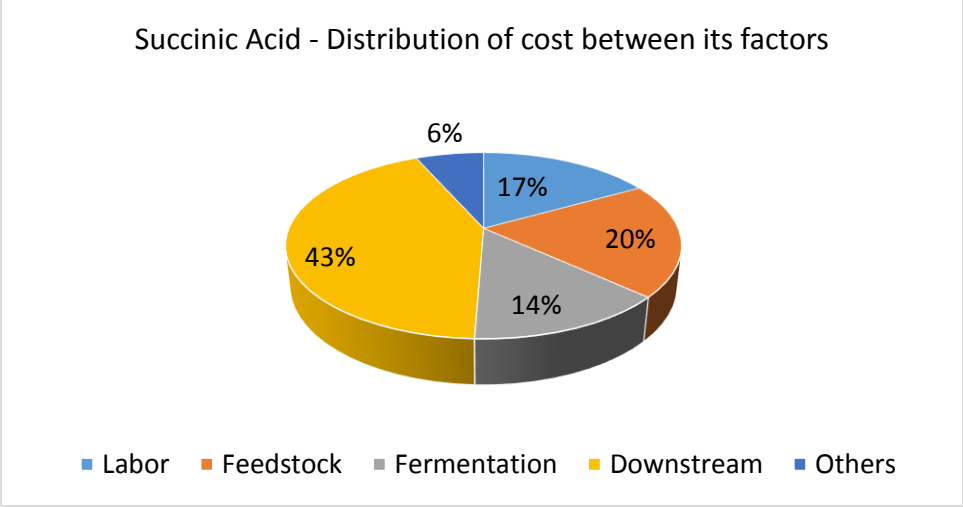

Figure 9 Case- II: Succinic acid – ESTEA's cost distribution including capital and operating cost between its factors of labor, feedstock, fermentation, downstream and others

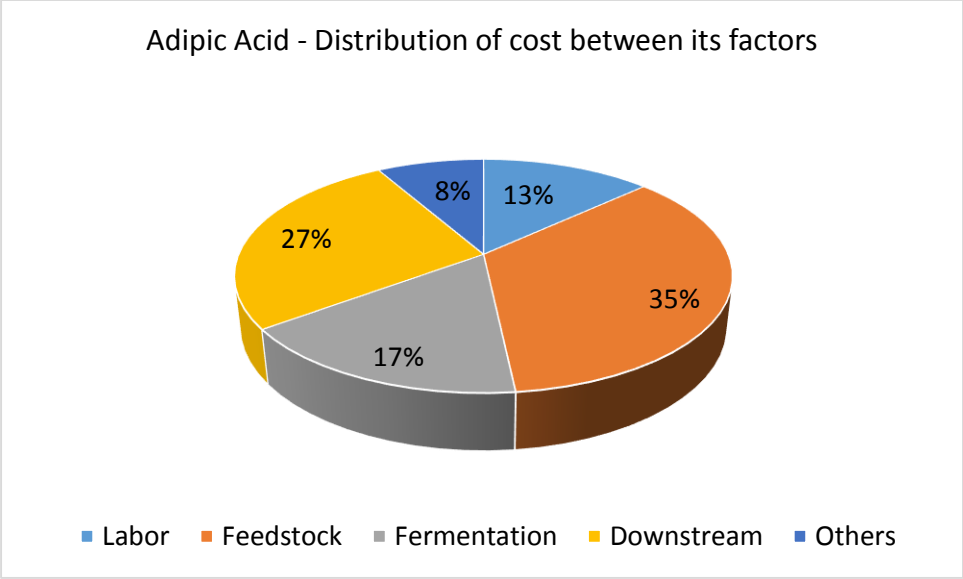

Figure 10 Case- III: Adipic acid – ESTEA's cost distribution including capital and operating cost between its factors of labor, feedstock, fermentation, downstream and others

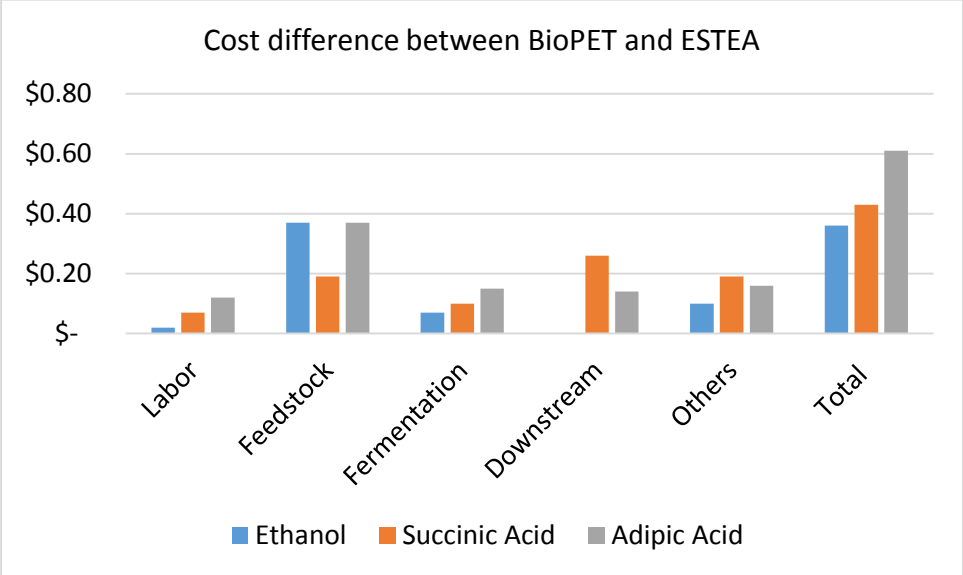

Figure 11 Cost difference between BioPET and ESTEA for Ethanol, Succinic acid and Adipic acid including all measured cost factors

Table 7 illustrate cost factors for ethanol, succinic acid and adipic acid in both BioPET and ESTEA and their difference between calculated costs for each factors explain changes and modifications made in ESTEA. ESTEA is not capable of including byproducts cost calculation. For example DDGS (Distiller's Dried Grains with Solubles) is a nutrient rich byproduct of ethanol. For every 1kg of ethanol produced, 0.8 kg of DDGS comes out as by product (US Grains Council, 2012). DDGS is sold at a market price of $0.17/kg of DDGS (US Grains Council, 2012). DDGS market price is decremented in ethanol cost calculation in ESTEA and BioPET to provide MESP of Ethanol. Figure 7 represents calculated cost differences between BioPET and ESTEA models. Cost differences are measured for cost factors/categories of labor, feedstock, fermentation, downstream and others as discusses earlier. Table 8 compares ESTEA estimated MESP with that of BioPET, SuperPro and literature values. Literature value for ethanol MESP are pulled from *National Renewable Energy Laboratory* report (Humbird et al., 2011) at $0.72/kg ethanol, succinic acid at $1.80 (Villadsen, 2013) and adipic acid at $2.78 (Pavone, 2012).Using these as the line marker, estimated MESPs from BioPET, ESTEA and SuperPro are compared, to derive the percentage deviation of MESP from literature value. Figure 8 illustrates percentage deviation of MESPs from literature values.

Table 8 Case- I: Ethanol – Comparison between BioPET and ESTEA calculated labor, feedstock, fermentation, downstream, others and MESP

Cost Categories	BioPET	ESTEA	Cost Difference
Ethanol			
Labor	$ 0.02	$ 0.04	$ 0.02
Feedstock	$ 0.30	$ 0.67	$ 0.37
Fermentation	$ 0.10	$ 0.17	$ 0.07
Downstream	$ 0.03	$ 0.03	$ 0.00
Others	$ 0.15	$ 0.05	$ 0.10
Total (MESP)	**$ 0.43**	**$ 0.79**	**$ 0.36**
Succinic Acid			
Labor	$ 0.21	$ 0.28	$ 0.07
Feedstock	$ 0.14	$ 0.33	$ 0.19
Fermentation	$ 0.13	$ 0.23	$ 0.10
Downstream	$ 0.45	$ 0.71	$ 0.26
Others	$ 0.30	$ 0.11	$ 0.19
Total (MESP)	**$ 1.23**	**$ 1.66**	**$ 0.43**
Adipic Acid			
Labor	$ 0.15	$ 0.27	$ 0.12
Feedstock	$ 0.35	$ 0.72	$ 0.37
Fermentation	$ 0.19	$ 0.34	$ 0.15
Downstream	$ 0.41	$ 0.55	$ 0.14
Others	$ 0.33	$ 0.17	$ 0.16
Total (MESP)	**$ 1.44**	**$ 2.05**	**$ 0.61**

Table 9 Case- I: Ethanol – MESPs from different models/software - % deviation of MESPs

Models	$/kg	% deviation from literature
Ethanol		
BioPET	$ 0.48	33%
ESTEA	$ 0.74	2%
SuperPro	$ 0.60	16%
Literature	$ 0.72	-
Succinic Acid		
BioPET	$ 1.23	32%
ESTEA	$ 1.66	7%
SuperPro	$ 1.35	25%
Literature	$ 1.80	-
Adipic Acid		
BioPET	$ 1.44	48%
ESTEA	$ 2.05	26%
SuperPro	$ 1.74	37%
Literature	$ 2.78	-

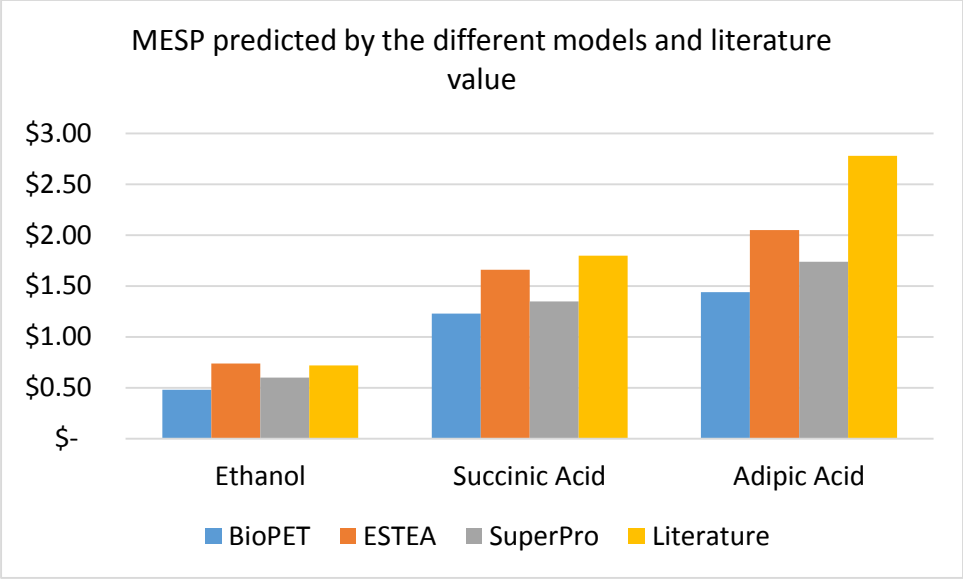

Figure 12 MESP comparison between models and literature value for ethanol, succinic acid and adipic acid

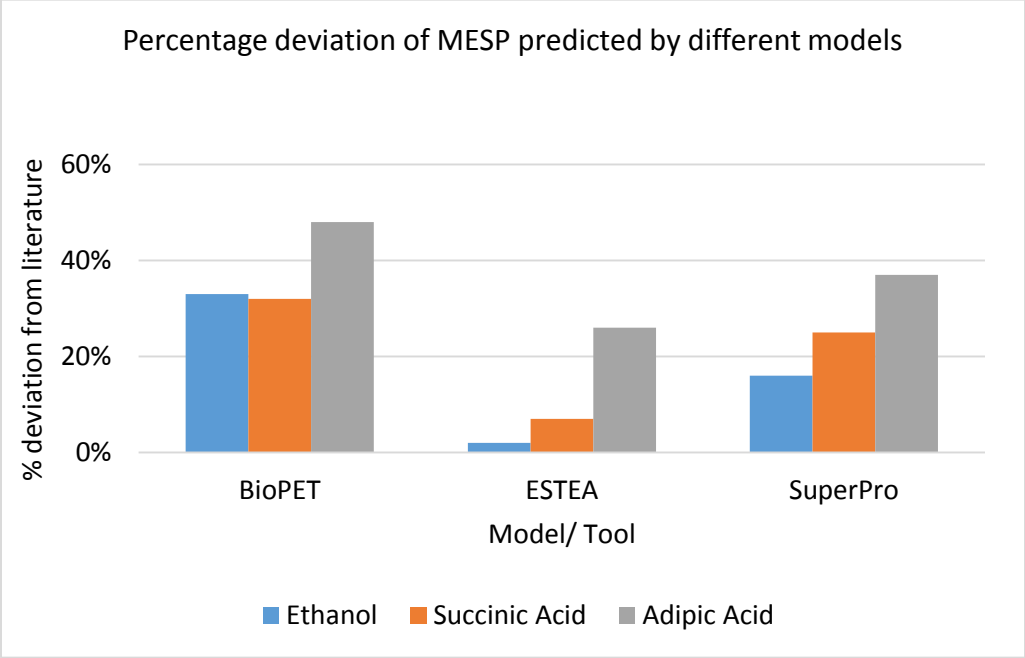

Figure 13 Percent deviation of MESPs calculated by models, when compared with its literature value for ethanol, succinic acid and adipic acid

Results from ESTEA were more consistent and near literature results than BioPET and SuperPro. ESTEA estimated Ethanol at $0.74, Succinic Acid at $1.66 and Adipic acid at $2.78. In all three cases, BioPET's estimated MESP were less than ESTEA's estimations. Common observations include:

- On comparing results between ESTEA and BioPET, major difference in cost estimation was found in feedstock and fermentation costs. ESTEA estimated higher feedstock and fermentation costs than BioPET – (Feedstock cost used in BioPET: $0.15/kg; ESTEA: $0.30/kg), (Water cost in BioPET: $0.0005/kg; ESTEA: $0.004/kg). These corrections in ESTEA have made the calculation differences.
- Maintenance and repair, operating supplies, patents, and plant overhead costs are grouped as "others" in ESTEA. BioPET estimates others larger than ESTEA in all 3 cases at a minimum of $0.10/kg of product and max $0.20/kg of product.
- Variation in labor cost – ESTEA estimated labor based on operators per shift, clerical labor fraction and non - operating labor fraction whereas BioPET estimations are based on assumed percent of total capital investment. These labor costing changes were now more focused on number of unit operations active. This can be argued by comparing the cost difference for labor in case of ethanol and adipic acid, higher the unit operations, higher is the labor, which was not clearly identified in BioPET
- BioPET predicted values 30% lower compared to literature values in all three cases. SuperPro estimates deviated from 16% to 37% from literature. In all three cases results from ESTEA was very closer to literature value than SuperPro and BioPET. In case of ethanol, ESTEA's predicted MESP had only 2% deviation. MESP predicted for adipic acid had an average of 37% deviation from literature value, this may be due

to usage of simplified process for modeling. As there were only limited information and different source of information for modeling and literature cost reference, possibility of greater variation in results exist. But overall, ESTEA's results were much closer to literature values than both SuperPro and BioPET.

- Plant size highly influenced feedstock and fermentation costs percentage. The effect of different parameters on MESP is discussed further in chapter 3.
- Generally feedstock forms >65% of total cost. But in case of Adipic acid and succinic acid, high downstream processing cost and lower annual production (plant size 15 kTA) and high fermentation yields decrease the relative contribution of fermentation vs. downstream processing costs.

The effect of downstream processing efficiency on feedstock requirement and overall costs are explored in chapter 3.

Validation - LCA

Similarly to ESTEA's economic validation against Super Pro, the BREW Project (Patel et. al., 2006) was used to validate ESTEA LCA's accuracy and functionality. Since the BREW Project only evaluated three biomass feedstocks—corn grain, corn stover, and sugarcane—switchgrass was not analyzed in the validation process. Three bioprocesses were chosen (ethanol, succinic acid, and adipic acid) to compare the GHG emissions estimates of BREW with those of ESTEA. In order to make these comparisons, process inputs from BREW were adapted to fit the input requirements of ESTEA.

As shown in Figure 9, when compared against the BREW Project (Patel et. al., 2006), ESTEA LCA estimated greenhouse gas emissions with reasonable accuracy for both succinic acid and adipic acid processes; succinic acid estimates were much closer in value than adipic acid estimates, but both processes followed similar trends for ESTEA and BREW between feedstocks. ESTEA overestimated GHG emissions for the ethanol process when compared to BREW In performing initial research for this project, no other published literature showed negative GHG emissions for an ethanol production process (cradle-to-plant gate), although some did have negative estimates when energy returns from ethanol use after production were taken into account. With this being the case, it may seem to have been better to validate ESTEA LCA against a different life cycle assessment, but we chose to stay with BREW due to the detail provided on the process inputs used, as well as its

analysis of several different bioprocesses and biomass feedstocks. The ESTEA vs. BREW results are shown below.

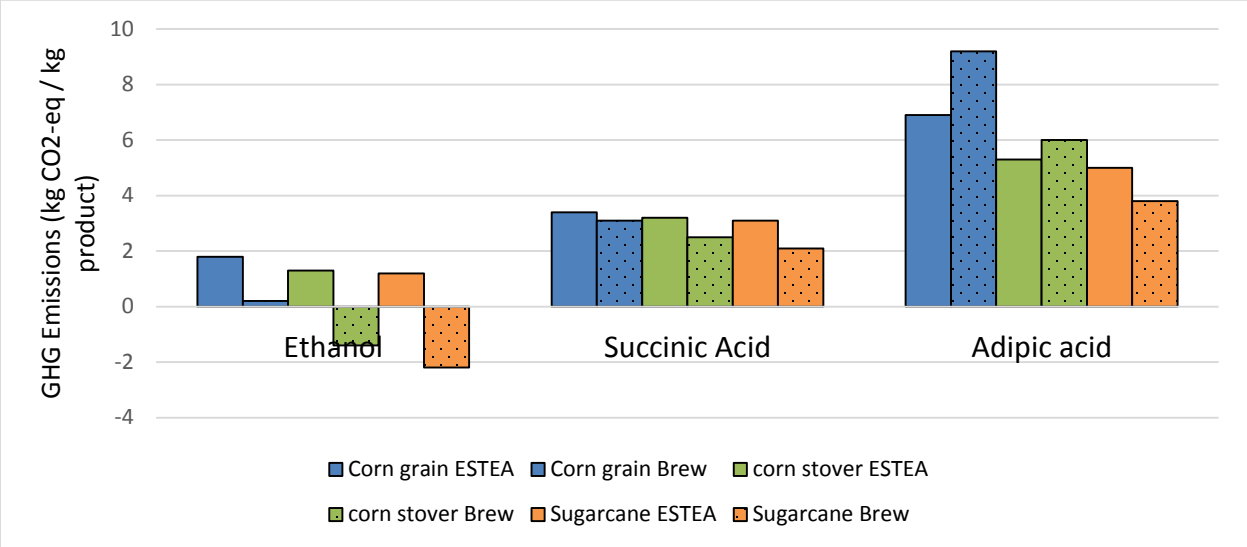

Figure 14 GHG emissions by feedstock for Ethanol, Succinic acid, and Adipic acid processes from ESTEA analysis and BREW published data

GHG emissions estimates for feedstock production have a large range, particularly for corn grain and corn stover (Figure 9). This being the case, it is possible that ESTEA's estimations could vary greatly for these two feedstocks depending on location of feedstock production and allocation strategies, among other things. In the future, methods other than a straight average may be used to compile the data in order to see if estimation accuracy can be improved. The tool might also be improved by the addition of GHG emissions calculations for the conversion of biomass feedstocks to fermentable sugars, since there are several different potential processes with varying emissions, energy usages, and yields. Lastly, a fossil energy use analysis for processing may be added to the tool to provide users

with additional information as part of the results given by ESTEA. Overall, ESTEA LCA currently calculates reasonable coarse estimate.

Results and discussions

View of GUI and Key Output

Results of Minimum Estimated Selling Price and Greenhouse Gas Emissions are displayed in GUI. GUI also provide a dynamic view of cost estimation results in the form of Cost breakdown by Cost Category (Figure 10) which displays the operating cost distribution among electricity, water, steam, labor, loan and many other miscellaneous factors. The other chart, Cap & Op Cost by Unit Operation (Figure 11) explains cost contribution of fermentation, separation, catalysis and purification, the key unit processes. This chart is based on percentage cost contributed by unit processes as cost per kg of product produced, which is calculated based on operating, capital, labor and other costs.

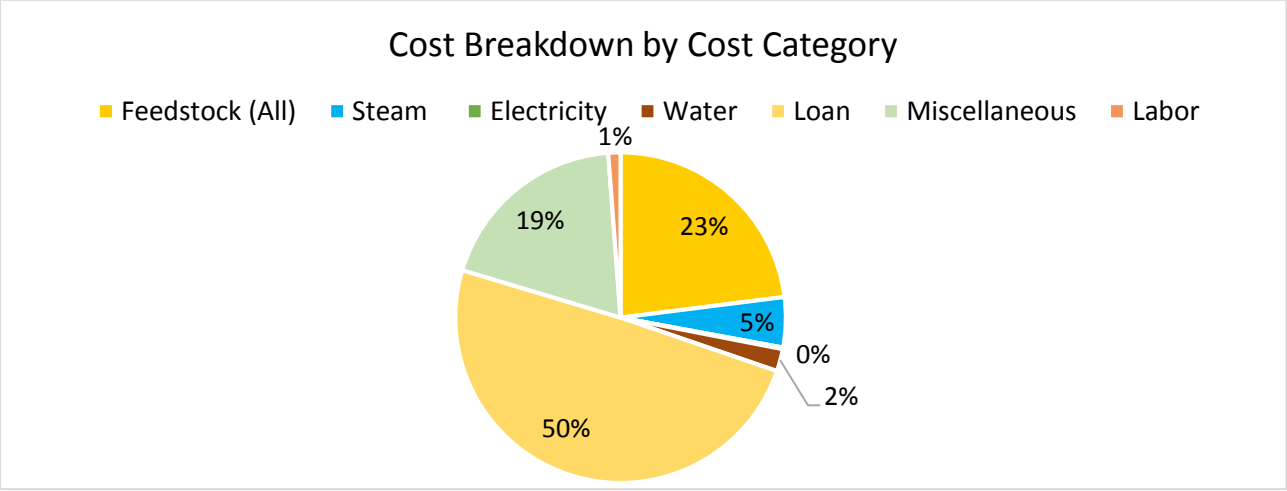

Figure 15 Distribution of different costs factors between Unit Processes

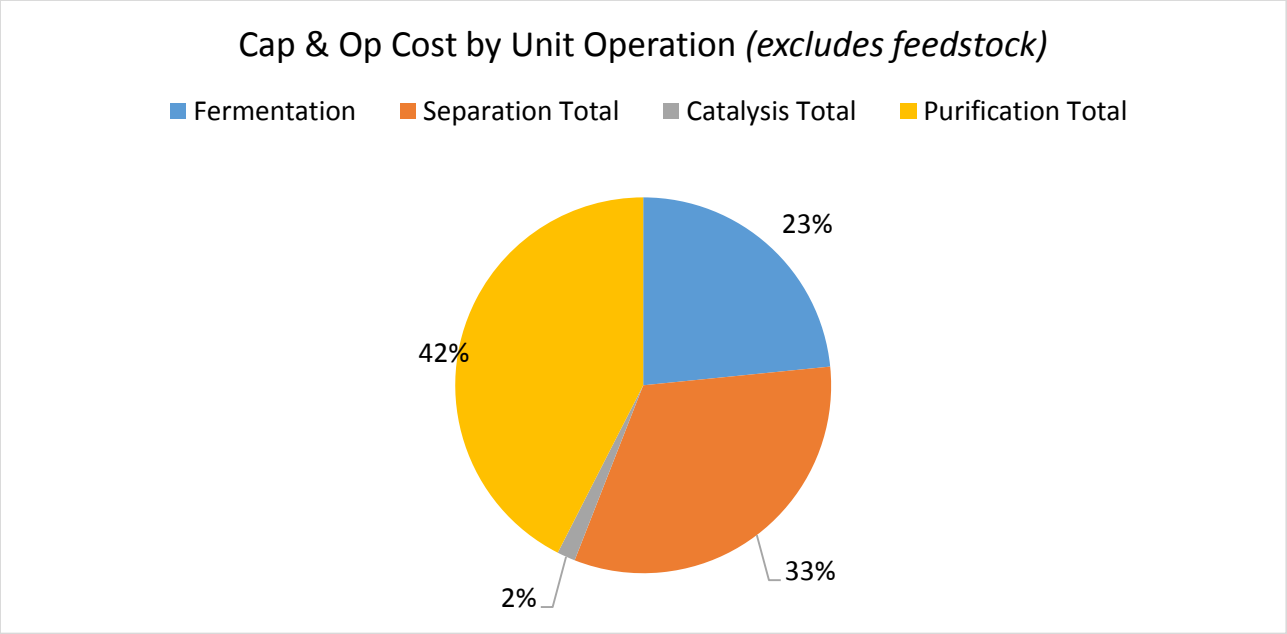

Figure 16 Percentage cost contribution across Unit Processes

Key Output sheet contain various other charts on cost and GHG calculations. ESTEA is capable of performing several analyses on cost and GHG emissions and the Key Output sheet contains all those analyses and their results. ESTEA provides cost comparison of the estimated chemical with that of other commercial chemicals in current market (Figure 12). Top chemicals in the market based on their price rank, are chosen for comparison (Chemicals cost are based on LUX research – CBiRC report 2013). The idea of this chart is to provide user a knowledge of where the product would stand in the market along with other chemical compounds. The clustered column chart has first column as the ESTEA's estimated chemical price, followed by other top chemicals arranged in the increasing cost per kg.

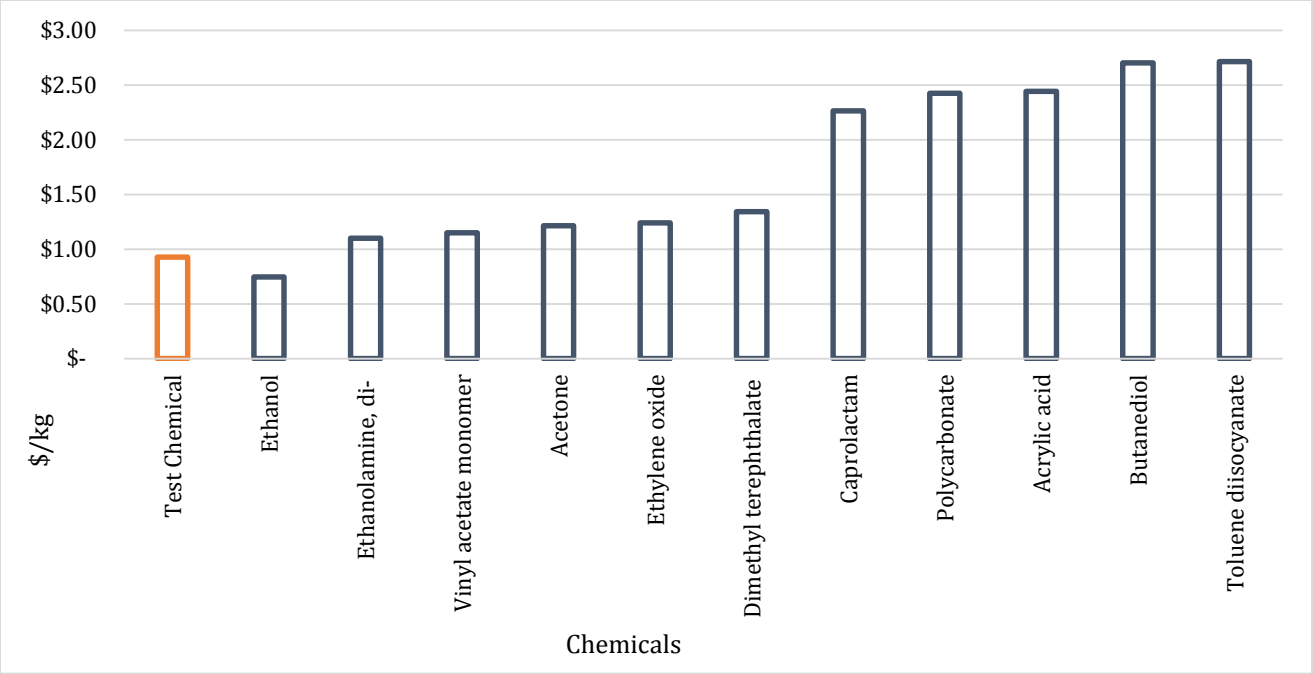

*Figure 17 Cost comparison between ESTEA estimated MESP of test chemical and other top chemicals in the market**

*Commercial price value of chemicals are from CBiRC's LUX report made from online price data websites (ICIS, 2013) (Alibaba.com, 2013) (Today in Energy, 2013).

Percent greenhouse gas emission estimations including emissions related to feedstock production, steam, and electricity consumption for adipic acid process are pictured in Figures 13 and 14.

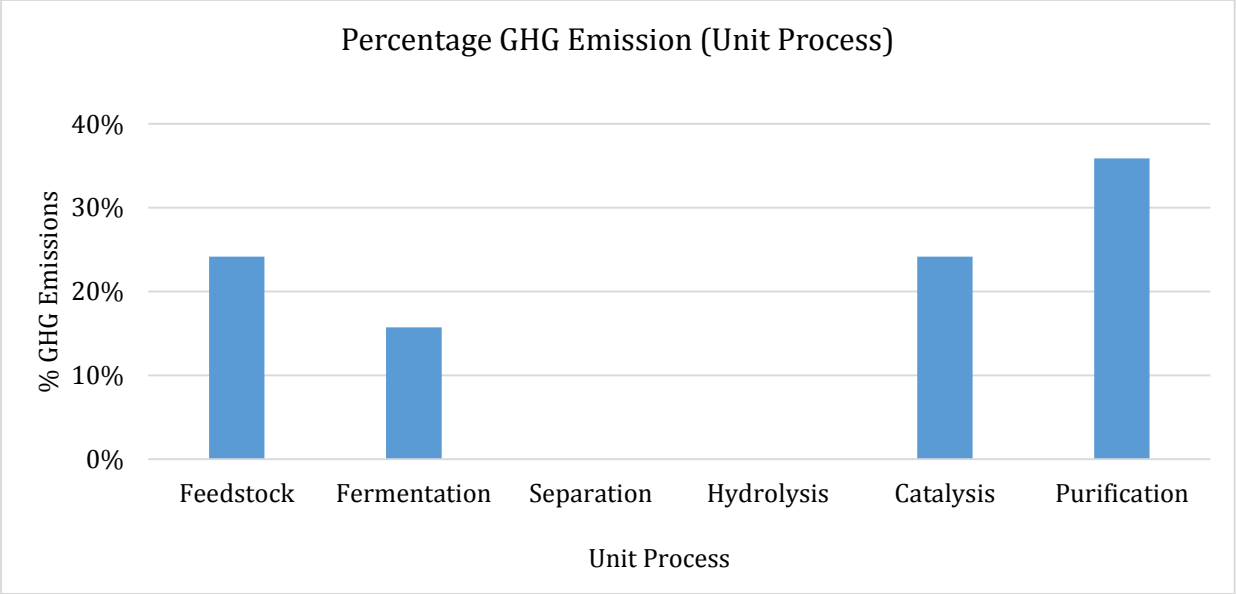

Figure 18 Percent GHG Emissions from unit processes (Feedstock, Fermentation, and Downstream Processing of Adipic Acid process)

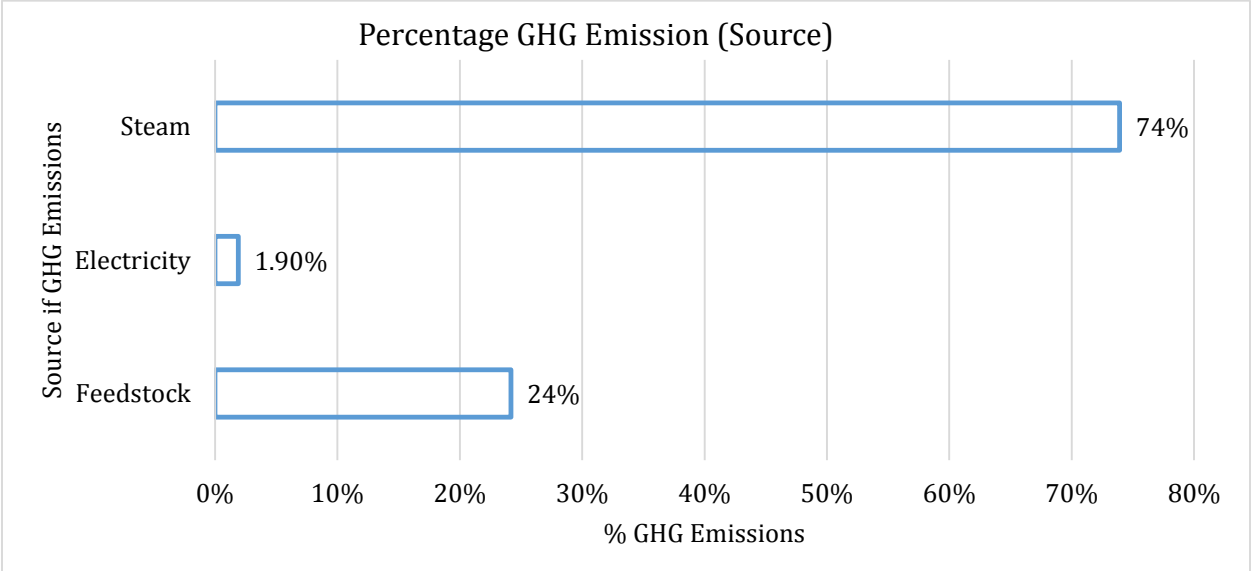

Figure 19 Percentage GHG emissions from Steam, Electricity consumption and feedstock processing of Adipic Acid production

Fermentation analyses:

To understand the effect of key fermentation parameters on the MESP of a bio-based chemical, ESTEA provides charts to visualize MESP changes as a function of fermentation parameter. To predict the effect of a single parameter (productivity, titer, and yield) on MESP, individual charts were developed. These charts are based on setting a constant value for any two of the three key fermentation parameters (titer, productivity and yield) and varying the third from its lower limit by a constant factor. A set of 100 values, incremented at 4% total span are plotted. Figure 15 explains the relationship between MESP and productivity when titer and yield are set to a constant value for a unit process. Similarly MESP vs Titer and MESP vs Yield (not shown here) charts in ESTEA distinctly overviews the parametrical dependency of MESP.

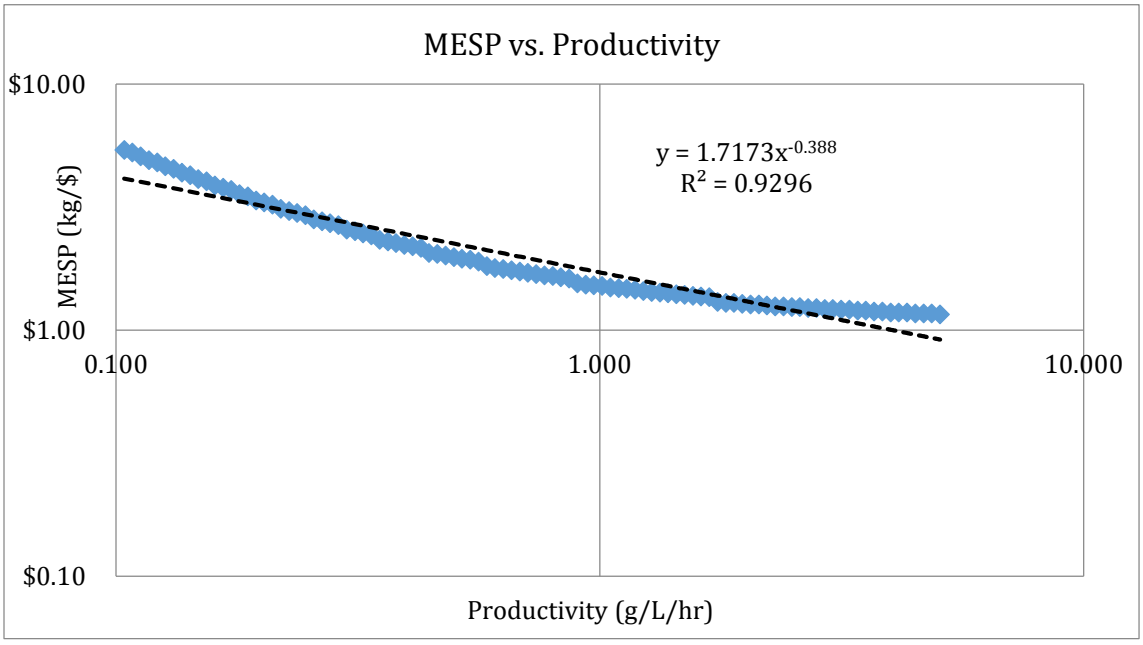

Figure 20 Relationship between MESP and Productivity when titer and yield of fermentation are constant

Radar Plot - fermentation

Yet another fermentation analysis involves estimating the minimum estimated selling price of the chemical by varying all three fermentation parametric values for every iteration. On a broader aspect, productivity, titer, and yield of fermentation are varied between their limits of 0.5 to 4.9 g/L/h, 50 to 200 g/L and 50% – 150%. Productivity is increased by a value of 0.4, titer by 25, and yield by 5%. The analysis is performed using VBA code that estimates all MESP for all possible combination of parametric values. A Radar plot (Figure 18) is generated based on the resulting values where MESP is displayed as the radius at any point. For easy interpretation, the plot can be categorized into cycles. Figure 16 and 17 explain the course of one complete cycle. A cycle starts at the least titer and yield for a given productivity. The yield is then increased to its maximum value with no change in titer and productivity, leading to a drop in MESP. Once the yield reaches its max value, titer is increased to its next value and the yield change is repeated for that titer – this sudden "reset" of the yield at the new titer gives rise to a saw tooth pattern in the radar plot. This chain continues till titer reaches its max limit. And this completes a full cycle (Figure 18). The next cycle starts by increasing the productivity and repeating titer and yield changes. A radar plot will thus MESP calculated by varying yield, titer and productivity. The sharp toothed radar plot in Figure 18 implies the high impact of yield on MESP compared to titer and productivity. This chart helps in identifying every possible combination of fermentation parametric values for the given unit processes and plant properties. This helps the user with a broad spectrum of MESP results.

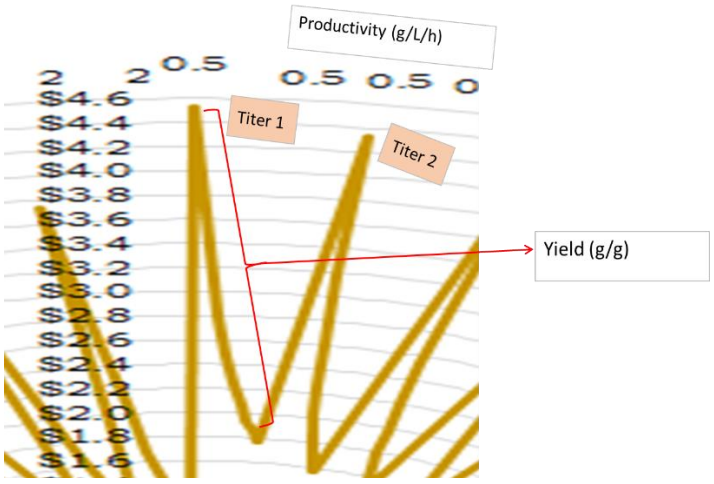

Figure 21 Radar plot – MESP drop reflected by increasing yield for every titer value at constant productivity

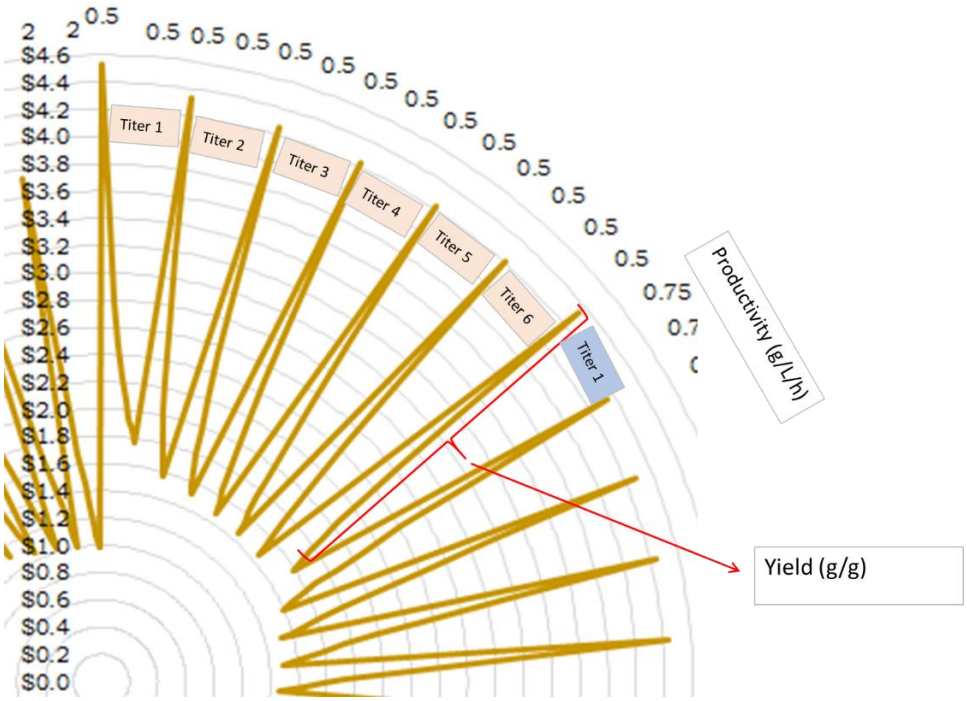

Figure 22 Radar plot – A complete cycle indicating MESP relationship with increasing yield and titer values for a single productivity

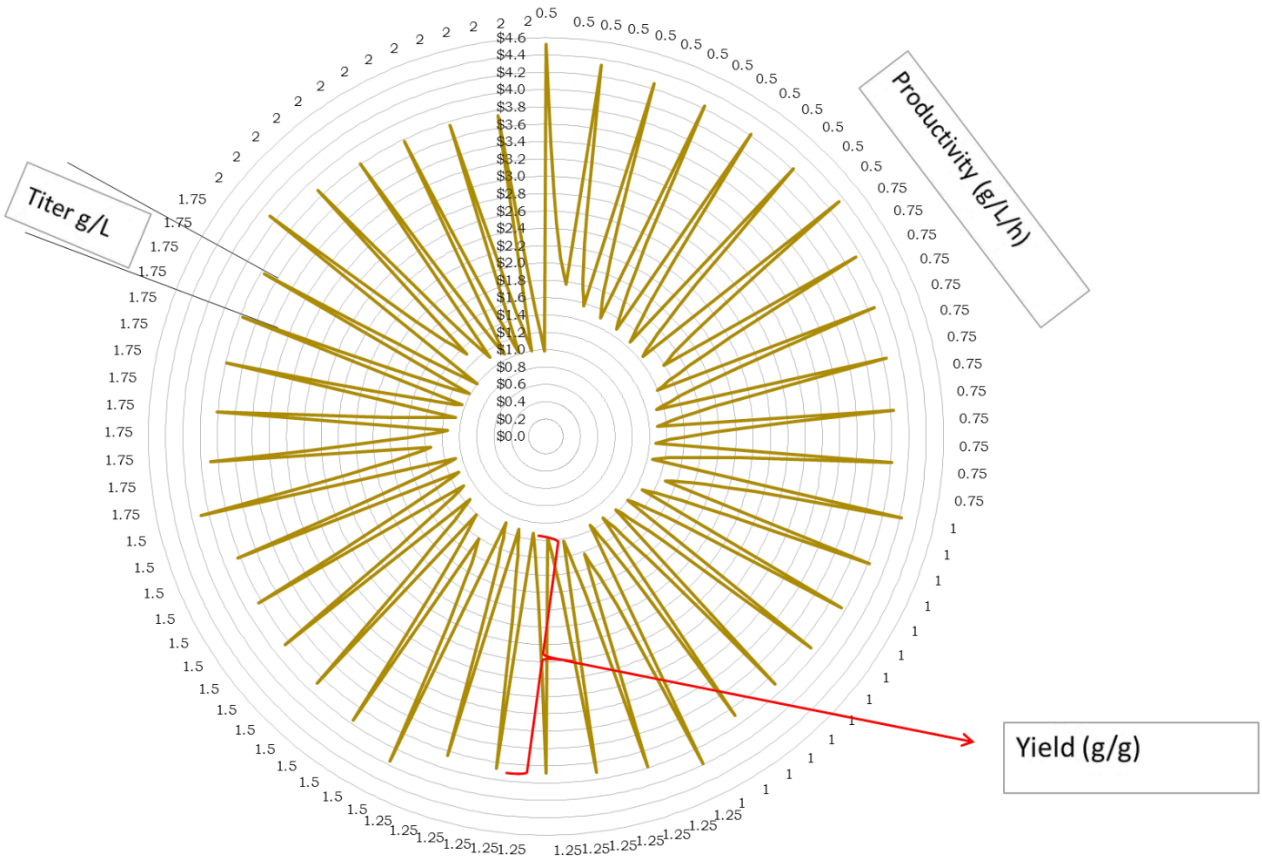

Figure 23 Radar plot – Fermentation parameters of titer, productivity, yield and their effect on MESP

Tornado plotting

To understand the sensitivity of process input parameters and to measure the impact of parametric values on costing, we developed few more charts using VBA in ESTEA. Tornado plot is one such macro based chart on variance of MESP/ GHG from the base case when the parametric values are subjected to change. User defined values on GUI are taken as the base case values. On selecting Create Tornado plot, the macro asks if the user would like to perform a +/- 10% uncertainty to parametric values. On choosing yes, cost calculations for +/- 10% uncertainty of parametric values are evaluated. On choosing No

option, a default uncertainty provided by ESTEA is used to evaluation. For every +/- uncertainty value of parameters, the MESP is calculated. Macro produces Tornado plot in Key Output sheet plotting the change in MESP from base case (Figure 19). The change in GHG emissions through uncertainty of parametric values produces Tornado for GHG (Figure 20) in parallel to MESP tornado.

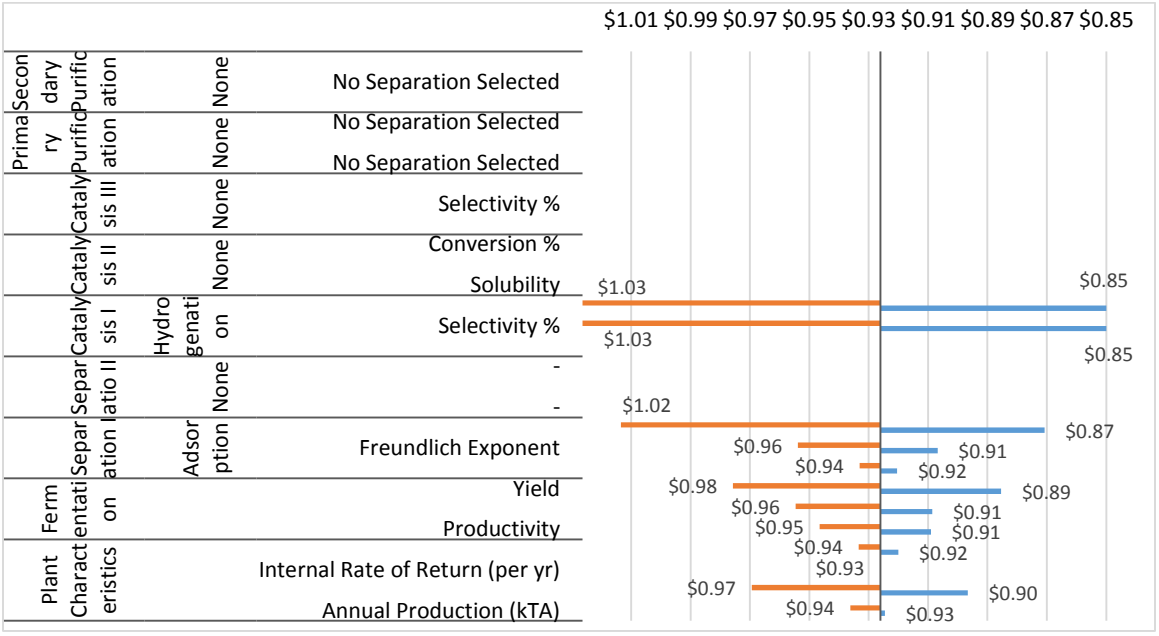

Figure 24 Tornado Plotting – MESP

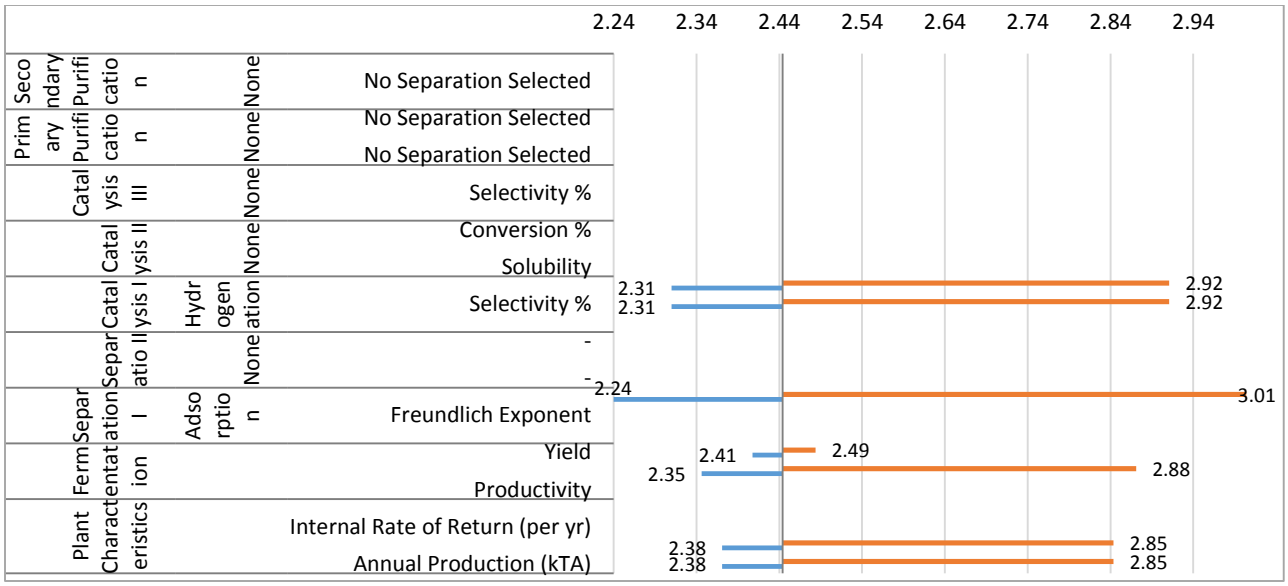

Figure 25 Tornado Plotting – GHG Emissions

Conclusion

BioPET has been reorganized as ESTEA, to make it clearer, simpler and easier to understand. ESTEA has new additions including: Fermentation parameter analyses, Tornado plotting, Radar charts, Hypothetical model, and Life cycle assessment of greenhouse gas emission estimation calculations. These new changes have evolved BioPET to an Early Stage Techno Economic Analysis - ESTEA tool. ESTEA has been validated through existing model comparison and with BREW project. We also worked on hypothetical model analysis in order to infer "rules-of-thumb on relationship between key process parameters and MESP. These are described in detail in the following chapter. Though ESTEA is incapable of replacing superior cost estimations models like SuperPro and Aspen cost estimator due to level of detail these software programs could provide, it finds a specific place at early stages of process development.

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CHAPTER 3. UNDERSTANDING THE LINKAGES BETWEEN FUNDAMENTAL PROCESS PARAMETERS AND PRODUCT COST IN JOINT FERMENTATIVE/CATALYTIC PROCESS SYSTEMS: A MODELING APPROACH

A paper to be submitted to *Journal of Cleaner Production*

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Introduction

Economic models can illuminate the effect and influence of numerous elements in a complex process chain. Furthermore, models can allow the sensitivity of the overall process to specific elements can be discerned, thereby allowing an understanding of how uncertainties in process parameters might influence operation of the process. Building on the efforts of Claypool and Raman (2013), Viswanathan and Raman developed ESTEA (Early Stage Techno Economic Analysis) as a second-generation, in-house, Microsoft Excel-based model. This model allows estimation of the cost and greenhouse gas impacts of making chemicals via fermentation of a bio-derived feedstock, followed by catalysis of a fermentatively produced intermediate. There are existing rules of thumb on scaling and designing processes, including equipment factors, estimation methodologies, design

concepts, sizing guidelines of process vessel and piping, and such that can be used to inform process engineering (Woods, 2007; Hall, 2012; Dysert, 2003). The primary goal of this work is identify patterns in the parameter-cost- space that suggests overarching design principles. That is, we sought to discern and explain simple generalizations, or "rules-of-thumb" regarding the relationship between key process parameters and cost estimated.

Materials and methods

Early Stage Technoeconomic Analysis Tool (ESTEA):

Strong technoeconomic analysis capabilities exist in commercially available process modeling softwares such as Aspen Economic Analyzer and Intelligen SuperPro Designer, both of which provide estimations of capital and operating costs. However, both these tools also require a level of detail regarding process configuration and parameter values typically unavailable at early stages of process evaluation. The spreadsheet-based BioPET model was created to overcome this challenge by providing an explicit early-stage technoeconomic analysis tool for fermentative-catalytic processing schemes (Claypool and Raman, 2013). Ease of use and minimal data input for process evaluation were the key criteria used in the development of BioPET. As described in Viswanathan et al., 2014, ESTEA is a refinement of BioPET, which includes simplified data flow, additional sensitivity and graphical analyses capabilities, a self-contained reference section for every unit operation, and additional separation process capabilities. ESTEA also provides an estimate of greenhouse gas emissions associated with the production of the target biorenewable chemical.

Hypothetical fermentative-catalytic process

In this paper we modeled a hypothetical process in ESTEA and performed multiple analyses to understand the dependence of MESP (Minimum Estimated Selling Price) on specific process parameters. The hypothetical process assumed is shown in Figure 1. Table 1 include plant characteristics and Table 2 include process specific input parameters used for hypothetical process modeling in ESTEA. Sugar from corn grain, priced at $0.30 serves as the feedstock. A plant size allowing the production of 30 kilo tonne per annum (kTA) while operating for 330 days a year is assumed process. Feedstock is fermented, producing an aqueous beer containing the intermediate product. Immediately after fermentation, the beer is subjected to separation involve solids removal through centrifugation and excess water removal through a simple distillation column. For simplicity, we assume complete solids removal from the broth during centrifugation. To concentrate the feed before catalysis, we assume approximately 60% of water is removed in distillation column. Concentrated broth along with Hexanol as solvent, is set as feed to the catalysis process, that converts the intermediate product to the desired product – which we refer to as hypothetical chemical (HYC) in the presence of Ni-Raney as catalyst. The HYC produced is crystallized and dried during the final purification process.

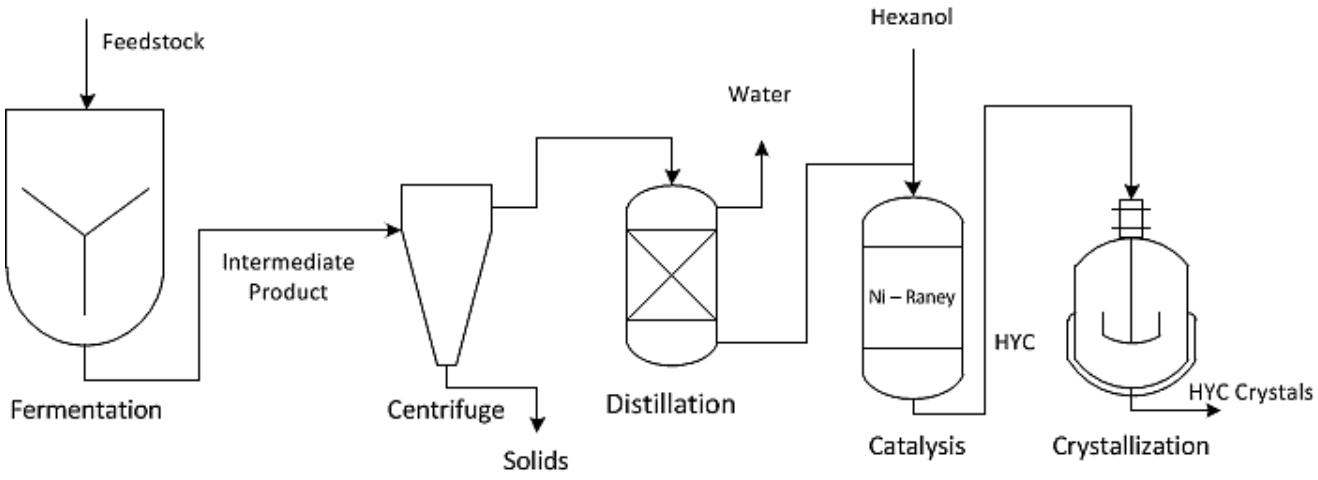

Figure 26 *Process flow diagram illustrating feedstock in, fermentation, centrifugation, adsorption, catalysis and purification.*

The following Table represents assumed ESTEA Unit Operations and their parametric values for the hypothetical model

Table 10 ESTEA's base-case assumed plant properties for HYC process modeling

Parameter	Value
Feedstock Price	$0.30/kg
Feedstock Type	Corn Grain
Lang Factor	6
Annual Production (kTA)	30
Operating days (per yr.)	350
Internal Rate of return (per yr.)	10%
Plant operating life (yr.)	10

Table 11 ESTEA's base-case unit operations and respective parametric values

Fermentation	*Extra – Cellular Product*
Productivity (g/L/h)	2
Titer (g/L)	60
Yield (kg/kg)	45%
Separation	*Distillation*
Relative Volatility	10
Product Purity	0.70
Yield	95%
Catalysis	*Hydrogenation*
Catalyst Metal	Ni – Raney
Solubility	5%
Selectivity	90%
Conversion	95%
Purification	*Crystallization*
Relative Volatility	10
Purity	0.7
Yield	95%
Solvent I	*Hexanol*
Solvent: Aqueous Ratio	0.8
Solvent Density (kg/m^3)	867
Solvent Cost ($/kg solvent)	$0.99
% Solvent Recovered	95%
Hexanol Feed Stage	Catalysis1
Hexanol Recovery Stage	Purification1

Feedstock – fermentation and plant size influence on MESP

ESTEA calculates feedstock requirement based on fermentation specifications. Feedstock requirement is calculated as shown in equation 3:

$$\frac{\text{Titer}}{\text{Yield}} \text{ *Annual Batches *Usable fraction of Fermenter *No. of Fermenters *Fermenter Size} \quad (3)$$

To understand the impact of fermentation parameters, we performed a sensitivity analysis for fermentation parameters of productivity, titer and yield on fermentation cost,

feedstock cost and MESP. We simplified the base-case process to include only fermentation (no downstream processing). Other ESTEA input parameters used were from Table 1 and2.

The other analysis involves predicting plant size influence on MESP. This was done by varying plant capacity from 1kTA to 100kTA and observing the effect on MESP.

Process yield - MESP sensitivity analysis

To understand the impact of process yields and solvent recovery efficiency on MESP, twelve different cases covering a range of process conditions were explored. Specifically we used three levels of process conditions as follow: *optimistic*, assuming high yields/solvent recovered for unit process, *pessimistic* with poor yields/solvent recovered (but still potentially in the realm of economically viable) for all, and *intermediate* using yields/solvent recovered between the *optimistic* and *pessimistic* cases. Table 3 describes the *optimistic*, *intermediate*, and *pessimistic* yields/percent solvent recovery used in this model. We assumed that four unit operations comprised the process (fermentation, separation, catalysis, purification), and we included a solvent unit, making five total devices. We then modeled the impact of a single device operating at optimistic or pessimistic conditions while holding all other devices at base-case conditions. Along with a base case with parameters as on original design and a best case with optimistic values for all unit processes, we modeled 12 cases. These and their corresponding case IDs are shown in Table4For each cases, cost contribution from raw material consumption and unit processes are measured. The sensitivity of MESP for all 12 cases is expressed as a

sensitivity coefficient, that is the as ratio of percentage change of MESP to percentage change in the input parameter. This analyses was done on VBA coding and excel formula.

Table 12 Optimistic, Intermediate and Pessimistic condition values assumed to perform all analyses

Process	Optimistic	Intermediate/Base Case	Pessimistic
Fermentation	49%	45%	40%
Downstream	99%	95%	90%
Solvent Recovery	99%	95%	90%

**Downstream involves separation, catalysis and purification unit operations.*

Table 13 Process Yield - MESP Sensitivity Analysis

Process scenarios – parametric values to measure MESP and later sensitivity

Case ID	Case	Parameters: Yield – Unit Processes/Recovery - Solvent				
		Fermentation	Separation	Catalysis	Purification	Solvent
1	Base Case	45%	95%	95%	95%	95%
2	Fermentation Strong	49%	95%	95%	95%	95%
3	Fermentation Weak	40%	95%	95%	95%	95%
4	Separation Strong	45%	99%	95%	95%	95%
5	Separation Weak	45%	90%	95%	95%	95%
6	Catalysis Strong	45%	95%	99%	95%	95%
7	Catalysis Weak	45%	95%	90%	95%	95%
8	Purification Strong	45%	95%	95%	99%	95%
9	Purification Weak	45%	95%	95%	90%	95%

Table 13 continued

10	Solvent Rec Strong	45%	95%	95%	95%	99%
11	Solvent rec Weak	45%	95%	95%	95%	90%
12	Best Case	49%	99%	99%	99%	99%

Cost analysis

We performed another analysis to predict the average 'MESP changer per unit operation' for a process. This analysis was sought to understand, *how the MESP increases on adding a unit operation (*under *optimistic*, *intermediate*, and *pessimistic conditions).* Every case was generated by adding a unit operation to its previous case. Thereby we generated 9 cases of increasing number of unit operations in the order of *n+*1, (n= number of unit operation in the previous case) as represented in Figure 2. From Figure 2, *Case 1 ->* Fermentation only; *Case 2 ->* Fermentation + Separation I; *Case 3 ->* Fermentation + Separation I + Hydrolysis I, and so on. These cases were then tested using *Optimistic, intermediate and pessimistic* assumptions previously described. Figure 3 elaborates the analyses as: 9 different cases tested under 3 different conditions to provide 27 different scenarios. A key observation from prior parts of this work was that MESP was highly sensitive to solvent For this reason, the optimistic case assumed *no solvent use*, the intermediate case assumed *99%* solvent recovery per unit operation, and the pessimistic case assumed *95%* solvent recovery per unit operation

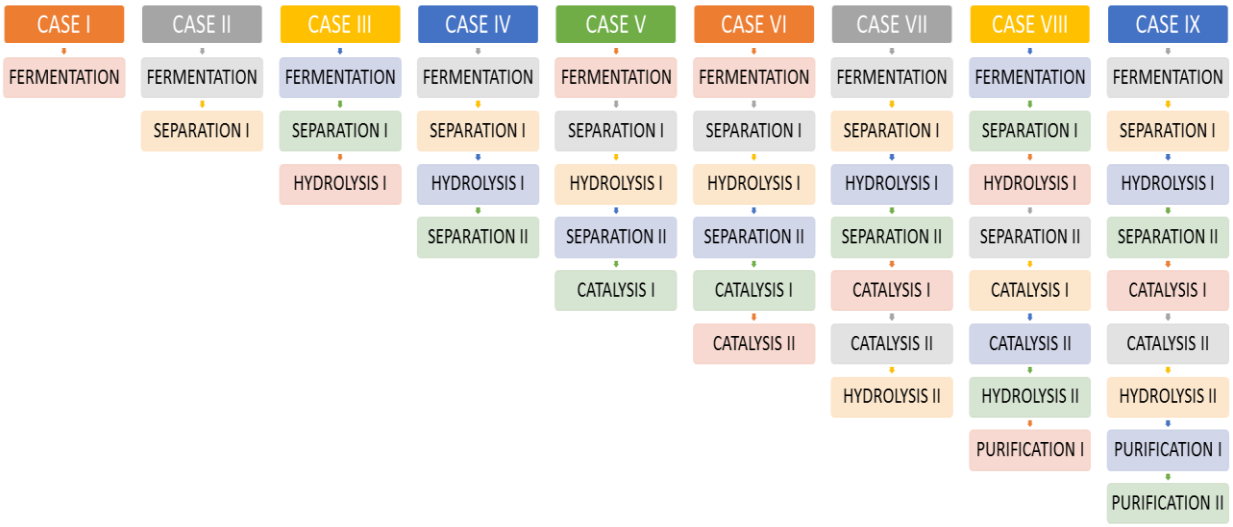

Figure 27 Representation of sequential unit operations addition from Case I through IX

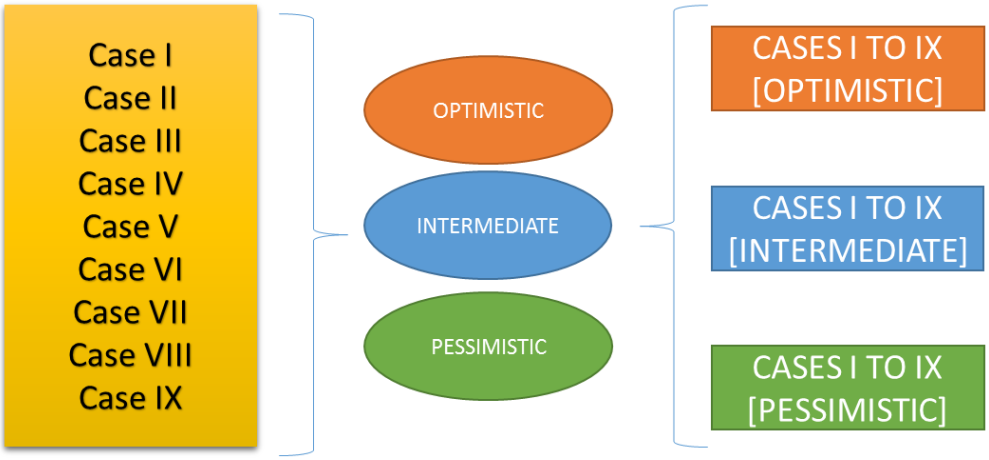

Figure 28 Cases and Conditions to generate cost analysis modeling

Results and discussion.

Using base-case values, ESTEA predicted MESP HYC$1.83/kg. As illustrated in Figure 5, raw materials including solvent hexanol and feedstock together form 60% of MESP, 15% of MESP accrues from fermentation, maintenance and other costs are 12% of

total costs, and downstream processing including separation, catalysis and purification form 14% of the total cost. Comparing this price to the prices of other high-volume commodity chemicals (Figure 4), suggests that under the given process assumptions, the fermentative-catalytic process is relatively expensive compared to ethanol, positioning at the start of $2.00/kg products such as Caprolactam, Butanediol, Acrylic acid.

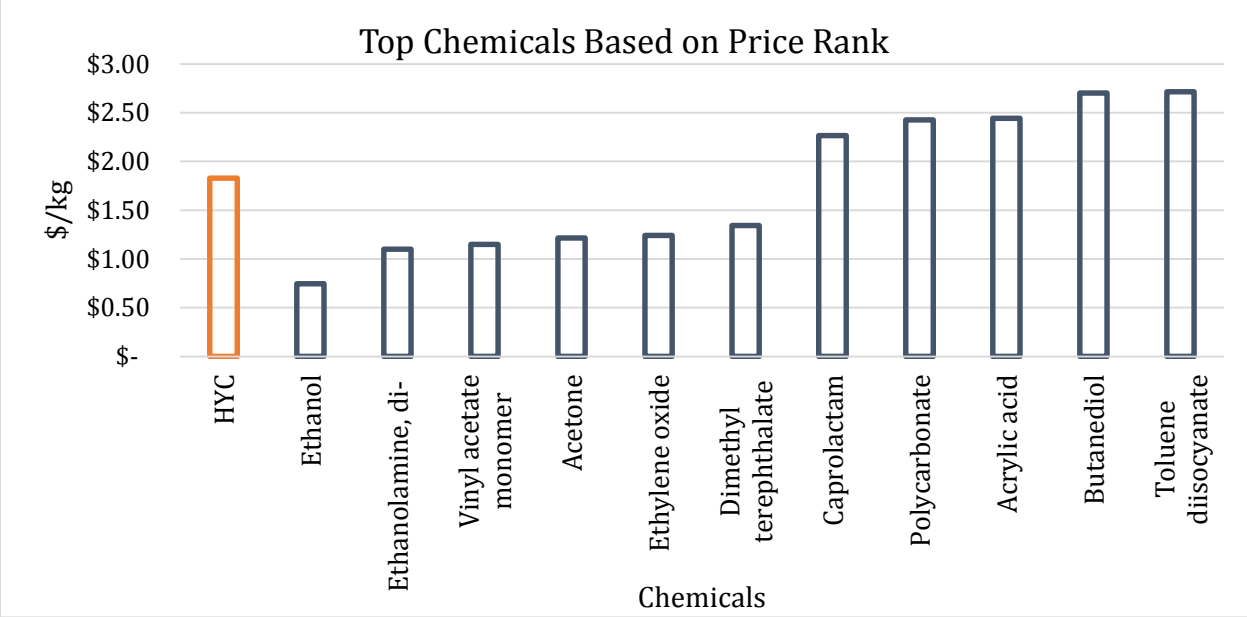

*Figure 29 Cost comparison between estimated MESP of HYC vs Top Chemicals Based on Market price ($/kg)**

**The estimated market price of all chemicals are derived from Lux Research – CBiRC_Top Chemicals_May 2013. Which are based on multiple reports*

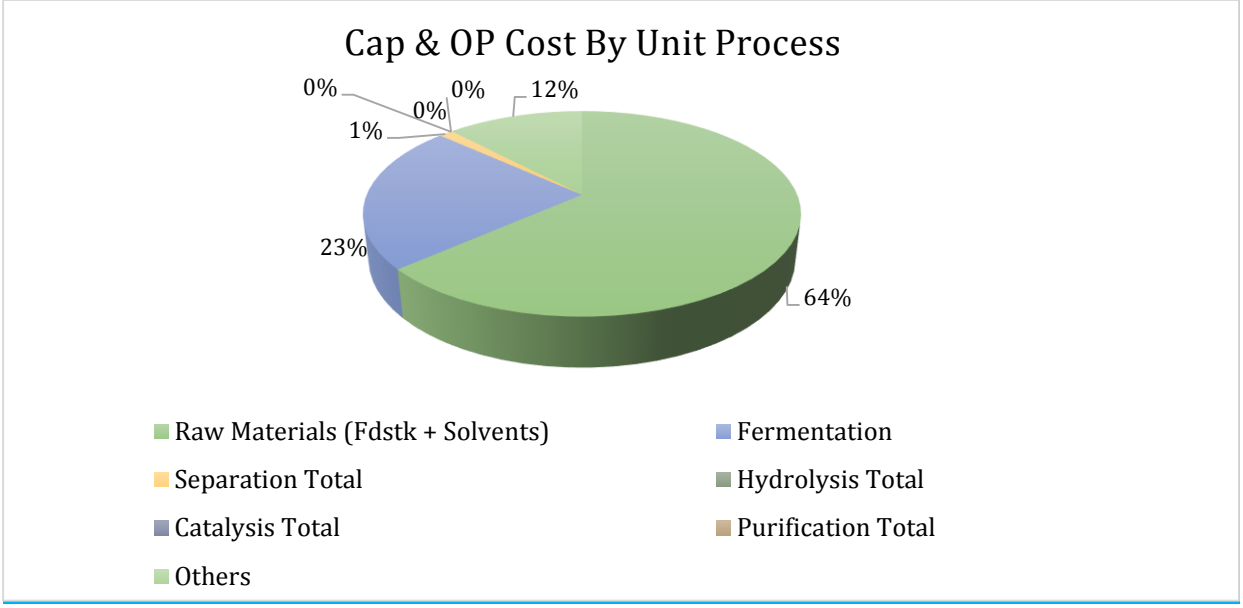

Figure 30 Capital and Operating Cost Distribution by Unit Processes

Fermentation, feedstock – MESP and plant size – MESP sensitivity analysis results

MESP dependence on plant size is studied by generating 100 values from 1kTA per annum to 100 kTA plant size, corresponding MESPs are measured. Figure 6 illustrates the impact of plant size on MESP using a semi-log plot. Fitting a power trend line to these data shows that the scaling = 0.72; this value is higher than the conventional 0.6 often used for chemical processing plants, and may reflect the inherent higher complexity of joint fermentative-catalytic processes

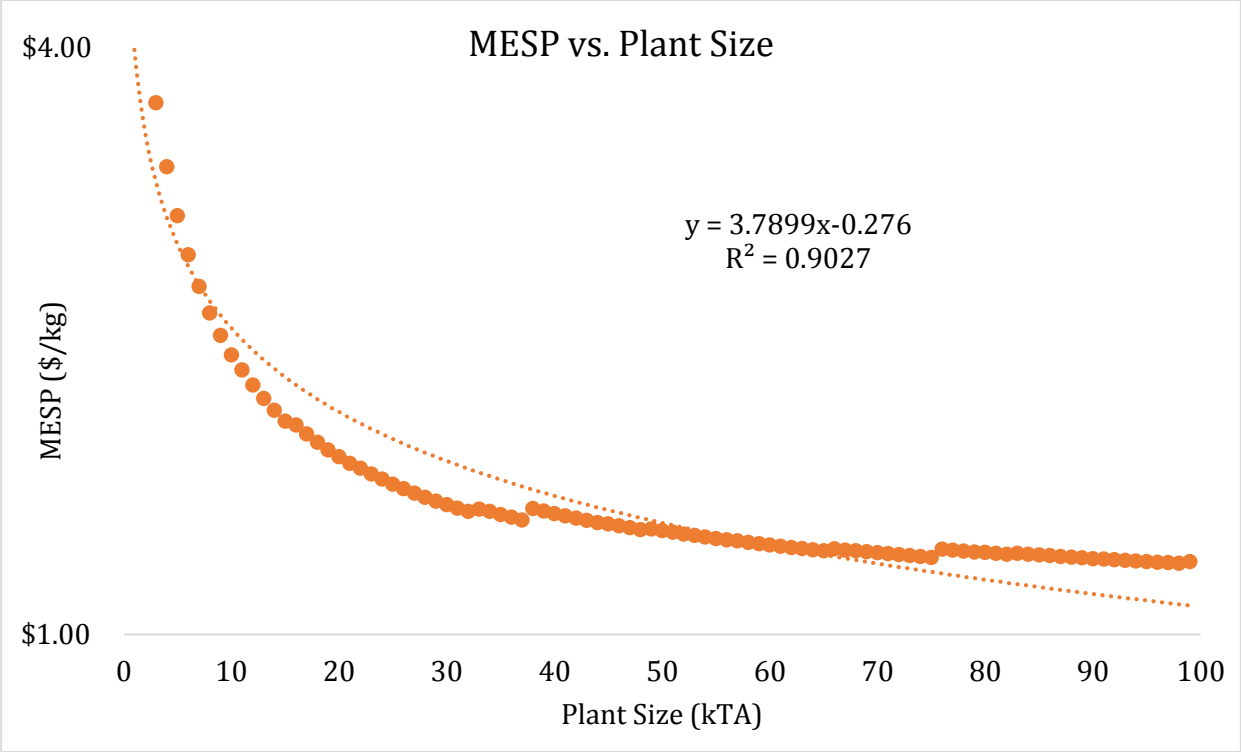

Figure 31 Influence of plant size (kTA) on MESP showing rapid decrease in MESP between 5kTA – 40kTA and gradual saturation after 70kTA

Figure 7 shows the sensitivity coefficients of feedstock cost, fermentation cost, and MESP on key critical, of three fermentation input parameters. The leftmost graph shows that only yield influences feedstock requirement– this is unsurprising since only yield ultimately impacts the total feedstock requirement; the other parameters influence reactor sizing and solvent requirements in various ways. . The rightmost part of Figure 7 shows that MESP is most influenced by yield in this model, suggesting that metabolic engineering prioritize yield over titer and productivity (although these are often linked).

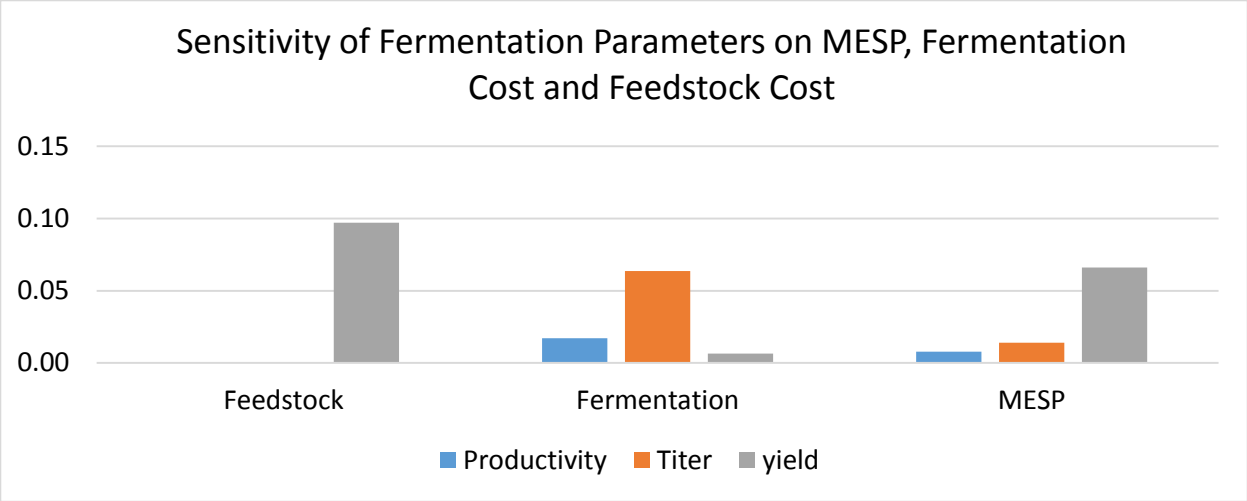

Figure 32 Sensitivity Coefficients of Feedstock Cost, Fermentation Cost, and MESP to Fermentation Parameters – Productivity, Titer, and Yield

Process Yield – MESP sensitivity analysis results

Process yield – MESP sensitivity analysis is performed using earlier discussed Table 1 and 2 input values. Figures 8 represent calculated percentage cost contributions from raw materials consumption and unit processes employed. It may be observed that optimistic cases have lower MESPs than base case, which are represented by *dips* and pessimistic cases having higher MESPs represented by *peaks*. Figure 9 represents measured values of Sensitivity Coefficients for unit process percentage yields or solvent recovered across all 12 Cases. Certain observations on costs distribution across cases include:

- Raw materials dominate costs irrespective of case. On average, 60% of costs is through raw materials consumption
- Fermentation costs were on average 15% of MESP. The interesting fact is, for a few case comparisons between their optimistic and pessimistic conditions such as fermentation strong/weak, percent solvent recovered strong/weak, the

reduction/increase in feedstock required is balanced on other end by the fermentation cost

- Solvent recovery is an essential factor of consideration.as discussed before, solvents and feedstock form 60% of MESP. From Figure 9, irrespective of cases, sensitivity coefficients measured for solvent recovery are higher than other process parameters
- Looking into percent cost distribution for optimistic and pessimistic conditions for solvent recovery, losing high solvent makes the process most expensive than any other yield loss. On the other hand, maximum solvent recovery at 99% provides MESP close to the best case value. This illustrates that, if solvent are employed, recovery of them are highly important as they are highly cost deciding factors

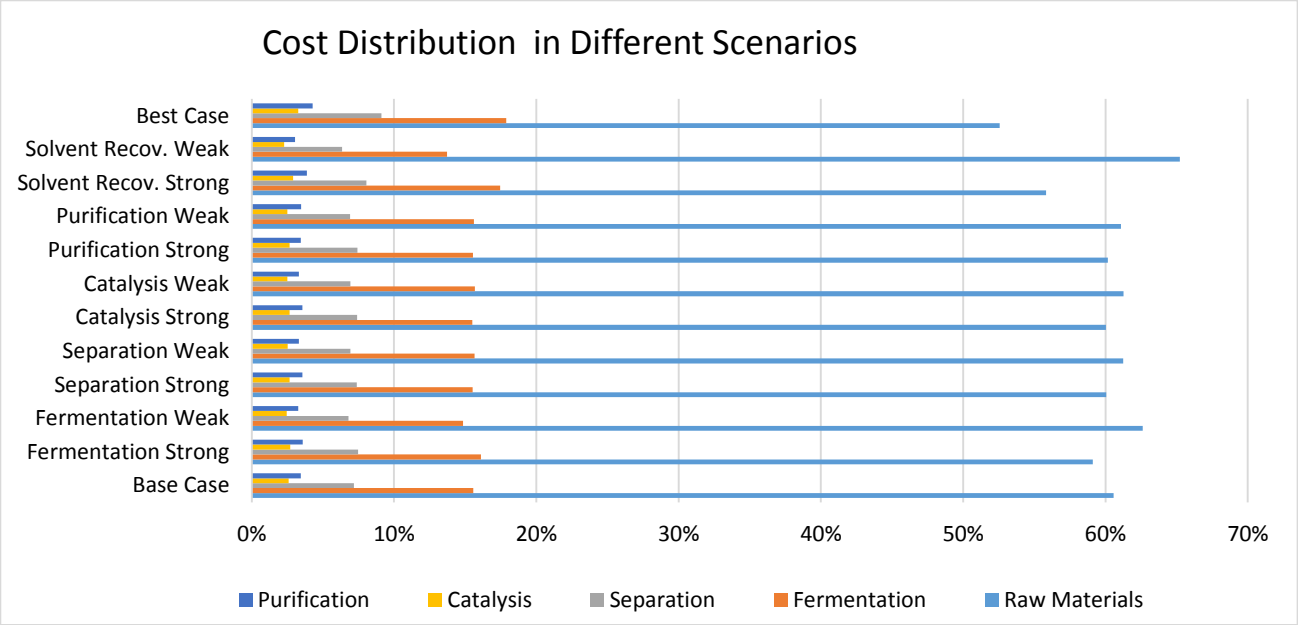

Figure 33 Case wise Cost Contribution by Unit Processes (In terms of percentage of cost)

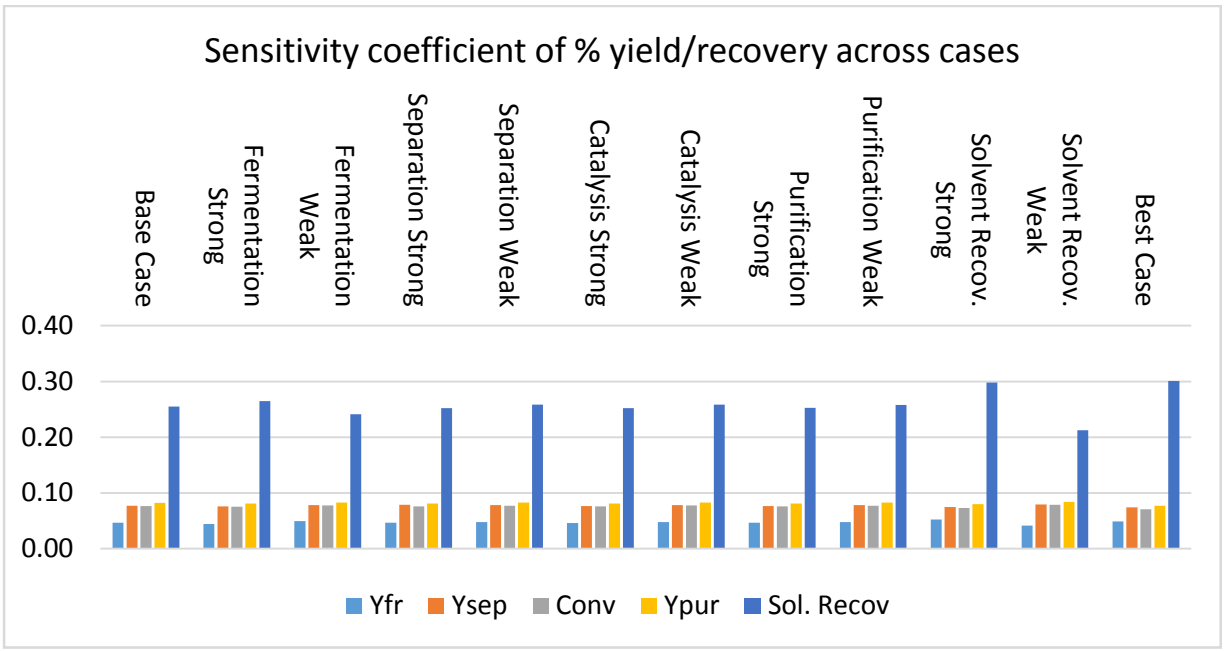

Figure 34 Measured values of Sensitivity Coefficient for Unit Process Percent Yields/Recovery Across all Cases

Cost analysis results

Figure 10 shows how MESP varies with the number of unit operations under different parameter scenarios. The three linear fits were made to the MESP for optimistic, intermediate and pessimistic conditions, with increasing number of unit processes as case ID. The linear regression of MESP on case ID, yielded R^2 values greater than 94% for all three conditions; a surprising level of linearity. The slope of the linear regression equation can be interpreted as the average additional cost per unit operation. From this, we can see that a "pessimistic" system, incurs an average offset of $1.23/kg and slope $0.18/kg, while an "optimistic" system has $0.94 as offset and $0.08/kg as slope. Interestingly this latter value corresponds closely to a rule of thumb of "five cents per pound per unit operation" that is sometimes used in industry (Shanks, pers. Comm. 2015). Another key observation include; complex process having nearly 9 downstream processes will have MESP per unit operation for optimistic case at $0.08 cents/kg and it rises to $0.18/kg for a pessimistic unit process.

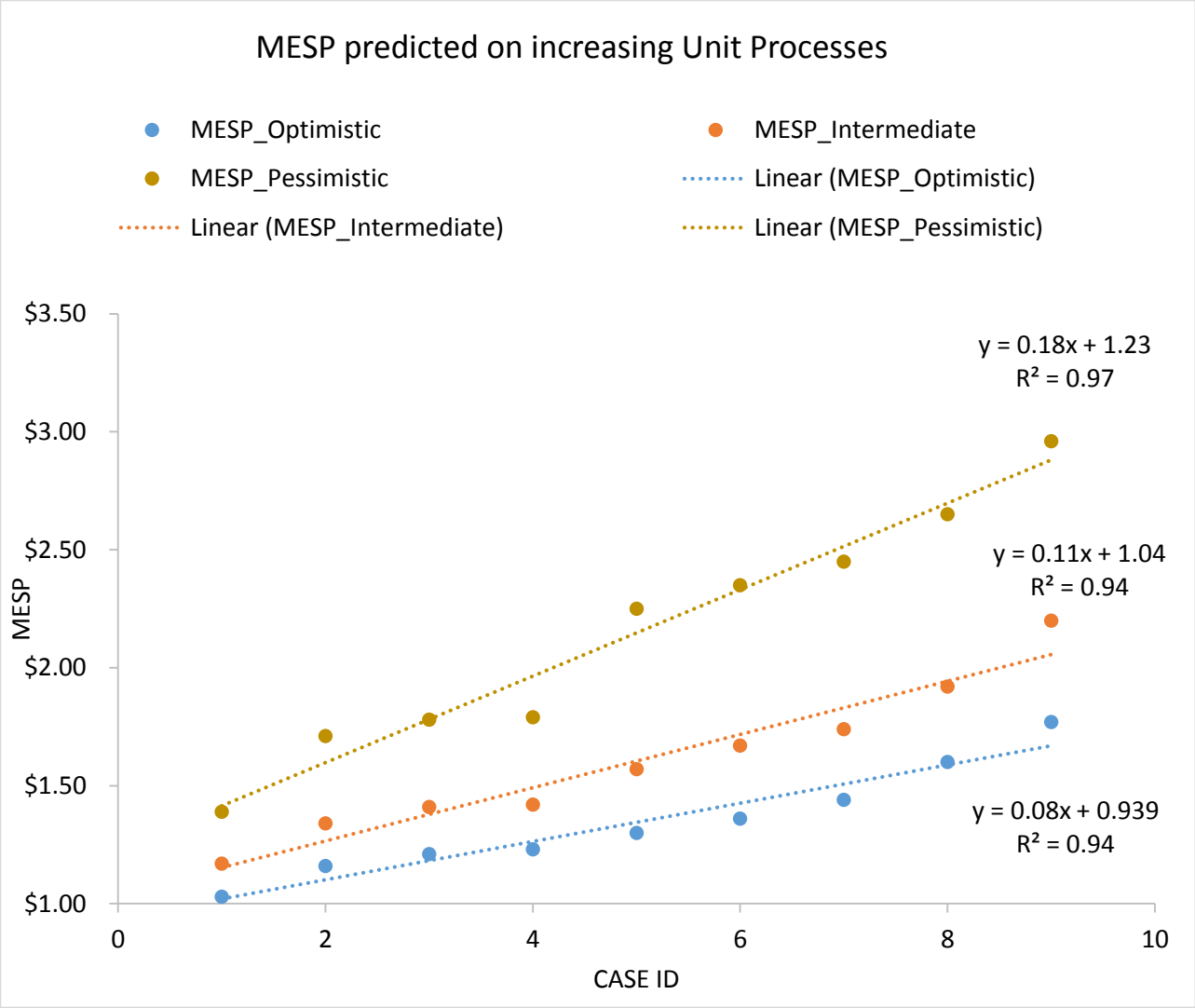

Figure 35 ESTEA-estimated MESP on Increasing Number of unit Processes (refer to Figure 2 for details), on optimistic, intermediate and pessimistic conditions of process yields

Rules of thumb

The results above suggested several possible rules-of-thumb that are applicable to a broad range of fermentative-catalytic process streams. These rules can be taken to be easily-implemented, coarse estimates of product cost that can be used to help guide early-stage decision making regarding fermentative-catalytic processes. These are as follow:

- Feedstock (glucose) costs will typically account for at least half of total costs of production.
- Solvent can increase raw material costs by 4-13% (99% - 90% solvent recovery).
- Additional unit operations will add between $0.08 and $0.18/kg to product cost.

Conclusion

In this work, we derived simple generalizations regarding relationships between key process parameters and cost of the product. We modeled a hypothetical fermentative – catalytic process producing a bio-based product. We worked on several analyses to predict relationship between MESP and key process parameters are studied. Certain combinations of key parameters were discusses to provide insight into the generalized cost structure of biorenewable chemicals. We also worked on fermentation – feedstock costs dependence on fermentation parameters and studied their sensitivity on MESP. We also worked on deriving MESP per unit operation operated. This effort is then translated into a series of key “rules of thumb” for biorenewable chemical production, illustrating ranges of key parameters needed to achieve certain cost goals.

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CHAPTER 4. GENERAL CONCLUSIONS

Though early-stage technoeconomic evaluation is necessary to understand the progress of research and development of joint fermentative-catalytic processes at early stages, they remain poorly explored. In this work, we modeled a cost estimation tool specific to biorefinery processes, performed multiple analyses and developed several rules of thumb. In chapter 2, we reorganized BioPET as ESTEA in order to make it clear, simpler and easier to understand, and also to add in analyses based on fermentation, charts such as Tornado plotting, Radar charts, Hypothetical modeling. We included a greenhouse gas emissions estimation as a primitive block. Major changes have been made to labor cost calculations, BioPET's primitive mass balance has been replaced by a full-fledged component flow balance in ESTEA. Cost calculation corrections have been made to catalysis modeling, hydrolysis unit operation, solvents and excess water addition are key additional work done to ESTEA. Separate inventories have been created for parameters related to process calculation, labor calculation and cost calculation. The second part of chapter 2 involves validation of ESTEA. GHG emissions block was validated with BREW project for different feedstocks. Process design for three different Biobased chemicals were modeled. These models were validated with existing models from BioPET and SuperPro. The validation predicted a 10% deviation for ESTEA's results from SupePro's numbers.

Using ESTEA as described in chapter 2, in chapter 3 we derived certain rules of thumb for cost estimation based on key process parameters. We assumed a hypothetical fermentative – catalytic process and modeled it in ESTEA. We ran on a handful of analyses in ESTEA through VBA coding and excel based formulas. The effect of unit process yields,

fermentation parameters such as productivity, titer, yield and operating plant capacity on MESP measured is studied for the hypothetical process. Through these studies, derived cost exponent for plant size, fermentation – feedstock cost relationship, sensitivity of process yields/solvent recovery, and $/kg/Unit operation for optimistic, intermediate and pessimistic process conditions. With the above results, we derived certain rules of thumb to be considered while modeling a fermentative-catalytic process.

Overall, ESTEA has been modeled as a platform to evaluate biobased products. ESTEA is capable of providing results more accurate than its predecessor (BioPET) along with primitive GHG estimations, various analyses and charts to explore process parameters and cost estimations that shall provide insight of the processes.

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