From Waste to Wonder: Bacterial Synthesis of 1,3-Propanediol from Crude Glycerol

Homework Assignment #4
CHE397 – Senior Design II

Ayush Patel
Thanh Nguyen
Jesse Anderson
Andres Rodriguez-Castro
Abdul Hamideh

Mentor: Dennis O'Brien

Table of Contents

Project Charter **4**
Design Plan **5**
Diversity, Equity, and Inclusion (DEI) Statement **5**
Executive Summary **6**
Introduction **6**
  Problem Definition and Significance 6
  Market Analysis 8
    Supply-Demand Analysis 8
    Global Share/Value Chain 8
    Pricing of Raw Materials and Products 9
    Business Plan 12
  Judging Criteria 13
  Sustainability 13
Process Description **15**
  Competing Processes 15
    DuPont (Degussa) Acrolein-Based Catalytic Hydrogenation Process 15
    Shell Chemical Co. One-Step Hydroformylation of Ethylene Oxide Process 16
  Chosen Process 18
    Chemistry of the Process 18
    Process Description 21
    Alternatives to the Chosen Process 27
  Operating Conditions and Assumptions 28
  Process Control 29
    Seed Fermentation 29
    Main Fermentation 31
    Centrifugation 32
    Ultrafiltration 32
    Reverse Osmosis 33
    Distillation 34
      T-102 P&ID 35
  Process Safety Analysis 36
    HAZOP Analysis 36
      HAZOP T-102 P&ID 41
    Operational Safety Analysis 43
    Environmental Analysis 45
      Air Emissions 45
      Water Discharges 47
      Solids Waste 47
    Material Safety 47

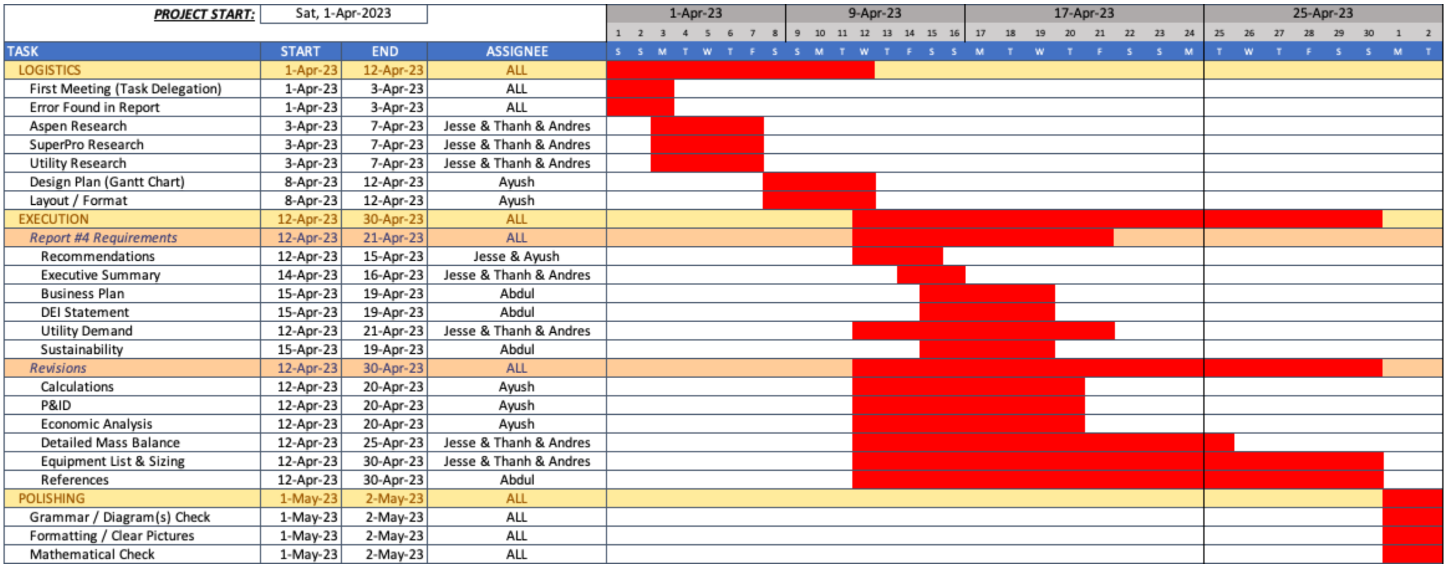
Process Economics Analysis 53
    Inside Battery Limits (ISBL) 53
    Outside Battery Limits (OSBL) 53
    Fixed Capital Cost 54
    Contingency 54
    Engineering Cost 54
    Working Capital 55
    Total Capital Cost 55
    Variable Cost of Production (VCOP) 55
    Maintenance Cost 56
    Fixed Cost of Production (FCOP) 56
    Revenue 57
    Simple Payback Time 58
    Return on Investment (ROI) 58
    Gross Margin 58
    Gross Profit 59
    Net Present Value (NPV) 59
    Discount Cash Flow Rate of Return (DCFROR) 61
    Sensitivity Analysis 61
Recommendations 62
Appendix 64
Design Basis 64
Block Flow Diagram (BFD) 65
Process Flow Diagram (PFD) 66
Detailed Mass Balance 74
Equipment List & Sizing 81
Sample Hand Calculation 88
    Distillation Column – Hand Calculation 88
    Distillation Column – Aspen Data 90
    Analysis: Hand vs. Aspen 91
    Liquid Ring Pump Calculation 92
Utility Demand 93
    Recycle 94
    Cooling Water 94
    Steam 95
    Electricity 95
    Nitrogen 96
    Utility Sourcing 97
Process Economics Analysis Data 97
References 113

Project Charter

Title	Goal	In Scope	Out of Scope
Proposal Report $^{\#}$4	The primary objective of this report is to refine and enhance our previous findings by incorporating feedback from mentors and the professor, ensuring that our analysis accurately reflects the current state of affairs. To achieve this, we will augment the report with three essential sections. Firstly, an executive summary will provide high-level executives with a concise overview of the market analysis, production quantity, plant location, cost analysis, and key recommendations. This tailored section aims to convey pertinent information to those without extensive technical process knowledge. Secondly, the recommendations section will deliver our overall conclusion regarding the proposed process. This includes highlighting any concerns, stating whether we endorse moving forward, and elaborating on uncertainties, risks, and potential future steps. Lastly, the report will conclude with a comprehensive evaluation of the plant's utilities demand, ensuring that all energy requirements are clearly outlined and finalized.	1. Correction and update of previous reports based on mentor and professor feedback 2. Executive summary: a. Brief market analysis b. Amount of product c. Plant location d. Cost analysis e. Recommendations 3. Recommendations section: a. Process concerns b. Endorsement or disapproval of moving forward c. Uncertainties and risks d. Future steps 4. Utilities demand: a. Finalization of the utility demand for the entire plant	1. Experiment with different materials of construction to determine their benefits. 2. A robust analysisof the utility demand. 3. Carbon Capture/Nitrous Oxide Scrubbing. 4. Heat Exchanger Network (HEN) design.

Deliverables	Team Members
• Project Charter • Design Plan • Executive Summary • DEI Statement • Business Plan • Sustainability • Recommendations • Finalized Utility Demand • References	Ayush Patel Thanh Nguyen Jesse Anderson Andres Rodriguez-Castro Abdul Hamideh

Design Plan



PROJECT START: Sat, 1-Apr-2023

TASK	START	END	ASSIGNEE
LOGISTICS	1-Apr-23	12-Apr-23	ALL
First Meeting (Task Delegation)	1-Apr-23	3-Apr-23	ALL
Error Found in Report	1-Apr-23	3-Apr-23	ALL
Aspen Research	3-Apr-23	7-Apr-23	Jesse & Thanh & Andres
SuperPro Research	3-Apr-23	7-Apr-23	Jesse & Thanh & Andres
Utility Research	3-Apr-23	7-Apr-23	Jesse & Thanh & Andres
Design Plan (Gantt Chart)	8-Apr-23	12-Apr-23	Ayush
Layout / Format	8-Apr-23	12-Apr-23	Ayush
EXECUTION	12-Apr-23	30-Apr-23	ALL
Report #4 Requirements	12-Apr-23	21-Apr-23	ALL
Recommendations	12-Apr-23	15-Apr-23	Jesse & Ayush
Executive Summary	14-Apr-23	16-Apr-23	Jesse & Thanh & Andres
Business Plan	15-Apr-23	19-Apr-23	Abdul
DEI Statement	15-Apr-23	19-Apr-23	Abdul
Utility Demand	12-Apr-23	21-Apr-23	Jesse & Thanh & Andres
Sustainability	15-Apr-23	19-Apr-23	Abdul
Revisions	12-Apr-23	30-Apr-23	ALL
Calculations	12-Apr-23	20-Apr-23	Ayush
P&ID	12-Apr-23	20-Apr-23	Ayush
Economic Analysis	12-Apr-23	20-Apr-23	Ayush
Detailed Mass Balance	12-Apr-23	25-Apr-23	Jesse & Thanh & Andres
Equipment List & Sizing	12-Apr-23	30-Apr-23	Jesse & Thanh & Andres
References	12-Apr-23	30-Apr-23	Abdul
POLISHING	1-May-23	2-May-23	ALL
Grammar / Diagram(s) Check	1-May-23	2-May-23	ALL
Formatting / Clear Pictures	1-May-23	2-May-23	ALL
Mathematical Check	1-May-23	2-May-23	ALL

ALL Indicates: Ayush Patel, Thanh Nguyen, Jesse Anderson, Andres Rodriguez-Castro, Abdul Hamideh

Diversity, Equity, and Inclusion (DEI) Statement

"Cultivating a Culture of Inclusivity: Paving the Way for Diversity and Equity"

We are proud to be a leading manufacturer of 1,3 propanediol (PDO), an eco-friendly and versatile ingredient essential to the skin care and carpet textile industries. Our commitment to diversity, equity, and inclusion (DEI) transcends our workplace culture and permeates our products, services, and relationships with our valued customers. By collaborating with diverse suppliers and partners, developing innovative products for our diverse clientele, and providing exceptional customer service, we strive to foster a culture of empathy, understanding, and respect. Our dedication to supporting our customers in their own DEI efforts, sharing best practices and resources, and engaging in community outreach to create opportunities for underrepresented groups, further demonstrates our pledge to a more equitable and inclusive industry. By integrating our DEI values into every aspect of our business, we are dedicated to making a positive impact on the skin care and carpet textile sectors, and together with our customers and partners, we will pave the way for diversity and equity, creating a more inclusive, sustainable, and innovative future for all.

Executive Summary

1,3-propanediol (1,3-PDO) will be produced from a safe and non-pathogenic organism, *Lactobacillus Reuteri CH53*. This commodity chemical has a CAGR of 8.3%, indicating that this process will continue to make money for some time after plant erection. This product is used both as a feedstock for Polytrimethylene Terephthalate and the skin care industry. The projected production rate is 61,500 tons per year with a purity of 99.54%, resulting in an annual gross profit of $107 MM. Additionally, the project includes the sale of byproducts such as ethanol (99.99% purity), acetic acid (99.16% purity), and lactic acid (98.16% purity), which will generate additional revenue of $71 MM. After a plant life of 20 years, the project's Net Present Value (NPV) is estimated to be $266 MM, taking into account a tax rate of 29.75% and a discount rate of 14%.

It is recommended that further analysis into the exact cost of the bacteria be conducted and sampling of the resultant broth containing 1,3-PDO be analyzed for hazardous proteins to assess if the current degree of purification is adequate. The process can currently move forward however a benchtop scale assessment of the above is highly recommended to assess any potential irritants within the broth. If such irritants are found it may require one additional ultrafiltration unit. Additionally, the product colority may exhibit changes after distillation, if this colority is present it may necessitate an additional preprocessing step in which the broth will be desalinated.

Introduction

Problem Definition and Significance

The purpose of this design is to successfully fabricate a process that produces 1,3- propanediol via a biogenetic route over the existing petrochemical route. The traditional petrochemical route of synthesizing 1,3 propanediol (PDO), while not as widely used, involves the use of acrolein and a caustic acid-based catalyst used in the hydration reaction. Another popular petrochemical process that is still used is based on the hydroformylation reaction using a cobalt-iron or cobalt-iron-ligand catalyst and ethylene oxide. Additionally, it is prone to many side reactions. As a result, a biochemical route for this process is a more desired process considering that it will be capable of keeping up with the global market demands of 1,3-propanediol while minimizing the production of toxic chemicals. 1,3-propanediol is also a sustainable and beneficial compound to produce as it is used in a variety of industries. The market for this product is heavily invested in since it is widely used in applications such as cosmetics, PTT, cleaning products, etc [1]. PTT is one of the most important commercial polyesters and is used in fibers for carpets and textiles [1]. Therefore, 1,3-propanediol is a high-demand compound for these industries, meaning that this product will guarantee a profitable production process. Fewer toxic chemicals are emitted because in this biobased process, we synthesize 1,3-propanediol from a fermentation process. Fermentation is a metabolic process in which microorganisms such as bacteria convert carbohydrate (sugar) based compounds into alcohols and other organic compounds, resulting in less synthesized toxic chemicals. In the fermentation setup for this process, crude glycerol will be the main substrate that is synthesized into 1,3-propanediol as one of the byproducts in the fermentation broth. The broth is then moved into a series of separation steps to extract the desired product. The previous petrochemical processes have been phased out and nowadays PDO is manufactured using DuPont's proprietary bio-based process using an engineered bacteria strain of *E. Coli*. The fermentation process using this bacteria strain results in 1,3-propanediol as one of the products. This process presents several advantages over the petrochemical route;

however, the strain used runs the risk of being pathogenic (O antigen) and capable of mutations across time. Additionally, the *E. Coli* strain can create many side products such as saccharides, CO_2, proteins, ammonia salts of organic acids, 1-2-4 butanetriol, carbonyl compounds, and UV absorbers. Therefore, for this design project, the simple basis model by DuPont was redesigned with added optimization routes that were taken to improve the overall production of 1,3-propanediol. These include changes such as using a more optimal strain of bacteria that is anaerobic will lead to reductions in the carbon footprint of the process. Additionally, using a bacteria which is anaerobic and preferentially uses that pathway for cell division will yield fewer side products which in turn means less energy used for distillation leading to an overall less costly product. Other changes implemented involve using a different source of nitrogen for fermentation [2] and utilizing a set of hydrocyclone units to remove most of the biomass prior to ultrafiltration. These changes should lead to more economical and efficient production of 1,3-propanediol.

Market Analysis

Supply-Demand Analysis

Overall, the market for 1,3-propanediol is expected to grow in the coming years, driven by increasing demand for bio-based and sustainable products, but also facing some challenges such as cost and competition. The supply of PDO is largely dependent on the availability and price of the raw materials used to produce it, such as propylene and glycerol. Additionally, the cost of producing PDO can be affected by factors such as energy prices and the availability of technology for converting raw materials into PDO. Poly trimethylene-terephthalate (PTT) and skin care/cosmetics are the biggest user applications for 1,3 PDO. The graph below illustrates the growth of PTT in market size, which results in a higher demand for 1,3 PDO.

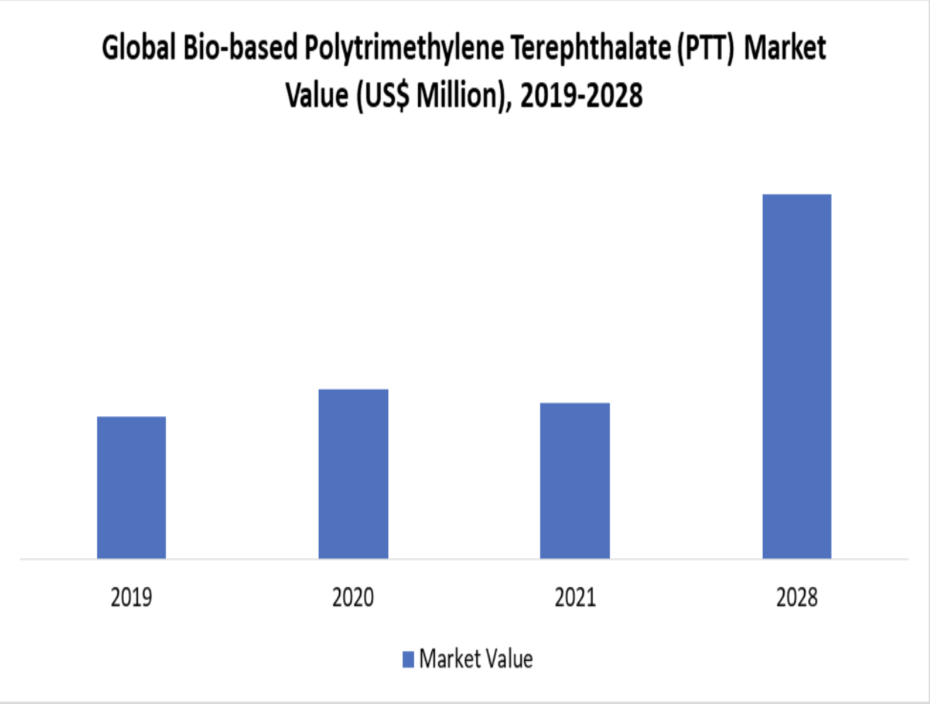


Figure 1 - Bio-based PTT Market Value [26]

Global Share/Value Chain

Market analysis is the most vital factor when considering an idea, product, or business model of choice. The reason is to provide hindsight if a product is worth funding and making capital from. If a positive market is present regarding your product, then it might be prosperous. However, if a product has a negative market, then one might consider neglecting it, as it will potentially fail. 1,3-Propanediol (PDO) is a chemical compound that is used in a variety of industrial and consumer products, including industrial and institutional care (deicing solutions) and personal care items. The market for 1,3-propanediol is driven by its increasing use in a variety of applications, including the production of Poly-trimethylene-terephthalate (PTT), polyesters, and polyurethanes as well as other industrial chemicals. Fortunately, there is a positive trend in the 1,3 PDO market globally. With a global market size of $398.0 MM (2022) [60] and a market volume of 146,000 MT/Yr [18]. 1,3 PDO is projected to proliferate exponentially with a compound annual growth rate (CAGR) of 8.3% [19]. The following data will depict and illustrate the market of 1,3 PDO and identify its applications and how fruitful of a market it is.

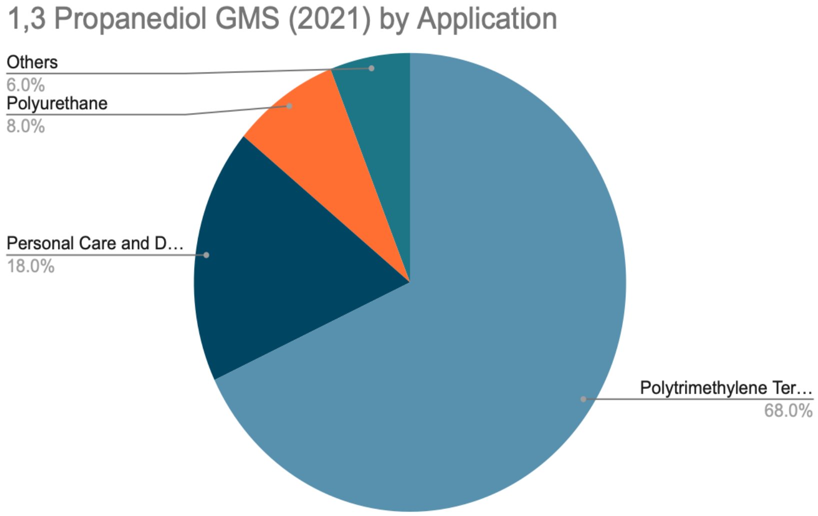


Figure 2 - Global Market Size for 1,3 Propanediol by Application (2021) [22]

Pricing of Raw Materials and Products

Raw materials are one of the most vital constituents to consider in a chemical process. Determining the choice of raw materials for the feedstock may influence how the process flows and how pure the end product is. There may be various manufacturers' producing the raw materials for your process. One must recognize the quality of the raw materials as well as the pricing. As for 1,3 PDO, the table below depicts the raw material pricing, and why specific raw materials were chosen over other alternatives. As for the pricing of the final product, 1,3 PDO is priced at a staggering $2180/MT [18].

Table 1 - Raw Material/Product Market Value [8], [9], [27], [28]

Material	Cost	Unit
Corn Steep Liquor (CSL)	200	$/ton
Crude Glycerol	170	$/ton

Sodium Hydroxide (NaOH)	492	$/ton
Dextrose	867	$/ton
Water	1.0265	$/ton
H_3PO_4	269.6	$/ton
Sulfuric Acid (H_2SO_4)	260	$/ton
Liquid Nitrogen	1623	$/ton
1,3 PDO	2180	$/ton
Ethanol	998	$/ton
Acetic Acid	1180	$/ton
Lactic Acid	1181	$/ton

Due to its availability, affordability, and high carbohydrate content, which can be hydrolyzed into sugar and fermented to make 1,3 PDO, originally corn stover was going to be our feedstock for the generation of 1,3 PDO. Corn stover is a renewable resource and may be used in place of fossil fuels to produce biofuel. Using it as a feedstock in the 1,3 PDO process can aid in reducing emissions of greenhouse gasses [12]. While using corn stover is preferable, the process is subject to a variable supply of corn stover which is economical to use. In a 2009 study, researchers at Purdue showed that the cost curve for corn stover increases exponentially after a certain point. Additionally, upon receipt the percentage of moisture or ash may make a particular batch very low quality or necessitate drying operations. Keeping this in mind, corn stover was kept out of the scope of this project due to our efforts were facilitated on generating PDO from *Lactobacillus reuteri* to compete with DuPont's *E. coli* process.

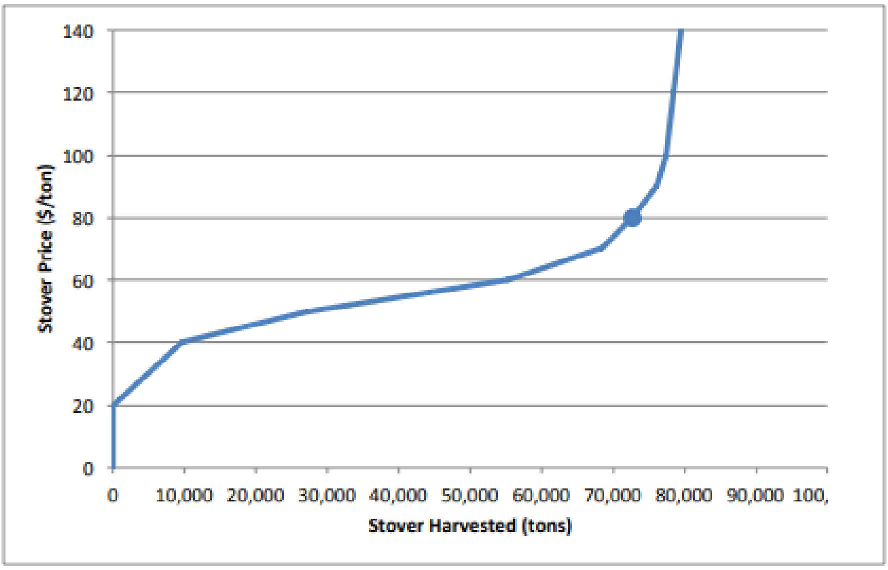


Figure 3 – Corn Stover Supply & Price Curve

Table 2 – Composition and Probability of High Quality Corn Stover

Category	Moisture	Ash	Penalty	Probability
Grade 1	<20%	<10%	\$0/ton	61.44%
Grade 2	≥20% & < 28%	<15%	\$8/ton	29.20%
Grade 3	≥28% & <36%	<15%	\$17/ton	0.83%
Grade 4	≥36%	>15%	100% price	8.52%

Corn steep liquor (CSL) is a nitrogen source needed for the increase in 1,3 PDO productivity and production. It has been employed as an essential source of organic nitrogen in the microbial fermentation of products including amino acids, polypeptides, and proteins because of its high organic nitrogen content [11]. Due to its high vitamin content, which significantly contributes to nutrition, CSL has also been used in the fermentation process as a nutritional and functional supplement. As a bulk agro-industrial by-product, CSL is significantly less costly than conventional nitrogen supplies like yeast extract and peptone, which are the major expenses in microbial fermentations. Thus, CSL is the optimal nitrogen source to use for the production of 1,3 PDO.

For the carbon source used, glycerol (crude) is a crucial raw material. Which is a by-product of biodiesel production. It is imperative to create sustainable crude glycerol production to increase the economic viability of biodiesel manufacturing. This has spurred numerous investigations [11] to determine how Lactobacillus might be used to produce a high-value product from crude glycerol.

As sulfuric acid (H_2SO_4), it was recognized to reduce the production of inhibitory compounds [10] during the pretreatment of corn stover with dilute H_2SO_4 (2%) to maximize sugar yield without the need for a detoxification step before fermentation.

Liquid nitrogen is substituted for gaseous nitrogen for economic advantages. Once expanded to a gaseous state, nitrogen is then used to purge the oxygen out to limit the aerobic metabolism of the *Lactobacillus reuteri* strain used in the process.

As one of the most affordable pH regulators, sodium hydroxide (NaOH) is used for maintaining pH levels when needed. Sulfuric acid is also used depending on how low/high the pH is detected. As for the chosen bacteria, *Lactobacillus reuteri CH53* or *L. reuteri CH53*, it is recognized as a safe and non-pathogenic bacterium that also increases the productivity of 1,3 PDO relative to other strains [11].

Sterilization and cleaning procedures in each fermentor will be carried out prior to and after the transfer of inoculum, respectively. The chemicals used in such operations are 0.5M Sodium Hydroxide, 20% w/w Phosphoric Acid and steam. These processes are absolutely essential to the continued operation of the bioreactors as any trace contaminants can cause mutations within our chosen strain of *L. reuteri* and/or limit the ability of the organism to metabolize carbon/nitrogen for its growth.

Who makes it now? And how much do they sell it for? There are a scarce amount of manufacturers for 1,3 propanediol (PDO) which allows us to comfortably permeate the market with less competition. Former petrochemical methods for producing PDO have been replaced by DuPont's unique bio-based process, which employs a genetically modified *E. Coli* bacteria strain. This fermentation approach generates 1,3-propanediol (PDO) as a byproduct, offering several benefits over traditional petrochemical techniques. However, the *E. Coli* strain used may potentially be pathogenic (O-antigen) and susceptible to mutations over time. Moreover, it can produce various side products like saccharides, CO_2, proteins, organic acid ammonia salts, 1-2-4 butanetriol, carbonyl compounds, and UV absorbers. Additionally, the general price per ton sold for 1,3 PDO by other competitors in the market is estimated to be $2180/ton.

So what makes us different? And how much of the market is desirable for us to capture? For this design project, DuPont's basic model was restructured with additional optimization pathways to enhance 1,3 PDO production. This included using an optimized anaerobic bacterial strain, which reduces the process's carbon footprint and generates fewer side products, leading to lower energy consumption for distillation and a more cost-effective product. Other modifications incorporated an alternative nitrogen source for fermentation and the use of hydrocyclone units to remove most biomass before ultrafiltration, as well as the choice of water removal by reverse osmosis in which the water is removed using a membrane filter to recycle ~%86 of the water back into the process. These adjustments aim to make 1,3 PDO production more economical and efficient.

With a market volume of an estimated 146,000 tons of PDO produced, we would like to capture 40% of the market share and periodically increase production as demand rises in the PDO market. This practically justifies the production of our plant of an estimated 61,500 tons/yr.

What other alternatives are being used now? Propylene glycol, typically produced from petrochemicals, is an alternative of PDO used in skin care and other applications. However, unlike PDO, propylene glycol produced from petrochemicals is harmful due to its reliance on nonrenewable fossil fuel resources and the associated environmental consequences. The extraction, refining, and processing of crude oil, from which propylene glycol is derived, results in air and water pollution, greenhouse gas emissions, and habitat destruction. Furthermore, the production process generates chemical waste and byproducts that can harm ecosystems and human health if not properly managed. By using petrochemicals as the raw material for propylene glycol, we perpetuate our dependence on fossil fuels and contribute to the ongoing negative environmental impacts.

Who wants/needs our product? And what is it used for? 1,3 PDO is a versatile chemical compound that has found widespread applications in various industries, including skincare and carpet manufacturing. Its unique properties and benefits make it an attractive choice for these sectors, which are explored in more detail below.

In the skincare and cosmetics industry, PDO offers several advantages. As an effective humectant, it helps retain and preserve moisture, making it an ideal ingredient for moisturizers, lotions, and serums that aim to keep the skin hydrated and maintain its elasticity. Furthermore, PDO can enhance the texture and stability of cosmetic formulations, resulting in a more pleasant user experience and easier application, especially for products like creams and lotions. Additionally, PDO is considered non-irritating and hypoallergenic, making it suitable for use in products designed for sensitive skin or daily use. Finally, its ability to act as a solvent for various ingredients improves the overall performance and effectiveness of skincare formulations.

The carpet manufacturing industry also benefits from PDO's unique properties. One such property is its antimicrobial nature, which inhibits the growth of bacteria, fungi, and other microorganisms. Incorporating

PDO into carpet manufacturing can contribute to a cleaner, healthier indoor environment by reducing allergens and odors associated with microbial growth. In addition, PDO is a biodegradable and environmentally friendly compound derived from renewable resources such as corn or glycerol. This makes it an attractive option for carpet manufacturers seeking to reduce their environmental footprint and create sustainable products.

Moreover, PDO functions as an effective plasticizer in carpet production, improving the flexibility and durability of carpets. This results in longer-lasting carpets that are more resistant to wear and tear. Another advantage of using PDO in carpet manufacturing is its ability to enhance the dyeability of fibers, leading to carpets with more vibrant and long-lasting colors. This aspect is particularly important for commercial applications where aesthetics are a key consideration.

Judging Criteria

Our chosen process is more environmentally friendly as it does not involve byproducts such as acrolein, ethylene oxide, acid catalyst, cobalt-iron catalyst, syngas, and 3,3'-oxybis-1-propanol. It does this by way of using an engineered bacteria which selectively catalyzes the reaction of glycerol to form 1,3 Propanediol. Additionally, this process uses less energy in the reactors as the reactors run at 98.6 ºF vs 212-572 ºF as in the Shell process. The bacteria we use is capable of anaerobically processing glycerol, thus drastically reducing the production of CO_2 [15]. Comparing the manufacturing of Bio-PDO to propanediol made from petroleum, there is a 40% reduction in energy use and a 20% reduction in greenhouse gas emissions [21].

Several economic and environmental implementations were considered for the production of 1,3 PDO. One of the most imperative economical substitutes made was Corn Steep Liquor (CSL) for any other nitrogen source. Despite CSL containing lesser nitrogen content than other major sources like yeast or beef extract, CSL is up to a fifth of the cost of yeast per ton and yields higher productivity than alternative Nitrogen sources such as beef extract. Additionally, CSL increases the yield of 1,3 propanediol due to the presence of vitamins such as B12 and other nutritional cofactors [11]. Another economical advantage was substituting nitrogen gas for liquid nitrogen. Liquid nitrogen is more cost-effective which could then be expanded to a gaseous form in order to sparge into the streams to expel oxygen levels and reduce potential risks of explosions as previously mentioned.

Sustainability

As a 1,3 propanediol (PDO) manufacturer utilizing crude glycerol, corn steep liquor (CSL), and *Lactobacillus reuteri CH53* in our production process, it is commendable that we are focusing on sustainable practices. This approach has several positive implications for the environment and the industry as a whole.

Firstly, utilizing crude glycerol as a primary feedstock showcases a sustainable approach to manufacturing. Crude glycerol is a byproduct of biodiesel production and is often considered a waste material. By incorporating it into our PDO production, we are effectively upcycling this waste and reducing the environmental burden associated with its disposal. Furthermore, using a renewable resource like crude glycerol reduces the reliance on petroleum-based feedstocks, which are finite and have a larger carbon footprint.

The incorporation of corn steep liquor (CSL) as a cost-effective nitrogen source is another significant aspect of our sustainable process. CSL is a byproduct of the corn wet-milling process, which makes it an abundant and renewable resource. By utilizing CSL, we not only reduce production costs but also contribute to a circular economy. This approach minimizes waste generation and promotes the efficient use of resources, ultimately lessening the environmental impact of our production process.

Lactobacillus reuteri CH53, a bacterium recognized as safe, further enhances the sustainability of our PDO manufacturing process. By employing a safe and non-pathogenic microorganism, we minimize the potential risks associated with the use of genetically modified or pathogenic organisms in industrial processes. Its ability to efficiently convert glycerol into PDO reduces the overall energy consumption and greenhouse gas emissions associated with the production process, further highlighting the sustainable nature of our approach.

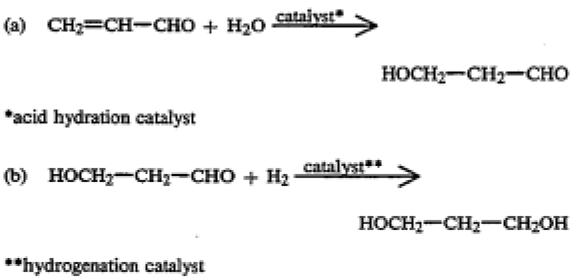
Overall, we are actively contributing to a more sustainable and eco-friendly industry by upcycling waste materials, reducing reliance on petroleum-based feedstocks, utilizing renewable resources, and employing safe microorganisms. Our approach serves as a model for other manufacturers seeking to minimize their environmental impact while maintaining cost-effective production methods.

Process Description

Competing Processes

DuPont (Degussa) Acrolein-Based Catalytic Hydrogenation Process

DuPont's acquisition of a catalytic hydrogenation process utilizing acrolein from Degussa pioneered a new method of high-yield production of 1,3-propanediol (1,3-PDO). Acrolein is acquired during the oxidation process of propylene and is commonly formed during the burning of animal and vegetable fats [1]. As shown in the block flow diagram (BFD), the process begins with the hydration of acrolein in the presence of an acid hydration catalyst and water in a reactor. The use of this catalyst is to add alcohol to the more substituted carbon atom, and hydrogen to the less substituted carbon atom of acrolein [2]. Using the reaction mixture, it is inputted into another reactor with 3-hydroxy propionaldehyde for its catalytic hydrogenation. Catalytic hydrogenation is a process that uses a catalyst to add hydrogen atoms to unsaturated compounds to create a more stable, saturated compound. It involves adding hydrogen gas to the unsaturated compound in the presence of a catalyst to lower the activation energy required for the reaction to occur [1]. This reaction mixture is then fed into a separation unit such as distillation, crystallization, etc., to separate the reacted acrolein from the unreacted, which, the unreacted acrolein will be fed back into the second reactor, as shown in the BFD. Using a distillation column, the hydrogenated reaction mixture containing water, 1,3-PDO, and by-products (with a boiling point higher than 1,3-PDO) is inserted. The column is heated above 415.4ºF, to separate the product and 3,3'-oxybis-1-propanol from the by-products. The product and byproducts exit from the process and the 3,3'-oxybis-1-propanol is fed into a fixed bed reactor containing an aqueous solution with an acid solid catalyst such as gamma-aluminum oxide, acid ion exchangers, natural and synthetic zeolites, etc. This is done to cleave the ether 3,3'-oxybis-1-propanol to be sent back into the distillation column to help with the 1,3-PDO production [3].



(a) $CH_2{=}CH{-}CHO + H_2O \xrightarrow{catalyst^*} HOCH_2{-}CH_2{-}CHO$

*acid hydration catalyst

(b) $HOCH_2{-}CH_2{-}CHO + H_2 \xrightarrow{catalyst^{**}} HOCH_2{-}CH_2{-}CH_2OH$

**hydrogenation catalyst

Figure 4 – (a) acid hydration of acrolein & (b) hydrogenation to produce 1,3-PDO [3]

One advantage of this process is that it has a high yield of 1,3-PDO. With an estimated 83% yield [3], this process is able to minimize the formation of byproducts and maximize the production of the desired product. This occurs because the catalysts used in the hydrogenation step are highly selective and produce 1,3-propanediol with high purity, reducing the need for further purification steps. This is done by utilizing an acid solid catalyst and using it to react with the 3,3'-oxybis-1-propanol inside a fixed bed reactor to create ether 3,3'-oxybis-1-propanol for further 1,3-PDO production. This process is also cost-effective because it uses acrolein which is a byproduct of ethylene production. Also, the starting materials are readily available and inexpensive. Additionally, the hydration reaction is simple and can be easily carried out at low temperatures and pressures, which reduces the cost and energy requirements of the process. However, acrolein is a highly volatile, toxic, and flammable material, which requires special handling during the production process, increasing the overall safety and environmental risks [4]. This causes the process to pose a negative environmental impact because it may also generate harmful emissions such as acrolein and other volatile organic compounds during the production process [5]. To add, the hydrogenation process generates significant amounts of by-products, which can increase the cost of downstream purification, specifically during the cleaving of the ether 3,3'-oxybis-1-propanol.

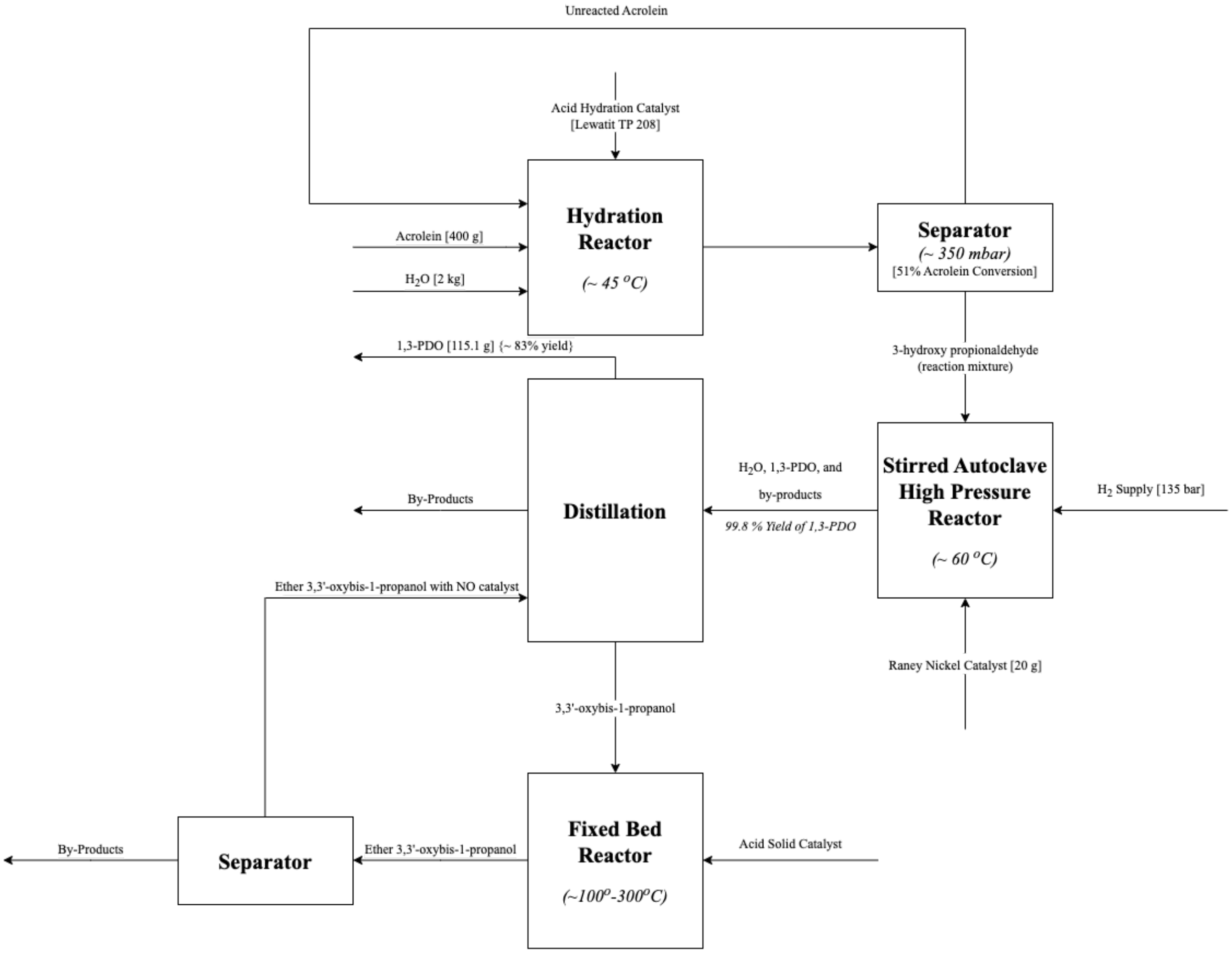


Figure 5 – BFD derived from DuPont's patent of the process [3]

Shell Chemical Co. One-Step Hydroformylation of Ethylene Oxide Process

Shell Chemical Co. designed a new method of forming 1,3-PDO by utilizing a bimetallic catalyst and was able to condense the existing two-step process into a one-step process. The one-step process includes the contact between ethylene oxide, hydrogen-rich synthesis gas (syngas), and the bimetallic catalyst in a "liquid-phase solution in an inert reaction solvent at a temperature of about 30 to 150° C., and an elevated pressure," [6]. Recovery of 1,3-PDO from the crude oxonated product solution is important because methods of recovering and recycling the catalyst are necessary to reduce production costs. Overall, the process can be done via batch or continuous process using either a bubble column or a stirred autoclave. The process of producing the self-assembled catalyst is proprietary to Shell. It is either composed of cobalt-iron or cobalt-iron-ligand and is solubilized in an ether solvent. As shown in the BFD, the iron (iron pentacarbonyl) and cobalt (dicobalt octacarbonyl) source is introduced into the reactor with 1,3-dioxolane (ether solvent) and N, N'-dimethyldodecylamine with syngas. The reactor's conditions depend on the type of catalyst materials being used. Ideally, the reaction temperatures should preferably range from 60-110 ºC and pressures from 1900-2100 psi. For these specific materials, the reactor should be pressurized to 1400 psi and at 90 °C. The contents of the reactor will then be continuously stirred for three hours, during which the reactor will be vented and contents are cooled to 5 °C. Once cooled, ethylene oxide and syngas are introduced into the reactor and the reactor is pressurized to 1900 psi and at 90 °C for two hours to perform hydroformylation. The contents are again cooled and sent into a settling tank operating at atmospheric pressure. Once cooled, the reaction mixture separates into two distinct phases: one rich in the reaction product 1,3-propanediol (1,3-PDO), and the other rich in the catalyst and solvent cobalt-iron. While the 1,3-PDO is extracted from the result combination using traditional techniques such as fractional distillation, phase separation, selective crystallization, or selective extraction, the high-catalyst and solvent-containing phase is recycled and reused in the process [6]. Reports suggest that this process can produce 1,3-PDO in approximately 90% yield [1].

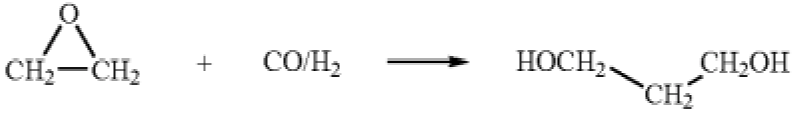


Figure 6 – Selective hydroformylation of ethylene oxide to 1,3-PDO in one step [6]

The self-assembly process of the bimetallic catalyst can be a low cost depending on the type of materials that are used [6]. Additionally, the one-step process reduces the need for multiple reactions, reducing the energy use and cost of the overall process. With the 1,3-PDO production having approximately 90% yield, it is a high-yielding process and because it is a one-step process, it eliminates the need for multiple reactions, reducing the loss of product in the process [1]. Because ethylene oxide is from petroleum-derived raw materials such as ethylene, it poses an environmental problem [1]. To include, ethylene oxide is highly toxic and requires proper handling and disposal and requires special precautions to ensure worker safety and environmental protection [7]. Additionally, 1,3-PDO that is formed via hydroformylation contains almost ten times more impurities than other current processes like hydrogenation [1]. The Fe-Co catalyst is a complex process and the reactor conditions and timing have to be precisely executed, specifically for the reintroduction of syngas with ethylene oxide, which makes it difficult to successfully perform [6].

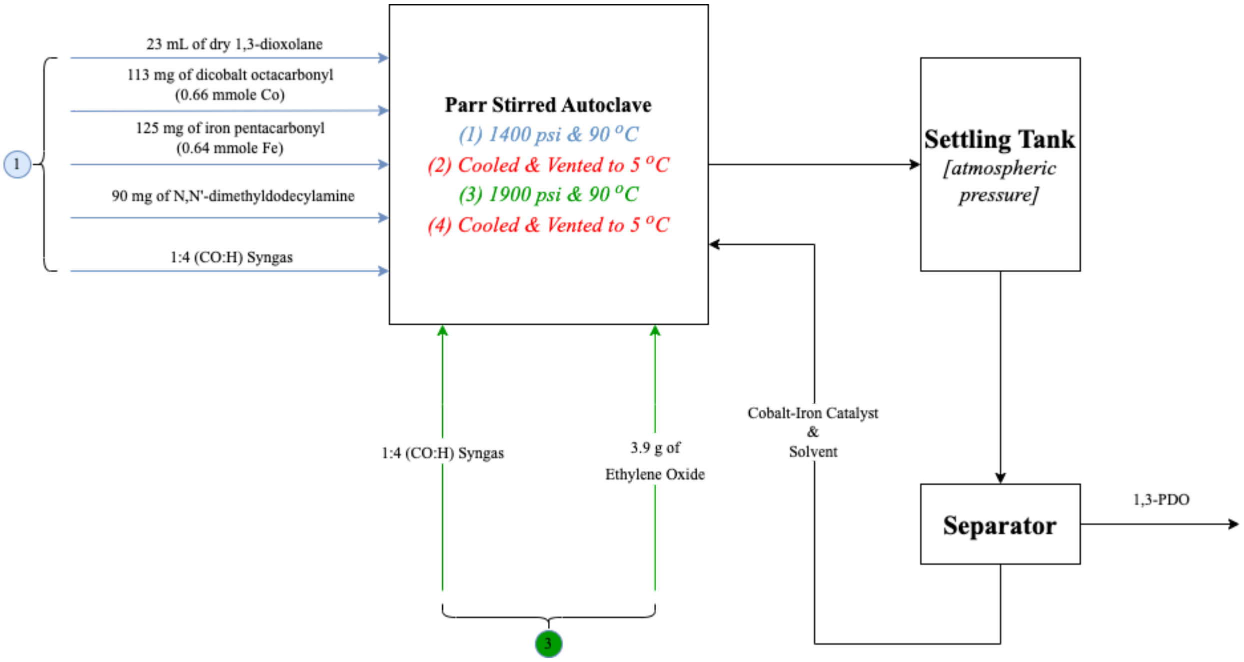


Figure 7 – BFD derived from Shell's patent of the process [6]

Chosen Process

Chemistry of the Process

In this process, 1,3-PDO is produced from microbial glycerol fermentation by using the specific bacteria strain *Lactobacillus reuteri CH53* that converts glycerol to 1,3-PDO in an anaerobic condition. The general mechanism of microbial glycerol fermentation involves two main metabolic branches: reduction and oxidation [22, 23].

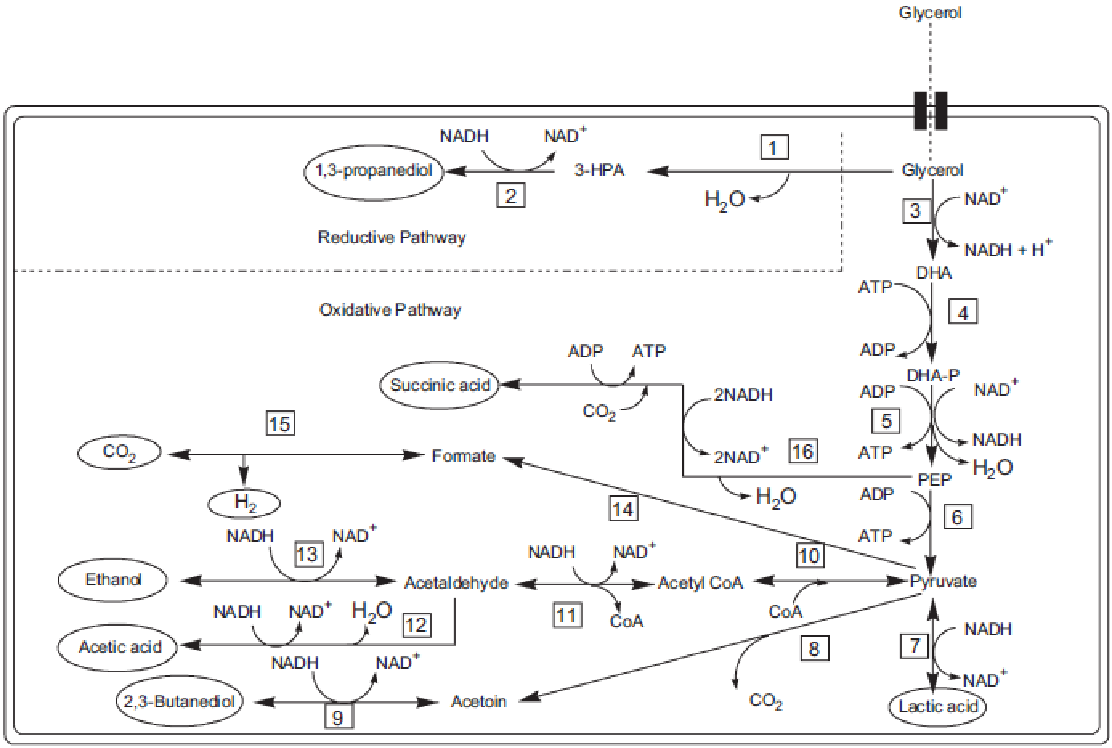


Figure 8 - General reductive and oxidative pathways of microbial glycerol fermentation. Ellipsoids represent the final products in the corresponding pathways. Numbers represent the enzymes the specific reactions: (1) glycerol dehydratase, (2) 1,3-propanediol oxidoreductase, (3) glycerol dehydrogenase, (4) dihydroxyacetone kinase (DHAK) [22]

In the oxidative pathway, with the presence of NAD+, an oxidizing agent, glycerol dehydrogenase (GDH) oxidizes glycerol to produce dihydroxyacetone (DHA) which is converted to dihydroxyacetone-phosphate (DHAP) by using ATP, the energy packets, in the presence of dihydroxyacetone kinase (DHAK). DHAP then enters the process of glycolysis which results in different final products. The final products may vary for different bacteria: acetic acid and butyrate for *Clostridium butyricum*; acetic acid, ethanol, 2,3-butanediol (2,3-BDO), succinic acid, and formic acid for *Klebsiella pneumoniae*; butanol for *Clostridium pasteurianum*; and lactic acid, acetic acid, and ethanol for *Lactobacillus* genus [22, 11]. It is important to note that along the oxidative pathway, a good amount of NADH + H+, acting as reducing agents, and ATP are generated, as observed in labels 5 and 6 in Figure 6.

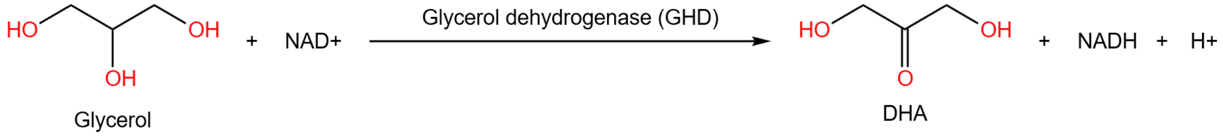


Figure 9 – Glycerol dehydrogenase (GHD) mechanism

In the reductive pathway, glycerol dehydratase (GHDt) acts as a catalyst and converts glycerol to 3-hydroxypropionaldehyde (3-HPA), resulting in water as a byproduct. GHDt heavily depends on vitamin B12 in many glycerol-fed bacteria, such as *Klebsiella*, *Lactobacillus*, and *Citrobacter* genera [22]. 3-HPA is then reduced to 1,3-PDO by 1,3-PDO oxidoreductase (PDOR) while NADH is oxidized to NAD+. It is noted that the reductive pathway depends on NADH +, H+, and ATP, which are generated in the oxidative pathway. For most bacteria, although the reductive pathway is the desired route to maximize the production of 1,3-PDO, a certain amount of glycerol is still used in the oxidative pathway for the bacteria to grow and maintain the 1,3-PDO production.

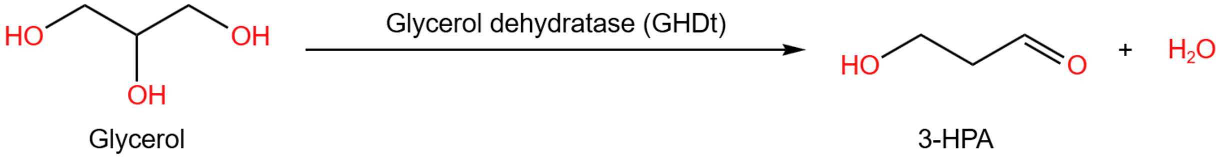


Figure 10 – Glycerol dehydratase (GHDt) mechanism

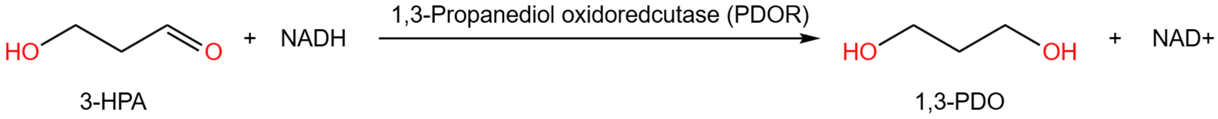


Figure 11 – 1,3-Propanol oxidoreductase (PDOR) mechanism

Lactobacillus reuteri is a hetero-fermentative bacterium that is non-pathogenic and not genetically engineered since it can be found in the gastrointestinal tracts of humans, pigs, and other animals [11]. This bacterium can be used to produce 1,3-PDO from glycerol due to its ability to generate GHDt and PDOR enzymes [11]. An interesting point about bacteria in the *Lactobacillus* genus is that they do not have a GDH enzyme that converts glycerol into DHA, meaning that they do not use any glycerol in the oxidative pathway [22, 11]. Therefore, co-fermentation, a process involving the use of more than one carbon source for fermentation, is required for this bacteria genus. Specifically, *L. reuteri* requires a co-fermentation of glycerol and glucose in which glucose is used as the electron acceptor that initiates the oxidative pathway to generate the necessary reducing agents and energy packets used in the reductive pathway. The products obtained from the glucose fermentation in *L. reuteri* are lactic acid, acetic acid, CO_2, and ethanol [22, 15].

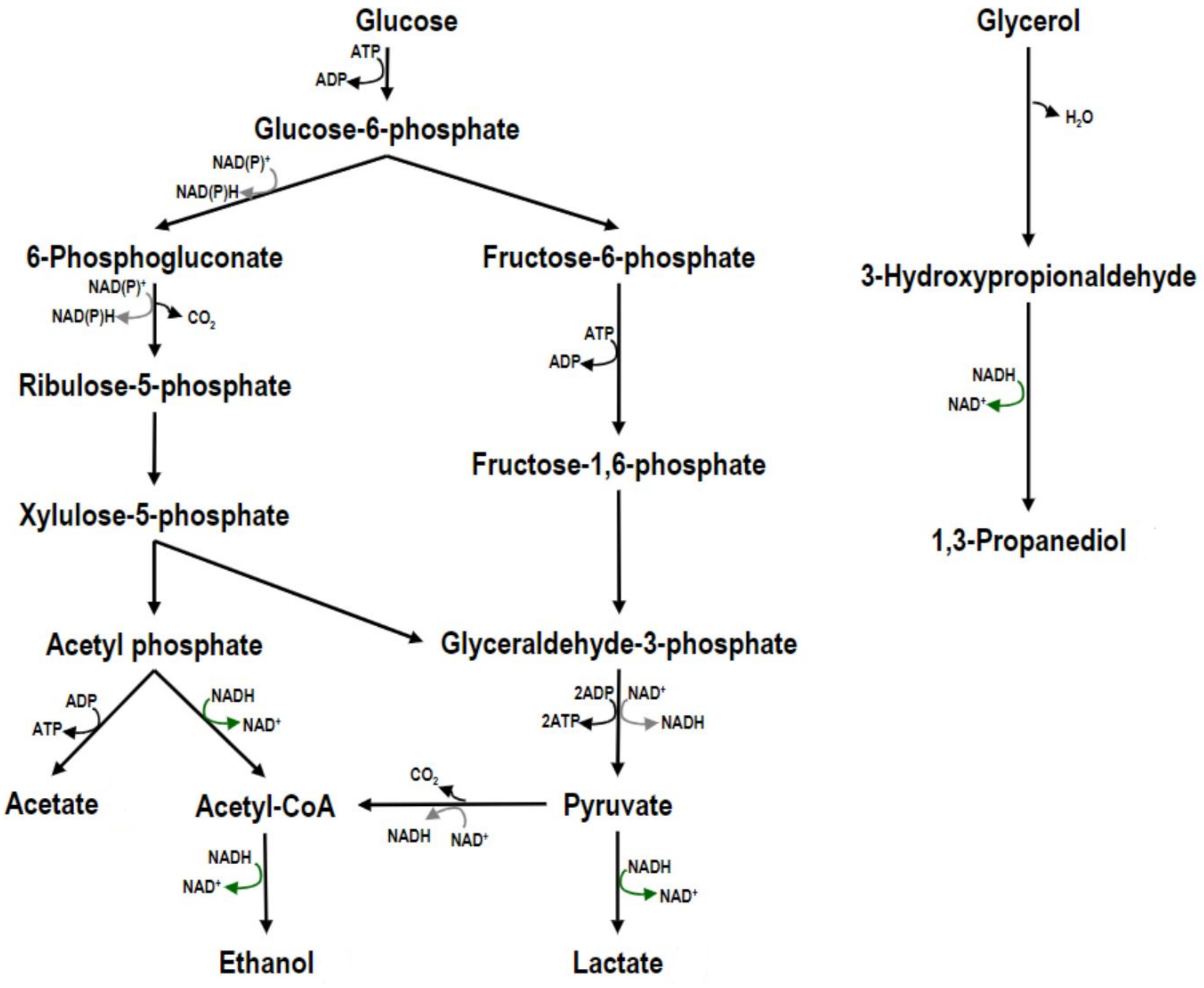
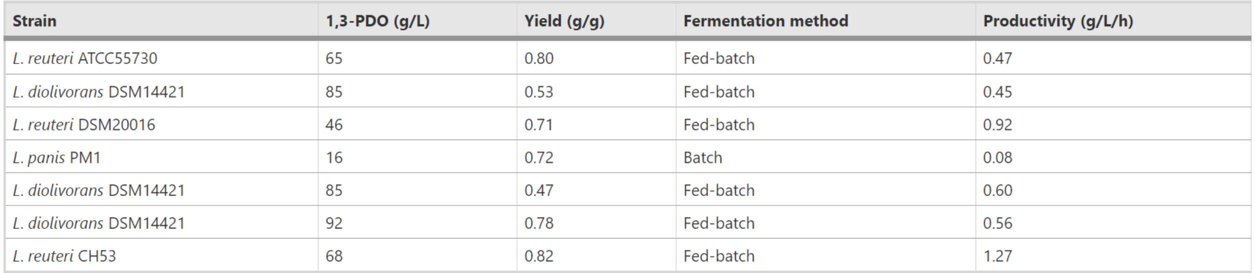


Figure 12 – Mechanism of glycerol-and-glucose co-fermentation for L. reuteri [15][59]

The main carbon source in this process is crude glycerol, a byproduct in many biodiesel processes. This is another reason for choosing *L. reuteri CH53* as this strain can process crude glycerol, instead of pure glycerol [11]. Glucose, acting as a co-substrate in this biosynthesized process, is obtained from the corn stover. It is reported that by using the diluted acid pretreatment to the corn stover, the average amount of glucose recovery is 18.4 g/L (66.8% yield) [14]. In addition to glycerol and glucose, nitrogen is also an important component in microbial fermentation since it is necessary to grow bacteria in nitrogenous culture media. It is reported that corn steep liquor (CSL) can be used as a cheap but efficient nitrogen source for this process [11]. Specifically, total nitrogen contents account for 4.1 wt% of CSL [11]. CSL can also be used as a sufficient source of vitamins, amino acids, and biotin [11].

The strain *L. reuteri CH53* can be cultured in either aerobic or anaerobic conditions. Studies show that anaerobic conditions will give a better production of 1,3-PDO than that of aerobic conditions since about 70%

of glycerol was left unreacted under aerobic conditions while only less than 2% of glycerol remained as residual under anaerobic conditions [11]. Therefore, anaerobic fermentation is used in this process. In addition, this strain is used because it is reported to be the most efficient strain in the genus to convert glycerol to 1,3-PDO [11]. In anaerobic conditions and using CSL as the nitrogen source, the yield of 1,3-PDO from *L. reuteri CH53*, with a productivity of 1.27 g/L/h, can be up to 0.82 g 1,3-PDO per g glycerol, which is 98.8% of the theoretical maximum yield (0.83 g 1,3-PDO per g glycerol) [11].



Strain	1,3-PDO (g/L)	Yield (g/g)	Fermentation method	Productivity (g/L/h)
L. reuteri ATCC55730	65	0.80	Fed-batch	0.47
L. diolivorans DSM14421	85	0.53	Fed-batch	0.45
L. reuteri DSM20016	46	0.71	Fed-batch	0.92
L. panis PM1	16	0.72	Batch	0.08
L. diolivorans DSM14421	85	0.47	Fed-batch	0.60
L. diolivorans DSM14421	92	0.78	Fed-batch	0.56
L. reuteri CH53	68	0.82	Fed-batch	1.27

Figure 13 – 1,3-PDO production of different bacteria in the L. genus under anaerobic conditions and CSL as the nitrogen source [11]

The reactor will be a fed-batch type reactor as this type of reactor allows for a high yield and productivity compared to batch reactors while avoiding the pitfalls of immobilized cell reactors such as high capital costs and fouling of ports due to cellular aggregation.In a fed-batch process, a batch of cells or microorganisms is first put into a bioreactor with a medium rich in nutrients for a specific time cycle duration. To maintain the optimum nutritional content and encourage optimal growth, extra nutrients and substrates are gradually supplied to the bioreactor as the cells expand and utilize the existing resources. Glycerol and glucose will be fed to the reactor continuously to sustain fermentation until the desired concentration of either cellular biomass or glycerol is reached then the resulting product will be transferred to the next unit [65].

Process Description

The process has four main steps: (1.) preparation, (2.) fermentation, (3.) biomass separation, and (4.) distillation [16,17].

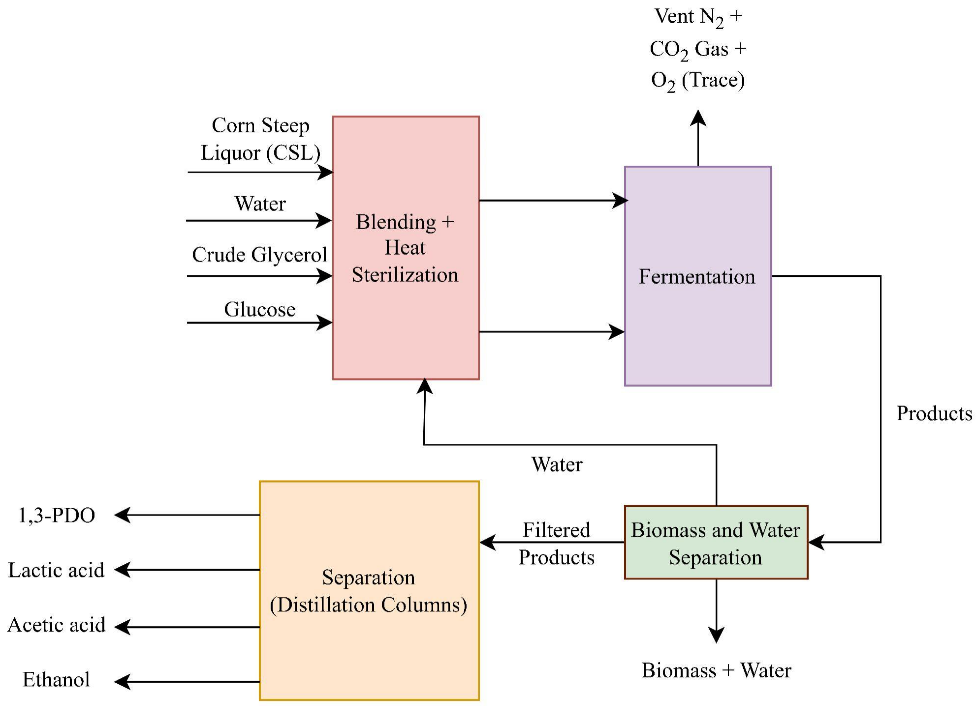


Figure 14 – BFD for the chosen process

On Demand Variable Corn-Stover Preparation

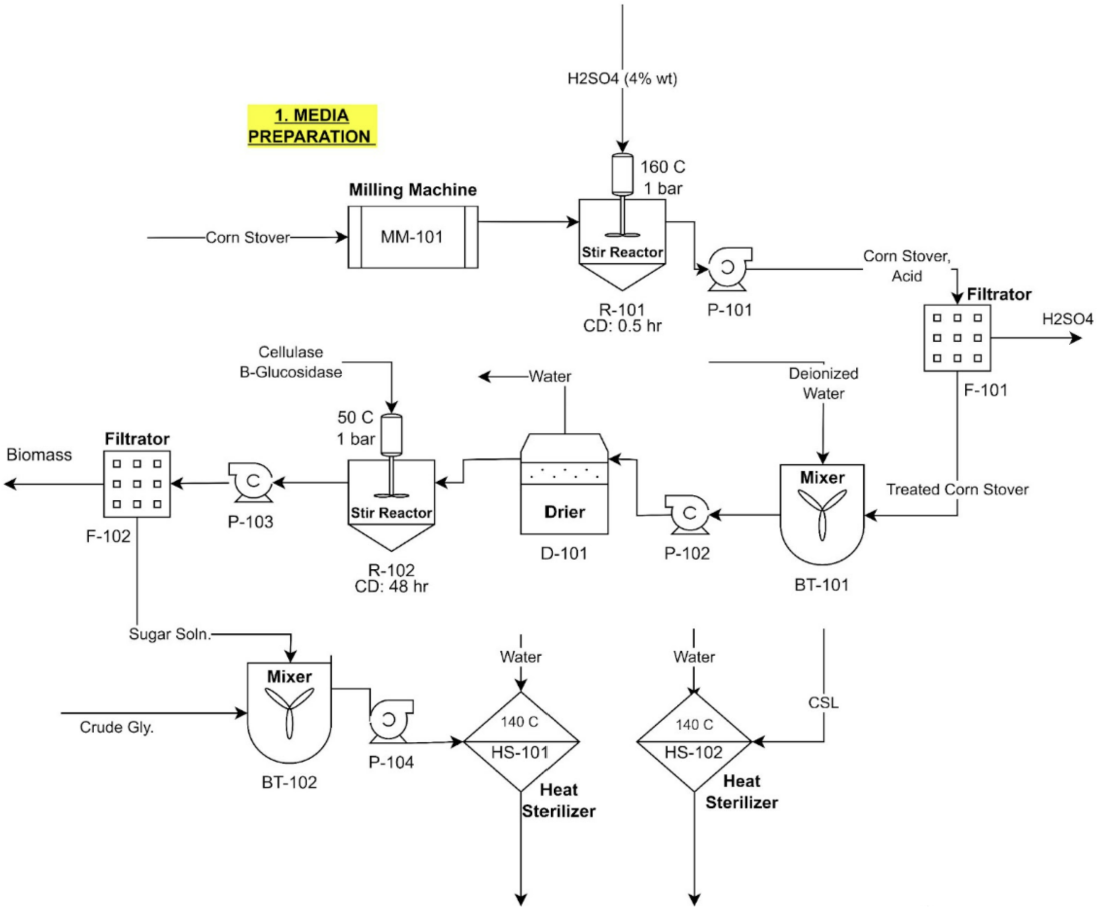


Figure 15 – On-Demand Media Preparation

Note that this is an on demand process meaning that this part of the process will only be employed when market conditions dictate its use. Generally, an estimate of 25% of our glucose production can come from corn. The corn glucose simulation in SuperPro revealed that the process was feasible, but further analysis of market conditions showed that the process would best be used on an as needed basis. While originally corn stover was going to be used on an as needed basis, it may be more economically feasible with resources such as tax credits or domestic production credits or carbon offset credits as the importing of glucose from China generates more CO_2 than domestic production.

Before removing corn stover from our design scope, this step was to extract sugars, including glucose, from corn stover. This process of extraction is performed at atmospheric pressure. Corn stover is milled by using a milling machine, and the milled corn stover is then transferred into a stirred reactor for acid treatment. Diluted 2 wt% H_2SO_4 solution is added to the stirred reactor [14]. The mixture is allowed to be stirred at the temperature of 320ºF for 30 minutes and then filtered to remove the acid [14]. The treated corn stover is quickly mixed with deionized water in a mixer at ambient temperature for 10 minutes and then dried to completely remove the water with the residual acid. The corn stover is then moved into the second stir reactor. Cellulase and β-glucosidase are added into that stir tank. The stirring is done at a temperature of 122ºF and a rotational speed of 145 rpm for 2 days [14]. During this stirring, sugars are gradually enzymatically extracted from the corn stover. The mixture is finally filtered to remove the unwanted biomass, and the sugar solution is transferred to storage.

1. *Preparation*

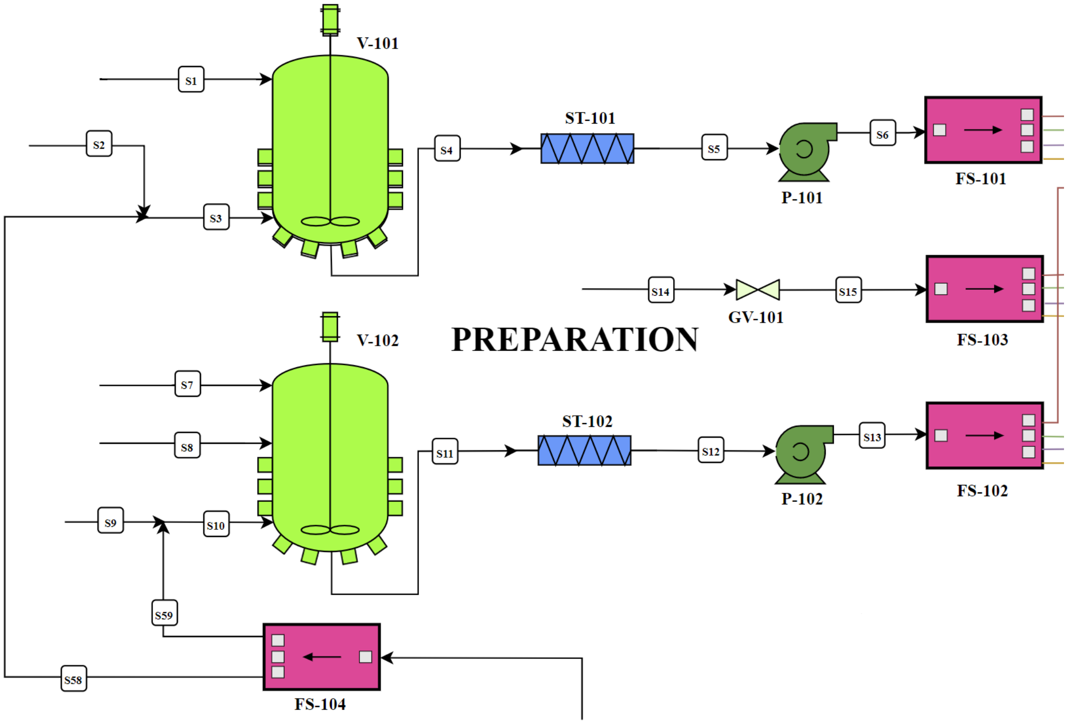


Figure 16 – PFD of the first step (preparation)

The first step of the process involves the preparation of the raw materials in which corn steep liquor (CSL) is used as the nitrogen source and glucose and glycerol as the carbon sources for the chosen bacteria.

CSL is mixed with water in a blending tank at ambient conditions. The mixture is then heat-sterilized at 280°F and then cooled down to 97.2°F before sending it to a flow splitter that splits into 4 smaller streams with a percentage ratio 90:9:0.9:0.1. Those four split streams will be sent in the following order (to the next step): "0.1%" stream to the first seed fermentor, "0.9%" stream to the second seed fermentor, "9%" stream to the third seed fermentor, and "90%" stream to the product fermentor. Glucose and glycerol are mixed together with water in a blending tank, and the mixture is then sent to a similar series of procedures. It is noted that most of the water used in these mixing comes from the recycle stream in the final step.

2. *Fermentation*

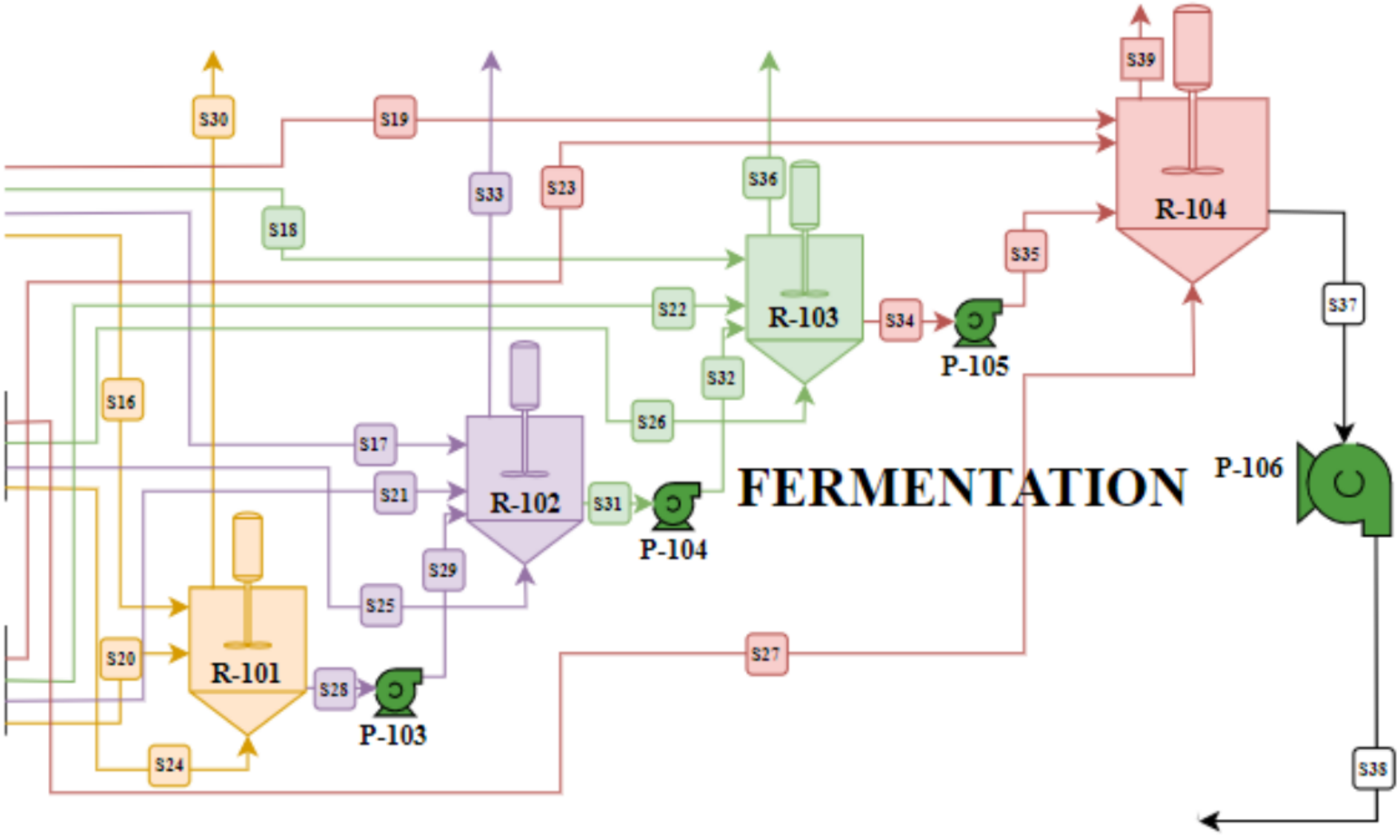


Figure 17 – PFD of the second step (fermentation)

The next major step is the fermentation process. Crude glycerol is mixed with the extracted sugar solution so that the molar ratio of glucose to glycerol is 0.5 [11]. The mixture is sterilized using heat sterilization at 284 °F and atmospheric pressure with the addition of water. The sterilized stream is then sent to a storage tank. At the same time, CSL, which includes vitamin B12 and other necessary nutrients, also undergoes heat sterilization at the same temperature and pressure and then are transferred to storage. When ready, two streams from those storage tanks (glycerol and sugar mixture stream, and CSL stream are sent to the first seed fermentor where the inoculum of *L. reuteri* is first introduced. The bacteria population is left to grow for approximately 9 hours at 98.6 °F, 14.7 psia, and a pH of 5.5 with an agitation speed of 100 rpm [11]. During the incubation period, nitrogen gas with a flow rate of 1 vvm (volume of air/volume of medium/time unit) (1 L/L/min) is sparged into the fermenter to maintain the anaerobic condition, and remove any dissolved O_2 [11]. After incubation, the inoculum is sent to the second fermentor with the new glycerol and glucose mixture stream, and CSL stream. The second feed fermentor operates under the same conditions as the first seed fermentor. Two more fermentors are introduced to get the cellular biomass sufficient for 1,3 PDO production at scale. After the third incubation period, the inoculum is finally sent to the product fermentor. A new set of the two streams (glycerol and glucose mixture, and CSL is sent to the product fermentor that is set at the same operating conditions as the first three fermentors. However, the reaction is left for 24 hours instead of 9 hours and the reactor is periodically refreshed with new growth media to keep growth steady.

3. *Biomass Separation*

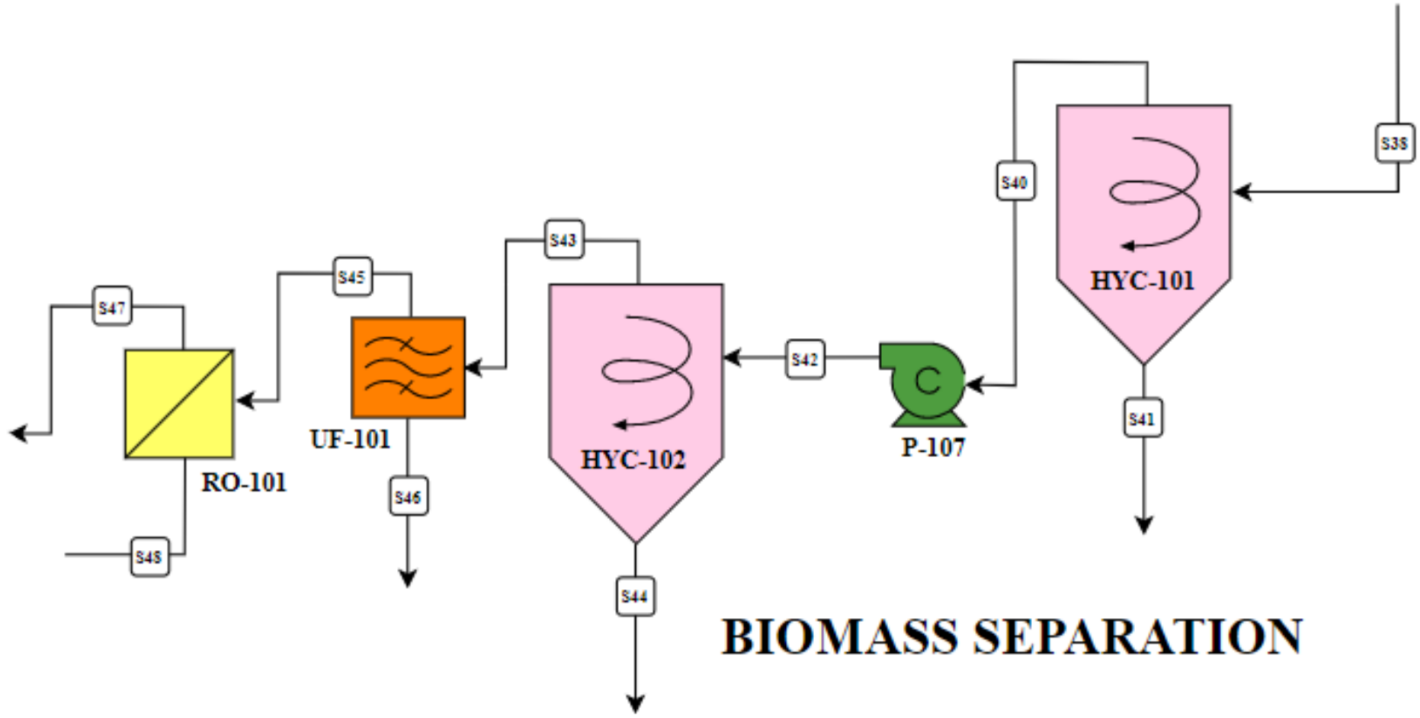


Figure 18 – PFD of the third step (Biomass Separation)

The fermentation broth obtained from the final fermentation unit is sent to two hydrocyclone units. These units act to separate much of the biomass and some of the water content of the broth. The water content of the stream entering the hydrocyclones is roughly 70%, and the removed biomass can be deposited as a slurry to dry and later be used as a fuel stock for heat generation or for cattle feed. From here, the stream is sent to an ultrafiltration unit to remove any remaining biomass particles. After that, the filtered product stream is sent to a reverse osmosis unit to remove all the remaining water. The treated stream will then enter the first distillation column and the excess water will be recycled in the process.

4. *Distillation*

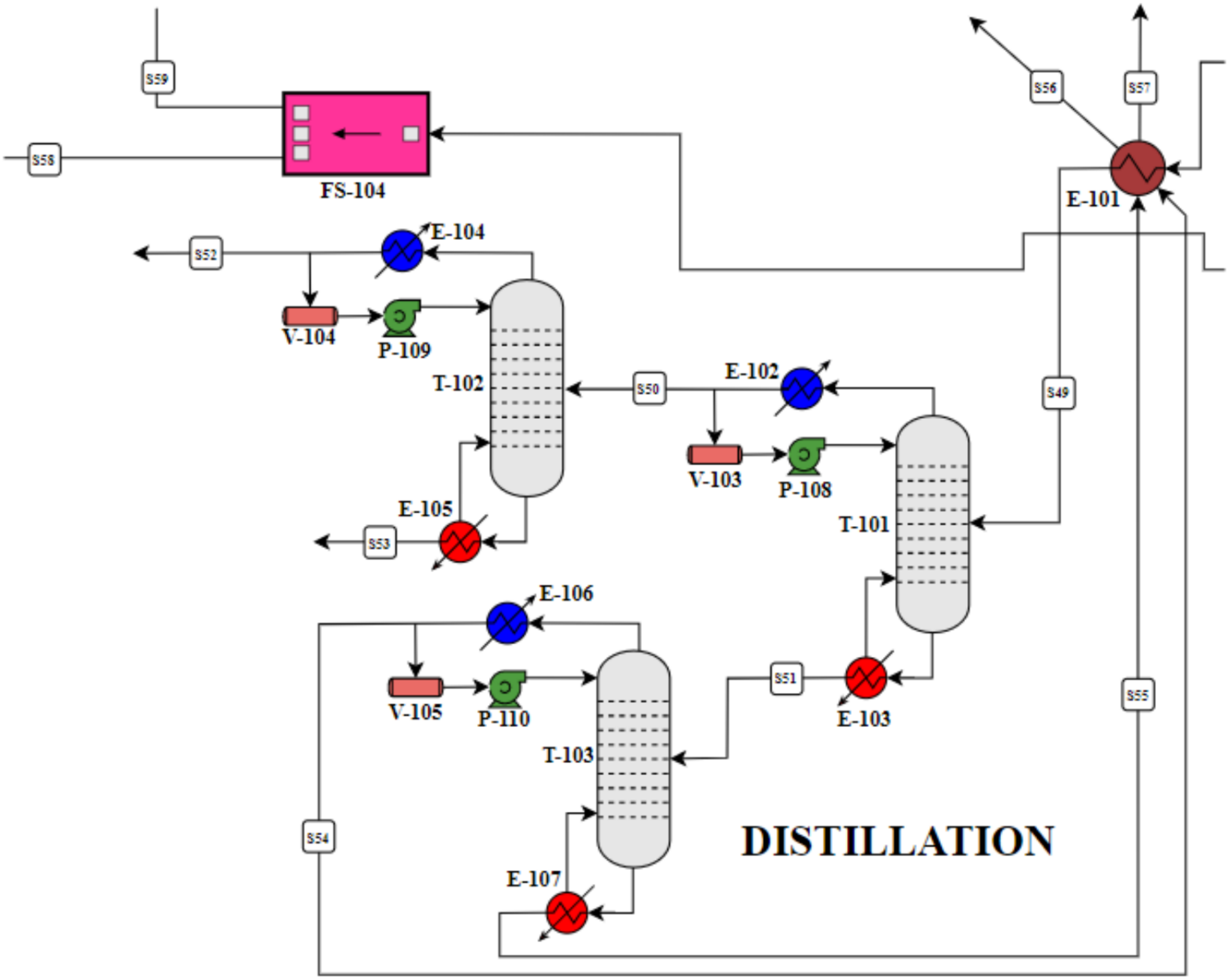


Figure 19 – PFD of the final step (Distillation)

The purification step contains three distillation columns, aiming for a purity of 99.5% for 1,3-PDO as well as maintaining high purities (above 98%) for other products (lactic acid, acetic acid, and ethanol). The filtered product stream, obtained after the process of reverse osmosis, enters a heat exchanger to receive the excessive heat from the downline product streams and then is sent to the first column. The first column is operated at 164°F at the top and 323°F at the bottom and at a pressure of 2.18 psia. Light products (acetic acid and ethanol) are obtained at the top while heavy products such as lactic acid and 1,3-PDO are collected at the bottom. The distillate stream of the first column (acetic acid and ethanol) is sent to the second column which operates at 97.7°F at the top and 148.9°F at the bottom and at a pressure of 2.18 psia. Ethanol with a purity of 99.9999% is obtained at the top, and acetic acid with a purity of 99.16% is obtained at the bottom of the second column. The heavy products of the first column (lactic acid and 1,3-PDO) are sent to the third distillation column. This column is operated at 286.3°F at the top and 310.7°F at the bottom and at a pressure of 2.18 psia. 99.54%-purity of 1,3-PDO is collected at the top while lactic acid with a purity of 98.16% is obtained at the bottom of the third column. The distillate as well as the bottom streams of the third column are sent to the heat exchanger before the first distillation column to recycle the heat from the system.

5. *Advantages*

Lactobacillus reuteri CH53 is capable of selectively catalyzing the production of 1,3 PDO from glycerol and a glucose source [15]. It is also a facultative anaerobic bacteria and as a result, will produce negligible amounts of CO_2 from its metabolism. The process does not require high-temperature reactors and is a sustainable process [17]. Consumers are likely to pay a premium for sustainably produced products that use the bio-based 1,3 propanediol relative to the petrochemical route. Corn steep liquor (CSL) is able to increase the yields of bacteria that use glycerol to generate PDO as it serves as both a nitrogen source and a source of nutrients for the bacteria [11]. The usage of corn stover (if used) as a cosubstrate is able to reduce the production of carbon dioxide as it is preferentially reduced in the metabolic pathway [10, 11, 15].

6. *Disadvantages*

For each run there is an inherent risk of contamination which could potentially ruin a batch. There is also a risk of mutations within the cell line which could cause the lactobacillus strain to not produce PDO at the same rate. This is controlled by decisions made at the company scale in which the cell line will be regularly taken out of frozen storage and cultured to generate more cells that are optimal. The filtration units run the risk of being fouled and as a result, at the first filtration step, there will be one ultrafiltration unit to reduce this risk. The economic feasibility of this process is dependent on a number of factors including availability/price, transportation costs, cost of raw materials, and other such factors.

Alternatives to the Chosen Process

In the 2000s, to reduce the number of nonrenewable chemicals being used in 1,3-PDO production, DuPoint developed a new microbial process that produces 1,3-PDO from glucose fermentation by engineering an *E. coli* strain that converts glucose to 1,3-PDO. However, this process had some disadvantages, such as the use of a pathogenic and mutagenic *E. coli* strain, the production of many undesired byproducts, such as proteins, saccharides, and UV absorbers, as well as the generation of a concerning amount of CO_2 due to being operation in aerobic conditions. This has shifted the study of microbial production of 1,3-PDO to glycerol fermentation, and glycerol fermentation has shown good results in achieving economical and friendly environmental production of 1,3-PDO.

There are many other bacteria strains that can replace the strain *L. reuteri CH53*. Other bacteria genera, such as *Klebsiella*, *Citrobacter*, and *Clostridium*, can also naturally convert glycerol to 1,3-PDO [11]. For example, *Klebsiella pneumoniae* can produce 102.7 g/L 1,3-PDO while *Clostridium butyricum* can produce 94 g/L 1,3-PDO [11]. However, these bacteria are pathogenic, and there is a need for genetic modification to the strains [11].

There are also different reactors to produce 1,3 PDO such as immobilized cell reactors and batch reactors [22]. In the process outlined in this paper, a fed-batch reactor system is used to ensure steady growth over a long time period. An immobilized cell reactor was not chosen due to mass transfer limitations inherent to having a fixed bacteria(catalyst) and a simple batch reactor was not chosen as downstream it would be more difficult to separate the glycerol and glucose. By using a fed batch system it is possible to control to a greater extent the amount of product produced and ultimately the amount of reactant downstream.

When corn stover was still prevalent in our design, it was pretreated with diluted acid before glucose extraction. Corn stover can also be pretreated with 2 wt% NaOH which can result in a higher glucose yield (81.73%) than that from 2 wt% H_2SO_4 (66.8%) [14]. However, NaOH is much more expensive than H_2SO_4, making the use of H_2SO_4 the economically better option. It is reported that beef extract is a better nitrogen source than CSL since beef extracts contain 11.4% nitrogen content while CSL only has 4.1% [11]. However, similar to NaOH, beef extract is more expensive than CSL, favoring the use of CSL as the nitrogen source in this process. The corn stover for glucose is a future recommendation to be implemented at some point in the future. As of right now, it may be wise to contract with local glucose manufacturers to limit the liability of possible corn stover market volatility and issues with corn stover quality.

Operating Conditions and Assumptions

1.) The plant operates 8,000 hr/year.
2.) The basis of 1,3 propanediol is 61,500 tons/year using 74,600 tons/year of glycerol and 60,600 ton/yr of glucose.
3.) Assume each reactor takes ~9 hours to “react”, the final reactor will take longer at ~24 hours.
4.) Each reactor is ~10% of the size of the one after it.
5.) The conversion of glycerol to 1,3 PDO is 0.82, the amount of 1,3 PDO in the broth is 68 g/L, and the productivity of the strain is 1.27 g/L/hr [11].
6.) Assume for the process for every 68 kg of 1,3 PDO produced 28 kg of biomass will be produced.
7.) Assume for the process that for every 100 kg of 1,3 PDO produced, we use 44 kg of CSL [11].
8.) Assume that all cellulose, hemicellulose, and lignins are broken down completely by cellulase and beta glucosidase to glucose [14].
9.) Per Talarico, 1990, the primary byproducts of the metabolism of glycerol and glucose will be CO_2, lactate, acetate, and ethanol [15].
10.) Assume hydrocyclone and ultrafiltration steps remove 100% of the biomass and any trace proteins/salts are also removed in those steps.
11.) We assume that all of the nutritional needs of the organism is handled by the CSL as Ju, et al. showed that it provided the B12 and other nutritional cofactors required for 1,3 propanediol production [11].
12.) Assuming we will purchase the organism for $500,000, culture the cells, and freeze a portion of the cell line to use in case of deviations/mutations. This number was arrived at upon consultation with our mentor.
13.) Corn stover liquor contains ~4.1% nitrogen by weight, and corn stover will be treated with a dilute acid pretreatment and will yield 18.4 g/L glucose (66.8% glucose yield) [11, 14]. Acid is used as it is more economical.
14.) 1 kg of corn stover will yield a maximum of 0.86 kg of glucose, but after pretreatment, it will give 66.8% of this value; 0.578kg of glucose per kg of corn stover [14].
15.) All the byproducts such as ethanol, lactic acid, and acetic acid are derived from glucose [11].
16.) 82% of the glucose will react to generate ethanol, lactic acid, and acetic acid [14].
17.) Out of the three products, ethanol is 39.4 wt%, lactic acid is 37.3 wt%, and acetic acid is 23.3 wt% [11].

Process Control

This process has six main stages to produce and extract 1,3 propanediol using *Lactobacillus reuteri CH53*. These stages are highlighted in the block flow diagram, they are as follows: seed fermentation, main fermentation, centrifugation, ultrafiltration, reverse osmosis, and distillation. This initial portion of this process is centered around culturing a microorganism, therefore, conditions at which the process runs must be highlighted. The process controls of the important sections of the process will be analyzed below. There will also be an in detail analysis of T-103, the last distillation column that is a part of the purification section of the process.

Seed Fermentation

The initialization of this process starts with culturing *L. reuteri* in several seed fermentors that replicate until they reach an optimal optical density in order to produce the required yield amount of 1,3 Propanediol. For this to take place, specific conditions such as oxygen concentration, media preparation, and fermenter conditions (temperature, pH, pressure, etc.) must be satisfied. It should be noted that all the fermenters operate as a fed batch mixture.This implies that the quantity of glycerol and glucose added can be adjusted or restricted as required, depending on the desired amount required.

This process begins with culturing *L. reuteri* in a cell culture that is sufficient enough to produce the desired 1,3-propanediol tons per year. The units involved in this stage are R-101 (first seed fermenter), R-102 (second seed fermenter), R-103 (third seed fermenter), V-101 (blending tank), and V-102 (blending tank). The streams include S1 (corn steep liquor [CSL]), S2 and S3 (water) that is pulled into the first blender to create the corn steep liquor (CSL) solution. The second blending tank that will create the glycerol/glucose solution will be pulling in S7 (glycerol), S8 (glucose), and S10 (water). Portions of both solutions will end up in the seed fermenters where the inoculum is created and transferred to the next seed fermenter. The media enters R-101, R-102, R-103 at different proportions. This can be done by implementing a few steps, first by measuring the flow rate of the incoming stream, from here the desired split ratios can be set based on the desired proportions. A control must be placed in on the splitter to adjust it. The splitter needs to be adjusted so that it splits the stream into the desired proportions. This can be done by controlling the valves that control the flow of the stream to each fermenter by setting a ratio control on the flow rates coming out of the splitter. Ratio control is a type of feedback control system that can be implemented to continuously monitor the flow rates and adjust the splitter accordingly. It will receive input from flow sensors and adjust the valves to maintain the desired split ratios.

Another aspect to consider is the sterilization of the media before it enters the fermenters. The purpose of these sterilizers is to avoid contamination of the media that is fed into the fermenters. The sterilizer performs this by autoclaving. This is a high-temperature and high-pressure method of sterilization that involves heating the media to a temperature of around 97°C for a period of 10 minutes twice, where it is then cooled after both times. The sterilizers are designed as a four way path in which it is heated and cooled twice, similar to how sterilization works in the dairy industry. Thus, there are a few process control variables

Another important aspect to control in the seed fermenters is the pH. All three seed fermenters must be kept at a pH of 5.5. This will ensure that the cell culture survives and is kept at its optimal conditions. For this, the manipulated variable will be either sodium hydroxide or sulfuric acid. Sodium hydroxide will more than likely be the more used pH controller due to the carbon dioxide that is generated from the cell culture that will cause a pH drop. For this a split range controller is needed. This will allow the controller to open/close both the valves that control the flows for the acid and the base simultaneously. The split range controller will open either valve based on the pH disturbance and shut off completely when the desired pH range is reached. It should be noted that only the acid or base is allowed to flow, nt both at the same time. The controller will also be connected to an electrode that will be used to measure the pH in the fermenter at all times.

Oxygen level is another important variable to control in the fermenter since the fermentation process is run anaerobically. Before a new fresh batch is introduced into the fermenter, nitrogen gas will be used to purge out any impurities such as oxygen since it can hinder the metabolization of *L. reuteri.* The percent of oxygen during the fermentation process should be kept near 0% at all times. For this, a Clark electrode will be used to measure the oxygen concentration in the fermenter. Oxygen can arise in the fermenter due to aspects such as agitation speed, excessive foaming in the broth, or improper purging. If such a thing occurs, the oxygen concentration will be controlled by manipulating the nitrogen gas stream that each seed fermenter has. It can be controlled via a feedback controller to ensure oxygen is reduced as soon as it is sensed in the system. As mentioned, the fermenter is purged before a new batch, however, the fermenter can also be purged during the fermentation process. Therefore, after it is initially purged the valve is completely shut off and reopened during fermentation if any oxygen needs to be removed.

Temperature is another variable that must be controlled as microbes such as *L. reuteri* are extremely sensitive to temperature. Just like pH, temperature is essential to optimal conditions and the survival of the cells. Temperature does have a bit of a wider range compared to pH, thus cascade control will not be necessary. However, a split range controller must be used so both cooling water and steam can be provided in case the temperature in the fermenter increases or decreases. A split range controller as mentioned, will allow one manipulated variable to be used, as soon as the set point is reached the manipulated variable is shut off completely. Once the opposite stimuli is sensed the other manipulated variable is used and controlled. The seed fermenters can encounter temperature disturbances due to endothermic reactions or exothermic reactions that may occur. The steam and cooling water will be supplied through the fermenter's jacket to control the temperature in an effort to keep the fermenter at 98.6°F.

The growth of the cell culture in the seed fermenters is very important as this is what will cause our main fermenter to satisfy production requirements. Thus, the optical density will be controlled through the time scheduling in each seed fermenter. The seed fermenters keep increasing in size since the inocolumn they provide to the main production fermenter also increases in its amount. If the optical density in the seed fermenters does not reach its required optimal value, the time will be adjusted to a longer duration in the fermenter. The controller will be manipulating the time in this case and the optical density will be measured through a wavelength of 600 nm using a 96-well Microplate Reader [11].

The pressure of the seed fermenters should also be controlled. Seed fermenters are stainless steel and therefore pressure should not be a huge concern, but since constant purging might be occurring during the process, each fermenter has a valve that controls the venting flow rate. The venting flow rate will be controlled in order to keep pressure at a safe operating condition.a simple feedback controller will be good enough to take care of this issue.

The level must be controlled in both the blenders and the seed fermenters. To control this, the feeds into the blending tank and the seed fermenters will be manipulated. Since the feed of the seed fermenters is the output of the blenders, the blenders will technically have the input and output flow rates that dictate its level. If the level of the seed fermenters need to be kept from rising, this will in turn slow down the flow rates coming from the blenders, therefore the feed into the blenders will also slow down. This makes sense since the blenders and the fermenters are in series. However, since the fermenter operates in cycle durations for hours, level will not pose as big an issue as in a continuous process. A feedback controller will be implemented for the seed fermenters to ensure the level in the blenders and fermenters are kept under control. It should be noted that since the blenders are mixing more than one stream, they must be controlled at the same time at the appropriate ratio, therefore, a ratio controller will be used to manipulate the feeds of the blenders.

Finally, the agitation speed in the fermenter is monitored by measuring the rotary speed of the impeller. The manipulated variable in this case will be the power output provided by the motor from the impeller. The impeller speed can adjust the agitation due to factors such as a thicker cell culture/broth that hinders the impeller rotation. Whenever the rotary speed is measured to be too low, the motor power output will be increased. This will ensure the cell culture/broth is thoroughly mixed and is uniform throughout the entire fermenter to ensure a high efficiency fermentation process.

Main Fermentation

The main fermenter (R-104) is a larger version of all the seed fermenters. It receives the inoculate from all of the seed fermenters in which it continues the production on a larger scale. As a result, the unit's controls discussed for the seed fermenters are identical, especially since it also receives the media streams from the two blenders.

Therefore, the controls for the agitation, pH, pressure, and oxygen concentration for the fermenter would be exactly the same. The pH is controlled through a split range controller by manipulating the flow rates of the sodium hydroxide and the sulfuric acid, the pressure is controlled by manipulating the flow of the venting through a feedback controller, and the oxygen concentration is controlled by manipulating the flow of the nitrogen gas that is allowed into the fermenter via feedback controller.

As for the temperature, due to the huge increase in size of this fermenter compared to the seed fermenters, a cascade controller will be put in place to keep the temperature at the desired temperature. The cascade controller will be a better option in this case since the size of the fermenter will make it less sensitive to sudden changes. Therefore, since a cascade controller provides a better control of the system conditions and a faster response time. In this case, the manipulated variable will now be only the cooling water in the jacket to assure the fermenter stays relatively cool at 98.6 F.

In order to control the optical density in the main fermenter, it will be similar to how the optical density was controlled in the seed fermenter. The manipulated variable will be the scheduled time. If needed, this time extension will allow more glycerol/glucose mixture (main bacteria metabolizer from S23) to pour into the fermenter to further ease the optical density growth. This will be another manipulated variable that can be handled by an operator. If it is determined that the bacteria needs more of the carbon substrate to metabolize at a faster rate, the valve for this stream can be opened so more glycerol/glucose mixture can enter the fermenter. As mentioned, since the main fermenter is much bigger compared to the seed fermenters, as a result the controls for the scheduling time will be more rigorous and it is the reason as to why the flow of the glycerol/glucose mixture can further be manipulated compared to the seed fermenter. The time will be manipulated using a feedback controller.

Unlike the seed fermenter and the blending tank, the level is not controlled through the inlet stream, for the main fermenter the level is controlled through the outlet stream (S37). This will also be set as a feedback controller. This will prevent an overflow of the fermenter to avoid spills or any leaks. This same logic applies to the seed fermenters. There are no waste streams up to this point, therefore the pH of the mixture does not need to be controlled for any waste streams. If a waste stream was removed into another tank, the pH of the waste stream would need to be controlled to avoid corrosion in other equipment.

Centrifugation

This is the section that follows the fermentation step of the process in which the objective is to remove the biomass from the products. The main components are two hydrocyclones (HYC-101 and HYC-102). Aspects such as pressure, flow rates, and motor speed must be monitored and controlled throughout the process in which the biomass is removed along with some of the water contents in the solution. The power output of a hydrocyclone is determined by several factors, including the feed flowrate, the feed concentration, and the design of the hydrocyclone itself. In general, the power output of a hydrocyclone can be calculated using the following equation:

$$Power\ Output\ =\ Flowrate\ *\ Pressure\ Drop$$

The hydrocyclone consists of a cylindrical chamber with a conical base. The liquid suspension is fed tangentially into the chamber, creating a swirling motion that causes the solid particles to move towards the outer edge of the chamber. As the liquid swirls around the chamber and up out of the chamber, while the solid particles are forced to the outer edge and eventually move downward towards the conical base, where they are discharged as underflow.

Before entering the hydrocyclone (S37), the biomass and products are pumped to the hydrocyclone for the purpose of ensuring a more consistent flow rate as well as achieving optimal pressure before entering the hydrocyclone. Therefore, the pressure at the pump's (P-106) outlet is monitored, the manipulated variable would then be the flowrate of the biomass mixture that comes out of the pump. The flow rate of the biomass solution after the pump is tied to the pressure at which it is pumped, thus, controlling the pressure also controls the flow rate. A simple feedback control will be sufficient for this. It is important to control the flow rate since it can affect the separation efficiency of the hydrocyclone.This is how the pressure inside the hydrocyclone is also controlled, by manipulating the inlet stream.

To ensure that the pump (P-106) operates at the optimal conditions to provide the correct amount of work to the biomass solution, a control can also be set on the frequency converter of the pump. This will control the pump motor speed. If the throughput value (3704 gal/min) of the solution drops for any reason (such as any density changes in the biomass), the controller will manipulate the pump's motor speed. By manipulating the motor speed, the vibration of the hydrocyclone is also controlled. The vibration is detected using a proximity sensor that is connected to the controller operating in a feedback loop.

Finally, since both hydrocyclones remove a mixture of biomass and water, there will be two waste streams (S41 and S44), one from each hydrocyclone. Both waste streams will be disposed of by being transferred over to a disposal. The flowrate of the outlet from the disposal area will be manipulated in case of an unusual build up, controlling the level in the disposal area. This will be controlled through a feedback loop.

Ultrafiltration

In this section, the final step in removing biomass impurities takes place. Once the majority of the biomass is removed from the broth in the hydrocyclone it is then transferred to an ultrafiltration step (UF-101). This section will also have a waste stream where the water and biomass end up in a disposal and the retentate moves into the reverse osmosis step.

An important variable to control in filtration steps is the pressure of the streams. Filtration steps experience pressure drops, therefore, the pressure of the stream leaving the filter (S45) is monitored. To control this, one of the spare centrifugal pumps from the warehouse will be used to control the pressure of this stream. The manipulated variable will be the pump power that is supplied to the stream. This can be done through a simple feedback loop controller. This will ensure that the pressure of S45 is high enough to satisfy the pressure requirements for the reverse osmosis step. This will also ensure S45 can withstand the pressure drop that will occur in the reverse osmosis membrane.

Just as in the hydrocyclones, there will be one waste stream containing the biomass and water that is removed from the products. The controls will be exactly the same. The flow rate of the outlet from the disposal area will be manipulated to avoid an over accumulation. Again, a feedback controller will be used to control the level.

Finally, the manipulated variable that is adjusted to achieve the desired filtration purity set point in this case will be the crossflow velocity. This velocity is controlled by the flow rate of the inlet stream. Increasing crossflow velocity can reduce fouling and improve filtration purity but also decrease the filtration rate. However, this stream has already been set as the manipulated variable for satisfying the set point for the inlet pressure. Therefore, a cascade controller will be used. A cascade controller allows for two independent control loops. The cross flow velocity is more important as it controls purity so it will be the primary control loop that is regulated, and the secondary control loop variable will be the pressure of the stream.

Reverse Osmosis

In this section the primary goal is to remove the remaining large amounts of water before entering the distillation step. Due to the large water content, removing the water is necessary if a cost effective distillation is pursued. The choice of water removal is reverse osmosis in which the water is removed using a membrane filter. There are a few process controls for this type of system such as inlet stream flow rate, inlet stream pressure, the pH of the solution, temperature, recovery rate, and permeate flow rate. These factors will ensure the reverse osmosis system can operate effectively and efficiently.

First, the inlet flow rate will be a manipulated variable controlled through a feedback controller to ensure a consistent flow rate. Very high flow rates lead to possible membrane damage and very low flow rates lead to concentration polarization and reduced flux rates. Controlling the flow rate will also control the pressure of the stream which is necessary since it will prevent any damages to the membrane. This will also ensure that the stream enters the system at the correct pressure. As mentioned, the pressure drops from the previous separation equipment may affect the pressure more than expected so it may be required to control the flow rate using another spare pump from the warehouse that is listed in the equipment.

Secondly, the pH of the solution will be monitored. Since the solution stream has compounds such as acetic acid, lactic acid, and ethanol, it may be required to alter the pH in order to prevent any effects on the solubility and precipitation of the compounds, which will then further cause fouling to the membrane. Similar to the fermenter, the pH will be controlled by using sodium hydroxide and sulfuric acid in a split range control set up.

The recovery is another aspect that will be monitored. The recovery rate will monitor the percentage of the feed solution that is converted into permeate. This means that if the recovery rate is low, in this case, it signifies that a lower amount of water was recovered from the solution. The recovery will be set to be approximately 99%, thus, removing nearly all of the water. For this, the manipulated variable will be the rejected flow rate. By altering the flow rate of the reject stream, the recovery rate can maintain the desired range of the set point. Either a feed back or a feed forward controller can be used, but a feedback controller is more commonly used for reverse osmosis processes.

To ensure optimal separation, it is key to maintain the desired ΔP (pressure difference) across the membrane for reverse osmosis. Pressure sensors are used to measure the pressure before and after the membrane. This helps to ensure that the ΔP is maintained at the desired level. If the pressure difference deviates from the setpoint, the control system can adjust the flowrate of the feed and/or the permeate stream to maintain the desired ΔP.

In this process, the water that was removed as the permeate stream, will be recycled into the blending tanks. The blending tanks used for the media utilize huge amounts of water, thus, this water is used as a recycle stream to improve plant efficiency. Recycle streams are crucial to control as they may lead to snowballing effects in the plant. As a result, a valve is placed on the recycle stream where the stream is manipulated based on demands from the blending tanks. For this a typical feedback controller will be sufficient.

Distillation

Finally, the last section of the entire process is the final stage of purification, this will be the distillation setup to isolate 1,3-propanediol from all the other compounds. All 3 distillation columns will follow the same control analysis except for T-101 since there is a recycle stream present. The main concerns for the distillation columns will be monitored such as: satisfying the purity set point via temperature analysis, monitoring the sump level in the column and the reflux accumulator, and the pressure of the column. The last distillation column is the unit that was analyzed in detail for both the HAZOP analysis and the P&ID analysis. The process control for this column will be briefly analyzed below.

First, the column's sump level will be controlled through bottoms flowrate that exits the column. A feedback controller will be set to ensure the desired level set point of the column is respected. The level of the reflux accumulator is controlled by manipulating the flow rate of the distillate. This will also be controlled using a feedback controller.

Second, to satisfy 1,3-propanediol's purity, the reflux ratio will be altered. The purity will be monitored through the temperature of the overhead stream. If the temperature drops, leading to a lower purity, the reflux ratio will increase to keep the desired purity. A feed forward could be used for a faster and more efficient change in cases of purity drops, but a feedback controller will also be sufficient.

To monitor the pressure of the column, the flowrate of the overhead vapor entering the condenser will be used as the manipulated variable. When there is an excess pressure within the column, the valve will be opened wider, which will lead to an increased flowrate into the condenser. However, if this results in an accumulation of liquid in the reflux accumulation drum, the level controller for the drum will step in and increase the bottom flowrate exiting the drum to maintain an appropriate sump level as mentioned before. This entire process can be done by employing feedback controllers.

The recycle stream for the first distillation will follow the same controls analysis as mentioned for the reverse osmosis unit. It will also be controlled using a feedback controller.

Finally, the product stream can be manipulated to control the temperature of the inlet stream (S47) that comes from the reverse osmosis unit. It may be reduced if S47 needs to be less heated, or it can be increased if S47 is in need of heating. Here it is wise to use a feed forward controller since it is a double pipe heat exchanger that uses two different process streams that exchange heat with one another.

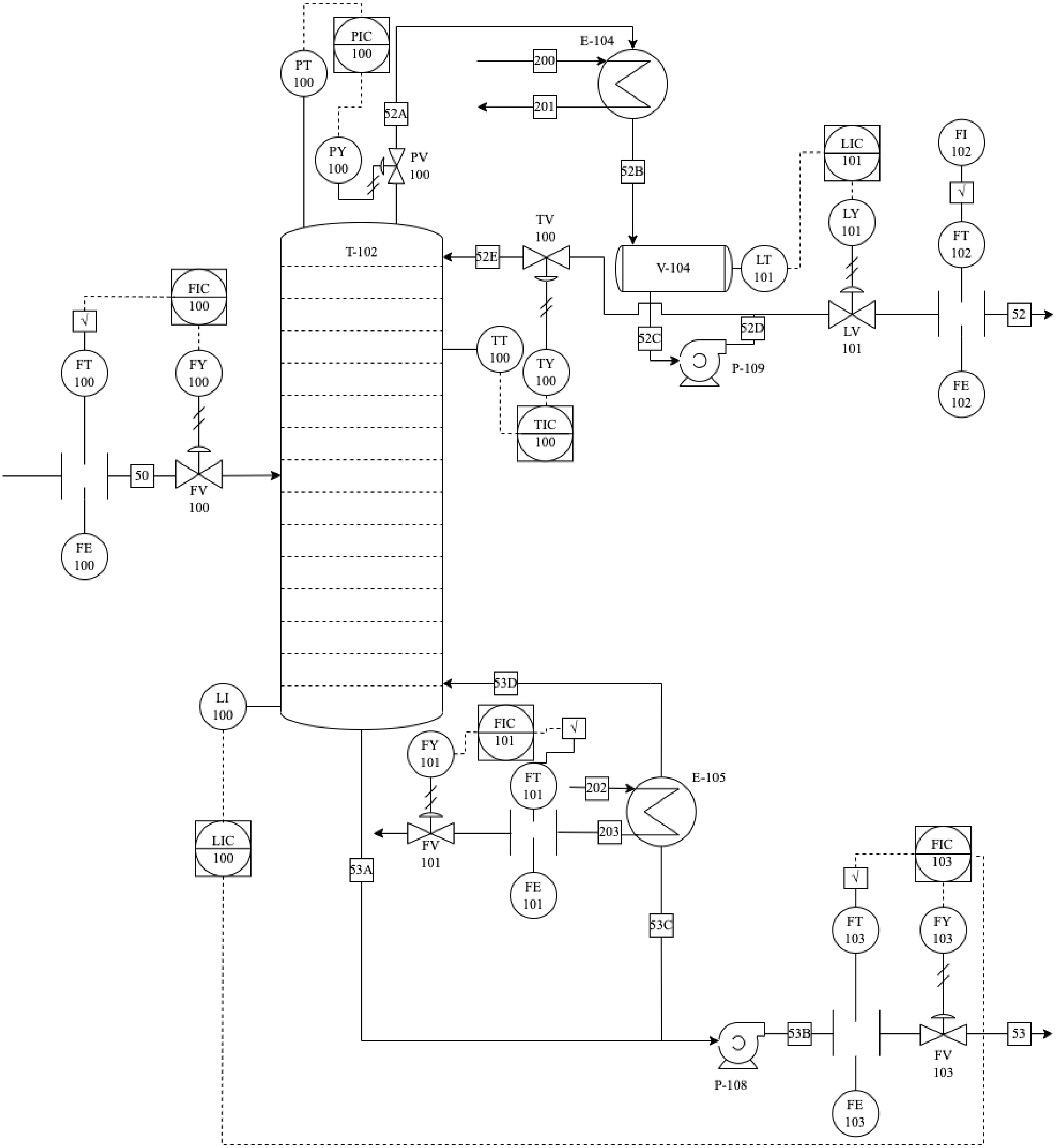


Figure 20 - T-102 Distillation Column Process Instrumentation Diagram (P&ID)

HAZOP Analysis

Table 3 - HAZOP Analysis

Stream/Equipment	Guide Word	Deviation	Cause(s)	Consequence(s)	Safeguard(s)	Action(s)
S50/T-102	No	Flow & Level	Pipe blockage, Control valve shut, Valves fail, Tube leakage and blocking, Pump failure	Column dry out from reboiler, No operation within the unit, no production out of column. Level of condensed vapor in the overhead receiver will be empty, and the level of liquid in the bottom of the column will be absent. Pumps may run dry.	Flow control loops. Install a low level alarm. Check maintenance procedure and schedule.	Allow control valve to stay open at desired point to allow flow in the column
	Less		Pipe blockage, Control valve reduced, Valves fail, Tube leakage and blocking, Pump failure	Inadequate separation, off-spec products, reduced production rate. Level of condensed vapor in the overhead receiver will drop, and the level of liquid in the bottom of the column will drop. Pumps may run dry.	Flow control loops. Install a low level alarm. Check maintenance procedure and schedule.	Level indicator controller will send signal to control valve at bottom stream to partially open valve
	More		Control valve is fully opened. Increase pumping capacity. Control valves failure.	Overloading in the column and build-up in the down comers lead to flooding Changes in product quality.	Flow control loops. Install a high level alarm. Decrease feed rate or reflux rate	Level indicator controller will send signal to control valve at bottom stream to partially close valve
Reboiler/E-105	Low	Pressure	Inadequate steam supply	Increased energy consumption. Off-spec product. Reduced distillate production.	Install a pressure controller loop to notify operators of low pressure within the column.	Maintains desired pressure in the bottom by increasing reboiler duty.

	High		Inadequate cooling duty from overhead, excessive steam supply, steam utility malfunction.	Low efficiency of separation. Rupture of column or other related equipment Product loss.	Install a high pressure alarm to notify operators of high pressure within the column.	Maintains desired pressure in the bottom by decreasing reboiler duty
Reboiler/E-105	Low	Temperature	Control valve opening reduced, less steam flow, control valve failure.	Low vapor flow which can result in flooding from liquid traveling from top of the column. Inadequate condensation, off-spec products	Implement temperature probe in reboiler for monitoring. Regular maintenance and monitoring of equipment	Maintains desired temperature within column increasing reboiler duty
	High		Control valve fully opened, more steam flow, control valve failure.	Excessive vapor flow can force liquid out of the overhead (Puking). Equipment damage, fire or explosion risk, increasing cooling water duty.	Implement temperature probe in reboiler for monitoring. Regular maintenance and monitoring of equipment	Maintains desired temperature within column decreasing reboiler duty

Condenser/E-104	Low	Pressure	Low vapor rate to the condenser, low reboiler duty, reduced feed rate.	Off-spec product. Reduced distillate production. Forces reboiler duty to exceed	Install a pressure gauge to display the operators of low pressure within the condenser. Regular maintenance and monitoring of equipment	Maintains desired pressure within overhead column by decreasing cooling duty
	High		High vapor rate to the condenser, high reboiler duty, increase in feed rate, less cooling water utility to condenser	Rupture of condenser or other related equipment Product loss. Forces cooling water duty to exceed .	Install a pressure gauge to display the operators of high pressure within the condenser. Regular maintenance and monitoring of equipment	Maintains desired pressure within the overhead column by increasing condenser duty.

Condenser/E-104	Low	Temperature	less steam flow from bottom, Reflux control valve failure	Inadequate condensation, off-spec products, decrease in cooling duty, increase in reboiler duty	Implement temperature probe for condenser to indicate operator(s) temperature deviation. Regular maintenance and monitoring of equipment	Temperature controller on reflux valve that regulates the amount of external reflux sent to the tower to control condensation in the overhead
	High		Excessive steam flow from bottoms, poor tray design.	Excessive vapor flow can force liquid out of the overhead (Puking). Equipment damage, increasing cooling water duty, reduced product quality, inefficient heat transfer.	Implement temperature probe for condenser to indicate operator(s) temperature deviation. Regular maintenance and monitoring of equipment	Temperature controller on reflux valve that regulates the amount of external reflux sent to the tower to control condensation in the overhead

Table 4 - HAZOP Analysis (continued)

Stream/Equipment	**Guide Word**	**Deviation**	**Cause(s)**	**Consequence(s)**	**Safeguard(s)**	**Action(s)**
Accumulator/ V-104	Low	Pressure & Level	Reduced flow rate into the overhead column, insufficient cooling from condenser, decrease in reboiler duty	Increasing cooling water duty, level of fluid in the accumulator decreases which leads to pressure drop within the accumulator, potential damage to pump.	Implement pressure and level control loops to monitor pressure and level within accumulator	Lower cooling duty to adjust low pressure in V-104/Low level is sensed in accumulator and allows distillate valve to close
	High		Increased flow rate into the overhead column, increased cooling from condenser, pump failure, increase in	Level of fluid in the accumulator builds up which leads to pressure build up within the accumulator, damaging the accumulator and surrounding units.	Install a pressure relief valve to reduce pressure in the unit. Reduce reboiler duty. Regular maintenance and monitoring of equipment	Pressure sensors allow the control valve for the vent to open. High level is sensed in accumulator

			reboiler duty			and allows distillate valve to open
Reboiler/E-105	Low	Level	Inadequate feed flow, steam flow too high	Insufficient separation, inefficiency, low product yield, pump may run dry.	Install level controller to recognize low level within bottom column	Increase feed flow, lower reboiler duty
	High		Valve for feed excessively open, valve for bottom shut, inadequate steam to reboiler.	Flooding, insufficient separation, column damage.	Install level controller to recognize high level within bottom column	Decrease feed flow, higher reboiler duty, open bottom stream valve.

Condenser/E-104	Low	Level	Low cooling water duty, inadequate reboiler duty, low feed flow	Off-spec product. Reduced distillate production. May force increase reboiler/condenser duty	Install flow meter before and after condenser	Increasing condenser duty or excessively opening feed feed flow valve until level is regulated
	High		High cooling water duty, excessive reboiler duty, high feed flow	Off-spec product. Increase in unnecessary distillate production. May force decrease in reboiler/condenser duty, level build-up in condenser which may lead to damage from flooding	Install flow meter before and after condenser	Decreasing condenser duty or closing feed feed flow valve until level is regulated

Bottom stream	No	Flow	Pump malfunction, no feed stream, no reboiler duty, pipe blockage, closed bottom valve.	Inefficiency in production, column build-up.	Maintain regular maintenance around equipment, check pipes for obstruction, make sure valves are open. Implement flow controller	Flow control allows the bottom stream control valve to open and release product.
	Less		Pump malfunction, low feed stream, low reboiler duty	Inefficiency in production, column build-up.	Maintain regular maintenance around equipment, check pipes for obstruction, make sure valves are open. Implement flow controller	Flow control allows bottom stream control valve to open and release product
	More		Increase in feed rate	Can reduce level in the sump of the column which may stimulate level alarms	make sure valves aren't excessively opened. Implement flow controller	Flow control allows bottom stream control valve to close reduce bottom flow

Reflux Stream	Low/ Less	Temperature & Flow	Less feed stream, less cooling duty, less reboiler duty, pump failure	Less production, potential vapor buildup, effect product composition	Maintain regular maintenance around equipment, check pipes for obstruction, make sure valves are open, implement temperature controller	Temperature control loop senses the change which decreases external reflux flow to the tower

	High/ More		Excessive reboiler duty, low cooling water duty	flooding in the column, effect product composition	Maintain regular maintenance around equipment, check pipes for obstruction, make sure valves are open, implement temperature controller	Temperature control loop senses the change which increases external reflux flow to the tower
Distillate stream	No	Flow	Pump malfunction, no feed stream, no cooling water/reboiler duty, pipe blockage, closed valve in distillate.	Inefficiency in production, column build-up.	Maintain regular maintenance around equipment, check pipes for obstruction, make sure valves are open. Implement flow controller	Flow control allows the distillate stream control valve to open and release product.
	Less		Pump malfunction, low feed stream, low cooling/reboiler duty, reflux ratio higher than usual	Inefficiency in production, column build-up.	Maintain regular maintenance around equipment, check pipes for obstruction, make sure valves are open. Implement level controller	Level controller allows distillate control valve to increase flow
	More		Increase in feed rate Reflux ratio lower than usual	Unnecessary distillate product, requires more vapor	make sure valves aren't excessively opened. Implement level controller	Level controller allows distillate control valve to reduce flow

HAZOP T-102 P&ID

Once incorporating all of the potential risks in the plant, specifically in T-102, the new P&ID incorporates all the necessary safety features required.

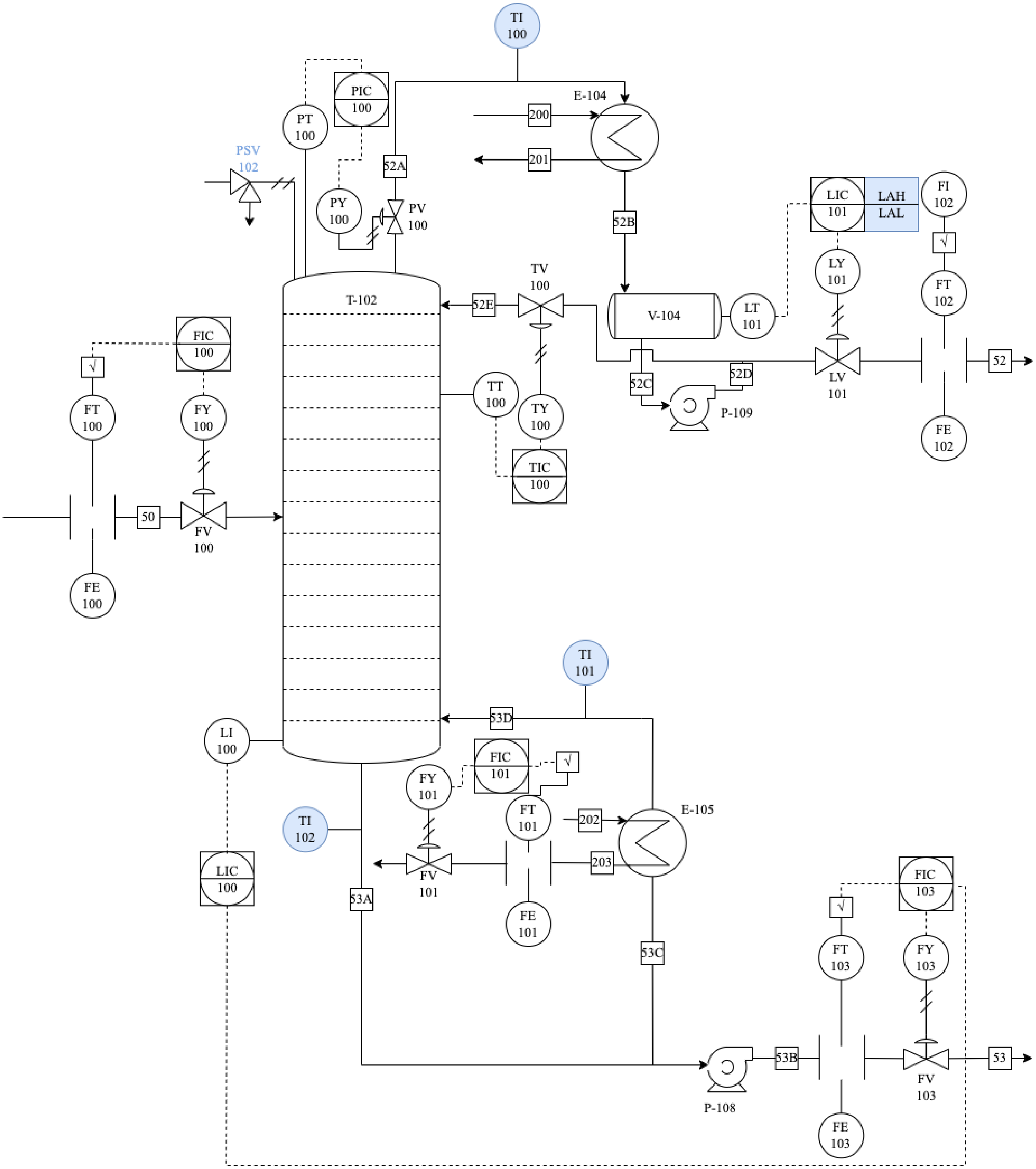


Figure 21 - HAZOP T-102 Distillation Column Process Instrumentation Diagram (P&ID)

Table 5 - Operational Safety Analysis

Block	Safety Concern	Prevention/Mitigation
Holding V-101,V-103, ST-101, ST102	Odor	Sterilize the blending tank before use and follow strict aseptic techniques during fermentation. Wear appropriate masks to prevent nausea form odor
	High Temperature/Hot Surface	Mandate the use of personal protective equipment (PPE) for all staff in proximity to the system.
	Pressure build-up	Install pressure relief vent to avoid pressure build-up and potential explosions.
	Physical Hazard	Blending tanks within the holding region include agitators. Emergency shutdowns should be recognized to halt the agitator.
Fermentation R-101, R-102, R-103, R-104	High Temperature/Hot Surface	Control the pressure and temperature in all seed fermenters; make use of the pressure relief valve. Mandate the use of PPE for all staff in proximity to the system.
	Pressure build-up	Accumulation of gasses like nitrogen and CO_2. Install pressure relief vent to avoid pressure build-up and potential explosions.
	pH	Control pH with regulators such as NaOH and H_2SO_4 to maintain a desired pH of 5.5. Wear appropriate respiratory masks, suits and shielded goggles.
	Odor	Make certain that all staff members are wearing appropriate PPE and protective jumpsuits. Wear appropriate masks to prevent nausea from odor. Contain and manage any unpleasant smells using an odor control system like wet scrubbers.

	Physical Hazard	Blending tanks within the holding region include agitators. Emergency shutdowns should be recognized to halt the agitator.
Biomass Separation CY-101, CY-102, UF-101	Noise and Vibration	For the hydro-cyclone units, proper design, installation, and maintenance of the entire system can help minimize vibrations and ensure smooth operation. Ensure operators are equipped with safety ear plugs to minimize potential loud noise.
	Membrane Fouling	For the ultrafiltration, implement a cleaning-in-place (CIP) system to clean the membranes regularly without disassembling the entire unit. Choose a membrane with suitable properties, such as pore size, hydrophilicity, and chemical resistance, to minimize fouling potential for the specific application.
Water Recycler RO-101	Membrane Fouling	For the reverse osmosis unit, implement a cleaning-in-place (CIP) system to clean the membranes regularly without disassembling the entire unit. Choose a membrane with suitable properties, such as pore size, hydrophilicity, and chemical resistance, to minimize fouling potential for the specific application.
Distillation E-101, T-101, T-102, T-103	High/Low Pressures	Implement pressure and vacuum monitoring and control systems with alarms and interlocks. Regularly inspect and maintain pressure relief devices.
	High/Low Temperatures	Adjust the reboiler heat input or the condenser cooling medium flow rate to maintain the desired temperature profile. Monitor and control the temperature at critical points in the column, such as the feed entry, overhead, and bottoms. Implement temperature control systems, such as controlling heating medium flow rate for evaporator.

	Liquid Overflow	Install level control and alarm systems to prevent column flooding or liquid entrainment in the overhead vapor line.
	Contains Flammable Materials	Refrain from contact of ignition sources.

Environmental Analysis

Air Emissions

An estimated 26,920.75 Ton/yr of Carbon dioxide (CO_2) is emitted from a total of four fermenter units; R-101, R-102, R-103 & R-104 as well as utility generation. Nitrogen and oxygen will also leave from the seed and main fermentation processes. CO_2 is classified as a hazardous air pollutant, and its monitoring falls under the jurisdiction of the EPA, as outlined in Section 112 of the Clean Air Act [52]. As per the regulations in Illinois, constructing an emission source and carrying out operations involving emission sources necessitate obtaining two permits: a construction permit and an operating permit. In order to prevent/mitigate such emissions, the aim is to send CO_2 to greenhouses for plant growth and higher crop yields. In order to fulfill crop growth, the supply of CO_2 levels for optimal plant growth should be considered. As per EPA,"Facilities are generally required to submit annual reports under Part 98 if GHG emissions from covered sources exceed 25,000 metric tons CO2e per year [61]." Large amounts of CO_2 will substantially decrease the photosynthetic rate of plants, so it is imperative to supply greenhouses at a ppm basis spec of 600 ppm to ensure optimal plant growth which will substantially decrease CO_2 emissions by 70% for a more eco-friendly process. After utilizing 70% of CO_2 to greenhousing, the total CO_2 emissions total at 22,917.11 Ton/yr [54]. No reporting is required since the amount emitting is lower than the minimum report amount of 25,000 metric tons per year.

In supplying greenhouses with 600 ppm CO_2 the rate of photosynthesis increases roughly 2 fold compared to ambient CO_2 levels of 300 ppm and allows the greenhouse to operate at a higher temperature which in turn can further increase the net photosynthetic rate to a rate nearly three times as fast [57,58].

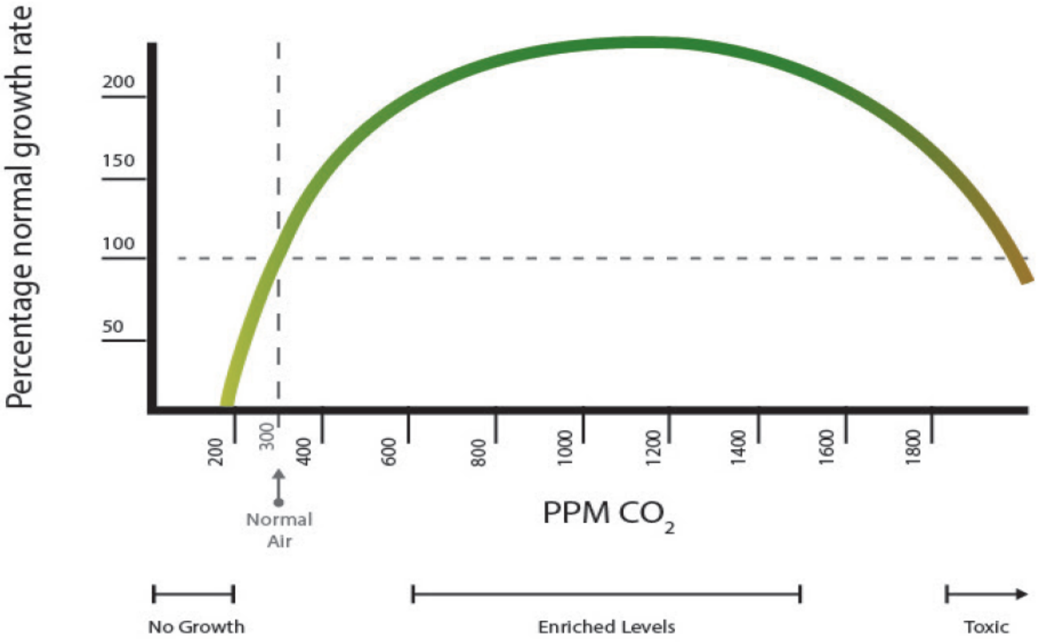


Figure 22 - The effect of CO_2 enrichment on growth rates. [57,58]

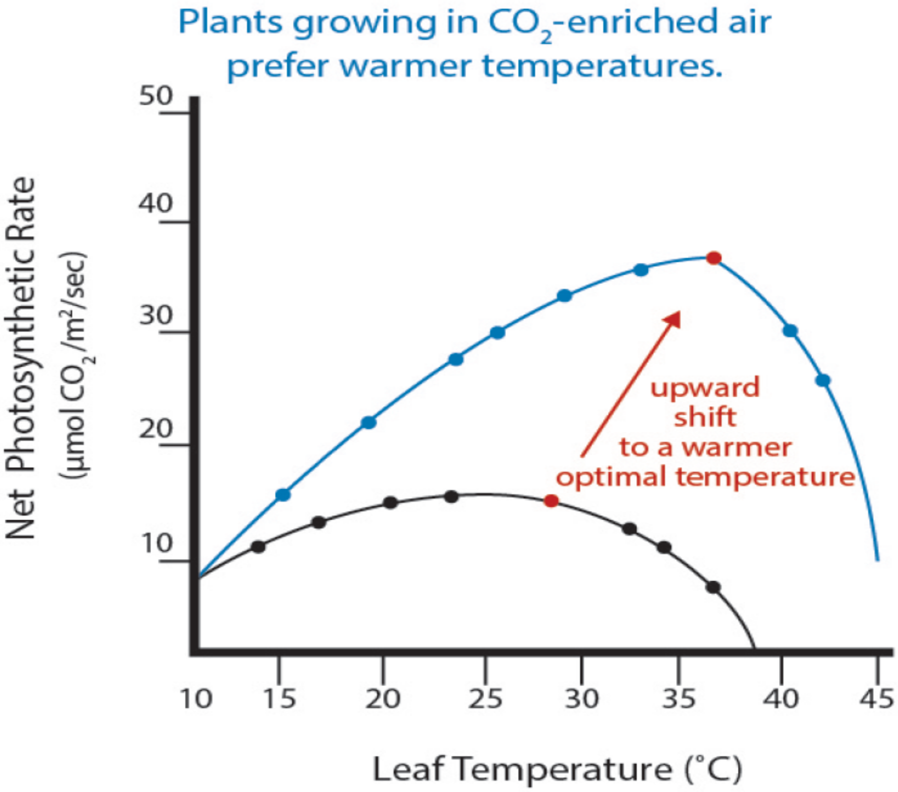


Figure 23 - Relationship between leaf temperature and net photosynthetic rate at ambient and elevated levels of CO_2 in Populas grandidentata [57,58]

Table 6 - Total Emissions

Component	Emissions Amount (Tons/year)	Source
Carbon dioxide	22,917.11	Fermentation & Utility generation
Nitrogen	2,137.31	Fermentation

Table 7 - Tolerable Emissions [56]

Tolerable Emissions/Yr (Ton/Yr)	Penalty Fee
100 tons to 13,888 tons	\$18/ton - \$21.50/ton

Water Discharges

An estimated 303,163.63 Ton/yr of water is recycled in this process for resource conservation, as well as reducing environmental impact. Water is recycled using reverse osmosis method and used through streams (3, 48, 58, 59). This is by separating large water amounts using RO-101 from incoming stream 45. Water waste is discharged at 49,676.36 Ton/yr along with biomass. As a total percentage, the amount of water recycled is approximately 85.9%. In Illinois, water discharges from industrial sites are regulated under the National Pollutant Discharge Elimination System (NPDES) permit program, which is authorized by the federal Clean Water Act and administered by the Illinois Environmental Protection Agency (IEPA). The NPDES program aims to control water pollution by regulating the discharge of pollutants into the waters of the United States. Industrial facilities that discharge processed wastewater, stormwater, or other pollutants into surface waters must obtain an NPDES permit from the IEPA [53]. In this process, the solids are discharged from the system alongside the water so the basis for treatment and discharge will be the biomass and water tonnage. That is, the rate for treating the discharge will use the relatively more expensive solids discharge rate but use the combined mass of water and biomass.

Solids Waste

The solid wastes leave streams (41, 44, 46) at an estimated 24,727.27 tons/yr of biomass and 49,676.36 tons/yr of water. Industrial plants that generate, store, treat, or dispose of solid waste are required to obtain permits from the IEPA. These permits outline the specific requirements and conditions for handling and disposing of waste materials. The Resource Conservation and Recovery Act (RCRA), passed in 1976, is the primary federal law governing solid waste management in the United States, including Illinois. The RCRA sets forth regulations and guidelines for the handling, storage, treatment, transportation, and disposal of solid waste generated by industrial plants and other facilities. In Illinois, the state's Environmental Protection Agency (IEPA) is responsible for enforcing the RCRA and ensuring compliance with federal and state regulations. Some of the ways the Solid Waste Act affects industrial plants in Illinois include permit requirements, waste characterization, waste minimization and other waste management acts [54].

Material Safety

Material safety involves identifying the potential hazards associated with a material, assessing the risks involved, and implementing appropriate measures to control or mitigate those risks. This may include using personal protective equipment (PPE), implementing engineering controls such as ventilation systems, establishing safe storage and handling procedures, and providing training and education to workers and other stakeholders. Material safety analysis is rigorously conducted for the components listed below for the 1,3 PDO process. These components include what comes in and out of the streams as raw materials, by products and final products. The majority of components have permissible exposure limits (PEL) standardized by OSHA. For this case, PEL values will be listed on the basis of 8 hour shifts in part per million (ppm).

The National Fire Protection Association (NFPA) codes and standards are widely used by governments, industries, and organizations to promote fire and life safety. They cover a wide range of topics, including building construction, fire protection systems, electrical systems, hazardous materials, and emergency response. Compliance with NFPA codes and standards is often required by law, insurance policies, and other regulations. The following table displays the classifications of NFPA levels for better comprehension [35].

Table 8 - NFPA Classification Level [55]

Classification Level	**Health Hazard**	**Flammability**	**Instability**
0	No hazard	Will not burn	Stable
1	Slight hazard - Exposure may cause irritation, but only minor residual injury possible	Flash point above 200°F (93°C)	Unstable if heated
2	Moderate hazard - Exposure could cause temporary incapacitation or residual injury unless prompt medical attention is given	Flash point between 100-200°F (38-93°C)	Violent chemical change possible at elevated temperature and pressure
3	Serious hazard - Exposure could cause major or permanent injury	Flash point below 100°F (38°C) and boiling point above 100°F (38°C)	Shock and heat may initiate a violent chemical change
4	Deadly hazard - Exposure could be fatal even with prompt medical attention	Very flammable - Will vaporize and readily ignite at normal temperature	May detonate even under normal conditions

Water: OSHA has established standards for the safe use of water in industrial processes, such as cooling water, process water, and wastewater. NFPA classification for water is Health: 0; Flammability: 0; Instability: 0. These standards include requirements for the treatment, storage, and disposal of these types of water, as well as guidelines for the use of personal protective equipment (PPE) to prevent worker exposure to harmful substances that may be present in the water [36].

Corn steep Liquor (CSL): Corn steep liquor (CSL) can be used as a cheap but efficient nitrogen source for this process. CSL is a byproduct of the corn wet milling process that can be used as a feed ingredient for livestock. NFPA classification for CSL is Health: 3; Flammability: 0; Instability: 0. While the Occupational Safety and Health Administration (OSHA) does not have specific standards for CSL, there are general regulations that apply to the handling, storage, and transportation of any hazardous materials that may be present in CSL. There are potential hazards when handling CSL. Chemical exposure, CSL may contain harmful chemicals such as sulfur dioxide and lactic acid, which can cause irritation or harm to the skin, eyes, and respiratory system if not handled properly. Confined space entry, CSL storage tanks or vessels may be considered confined spaces and may require special entry procedures to ensure worker safety. Recommendations by OSHA for handling these potential risks are the following. Proper storage, CSL should be stored in well-ventilated areas away from heat sources and incompatible materials. Personal protective equipment (PPE), workers handling CSL should wear appropriate PPE such as gloves, eye protection, and respiratory protection if necessary. Hazard communication, employers must inform workers of the hazards associated with CSL and provide training on safe handling procedures. Finally, employers should have an emergency response plan in place in case of spills or other accidents involving CSL [37].

Sodium Hydroxide: According to the OSHA's "Hazard Communication Standard" (29 CFR 1910.1200 OSHA HCS), Sodium hydroxide is not classified as hazardous. NFPA classification for Sodium Hydroxide is Health: 3; Flammability: 0; Instability: 1. However, it is important to note that NaOH can cause harm to the skin and metals as it is corrosive. Prolonged exposure to NaOH can lead to eye damage, irritation, or toxicity, thus necessitating the use of appropriate Personal Protective Equipment (PPE) when handling it. Wear chemical splash goggles and face shield, butyl rubber gloves, apron, and/or clothing as well as appropriate protective clothing to prevent skin exposure [38]. The PEL according to OSHA for NaOH is 1.2 ppm [39].

Glucose: This chemical is not considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200). NFPA classification for glucose is Health: 0; Flammability: 0; Instability: 0. However, If the substance comes in contact with eyes, flush them with water, including under the eyelids, for at least 15 minutes and seek medical assistance. If substance is inhaled, move to an area with fresh air and seek medical attention immediately if you experience any symptoms. If you stop breathing, perform artificial respiration [40].

Glycerol: The OSHA Hazard Communication Standard (29 CFR 1910.1200 OSHA HCS) does not classify Glycerol as a hazardous substance. NFPA classification for CSL is Health: 1; Flammability: 1; Instability: 0. However, it is essential to use the correct Personal Protective Equipment (PPE) to prevent skin or eye contact. Additionally, it is important to note that strong oxidizing agents are incompatible materials when used in conjunction with Glycerol [41]. The PEL according to OSHA for crude glycerol is 2 ppm [42].

Nitrogen (Liquid): Nitrogen is used for purging pipelines, tanks, and other equipment to remove impurities and prevent fires and explosions. Liquid nitrogen is a colorless, odorless, and extremely cold liquid (typically at -320 F) that can pose hazards to workers if not handled properly. NFPA classification for liquid nitrogen is Health: 3; Flammability: 0; Instability: 0. Appropriate PPE to consider is safety glasses with side-shields and cryogenic gloves that should be worn at all times. The Occupational Safety and Health Administration (OSHA) has several regulations and standards that apply to the handling and use of liquid nitrogen in the workplace.

Some potential hazards associated with liquid nitrogen include many risks. Cold burns, contact with liquid nitrogen can cause severe cold burns and frostbite to the skin and eyes. Oxygen displacement, liquid nitrogen can displace oxygen in confined spaces and lead to asphyxiation. Pressure build-up, If liquid nitrogen is stored in a sealed container, pressure can build up and cause explosions or other mechanical failures [43]. The PEL according to OSHA for nitrogen is 1000 ppm [39].

Lactobacillus Reuteri: Lactobacillus Reuteri CH53 is used to convert glycerol to 1,3-PDO in an anaerobic condition. When employing Lactobacillus Reuteri in the workplace, employers are responsible for providing a safe working environment for their employees. Employers must comply with OSHA's Hazard Communication Standard (HCS), which requires them to inform their employees about the hazards of the chemicals or substances they may come into contact with on the job. Handling bacteria from a safety standpoint requires careful attention to sanitation, personal protective equipment, proper handling techniques, training, and monitoring to prevent the spread of infectious diseases and accidental exposure to harmful bacteria. However, the body safety level for L. reuteri is classified as BSL 1. Which means the microbes are generally not associated with causing disease in healthy adults, and they pose a low risk to laboratory personnel and the environment. ATCC follows a risk assessment to determine the biosafety level of a material with guidance from the BMBL. It is the user's responsibility to know the hazards of the material according to their organization's policies and regulations. Personal protective equipment is recommended when handling vials. For cultures stored in liquid nitrogen, some vials may leak and explode upon thawing, so ATCC suggests storing them in the vapor phase instead [44].

Ethanol: Ethanol, also known as ethyl alcohol, is a colorless and flammable liquid that is commonly used as a solvent, fuel, and disinfectant. It is also used in the production of alcoholic beverages and personal care products. NFPA classification for ethanol is Health: 2; Flammability: 3; Instability: 0. According to OSHA, ethanol can pose a hazard to workers if it is not handled and used properly. The main hazards associated with ethanol include flammability, toxicity, and skin and eye irritation. To prevent these hazards, OSHA recommends that workers who handle ethanol use appropriate PPE, including gloves, goggles, and protective clothing (29 CFR 1910.133 OSHA HCS). Workers should also be trained in the safe handling and use of ethanol and should be aware of the potential hazards associated with this chemical. In addition, OSHA requires employers to provide adequate ventilation in areas where ethanol is used and stored to prevent the buildup of flammable vapors. When handling immense fires, employers are required to maintain appropriate fire suppression equipment such as alcohol resistant foams and carbon dioxide extinguishers as well as to train workers in fire prevention and response procedures [45]. The PEL according to OSHA for ethanol is 1000 ppm [39].

Lactic Acid: When handling lactic acid in the workplace, it is important to follow proper safety protocols and wear PPE such as protective clothing, gloves, and goggles, as well as ensuring proper ventilation and storage of the substance in accordance with (29 CFR 1910.1200 OSHA HCS). NFPA classification for lactic acid is Health: 2; Flammability: 1; Instability: 1. Employers are responsible for ensuring the safety of their employees when working with hazardous substances, including lactic acid. This includes providing appropriate training and safety equipment, as well as implementing safety procedures and monitoring for any potential health hazards [46]. The PEL according to OSHA for lactic acid is 10 ppm [39].

Acetic Acid: According to OSHA HCS (29 CFR 1910.1200 OSHA HCS). Acetic acid can be hazardous to workers if it is not handled properly. It can cause skin and eye irritation, respiratory irritation, and corrosion of metal equipment. NFPA classification for acetic acid is Health: 3; Flammability: 2; Instability: 0. Exposure to high concentrations of acetic acid vapor can also cause lung damage. In the workplace, OSHA requires that workers be protected from exposure to acetic acid. OSHA also requires that employers provide appropriate personal protective equipment (PPE) to workers who may be exposed to acetic acid. This may include nitrile gloves, goggles, and respirators [47]. The PEL according to OSHA for acetic acid is 10 ppm[39].

Dextrose: In accordance with (29 CFR 1910.1200 OSHA HCS OSHA HCS). NFPA classification for dextrose is Health: 0; Flammability: 0; Instability: 0. When handling dextrose in the workplace, it is important to follow safe handling practices and take appropriate precautions to prevent exposure. This may include wearing PPE such as gloves, goggles, and a respirator if necessary, as well as following proper storage and disposal procedures. Employers should also provide training on the safe use and handling of dextrose and ensure that employees are aware of any potential hazards or risks associated with the substance [48].

Phosphoric Acid: In accordance with (29 CFR 1910.1200 OSHA HCS OSHA HCS), phosphoric acid is classified as a corrosive substance under category 1, and has the potential to cause severe damage to the eyes and skin, as well as organ toxicity. NFPA classification for phosphoric acid is Health: 3; Flammability: 0; Instability: 1. To ensure safety when working with phosphoric acid near the CIP (clean-in-place) system, appropriate PPE such as nitrile gloves, side-shield glasses and long aprons should be worn at all times. It is also important to avoid inhaling any vapor or mist that may be generated during use [49]. The PEL according to OSHA for phosphoric acid is 0.25 ppm [39].

Carbon Dioxide: In the fermentation process, relatively small amounts of Carbon dioxide is released. NFPA classification for carbon dioxide is Health: 2; Flammability: 0; Instability: 0. In accordance with (29 CFR 1910.1200 OSHA HCS OSHA HCS), there is no listed acute toxicity for CO_2, which requires all personnel working near the fermenters to wear flame-resistant clothing. CO_2 can also lead to asphyxiation, so proper ventilation is necessary when working with it. PPE required when in contact are respirators, impervious gloves, side shield goggles and appropriate clothing [50]. The PEL according to OSHA for carbon dioxide is 5000 ppm [39].

Nitrogen (Gas): Nitrogen can create an oxygen-deficient atmosphere that can be hazardous to workers who are entering confined spaces or areas with limited ventilation. NFPA classification for nitrogen gas is Health: 0; Flammability: 0; Instability: 0. To minimize the risks associated with nitrogen, OSHA recommends implementing appropriate safety measures, including ensuring adequate ventilation in areas where nitrogen is being used or stored, providing appropriate personal protective equipment (PPE) such as gloves and face shields, and training workers on the safe handling and use of nitrogen. OSHA also recommends implementing an emergency action plan in the event of a nitrogen-related accident or incident [51]. The PEL according to OSHA for nitrogen is 1000 ppm [39].

1,3 Propanediol: 1,3 PDO is commonly used in the manufacture of cosmetics, personal care products, and food and beverage products. NFPA classification for 1,3 PDO is Health: 1; Flammability: 1; Instability: 1. It is generally considered to be safe for use in these applications, but caution should be taken when handling the chemical in its pure form. This chemical is not considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200) [51]. In such cases, the manufacturer or importer of the chemical must provide a Safety Data Sheet (SDS) that contains information on the hazards, handling, and emergency procedures related to the chemical.

Table 9 - Material Safety Summary

All information was retrieved from the MSDS cited above						
Components	**Boiling Point (F)**	**Flash Point (F)**	**Autoignition (F)**	**Flammability**	**Permissible Exposure Limit (8-hour shift)**	**Shelf-life**

					in ppm	
Water	212	N/A	N/A	N/A	N/A	Indefinite
CSL	212-219	N/A	N/A	N/A	N/A	Several months, under optimal storage conditions
Sodium Hydroxide	212	N/A	N/A	N/A	1.2	1 year
Glucose	N/A	N/A	N/A	N/A	N/A	1 year
Glycerol	554	320	752	N/A	2	Greater than 1 year, under optimal storage conditions
Nitrogen	-320.8	Product does not sustain combustion	N/A	N/A	1000	Greater than 1 year, under optimal storage conditions
Lactobacillus Reuteri	N/A	N/A	N/A	N/A	N/A	Weeks to months under optimal storage conditions. Store between 2-8 (C)
Ethanol	172.4	61.88	685.4	Class 3	1000	3 years
Lactic Acid	251.6	230	N/A	Class 1	10	Up to 3 years, under optimal storage conditions
Acetic Acid	242.6	104	800.6	Class 3	10	1 year
Dextrose	N/A	N/A	N/A	Class 1	N/A	1 year under optimal storage conditions
Phosphoric Acid	316.4	N/A	N/A	Class 0	0.25	Indefinite, under optimal

						storage conditions
Carbon Dioxide	N/A	N/A	N/A	N/A	5000	Indefinite, under optimal storage conditions
1,3 Propanediol	417.2	284	761	Class 1	N/A	1 year under optimal storage conditions

Process Economics Analysis

Inside Battery Limits (ISBL)

The Inside Battery Limits, or ISBL, plant cost is dependent on the cost of compiling and installing all of the equipment necessary for the plant. There are two phases of this cost: direct and indirect. Direct field costs include all of the major process equipment (vessels, reactors, columns, etc.), bulk items (piping, valves, wiring, etc.), civil works (roads, foundations, piling, etc.), and installation labor and supervision. Indirect field costs include construction costs (rentals, workshops, temporary utilities, etc.), field expenses and services (specialist costs, overtime pay, field canteens, etc.), construction insurance, labor benefits and burdens (social security, workers' compensation, etc.) and miscellaneous overhead items (legal costs, import duties, special freight costs, etc.). In our case, most of these costs cannot be considered because we are not actually building the plant and have no expertise in constructing a chemical plant. However, to calculate the total plant ISBL capital cost, which includes engineering costs, we must factor in the Lang factor. The Lang factor is responsible for accounting for the installation costs needed from the SuperPro and Aspen equipment cost data. The Lang factor that we will use is 3.63 because our plant is a mixed fluids-solids processing plant [32].

$$C = F * (\sum C_e) = 3.63 * (\$10.54\ MM) = \$38.27\ MM$$

Where:

- C = Total plant ISBL capital cost (including engineering costs)
- F = Lang factor (installation factor)
- C_e = Total delivered cost of all the major equipment items

Outside Battery Limits (OSBL)

The Outside Battery Limits, or OSBL, investment is the cost of the additional components added to the infrastructure of a new or existing chemical plant to meet new production requirements. This includes but is not limited to site security, emergency services, laboratories, offices, water pipes, circulation pipes, electric power lines, etc. For a plant that is in its early stages with no details of the plant site being known, the OSBL is estimated to be 40% of the ISBL cost [32]. Like ISBL, the OSBL infrastructure upgrades are typically made during the commissioning phase of the plant and need to be done before the plant begins operation.

$$OSBL = 0.4 * ISBL = 0.4 * \$38.27\,MM = \$15.31\,MM$$

Where:

- $OSBL$ = Outside Battery Limits (OSBL) costs
- $ISBL$ = Inside Battery Limits (ISBL) costs [including engineering costs]

Fixed Capital Cost

The fixed capital cost is a crucial component of the economic analysis of a plant, as it represents the upfront investment required to build and equip the facility. It is calculated by summing up the costs of all long-term assets that are required for the plant to operate, such as land, buildings, machinery, and equipment. The equation to calculate the fixed capital cost can be represented by summing up the ISBL and OSBL as follows:

$$FCC = ISBL + OSBL = \$38.27\,MM + \$15.31\,MM = \$53.58\,MM$$

- FCC = Fixed capital cost
- $ISBL$ = Inside Battery Limits (ISBL) costs [including engineering costs]
- $OSBL$ = Outside Battery Limits (OSBL) costs

Contingency

Contingency charges serve as a means to mitigate the potential impact of unforeseen circumstances on project costs, such as fluctuations in pricing or unexpected expenses. In the absence of an instantaneous facility construction process, it is imperative to incorporate contingency costs into the project budget to ensure adequate financial resources are available to handle these unpredictable changes. Rather than requesting additional funding mid-project, contingency charges are typically levied to the parent or contracting organization at the outset of the project. A minimum of 10% of the total capital investment, encompassing both the Inside Battery Limit (ISBL) and the Outside Battery Limit (OSBL), is commonly reserved for contingency expenses. The contingency charge calculation follows a predefined equation, however, we've implemented a contingency factor of 60% for our calculations. The implementation of this contingency factor is due to the fact that for a contingency factor of only 10% there is a 90% confidence that the project will come in over budget; however, for a 60% contingency there is a 95% confidence that the project will come in under budget per Towler and Sinnott[32].

$$Contingency = 0.60 * FCC = 0.60 * \$53.58\,MM = \$32.15\,MM$$

Where:

- FCC = Fixed capital cost

Engineering Cost

The fabrication of specialized equipment or structures that are to be used on site can sometimes exceed the purview of chemical process design. In such cases, a contractor is typically engaged to execute the design instead of the plant engineer. The engineering cost, which includes all expenses associated with the creation of the design and possibly extends to the entire manufacturing and installation process, is factored into the project budget. The calculation of engineering cost is governed by a predefined equation.

$$EC = 0.15 * FCC = 0.15 * \$53.58\,MM = \$8.04\,MM$$

Where:

- EC = Engineering cost
- FCC = Fixed capital cost

Working Capital

Working capital refers to the additional funds required, beyond the plant's construction costs, to start and sustain plant operations. It represents the money that is tied up in keeping the plant running and typically includes raw material and product inventories, cash on hand, accounts receivable, and credit for accounts payable, as well as spare parts inventory. Working capital can vary significantly depending on the plant's complexity and the products it produces. A general estimate for chemical and petrochemical plants is 15% of the fixed capital cost. It is important to note that working capital is not the same as miscellaneous start-up costs and cannot be depreciated. Companies can increase working capital turnover, a measure of efficiency, by reducing working capital through tighter management of inventories and accounts receivable.

$$WC = 0.15 * FCC = 0.15 * \$53.58\, MM = \$8.04\, MM$$

- WC = Working capital
- FCC = Fixed capital cost

Total Capital Cost

The total capital cost of a chemical plant can be calculated by summing up five key components, which include Inside Battery Limit (ISBL), Outside Battery Limit (OSBL), contingency, engineering cost, and working capital. We have already evaluated and estimated these individual components and the final value is calculated using the following formula:

$$TCC = ISBL + OSBL + Contingency + EC + WC = \$101.81\, MM$$

Where:

- TCC = Total capital cost
- $ISBL$ = Inside Battery Limits (ISBL) costs [including engineering costs]
- $OSBL$ = Outside Battery Limits (OSBL) costs
- EC = Engineering cost
- WC = Working capital

Variable Cost of Production (VCOP)

To calculate the overall variable cost of production (VCOP), there are a total of four aspects that must be considered: cost of raw materials, utility cost, waste disposal, and shipping costs [32]. The cost of raw materials utilized is done by compiling all of the materials fed into the reactor and their respective amount and converting it into $\frac{USD}{yr}$ using its market price. Table 39 demonstrates the cost of each material and the total cost of raw materials needed for this process.

Utility cost was given by SuperPro and Aspen for all of our utilities: cooling water, steam, and electrical power. The total for SuperPro was $\frac{\$0.65\, MM\, USD}{yr}$, for Aspen it was $\frac{\$0.49\, MM\, USD}{yr}$, and for our consumable membrane it was $\frac{\$0.21\, MM\, USD}{yr}$ totaling to an amount of $\frac{\$1.35\, MM\, USD}{yr}$.

The cost associated with waste disposal is a crucial consideration in the economic analysis of Variable Cost of Production (VCOP) for chemical plants. Most chemical processes generate materials that cannot be recycled or sold as by-products and must be safely disposed of as waste. To accurately calculate waste disposal costs, it is necessary to analyze the amount of waste coming out of the process and its cost to dispose of. Our waste materials include biomass and contaminated biomass water. A report from the U.S. Environmental Protection Agency (EPA) in 2016 mentioned that the cost of biomass waste disposal treatment ranges from \$30 to \$70 per metric ton [33]. This is dependent on what type of biomass is being formulated and on how hazardous it is. This information is unknown to us and cannot be used to gauge how much it costs in the industry. That is why we took an average of the range and came up with a cost of \$50 per metric ton of biomass waste. Wastewater treatment is required for the water coming out of the fermentors, however, our wastewater stream includes biomass so we assumed it to cost the same. The disposal cost for biomass was $\frac{\$1.32\ MM\ USD}{yr}$ and for wastewater was $\frac{\$2.66\ MM\ USD}{yr}$. The total came out to be $\frac{\$3.98\ MM\ USD}{yr}$.

The final aspect that needs to be covered for VCOP is shipping costs. Both truck and rail estimations have to be made because these are the two crucial modes of transportation for distribution. The price of transporting via truck and rail is $\frac{\$0.25\ USD}{1\ metric\ ton-mile}$ and $\frac{\$0.025\ USD}{1\ metric\ ton-mile}$ respectively [34]. Unfortunately, the transportation logistics of our products aren't quite clear and don't know who and where we would be distributing. To be safe, we'll demonstrate how much it would cost both truck and rail to transport 150 miles of all our materials including the raw materials, products, and by-products. It comes out to be $\frac{\$13.9\ MM\ USD}{yr}$ and $\frac{\$1.39\ MM\ USD}{yr}$ for trucking and railing services respectively. The total comes out to be $\frac{\$15.29\ MM\ USD}{yr}$. Once adding all of the different total costs, the total VCOP came out to be $\frac{\$88.59\ MM\ USD}{yr}$

Maintenance Cost

Maintenance costs in chemical engineering refer to the expenses involved in keeping a plant in good condition, regardless of the production level. These costs include the cost of replacing or repairing parts and equipment, as well as the cost of labor required to carry out the maintenance work. Typically estimated as a fraction of ISBL investment, maintenance costs range from 3% to 5%, depending on the type of process. In addition, if regular equipment replacement is required due to shorter life expectancy or excessive wear and tear, the design engineer should estimate the annualized replacement cost and add it to the maintenance costs. For our process, it will be 3% of our ISBL investment due to our process will primarily focus on liquids and gases.

$$MC = 0.03 * ISBL = 0.03 * \$38.27\ MM = \$1.15\ MM$$

Where:

- MC = Maintenance cost
- $ISBL$ = Inside Battery Limits (ISBL) costs [including engineering costs]

Fixed Cost of Production (FCOP)

According to Towler, there are a total of eleven criteria that are considered for the fixed cost of production (FCOP). Operating labor, supervision, direct salary overhead, maintenance, property taxes, insurance, rent of land, general plant overhead, allocated environmental charges, license and royalty fees, capital charges, and sales and marketing costs are all part of FCOP [32]. However, before any of these can be calculated, the operator shifts and salary must be first sorted. It is assumed that the total hours of plant operation is $\frac{7{,}960.33\ hr}{yr}$, which gets rounded up to $\frac{8000\ hr}{yr}$ (which is approximately 330 days). Each shift length is 8 $\frac{hr}{day}$, there are a total of 1,000 $\frac{shifts}{yr}$ or 3.0303 $\frac{shifts}{day}$. We chose 4.3 $\frac{shifts}{day}$ with 6 $\frac{operators}{shift}$ because it is both a batch (fermentation), which requires a minimum of 3 operators, and continuous (distillation) process and is a standalone site [32]. This will yield a total of 25.8 $\frac{operators}{day}$ with a salary of $64,785 per operator as a national United States Gulf Coast (USGC) average [32] back in 2014 (while accounting for inflation).

Operating labor is the number of operators required each day multiplied by the salary, which comes out to be $\frac{\$1.67\ MM\ USD}{1\ yr}$. Supervision is depicted to be 25% of the operating labor comes out to be $\frac{\$0.42\ MM\ USD}{1\ yr}$. Direct salary overhead is usually 40-60% of the operating labor plus supervision and accounts for the employee health insurance and other benefits. This plant is brand new and requires two different production methods (batch and continuous), we decided to have our overhead at 50%, which comes out to be $\frac{\$1.04\ MM\ USD}{1\ yr}$. Maintenance of both the materials and labor are dependent on the ISBL investment and it ranges from 3-5%. Again, due to our plant being new, we decided to have our maintenance at 3% because all of the equipment will be new, which comes out to be $\frac{\$1.15\ MM\ USD}{1\ yr}$. Property taxes and insurance for a complicated process is around 2% of the ISBL, which comes out to be $\frac{\$0.76\ MM\ USD}{1\ yr}$. Assuming we rent the building for our process, the rent will be usually around 1% of the sum of the ISBL and OSBL (FCC), which comes out to be $\frac{\$0.54\ MM\ USD}{1\ yr}$. The general plant overhead is around 65% of the total cost of operating labor, supervision, and direct salary overhead while adding the maintenance to cover corporate entities like human research, R&D, etc. This comes out to be $\frac{\$3.18\ MM\ USD}{1\ yr}$. The allocated environmental charges to cover superfund payments are typically 1% of the ISBL plus OSBL cost, which comes out to be $\frac{\$0.54\ MM\ USD}{1\ yr}$. Running license fees and royalty payments is typically 0.5% of the ISBL and comes out to be $\frac{\$0.19\ MM\ USD}{1\ yr}$. The capital charges are typically 1% of the ISBL plus OSBL cost to account for any financial assistance like loans that were used to acquire the plant, which comes out to be $\frac{\$0.54\ MM\ USD}{1\ yr}$. Finally, sales and marketing costs are entirely dependent on the owner of the plant and can range from zero to millions of dollars a year. For ease, we decided to make our sales and marketing cost the same as the average operator salary which is $\frac{\$64{,}785\ USD}{1\ yr}$ [32]. The total cost of the FCOP and CCOP (which is VCOP + FCOP) was $\frac{\$10.1\ MM\ USD}{1\ yr}$ and $\frac{\$98.68\ MM\ USD}{1\ yr}$ respectively.

Revenue

In the context of the production of 1,3-propanediol (1,3-PDO), the main product generated accounts for the majority of revenue. Assuming a base price of $\frac{\$2180\ USD}{ton}$ based on the current market price for the purity of our 1,3-PDO [27], this product represents a significant portion of our revenue. Our main competitor in the bio-based 1,3-PDO market is DuPont Tate & Lyle, which currently holds a 60% market share. However, our process costs less and uses energy more efficiently, while also producing sellable by-products, making it a more favorable option. The pricing for our by-products, including ethanol, acetic acid, and lactic acid, was determined using a similar market-based pricing analysis, with specific prices for each product being $\frac{\$738\ USD}{ton}$, $\frac{\$1180\ USD}{ton}$, and $\frac{\$1240\ USD}{ton}$, respectively. The calculation of revenue in chemical engineering involves taking into account for the quantities and market values of all products and by-products sold, and it is a key determinant of the overall profitability of a chemical production process.

$$Revenue = P * MV_P + \sum_{i=1}^{n} BP_n MV_{BP}^{n} = \frac{\$204.84\ MM\ USD}{yr}$$

Where:

- P = Amount of product produced
- MV_P = Market value of product
- n = Number of by-products
- BP = Amount of by-product produced
- MV_{BP} = Market value of by-product

Simple Payback Time

In chemical engineering, the economic feasibility of a process can be determined by utilizing various methods of economic analysis. One such method is the calculation of the simple payback time, which quantifies the duration of time required to recoup the initial investment cost. This metric serves as an indicator of the investment's attractiveness, with a shorter payback time indicating a more desirable investment compared to a longer payback time. To calculate the simple payback time, the total initial capital investment is divided by the average annual cash flow. The resulting value represents the number of years required to recover the investment cost shown below and a graphical representation of the simple payback period can be found in the Appendix.

$$Simple\ Payback\ Time = \frac{Total\ Investment}{Average\ Annual\ Cash\ Flow} = 1.89\ years \approx 2\ years$$

Return on Investment (ROI)

In the realm of investment analysis, the return on investment (ROI) is a commonly utilized metric for evaluating the viability of a potential investment. ROI measures the amount of return generated by an investment, relative to the investment's cost. A higher ROI indicates a more profitable investment opportunity, and as such, is regarded as a more attractive option. The ROI can be calculated by dividing the net annual profit generated by the investment by the total amount of the investment. This calculation provides a percentage value that represents the rate of return on the investment. Therefore, the ROI serves as a valuable tool for decision-making and aids in determining the economic feasibility of an investment.

$$ROI = \frac{Net\ Annual\ Profit}{Total\ Investment} = \frac{Revenue - CCOP}{TCC} * 100 = \frac{\$204.84\ MM\ USD - \$98.68\ MM\ USD}{\$101.81\ MM\ USD} * 100 = 104.26\%$$

Where:

- ROI = Return on investment
- $CCOP$ = Cash cost of production
- TCC = Total capital cost

Gross Margin

Gross margin is a significant measure in the chemical industry, as raw material costs often account for the bulk of the production costs (typically around 80% to 90% of the total cost of production). Since raw material and product prices of commodities are subject to high variability, margins are less susceptible to fluctuations if producers can pass on feedstock price increases to their customers. As a result, margins are often used in price forecasting. The level of gross margins varies significantly across different sectors of the chemical industry. For commodities such as bulk petrochemicals and fuels, margins are generally very low (less than 10% of revenues) and may occasionally even be negative. Commodity businesses are often cyclical due to investment cycles and tend to experience higher margins when supply is short. On the other hand, for products that are tightly regulated or subject to patent protection, such as food additives, pharmaceutical products, and biomedical implants, margins can be considerably higher, typically accounting for over 40% of revenues and often higher than 80% of revenues. In this way, gross margins provide insight into the profitability of different sectors of the chemical industry and can assist in predicting market trends and investment opportunities [32]. Our process came out to have a gross margin of roughly 52.42% of our revenues.

$$GM = Revenues - Raw\ Material\ Cost = \frac{\$204.84\ MM\ USD}{yr} - \frac{\$67.96\ MM\ USD}{yr} = \frac{\$136.88\ MM\ USD}{yr}$$

Where:

- GM = Gross Margins

Gross Profit

Gross profit in chemical engineering is a crucial financial metric that reflects the efficiency and financial health of a company within the industry. It is essential to distinguish gross profit from gross margin, as the former encompasses a broader range of costs and revenues. Gross profit takes into account all variable costs, including raw materials, fixed costs, and even revenues generated from by-products. In some chemical engineering companies, gross profit is calculated on a plant basis, which excludes general overhead charges and selling costs, such as selling, general, and administrative (SG&A) expenses. To determine the operating income of a company, the SG&A charges are subsequently deducted from the gross profit. This approach allows companies to better evaluate their operational efficiency and make informed decisions for future growth and profitability.

$$GP = Main\ Product\ Revenue - CCOP = \frac{\$204.84\ MM\ USD}{yr} - \frac{\$98.68\ MM\ USD}{yr} = \frac{\$106.15\ MM\ USD}{yr}$$

Where:

- GP = Gross Profits

Net Present Value (NPV)

Net present value (NPV) is a financial metric that measures the value of an investment by comparing the present value of its future cash inflows to the initial investment. NPV is considered a more useful measure than simple payback or ROI because it takes into account the time value of money, which recognizes that money today is worth more than the same amount of money in the future. The calculation of NPV involves determining the present value of each future cash inflow, which is obtained by discounting the cash flow by a discount factor that is based on the given interest rate. The sum of all the present values of future cash inflows, less the initial investment, gives the NPV [32].

For our plant, the NPV calculation considers several factors, including the cost of planning and constructing the plant, the production of the products, and the depreciation of fixed capital. The gross profit of the plant is calculated from the revenues generated by the main product, minus the cash cost of production (CCOP).

$$Gross\ Profit = Revenues - CCOP$$

Where:

- $CCOP$ = Cash cost of production

Depreciation is calculated using both the 5- or 7-year Modified Accelerated Cost Recovery System (MACRS) values, which are then multiplied by the total fixed capital of the plant.

$$Depreciation = MACRS * Total\ Fixed\ Capital$$

Where:

- $MACRS$ = Modified Accelerated Cost Recovery System

After calculating the gross profit and depreciation charge, the taxable income was determined as the difference between the two. The calculation of taxes paid was then performed, which involved multiplying the taxable income by the designated tax rate of 40%. It should be noted that taxes are paid for the previous year's taxable income and not for the current year. Furthermore, taxes are only applicable to valid taxable income that is positive and not negative or zero. This implies that if the taxable income for a given year is negative or zero, no taxes will be paid for that year. The calculation of taxes paid is a critical component in determining the net present value of an investment, as it directly affects the cash inflows for a given year. Thus, it is essential to consider all applicable tax laws and regulations when calculating the taxable income and taxes paid for any investment project.

$$Taxable\ Income = Gross\ Profit - Depreciation$$

$$Taxes\ Paid = Taxable\ Income\ (Previous\ Year) * Tax\ Rate$$

The cash flow for each year of the investment project is calculated by subtracting the taxes paid for that year from the gross profit. The resulting cash flow represents the actual amount of money that the investment generates for each year. The discount factor, which is based on the given interest rate, is then applied to each year's cash flow to obtain a modified present value of the cash flow. This modified present value represents the value of the cash flow in today's dollars, taking into account the time value of money. The calculation of the cash flow and discount factor is a critical step in determining the net present value of an investment project, as it reflects the actual cash inflows generated by the project over time. By incorporating the discount factor, the net present value takes into account the opportunity cost of tying up capital in the investment project, thus providing a more accurate measure of the investment's true value.

$$Cash\ Flow = Taxable\ Income - Cash\ Flow$$

$$Discount\ Factor = \frac{1}{(1+Interest)^2}$$

$$Present\ Value\ of\ Cash\ Flow = Cash\ Flow * Discount\ Factor$$

After calculating the present value of the cash flow for each year using the discount factor, the NPV values for the investment project can be calculated. Specifically, the NPV values for the 5-year and 7-year MACRS are calculated by adding up the present values of the cash flow for each year and then subtracting the initial investment. This calculation takes into account the time value of money and the opportunity cost of tying up capital in the investment project. The interest rate is a crucial factor in determining the NPV, as it affects the present value of the cash flow for each year. Thus, a higher interest rate leads to a lower present value of future cash flows, which in turn reduces the NPV of the investment. Conversely, a lower interest rate results in a higher present value of future cash flows and a higher NPV. The calculation of the NPV provides a clear measure of the investment's true value, allowing investors to make informed decisions about the viability of the investment project.

$$NPV = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n}$$

Where:

- NPV = Net present value
- CF_n = Cash flow in year n
- t = Project life in years
- i = Interest rate

The final NPV after the 20 years of the plant's operation was calculated, and the NPV values for the 5-year and 7-year MACRS were determined to be \$417.2 MM and \$430.7 MM, respectively. In both cases, the NPV value was positive, indicating a net profit in the investment in the plant. This result suggests that the investment in the plant is a viable option for investors, and they are likely to generate profits from the investment over the long term.

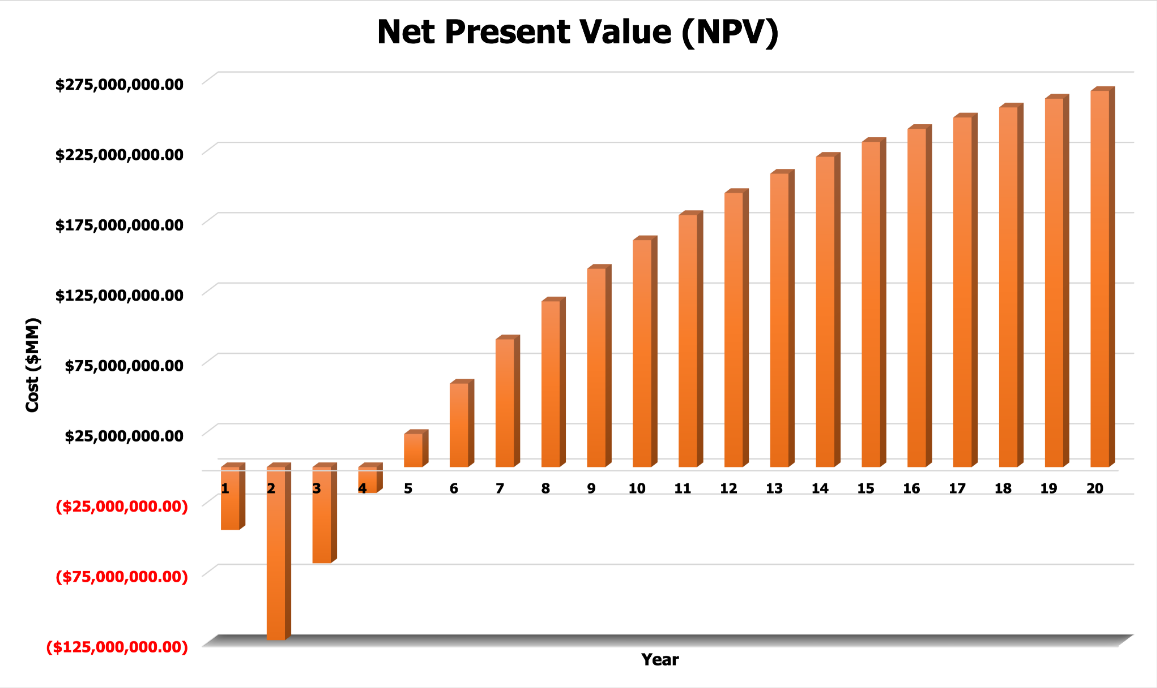


Figure 24 – Net Present Value (NPV) of Process

Discount Cash Flow Rate of Return (DCFROR)

The Discounted Cash Flow Rate of Return (DCFROR) is a financial metric that measures the maximum interest rate at which the cumulative net present value (NPV) of an investment equals zero. This is achieved by calculating the NPV of the investment at various interest rates and finding the rate at which the NPV equals zero. The DCFROR provides a useful way of comparing the performance of capital for different projects, regardless of the project's size or the actual interest rates prevailing at any time. It is a more useful method than NPV when comparing projects of very different size, as the DCFROR is independent of project size. When using DCFROR as an investment criterion, companies usually expect projects to have a DCFROR greater than the cost of capital. DCFROR can also be compared directly with interest rates and is sometimes known as the interest rate of return or internal rate of return (IRR). The value of 'i' is typically found by trial-and-error calculations or by using appropriate functions in spreadsheet software, such as Goal Seek. A more profitable project will be able to pay a higher DCFROR, making it an essential tool for decision-making in capital investment [32].

For our process, the DCFROR for the 5-year and 7-year MACRS was determined to be 59.33% and 61.10%, respectively. These are very high discount rates, meaning that investment into this project is profitable.

Sensitivity Analysis

The economic analysis of any project is heavily reliant on the accuracy of the initial investment and cash flow estimates. However, the actual cash flows achieved can be significantly influenced by changes in raw materials costs, operating costs, sales volume, and pricing. To assess the project's viability, a sensitivity analysis is conducted to examine the effects of uncertainties in the forecasts. The analysis begins with the calculation of the base case using the most probable values for various factors. Parameters in the cost model are then adjusted within a range of error for each factor, to determine the sensitivity of the cash flows and economic criteria to forecast errors. The results of the sensitivity analysis are usually presented in graphical plots of an economic criterion such as NPV or DCFROR versus the studied parameter, as shown below. The analysis helps to quantify the degree of risk involved in making judgments on the forecast performance of the project, providing investors with a more comprehensive understanding of the investment's viability.

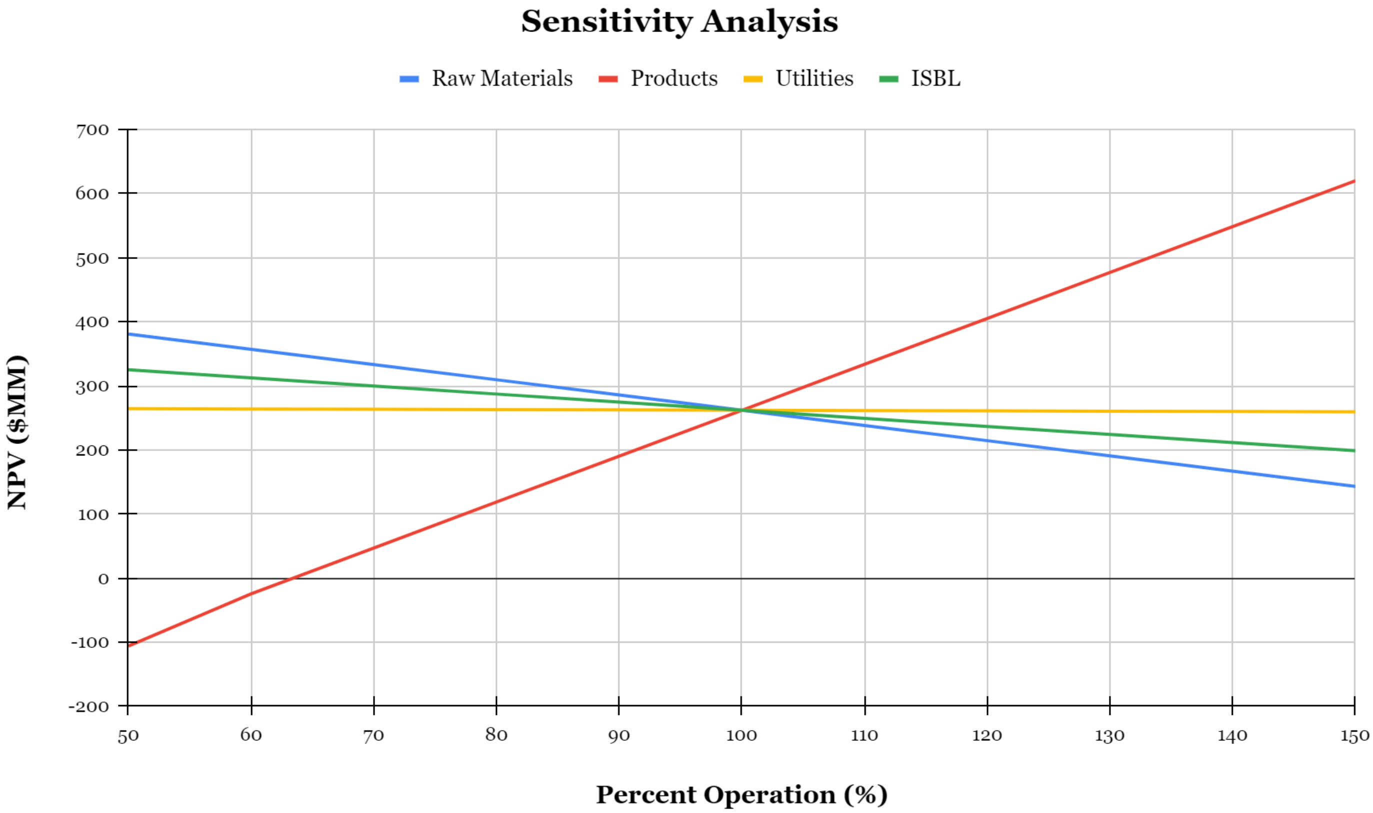


Figure 25 – Sensitivity Analysis Graph

It can be observed that changes in utilities do not affect the NPV of the process as much as changes in raw materials, products, and ISBL. Specifically, the process is more sensitive to the changes in products than the changes in raw materials and ISBL since the slope for the products is much steeper than the slope for the raw materials and ISBL. Within the ranges between 50% and 150% operation for the raw materials and ISBL, the NPV of the process is still positive. Meanwhile, at around 60% operation for the products, the NPV of the process becomes negative. Therefore, it is recommended that the process is operated with at least 60% of the products. Price changes for the products are expected to increase in the future due to global inflation and demand. An indication of positive compound annual growth rates for each product recognizes that the products will also increase in value due to market size growth.

Recommendations

In conclusion, this process is highly recommended as it is both profitable and is sustainable. With a payback period of 1.89 years and a NPV of $266 MM after 20 years, the project will quickly pay for itself. Looking ahead to the future, with a CAGR of 8.3%, the process will continue to make money in the future and it may be prudent to modularize the reactor setup to produce more product as needed.

It is very highly recommended to further analyze the costs of acquiring or genetically modifying *Lactobacillus Reuteri*, the assumed cost of $500,000 is likely too low, but the contingency of 60% is more than enough to accommodate either the acquiring of the strain or hiring a biotechnician to create a strain with an augmented 1,3-PDO synthesis gene. A study will need to be conducted at the bench top scale to verify the fermentation times of 9 hours for the seed fermentors and 24 hours for the production fermentor. If it is determined that those times are insufficient, it is possible that more reactors will need to be implemented to seed and/or the production fermentor will need to be run for a longer period of time. The assumption that all cellular biomass is nonviable for cell culture in the output of the hydrocyclones incurs a large waste disposal cost. Once the process is up, running the hydrocyclones' output will be sampled and cultured to assess the viability of recycling the biomass back into the process. The nonviable biomass will be assessed to determine if its grading is sufficient to use as feedstock for cattle. It is possible that the ultrafiltration unit will be insufficient to completely filter out trace proteins and implementing a sampling protocol to assess any antigenic proteins or irritants in the resulting product will be important. The ethanol and organic acids may pose a problem to the membranes used in the ultrafiltration and reverse osmosis units. The lifetime, based on typical manufacturers, was assumed to be 3 years of the membranes, but may vary which may shift the variable cost of production up or down. Depending on the final resulting 1,3-PDO colority, a desalination or ion exchange resin column may need to be implemented prior to the distillation steps. This may incur some additional cost, but any additional cost should be buffered by the contingency.

Moving forward, it is advised to contract with a local glucose vendor to secure a contract to source glucose for the first 5 years of plant operation as it will begin to be profitable. After this, acquiring corn stover and enzymatically treating it to produce glucose at a lower cost can be used provided the corn stover is of an adequate grade. This unit, while initially part of the process, was phased out in later stages as it was found that the possibility of losing money relative to buying glucose outweighed any benefit. It is also possible that the plant may need to expand to accomodate market demand. Luckily, Menard County has a low population density and land can be acquired to do so.

Overall, this process has a high probability of generating income for investors and has been thoroughly evaluated. The results indicate a clear potential for success and as such, it is recommended to move to the next stage of design. This will involve fine-tuning the details and implementing the plan, which will bring the process to fruition and bring a positive return on investment for all stakeholders involved. It is an exciting time for all involved and the future looks bright for this project.

Appendix

Design Basis

Location: Menard County, Southern Illinois due to it being the highest producer of corn with approximately 216.3 bushels (55,000 kg) of corn per acre [13]. We can reasonably assume that the corn stover content is 50%. The reason why Illinois was chosen is that it is in close proximity to transportation lines such as rail.

Amount of raw materials needed: 74,600 tons/year of Glycerol, 60,600 tons/yr of Glucose, 29,100 tons/yr of CSL, 73,900 tons/yr of Water, 5,800 tons/year of H_3PO_4 (20% w/w), 5,400 tons/year of NaOH (0.5 M), and 900 tons/yr of liquid N_2.

***Note: US production of corn in 2022 was 13.7 billion bushels of corn. At ~50% corn stover and 1 bushel of corn = 0.0254 metric tons of corn, we arrive at a value of 173,990,000 metric tons corn stover if we wish to create our glucose on site.** [24, 25]*

Plant's size: 3,358,340.05 ft^2. The Bio Tate and Lyle plant in Loudon Tennessee was used as a basis for our own production and was measured using Google Earth. The fed batch process where bacteria are used will be carried out indoors so better control is achieved as well as the filtration steps. The distillation will take place outdoors.

Annual Production: 61,500 tons/year of 1,3 PDO (99.54% purity), 2,330 tons/yr of Ethanol (99.9999% purity), 21,200 tons/year of Acetic acid (99.16% purity), and 36,900 tons/yr of Lactic acid (98.16% purity).

Block Flow Diagram (BFD)

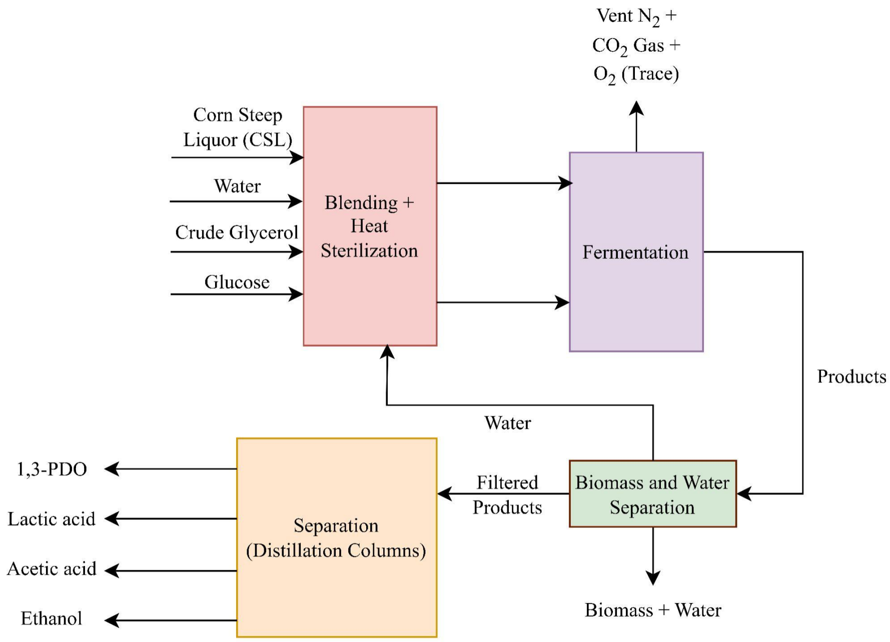


Figure 26 – BFD of the chosen process

Process Flow Diagram (PFD)

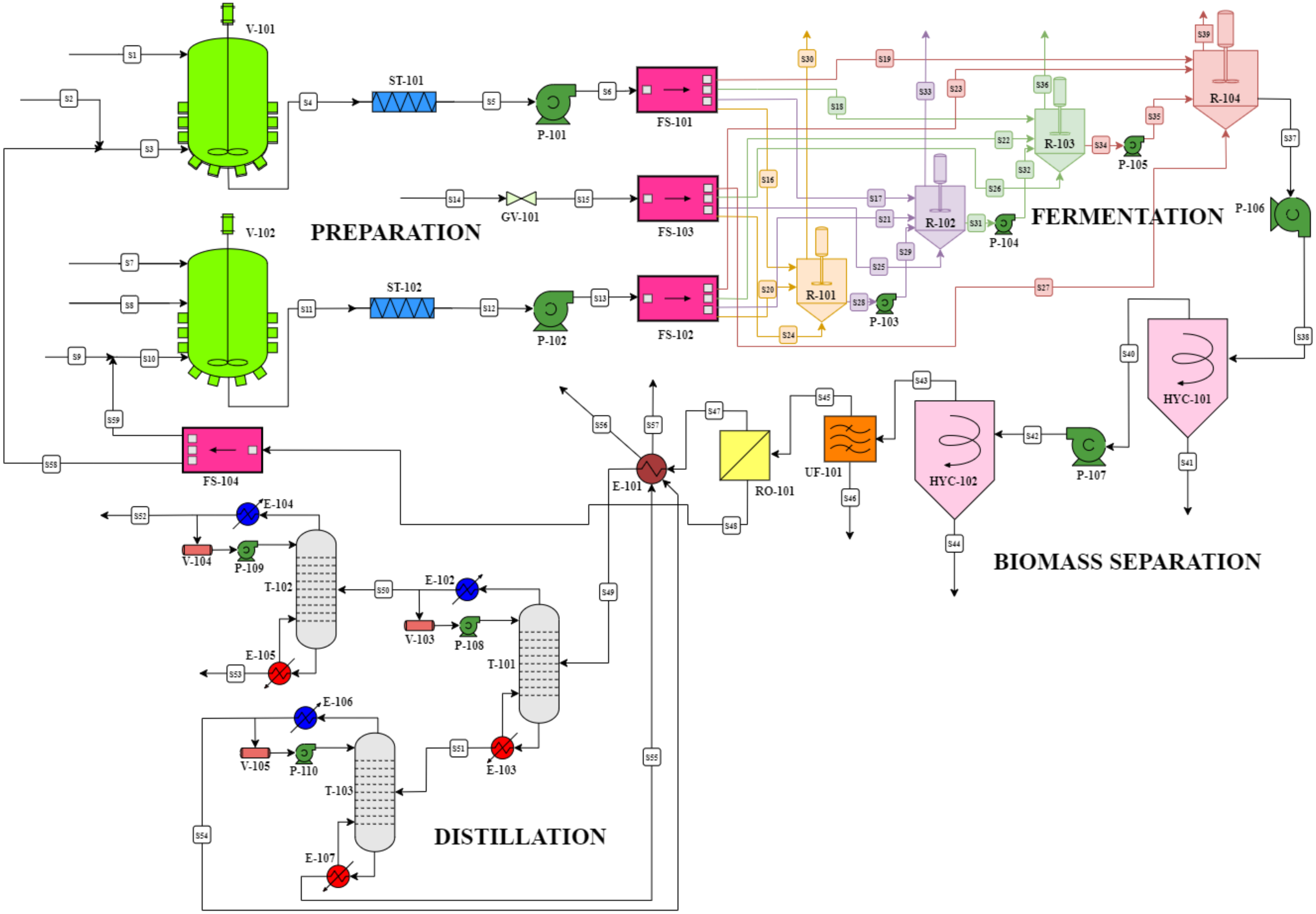


Figure 27 – PFD of the chosen process

1. **Blending Tanks** *(Note: All equipment type are mentioned in the 'Equipment List & Sizing' section, pg. 83)*

   There are 2 blending tanks at the beginning of the process. One used to mix water with corn stover liquor (ammonia and salt source), and the other was used to mix our glucose and glycerol with water (our sugar solution).

   a. ***V-101:*** Blending tank that mixes one stream containing corn stover liquor (CSL), a water stream, and a recycle stream. The water stream is used since water is necessary in the fermentation process since it makes an optimal environment for the bacteria to metabolize. The third stream is a recycled stream containing mainly water and some acetic acid to reduce the water load needed. This occurs at about 97.2ºF and 14.7 psia.
      i. *Volume*: 2,788 ft^3
      ii. *Height:* 31.73 ft
      iii. *Diameter:* 10.58 ft
      iv. *Design Pressure*: 22.04 psia
      v. *Material*: SS316
      vi. *Occupancy Time*: 3.25 hours
      vii. *Number of units:* 20

   b. ***V-102:*** Blending tank that mixes one stream containing glucose, a stream containing glycerol, and a recycle stream containing the water. As mentioned, the recycled stream also carries some acetic acid but this is fine as it will not impact the metabolism of our cell culture. This occurs at about 97.2ºF and 14.7 psia.
      i. *Volume*: 2,823 ft^3
      ii. *Height:* 31.86 ft
      iii. *Diameter:* 10.62 ft
      iv. *Design Pressure*: 22.04 psia
      v. *Material*: SS316
      vi. *Occupancy Time*: 3.25 hours
      vii. *Number of units:* 27

2. **Splitters**

   Due to the fact that 4 fermentation tanks will be used in this process where one fermenter feeds another, we must split out initial feed inputs into fours, so each tank can receive a fraction of initial feed input. The three streams that get split into fours are the streams that contain the glucose/glycerol water mix, the stream that contains the corn stover liquor water mix, and the feed input that contains nitrogen. The flow split percentage increases as the fermenter tank size increases, so a 90% split flow ends up in the production tank and the 0.9% split flow ends up in the first seed fermenter.

   a. ***FS-101***: Splits the flow that contains corn stover and water into the three seed fermenters and the production fermenter.
      i. Split % for 1st seed fermentation: 0.1%
      ii. Split % for 2nd seed fermentation: 0.9%
      iii. Split % for 3rd seed fermentation: 9.0%
      iv. Split % for the product fermentation: 90.0%

      - v. *Material*: CS
  - b. ***FS-102***: Splits the flow that contains glycerol, glucose, and water into the three seed fermenters and the production fermenter.
      - i. Split % for 1st seed fermentation: 0.1%
      - ii. Split % for 2nd seed fermentation: 0.9%
      - iii. Split % for 3rd seed fermentation: 9.0%
      - iv. Split % for the product fermentation: 90.0%
      - v. *Material*: CS
  - c. ***FS-103***: Splits the flow that contains nitrogen into the three seed fermenters and the production fermenter.
      - i. Split % for 1st seed fermentation: 0.1%
      - ii. Split % for 2nd seed fermentation: 0.9%
      - iii. Split % for 3rd seed fermentation: 9.0%
      - iv. Split % for the product fermentation: 90.0%
      - v. *Material*: CS

3. **Heat Sterilizers**

   Heat sterilization is a necessary protocol before a fermentation process since it ensures that the desired microorganisms can grow and metabolize without any competition from unwanted microorganisms. It kills off anything that might interfere with the cell culture in the fermenter. The type of sterilizers used will be a sanitary double pipe exchanger.
  - a. ***ST-101:*** Helps eliminate contamination from microorganisms, the high heat destroys any present bacteria, fungi, etc. that will interfere with production. This takes place at 284 F for the corn stover liquor water mix.
      - i. *Holding Tube Diameter:* 8.52 ft
      - ii. *Holding Tube Length*: 8.71 ft
      - iii. *Rated Throughput:* 391.02 gpm
      - iv. *Material*: SS316
      - v. *Number of units:* 4
  - b. ***ST-102:*** Helps eliminate contamination from microorganisms, the high heat destroys any present bacteria, fungi, etc. that will interfere with production. This takes place at 284 F for the glucose/glycerol water mix.
      - i. *Holding Tube Diameter:* 10.07 ft
      - ii. *Holding Tube Length*: 8.23 ft
      - iii. *Rated Throughput:* 427.59 gpm
      - iv. *Material*: SS316
      - v. *Number of units:* 5

4. **Fermentors**

   A fermentation process is a metabolic process where our bacteria converts organic compounds (the sugar solution being used) into other compounds. The seed fermenters are used before a production fermenter to establish a large quantity of actively growing cell cultures. In other words, it creates an inoculate solution containing the bacteria and the products produced. This inoculate solution can then be used to inoculate the production fermenter. This large population of active bacteria that is present in the inoculum will quickly colonize the large production fermenter, as opposed to making the production fermenter start from scratch. This yields a faster and much more efficient fermentation process. The type of fermenters used will be a jacketed stainless steel fermenter.

a. ***R-101:*** Begins fermentation process at 98.6ºF and 14.7 psia for 9 hours at a fixed pH of 5.5 with the lactobacillus bacteria strain present. The water mixtures of glycerol/sugar solution, CSL solution, along with nitrogen are then fed into the fermenter.
   i. *Volume*: 149 ft^3
   ii. *Height:* 11.94 ft
   iii. *Diameter:* 3.98 ft
   iv. *Design Pressure*: 22.04 psia
   v. *Material*: SS316
   vi. *Cycle Duration*: 9 hours
   vii. *Number of units:* 1
b. ***R-102:*** Continues fermentation process at 98.6ºF and 14.7 psia for 9 hours at a fixed pH of 5.5, and receives the inoculum stream from R-101 along with the same water mixture feeds used in R-101, but of course, the culture of bacteria is more advanced at this point.
   i. *Volume*: 1,485 ft^3
   ii. *Height:* 25.72 ft
   iii. *Diameter:* 8.57 ft
   iv. *Design Pressure*: 22.04 psia
   v. *Material*: SS316
   vi. *Cycle Duration*: 9 hours
   vii. *Number of units:* 1
c. ***R-103:*** Continues fermentation process at exact same conditions as the previous seed fermenters for 9 hours, and receives the inoculum stream from R-102 along with the same water mixture feeds used in R-101, but of course, the culture of bacteria is more advanced at this point. This seed fermentation series helps to ensure consistent and controlled conditions, helps improve the efficiency of the fermentation process and helps rid of contamination from other microorganisms.
   i. *Volume*: 1,650 ft^3
   ii. *Height:* 26.64 ft
   iii. *Diameter:* 8.88 ft
   iv. *Design Pressure*: 22.04 psia
   v. *Material*: SS316
   vi. *Cycle Duration*: 9 hours
   vii. *Number of units:* 9
d. ***R-104:*** Final fermentation step that receives the inoculum feed from R-103 along with water mixtures that were mentioned in the previous seed fermenters which produce our final yield of biomass and products including 1,3-propanediol. This fermenter takes place at the same conditions as seed fermenters but for 24 hours per cycle instead.
   i. *Volume*: 12,000 ft^3
   ii. *Height:* 51.62 ft

   - iii. *Diameter:* 17.21 ft
   - iv. *Design Pressure*: 22.04 psia
   - v. *Material*: SS316
   - vi. *Cycle Duration*: 24 hours
   - vii. *Number of units:* 11

5. **Hydrocyclones**

   Hydrocyclones are used to separate the biomass from liquid products that were produced from the fermenter. This is done by using centrifugal force to separate the particles. The centrifugal force causes the biomass to move towards the wall of the hydrocyclone, where it is collected. The liquid products move onto the next stage of the process.

   a. ***HYC-101***: The first hydrocyclone (8 inches in diameter) reduces the biomass composition in the solution from 6% to 1%. It operates at 98.6°F and at 14.7 psi.
      - i. *Rated Throughput:* 266.18 gpm
      - ii. *Overall Removal Efficiency*: 16.78%
      - iii. *Material*: SS316

   b. ***HYC-102***: The second hydrocyclone (8 inches in diameter) reduces the biomass composition in the solution from 1% to about 0.16%. It operates at 98.6°F and at 14.7 psi.
      - i. *Rated Throughput:* 231.72 gpm
      - ii. *Overall Removal Efficiency*: 2.98%
      - iii. *Material*: SS316

6. **Filtrators**

   Ultrafiltration is used to completely separate the trace amount of biomass from liquid products after going through the two hydrocyclones HYC-101 and HYC-102. This is done based on particle size, and since our biomass is composed of solid particles, the ultrafiltration will separate the biomass through a membrane. Reverse osmosis is included to remove water from the product stream. This separated water stream is recycled back to the beginning of the process (blending tanks V-101 and V-102).

   a. ***UF-101**:* This is the second step of the filtration process to remove more biomass and cell debris. This ultrafiltration step focuses on removing contaminants of somewhat high molecular weight. This device operates at 101.3°F and at a pressure of 60 psia. Note that due to huge amounts of biomass and water, all these filtration steps will be necessary.
      - i. *Filtration time*: 240 mins
      - ii. *Recovery percentage:* 99.5%
      - iii. *Pore size:* 0.450 microns
      - iv. *Type:* Dft RO Membrane
      - v. *Material*: SS316
      - vi. *Number of units:* 446
      - vii. *Membrane area per unit:* 860 ft^2

   b. ***RO-101:*** Reverse osmosis is introduced to separate the water from the product stream before entering the distillation columns. This operates at 101.3°F.
      - i. Filtration time: 300 mins
      - ii. *Recovery percentage:* 25.425%

   iii. *Pore size:* 0.450 microns
   iv. *Type:* Dft RO Membrane
   v. *Material:* SS316
   vi. *Number of units:* 73
   vii. *Membrane area per unit:* 1,070 ft^2

7. **<u>Recycle Heat Exchangers</u>**

   This is used to make the process less energy intensive.

   a. ***E-101:*** The feed stream into the first distillation column T-101 enters the heat exchanger E-101 (process multi heat exchanger) together with the product streams (distillate and bottom) of the third distillation column T-103 so that the excessive heat from the product streams is recycled into the feed stream.
      i. Heat transfer area: 353.97 ft^2
      ii. Tube design pressure: 0.304 psig
      iii. Tube design temperature: 336.3°F
      iv. Tube diameter: 0.0833 ft
      v. Tube length: 20 ft
      vi. Shell design pressure: 0.304 psig
      vii. Shell design temperature: 398.4°F
      viii. Duty: 1,303.93 MBtu/hr

8. **<u>Distillation</u>**

   Distillation is a method used to purify liquid mixtures based on the volatility of the components. This refers to the boiling points of all the individual components. The components with the lower boiling points get boiled up first while the heavier components remain in the column. For this process there are four distillation columns used to purify 1,3-Propanediol (1,3-PDO) as well as the other products (lactic acid, acetic acid, and ethanol)

   a. ***T-101:*** The top products include acetic acid and ethanol while the bottom products are 1,3-PDO and lactic acid. The operating conditions for the column are at 164°F for the top and 323°F for the bottom at 2.18 psia.
      i. T-101
         1. *Column Diameter:* 4.5 ft
         2. *Column Height:* 64 ft
         3. *Column Trays:* 26
         4. *Tray type:* Sieve
         5. *Tray spacing:* 2 ft
      ii. E-102
         1. *Condenser heat transfer area:* 10.9 ft^2
         2. *Condenser tube design pressure:* 0.304 psig
         3. *Condenser tube design temperature:* 250°F
         4. *Condenser tube diameter:* 0.0833 ft
         5. *Condenser tube length:* 20 ft
         6. *Condenser duty:* -169.1 MBtu/hr

- iii. E-103
    1. *Reboiler heat transfer area:* 1,001 ft^2
    2. *Reboiler tube design pressure:* 139.76 psig
    3. *Reboiler tube design temperature:* 397°F
    4. *Reboiler tube diameter:* 0.0833 ft
    5. *Reboiler tube length:* 20 ft
    6. *Reboiler duty:* 2,730.4 MBtu/hr
- iv. P-108 - Centrifugal pumps
    1. *Pump liquid* flow rate: 1.019 gpm
    2. *Pump fluid specific gravity*: 0.897
    3. *Pump design temperature*: 250°F
    4. *Pump efficiency:* 0.7

b. ***T-102:*** The top product is ethanol, and the bottom product is acetic acid. The column will operate at 97.7°F for the top and 148.9°F for the bottom at 2.18 psia.

- i. T-102
    1. *Column Diameter:* 4.5 ft
    2. *Column Height:* 64 ft
    3. *Column Trays:* 26
    4. *Tray type:* Sieve
    5. *Tray spacing:* 2 ft
- ii. E-104
    1. *Condenser heat transfer area*: 573.6 ft^2
    2. *Condenser tube design pressure:* 0.304 psig
    3. *Condenser tube design temperature:* 250°F
    4. *Condenser tube diameter*: 0.0833 ft
    5. *Condenser tube length:* 20 ft
    6. Condenser duty: -2,058.7 MBtu/hr
- iii. E-105
    1. *Reboiler heat transfer area:* 68.23 ft^2
    2. *Reboiler tube design pressure:* 35.305 psig
    3. *Reboiler tube design temperature:* 307°F
    4. *Reboiler tube diameter:* 0.0833 ft
    5. *Reboiler tube length:* 20 ft
    6. *Reboiler duty:* 984.7 MBtu
- iv. P-109 - Centrifugal pump
    1. *Pump liquid flow rate:* 14.7 gpm
    2. *Pump fluid specific gravity:* 0.787
    3. *Pump design temperature*: 250°F
    4. *Pump efficiency*: 0.7

c. ***T-103****:* The top product is 1,3-PDO, and the bottom product is lactic acid. The column functions at 286.3°F at the top and 310.7°F at the bottom at 2.18 psia.

- i. T-103
    1. *Column Diameter:* 13 ft

    2. *Column Height:* 178 ft
    3. *Column Trays:* 83
    4. *Tray type:* Sieve
    5. *Tray spacing:* 2 ft

ii. E-106

    1. *Condenser heat transfer area:* 610.3 ft^2
    2. *Condenser tube design pressure:* 0.304 psig
    3. *Condenser tube design temperature:* 337.8ºF
    4. *Condenser tube diameter:* 0.0833 ft
    5. *Condenser tube length:* 20 ft
    6. Condenser duty: -16,932 MBtu/hr

iii. E-107

    1. *Reboiler heat transfer area:* 3,025 ft^2
    2. *Reboiler tube design pressure:* 139.8 psig
    3. *Reboiler tube design temperature:* 397ºF
    4. *Reboiler tube diameter:* 0.0833 ft
    5. *Reboiler tube length:* 20 ft
    6. *Reboiler duty:* 16,536 MBtu/hr

iv. P-110 - Centrifugal pumps

    1. *Pump liquid flow rate:* 156.56 gpm
    2. *Pump fluid specific gravity:* 0.670
    3. *Pump design temperature:* 336.3ºF
    4. *Pump efficiency:* 0.7

Detailed Mass Balance

Table 10 – Mass Flow Data of Holding Section (S1-S6)

Mass Flow (lb/hr)						
Stream	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Pressure (psi)	14.7	14.7	14.7	14.7	14.7	29.2
Temperature (ºF)	77.0	77.0	97.8	97.2	95.0	95.3
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Total	7,290	6,830	48,520	55,820	55,820	55,820
Glycerol	---	---	trace	trace	trace	trace
Glucose	---	---	trace	trace	trace	trace
CSL	7,290	---	---	7,290	7,290	7,290
Water	---	6,830	48,520	48,520	48,520	48,520
1,3 PDO	---	---	trace	trace	trace	trace
Ethanol	---	---	trace	trace	trace	trace
Lactic Acid	---	---	trace	trace	trace	trace
Acetic Acid	---	---	trace	trace	trace	trace

Table 11 – Mass Flow Data of Holding Section (S7-S13)

Mass Flow (lb/hr)							
Stream	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**	**S13**
Pressure (psi)	14.7	14.7	14.7	14.7	14.7	14.7	29.2
Temperature (ºF)	77.0	77.0	77.0	97.8	92.2	95.0	95.3
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Total	18,740	15,210	6,830	48,520	82,480	82,480	82,480
Glycerol	18,740	---	---	trace	18,740	18,740	18,740

Glucose	---	15,210	---	trace	15,210	15,210	15,210
Water	---	---	6,830	48,520	48,520	48,520	48,520
1,3 PDO	---	---	---	trace	trace	trace	trace
Ethanol	---	---	---	trace	trace	trace	trace
Lactic Acid	---	---	---	trace	trace	trace	trace
Acetic Acid	---	---	---	trace	trace	trace	trace

Table 12 – Mass Flow Data of Holding Section (S14-S15)

Mass Flow (lb/hr)		
Stream	**S14**	**S15**
Pressure (psi)	362.59	14.50
Temperature (ºF)	-200.0	77.0
Phase	Liquid	Gas
Total	220.46	220.46
Glucose	---	220.46
N2	220.46	---

Table 13 – Mass Flow Data of Fermentation Section (R-101)

Mass Flow (lb/hr)						
Stream	**S16**	**S20**	**S24**	**S28**	**S29**	**S30**
Pressure (psi)	29.2	29.2	14.7	14.7	29.2	14.7
Temperature (ºF)	95.3	95.3	77.0	98.6	98.6	98.6
Phase	Liquid	Liquid	Gas	Liq/Solid	Liq/Solid	Gas
Total	55.8	82.5	0.22	136	136	2.30
Glycerol	trace	18.7	---	11.0	11.0	---
Glucose	trace	15.2	---	7.3	7.3	---

CSL	7.29	---	---	---	---	---
Water	48.5	48.5	---	97.0	97.0	---
1,3 PDO	trace	trace	---	6.3	6.3	---
Ethanol	trace	trace	---	0.6	0.6	---
Lactic Acid	trace	trace	---	4.4	4.4	---
Acetic Acid	trace	trace	---	2.9	2.9	---
N_2	---	---	0.22	---	---	0.36
CO_2	---	---	---	---	---	1.90
Biomass	---	---	---	6.8	6.8	---
O_2	---	---	---	---	---	0.04

Table 14 – Mass Flow Data of Fermentation Section (R-102)

Mass Flow (lb/hr)							
Stream	**S17**	**S21**	**S25**	**S29**	**S31**	**S32**	**S33**
Pressure (psi)	29.2	29.2	14.7	29.2	14.7	29.2	14.7
Temperature (°F)	95.3	95.3	77.0	98.6	98.6	98.6	98.6
Phase	Liquid	Liquid	Gas	Liq/Solid	Liq/Solid	Liq/Solid	Gas
Total	502	742	1.98	136	1,360	1,360	20.9
Glycerol	trace	169	---	11.0	110	110	---
Glucose	trace	137	---	7.3	73	73	---
CSL	66	---	---	---	---	---	---
Water	436	436	---	97.0	970	970	---
1,3 PDO	trace	trace	---	6.3	63	63	---
Ethanol	trace	trace	---	0.6	6.1	6.1	---
Lactic Acid	trace	trace	---	4.4	44	44	---

Acetic Acid	trace	trace	---	2.9	29	29	---
N_2	---	---	1.98	---	---	---	3.4
CO_2	---	---	---	---	---	---	17.1
Biomass	---	---	---	6.8	68	68	---
O_2	---	---	---	---	---	---	0.4

Table 15 – Mass Flow Data of Fermentation Section (R-103)

Mass Flow (lb/hr)							
Stream	**S18**	**S22**	**S26**	**S32**	**S34**	**S35**	**S36**
Pressure (psi)	29.2	29.2	14.7	29.2	14.7	29.2	14.7
Temperature (°F)	95.3	95.3	77.0	98.6	98.6	98.6	98.6
Phase	Liquid	Liquid	Gas	Liq/Solid	Liq/Solid	Liq/Solid	Gas
Total	5,020	7,420	19.8	1,360	13,630	13,630	209
Glycerol	trace	1,690	---	110	1,100	1,100	---
Glucose	trace	1,370	---	73	731	731	---
CSL	660	---	---	---	---	---	---
Water	4,360	4,360	---	970	9,700	9,700	---
1,3 PDO	trace	trace	---	63	633	633	---
Ethanol	trace	trace	---	6.1	61	61	---
Lactic Acid	trace	trace	---	44	438	438	---
Acetic Acid	trace	trace	---	29	292	292	---
N_2	---	---	19.8	---	---	---	34
CO_2	---	---	---	---	---	---	171
Biomass	---	---	---	68	680	680	---
O_2	---	---	---	---	---	---	4

Table 16 – Mass Flow Data of Fermentation Section (R-104)

Mass Flow (lb/hr)							
Stream	**S22**	**S23**	**S27**	**S35**	**S37**	**S38**	**S39**
Pressure (psi)	29.2	29.2	14.7	29.2	14.7	29.2	14.7
Temperature (°F)	95.3	95.3	77.0	98.6	98.6	98.6	98.6
Phase	Liquid	Liquid	Gas	Liq/Solid	Liq/Solid	Liq/Solid	Gas
Total	50,230	74,230	198	13,630	134,600	134,600	3,850
Glycerol	trace	16,870	---	1,100	24	24	---
Glucose	trace	13,690	---	731	94	94	---
CSL	6,560	---	---	---	---	---	---
Water	43,670	43,670	---	9,700	97,030	97,030	---
1,3 PDO	trace	trace	---	633	15,510	15,510	---
Ethanol	trace	trace	---	61	608	608	---
Lactic Acid	trace	trace	---	438	9,190	9,190	---
Acetic Acid	trace	trace	---	292	5,320	5,320	---
N_2	---	---	198	---	---	---	330
CO_2	---	---	---	---	---	---	3,480
Biomass	---	---	---	680	6,800	6,800	---
O_2	---	---	---	---	---	---	40

Table 17 – Mass Flow Data of Biomass Separation Section (S40-S48)

Mass Flow (lb/hr)									
Stream	**S40**	**S41**	**S42**	**S43**	**S44**	**S45**	**S46**	**S47**	**S48**
Pressure (psi)	14.7	14.7	29.2	14.7	14.7	14.7	14.7	14.7	14.7

Temperature (ºF)	98.9	98.9	99.2	99.2	99.2	100.9	100.9	101.3	101.3
Phase	Liq/Solid	Liq/Solid	Liq/Solid	Liq/Solid	Liq/Solid	Liquid	Liq/Solid	Liquid	Liquid
Total	117,200	17,430	117,200	114,600	2,580	114,000	579	30,630	83,370
Glycerol	24	---	24	24	---	24	trace	24	trace
Glucose	94	---	94	94	---	94	trace	94	trace
Water	85,390	11,640	85,390	83,680	1,710	83,370	311	---	83,370
1,3 PDO	15,510	---	15,510	15,510	---	15,450	58	15,450	trace
Ethanol	608	---	608	608	---	606	2.2	606	trace
Lactic Acid	9,190	---	9,190	9,190	---	9,160	34	9,150	trace
Acetic Acid	5,320	---	5,320	5,320	---	5,300	20	5,300	trace
Biomass	1,020	5,780	1,020	153	867	---	153	---	---

Table 18 – Mass Flow Data of Distillation Section (S49-S57)

Mass Flow (lb/hr)									
Stream	**S49**	**S50**	**S51**	**S52**	**S53**	**S54**	**S55**	**S56**	**S57**
Pressure (psi)	14.7	2.18	2.18	2.18	2.18	1.09	1.09	1.09	1.09
Temperature (ºF)	200.6	163.8	323.1	97.7	148.9	286.3	310.7	178.3	211.7
Phase	Liquid	Vapor	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Total	27,810	5,370	22,440	532	4,840	14,030	8,420	14,030	8,420
Glycerol	22	trace	22	0	0	trace	22	trace	22
Glucose	85	trace	85	0	0	trace	85	trace	85
1,3 PDO	14,030	21	14,010	trace	21	13,960	48	13,960	48
Ethanol	550	550	trace	532	18	trace	trace	trace	trace
Lactic Acid	8,310	trace	8,310	trace	1	48	8,260	48	8,260

Acetic Acid	4,820	4,800	20	trace	4,800	17	trace	17	trace

Table 19 – Mass Flow Data of Recycle Water Section

Mass Flow (lb/hr)							
Stream	**S48**	**S58**	**S59**	**S2**	**S3**	**S9**	**S10**
Pressure (psi)	14.7	14.7	14.7	14.7	14.7	14.70	14.70
Temperature (ºF)	101.3	101.3	101.3	77.0	97.8	77.0	97.8
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Total	83,370	41,690	41,690	6,830	48,520	6,830	48,520
Glycerol	trace	trace	trace	---	trace	---	trace
Glucose	trace	trace	trace	---	trace	---	trace
Water	83,370	41,690	41,690	6,830	48,520	6,830	48,520
1,3 PDO	trace	trace	trace	---	trace	---	trace
Ethanol	trace	trace	trace	---	trace	---	trace
Lactic Acid	trace	trace	trace	---	trace	---	trace
Acetic Acid	trace	trace	trace	---	trace	---	trace

Table 20 – Blending Tank List and Sizing

Label	Equipment	Material	Sizing Parameter	Value	Units
V-101	Blending Tank (Fixed propeller type mixer)	SS316	Volume	2,788	ft^3
			Height	31.73	ft
			Diameter	10.58	ft
			Design Pressure	22.04	psia
			Occupancy	3.25	hours
			Number of units	20	
V-102	Blending Tank (Fixed propeller type mixer)	SS316	Volume	2,823	ft^3
			Height	31.86	ft
			Diameter	10.62	ft
			Design Pressure	22.04	psia
			Occupancy	3.25	hours
			Number of units	27	

Table 21 – Heat Sterilizer List and Sizing

Label	Equipment	Material	Sizing Parameter	Value	Units
ST-101	Heat Sterilizer (Sanitary double pipe exchanger)	SS316	Holding Tube Diameter	8.52	ft
			Holding Tube Length	8.71	ft
			Rated Throughput	391.02	gpm
			Number of units	4	
ST-102	Heat Sterilizer (Sanitary double pipe exchanger)	SS316	Holding Tube Diameter	10.07	ft
			Holding Tube Length	8.23	ft

			Rated Throughput	427.59	gpm
			Number of units	5	

Table 22 – Fermentor List and Sizing

Label	Equipment	Material	Sizing Parameter	Value	Units
R-101	Seed Fermentor (Jacketed)	SS316	Volume	149	ft^3
			Height	11.94	ft
			Diameter	3.98	ft
			Design Pressure	22.04	psia
			Cycle Duration	9	hours
			Number of units	1	
R-102	Seed Fermentor (Jacketed)	SS316	Volume	1,485	ft^3
			Height	25.72	ft
			Diameter	8.57	ft
			Design Pressure	22.04	psia
			Cycle Duration	9	hours
			Number of units	1	
R-103	Seed Fermentor (Jacketed)	SS316	Volume	1,650	ft^3
			Height	26.64	ft
			Diameter	8.88	ft
			Design Pressure	22.04	psia
			Cycle Duration	9	hours
			Number of units	9	
R-104	Production Fermentor (Jacketed)	SS316	Volume	12,000	ft^3
			Height	51.62	ft
			Diameter	17.21	ft

			Design Pressure	22.04	psia
			Cycle Duration	24	hours
			Number of units	11	

Table 23 – Filtration List and Sizing

Label	Equipment	Material	Sizing Parameter	Value	Units
HYC-101	Hydrocyclone (Pulp stock centrifugal cleaner)	SS316	Rated Throughput	266.18	gpm
			Removal Efficiency	16.78	%
HYC-102	Hydrocyclone (Pulp stock centrifugal cleaner)	SS316	Rated Throughput	231.72	gpm
			Removal Efficiency	2.98	%
UF-101	Ultrafiltration Unit (White water filter)	DFT RO Membrane	Recovery	99.5	%
			Pore Size	0.450	microns
			Material	SS316	
			Number of Units	446	
			Membrane area per unit	860	ft^2
RO-101	Reverse Osmosis (Tubular fabric filter)	DFT RO Membrane	Recovery	24.425	%
			Pore Size	0.450	microns
			Material	SS316	
			Number of Units	73	
			Membrane area per unit	1,070	ft^2

Table 24 – Distillation Column List and Sizing

Label	Equipment	Material	Sizing Parameter	Value	Units
T-101	Distillation Column	SS316	Height	64	ft
			Diameter	4.5	ft
			Trays	26	
			Tray Type	Sieve	
			Tray Spacing	2	ft
T-102	Distillation Column	SS316	Height	64	ft
			Diameter	4.5	ft
			Trays	26	
			Tray Type	Sieve	
			Tray Spacing	2	ft
T-103	Distillation Column	SS316	Height	178	ft
			Diameter	13	ft
			Trays	83	
			Tray Type	Sieve	
			Tray Spacing	2	ft

Table 25 – Heat Exchanger List and Sizing

Label	Equipment	Material	Sizing Parameter	Value	Units
E-101	Recycle Heat Exchanger (Process multi stream heat exchanger)	SS316	Heat transfer area	353.965	ft^2
			Tube design pressure	0.304011	psig
			Tube design temperature	336.255	F
			Tube diameter	0.0833	ft
			Tube length	20	ft

			Duty	1,303.92	MBtu/hr
E-102	Distillation Column 1 Condenser (Fixed float U-tube heat exchanger)	SS316	Heat transfer area	10.8987	ft^2
			Tube design pressure	0.304011	psig
			Tube design temperature	250	F
			Tube diameter	0.0833	ft
			Tube length	20	ft
			Duty	-169.092	MBtu/hr
E-103	Distillation Column 1 Reboiler (U-tube kettle type reboiler)	SS316	Heat transfer area	1001.35	ft^2
			Tube design pressure	139.756	psig
			Tube design temperature	397	F
			Tube diameter	0.0833	ft
			Tube length	20	ft
			Duty	2,730.4	MBtu/hr
E-104	Distillation Column 2 Condenser (Fixed float U-tube heat exchanger)	SS316	Heat transfer area	573.55	ft^2
			Tube design pressure	0.304	psig
			Tube design temperature	250	F
			Tube diameter	0.0833	ft
			Tube length	20	ft
			Duty	-2,058.7	MBtu/hr
E-105	Distillation Column 2 Reboiler (U-tube kettle	SS316	Heat transfer area	68.2328	ft^2
			Tube design pressure	35.3052	psig

	type reboiler)		Tube design temperature	307	F
			Tube diameter	0.0833	ft
			Tube length	20	ft
			Duty	984.69	MBtu/hr
E-106	Distillation Column 3 Condenser (Fixed float U-tube heat exchanger)	SS316	Heat transfer area	610.322	ft^2
			Tube design pressure	0.304	psig
			Tube design temperature	337.826	F
			Tube diameter	0.0833	ft
			Tube length	20	ft
			Duty	-16,932.2	MBtu/hr
E-107	Distillation Column 3 Reboiler (U-tube kettle type reboiler)	SS316	Heat transfer area	3,024.77	ft^2
			Tube design pressure	139.756	psig
			Tube design temperature	397	F
			Tube diameter	0.0833	ft
			Tube length	20	ft
			Duty	16,536.17	MBtu/hr

Table 26 – Pump List and Sizing

Label	Equipment	Material	Sizing Parameter	Value	Units
P-101	Pump (Centrifugal)	SS316	Flow Rate	81.40	gpm
P-102	Pump (Centrifugal)	SS316	Flow Rate	136.78	gpm
P-103	Pump	SS316	Flow Rate	0.22	gpm

	(Centrifugal)				
P-104	Pump (Centrifugal)	SS316	Flow Rate	2.18	gpm
P-105	Pump (Centrifugal)	SS316	Flow Rate	21.75	gpm
P-106	Pump (Centrifugal)	SS316	Flow Rate	218.24	gpm
P-107	Pump (Centrifugal)	SS316	Flow Rate	218.24	gpm
P-108	Pump (Water-sealed vacuum pump)	SS316	Flow Rate	1.019	gpm
P-109	Pump (Water-sealed vacuum pump)	SS316	Flow Rate	14.70	gpm
P-110	Pump (Water-sealed vacuum pump)	SS316	Flow Rate	156.56	gpm

Table 27 - Liquid Ring Vacuum Pump List and Sizing

LR-101	Liquid Ring Vacuum Pump (Water-sealed vacuum pump)	SS316	Gas Flow Rate	1,508	cuft/min
			Speed	1,800	RPM
			Driver Power	60	HP
			Brake HP	56	HP
LR-102	Liquid Ring Vacuum Pump (Water-sealed vacuum pump)	SS316	Gas Flow Rate	1,508	cuft/min
			Speed	1,800	RPM
			Driver Power	60	HP
			Brake HP	56	HP

Distillation Column – Hand Calculation

The sample hand calculation will be done for the distillation column. There are three main columns in the primary design, T-102 will use in this instance. To determine the sizing of the column, diameter, number of trays, and height need to be calculated. Generally, the overall height of the column will depend on the plate spacing, which can range from 0.5 meters to 1 meter depending on the diameter of the column. Close spacing is typically employed for small-diameter columns or areas with limited headroom. For columns that exceed 1 meter in diameter, plate spacings ranging from 0.3 to 0.6 meters are generally utilized, and an initial estimate of 0.5 m can be assumed.

The maximum allowable vapor velocity (u_V) can be calculated using the Souders and Brown equation:

$$\hat{u}_V = \left[\frac{\rho_L - \rho_V}{\rho_V}\right]^{0.5} (-\ 0.171 l_t^2 + 0.27 l_t - 0.047)$$

Where:

- ρ_L = Liquid Density $\left(\frac{kg}{m^3}\right) = 785.068 \frac{kg}{m^3}$
- ρ_V = Vapor Density $\left(\frac{kg}{m^3}\right) = 101.49 \frac{kg}{m^3}$
- u_V = Maximum Allowable Vapor Velocity $\left(\frac{m}{s}\right)$
- l_t = Plate Spacing $(m) = 0.610\ m\ [Chosen]$

$$\hat{u}_V = \left[\frac{785.068 - 101.49}{101.49}\right]^{0.5} (-\ 0.171 (0.61^2) + 0.27 * 0.61 - 0.047) = 0.143 \frac{m}{s}$$

After calculating the maximum allowable vapor velocity, it can be used to calculate the diameter of the column (D_C) using the following equation:

$$D_C = \sqrt{\frac{4\hat{V}_W}{\Pi \rho_V u_V}}$$

Where:

- $\hat{V}_W$ = Maximum Vapor Flow Rate $\left(\frac{kg}{s}\right) = 24.76 \frac{kg}{s}\ [Aspen\ Data]$
- ρ_V = Vapor Density $\left(\frac{kg}{m^3}\right) = 101.49 \frac{kg}{m^3}$
- u_V = Maximum Allowable Vapor Velocity $\left(\frac{m}{s}\right) = 0.143 \frac{m}{s}$
- D_C = Diameter of the Column (m)

$$D_C = \sqrt{\frac{4*24.76}{\Pi*101.49*0.143}} = 1.50\ m = 4.499\ ft$$

To calculate the number of trays in the distillation column Fenske-Underwood equation needs to be used:

$$N_{min} = \frac{log\left[\left(\frac{x_{LK}}{X_{HK}}\right)_D \left(\frac{y_{HK}}{y_{LK}}\right)_B\right]}{log(\alpha)}$$

Where:

- x_{LK} = Light key component composition in Distillate
- y_{HK} = High key component composition in Distillate
- y_{LK} = Light key component composition in Bottom
- x_{HK} = High key component composition in Bottom
- α = Relative Volatility $\left(\frac{K_{LK}}{K_{HK}}\right)$
- N_{min} = Minimum Number of trays needed in the distillation column

Using the boiling points of the five components (lactic acid, ethanol, acetic acid, and 1,3-PDO), we can determine the light and high key components. However, the compositions of the bottom and distillate don't necessarily line up with the traditional methods of calculating the minimum number of trays in the column. As shown in the table below, these are the mole fractions of the components in the distillate and bottoms.

Table 28 – Mole Fraction of Components

Mole Fraction of Components	
Identification	**Mole Fraction**
x-LK_D, Mole Fraction of Ethanol in Distillate	0.999
x-HK_D, Mole Fraction of Acetic Acid in Distillate	8.65E-7
x-LK_B, Mole Fraction of Ethanol in Bottoms	0.00486
x-HK_B, Mole Fraction of Acetic Acid in Bottoms	0.9915

$$N_{min} = \frac{log\left[\left(\frac{0.999}{8.65E-7}\right)_D\left(\frac{0.00486}{0.9915}\right)_B\right]}{log(0.88)} = 14.765 \cong 15\ trays$$

Since the minimum number of trays needed is obtained, it is now possible to calculate the tray efficiency by finding ΔV_{feed}:

$$\Delta V_{feed} = F(1 - q)$$

Where:

- ΔV_{feed} = Change in Vapor Feed $\left(\frac{kmol}{s}\right)$
- F = Feed Flow Rate $\left(\frac{kmol}{s}\right) = 0.012\frac{kmol}{s}$
- q = Feed Quality $= 0.518$

Using the values from Aspen, the vapor difference was calculated:

$$\Delta V_{feed} = 0.012(1 - 0.518) = 0.006\frac{kmol}{s}$$

Once ΔV_{feed} is found, goal seek via Excel is utilized to find ϕ from the following equation:

$$\Delta V_{feed} = \sum_{i=1}^{c} \frac{\alpha_{i-ref} F z_i}{\alpha_{i-ref} - \phi} \rightarrow 0.006 = \frac{0.88*0.012*0.129}{0.88-\phi} + \frac{0.25*0.012*0.867}{0.25-\phi} + \frac{0.097*0.012*0.00017}{0.097-\phi} + \frac{0.088*0.012*0.0045}{0.088-\phi}$$

$$\phi = 0.918$$

Once the feed flash is found, the V_{min} can be found:

$$V_{min} = \sum_{i=1}^{c} \frac{\alpha_{i-ref} D x_{i,dist}}{\alpha_{i-ref} - \phi} = \frac{0.0102*0.0049*0.4}{0.4-0.918} + \frac{0.0102*0.9915*0.112}{0.112-0.918} + \frac{0.0102*0.0002*0.778}{0.778-0.918} + \frac{0.0102*0.00034*1.25}{1.25-0.918}$$

$$V_{min} = 0.055 \frac{kmol}{s}$$

Now, L_{min} can be found:

$$L_{min} = V_{min} - D \rightarrow L_{min} = 0.0521 \frac{kmol}{s} - 0.0102 \frac{kmol}{s} = 0.042 \frac{kmol}{s}$$

Now, $\left(\frac{L}{D}\right)_{min}$ can be found:

$$\left(\frac{L}{D}\right)_{min} = \frac{0.042}{0.055} = 0.764$$

Using the given reflux ratio, the Gilliland correlation graph is used along with the given reflux ratio from Aspen, it was found that the actual number of trays was 32.192, which was rounded down to 32 trays.

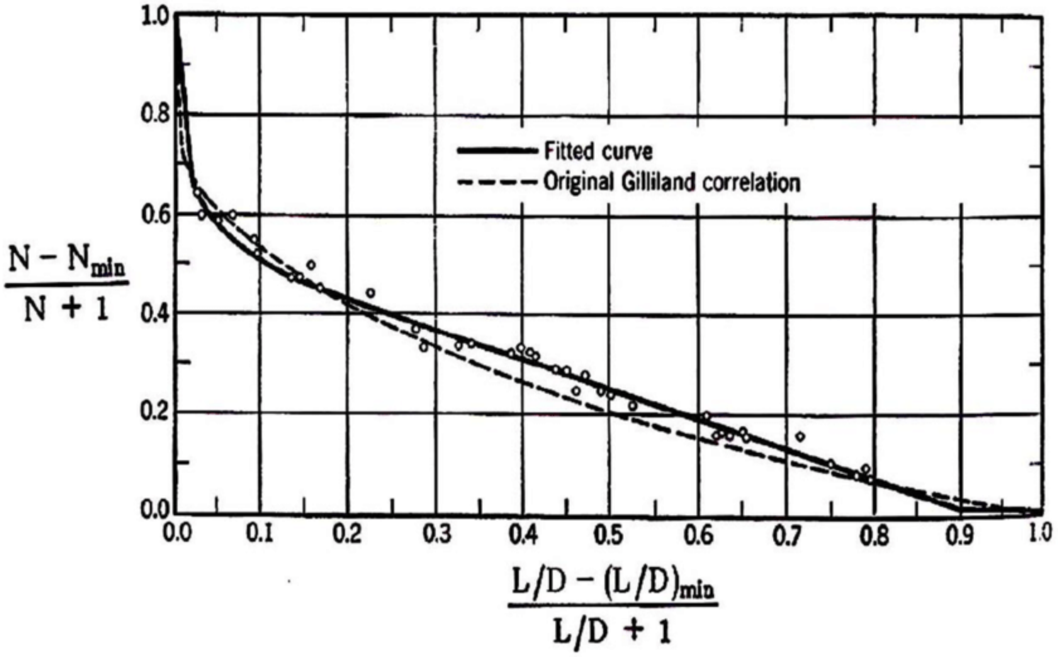


Figure 28 – Gilliland Correlation Graph [31]

Since the number of trays needed is obtained, it is now possible to calculate the height of the column:

$$Height = \#\, of\ trays * l_t + 10\, ft = 68.56\, ft$$

Distillation Column – Aspen Data

The following data table represents the Aspen data collection of the distillation columns and will be used to compare to the hand calculations.

Table 29 – Aspen Data of Distillation Columns

Multi-diameter tower

User tag number	**COL3-tower**	**COL2-tower**	**COL1-tower**
Remarks 1	Equipment mapped from 'COL3'.	Equipment mapped from 'COL2'.	Equipment mapped from 'COL1'.
Diameter [meter]	3.96	1.37	1.37
Bottom tangent to tangent height [meter]	54.25	19.5072	19.50
Design gauge pressure Bottom [barg]	1.034	1.034	1.03
Design temperature Bottom [C]	182.63	121.11	189.51
Operating temperature Bottom [C]	173.11	64.96	162.25
Number of trays	83	26	26
Bottom Tray type	SIEVE	SIEVE	SIEVE
Bottom Tray spacing [meter]	0.61	0.61	0.61
Molecular Wt Overhead Prod.	90.50	60.05	80.94

Analysis: Hand vs. Aspen

Using the results from the hand calculations and the Aspen data, the table below compares both values and derives the percent error between the two values.

Table 30 – Hand vs. Aspen Calculations with Error Analysis

	Hand Calculation	**Aspen**	**Percent Error**
Column Trays	32.00	26.00	23.07
Column Diameter (ft)	4.50	4.12	8.12
Column Height (ft)	68.56	58.52	17.15

In chemical engineering, accuracy is critical to ensure the efficient and safe operation of chemical processes. Aspen Plus simulation and doing calculations by hand are two methods that can be used to calculate and model chemical processes, but they differ in terms of their accuracy. The slight error in hand calculations is due to the fact that they are generally simpler and involve approximations and assumptions, which can lead to inaccuracies. On the other hand, the Aspen Plus software is more accurate because it utilizes advanced algorithms and models to simulate complex chemical processes and calculate various properties, such as thermodynamic and transport properties, which can be challenging or impossible to calculate by hand. By incorporating a wide range of variables and factors, such as process equipment, operating conditions, and feedstock properties, Aspen provides a more comprehensive and accurate analysis than hand calculations. Moreover, Aspen can perform sensitivity analyses and optimization studies to identify the critical factors impacting process performance and determine optimal operating conditions. Although hand calculations can provide quick estimates of process variables, they may be subject to uncertainties due to the application of formulas. As such, new equations and methods of calculating key components of the distillation column will be implemented in subsequent reports to ensure greater accuracy and reduce uncertainties.

Liquid Ring Pump Calculation

To determine the sizing of the liquid ring vacuum pump a calculation will be performed to determine the pumping speed in gallons per minute of the pump. To do so, Atlas Copco Vacuum Solutions's [62], a manufacturer of vacuum pumps, derived an equation to calculate the speed.

$$Speed = \frac{V * ln(\frac{P_1}{P_2})}{Time}$$

Where:

- V = Volume of the liquid
- P_1 = Pressure of the inlet
- P_2 = Pressure of the outlet

A typical pump down time of 6 hours to vacate the columns was used for the vacuum pump calculation. The calculation was done for the largest column which is 13 ft wide and 178 ft tall for a volume of 94,505 ft^3, or 707,000 gallon. The other columns come in at a volume of 4,071 ft^3 so installing two vacuum pumps allows not only for the vacation of all towers, but will also accommodate the associated piping. The pressure will drop from 14.7 psi to 2.18 psi.

$$Speed = \frac{0.71\ MM\ gallon * ln(\frac{14.7}{2.18})}{6\ hours} = 224.89 \frac{MM\ gallons}{hr} = 3,748.13 \frac{gallons}{min} = 501\ \frac{ft^3}{min}$$

To accommodate possible future expansions in capacity, the liquid ring vacuum pump was sized at a three times capacity sizing of 1,500 ft^3 per min.

Utility Demand

The majority of the initial utility cost analysis was conducted utilizing Aspen software. Our simulation process employed both Aspen and SuperPro Designer. We found that SuperPro's cost analysis produced results that were often inaccurate, leading to erroneous conclusions. The use of industrial cooling water and steam is required to operate our heat transfer agents. Electricity was required to power the equipment throughout the process. Nitrogen gas is viable for purging oxygen out of the apparatus. Phosphoric acid and sodium hydroxide are two essential components necessary to maintain sanitation throughout the pipes and equipment of the process. Cooling water is crucial for the functioning of our distillation columns as it is fed into the condenser after the distillate has been produced in the tower. Industrial water is utilized during the heat sterilization of the crude glycerol, which occurs toward the end of the media preparation stage. Steam is used for the live stream of the column's bottom product and to clean the system's pipes and pumps. Electrical consumption is necessary for the operation of pumps, heat sterilizers, mixers, driers, seed fermentors, and stirred reactors. Notably, the reflux pump in column 1 consumed the highest amount of electricity due to the fact that it moves more than twice as much liquid as any other pump.

Table 31 – Total Utility Usage

Heat Transfer Agent	**Usage unit (tons/hr)**	**Duty (MBTU/hr)**
Cooling Water	1,328.60	-16,239.54
Low Pressure Steam	10.25	10,087.37
Medium Pressure Steam	11.01	19,266.6
Power	**Usage (KW-h)**	
Electricity	2,034.00	
Purging	**L/L/M**	
Nitrogen	4.00	
Sanitation	**tons/hr**	
H_3PO_4	0.72	
NaOH	0.66	

Recycle

Table 32 – Heat Recycling Analysis

Equipment	**Duty (MBtu/hr)**	**Comments**
E-101	2,608.34	Overhead of Column 1 used as a recycled water stream and also to preheat the feed stream.

Cooling Water

Table 33 – Cooling Water Utility Analysis

Equipment	**Duty (MBtu/hr)**	**Comments**
E-102	-169.10	Used for condensing vapor in the overhead T-101 column
E-104	-2,058.70	Used for condensing vapor in the overhead T-102 column
E-106	-16,932.20	Used for condensing vapor in the overhead T-103 column
ST-102	2.43	Used for sterilizing mixture of

		glycerol, glucose, and water
ST-101	2.08	Used for sterilizing mixture of CSL and water
R-101	0.00050	Used in clean-in-place procedure as well as maintaining the reactor temperature constant
R-102	0.0062	Used in clean-in-place procedure as well as maintaining the reactor temperature constant
R-103	0.0056	Used in clean-in-place procedure as well as maintaining the reactor temperature constant
R-104	0.015	Used in clean-in-place procedure as well as maintaining the reactor temperature constant
Total	-19,155.40	---

Steam

Table 34 – Steam Utility Analysis

Equipment	**Duty (MBtu/hr)**	**Comments**
E-103	2,730.4	Used for vaporizing volatile components in T-101
E-105	984.69	Used for vaporizing volatile components in T-102
E-107	16,536.17	Used for vaporizing volatile components in T-103
ST-102	1.58	Used for sterilizing mixture of glycerol, glucose, and water
ST-101	0.87	Used for sterilizing mixture of CSL and water
R-101	0.0019	Used for steam-in-place procedure
R-102	0.0084	Used for steam-in-place procedure
R-103	0.081	Used for steam-in-place procedure

R-104	0.37	Used for steam-in-place procedure
Total	20,254.20	---

Electricity

Table 35 – Electricity Utility Analysis

Equipment	Rating (HP)	Comments
V-101	95.27	Powering Motor for Agitation
V-102	130.24	Powering Motor for Agitation
R-101	25.00	Powering Motor for Agitation
R-102	150.00	Powering Motor for Agitation
R-103	150.00	Powering Motor for Agitation
R-104	250.00	Powering Motor for Agitation
P-101	18.90	Move CSL + Water before splitter
P-102	25.90	Move Glycerol + Glucose + Water before splitter
P-103	1.36	Move inoculum from R-101 to R-102
P-104	2.36	Move inoculum from R-102 to R-103
P-105	4.50	Move inoculum from R-103 to R-104
P-106	44.80	Move inoculum from R-101 to R-102
P-107	39.00	Move fermentation broth to holding tank V-105
P-108	0.12	Pumps reflux back to T-101
P-109	1.67	Pumps reflux back to T-102
P-110	13.69	Pumps reflux back to T-103
HYC-101	2.27	Separate biomass from fermentor

HYC-102	1.98	Separate remnant biomass from first HYC-102
UF-101	21.43	Per unit value, there are 446 units. Uses ultrafiltration to remove residual biomass.
RO-101	26.64	Per unit value, there are 73 units. Uses reverse osmosis to recycle water in the process.

Nitrogen

Table 36 – Nitrogen Utility Analysis

Equipment	Usage Value	Usage Units	Comments
R-101	1.00	L/L/Min	To deplete oxygen levels
R-102	1.00	L/L/Min	To deplete oxygen levels
R-103	1.00	L/L/Min	To deplete oxygen levels
R-104	1.00	L/L/Min	To deplete oxygen levels
Total	4.00	L/L/Min	---

Utility Sourcing

Cooling water is sourced by a natural reservoir in the Menard County district for feasible water access. Cooling water is utilized in the condensers for condensing vapor that ascends from the partial reboiler and obtaining a top product.

Steam is typically used in a distillation column to help control the temperature and pressure of the system. By introducing steam into the bottom column, the boiling point of the liquid mixture can be raised, which can help to separate components that would otherwise have similar boiling points. Steam can also help to prevent fouling or clogging of the trays or packing material, which can improve the efficiency of the distillation process. Steam is sourced on-site by fundamentally using water and a heat exchanger. Low-pressure, Medium-pressure steam are used for various units that operate in different pressure conditions.

Nitrogen can be considered a utility in various industries and applications because of its unique properties and versatility. Nitrogen is used for purging pipelines, tanks, and other equipment to remove impurities and prevent fires and explosions. It is an inert gas that displaces oxygen and other combustible gasses, reducing the risk of ignition and explosion. Sourcing nitrogen will be provided in a liquid state transported by tankers, then expanded to gas for purging the units in order to deplete oxygen levels. Expanding nitrogen is a common process in industry where the nitrogen flows through valve/nozzle into a low-pressure region which then absorbs heat from the surrounding and evaporates into a gaseous state.

Electricity is a prominent utility for pumps to transfer fluids to other streams and filtration units within the plant. The motor is primarily operated by electricity which then mechanically drives the impeller to transfer the fluid through the system. Since agitators are powered by motors, electricity is an imperative utility to operate the motor and have effective agitation within the tank at a certain RPM. With the plant being connected to electrical grids, electricity is sourced and purchased by a local utility provider, Menard Electric Cooperative.[63]

Sodium hydroxide and phosphoric acid, responsible for sanitation of equipment and piping, will be supplied by HAWKINS, a prominent distributor of industrial chemicals around the United States. Luckily, HAWKINS has a distribution site in the southern Illinois region, which is an advantageous factor for quick and easy delivery.[64]

Process Economics Analysis Data

Table 37 - Equipment Costs

Equipment Costs			
SuperPro			
Label	**Equipment**	**Material**	**Price (MM USD)**
V-101	Blending Tank	SS316	$0.10
V-102	Blending Tank	SS316	$0.12
R-101	Seed Fermentor	SS316	$0.13
R-102	Seed Fermentor	SS316	$0.51
R-103	Seed Fermentor	SS316	$0.64
R-104	Fermentor	SS316	$2.73
P-101	Centrifugal Pump	SS316	$0.020
P-102	Centrifugal Pump	SS316	$0.028
P-103	Centrifugal Pump	SS316	$0.0048
P-104	Centrifugal Pump	SS316	$0.0048
P-105	Centrifugal Pump	SS316	$0.010
P-106	Centrifugal Pump	SS316	$0.039
P-107	Centrifugal Pump	SS316	$0.039
RO-101	Reverse Osmosis Filter	SS316	$2.39
HYC-101	Hydrocyclone	SS316	$0.034
HYC-102	Hydrocyclone	SS316	$0.034
UF-101	Ultrafilter	SS316	$0.062
ST-101	Sterilizer	SS316	$0.082
ST-102	Sterilizer	SS316	$0.082

P-101 WHSPARE	Warehouse Spare Pump	SS316	$0.017
P-102 WHSPARE	Warehouse Spare Pump	SS316	$0.025
P-103 WHSPARE	Warehouse Spare Pump	SS316	$0.0040
P-104 WHSPARE	Warehouse Spare Pump	SS316	$0.0040
P-105 WHSPARE	Warehouse Spare Pump	SS316	$0.0081
P-106 WHSPARE	Warehouse Spare Pump	SS316	$0.034
P-107 WHSPARE	Warehouse Spare Pump	SS316	$0.033
Bacteria	Media	*L. reuteri CH53*	$0.50
Aspen			
Label	**Equipment**	**Material**	**Price (MM USD)**
E-101	Heat Exchanger	SS316	$0.028
E-102	Heat Exchanger	SS316	$0.011
E-103	Heat Exchanger	SS316	$0.052
E-104	Heat Exchanger	SS316	$0.039
E-105	Heat Exchanger	SS316	$0.016
E-106	Heat Exchanger	SS316	$0.040
E-107	Heat Exchanger	SS316	$0.11
V-103	Accumulator	SS316	$0.016
V-104	Accumulator	SS316	$0.016
V-105	Accumulator	SS316	$0.021
T-101	Distillation Column	SS316	$0.14
T-102	Distillation Column	SS316	$0.14
T-103	Distillation Column	SS316	$1.09
LRP-101	Liquid Ring Pump	SS316	$0.28
LRP-102	Liquid Ring Pump	SS316	$0.28
LRP-101 WHSPARE	Warehouse Spare Pump	SS316	$0.27
LRP-102 WHSPARE	Warehouse Spare Pump	SS316	$0.27
P-108	Centrifugal Pump	SS316	$0.0048
P-109	Centrifugal Pump	SS316	$0.0048

P-110	Centrifugal Pump	SS316	$0.0068
P-108 WHSPARE	Warehouse Spare Pump	SS316	$0.0061
P-109 WHSPARE	Warehouse Spare Pump	SS316	$0.0043
P-110 WHSPARE	Warehouse Spare Pump	SS316	$0.0043
Total Cost (MM USD)			**$10.54**

Table 38 - Capital Cost

Capital Cost Data		
Topic	**Amount**	**Unit**
ISBL	$38.27	MM USD
F	3.63	
C_e	$10.54	MM USD
OSBL	$15.31	
FCC	$53.58	
Contingency	$32.15	
EC	$8.04	
WC	$8.04	
TCC	$101.81	

Table 39 - Cost of Raw Material

Raw Material Fed Cost			
Chemical	**Amount (MM ton/yr)**	**Cost (USD/ton)**	**Total Cost (MM USD/yr)**
CSL	0.029	$200.00	$5.80
Glucose/Dextrose	0.060	$723.50	$43.80
Glycerol	0.074	$170.00	$12.68
H3PO4 (20% w/w)	0.0058	$269.60	$1.56
NaOH (0.5 M)	0.0053	$492.00	$2.61
Nitrogen	0.00088	$1,623.00	$1.42
Water	0.074	$1.03	$0.076
Total	*0.25*	*$3,479.13*	*$67.96*

Table 40 - Utility Cost

Utility Cost		
Software	**Amount**	**Unit**
SuperPro	$0.65	MM USD/yr
Aspen	$0.49	
Consumable Membrane	$0.21	
Total	*$1.35*	

Table 41 - Waste Disposal Cost

Waste Disposal Cost			
Disposal Type	**Amount (MM ton/yr)**	**Cost (USD/ton)**	**Total Cost (MM USD/yr)**
Biomass	0.026	$50.00	$1.32
Biomass Waste Water	0.053	$50.00	$2.66
Total	*0.080*	*$100.00*	*$3.98*

Table 42 - Shipping Cost

Shipping Cost								
Chemical	**Amount (MM ton/yr)**		**Price (USD/ton-mile)**	**Cost (MM USD/yr)**		**Price (USD/ton-mile)**	**Cost (MM USD/yr)**	**Total Cost (MM USD/yr)**
Raw Materials	0.37	*Truck*	$0.25	$13.90	*Rail*	$0.03	$1.39	*$15.29*
Product								
By-product			**Distance (mile/yr)**			**Distance (mile/yr)**		
			150			150		

Table 43 - VCOP

Variable Cost of Production (VCOP)		
Criteria	**Cost (MM USD/yr)**	**VCOP (MM USD/yr)**
Raw Material Fed Cost	$67.96	**$88.59**
Utility Cost	$1.35	
Waste Disposal Cost	$3.98	
Shipping Cost	$15.29	

Table 44 - Job Description Parameters

Parameters of Job Description

Label	Amount	Unit
Hours Worked	8000	hr/yr
Days Worked	334	day/yr
Shift Length	8	hr/day

Table 45 - Operating Labor Parameters

Operating Labor

Label	Amount	Unit
# of annual shifts	1000	shifts/yr
# of daily shifts	4.3	shifts/day
# of operators per shift	6	operator/shift
# of operators per day	25.8	operator/day
Average Salary of Operator	$64,785.00	USD/yr

Table 46 - FCOP & CCOP Calculations

Fixed Cost of Product (FCOP)

Label	Cost (MM USD/yr)
Operating Labor	$1.67
Supervision	$0.42
Direct Salary Overhead	$1.04
Maintenance	$1.15
Property Taxes & Insurance	$0.76
Rent of Building	$0.54
General Plant Overhead	$3.18
Allocated Environmental Charges	$0.54
License & Royalty Fees	$0.19
Capital Charges	$0.54
Sales & Marketing Costs	$0.065
FCOP	**$10.10**
CCOP	**$98.68**

Table 47 - Revenue

Revenue			
Chemical	**Amount (MM ton/yr)**	**Price (MM USD/ton)**	**Revenue (MM USD/yr)**
1,3-PDO	0.061	$0.0022	$133.39
Ethanol	0.002	$0.00074	$1.72
Acetic Acid	0.021	$0.0012	$24.82
Lactic Acid	0.036	$0.0012	$44.90
Total	0.12	$0.0053	$204.84

Table 48 - Simple Payback & ROI Parameters

Simple Payback & ROI Parameters		
Label	**Amount**	**Unit**
TCC	$101.81	MM USD
Revenue	$204.84	MM USD/yr

Table 49 - Simple Payback Calculations

Payback Period
1.89

Table 50 - ROI Calculations

ROI
104.26%

Table 51 - Simple Payback Data

Years	**Cumulative Cashflow (MM USD/yr)**
-2	-$12.73
-1	-$25.45
0	-$50.91
1	-$101.81
2	$0.61
3	$205.44
4	$410.28
5	$615.12

6	$819.96
7	$1,024.79
8	$1,229.63
9	$1,434.47
10	$1,639.30
11	$1,844.14
12	$2,048.98
13	$2,253.81
14	$2,458.65
15	$2,663.49

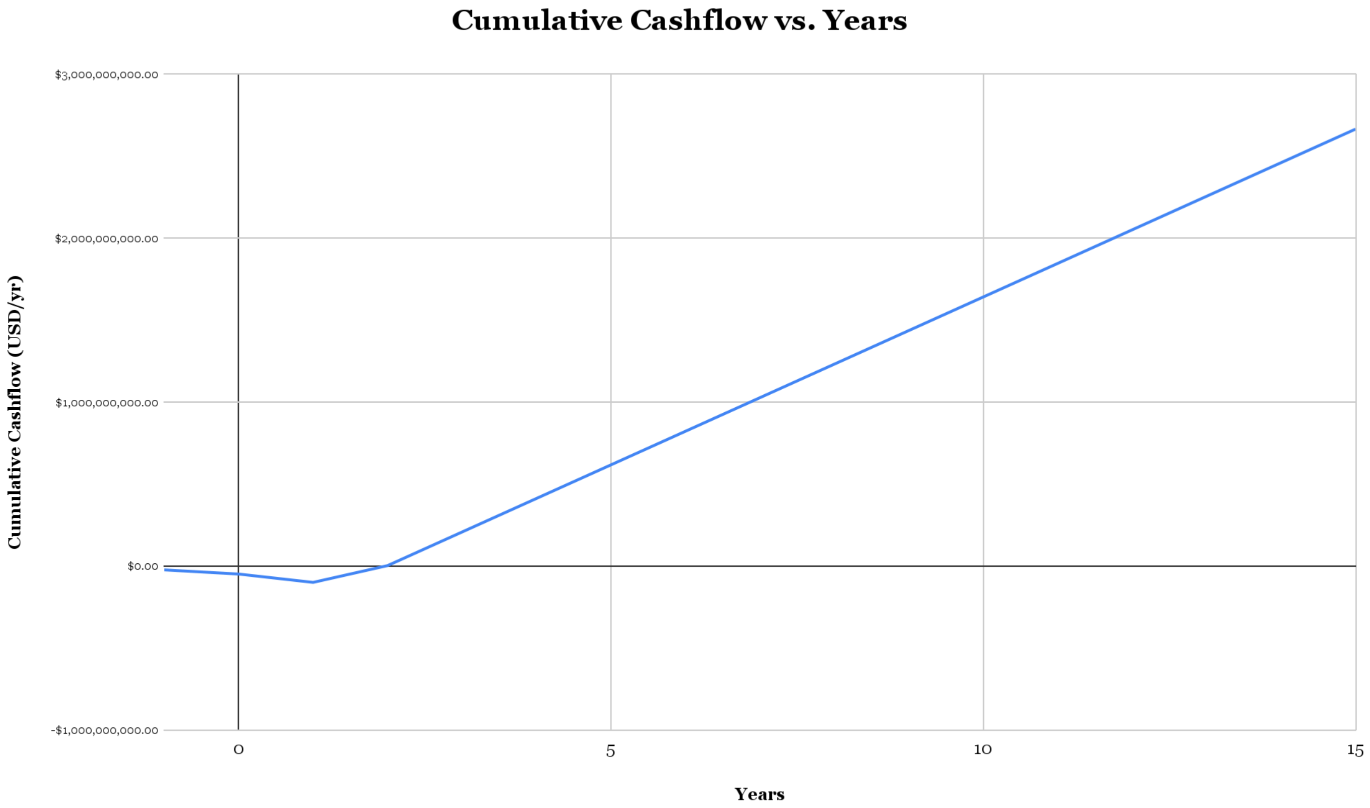


Figure 29 - Simple Payback Curve

Table 52 - NPV 5-Year Recovery Parameters

5-Year Parameters		
Label	**Amount**	**Unit**
TCC	$101.81	MM USD

Gross Profit	$106.15	MM USD/yr
TCC-WC	$93.77	MM USD
Tax	29.75%	
Discount Rate	0.14	

Table 53 - NPV 5-Year Depreciation Parameters

Depreciation	
Years	**Percent**
1	20.00%
2	32.00%
3	19.20%
4	11.52%
5	11.52%
6	5.76%

Table 54 - NPV 5-Year Recovery

5-Year Recovery (MM USD)								
Year	**Pre-tax CF**	**Depreciation**	**Taxable Income**	**Tax**	**Pretax CF-tax**	**Discount Factor**	**Present Value**	**NPV**
1.000	-$50.91	$0.00	-$50.91	$0.00	-$50.91	0.877	-$44.65	-$44.65
2.000	-$101.81	$0.00	-$101.81	$0.00	-$101.81	0.769	-$78.34	-$122.99
3.000	$106.15	$18.75	$87.40	$26.00	$80.15	0.675	$54.10	-$68.89
4.000	$106.15	$30.01	$76.14	$22.65	$83.50	0.592	$49.44	-$19.46
5.000	$106.15	$18.00	$88.15	$26.22	$79.93	0.519	$41.51	$22.06
6.000	$106.15	$10.80	$95.35	$28.37	$77.79	0.456	$35.44	$57.49
7.000	$106.15	$10.80	$95.35	$28.37	$77.79	0.400	$31.09	$88.58
8.000	$106.15	$5.40	$100.75	$29.97	$76.18	0.351	$26.71	$115.29
9.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.308	$22.93	$138.22
10.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.270	$20.12	$158.33
11.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.237	$17.64	$175.98
12.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.208	$15.48	$191.46
13.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.182	$13.58	$205.03

14.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.160	$11.91	$216.94
15.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.140	$10.45	$227.39
16.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.123	$9.16	$236.55
17.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.108	$8.04	$244.59
18.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.095	$7.05	$251.64
19.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.083	$6.19	$257.83
20.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.073	$5.43	$263.26

Table 55 - NPV 7-Year Recovery Parameters

7-Year Parameters		
Label	**Amount**	**Unit**
TCC	$101.81	MM USD
Gross Profit	$106.15	MM USD/yr
TCC-WC	$93.77	MM USD
Tax	29.75%	
Discount Rate	0.14	

Table 56 - NPV 7-Year Depreciation Parameters

Depreciation	
Years	**Percent**
1	14.30%
2	24.50%
3	17.50%
4	12.50%
5	8.90%
6	8.90%
7	8.90%
8	4.50%

Table 57 - NPV 7-Year Recovery

7-Year Recovery (MM USD)								
Year	**Pre-tax CF**	**Depreciation**	**Taxable Income**	**Tax**	**Pretax CF-tax**	**Discount Factor**	**Present Value**	**NPV**

1.000	-$50.91	$0.00	-$50.91	$0.00	-$50.91	0.877	-$44.65	-$44.65
2.000	-$101.81	$0.00	-$101.81	$0.00	-$101.81	0.769	-$78.34	-$122.99
3.000	$106.15	$13.41	$92.74	$27.59	$78.56	0.675	$53.03	-$69.97
4.000	$106.15	$22.97	$83.18	$24.75	$81.41	0.592	$48.20	-$21.77
5.000	$106.15	$16.41	$89.74	$26.70	$79.45	0.519	$41.27	$19.50
6.000	$106.15	$11.72	$94.43	$28.09	$78.06	0.456	$35.56	$55.06
7.000	$106.15	$8.35	$97.81	$29.10	$77.05	0.400	$30.79	$85.85
8.000	$106.15	$8.35	$97.81	$29.10	$77.05	0.351	$27.01	$112.87
9.000	$106.15	$8.35	$97.81	$29.10	$77.05	0.308	$23.69	$136.56
10.000	$106.15	$4.22	$101.93	$30.32	$75.83	0.270	$20.45	$157.02
11.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.237	$17.64	$174.66
12.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.208	$15.48	$190.14
13.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.182	$13.58	$203.72
14.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.160	$11.91	$215.63
15.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.140	$10.45	$226.07
16.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.123	$9.16	$235.24
17.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.108	$8.04	$243.28
18.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.095	$7.05	$250.33
19.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.083	$6.19	$256.51
20.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.073	$5.43	$261.94

Table 58 - NPV Results

NPV Results (MM USD/yr)	
5-Year Recovery	**7-Year Recovery**
$1,340.77	$1,317.69

Table 59 - DCFROR 5-Year Recovery Parameters

5-Year Parameters		
Label	**Amount**	**Unit**
TCC	$101.81	MM USD
Gross Profit	$106.15	MM USD/yr
TCC-WC	$93.77	MM USD

Tax	29.75%	[redacted]
Discount Rate	0.46	[redacted]

Table 60 - DCFROR 5-Year Depreciation Parameters

Depreciation	
Years	**Percent**
1	20.00%
2	32.00%
3	19.20%
4	11.52%
5	11.52%
6	5.76%

Table 61 - DCFROR 5-Year Recovery

5-Year Recovery (MM USD)								
Year	**Pre-tax CF**	**Depreciation**	**Taxable Income**	**Tax**	**Pretax CF-tax**	**Discount Factor**	**Present Value**	**NPV**
1.000	-$50.91	$0.00	-$50.91	$0.00	-$50.91	0.686	-$34.94	-$34.94
2.000	-$101.81	$0.00	-$101.81	$0.00	-$101.81	0.471	-$47.96	-$82.90
3.000	$106.15	$18.75	$87.40	$26.00	$80.15	0.323	$25.92	-$56.99
4.000	$106.15	$30.01	$76.14	$22.65	$83.50	0.222	$18.53	-$38.45
5.000	$106.15	$18.00	$88.15	$26.22	$79.93	0.152	$12.17	-$26.28
6.000	$106.15	$10.80	$95.35	$28.37	$77.79	0.105	$8.13	-$18.15
7.000	$106.15	$10.80	$95.35	$28.37	$77.79	0.072	$5.58	-$12.57
8.000	$106.15	$5.40	$100.75	$29.97	$76.18	0.049	$3.75	-$8.81
9.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.034	$2.52	-$6.29
10.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.023	$1.73	-$4.56
11.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.016	$1.19	-$3.38
12.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.011	$0.82	-$2.56
13.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.008	$0.56	-$2.00
14.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.005	$0.38	-$1.62
15.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.004	$0.26	-$1.35

16.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.002	$0.18	-$1.17
17.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.002	$0.12	-$1.05
18.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.001	$0.09	-$0.96
19.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.001	$0.06	-$0.90
20.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.001	$0.04	-$0.86

Table 62 - DCFROR 7-Year Recovery Parameters

7-Year Parameters		
Label	**Amount**	**Unit**
TCC	$101.81	MM USD
Gross Profit	$106.15	MM USD/yr
TCC-WC	$93.77	MM USD
Tax	29.75%	
Discount Rate	0.45	

Table 63 - DCFROR 7-Year Depreciation Parameters

Depreciation	
Years	**Percent**
1	14.30%
2	24.50%
3	17.50%
4	12.50%
5	8.90%
6	8.90%
7	8.90%
8	4.50%

Table 64 - DCFROR 7-Year Recovery

7-Year Recovery (MM USD)								
Year	**Pre-tax CF**	**Depreciation**	**Taxable Income**	**Tax**	**Pretax CF-tax**	**Discount Factor**	**Present Value**	**NPV**
1.000	-$50.91	$0.00	-$50.91	$0.00	-$50.91	0.689	-$35.05	-$35.05
2.000	-$101.81	$0.00	-$101.81	$0.00	-$101.81	0.474	-$48.26	-$83.31

3.000	$106.15	$13.41	$92.74	$27.59	$78.56	0.326	$25.64	-$57.67
4.000	$106.15	$22.97	$83.18	$24.75	$81.41	0.225	$18.29	-$39.38
5.000	$106.15	$16.41	$89.74	$26.70	$79.45	0.155	$12.29	-$27.08
6.000	$106.15	$11.72	$94.43	$28.09	$78.06	0.107	$8.32	-$18.77
7.000	$106.15	$8.35	$97.81	$29.10	$77.05	0.073	$5.65	-$13.12
8.000	$106.15	$8.35	$97.81	$29.10	$77.05	0.051	$3.89	-$9.22
9.000	$106.15	$8.35	$97.81	$29.10	$77.05	0.035	$2.68	-$6.55
10.000	$106.15	$4.22	$101.93	$30.32	$75.83	0.024	$1.82	-$4.73
11.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.016	$1.23	-$3.50
12.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.011	$0.85	-$2.65
13.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.008	$0.58	-$2.07
14.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.005	$0.40	-$1.67
15.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.004	$0.28	-$1.39
16.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.003	$0.19	-$1.20
17.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.002	$0.13	-$1.07
18.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.001	$0.09	-$0.98
19.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.001	$0.06	-$0.92
20.000	$106.15	$0.00	$106.15	$31.58	$74.57	0.001	$0.04	-$0.88

Table 65 - DCFROR Results

DCFROR Results (MM USD/yr)	
5-Year Recovery	**7-Year Recovery**
-$300.85	-$306.17

Table 66 - Gross Margin Results

Gross Margin	
Label	**Amount (MM USD/yr)**
Revenues	$204.84
Raw Material Cost	$67.96
GM	**$136.88**

Table 67 - Gross Profit Results

Gross Profit	
Label	**Amount (MM USD/yr)**
Main Product Revenue	$204.84
CCOP	$98.68
GP	**$106.15**

Table 68 - Sensitivity Analysis Data

Sensitivity Analysis			
Percent Operation (%)	**NPV (MM USD)**		
	Raw Materials	**Products**	**Utilities**
50	$380.73	-$105.98	$264.30
60	$356.98	-$24.50	$263.83
70	$333.22	$47.11	$263.36
80	$309.46	$118.72	$262.88
90	$285.70	$190.33	$262.41
100	$261.94	$261.94	$261.94
110	$238.18	$333.55	$261.47
120	$214.42	$405.16	$260.99
130	$190.66	$476.77	$260.52
140	$166.90	$548.38	$260.05
150	$143.14	$619.99	$259.58

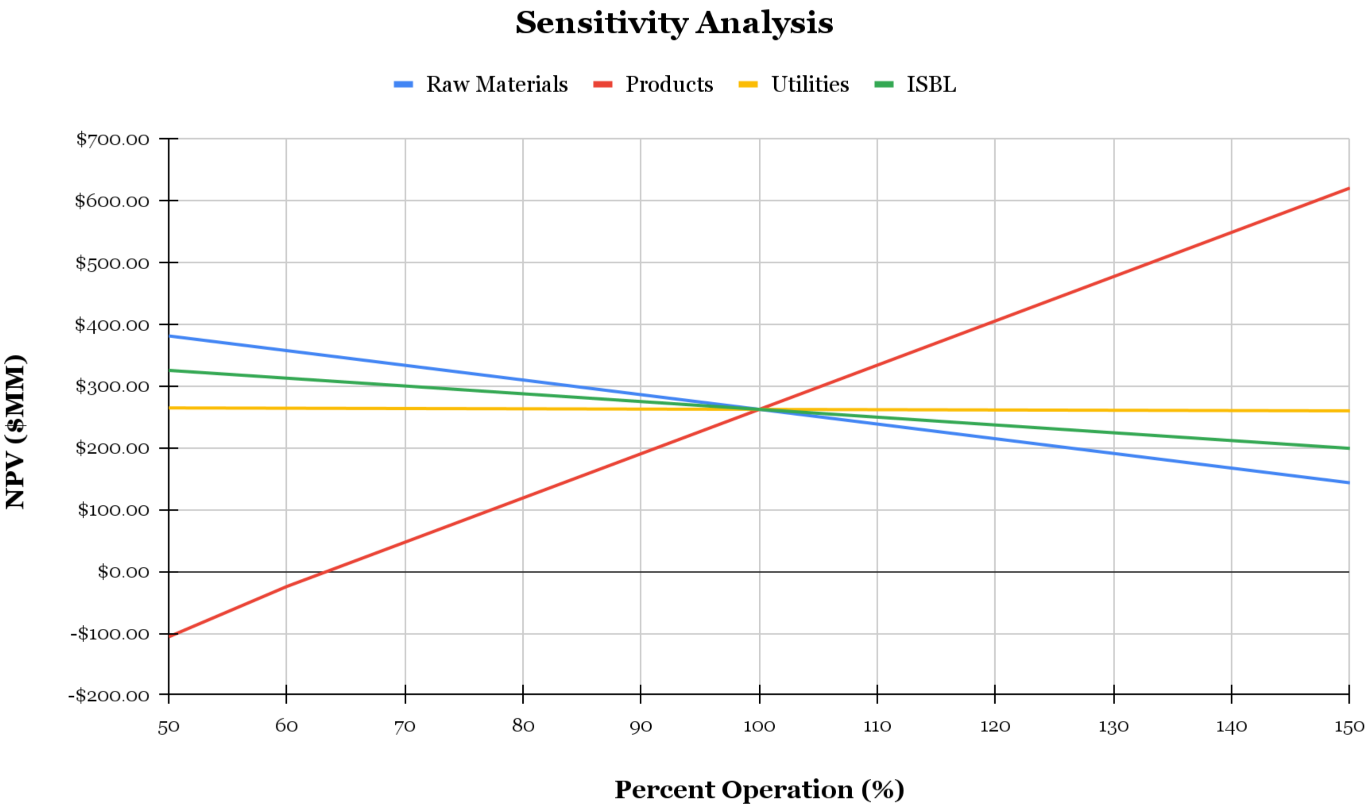


Figure 30 - Sensitivity Analysis Curve

References

[1] Kraus, G. A. (2008). Synthetic methods for the preparation of 1,3-propanediol. *CLEAN - Soil, Air, Water*, *36*(8), 648–651. https://doi.org/10.1002/clen.200800084

[2] *Acid catalyzed hydration of alkenes reaction and mechanism*. MCAT and Organic Chemistry. (2019, January 20). Retrieved January 25, 2023, from https://leah4sci.com/acid-catalyzed-hydration-of-alkenes-reaction-and-mechanism/

[3] Haas, T., & Arntz, D. (1994, November 15). Process for the Preparation of 1,3-Propanediol.

[4] Australian Government. (n.d.). *Acrolein (2-propenal)*. DCCEEW. Retrieved January 27, 2023, from https://www.dcceew.gov.au/environment/protection/npi/substances/fact-sheets/acrolein-2-propenal#:~:text=Physical%20properties,by%20the%20National%20Pollutant%20Inventory.

[5] Petrides, D., & Ferreira, R. D. G. (2020). Production of 1,3 Propanediol (PDO) via Fermentation - Process Modeling and Techno-Economic Assessment (TEA) using SuperPro Designer. https://doi.org/10.13140/RG.2.2.17939.63521

[6] Knifton, J. F., James, T. G., Slaugh, L. H., Weider, P. R., Allen, K. D., & Powell, J. B. (2009, May 26). One-step production of 1,3-propanediol from ethylene oxide and syngas with a cobalt-iron catalyst.

[7] US Department of Labor. (n.d.). *Ethylene Oxide*. Occupational Safety and Health Administration. Retrieved January 28, 2023, from https://www.osha.gov/ethylene-oxide#:~:text=Acute%20exposures%20to%20EtO%20gas,changes%2C%20neurotoxicity%2C%20and%20sensitization.

[8] *Chemical Price Analysis, chemical latest prices*. ChemAnalyst. (n.d.). Retrieved January 29, 2023, from https://www.chemanalyst.com/Pricing/Pricingoverview

[9] *Liquid Nitrogen Price List | Procurement | University of Arkansas*. (n.d.). Procurement.uark.edu. https://procurement.uark.edu/e-procurement/liquid-nitrogen-price-list.php

[10] Schell, D. J., Farmer, J., Newman, M., & Mcmillan, J. D. (2003). Dilute-Sulfuric Acid Pretreatment of Corn Stover in Pilot-Scale Reactor: Investigation of Yields, Kinetics, and Enzymatic Digestibilities of Solids. *Applied Biochemistry and Biotechnology*, *105*(1-3), 69–86. https://doi.org/10.1385/abab:105:1-3:69

[11] Ju, J.-H., Wang, D., Heo, S.-Y., Kim, M.-S., Seo, J.-W., Kim, Y.-M., Kim, D.-H., Kang, S.-A., Kim, C.-H., & Oh, B.-R. (2020). Enhancement of 1,3-propanediol production from industrial by-product by Lactobacillus reuteri CH53. *Microbial Cell Factories*, *19*(1). https://doi.org/10.1186/s12934-019-1275-x

[12] Huang, K., Peng, X., Kong, L., Wu, W., Chen, Y., & Maravelias, C. T. (2021). Greenhouse Gas Emission Mitigation Potential of Chemicals Produced from Biomass. *ACS Sustainable Chemistry & Engineering*, *9*(43), 14480–14487. https://doi.org/10.1021/acssuschemeng.1c04836

[13] Grant, D. (2021, March 2). *Illinois Counties Rank Among Best for Crop Output Nationally*. FarmWeekNow. Retrieved January 29, 2023, from https://www.farmweeknow.com/profitability/illinois-counties-rank-among-best-for-crop-output-nationally/article_77d3b492-7b91-11eb-ac70-dbe79624b942.html

[14] Aboagye, D., Banadda, N., Kambugu, R., Seay, J., Kiggundu, N., Zziwa, A., & Kabenge, I. (2017). Glucose recovery from different corn stover fractions using dilute acid and alkaline pretreatment techniques. *Journal of Ecology and Environment*, *41*(1). https://doi.org/10.1186/s41610-017-0044-1

[15] Talarico, T. L., & Dobrogosz, W. J. (1990). Purification and characterization of glycerol dehydratase from *lactobacillus reuteri*. *Applied and Environmental Microbiology*, *56*(4), 1195–1197. https://doi.org/10.1128/aem.56.4.1195-1197.1990

[16] *Adkesson, D. M. A. M., Alsop, A. W., & Ames, T. T. (2005, March 31). PURIFICATION OF BIOLOGICALLY PRODUCED 1,3-PROPANEDIOL.*

[17] *Cervin, M. A., Soucaille, P., & Valle, F. (2010, June 29). PROCESS FOR THE BIOLOGICAL PRODUCTION OF 13-PROPANEDIOL WITH HIGH YIELD.*

[18] *(2023). Biotechnology for Biofuels and Bioproducts [Review of Biotechnology for Biofuels and Bioproducts]. Biotechnologyforbiofuels.biomedcentral.com.* https://biotechnologyforbiofuels.biomedcentral.com/articles/10.1186/s13068-019-1529-1/tables/1

[19] *https://www.marketresearchfuture.com, M. R. F. (n.d.). 1, 3-Propanediol Market Size, Share, Growth | Report, 2030. Www.marketresearchfuture.com. Retrieved January 30, 2023, from https://www.marketresearchfuture.com/reports/1-3-propanediol-market-5722*

[20] Du, C., & Webb, C. (2011). Cellular systems. *Comprehensive Biotechnology*, *2*, 11–23. https://doi.org/10.1016/b978-0-08-088504-9.00080-5

[21] RSS-Feed, bio-based eu/news- das F. für bio-basierte Ö., Biowerkstoffe und Industrielle Biotechnologie-. (n.d.). *U.S.A.: World's first propanediol production from corn sugar opened*. Renewable Carbon News. Retrieved January 30, 2023, from https://renewable-carbon.eu/news/u-s-a-worlds-first-propanediol-production-from-corn-sugar-opened/

[22] Vivek, N., Pandey, A., & Binod, P. (2017). Production and applications of 1,3-propanediol. *Current Developments in Biotechnology and Bioengineering*, 719–738. https://doi.org/10.1016/b978-0-444-63662-1.00031-2

[23] Liu, H., Xu, Y., Zheng, Z., & Liu, D. (2010). 1,3-Propanediol and its copolymers: Research, development and industrialization. *Biotechnology Journal*, *5*(11), 1137–1148. https://doi.org/10.1002/biot.201000140

[24] *Converting Grain Units*. U.S. GRAINS COUNCIL. (2021, June 2). Retrieved January 29, 2023, from https://grains.org/markets-tools-data/tools/converting-grain-units/

[25] *United States Department of Agriculture*. USDA. (n.d.). Retrieved January 29, 2023, from https://www.nass.usda.gov/Charts_and_Maps/Field_Crops/cornprod.php

[26] https://www.datamintelligence.com, D. I. (n.d.). *Bio-based Polytrimethylene Terephthalate (PTT) Market Size*. DataMIntelligence. Retrieved January 30, 2023, from https://www.datamintelligence.com/research-report/bio-based-polytrimethylene-terephthalate-market

[27] 1,3-propanediol price trend and forecast. PR. (n.d.). Retrieved February 26, 2023, from https://www.procurementresource.com/resource-center/1-3-Propanediol-price-trends

[28] Techno-economic analysis of bio-based lactic acid production utilizing ... (n.d.). Retrieved February 26, 2023, from https://www.researchgate.net/publication/339098455_Techno-Economic_Analysis_of_Bio-Based_Lactic_Acid_Production_Utilizing_Corn_Grain_as_Feedstock

[29] Dextrose price trend and forecast. PR. (n.d.). Retrieved February 26, 2023, from https://www.procurementresource.com/resource-center/dextrose-price-trends

[30] Thompson, J., & Tyner, W. (2011, September). Corn Stover for Bioenergy Production: Cost Estimates and Farmer Supply Response. Retrieved February 20, 2023, from https://www.extension.purdue.edu/extmedia/EC/RE-3-W.pdf

[31] Alghamdi, B. (n.d.). Alkylation of benzene by propylene to cumene. *Chemical Process Design*, 173–200. https://doi.org/10.1002/9783527621583.ch6

[32] Towler, G. P., & Sinnott, R. K. (2013). *Chemical Engineering Design: Principles, Practice, and Economics of Plant and Process Design* (2nd ed.). Boston, MA: Butterworth-Heinemann.

[33] U.S. Environmental Protection Agency. (2016). *Costs of managing wastes generated by industrial facilities - Executive summary*. Retrieved March 23, 2023, from https://www.epa.gov/sites/default/files/2016-09/documents/waste_generation_and_management_costs_-_executive_summary.pdf

[34] Nunez, K. (2011). Managing Supply Chain's Transaction Costs Through Logistics. *Journal of Applied Business Research (JABR), 22*(1), 21-30. doi:10.19030/jabr.v22i1.1442

[35] Safeopedia. (n.d.). National Fire Protection Association (NFPA). Retrieved March 25, 2023, from https://www.safeopedia.com/definition/94/national-fire-protection-association-nfpa

[36] LabChem. (2015). Safety Data Sheet: Water, Deionized [PDF]. https://www.labchem.com/tools/msds/msds/LC26750.pdf

[37] Santa Cruz Biotechnology. (2018). Safety Data Sheet: Potassium Ferricyanide [PDF]. https://datasheets.scbt.com/sc-214762.pdf

[38] National Oceanic and Atmospheric Administration. (n.d.). Sodium Hydroxide Solution. CAMEO Chemicals. https://cameochemicals.noaa.gov/chemical/9073

[39]Occupational Safety and Health Administration. (2021). Annotated PELs Table Z-1. Retrieved March 24, 2023, from https://www.osha.gov/annotated-pels/table-z-1

[40] Fisher Scientific. (2021). Safety Data Sheet: D-(+)-Glucose Monohydrate, 99+%, for analysis, ACROS Organics™ [PDF]. https://www.fishersci.com/store/msds?partNumber=AC450740010&productDescription=D%28%2B%29-GLUCOSE+MONOHYDRATE+1KG&vendorId=VN00032119&countryCode=US&language=en

[41] Cargill. (2016). Glycerin Crude MSDS. Retrieved from https://www.cargill.com/doc/1432075994011/glycerin-crude-msds.pdf

[42] Cargill, Incorporated. (2017). Glycerin Crude Material Safety Data Sheet. Retrieved March 24, 2023, from https://www.cargill.com/doc/1432075994011/glycerin-crude-msds.pdf

[43] National Oceanic and Atmospheric Administration. (n.d.). Nitrogen. https://cameochemicals.noaa.gov/chemical/4069

[44] ATCC. (n.d.). ATCC® Minis – Malaria Parasite, Plasmodium falciparum 3D7, MRA-102G™. Retrieved March 24, 2023, from https://www.atcc.org/products/23272

[45] Fisher Scientific. (2019). Ethanol absolute, molecular biology grade [Safety Data Sheet]. Fisher Scientific. https://fscimage.fishersci.com/msds/89308.htm

[46] Fisher Scientific. (n.d.). Safety Data Sheet: Lactic acid, USP/FCC, 500 mL. https://www.fishersci.com/store/msds?partNumber=A159500&productDescription=LACTIC+ACID+USP%2FFCC+500ML&vendorId=VN00033897&countryCode=US&language=en

[47] Fisher Scientific. (n.d.). Acetic acid, Glacia 2.5L. Fisher Scientific. Retrieved March 25, 2023, from https://www.fishersci.com/msdsproxy%3FproductName%3DAC423220025%26productDescription%3DACETIC%2BACID%252C%2BGLACIA%2B2.5L%26catNo%3DAC42322-0025%2B%26vendorId%3DVN00033901%26storeId%3D10652

[48] Fisher Scientific. (n.d.). Safety Data Sheet: Dimethyl sulfoxide. https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-d/S25295B.pdf

[49] Fisher Scientific. (n.d.). Potassium hydroxide pellets [Safety Data Sheet]. Fisher Scientific. https://fscimage.fishersci.com/msds/18691.htm

[50] Sigma-Aldrich Co. LLC. (2020). Safety Data Sheet - Carbon Dioxide (295108). https://www.sigmaaldrich.com/US/en/sds/ALDRICH/295108

[51] Fisher Scientific. (2015). Safety Data Sheet - 1,3-Propanediol, 98% (AC131400010). https://www.fishersci.com/store/msds?partNumber=AC131400010&productDescription=1%2C3-PROPANEDIOL%2C+98%25+1LT&vendorId=VN00032119&countryCode=US&language=en

[52] U.S. Environmental Protection Agency. (n.d.). Summary of the Clean Air Act. Retrieved March 25, 2023, from https://www.epa.gov/laws-regulations/summary-clean-air-act

[53] Environmental Protection Agency. (2022, January 10). Summary of the Clean Water Act. Retrieved March 24, 2023, from https://www.epa.gov/laws-regulations/summary-clean-water-act

[54] Manitoba Agriculture and Resource Development. (n.d.). Carbon Dioxide (CO2) Supplement in Greenhouses. Retrieved March 24, 2023, from https://www.gov.mb.ca/agriculture/crops/crop-management/co2-supplement.html

[55] University of Washington. (n.d.). Caution Signs and Warning Signs. Environmental Health & Safety. Retrieved March 24, 2023, from https://www.ehs.washington.edu/research-lab/caution-signs-and-warning-signs

[56] Environmental Protection Agency. (n.d.). Clean Air Act Permitting for Greenhouse Gases. Retrieved March 26, 2023, from https://www.epa.gov/nsr/clean-air-act-permitting-greenhouse-gases#UARG

[57]*Greenhouse Carbon Dioxide Supplementation - Oklahoma State University*. Greenhouse Carbon Dioxide Supplementation | Oklahoma State University. (2017, March 1). Retrieved March 26, 2023, from https://extension.okstate.edu/fact-sheets/greenhouse-carbon-dioxide-supplementation.html

[58]Jurik, T. W., Weber, J. A., & Gates, D. M. (1984). Short-term effects of CO2 on gas exchange of leaves of bigtooth aspen (populus grandidentata) in the field. *Plant Physiology*, *75*(4), 1022–1026. https://doi.org/10.1104/pp.75.4.1022

[59]Ju, J.-H., Heo, S.-Y., Choi, S.-W., Kim, Y.-M., Kim, M.-S., Kim, C.-H., & Oh, B.-R. (2021). Effective bioconversion of 1,3-propanediol from biodiesel-derived crude glycerol using organic acid resistance–enhanced lactobacillus reuteri JH83. *Bioresource Technology*, *337*, 125361. https://doi.org/10.1016/j.biortech.2021.125361

[60] Grand View Research. (2021). 1,3-Propanediol (PDO) Market Size, Share & Trends Analysis Report By Application (Polytrimethylene Terephthalate, Personal Care & Detergents, Engine Coolants), By Region, And Segment Forecasts, 2020 – 2027. Retrieved April 11, 2023, from https://www.grandviewresearch.com/industry-analysis/1-3-propanediol-pdo-market

[61] Learn About the Greenhouse Gas Reporting Program (GHGRP) Website: https://www.epa.gov/ghgreporting/learn-about-greenhouse-gas-reporting-program-ghgrp

[62] *Vacuum fundamentals*. Atlas Copco. (n.d.). Retrieved April 30, 2023, from https://www.atlascopco.com/en-us/vacuum-solutions/vacuum-fundamentals

[63] Menards. (n.d.). Home improvement at Menards®. Retrieved May 1, 2023, from https://www.menards.com/

[64] Hawkins, Inc. (n.d.). Home. Retrieved May 1, 2023, from https://www.hawkinsinc.com/

[65] Allman, T. (2021, November 9). *The difference between batch, fed-batch and continuous processes*. Blog. Retrieved May 2, 2023, from https://www.infors-ht.com/en/blog/the-difference-between-batch-fed-batch-and-continuous-processes