Scale-Up Design for Biodegradable Vanillin-Based Polymer Production

A Technical Report submitted to the Department of Chemical Engineering

Presented to the Faculty of the School of Engineering and Applied Science
University of Virginia • Charlottesville, Virginia

In Partial Fulfillment of the Requirements for the Degree
Bachelor of Science, School of Engineering

Jillian Dane
Spring, 2020

Technical Project Team Members
Christopher Brodie
Ethan Bush
Gavin Restifo
Rebecca Richardson

On my honor as a University Student, I have neither given nor received
unauthorized aid on this assignment as defined by the Honor Guidelines
for Thesis-Related Assignments

Scale-Up Design for Biodegradable Vanillin-Based Polymer Production

Spring 2020

Project Team Members:
Christopher Brodie, Ethan Bush, Jillian Dane, Gavin Restifo, Rebecca Richardson

ABSTRACT

Lignin-derived biopolymers are a promising class of degradable materials with potential applications in the textile and plastic industries. Despite an abundance of laboratory-scale syntheses, few biopolymers are produced at the industrial scale in comparison to conventional plastics such as polyethylene terephthalate (PET). We show plant design and economic analysis for the at-scale production of poly(dihydroferulic acid) (PHFA), a novel biodegradable polymer with properties mimicking those of PET. Process design closely follows the synthetic scheme originally developed and patented by Mialon *et al.* with modifications made to ensure feasible scalability and process safety. With a target output of 330,000 MT of PHFA per year, the plant would occupy 1.2% of the global PET market and produce an annual after-tax cash flow of over $30 million. With an initial capital investment of 210 million USD, this cash flow ensures an internal rate of return of 12%. Through its economic and logistical viability, the PHFA manufacturing process highlights the potential for improving environmental sustainability of widely used materials and the reduction of plastic waste in the future.

TABLE OF CONTENTS

1. INTRODUCTION

1.1 Design Motivation

In the span of half a century, the low cost-to-performance ratio of synthetic plastic has driven its use across a wide range of applications. Single-use packaging, textiles, building construction, vehicles, medical devices, and innumerable consumer products are created from plastic, but of the 8.3 billion metric tons (MT) of plastic produced between 1950 and 2017, 6.3 billion MT were thrown away without recycling.[1] Moreover, the plastic recycling rate in the U.S. peaked in 2014 at only 9.5%, reflecting the cultural and economic barriers to keeping plastic waste streams out of the environment.[2] In the early 1990s, the annual rate of plastic production reached 100 million MT, surpassing that of steel. At this time, researchers began to notice that the majority of waste accumulating in the ocean was non-degrading plastic.[2,3] Today, the National Ocean Service estimates that 8 million MT of plastics enter the ocean each year.[4] In order to limit further impacts of discarded plastic, it may be possible to design functional replacements for conventional polymers that degrade on relatively short timescales into harmless byproducts in both marine and landfill conditions.[5]

Another concern with most traditional polymers is their dependence on a non-renewable feedstock: 99% of plastic is currently derived from fossil fuels.[6] Consequently, the plastic industry is expected to account for 20% of global oil use by 2050 without a change in feedstock, which motivates academic research into alternative polymer chemistries that utilize renewable feedstocks.[7] One reaction that is gaining particular interest from researchers involves the depolymerization of lignin, a natural polymer representing 30% of the world's biomass, to obtain aromatic compounds for continued processing.[8,9] Mialon et al., researchers at The George and Josephine Butler Laboratory for Polymer Research at the University of Florida, reported a novel, biodegradable, and lignin-derived thermoplastic replacement for polyethylene terephthalate (PET) in 2010. The final product of their reported reaction, poly(dihydroferulic acid) (PHFA), exhibits thermal and mechanical properties comparable to those of PET, the third most common synthetic polymer that accounts for nearly twenty percent of global plastic production.[10] The monomer, dihydroferulic acid, is a modified form of vanillin which is a product of wood-derived lignin depolymerization. The other reagent, acetic anhydride, can also be extracted from wood, resulting in a fully wood-sourced material.[10]

A patent and trademark, under the name Gatoresin™, for PHFA followed its discovery, indicating its perceived viability.[11,12] The technology then led to the founding of US Bioplastics, with Miller as the CTO. The company received initial funding, but never acquired the resources to build a pilot facility for the production of the material.[13] Given the promise of the bioplastic itself and the recent increase in demand for bioplastics, it is worth considering the development of a new design for industrial scale production of this material. Currently, lignin-based vanillin is produced at small-scales and high costs relative to its petrochemical-based counterpart. From a basic input-output cost balance, detailed further in a later section, production of PHFA from natural vanillin is not economically feasible since the PET-alternative will be sold at prices typical of bulk commodity plastics. Thus, the industrial process design will initially utilize petrochemical vanillin to produce PHFA based on the synthetic scheme detailed by the Mialon group. Theoretically, continued advances in technology to decrease the manufacturing costs of renewably-sourced vanillin combined with implementation of policies that increase the demand for sustainable materials will allow for eventual transition to a lignin-derived plant.

1.2 Specification of Product

1.2.1 Thermal Properties of PHFA

PHFA exhibits a glass transition temperature of 73 °C and melts at 234 °C, while its cooling-cycle crystallization temperature is 207 °C. PET has a similar glass transition temperature, which typically varies between 67 °C and 81 °C depending on the individual sample grade, while it melts at 237 °C and undergoes cooling-cycle crystallization at 190 °C (**Figure 1-1**). This disparity in melting points is not expected to impair the applicability of the PHFA product, as most PET is not exposed to such high temperatures during regular use, and will likely make further processing of PHFA easier and more cost-effective to execute than that of PET. Additionally, the higher cooling-cycle crystallization temperature of PHFA implies that it may have a faster crystallization rate than PET.[10]

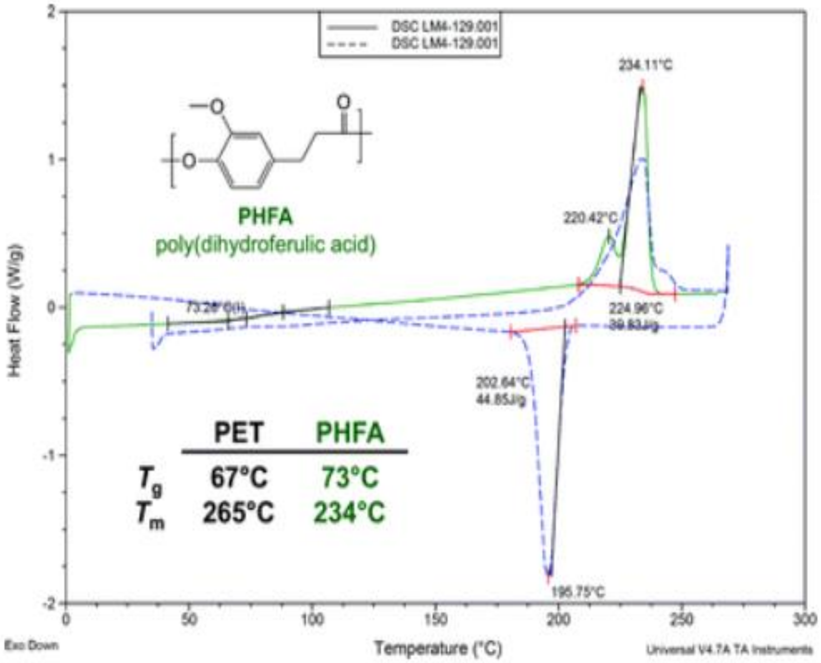


Figure 1-1. Differential Scanning Calorimetry Data and Structure of PHFA (Mialon, 2010)

1.2.2 Molecular Weight & Purity of PHFA

A polymerization scheme's target number average molecular weight, M_n, varies with the desired applications of the product. As commercial PET typically has M_n between 15,000 and 40,000, the product PHFA must possess a comparable range. Relatively low molecular weight PET tends to be used in packaging and textiles, while high molecular weight PET products are favored for thermoplastic applications.[10] The product polymer must be at least 98% pure PHFA by weight, as unreacted monomers and oligomers are common impurities in plastics, particularly those obtained via step polymerization. Other expected impurities include traces of the polymerization reaction byproduct, acetic acid, and low-molecular weight hydrogenation side products such as aliphatic alcohol or carboxylic acid products.[11]

1.2.3 Degradation of PHFA

PHFA degrades benignly into the environment chemically (in a landfill) or enzymatically (biodegradation under composting conditions), since the dihydroferulic acid building block is a metabolite recognizable by existing microbes.[10] Initial target applications include beverage bottles, retail food containers, and eco-friendly soft textiles due to the overlap between the M_n of PHFA produced by reaction conditions selected from the Mialon paper (M_n ~ 18,000) and the M_n range of PET generally favored by those industries.[14]

1.3 Description of Raw Materials

Our production line will utilize a three-step reaction to produce our polymer. The first step of the process will use vanillin, acetic anhydride, sodium acetate, and a small fraction of pyridine to decrease viscosity. Vanillin at the beginning of operation will be bought in bulk from a chemical company, but after the price-point adjusts it could be purchased in the form produced by Brownhill et al. in their undergraduate capstone project[15], where it was derived from black liquor produced by a paper production facility. The second step will use hydrogen and palladium-carbide catalyst, and potentially a solvent mixture of tetrahydrofuran and methanol. The hydrogen used in this step will be produced through steam-methane-reforming, which will require the use of natural gas and steam. The final step of the reaction will not require any new raw materials, but additional purification steps may require further use of solvents.

1.4 Production Scale

Given the similarities between the chemical structures of PHFA and PET, the proposed mechanism of PHFA industrial synthesis, detailed in the following section, is quite similar to that for PET production. Thus, the nominal capacity of a typical PET facility may serve as a guideline for the scaling of our PHFA process. In 2007, the industry-best capacity for PET production in North America was 330,000 MT per year at the Eastman Chemical facility in Columbia, South Carolina.[16] The largest PET manufacturing facility to date, integrated with a purified terephthalic acid (PTA) plant to achieve a proposed annual capacity of 1.1 million MT, began construction in 2017 in Corpus Christi, Texas.[17] The plant was acquired by a joint venture known as CC Polymers, including global PET manufacturers Alpek and Indorama. The PET producers are joined by Far Eastern Investment, a subsidiary of polyester producer Far Eastern New Century Corporation. The plant is set to continue construction and will begin production as early as 2020, at which point each stakeholder will receive a third of the PET produced at the site.[17]

Given the project goal of mass producing PHFA to compete in the PET market, it is necessary to select a plant scale that make markets penetration feasible. Global PET production capacity was 27.8 million MT in 2015. China is the leading producer, controlling 27% of the market share followed by Europe and North America, controlling 17% each.[18] The scale of the

Eastman plant in Columbia -- 330,000 MT per year -- is on the lower end of PET plants today but is of a large enough capacity to produce reductions in capital costs while maintaining realistic sales volumes. At a proposed capacity of 330 thousand MT per year, this PHFA plant will represent 1.2% of the global PET market and 7.0% of the North American market.

2. PREVIOUS WORK

In the 2018 Undergraduate Thesis ‘Design of the Production of Vanillin from Kraft Black Liquor,’ Brownhill et al. report plant design for production of food-grade vanillin from kraft black liquor. A lignin-rich byproduct of paper pulp production, black liquor was investigated as a potential source material for PHFA production. Though the vanillin produced by the process outlined in this thesis would have been a more environmentally sustainable source material for PHFA production, purchase of petrochemically-derived vanillin was necessary for the PHFA plant to be economically viable. It was theorized that the environmental sustainability of the PHFA manufacturing process could be improved over time by switching from petrochemical to biomass-derived vanillin feedstocks later in the lifespan of the plant.

3. DESIGN DISCUSSION

3.1 Overview of Chemical Pathway

The central reactive pathway is presented in **Figure 3-1**, showing the separation of steps that was employed to distinguish between the corresponding sections of the facility. The acetyl group additions by the Perkin and O-acetylation reactions may be performed in either order or simultaneously, although the proposed process is designed to complete O-acetylation in one step, followed by the Perkin reaction.

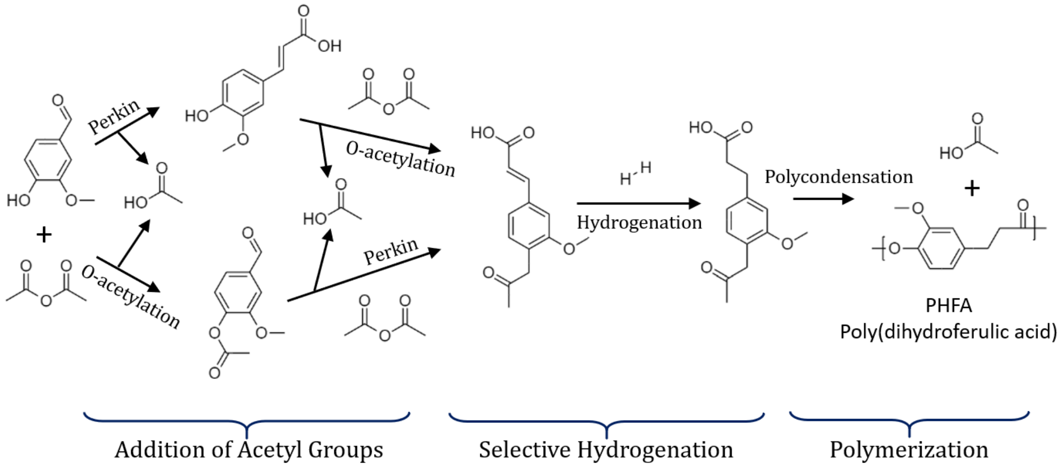


Figure 3-1. Visualization of chemical pathway for synthesizing PHFA

3.2 Acetylation of Vanillin with Acetic Anhydride to Form Acetylferulic Acid

Initially, both the O-acetylation and Perkin reactors were designed as CSTRs with 80% conversion, with any unreacted vanillin, vanillin acetate, and ferulic acid being separated by distillation from the premonomer and recycled to the feed stream. Since the normal boiling point of acetylferulic acid is at least 70 °C above vanillin and the mono-acetylated intermediates, and also because the acetylation groups may be added in any order, it seemed feasible to recycle unreacted effluent from the Perkin reactor to the O-acetylation reactor. However, even with 80% conversion, parallel O-acetylation CSTRs required 140 m^3 in total before considering the effect of recycle flow – and since the Perkin reaction proceeds at least an order of magnitude more slowly, the design was determined to be impractical, if not impossible. In addition, efforts to separate components present in Section 1 showed that distillation was highly energy-intensive, so the reactors were redesigned to approach full conversion (in excess of 99.5%) in a single pass. To improve conversion, both reactors were redesigned from CSTRs to PFRs, which also simplifies heat removal.

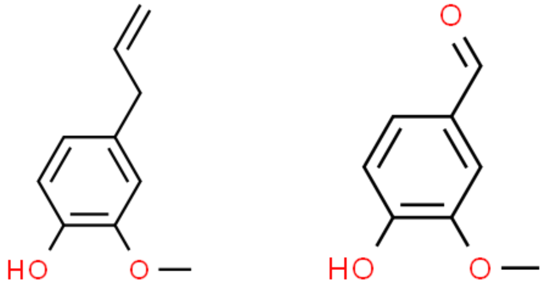


Figure 3-2. Comparison of eugenol (left) and vanillin (right) structures. O-acetylation occurs at the phenol group *via* acetic anhydride.

The O-acetylation reactor utilizes kinetic data from the liquid phase O-acetylation of eugenol by acetic anhydride, which is comparable to the reaction of vanillin (see **Figure 3-2**).[19] It is likely that this kinetic substitute would yield conservative results, if it is inaccurate, since the electron-withdrawing aldehyde in vanillin may encourage the reaction. The catalyst is a sodium zeolite (4Å pore size), which is available as beads suitable for a packed bed (a resin catalyst was also reported, but had poor activity retention). Similarly, kinetic data for the Perkin reaction was found for acetic anhydride and benzaldehyde, which lacks the acetate and methyl ether groups present in the vanillin acetate intermediate.[20] The kinetic study included multiple solvents and catalysts, allowing selection of conditions that would be most safe and cost-effective in this facility. We opted to use an excess of acetic anhydride instead of adding a solvent, to reduce separation costs and safety concerns, even though the rate constant is doubled in the presence of high-polarity solvents. Of the tertiary amine liquid catalysts, we chose that with the highest activity, namely, 4-dimethylaminopyridine (DMAP).

Solving temperature, pressure, and concentration differential equations simultaneously, using the activation energy data and Aspen-calculated mixture properties, results in detailed specifications for the O-acetylation PFR. The reaction occurs rapidly, so the total volume of packed bed is small relative to the volumetric flow. Only 10 vertical tubes, 25 cm in diameter with 20 cm zeolite packed beds, are required to exceed 99.5% conversion, and these tube dimensions also yield an acceptable pressure drop of 1.395 bar for Molecular Sieve 4Å beads with a commercially-available diameter of 3.2 mm. The throughput, over 500 m^3/hr, is so large relative to the tube surface area, 1.57 m^2, that heat removal by external cooling fluid is ineffective. Therefore, heat generated by the reaction primarily raises the temperature of the reactant stream from 56.9 °C to 78.9 °C, with negligible losses across the tube walls. This benefits the following separations, since less additional heat is needed to reach vapor-liquid equilibrium, and also increases conversion.

The DMAP-catalyzed Perkin reaction occurs far more slowly than the O-acetylation, with a residence time of 14.1 hours required for 99.5% conversion, even assuming ideal PFR kinetics. The residence time could potentially be reduced by optimizing feed concentrations, but since an experimental rate is provided for the designed conditions, and the generalized empirical rate equation does not suggest much potential for improvement, we did not alter the feed ratios. Additionally, temperature-dependent kinetics are only reported for triethylamine catalysis, so the Perkin reactor is constrained to 140 °C. The long residence time is achieved by 200 tubes, 52 m in length and 80 cm in diameter. Since this would be inconvenient to build as a single vertical pass, three passes are used (fall, rise, then fall to the outlet). To keep the reaction fluid near 140 °C, cooling is required, although this is nearly trivial given the sluggishness of the reaction and a heat transfer surface area in excess of 26,000 m^2 in the tubes. High-flow (320 m^3/s for a 10 °C increase) vertically blown air provides sufficient heat removal, although the airspeed must vary across the length of the tubes such that heat transfer is proportional to the heat generated by reaction. In addition to the high residence time, the Perkin reactor is hindered by a significant side reaction, also catalyzed by DMAP: acetic anhydride decomposes into acetone and carbon dioxide. The competition of this reaction with the desired acetylation may be reduced with less of an excess of anhydride, but again, it was decided that the kinetic data could not be extrapolated to other conditions.

3.3 Purification of Premonomer and Side Products in Acetylation Process

Early in the design process, it appeared that the main challenge of separations within Section 1 would be throughput, since the differences in volatility between the components are sufficient for distillation, and acetylferulic acid is the least volatile component present. **Table 3-1** gives the normal boiling points for the liquid components, that is, excluding carbon dioxide. Even using the simplified analysis of comparing boiling points, it is clear that the separation acetic acid and acetic anhydride would be the most resource-intensive. Acetic acid must be removed from anhydride-rich streams before and after the Perkin reactor, both to enable its sale as a coproduct and to keep it from protonating DMAP within the reactor. Unfortunately, acetic acid and acetic anhydride form an anhydride-rich azeotrope near or below atmospheric pressure, so in both cases, pressure-swing distillation with a 10 bar column followed by a 1.2 bar

Table 3-1. Relevant Normal Boiling Points for Section 1 Separations (°C)

Acetone	56
Acetic acid	118
Acetic anhydride	140
DMAP	195
Vanillin	285
Vanillin acetate	291
Ferulic acid	395
Acetylferulic acid	468

column was employed. Hydrogen bonding and acid-base interactions create non-ideality in both liquid and vapor phases throughout Section 1.

Due to vapor-phase nonideality inherent to acetic acid, pressure-swing distillation was required to remove acetic acid from the organic reactants and anhydride. Separations within Section 1 begin when effluent from the O-acetylation reactor, R-101, is subjected to columns T-101 and T-102 in order to remove acetic acid produced by O-acetylation before the organic reactants enter the Perkin PFR, R-102. T-101 operates at a pressure of 10 bar, while T-102 operates at 1.2 bar. Acetic acid and acetic anhydride compose over 99.9% of the distillate by mass, while the bottoms stream contains the heavier organic components including vanillin acetate and unreacted vanillin. With a tray effectiveness value of 0.70, the default value for that parameter in Aspen, T-101 possesses 32 trays while T-102 has 40. Effluent from the Perkin reactor is fed to T-103 in order to separate the heavy organic components such as acetylferulic acid and DMAP from acetic anhydride and acetic acid. T-103 possesses 6 trays. The distillate of T-103 is fed to T-104 in order to separate the DMAP from the light components, acetic acid and acetic anhydride, while the bottoms of T-103 is fed to T-105 in order to separate DMAP from the heavy organic components, mainly acetylferulic acid. The bottoms of T-104 and distillate of T-105 consist of purified DMAP, and are mixed to form a recycle stream that eventually returns to the Perkin reactor to preserve catalyst. The final separation occurs via T-106 and T-107, in which acetic acid is separated from acetic anhydride. T-106 and T-107 both require 40 trays in order to achieve the separation. Though the specifications of the separations were configured using Aspen and presented in the process flow diagram **Figure 4-1**, the reactors were designed using Python, creating manual tear stream locations at the input and output of each reactor in the Aspen file for manual iteration.

3.4 Selective Hydrogenation of Acetylferulic Acid to Acetyldihydroferulic Acid

Kinetic data for accurate modeling was taken from Begley et al. and Surface and Nanomolecular Catalysis.[21] The molecule these parameters were measured from, 1-phenylpropene, has similar functionality to Acetylferulic Acid, and it is assumed that the kinetics will accurately portray the reaction that we are modeling, although lab and pilot plant testing is necessary to collect more accurate kinetic and physical data prior to plant production. Begley et al. performed the hydrogenation reaction in isopropanol at 313 K and 1 barg of pure hydrogen with 2.5 wt% Rh/SiO_2 catalyst. The kinetics were fit to a pseudo first order rate equation with respect to the alkene, which is used for the model here. A paper published at the University of KwaZulu-Natal found that the rate of liquid phase hydrogenations is dependent on the solvent used. For accuracy of our kinetic parameters, isopropanol is used in the reactor design.

Solubility was estimated with Aspen, and it was found that at a 1:1 ratio by volume at 5 barg and 120ºC there would be no solids present. Viscosity and heat capacity were then estimated in Aspen assuming this composition. Mass and energy balances for CSTRs, shown in the appendix, were performed with a chosen conversion to yield reactor volume and heat produced. As separations from the hydrogenated and unhydrogenated species are impractical and unhydrogenated species will contribute to crosslinking at the conditions in the polymerization reactor described below, conversion for each reactor was chosen such that the reactor was small enough to allow pricing using CAPCOST and so that overall conversion exceeded 99.9%. A conversion of 87.2% per reactor yields 99.95% conversion in a series 4 reactors, each with a liquid volume of 26.6 m^3. Catalyst mass was scaled from the lab setup to yield 3.35 kg of catalyst dispersed in each reactor.

For the physical reactor design, a diameter of 2.5 m and height of 6.25 m was chosen to yield a total volume of 30.7 m^3 with an L/D of 2.5. This provides an adequate vapor space above the liquid with 86.6% of the volume being liquid. Cooling these reactors is done through pumping reactor contents through heat exchangers with cooling water to remove heat. Complete reactor design is specified below in **Table 4-2** and the exchanger and pumping equipment is fully specified in **Tables 4-6** and **4-10**. This pumping will provide supplementary mixing to baffles and a multi-blade agitator.

Aspen was used to perform the additional mass balances in each reactor with respect to the other components in the system. At these conditions, isopropanol readily moved into the vapor with unreacted hydrogen gas. The vapor collected from each reactor is cooled to 50℃ and phase separated to separate the solvent and unreacted hydrogen that is saturated with solvent vapor. These streams are recycled into their respective feed streams. The liquid product from the reactors is heated using steam at 350 psi to 200℃ and isothermally flashed from 5 barg to 1 barg. This flash drum requires pumping of the liquid contents through a heater and back into the drum, like the reactors described above. The liquid product is then sent as the feed to the initial polymerization heater and the vapor is compressed back to 5 barg then cooled to 50℃, separated by phase, and each stream is sent to their respective recycle. The vapor recycles are primarily unreacted hydrogen with some isopropanol, and the liquid recycle is primarily isopropanol with some trace monomer. The compressor, exchangers, and separation equipment are specified in **Tables 4-4**, **4-6**, and **4-8**. The separation drums were sized using Aspen, exchangers were designed using Exchanger Design & Rating, a program built off Aspen, and the pumps and compressor were designed using Aspen and Analysis, Synthesis and Design of Chemical Processes by Richard Turton.

Isopropanol remains in the monomer stream, which is further separated prior to polymerization, described below in Section 3.4. Additional isopropanol is included in the feed to the process to maintain the solution in each piece of equipment, requiring 55,000 L/hr of solvent in the feed to the reactors and 700 kg/hr of hydrogen gas split between the reactors. 86.5% of the hydrogen is sent to the first, 10% to the second, and 2.5% to the third with the remaining to the final reactor. With the feed of 61,250 kg/hr of acetylferulic acid, 62,000 kg/hr of acetyldihydroferulic acid is produced and about 50 kg/hr of unreacted acetylferulic acid remains. Material balances yield a makeup of 433 kg/hr of isopropanol and 520 kg/hr of hydrogen gas.

3.5 Acetyldihydroferulic Acid Purification for PHFA production

Purification of the monomer was completed through a system of heat exchangers (E-201, 202, 207, 208, 209) and flash drums (V-201, 202, 203). The vapor collected from each hydrogenation reactor described above is collected into one stream and cooled to 50℃ in exchanger E-208. This enters hydrogen-isopropanol settler V-201. The vapor is primarily hydrogen and the liquid primarily isopropanol, and both are pumped and heated, discussed below. The liquid product flowing from the final hydrogenation reactor R-204 is heated to 200℃ in hydrogenation effluent heater E-207. This enters the monomer-solvent flash drum V-202 where the fluid is flashed to 1 barg. This vessel will be kept isothermal by pumping the liquid through monomer solvent flash heater E-212 with monomer solvent flash pump P-211 A/B and back into the vessel. The liquid product from this is primarily monomer with some remaining isopropanol and is sent to the polymerization reactor scheme. The vapor product is pressurized in effluent vapor compressor C-201 to 5 barg, cooled in effluent vapor condenser E-209 to 50℃, and phase separated in effluent vapor separator V-203. The liquid from effluent vapor separator V-203 and hydrogen-isopropanol settler V-201 are mixed, pumped through liquid isopropanol recycle pump P-210 A/B, heated with liquid isopropanol recycle heater E-211 and fed as liquid recycle, while the vapor from effluent vapor separator V-203 and hydrogen-isopropanol settler V-201 is heated in vapor recycle heater E-210 and recycled. A simulation of the entire process was performed in Aspen, with the stream results shown in **Tables 4-14 and 4-15.**

Equipment design for each of the drums and heat exchangers was performed with Aspen and is shown in table 4.2. As residual acetic acid is only sparsely present from previous production processes, every vessel may be made of carbon steel. Cooling water at 30℃ was used for the coolers (E-203 A/B, 204, 205, 206, 208, 209) and was designed to be sent to cooling towers at 45℃. High pressure steam at 350 psi was used for the heaters (E-201, 202, 207, 210, 211, 212).

Centrifugal pumps (P-202-209) associated with each reactor, both for the reactor products and the pump-around cooling and heat exchangers (P-210, 211) were designed using their necessary hydraulic power and are specified in table 4-8. For each pump, the throughput was defined from the material balances completed in Aspen, and the drop was calculated using Exchanger Design and Rating in Aspen when available, or was estimated to be 0.5 atm when there was no available information

3.6 Pre-Polymerization of Acetyldihydroferulic Acid to Low-Viscosity PHFA

Industrially, PET is produced via a copolymerization reaction of purified terephthalic acid (TPA) and ethylene glycol (EG).[22] Due to differences in required residence times for initial esterification of TPA and EG and downstream polycondensation, the process is typically designed in two steps. First, TPA and EG are mixed in an esterification reactor which yields a TPA-EG comonomer and low molecular weight oligomers. This oligomer mixture is then sent to a set of parallel polycondensation reactors, run at 265-275ºC and 2500-3500 Pa, to achieve a degree of polymerization between 15 and 20.[22] Thermodynamic studies of PET polymerization suggest an equilibrium constant around K=0.5.[22] Thus, the reaction is run at high temperature and low pressure to aid in the removal of EG from the polymer melt which drives the reaction towards the products.

The major product of upstream PET esterification, bis-hydroxyethyl terephthalate (BHET) is a comonomer formed by the combination of one TPA and two EG molecules in the reaction displayed below.[22]

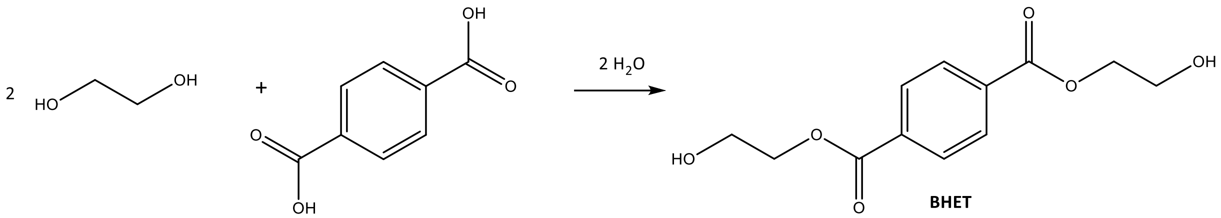


Figure 3-3. Reaction of ethylene glycol and terephthalic acid to produce BHET

Because BHET is structurally similar to acetyldihydroferulic acid, the kinetics of BHET in pre-polymerization reactors was used to model ADHF polymerization. Chen-Chong and Baliga studied the polycondensation of BHET at 278ºC in the presence of 0.025 wt% Sb_2O_3 catalyst by monitoring the course of intrinsic viscosity. Their study supported a second order irreversible reaction model for early stages of polymerization.[23]

Mass transfer effects for acetic acid in the polymer melt were largely neglected in the design of the continuous stirred tank reactors used for pre-polycondensation. To support the assumption that the removal of acetic acid from the reactor is readily achieved at the reactor operating temperature and pressure, a degree of polymerization at the low-end of the typical range – 15 – was selected.

Wallace Carothers developed a model to relate extent of polycondensation reaction (p) to the number average degree of polymerization ($\bar{x}_n$) based on the molar ratio of reactive end groups. For ARB polycondensation reactions, exemplified by the polymerization of ADHF, the ratio (r) of ‘A’ to ‘B’ groups is always 1. The general form of the equation and the simplified form for ARB reactions is displayed in Equation 10-5 in the Appendix. Thus, the Carothers equation suggests that an extent of reaction of p = 93% is required to achieve a degree of polymerization of 15.

Mass balances on CSTRs in parallel performed using MATLAB indicate that a 93% fractional conversion of ADHF is achieved using 4 CSTRs in parallel, each with a volume of 32.8 m^3. Scaling up the reaction performed by Chen-Chong and Baliga, 12.4 kg of Sb_2O_3 is required in each reactor.[23] Commercially, Sb_2O_3 is sold in powder form with a mesh size on the order of 5μm the name Senarmontite.[24] For application in the CSTRs, this powder must be processed by a third party to create particles with a nominal size around 1mm. At this size, the catalyst beads are both suspendable and filterable by a screen at the outlet of the reactor. The Sb_2O_3 powder could be pelletized or coated onto an inert and light-weight matrix.

One 32.8 m^3 reactor, filled with 12.4 kg of Sb_2O_3 in 1mm beads and operating at 278ºC, processes 15,500 kg/hr of ADHF into 10,900 kg/hr of polymer melt and 3570 kg/hr acetic acid with unreacted 1030 kg/hr ADHF. Aspen was used to determine the composition of the vapor and polymer-melt reactor effluents. The reactor was modeled as an adiabatic flash block at 278ºC using the steady-state reactor composition to set the composition of the block’s inlet stream. Because the polymer is not a recognized component in Aspen, the polymer was represented by an equal mass of ADHF. First, a sensitivity analysis was first performed to determine the effect of pressure on the split of acetic acid between the vapor and polymer melt phases. From this analysis, it was determined that a vacuum pressure of 0.2 bar was sufficient in removing 99% of the acetic acid from the polymer melt. Decreasing the vacuum pressure further removed more acetic acid from the polymer melt but also increased the amount of unreacted ADHF monomer that was pulled into the vapor phase. This monomer will be removed from acetic acid in later separations but is not set to be recycled to the process. Thus, it was important to minimize loss of ADHF to the vapor to diminish waste production and to ensure sufficient monomer remains in the polymer melt to achieve high degree of polymerization in the finishers. The complete compositions of the polymer melt and vapor vent are available in **Table 4-15.**

The transesterification reaction occurring in the CSTRs is considered to be heat neutral. Assuming each CSTR is adequately insulated, the only heat loss is the CSTR is due to the vaporization of acetic acid. To add heat to the reactors to maintain a working temperature of 278ºC, the feed will be preheated. The heat of vaporization of acetic acid and the heat capacity of reactor internals at operating conditions were determined using Aspen. Using this data and a CSTR energy balance, it was determined that pre-heating the monomer feed to 311.5ºC creates a steady-state reactor temperature of 278ºC.

A fired heater with a duty of 3360 kW will be utilized to pre-heat the feed. There is some concern that the monomer fluid could begin to polymerize in the fired heater as the temperature is increased. Thus, trial experiments should be performed to determine the degree of polymerization achieved at these conditions. Likewise, it would be prudent to install flow meters in the fired heater to allow for the monitoring of pipes to ensure blockages are not formed by molten polymer.

3.7 Finishing Processes of the Low Viscosity Polymer Melt

The full polymerization requires roughly two hours of residence time and is driven by the mass-transfer of acetic acid. To accomplish this full polymerization, our team will be purchasing BUSS COMPEO 176 compounders. Below is a schematic of the extruder:

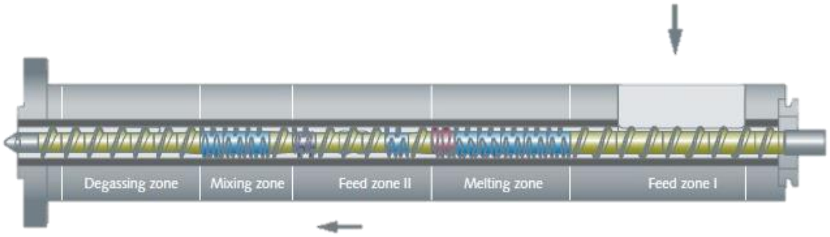


Figure 3-4. Schematic of polymerization reactor.[25]

These extruders are used in PET production, promising a throughput capability between 4800 and 6400 kg/h.[25] BUSS compounders are highly customizable for our process, but the data to be able to determine the degree of polymerization for our product was not available. Therefore, trials would need to be done to determine the extent to which the reaction occurs within these extruders and to make adjustments to the operating parameters to achieve a final product with a commercially applicable degree of polymerization. Given the range of throughputs, we have determined that we will need between 15 and 20 of these extruders. Each extruder is designed with 176 mm screws and operates at 600 rpm and has a max drive power of 1650 kW.[25]

For the purpose of waste treatment, it is necessary to obtain an estimate of the amount of acetic acid that would be produced in the devolatilization stage. Although the actual degree of polymerization will be highly dependent on extruder operating conditions, it is known that the target degree of polymerization is around 100 which corresponds to a total extent of reaction of 99%. Using this extent of reaction and the relationship between the amount of monomer reacted and the amount of condensate formed in an ARB polymerization, it is estimated that the bay of finishing extruders will generate 775 kg/hr of acetic acid vapor. Additionally, any volatile components that remained in the polymer melt after pre-polymerization will be vaporized in the finishers. Assuming complete removal of all acetic acid and isopropanol from the polymer melt, the extruders will produce a total of 916 kg/hr acetic acid vapor and 1.2 kg/hr isopropanol vapor. These streams will be combined with the liquid waste from the downstream acetic acid purification which will be repurposed as fuel in the plant’s fired heaters.

3.8 Recovery of Acetic Acid for Sale

The acetic acid purification process takes in three streams from various parts of the production. Two of the streams come from the acetylation portion of the production line and are mixed together with the acetic acid that is getting pulled off of the pre-polymerization CSTRs. This design utilizes two 26 equilibrium-stage distillation columns, assuming a tray efficiency of 70%. Each column also uses a total condenser and U-tube kettle reboiler.

3.9 Simulation of Processes in Aspen Plus

Acetylferulic acid and acetyldihydroferulic acid were the only compounds in the facility not found in Aspen’s component property databanks. Therefore, the UNIFAC group-contribution method was used to estimate parameters in Aspen for these components, with the assumption of a negligible magnetic dipole moment for both (MUP property set to zero).

Unless otherwise noted, the NRTL-HOC property method and the default values for efficiencies were used for Aspen simulations.

4. FINAL RECOMMENDED PROCESS DESIGN

As reported in the patent and research article of Miller et al., PHFA was developed using bench-top-scale batch syntheses on the order of tens of grams.[10,11] Additionally, the published method utilized solvents and separation techniques that would not permit direct scale-up. For instance, the monomer was isolated from the hydrogenation reaction mixture by vacuum filtration through celite, drying over magnesium sulfate, dissolving in tetrahydrofuran, precipitating in hexanes, vacuum filtration, recrystallization in 5:1 ethyl acetate and water, and finally drying on a Schlenk line. A similar process was employed following acetylation of vanillin, and also following the polymerization. In the latter case, the crude solid product was dissolved in a trifluoroacetic acid and dichloromethane mixture in order to increase the purity of the PHFA product by precipitation. Overall yields for each reaction-separation step were reported in the range of 62-91%. These methods would not be suitable for any significant scale-up.

To achieve the target throughputs resulting in 45.8 t PHFA/hr, continuous operation is the only feasible option for our facility, since the material logistics within the plant required for batch operation would greatly increase capital and operating costs at this scale. This decision alone meant that the PHFA production scheme would need to be modified from that of the patent. For the purposes of safety and reduced environmental hazard, as well as economic considerations, minimizing the use of solvents throughout the process was a priority, and fluorinated/chlorinated solvents were not considered as options. The energy demand of drying processes would also be prohibitive. As such, the production method had to be redesigned from the basis of the chemical pathway: Perkin and O-acetylation reactions with vanillin and acetic anhydride, selective hydrogenation to obtain the monomer, and step-growth polymerization to produce PHFA.[10]

4.1 Overview of Process Flow

The addition of acetyl groups to vanillin, yielding acetylferulic acid, was designated Section 1 of the facility. The process flow diagram and equipment key are provided in **Figure 4-1**. Vanillin and acetic anhydride are loaded as received into the Vanillin Feed Tank, TK-101, and the Anhydride Feed Tank, TK-102, then combined to create a liquid feed stream with an anhydride-rich recycle stream, and reacted in O-Acetylation Plug Flow Reactor R-101 A/B to form vanillin acetate. The feed is swapped between R-101 A and R-101 B to prevent downtime when the packed bed is regenerated or replaced. Acetic acid is removed from the effluent by successive vapor-liquid equilibrium separations, starting with V-101, the O-Acetylation Effluent Flash Drum, and followed by the High Pressure and Low Pressure Acid Columns, T-101 and T-102. Another anhydride recycle stream and a make-up stream of acetic anhydride and DMAP catalyst are added before feeding to the Perkin Plug Flow Reactor, R-102. Anhydride is partially consumed in a side reaction that creates acetone and carbon dioxide, the latter of which is vented from R-102. The effluent of R-102 contains acetone, trace concentrations of unreacted vanillin and mono-acetylated intermediates (vanillin acetate and ferulic acid), all DMAP that enters the reactor, acetic acid generated by acetylation, the remaining acetic anhydride (still in excess), and the acetylferulic acid premonomer. The Perkin Effluent Column, T-103, divides the components with volatilities greater and less than DMAP, with DMAP present in both the distillate and bottoms. DMAP is removed for recycling in T-104, the Light DMAP Column, and T-105, the Heavy DMAP column. The distillate of T-104 is primarily anhydride, which is isolated using pressure-swing by T-106 and T-107, the High

Pressure and Low Pressure Anhydride Columns. The distillate of T-107, a mixture of acetone, acetic acid, and acetic anhydride is routed to Section 3 for purification of acetic acid. The Heavy DMAP Column bottoms stream is the product of Section 1, acetylferulic acid, which is piped into Section 2.

Section 2 corresponds to the selective hydrogenation of acetylferulic acid, and generates the monomer of PHFA, acetyldihydroferulic acid. The process flow and equipment key are provided in Figure 4-2. Acetylferulic acid is dissolved in isopropanol and heated to form a feed solution for the series of hydrogenation reactors R-201 to R-204, which are the First through Fourth Hydrogenators. Hydrogen is bubbled continuously through each reactor. Hydrogen and isopropanol vapor pulled from the headspace of the reactors are separated by the Hydrogen-Isopropanol Settler, V-201, and both are recycled to combine with the respective feed streams. The conversion is high enough that the trace amounts of acetylferulic acid do not need to be separated from the monomer before sending to polymerization in Section 3, so only the isopropanol solvent is removed from the final effluent using Monomer-Solvent Flash Drum V-202. This solvent stream is also recycled to the isopropanol feed stream.

The PHFA polymer product and acetic acid co-product are made in Section 3. The process flow diagram and equipment key are provided in **Figure 4-3**. Acetyldihydroferulic acid undergoes initial polycondensation to a low degree of polymerization in the parallel set of Pre-polymerization Reactors, R-301 A/B/C/D. Finishing polymerization occurs in the array of Polymerization Extruders, R-302, and the product is then pelletized by PHFA Pelletizer P-302 to generate the sellable form of the product. The Pre-polymerization Vacuum Pump, P-301, maintains dynamic vacuum on the R-301 to remove acetic acid as it is generated. This acetic acid vapor is combined with the acetic acid leaving Section 1 and purified for sale in Acetic Acid

Distillation Columns, T-301 and T-302. The bottom stream of T-301 and distillate of T-302 are liquid waste containing unreacted compounds. This liquid waste, containing only organic compounds, will be utilized as fuel in the fired heaters throughout the plants.

TK-101	TK-102	P-101 A/B	P-102 A/B	E-101	R-101 A/B	P-103 A/B	E-102	TK-103	V-101	T-101	E-103	E-104
Vanillin Feed Tank	Anhydride Feed Tank	O-Acetylation Feed Pump	Anhydride Recycle Pump	O-Acetylation Feed Heater	O-Acetylation Plug Flow Reactor	O-Acetylation Effluent Pump	O-Acetylation Effluent Heater	DMAP Storage Tank	O-Acetylation Effluent Flash Drum	High Pressure Acid Column	High Pressure Acid Column Condenser	High Pressure Acid Column Reboiler
T-102	E-105	E-106	P-104 A/B	P-105 A/B	P-106 A/B	E-107	R-102	E-108	T-103	E-109	E-110	P-106 A/B
Low Pressure Acid Column	Low Pressure Acid Column Condenser	Low Pressure Acid Column Reboiler	Anhydride Recovery Pump	Anhydride Recovery Pump	Perkin Supplement Pump	Perkin Feed Cooler	Perkin Plug Flow Reactor	Perkin Effluent Heater	Perkin Effluent Column	Perkin Effluent Column Condenser	Perkin Effluent Column Reboiler	Perkin Column Bottoms Pump
T-104	E-111	E-112	T-105	E-113	E-114	P-107 A/B	T-106	E-115	E-116	T-107	E-117	E-118
Light DMAP Column	Light DMAP Column Condenser	Light DMAP Column Reboiler	Heavy DMAP Column	Heavy DMAP Column Condenser	Heavy DMAP Column Reboiler	DMAP Column Distillate Pump	High Pressure Anhydride Column	High Pressure Anhydride Column Condenser	High Pressure Anhydride Column Reboiler	Low Pressure Anhydride Column	Low Pressure Anhydride Column Condenser	Low Pressure Anhydride Column Reboiler

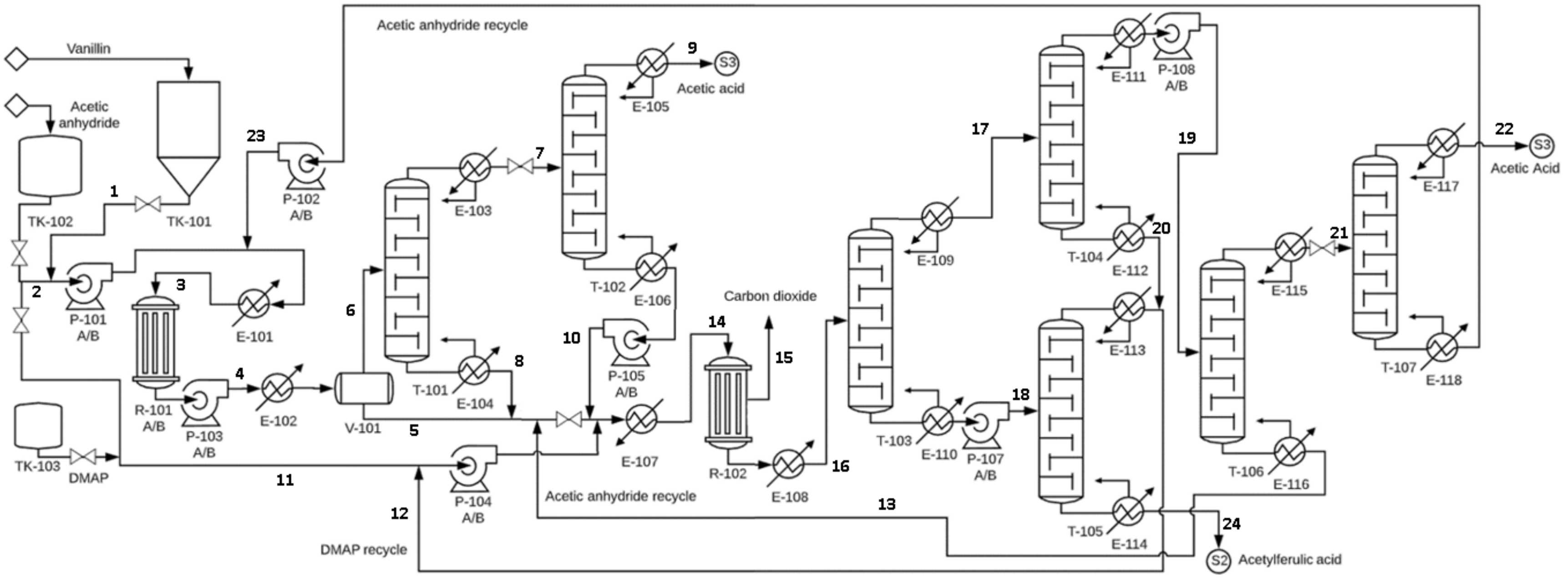


Figure 4-1. Process Flow Diagram and Equipment Key for Section 1. Vanillin and acetic anhydride are reacted in two acetylation steps to form acetylferulic acid, the premonomer of PHFA. The acetic acid side product is separated out for purification in Section 3.

TK-201	P-201	E-201	E-202	R-201	P-202 A/B	P-203 A/B	E-203	R-202	P-204 A/B	P-205 A/B	E-204
Premonomer Feed Pump	Premonomer Feed Pump	Hydrogen Heater	Premonomer Dissolution Heater	First Hydrogenator	First Effluent Pump	First Cycling Pump	First Cycling Cooler	Second Hydrogenator	Second Effluent Pump	Second Cycling Pump	Second Cycling Cooler
R-203	P-206 A/B	P-207 A/B	E-205	R-204	P-208 A/B	P-209 A/B	E-206	E-207	E-208	V-201	
Third Hydrogenator	Third Effluent Pump	Third Cycling Pump	Third Cycling Cooler	Fourth Hydrogenator	Fourth Effluent Pump	Fourth Cycling Pump	Fourth Cycling Cooler	Hydrogenator Effluent Heater	Vapor Pull Cooler	Hydrogen-Isopropanol Settler	
V-202	C-201	E-209	V-203	E-210	P-210 A/B	E-211	E-212	P-211 A/B	C-202	E-213	
Monomer-Solvent Flash Drum	Effluent Vapor Compressor	Effluent Vapor Condenser	Effluent Vapor Settler	Vapor Recycle Heater	Liquid Isopropanol Recycle Pump	Liquid Isopropanol Recycle Heater	Monomer-Solvent Flash Heater	Monomer-Solvent Flash Pump	Isopropanol Recovery Compressor	Isopropanol Recovery Condensor	

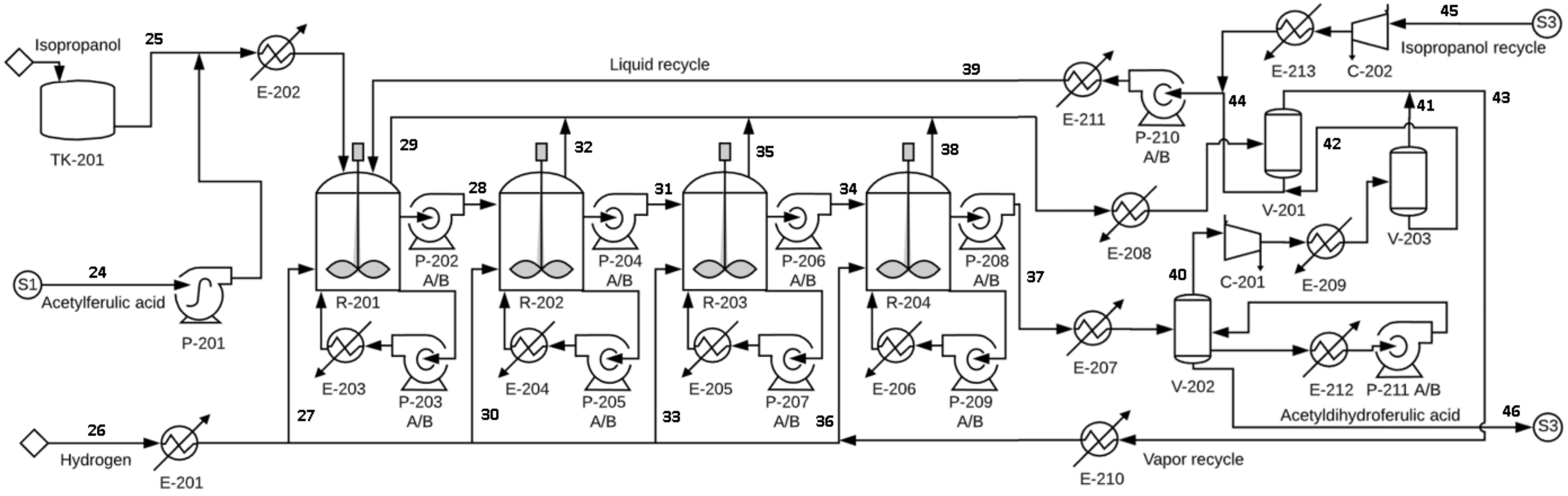


Figure 4-2. Process Flow Diagram and Equipment Key for Section 2. Acetylferulic acid and hydrogen are reacted in a series of CSTRs, with isopropanol as a solvent, to form acetyldihydroferulic acid, the monomer of PHFA. Isopropanol in the acetyldihydroferulic acid stream is recovered in Section 3 and recycled.

H-301	V-301	R-301 A/B/C/D	P-301	R-302	P-302	T-301	E-301	E-302	T-302	E-303	E-304
Monomer Fired Heater	Monomer Feed Settler	Pre-polymerization Reactors	Pre-polymerization Vacuum Pump	Polymerization Extruders	PHFA Pelletizer	First Acetic Acid Distillation Column	First Acetic Acid Distillation Reboiler	First Acetic Acid Distillation Condenser	Second Acetic Acid Distillation Column	Second Acetic Acid Distillation Reboiler	Second Acetic Acid Distillation Condenser

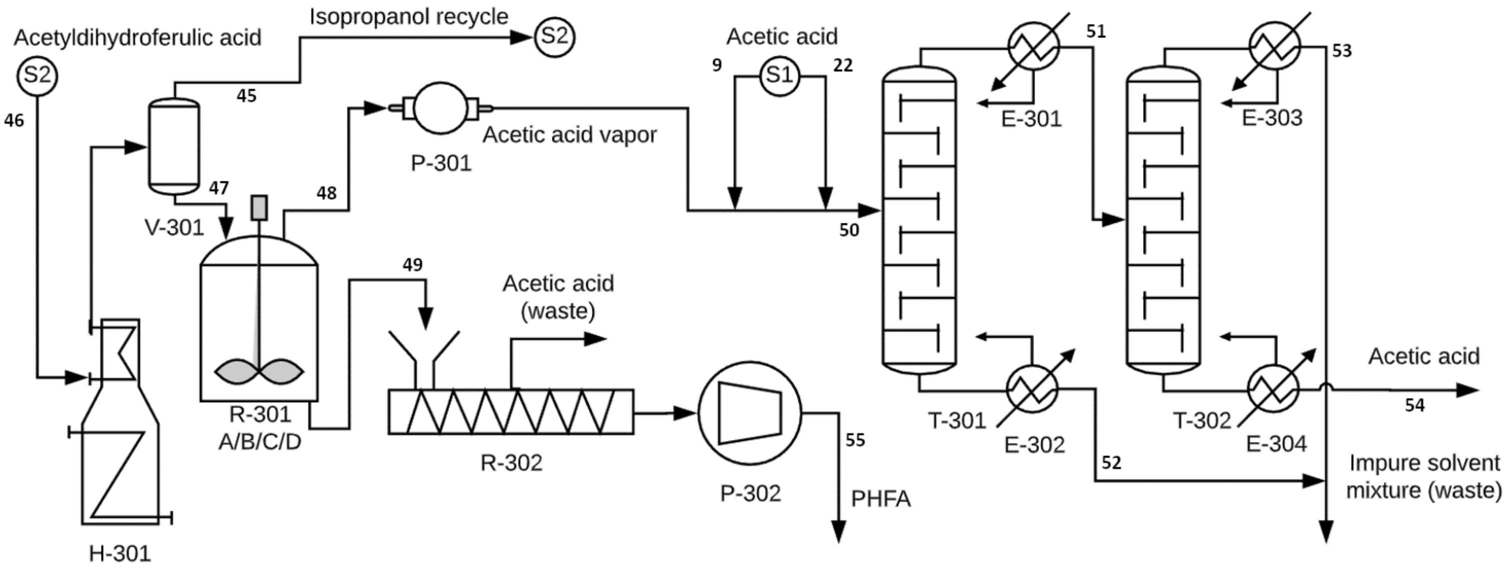


Figure 4-3. Process Flow Diagram and Equipment Key for Section 3. Acetyldihydroferulic acid is pre-polymerized in parallel CSTRs, finished in devolatilizing extruders, and pelletized for sale as PHFA. Acetic acid generated by pre-polymerization is combined with that sent from Section 1 and purified for sale.

4.2 Equipment Tables

Relevant equipment specifications for the unit operations in the PHFA plant are displayed in the following tables of this section. Equipment pricing, represented as the total module cost, is also included for each piece of equipment. The bare module equipment price was calculated using Richard Turton's CAPCOST software. The total module costs displayed in this section include the costs of contingencies and fees, represented as 15% and 3% respectively of bare module cost.[26]

Distillation column specifications were pulled from the Aspen simulation engine. Tower specifications and total module prices from CAPCOST are displayed in **Table 4-1** below.

Table 4-1. Distillation Column Equipment Specifications

Column Name	# Sieve Trays	Height (m)	Diameter (m)	Pressure (bar)	MOC	Total Module Cost
T-101	32	23.2	3.2	10	SS	$ 4,790,800
T-102	40	28.0	2.9	1.2	SS	$ 2,183,000
T-103	6	7.3	3.4	1.2	SS	$ 888,540
T-104	20	15.8	5.2	1.2	SS	$ 4,118,200
T-105	6	7.3	1.8	1.2	SS	$ 324,500
T-106	40	28.0	5.6	10	SS	$ 20,886,000
T-107	40	28.0	6.0	1.2	SS	$ 9,428,200
T-301	26	19.5	6.1	1.2	SS	$ 6,832,200
T-302	26	19.5	2.9	1.2	SS	$ 1,522,200

Specifications for the reactors in the PHFA plant are displayed in **Table 4-2** and **Table 4-3** below. The price of the PFRs was approximated using CAPCOST's pricing data for floating head shell and tube heat exchangers. The total module cost in the table represents the price of one reactor only. For reactors in parallel, the total plant cost is equal to the number of reactors in parallel times the total module cost.

Table 4-2. CSTR Equipment Specifications

Reactor Name	Volume	Height (m)	Diameter (m)	Total Module Cost
R-201	30.7	6.25	2.5	$ 556,960
R-202	30.7	6.25	2.5	$ 556,960
R-203	30.7	6.25	2.5	$ 556,960
R-204	30.7	6.25	2.5	$ 556,960
R-301 A/B/C/D	40.1	6.75	2.75	$ 888,540

Table 4-3. PFR Equipment Specifications

Reactor Name	Pressure (bar)	Tube Length (m)	Tube Diameter (cm)	Number Tubes	Number Passes	Heat Transfer Coefficient (W/m^2*K)	Total Module Cost
R-101 A/B	3.5	0.2	25	10	1	100	$ 152,220
R-102	5	52	80	200	3	100	$ 29,854,000

Flash drum and heat exchanger specifications were also obtained from the Aspen simulation engine. Vessel specifications and costs are displayed in **Table 4-4** below. Heat exchanger data is displayed by plant section in **Table 4-5**, **Table 4-6**, and **Table 4-7** below.

Table 4-4. Flash Drum and Settler Equipment Specifications

Vessel Name	Volume (L)	Height (m)	Diameter (m)	Max Pressure (barg)	MOC	Total Module Cost
V-201	3270	3.7	1.1	5	CS	$ 41,300
V-202	66700	9.4	3.1	5	CS	$ 481,440
V-203	8618	4.7	1.5	5	CS	$ 81,420
V-301	8618	4.7	1.5	1	SS	$ 74,222

Table 4-5. Section 1 Heat Exchanger Equipment Specifications

HX Name	Total Heat Duty (kW)	Heat Transfer Area (m^3)	Exchange Fluid	Tube Length (m)	Total Module Cost
E-101	171	8.4	Steam	6.1	$ 217,120
E-102	7420	237	Steam	6.1	$ 449,580
E-103	21700	85.5	Cooling H_2O	6.1	$ 264,320
E-105	9820	114	Cooling H_2O	6.1	$ 292,640
E-107	29200	267	Cooling H2O	6.1	$ 479,080
E-109	28200	161	Cooling H_2O	6.1	$ 349,280
E-111	42300	516	Cooling H2O	6.1	$ 804,760
E-112	765	61.4	Steam	6.1	$ 680,860
E-113	2200	11.8	Cooling H2O	6.1	$ 210,040
E-115	36900	145	Cooling H2O	6.1	$ 335,120
E-117	41300	481	Cooling H2O	6.1	$ 757,560

Table 4-6. Section 2 Heat Exchanger Equipment Specifications

HX Name	Total Heat Duty (kW)	Heat Transfer Area (m^3)	Exchange Fluid	Tube Length (m)	Total Module Cost
E-201	252	11.96	Steam	1.20	$ 113,752
E-202	2030	42.56	Steam	1.95	$ 115,522
E-203	6700	55.28	Cooling H_2O	1.50	$ 219,480
E-204	2210	19.26	Cooling H_2O	2.55	$ 106,908
E-205	331	3.39	Cooling H_2O	1.35	$ 115,876
E-206	50	2.44	Cooling H_2O	1.20	$ 115,876
E-207	9130	248.70	Steam	5.10	$ 247,800
E-208	1140	34.84	Cooling H_2O	5.10	$ 110,094
E-209	11100	172.45	Cooling H_2O	4.05	$ 193,520
E-210	56	1.22	Steam	1.20	$ 117,646
E-211	2730	48.46	Steam	3.75	$ 119,180
E-212	433	20.56	Cooling H_2O	1.20	$ 115,108
E-213	312	2.05	Steam	1.20	$ 108,442

Table 4-7. Section 3 Heat Exchanger Equipment Specifications

HX Name	Total Heat Duty (kW)	Heat Transfer Area (m^3)	Exchange Fluid	Tube Length (m)	Total Module Cost
E-301	32000	458	Cooling H_2O	6.1	$ 546,340
E-302	20600	1440	Steam	6.1	$ 1,652,000
E-303	7680	165	Cooling H_2O	6.1	$ 266,680
E-304	7800	252	Steam	6.1	$ 346,920

Compressor power requirements were obtained from Aspen simulations and are displayed in **Table 4-8** below. Pump power requirements were calculated using the product of volumetric flow rate and differential power. A pump efficiency of 70% was assumed. Pump specifications and pricing are listed by plant section in **Table 4-9** and **Table 4-10** below. The plant costs listed in the tables include the price of the specified pump and its spare for those pumps denoted with an ‘A/B’.

Table 4-8. Compressor Equipment Specifications.

Compressor Name	Hydraulic Power (kW)	Total Module Cost
C-201	1010	$ 726,880
C-202	33.3	$ 1,368,800
P-301 A/B	903	$ 5,274,600

Table 4-9. Section 1 Pump Specifications.

Pump Name	Volumetric Flow (m^3/s)	Outlet Pressure (barg)	Differential Head (Pa)	Hydraulic Power (W)	Total Module Cost
P-101 A/B	0.032	1.58	50,000	1,600	$ 47,200
P-102 A/B	0.015	1.58	140,000	2,130	$ 50,622
P-103 A/B	0.043	8.99	880,000	37,700	$ 149,860
P-104 A/B	0.012	1.99	180,000	2,080	$ 50,976
P-105 A/B	0.0056	8.99	880,000	4,900	$ 67,968
P-106 A/B	0.018	0.19	50,000	910	$ 43,896
P-107 A/B	0.098	8.99	880,000	86,000	$ 238,360

Table 4-10. Section 2 Pump Specifications.

Pump Name	Volumetric Flow (m^3/s)	Outlet Pressure (barg)	Differential Head (Pa)	Hydraulic Power (W)	Total Module Cost
P-201 A/B	0.011	5	50,700	540	$ 34,574
P-202 A/B	0.028	5	50,700	1,420	$ 37,170
P-203 A/B	0.078	5	25,000	1,960	$ 39,176
P-204 A/B	0.028	5	50,700	1,420	$ 37,170
P-205 A/B	0.053	5	14,000	745	$ 34,692
P-206 A/B	0.028	5	50,700	1,410	$ 37,170
P-207 A/B	0.008	5	15,000	118	$ 34,574
P-208 A/B	0.028	5	50,700	1,410	$ 37,052
P-209 A/B	0.001	5	2,000	2.41	$ 34,574
P-210 A/B	0.021	5	45,000	922	$ 35,282
P-211 A/B	0.170	5	2340	398	$ 34,574

Fired heater duties were pulled from generic heater blocks in Aspen simulations. Equipment prices and duties are displayed in **Table 4-11** below.

Table 4-11. Fired Heater Specifications.

Fired Heater Name	Heat Duty (kW)	Total Module Cost
E-104	12,700	$ 4,720,000
E-106	5,950	$ 3,398,400
E-108	5,196	$ 3,233,200
E-110	14,695	$ 5,085,800
E-114	6,983	$ 3,610,800
E-116	66,405	$ 13,688,000
E-118	31,707	$ 8,012,200
H-301	3,360	$ 2,159,400

Storage tanks for the main liquid feedstocks were designed to hold a 2 weeks supply of vanillin, acetic anhydride, DMAP, and isopropanol. All volumes were calculated using densities at a temperature between 25ºC and 30ºC. The volumes displayed in **Table 4-12** below allow for a vapor space of roughly 20% of the total tank volume.

Table 4-12. Storage Tank Specifications.

Tank Name	Volume (m^3)	Total Module Cost
TK-101	8,000	$ 561,680
TK-102	20,000	$ 1,157,580
TK-103	145	$ 82,364
TK-201	120	$ 79,060

4.3 Material & Energy Balances

Table 4-13. Stream Tables (1-20, See Figure 4-1)

		1	2	3	4	5	6	7	8	9	10
Temperature (°C)		20.0	20.0	56.9	79.2	292.0	292.0	230.8	240.9	132.8	144.9
Pressure (bar)		2.6	2.6	2.6	10.0	10.0	10.0	10.0	10.0	1.2	10
Flow (MT/hr)	Vanillin	40.0	-	40.0	0.0	0.0	0.0	0.0	0.0	-	0.0
	Acetic anhydride	-	89.3	130.8	104.2	18.2	86.0	19.3	66.7	2.7	16.6
	Vanillin acetate	-	-	-	51.0	51.0	0.0	0.0	0.0	-	0.0
	Acetic acid	-	-	1.5	17.1	1.7	15.4	13.8	1.6	11.9	1.9
	DMAP	-	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Total	40.0	89.3	172.3	172.3	70.9	101.4	33.1	68.3	14.6	18.5

		11	12	13	14	15	16	17	18	19	20
Temperature (°C)		20.0	217.3	242.1	140.0	162.6	162.6	161.2	321.4	138.7	169.6
Pressure (bar)		1.2	1.2	10.0	3.0	2.0	2.0	1.2	1.2	10	1.2
Flow (MT/hr)	Vanillin	-	0.0	0.0	0.0	-	0.0	0.0	0.0	0.0	0.0
	Acetic anhydride	15.3	25.9	239.4	359.2	-	323.7	301.9	22.8	298.9	3.0
	Vanillin acetate	-	0.0	-	51.0	-	0.3	0.0	0.3	-	0.0
	Acetic acid	-	0.2	1.4	6.8	-	22.4	22.4	0.0	22.2	0.2
	Acetylferulic acid	-	0.3	-	0.0	-	61.8	0.0	61.8	-	0.0
	DMAP	0.6	17.8	0.0	18.4	-	18.4	3.8	14.6	0.0	3.8
	Acetone	-	0.0	0.0	0.0	0.0	5.0	5.0	0.0	5.0	0.0
	CO2	-	0.0	-	-	3.8	-	-	-	-	-
	Ferulic acid	-	0.0	-	0.0	-	0.0	0.0	0.0	-	0.0
	Total	15.9	44.7	240.8	435.4	3.8	431.6	333.1	99.5	326.1	7.0

Table 4-14. Stream Tables (21-40, See Figures 4-1 and 4-2)

		21	22	23	24	25	26	27	28	29	30
Temperature (°C)		211.5	130.9	145.0	472.7	30.0	30.0	120.0	120.0	120.0	120.0
Pressure (bar)		1.2	1.2	1.2	1.2	6.0	6.0	6.0	6.0	6.0	6.0
Flow (MT/hr)	Vanillin	-	-	-	0.0	-	-	-	0.0	-	-
	Acetic anhydride	59.5	10.4	49.1	0.0	-	-	-	0.0	-	-
	Vanillin acetate	-	-	-	0.3	-	-	-	0.3	-	-
	Acetic acid	20.8	19.3	1.5	-	-	-	-	-	-	-
	Acetylferulic acid	-	-	-	61.5	-	-	-	9.2	0.0	-
	DMAP	0.0	-	0.0	0.1	-	-	-	0.1	-	-
	Acetone	5.0	5.0	-	-	-	-	-	-	-	-
	Acetyldihydro-ferulic acid	-	-	-	-	-	-	-	52.6	0.0	-
	Isopropanol	-	-	-	-	43.3	-	0.0	38.1	5.2	0.0
	Hydrogen	-	-	-	-	-	700.0	605.5	0.0	0.2	70.0
	Total	85.3	34.7	50.6	61.9	43.3	700.0	605.5	100.3	5.4	70.0

		31	32	33	34	35	36	37	38	39	40
Temperature (°C)		120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	200.0
Pressure (bar)		6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	2.0
Flow (MT/hr)	Vanillin acetate	0.3	-	-	0.3	-	-	0.3	-	-	0.0
	Acetylferulic acid	1.4	-	-	0.2	-	-	0.0	-	0.0	0.0
	DMAP	0.1	-	-	0.1	-	-	0.1	-	-	0.0
	Acetyldihydro-ferulic acid	60.5	0.0	-	61.7	0.0	-	61.9	0.0	0.0	0.0
	Isopropanol	38.0	0.1	0.0	37.7	0.2	0.0	37.6	0.2	41.7	36.2
	Hydrogen	0.0	0.0	17.5	0.0	0.0	7.0	0.0	0.0	0.0	0.0
	Total	100.3	0.1	17.5	100.0	0.2	7.0	99.9	0.2	41.7	36.2

Table 4-15. Stream Tables (41-55, See Figures 4-2 and 4-3)

		41	42	43	44	45	46	47	48
Temperature (°C)		50.0	50.0	120.0	120.0	311.5	200.0	311.5	278.0
Pressure (bar)		6.0	6.0	6.0	6.0	2.0	2.0	2.0	0.2
Flow (MT/hr)	Acetic anhydride	-	-	-	-	-	-	-	-
	Vanillin acetate	-	-	-	-	-	0.3	0.3	0.3
	Acetic acid	-	-	-	-	-	-	-	3.5
	Acetylferulic acid	-	0.0	-	0.0	-	0.0	0.0	-
	DMAP	-	0.0	-	-	-	0.1	0.1	-
	Acetyldihydroferulic acid	-	0.0	-	0.0	0.0	61.9	61.9	0.5
	Isopropanol	0.0	36.2	0.2	41.7	1.0	1.4	0.4	0.1
	Hydrogen	0.0	0.0	0.2	0.0	-	0.0	0.0	0.0
	PHFA	-	-	-	-	-	-	-	-
	Total	0.0	36.2	0.4	41.7	1.0	63.7	62.7	4.4

		49	50	51	52	53	54	55
Temperature (°C)		278.0	178.7	111.0	141.6	75.3	123.6	30.0
Pressure (bar)		2.0	1.2	1.2	1.2	1.2	1.2	1.1
Flow (MT/hr)	Acetic anhydride	-	13.1	0.0	13.1	-	0.0	-
	Vanillin acetate	0.0	0.3	-	0.3	-	-	0.0
	Acetic acid	0.0	45.4	39.6	5.8	3.3	36.3	-
	Acetylferulic acid	0.0	-	-	-	-	-	0.0
	DMAP	0.1	-	-	-	-	-	0.1
	Acetone	-	5.0	5.0	0.0	5.0	0.0	-
	Acetyldihydroferulic acid	11.9	0.2	-	0.2	-	-	0.0
	Isopropanol	0.3	0.4	0.4	0.0	0.4	0.0	0.0
	Hydrogen	-	-	-	-	-	-	-
	PHFA	46.0	-	-	-	-	-	57.8
	Total	58.3	64.4	45.0	19.4	8.7	36.3	57.9

Table 4-16 Energy Balance Summary of Heat Exchangers and Fired Heaters

Equipment Name	Heat Duty (kW)	Equipment Name	Heat Duty (kW)	Equipment Name	Heat Duty (kW)
Section 1		Section 2		Section 3	
E-101	171	E-201	252	E-301	-32,000
E-102	7,420	E-202	2,030	E-302	20,600
E-103	-21,700	E-203	-6,700	E-303	-7,680
E-104	12,700	E-204	-2,210	E-304	7,800
E-105	-9,820	E-205	-331	H-301	3,360
E-106	5,950	E-206	-50		
E-107	-29,200	E-207	9,130		
E-108	5,196	E-208	-1,140		
E-109	-28,200	E-209	-11,100		
E-110	14,695	E-210	56		
E-111	-42,300	E-211	2,730		
E-112	765	E-212	-433		
E-113	-2,200	E-213	312		
E-114	6,983				
E-115	-36,900				
E-116	66,405				
E-117	-41,300				
E-118	31,707				
Net Energy Consumption (kW)	-59,628		-7,454		-7,920

Table 4-17 Energy Balance Summary of Pumps and Compressors

Equipment Name	Shaft Work (W)	Equipment Name	Shaft Work (W)	Equipment Name	Shaft Work (W)
Section 1		Section 2		Section 3	
P-101 A/B	1,600	P-201 A/B	540	P-301 A/B	903
P-102 A/B	2,130	P-202 A/B	1,420		
P-103 A/B	37,700	P-203 A/B	1,960		
P-104 A/B	2,080	P-204 A/B	1,420		
P-105 A/B	4,900	P-205 A/B	745		
P-106 A/B	910	P-206 A/B	1,410		
P-107 A/B	86,000	P-207 A/B	118		
		P-208 A/B	1,410		
		P-209 A/B	3		
		P-210 A/B	922		
		P-211 A/B	398		
		C-201	1,010		
		C-202	33		
Net Energy Consumption (W)	135,320		11,388		903

4.4 Process Economics

4.4.1 Capital Costs

Table 4-17 below contains the total module cost for each category of equipment. The price of the BUS-COMPEO 176 extruders was not readily available to students. Thus, the price for each extruder-pelletizer pair was estimated at $1,000,000 each.[27] The prices for all other equipment were calculated using CAPCOST and a CEPCI of 596.1.[28]

Table 4-17. Capital Cost Investment for PHFA Plant.

Equipment Category	Total Module Cost
Reactors	$ 35,940,440
Distillation Columns	$ 50,973,640
Heat Exchangers	$ 9,452,272
Fired Heaters	$ 43,907,800
Extruders + Pelletizers	$ 20,000,000
Pumps	$ 1,044,890
Compressors	$ 7,370,280
Vessels	$ 678,382
Storage Tanks	$ 1,880,684
Total Cost	$ 171,248,388

It is assumed that this facility will be a greenfield construction. Thus, the costs for site development, auxiliary buildings, and other facilities must be included. According to the Turton text, the grassroots cost may be approximated as 50% of the base bare module cost obtained vai CAPCOST.[26] Using this estimation, the grassroots auxiliary cost for the PHFA plant is $39,523,750. Combining this cost with the total module cost displayed in **Table 4-17** above gives the total plant capital investment – $210,772,138.

4.4.2 Operating Costs

For all operating cost calculations, it was assumed that an operating year contains 300 days or 7200 hours. As in section 4.4.1, CAPCOST was used to determine the costs for cooling water, steam, and electricity. Fuel costs for the fired heaters were calculated using the heat duty of the heater and assuming a 90% fuel efficiency. The price of natural gas fuel, obtained from CAPCOST, was $3.16 per GJ. The energy obtained from burning the waste streams in section 3 was estimated using an RGibbs reactor in Aspen and combusting the waste in the presence of excess oxygen. This energy was counted as a credit towards the total fuel energy requirement. A complete breakdown of utility costs and credits by plant section is available in *Appendix 10.2.1* **Table 10-1.** The total utility costs for the plant are displayed in **Table 4-18** below.

Table 4-18. Utility Costs

Utility	Cost (Per year)
Cooling Water	$2,011,891
Steam	$7,287,192
Electricity	$1,033,685
Fuel	$9,596,793
Total	$41,613,456

Operating costs of labor were calculated using the Alkhayat and Gerrard correlation for the number of operators required per shift based on the number of processing steps.[29] Based on recommended values in the Turton text, it was assumed that 4.5 operators would be hired for each operator needed in the plant at any time. A salary of $66,910 per year was used to calculate the operating cost of labor each year. Full details of the calculation can be seen in *Appendix 10.2.2*. A summary is provided in **Table 4-19** on the following page. This value accounts only for labor on the floor. The price of supervisory and support staff will be calculated using a separate correlation in a later section.

Table 4-19. Operating Cost of Labor

Labor Statistic	Value
# Operators per Shift	4.43
Total Operators Hired (Rounded to Next Whole #)	20
Operator Salary	$66,910/yr
Total Cost of Operating Labor	$1,338.200/yr

The costs of raw materials are displayed in **Table 4-20** and **Table 4-21**. The price of vanillin listed in the table is reflective of bulk petrochemical vanillin. Although the goal of the plant is to eventually use biomass-derived vanillin, the input-output economic analysis performed in the Design Basis Memorandum suggested that use of sustainably-sourced vanillin, priced at $8/lb ($17,600/MT) in the 2018 vanillin thesis, is not economically feasible.

The global vanillin market size was approximately 395 million USD in 2016 with 99% of these sales consisting of synthetic vanillin. With a throughput of 330,000 MT/yr of PHFA, the plant requires 144 million USD of vanillin annually, representing roughly 50% of the global vanillin market. Thus, there is significant potential for market strain and subsequent vanillin price increases if the plant were to be commissioned.

The price of acetic anhydride was taken from the prices seen in China, as this presented the lowest price and could present a potential location for the production facility. Prices of DMAP and IPA were also selected from bulk prices seen in China. The price of hydrogen is estimated from a pamphlet provided by Air Products. They estimate the commercial cost of delivered hydrogen to be $7000/MT. Since the hydrogen for the PHFA plant will be produced by an onsite generator controlled by a third-party, a 2x price premium is applied to the raw material price to account for additional fees to the owner of the generation station.

Table 4-20. Raw Material Costs for Liquid Feedstocks

Liquid Feed	Mass per Operating Year (MT/yr)	Price (USD/MT)	Annual Cost (USD/yr)
Vanillin	288,000	500[30]	$ 144,000,000
Acetic Anhydride	753,055	790[31]	$ 594,913,608
DMAP	4,398	200[32]	$ 879,552
IPA	3,118	950[33]	$ 2,961,720
H_2	3,744	14,000[34]	$ 52,416,000
Total	-	-	$ 795,170,880

Data on catalyst lifetime were not available in the literature. Thus, it was assumed that each catalyst had a lifetime of 1 operating year. Prices of catalysts were scaled up from the price for the largest quantity available to the public online. For the antimony trioxide catalyst which is only available in powdered form and must be pelletized for use in the pre-polymerization CSTRs, the price reflected in the table below is 3x the price of the raw powder. The total price of these catalysts is only 0.01% of the total raw materials cost per year. Thus, it is believed that each of the above approximations has a negligible effect on calculation of plant profitability.

Table 4-21. Raw Material Costs for Solid Catalysts

Solid Catalyst	Mass per Operating Year (kg/yr)	Price (USD/kg)	Annual Cost (USD/yr)
Na Zeolite	142	88[35]	$ 12,500
2.5 wt% Rh/SiO_2	13.4	4,600[36]	$ 61,700
Sb_2O_3	49.6	387[24]	$ 19,200
Total	-	-	$ 93,400

Additional operating costs can be estimated as a percentage of fixed capital investment and costs of operating labor, utilities, waste treatment, and raw materials. For ease of reading, these costs are reproduced in **Table 4-22** below. The price of waste treatment was assumed to be zero. The entirety of liquid waste produced in the PHFA plant is burned as fuel in plant fired heaters. In reality, solid waste would certainly be produced including spent catalysts and PHFA waste from the extrusion-palletization process. Since the cost waste production is not easily estimated, it is assumed to be negligible compared to the magnitude of other operating costs.

Table 4-22. Relevant Capital and Operating Costs for Total Cost of Manufacture Estimations

Category	Cost	
Total Module Cost	$	171,248,388
Operating Labor	$/yr	1,338,200
Utilities	$/yr	19,929,562
Waste Treatment	$/yr	0
Raw Materials	$/yr	795,264,280

Additional operating costs can be split into the following three categories: direct operating costs (**Table 4-23**), fixed operating costs (**Table 4-24**), and general manufacturing expenses (**Table 4-25**). Estimations for each line item in these categories is provided in the Turton text.[29] Using these correlations, the total cost of manufacturer for the PHFA plant is $1,050,411,118 per year. This cost includes depreciation, estimated using a straight-line depreciation model yielding a 5% cost per year for the 20-year plant lifetime. Detailed calculations are included in *Appendix 10.2.3.*

Table 4-23. Direct Operating Costs

Category	Cost
Raw Materials	$ 795,264,280
Waste Treatment	$ 0
Utilities	$ 19,929,562
Operating Labor	$ 1,338,200
Direct Supervisory & Clerical Labor	$ 240,876
Maintenance & Repair	$ 10,274,903
Operating Supplies	$ 1,541,235
Laboratory Charges	$ 200,730
Patents and Royalties	$ 31,371,865
Total	$ 860,161,651

Table 4-24. Fixed Operating Costs

Category	Cost
Depreciation	$ 8,562,419
Local Taxes & Insurance	$ 5,479,948
Plant Overhead Costs	$ 7,112,388
Total	$ 21,154,755

Table 4-25. General Manufacturing Expenses

Category	Cost
Administrative Costs	$ 1,778,097
Distribution & Selling Costs	$ 115,030,172
Research & Development	$ 52,286,442
Total	$ 169,094,711

4.4.3 Operating Profit

Table 4-26 below contains the production rate and prices of the PHFA plant saleable materials. An initial cost of $3000/MT was estimated for our PHFA product as this is approximately the price of PET. Based on conversations with Ron Unnerstall, the price of industrial grade acetic acid (99.99% purity) typically ranges from $200 to $500 per MT. A conservative value of $350/MT was used for initial revenue calculations.

Table 4-26. Product Prices and Gross Revenues

Product	Mass per Operating Year (MT/yr)	Price (USD/MT)	Annual Revenue (USD/yr)
PHFA	330,480	3,000[18]	$ 991,440,000
Acetic Acid	261,360	350	$ 91,476,000
Total	-	-	$ 1,082,916,000

To calculate the after-tax cash flow of the PHFA plant, a federal tax rate of 35% was assumed. **Table 4-27** below contains a summary of the annual net profit and cash flow.

Table 4-27. Product Prices and Gross Revenues

Product	Annual Cost/Profit
Gross Revenue	$ 1,082,916,000
Cost of Manufacture	$ 1,050,411,118
Taxable Profit	$ 32,504,881
Income Tax	$ 11,376,708
Net Profit	$ 21,128,173
Depreciation	$ 8,562,419
After-Tax Cash Flow	**$ 29,690,592**

4.4.4 Return on Investment

It was assumed that the initial capital investment for the PHFA plant would occur in two phases. The first year of construction, denoted as Year -1, one-third of the total capital investment would be spent. The next year, denoted as Year 0, the remaining two-thirds of the total capital investment would be spent and the plant is completed. A discrete cash flow diagram is displayed in **Figure 4-4** below for an assumed plant life of 20 years.

Assuming an interest rate of 9%, the net present value of each expenditure and profit may be calculated. The cumulative cash flow, discounted to Year 0, is displayed in **Figure 4-5** on the following page.

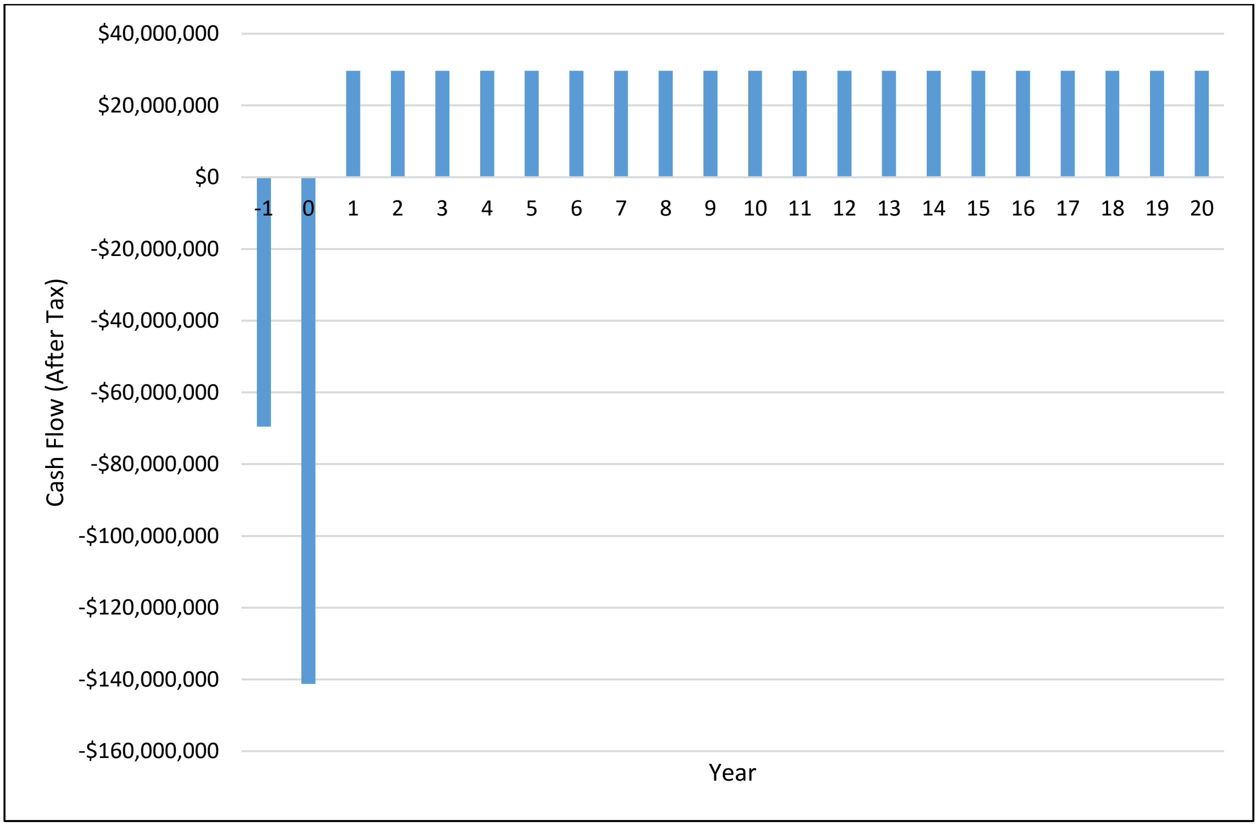


Figure 4-4. Discrete cash flow diagram for PHFA plant over 20-year lifetime.

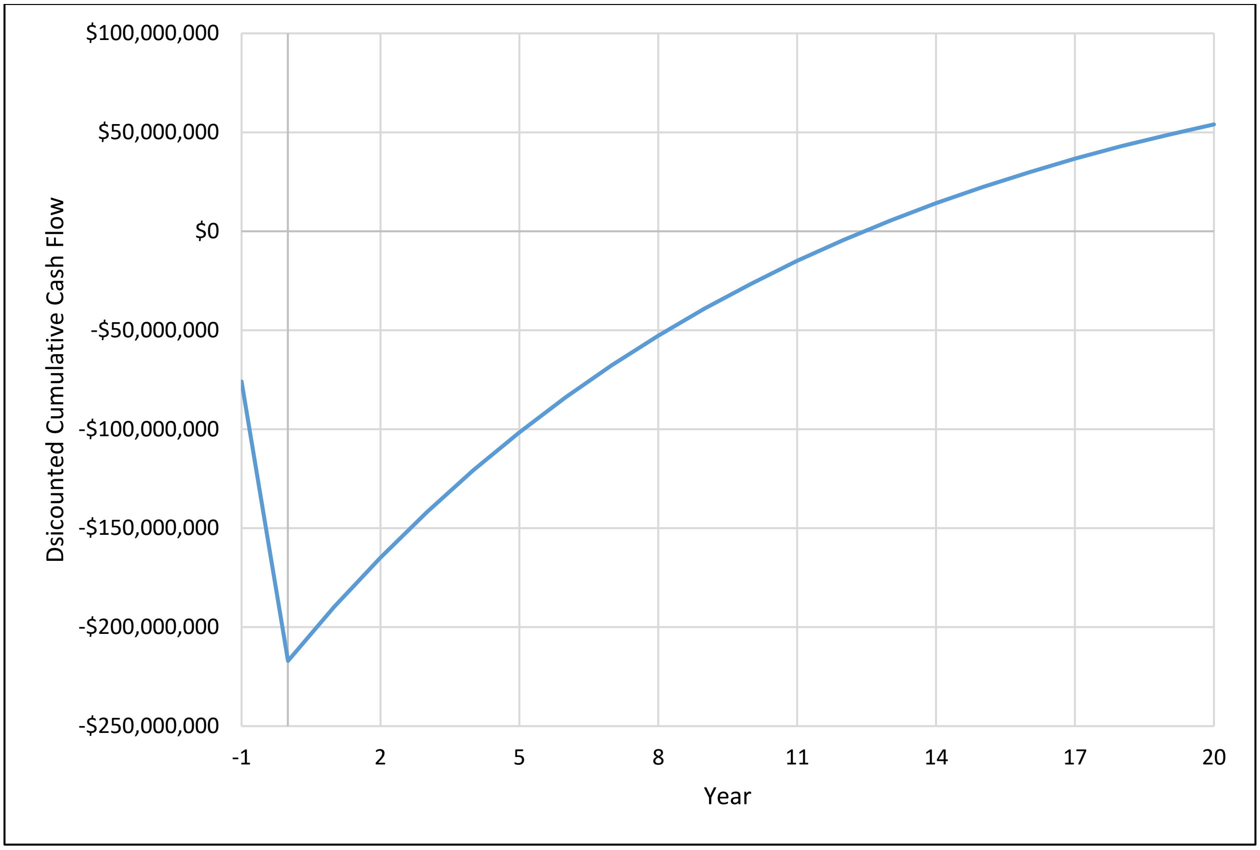


Figure 4-5. Cumulative cash flow diagram for PHFA plant. Cash flows are discounted to Year 0 using an interest rate of 9%.

Using the conservative product prices displayed in **Table 4-20** above for PHFA and acetic acid, construction of the PHFA plant as designed yields an internal rate of return (IRR) of 12%. Holding all else constant, the IRR is greatly influenced by the market price of PHFA. Likewise, increasing the price of acetic acid within the range recommended by Ron Unnerstall increases the plant IRR.

Table 4-28 on the following page displays a range of product price scenarios and their corresponding IRR. The base case, with PHFA priced at $3,000/MT and acetic acid priced at $350/MT provides an IRR of 12% as mentioned above. In the worst-case scenario where the price of acetic acid falls to $200/MT, the construction of the plant is not profitable. Adding a slight price premium to the PHFA, justified based on its biodegradability, IRR improves drastically. Assuming a moderate acetic acid price of $350/MT, a PHFA price of $3,250 yields an IRR of 35%. In the best-case scenario, where acetic acid sells at its maximum price of $500 and a 17% price premium is applied to PHFA for a market price of $3,500/MT, the IRR rises to 64%.

Table 4-28. Investment Scenarios for PHFA Plant Based on Product Market Price

Internal Rate Of Return		Price Acetic Acid (USD/MT)		
		$200	$300	$500
Price PHFA (USD/MT)	$3,000	-7%	12%	24%
	$3,250	25%	35%	45%
	$3,500	46%	55%	64%

As noted in the raw materials section above, petrochemical vanillin is used to ensure profitable production. However, the aim construction of the PHFA plant is to provide the framework to transition to sustainably-derived vanillin when the market price permits it. The maximum price of vanillin that will allow the PHFA plant to break even is quantified as the price at which the plant IRR is 0%.

Table 4-29 on the following page displays a range of pricing scenarios for the saleable products and the corresponding maximum vanillin price. The maximum potential price of PHFA is $6,000/MT, corresponding to a 100% price increase from PET. Such a premium would be justifiable by both the biodegradability of the plastic and the sustainably-sourced pre-monomer.

Table 4-29. Investment Scenarios for Sustainably-Sourced Vanillin

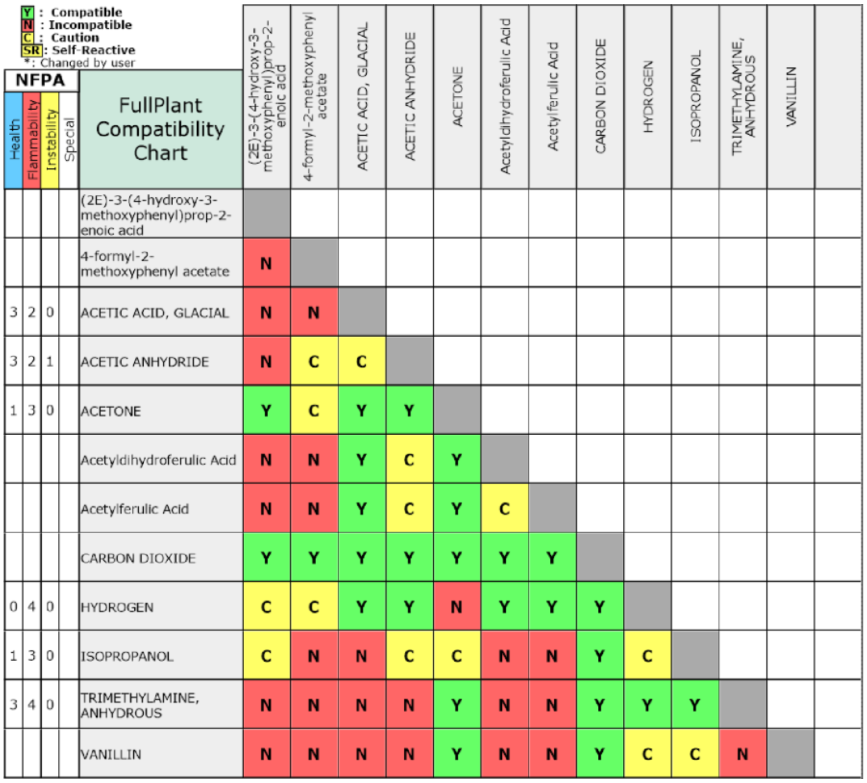
Price Acetic Acid (USD/MT)	Price PHFA (USD/MT)	Break-Even Price of Vanillin (USD/MT)
$350	$3,000	$585
$350	$4,000	$1,515
$350	$5,000	$2,445
$350	$6,000	$3,375
$500	$6,000	$3,485

The price of petrochemical vanillin is $500/MT. Lignin-derived vanillin, on the other hand, costs $17,600/MT. At the base-case economic conditions, the maximum price of vanillin to break even is $585/MT. Even under the best-possible market conditions where acetic acid sells for $500/MT and PHFA sells at a premium of $6,000/MT, the maximum allowable price of vanillin is only $3,485/MT – approximately 1/5 the price of sustainable vanillin.

5. SAFETY AND ENVIRONMENTAL CONSIDERATIONS

5.1 Materials Compatibility

A chemicals reactivity worksheet (CRW) was prepared using a tool (CRW4) provided by AIChE. Custom chemicals were added for the intermediates, pre-monomer, and monomer using their functional groups. This may show some hazards that may not occur due to the nature of the molecular structure. The chart shown below in **Figure 5-1** shows which chemicals are incompatible with each other. A few notable aspects are the incompatibility between isopropanol and acetic acid. Some isopropanol will remain in our recovery process, and will react through heating with acetic acid to produce isopropyl acetate. This will present an impurity in our final products, but the amount will be small and is neglected. The other reactivity hazards are intended or likely will not occur at the conditions we are operating.



Y : Compatible
N : Incompatible
C : Caution
SR : Self-Reactive
*: Changed by user

NFPA																	
Health	Flammability	Instability	Special	FullPlant Compatibility Chart	(2E)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid	4-formyl-2-methoxyphenyl acetate	ACETIC ACID, GLACIAL	ACETIC ANHYDRIDE	ACETONE	Acetyldihydroferulic Acid	Acetylferulic Acid	CARBON DIOXIDE	HYDROGEN	ISOPROPANOL	TRIMETHYLAMINE, ANHYDROUS	VANILLIN	
				(2E)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid													
				4-formyl-2-methoxyphenyl acetate	N												
3	2	0		ACETIC ACID, GLACIAL	N	N											
3	2	1		ACETIC ANHYDRIDE	N	C	C										
1	3	0		ACETONE	Y	C	Y	Y									
				Acetyldihydroferulic Acid	N	N	Y	C	Y								
				Acetylferulic Acid	N	N	Y	C	Y	C							
				CARBON DIOXIDE	Y	Y	Y	Y	Y	Y	Y						
0	4	0		HYDROGEN	C	C	Y	Y	N	Y	Y	Y					
1	3	0		ISOPROPANOL	C	N	N	C	C	N	N	Y	C				
3	4	0		TRIMETHYLAMINE, ANHYDROUS	N	N	N	N	Y	N	N	Y	Y	Y			
				VANILLIN	N	N	N	N	Y	N	N	Y	C	C	N		

Figure 5-1. Chemical Reactivity Worksheet including all chemicals present on site. N represents an incompatible mixture, C represents a mixture that may be hazardous, and Y represents a mixture that will not present any reactivity hazards.

5.2 Maximum Credible Events

A maximum credible event (MCE) is the worse event that could realistically occur, and therefore requires extensive safeguards. Modeling of these events determines how facilities such as the one planned above should be sited and what hazards will be present during operation. These models can also help determine locating various sections of the process or operator buildings during plant construction. Below in section 5.3, the modeling software ALOHA will be used to determine the potential impacts of MCE release scenarios.

5.3 ALOHA modeling for Loss of Primary Containment (LOPC) Incidents

Areal Locations of Hazardous Atmospheres, or ALOHA, is a modeling software developed by CAMEO and supplied by the US EPA. This allows for modeling of various types of LOPC incidents in chemical processes. For this plant, releases of Acetic Anhydride, Acetic Acid, and Isopropanol are modeled assuming a release from the largest piping section that the materials will travel through, assuming a 2 m/s liquid velocity and 30°C. This was then scaled to the nearest standard pipe bore. For Process Hazard Analyses (PHAs), a realistic process pipe rupture will be full bore for diameters less than 2 in, 3.14 in^2 for diameters from 2-4 in, and 20% of pipe area for bores greater than 4 in. A liquid source model, shown in Equation 5-1 can be used to determine the release rate. **Table 5-1** below summarizes the releases.

Table 5-1. Release calculation pathway for chemicals of interest.

Material	Volumetric Flow (m^3/s)	Pipe Bore (in)	Rupture Assessment	Rupture Area (m^2)	Release Flow (kg/s)
Acetic Anhydride	0.0269	6	20% of pipe area	0.00365	119.89
Acetic Acid	0.0097	4	2-in area	0.00203	65.34
Isopropanol	0.00016	0.5	Full bore	0.000127	3.53

$$Q_m = A * C_0\sqrt{2 * \rho * g_c * P_g} \qquad \text{(Equation 5-1)}$$

Equation 5-1 is the source model for liquid flow through a hole. The discharge coefficient, C_0, was chosen to be 1 to be conservative. g_c, the gravitational constant, is equal to 1 when using SI units, and P_g is the gauge pressure, assumed to be 500000 Pa. This yields the mass flow rate from the orifice in units of mass/time.

Using this data, a release scenario can be modeled in the ALOHA software given atmospheric conditions. In a worst-case scenario, the atmosphere will be classified as very stable, making vapor clouds dissipate slowly. For a conservative estimate, the atmospheric conditions are chosen to be 3 mph winds, partly cloudy, night-time, with 25% humidity at 30°C. This yields a Class E atmosphere, which is quite stable, and the release was estimated to last for 30 minutes.

Figure 5-2 below displays the threat zones based on the ERPG 1 hour limits for exposure to vapor Acetic Anhydride. Evacuation is necessary for all regions affected by greater concentrations than the ERPG-2 value, in this case 15 ppm. This area is nearly 15 mi^2, and the consequences of a release of this magnitude are extremely significant. With the potential for this, the plant should be sited far from any major population and local emergency response should be well educated on this hazard.

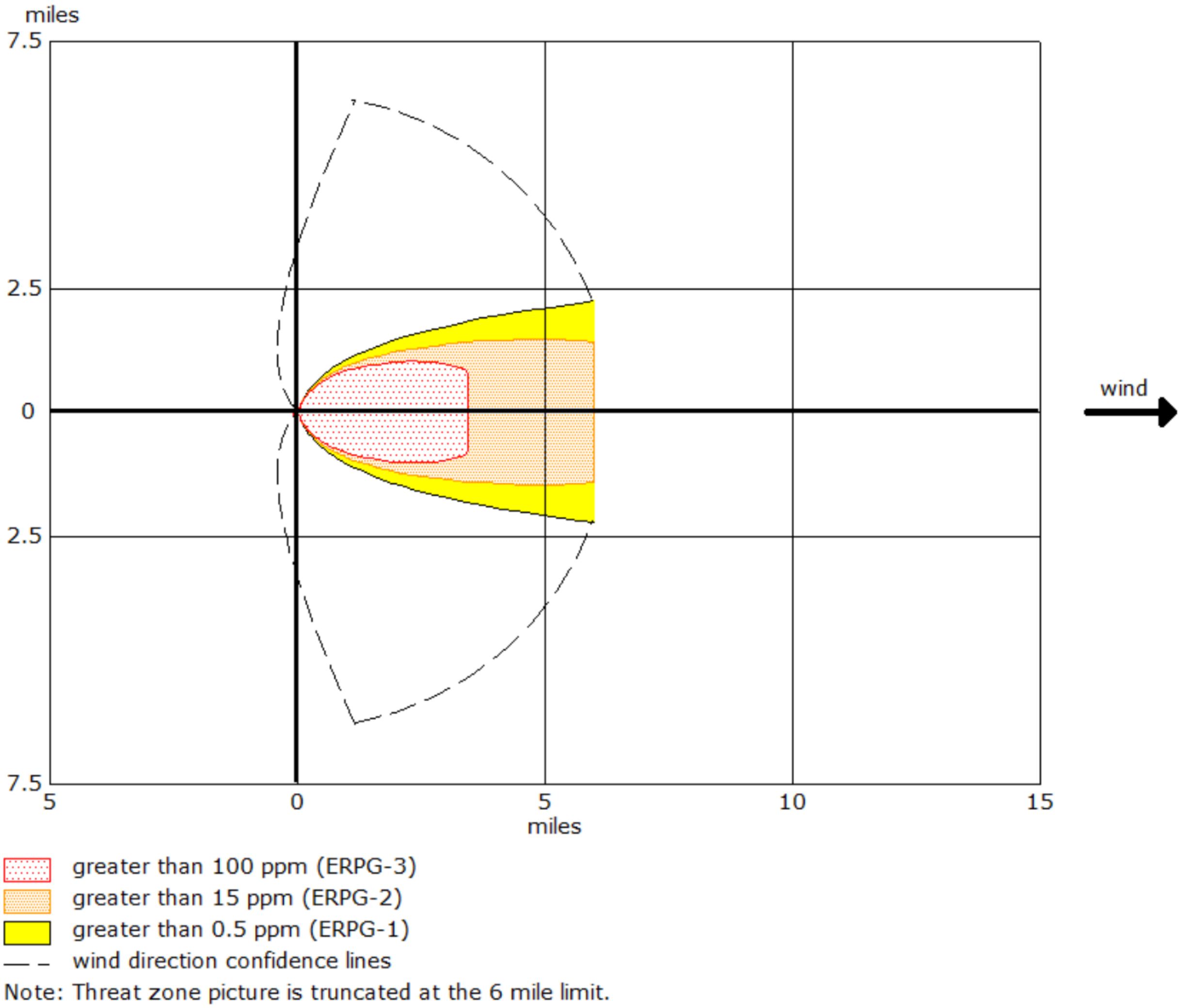


Figure 5-2. Toxic threat zone produced using ALOHA modeling for the Acetic Anhydride release. The software does not estimate threat zones further than 6 miles away due to poor reliability over large distances. ALOHA does not model the reactivity of Acetic Anhydride and assumes that the chemical is inert. If the release were to interact with water, it may change the behavior and the toxic threat zone.

While one may think that more concern should be placed on an Acetic Anhydride release due to its toxicity, similar concern should be placed on a similar release scenario from the Acetic Acid product piping. Below in **Figure 5-3** is the toxic threat zone at the same conditions in the Acetic Anhydride release. A smaller area would need to be evacuated in this scenario, only about 8 mi^2.

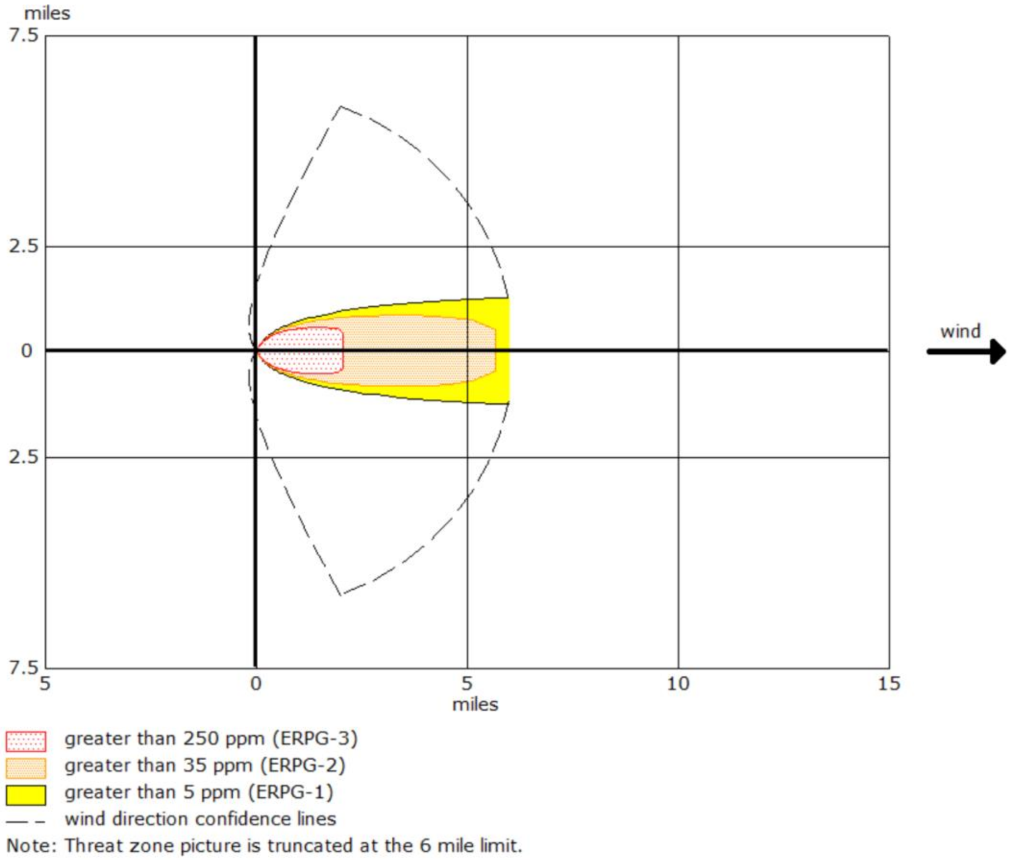


Figure 5-3. Toxic threat zone produced using ALOHA modeling for the Acetic Acid release.

For a release of Isopropanol, as the release is significantly smaller, the toxic threat likely remains within the plant itself. The toxic threat zone is shown below in **Figure 5-4.**

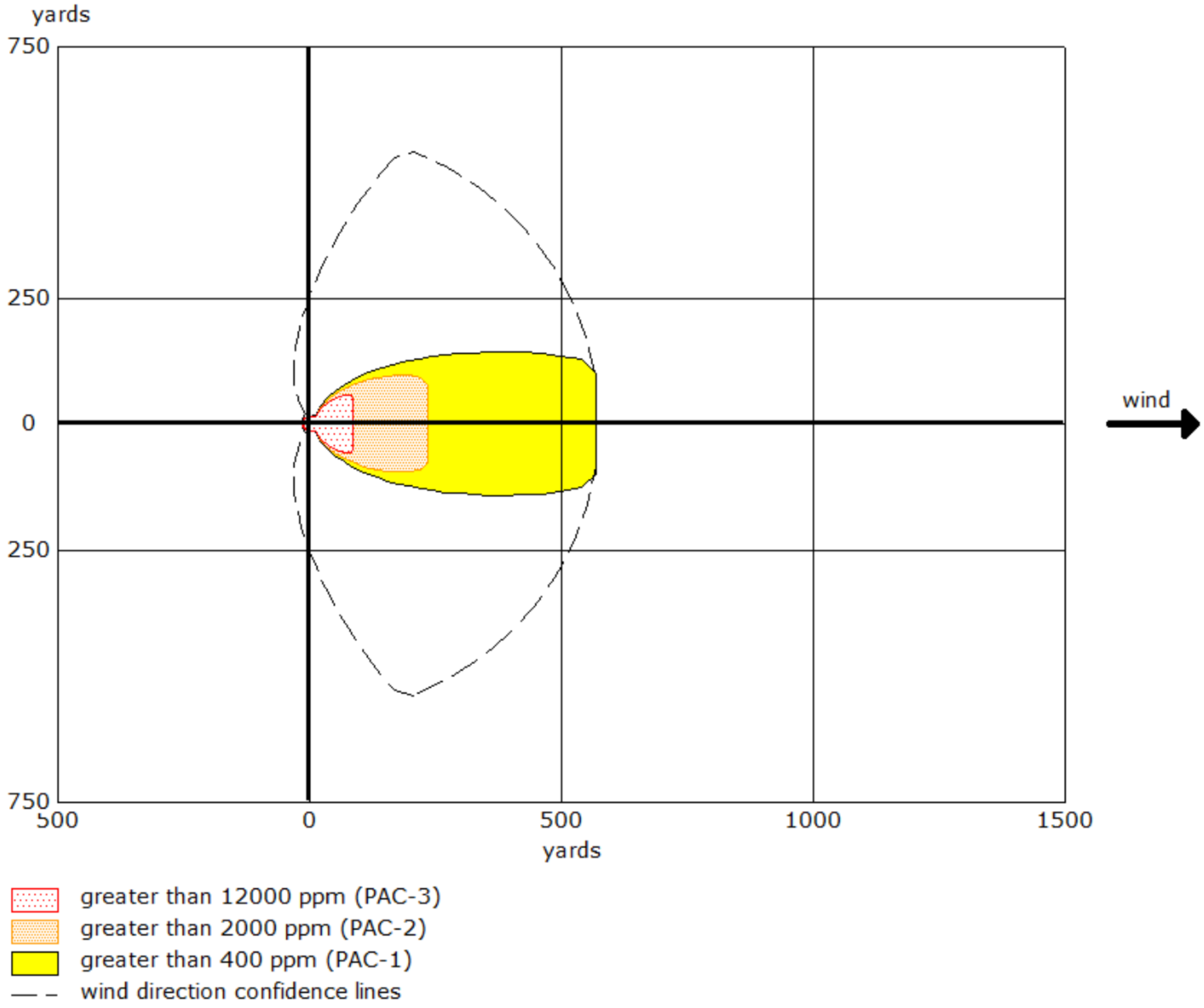


Figure 5-4. Toxic threat zone for the release scenario described above for Isopropanol.

In this release, a potentially more important scenario would be a vapor cloud explosion (VCE), shown in **Figure 5-5** below. Notably, there will be no building destruction due to this explosion, but any workers in close vicinity to the process may be seriously injured, and no occupied buildings should be nearby.

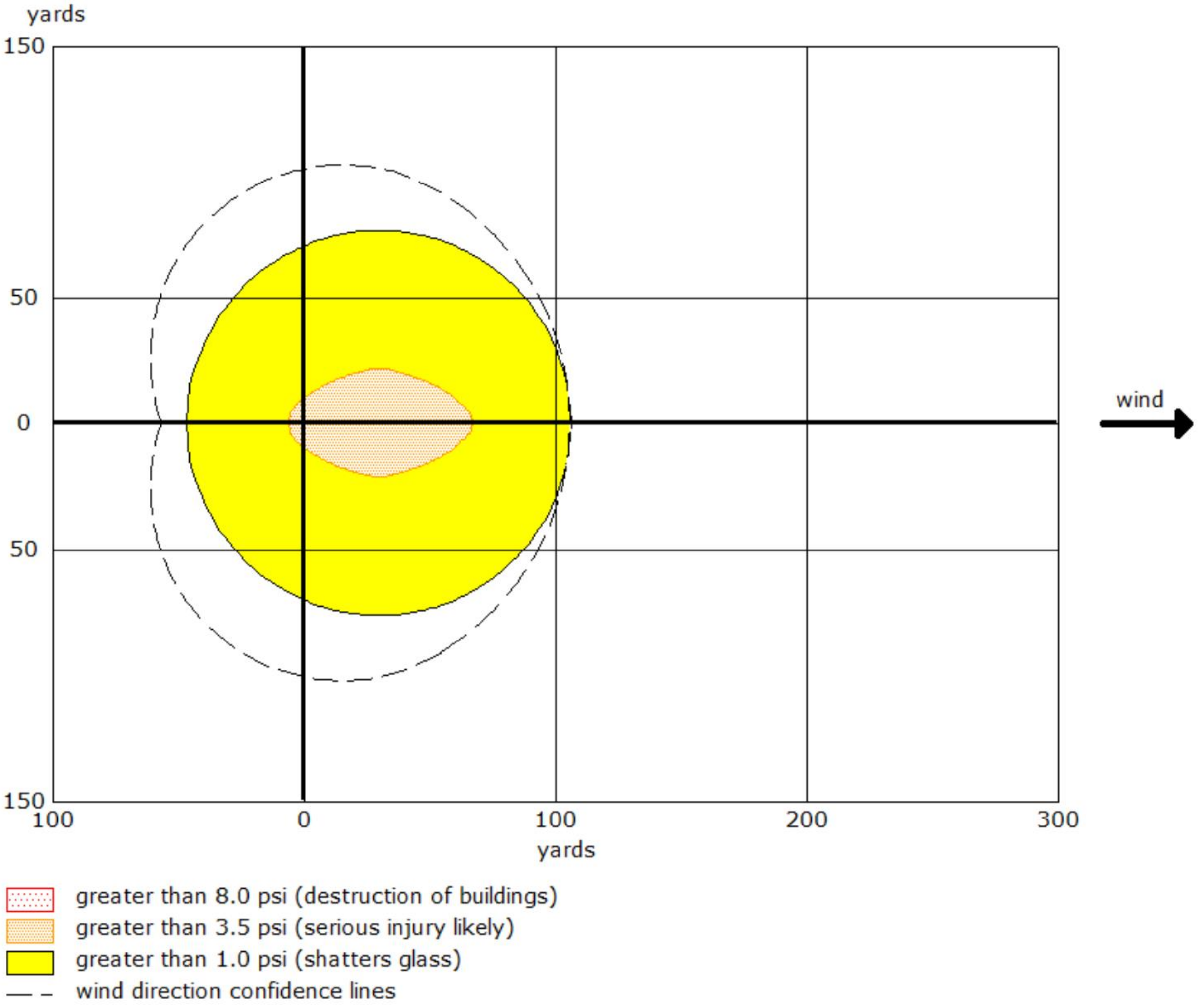


Figure 5-5. Overpressure plot for a VCE in the Isopropanol release scenario described above.

5.4 CO_2 Production

The two sources of CO_2 in the proposed process are the production of hydrogen feed to the hydrogenation reactors and the vent from R-102, the Perkin PFR. With perfect reforming, 2860 kg/hr of CO_2 will be produced when producing the necessary 520 kg/hr of hydrogen, and 3772 kg/hr will vent from the Perkin PFR R-102. This presents a concern, as the major motivation for this product was the potential for it to be environmentally sustainable. In the future of this project, a carbon capture unit may be designed and incorporated to prevent this pollution.

5.5 Waste Streams

Residual waste streams resulting from purification of our side product, Acetic Acid, will be disposed of through combustion. Recovery of these materials for recycle is not economically feasible and will not be impactful with our production scheme. However, because the waste streams are entirely organic, they may be used as fuel in the fired heaters across the plant.

5.6 Toxicity of Catalysts

The Sb_2O_3 catalyst used in the pre-polymerization of ADHF to produce low-viscosity PHFA is classified as a probable human carcinogen.[37] Although the catalyst will be processed into pellets for use in the polymerization CSTR reactors, it is likely that small quantities of Sb_2O_3 will move through the filter screen with the polymer melt due to abrasion of the pellets. Thus, this catalyst is not suitable for applications in which the final product will come in contact with skin or ingestible items such as textiles or bottles. Thus, it will be necessary to perform active work in developing a more biosafe catalyst.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Financial Considerations

Based on the investment scenarios presented in Section 4.4.4 above, it is recommended that plans to construct the PHFA plant move forward. Admittedly, the worst-case scenario for product market prices yields a negative IRR. However, small changes in the sale price for one of the products enables the facility to break-even. A $30/MT price increase for PHFA or a $35/MT increase for acetic acid, corresponding to 1% or 17.5% increments respectively, yields an IRR of 0%. The international chemical economy will largely dictate the acetic acid price. The same is true for the baseline PHFA price since it is based on the market price of PET. However, leveraging the biodegradability of PHFA should enable the capture of slightly more sales revenue should need be. In fact, imposing an 8% increase in PHFA price based on its sustainability, the minimum IRR for the PHFA plant is 25%. With a slightly steeper price adjustment of 16%, the minimum IRR is 46%. Given these market scenarios, we are confident that the PHFA plant can remain profitable amidst market uncertainty.

There are some financial risks which are not captured by the IRR measure. The most significant identifiable risk is that of the vanillin market price. As demonstrated in the investment scenario in **Table 4-29** , the maximum allowable vanillin price for the base product price conditions is $585/MT which is only $85/MT greater than the currently identified market price of vanillin. A small price increase in vanillin could be combatted with a slight sustainability premium on PHFA. Large increases may not be financially sustainable. However, such an invent would likely coincide with increased work on the development of more efficient sustainably-derived vanillin at which time the total available market for vanillin will increase, allowing prices of raw materials to fall and product prices to increase based the sustainability factor.

6.2 Recommendations for Future Work

Other financial uncertainties are captured in the economic analysis in the form of insurance payments and contingencies for capital costs. The largest remaining risk to the success of the PHFA plant comes in the form of scale-up issues. All of the kinetic and thermodynamic data from which the unit operations were designed were estimated using either lab-scale reactions or estimated properties. As such, it is our recommendation that serious work be performed to obtain actual properties of each component in the system. Of specific importance are the VLE properties of all monomer intermediates which are involved in difficult and costly separations. Additionally, kinetic data for each monomer-functionalization and polymerization reaction should be obtained for the PHFA process to ensure the safe and efficient operation of all reactors. Once this data is obtained, it would be prudent to construct a pilot plant before the full-capacity plant. Construction of the pilot plant will illuminate key shortcomings in the scale-up of laboratory data and will enable the fine-tuning of operating conditions such as those of the finishing extruders.

7. ACKNOWLEDGMENTS

A special thank you to Professor Rachel Letteri for lending her expertise in polymer chemistry during the design of the polymerization stage of the PHFA plant. Her guidance and mentorship were invaluable.

8. TABLES OF NOMENCLATURE

Table 8-1. Regularly Used Acronyms

Acronym	Meaning
ARB	Polycondensation of A with B
ADHF	Acetyldihydroferulic Acid
ALOHA	Areal Locations of Hazardous Atmospheres
BHET	Bis-hydroxyethyl terephthalate
CEPCI	Chemical Engineering Plant Cost Index
CRW	Chemicals Reactivity Worksheet
CSTR	Continuous Stirred Tank Reactor
DMAP	4-dimethylaminopyridine
EG	Ethylene Glycol
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guidelines
PET	Polyethylene Terephthalate
PHFA	Poly(dihydroferulic acid)
HX	Heat Exchanger
IPA	Isopropanol
IRR	Internal Rate of Return
LOPC	Loss of Primary Containment
MCE	Maximum Credible Event
MOC	Materials of Construction
MT	Metric Ton
PFR	Plug Flow Reactor
PHA	Process Hazard Analysis
TPA	Terephthalic Acid
USD	United States Dollar ($)
VCE	Vapor Cloud Explosion

Table 8-2. Mathematical Nomenclature

Term	Meaning
A	Pipe Cross Sectional Area
A_r	Rupture Area
C_0	Discharge Coefficient
C_n	Molar Concentration in CSTR
C_n^0	Molar Concentration of CSTR Feed
D	Pipe Diameter
E	Activation Energy
f_n	Fractional Conversion
g_c	Gravitational Constant
k	Rate Constant
k_0	Arrhenius Rate Constant
K	Polymerization Equilibrium Constant
m	Mass Flow Rate
M_n	Number Average Molecular Weight
ρ	Density
ρ_m	Molar Density
p	Extent of Polycondensation Reaction
P_g	Gauge Pressure in Piping
Q_m	Mass Flow Rate Through an Orifice
r	Molar Ratio of ‘A’ to ‘B’ Functional Groups in a Polymerization
r_{CSTR}	Reaction Rate
R	Gas Constant
τ	Space Time
T	Temperature
ν_n	Stoichiometric Coefficient for component n
v	Volumetric Flow Rate

V	Volume
$\bar{x}_n$	Number Average Degree of Polymerization
$\overline{x}_n^{ARB}$	Number Average Degree of Polymerization for an ARB polycondensation

9. REFERENCES

(1) Oakes, K. The Search for a Cleaner, Greener Plastic. *The Observer*. July 7, 2019.

(2) Lerner, S. Waste Only: How the Plastics Industry Is Fighting to Keep Polluting the World. *The Intercept*. July 20, 2019.

(3) Buranyi, S. The Plastic Backlash: What's behind Our Sudden Rage – and Will It Make a Difference? *The Guardian*. November 13, 2018.

(4) US Department of Commerce, N. O. and A. A. NOAA's National Ocean Service https://oceanservice.noaa.gov/hazards/marinedebris/plastics-in-the-ocean.html (accessed Sep 26, 2019).

(5) Kjeldsen, A.; Price, M.; Lilley, C.; Guzniczak, E.; Archer, I. *A Review of Standards for Biodegradable Plastics*; Industrial Biotechnology Innovation Centre, 2018; p 33.

(6) Azoulay, D.; Villa, P.; Arellano, Y.; Gordon, M.; Moon, D.; Miller, K.; Thompson, K. *Plastic & Health: The Hidden Costs of a Plastic Planet*; Kistler, A., Series Ed.; Center for International Environmental Law, 2019.

(7) United Nations Environment Programme. *Single-Use Plastics, a Roadmap for Sustainability.*; 2018.

(8) Nicastro, K. H.; Kloxin, C. J.; Epps, T. H. Potential Lignin-Derived Alternatives to Bisphenol A in Diamine-Hardened Epoxy Resins. *ACS Sustain. Chem. Eng.* **2018**, *6* (11), 14812–14819. https://doi.org/10.1021/acssuschemeng.8b03340.

(9) Ganewatta, M. S.; Lokupitiya, H. N.; Tang, C. Lignin Biopolymers in the Age of Controlled Polymerization. *Polymers* **2019**, *11* (7). https://doi.org/10.3390/polym11071176.

(10) Mialon, L.; Pemba, A. G.; Miller, S. A. Biorenewable Polyethylene Terephthalate Mimics Derived from Lignin and Acetic Acid. *Green Chem.* **2010**, *12* (10), 1704–1706. https://doi.org/10.1039/C0GC00150C.

(11) Mialon, L.; Miller, S. A. United States Patent: 9080011 - Poly(Dihydroferulic Acid) a Biorenewable Polyethylene Terephthalate Mimic Derived from Lignin and Acetic Acid and Copolymers Thereof. 9080011, July 14, 2015.

(12) Florida Institute funds US Bioplastics https://www.florida-institute.com/news/florida-institute-funds-us-bioplastics (accessed Oct 20, 2019).

(13) Wayback Machine https://web.archive.org/web/20140315000000*/usbioplastics.com (accessed Oct 20, 2019).

(14) European Chemicals Agency. Guidance for Monomers. EHCA 2012.

(15) Brownhill J.; Ledoux, J. A.; Lee, Y.; Kammauff, W.; Ryberg C. S. Design of the Production of Vanillin from Kraft Black Liquor, University of Virginia, Charlottesville, VA, 2018.

(16) Richardson, D. N. PET Manufacturing: Revolution by Evolution. **2008**, 19.

(17) Brown, T. Alpek, Indorama, Far Eastern consortium to acquire M&G Texas PTA-PET plant for $1.12bn https://www.icis.com/explore/resources/news/2018/03/21/10204733/alpek-indorama-far-eastern-consortium-to-acquire-m-g-texas-pta-pet-plant-for-1-12bn (accessed Dec 11, 2019).

(18) Polyethylene Terephthalate Production, Price and Market https://www.plasticsinsight.com/resin-intelligence/resin-prices/polyethylene-terephthalate/ (accessed Nov 20, 2019).

(19) Laroque, D. A.; Maria JA Silva, R. A. L.; Pereira, G. N. Synthesis of Eugenyl Acetate in Solvent-Free Acetylation: Process Optimization and Kinetic Evaluation. *J. Chem. Eng. Process Technol.* **2015**, *06* (04). https://doi.org/10.4172/2157-7048.1000247.
(20) Kasprzyk, H.; Kinastowski, S. Kinetic Investigations on the Perkin Reaction Catalyzed by Tertiary Amines. 10.
(21) Begley, L. C.; Kakanskas, K. J.; Monaghan, A.; Jackson, S. D. Effect of Molecular Structure on the Hydrogenation and Isomerisation of Propenylbenzene Isomers. *Catal. Sci. Technol.* **2012**, *2* (6), 1287–1291. https://doi.org/10.1039/C2CY20105D.
(22) Rieckmann, T.; Völker, S. Poly(Ethylene Terephthalate) Polymerization – Mechanism, Catalysis, Kinetics, Mass Transfer and Reactor Design. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*; John Wiley & Sons, Ltd, 2004; pp 29–115. https://doi.org/10.1002/0470090685.ch2.
(23) Lin, C.-C.; Baliga, S. A Study on the Polycondensation of Bis-hydroxyethyl Terephthalate. *J. Appl. Polym. Sci.* **1986**, *31* (8), 2483–2489. https://doi.org/10.1002/app.1986.070310809.
(24) Antimony(III) oxide 230898 https://www.sigmaaldrich.com/catalog/product/aldrich/230898 (accessed Mar 23, 2020).
(25) BUSS. Compeo: The New Compounder Generation. Increadibly Different. BUSSCorp.
(26) Online, S. B. Chapter 7 Estimation of Capital Costs - Analysis, Synthesis, and Design of Chemical Processes, Fifth Edition https://learning.oreilly.com/library/view/analysis-synthesis-and/9780134177502/ch08.xhtml (accessed Apr 5, 2020).
(27) Twin Screw Extruder Granulator Waste Plastic Recycling Pelletizer Price Of Plastic Extrusion Machine - Buy Waste Plastic Recycling Pelletizer,Price Of Plastic Extrusion Machine,Twin Screw Extruder Granulator Product on Alibaba.com https://www.alibaba.com/product-detail/Twin-Screw-Extruder-Granulator-Waste-Plastic_62307715817.html?spm=a2700.galleryofferlist.0.0.299428daAe5WHk (accessed Mar 31, 2020).
(28) Anonymous. Economic Indicators. *Chem. Eng. N. Y.* **2020**, *127* (2), 56.
(29) Online, S. B. Chapter 8 Estimation of Manufacturing Costs - Analysis, Synthesis, and Design of Chemical Processes, Fifth Edition https://learning.oreilly.com/library/view/analysis-synthesis-and/9780134177502/ch08.xhtml (accessed Apr 5, 2020).
(30) Natural Vanillin Price Bulk Powder Vanillin - Buy Vanillin Food Additives,Cas 121-33-5,Food Grade Product on Alibaba.com https://www.alibaba.com/product-detail/Natural-Vanillin-Price-Bulk-Powder-Vanillin_62064545312.html?spm=a2700.7724857.normalList.204.6a437b75fTCepK (accessed Nov 20, 2019).
(31) Hot Sale Glacial Acetic Acid Glacial Acetic Acid Price Anhydride Price - Buy Acetic,Acetic Anhydride Price,Glacial Acetic Acid Price Product on Alibaba.com //www.alibaba.com/product-detail/Hot-sale-glacial-acetic-acid-glacial_60408188343.html (accessed Nov 20, 2019).
(32) 4-dimethylaminopyridine Cas 1122-58-3 With Purity 99% - Buy 4-dimethylaminopyridine,Cas 1122-58-3,1122-58-3 Product on Alibaba.com //www.alibaba.com/product-detail/4-Dimethylaminopyridine-CAS-1122-58-3_60715250521.html (accessed Mar 31, 2020).

(33) Purity 99.9% Isopropyl Alcohol /ipa - Buy Isopropyl Alcohol 99%,Isopropyl Alcohol,Ipa Product on Alibaba.com //www.alibaba.com/product-detail/Purity-99-9-Isopropyl-alcohol-IPA_62501227701.html (accessed Mar 31, 2020).
(34) Bonner, B.; Products, A. Current Hydrogen Cost. 20.
(35) Molecular sieves, 4 Å 334294 https://www.sigmaaldrich.com/catalog/product/sigald/334294 (accessed Mar 31, 2020).
(36) 0066-SIRhA01 https://shop.riogeninc.com/product.sc?productId=6208&categoryId=3 (accessed Mar 31, 2020).
(37) PubChem. Senarmontite https://pubchem.ncbi.nlm.nih.gov/compound/14794 (accessed Mar 23, 2020).

10. APPENDIX

10.1 Sample Calculations

While many calculations were performed using the Aspen software to simulate our systems, some calculations were completed by hand. Throughout the rest of section 10.1, the relevant equations and a sample calculation using those equations is supplied.

10.1.1 CSTR Material Balances

For a given CSTR, the material balance can be organized using Accumulation = input – output + generated. This is shown below assuming no accumulation of material within the reactor.

$$0 = vC_n^0 - vC_n + \nu_n r_{CSTR} V \qquad \text{(Equation 10-1)}$$

Assuming a first order rate expression as well as an expression for space time in the reactors leads to the final material balance equation 10-4

$$r_{CSTR} = kC_n = k_0 e^{-\frac{E}{RT}} C_n \qquad \text{(Equation 10-2)}$$

$$\tau = \frac{v}{V} \qquad \text{(Equation 10-3)}$$

$$0 = C_n^0 - C_n - \tau k_0 e^{-\frac{E}{RT}} C_n \qquad \text{(Equation 10-4)}$$

For a given reaction if a specific conversion is desired (alternatively, a specific concentration in the reactor is desired) then the space time can be calculated. From this, a given reactor volume can be calculated in order to achieve a volumetric throughput.

The CSTRs used here were either heat neutral, like the pre polymerization reactors R-301 A/B/C/D, or were kept isothermal through heat removal from a pump around heat exchanger like the hydrogenator reactors R-201-204. Although the hydrogenation reaction produces significant heat, the heat of reaction was used as the required duty for the heat exchangers in order to keep the reactor isothermal.

A sample calculation will be performed for the first hydrogenation reactor, R-201. Given the conversion of 0.872, with the feed being a mixture of 50/50 isopropanol by volume, the concentration into and out of the reactor in the reactor can be calculated.

$$\rho_m = 6.5\frac{mol}{L}, 6.5\frac{mol}{L} * 0.5 = C_n^0 = 3.25\frac{mol}{L}$$

$$C_n = C_n^0(1 - f_n) = 3.25\frac{mol}{L}(1 - 0.872) = 0.416\frac{mol}{L}$$

The values for k_0, E, and T, are $133187\frac{1}{hr}$, $29\frac{kg}{mol}$, and $120\ °C$ respectively. The CSTR material balance equation can be manipulated into the following form:

$$(C_n - C_n^0)/(k_0 e^{-\frac{E}{RT}} C_n) = \tau = 0.3647$$

Then, the reactor volume can be calculated:

$$V = \frac{v}{\tau} = 26576\ L = 26.576\ m^3$$

This is the necessary liquid volume in the reactor, and the actual volume must be larger due to the vapor phase flow and headspace.

10.1.2 Carothers Equation for Degree of Polymerization

$$\bar{x}_n = \frac{1+r}{1+r-2rp} \ | \ \bar{x}_n{}^{ARB} = \frac{1}{1-p} \qquad \text{(Equation 10-5)}$$

For an ARB polymerization such as that of PHFA, r = 1. The sample calculation below is used to determine the extent of reaction required in the pre-polymerization CSTRs (R-301 A/B/C/D) with a goal degree of polymerization of 15.

$$\bar{x}_n{}^{ARB} = \frac{1}{1-p} = 15 \ \rightarrow p = 0.933$$

10.1.3 Source Model for Liquid Flow Through an Orifice.

A sample calculation will be performed using the Acetic Anhydride release as a model scenario. Assuming a liquid velocity of 2 m/s and a temperature of 30°C, the pipe bore can be calculated shown below.

$$\frac{m}{2\rho} = A = \frac{104591\,\frac{kg}{hr} * \frac{1}{3600}\,\frac{hr}{s}}{2\,\frac{m}{s} * 1080\,\frac{kg}{m^3}} = 0.01345\ m^2 = 20.84826\ in^2$$

The equation for a circle is then used to find the pipe bore

$$D = \sqrt{\frac{4A}{\pi}} = 5.1522\ in$$

Following the guidelines for a PHA, the assumed rupture area would be 20% of the total pipe area as the diameter is greater than 4 inches. The discharge coefficient is conservatively chosen to be 1. The source model equation 5-1 can then be used, yielding the mass flow through the rupture area.

$$Q_m = 0.2 * 0.01345\ m^2 * 1 * \sqrt{2 * 1080\,\frac{kg}{m^3} * 1 * 500000\ Pa} = 88.41\,\frac{kg}{s}$$

10.2 Supplementary Economic Calculations

10.2.1 Break Down of Utility Prices and Credits by Section

Table 10-1. Utility Prices and Credits by PHFA Plant Section

Cooling Water	
Section 1	$ 1,585,200.00
Section 2	$ 129,453.00
Section 3	$ 297,238.00
Total	$ 2,011,891.00
Steam	
Section 1	$ 1,225,885.00
Section 2	$ 1,894,823.00
Section 3	$ 4,166,484.00
Total	$ 7,287,192.00
Electricity	
Section 1	$ 86,208.00
Section 2	$ 509,321.00
Section 3	$ 438,156.00
Total	$ 1,033,685.00
Fuel	
Section 1	$ 13,062,176.00
Section 2	$ -
Section 3	$ 305,888.00
Credit for Waste Burning	$ (3,771,270.40)
Total	$ 9,596,793.60

10.2.2 Calculation of Cost of Operating Labor

The number of operators per shift can be estimated using the Alkhayat-Garrard correlation as displayed in Equation 10-6 below.

$$N_{OL} = \sqrt{6.29 + 31.7P^2 + 0.23N_{NP}} \qquad \text{(Equation 10-6)}$$

P represents the number of processing steps involving the handling of particulate solids. N_{NP} is the number of liquid/vapor steps such as compression, heating and cooling, mixing, and reactions. Pumps and vessels are not included in the N_{NP} count. The total number of liquid/vapor steps are listed in **Table 10-XX** below. For the purposes of calculations, it was assuming that there are 0 solid handling steps. In reality, there will be some handling of solid catalyst during reactor downtime.

Table 10-2. Number of Processing Steps

Category	Number of Unit Ops (N_{NP})
Compressors	3
Exchangers	28
Furnaces	8
Reactors	10
Towers	9
Total	58

10.2.3 Calculation of Operating Expenses

The total cost of manufacture (COM) is equal to the sum of direct manufacturing costs (DMC), fixed manufacturing costs (FMC), and general expenses (GE). Each line item within these categories may be estimated based on the following categories of expenses: fixed capital investment (FCI), cost of operating labor (C_{OL}), cost of utilities (C_{UT}), cost of waste treatment (C_{WT}), and cost of raw materials (C_{RM}). The tables below contain the recommended correlation used for each category of operating costs.

Table 10-3. Direct Operating Costs

Category	Cost
Raw Materials	C_{RM}
Waste Treatment	C_{WT}
Utilities	C_{UT}
Operating Labor	C_{OL}
Direct Supervisory & Clerical Labor	$0.18 \cdot C_{OL}$
Maintenance & Repair	$0.06 \cdot FCI$
Operating Supplies	$0.009 \cdot FCI$
Laboratory Charges	$0.15 \cdot C_{OL}$
Patents and Royalties	$0.03 \cdot COM$
Total	$C_{RM} + C_{WT} + C_{UT} + C_{OL} + 0.03 \cdot COM + 0.069 \cdot FCI$

Table 10-4. Fixed Operating Costs

Category	Cost
Depreciation	$0.05 \cdot FCI$
Local Taxes & Insurance	$0.032 \cdot FCI$
Plant Overhead Costs	$0.708 \cdot C_{OL} + 0.036 \cdot FCI$
Total	$0.708 \cdot C_{OL} + 0.168 \cdot FCI$

Table 10-5. General Manufacturing Expenses

Category	Cost
Administrative Costs	$0.177 \cdot C_{OL} + 0.009 \cdot FCI$
Distribution & Selling Costs	$0.11 \cdot COM$
Research & Development	$0.05 \cdot COM$
Total	$0.177 \cdot C_{OL} + 0.009 \cdot FCI + 0.16 \cdot COM$

Adding the total DMC, FMC, and GE expenses and solving for total manufacturing cost yields the following expression:

$$COM = 0.28FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM}) \quad \text{(Equation 10-7)}$$