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**Lignin to Adipic Acid**

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## Executive Summary

PetroPalooza is a petrochemical company that makes adipic acid with the conventional process. The National Renewable Energy Laboratory (NREL) has recently derived a process that converts lignin into adipic acid. The purpose of our project is to determine if the process NREL developed is a threat to the conventional petrochemical process of creating adipic acid. In order to determine if the NREL process is a threat, the steps that NREL took were scaled to an industrial size process. To be competitive, the lignin to adipic acid pathway needs to make a profit, and have the possibility of producing the same amount of adipic acid as the conventional process in the future. According to the results of our research thus far, the NREL process would not be competitive with the petrochemical process because the scaled up NREL process is not profitable, and does not produce as much adipic acid as the conventional process. The estimated capital investment for our industrially scaled NREL process is approximately \$16,000,000. The net present value at 10 years with a depreciation of 10% was found to be approximately negative \$17,000,000, and the IRR was found to be -6%. The net present value at 20 years with a depreciation of 10% was found to be approximately negative \$16,000,000, and the IRR was found to be -11%. The risk involved with the production of adipic acid through lignin is that the process technology is new. For future work, the amount of M9 needs to be further investigated, the lignin to bacteria ratio needs to be increased, the regeneration of activated carbon needs to be reviewed further, heat exchangers need to be reviewed for the crystallizers, different types of solid-liquid filters need to be examined, the catalyst in the trickle bed reactor needs to be examined, and the optimum conditions of the trickle bed reactor need to be determined.

## Scope

### *Design Problem*

As a petrochemical company that currently makes adipic acid, PetroPalooza wants to know whether the National Renewable Energy Laboratory's (NREL's) lignin to adipic acid process will be a competitor in industry in the near future. To determine this, an industrial process must be designed based on the lab scale procedures and results from NREL. The materials and methods, Vardon, D.R. *et al.* (2015) and Vardon, D.R. *et al.* (2016), were thoroughly analyzed and industrial unit operations with similar functions to the laboratory equipment were researched to determine if an industrial lignin to adipic acid process was determined to be technically feasible. Then, economic and sensitivity analyses were performed to determine if the process is economically feasible.

### *Design Constraints*

The design of an industrial sized lignin to adipic acid plant comes with many constraints. The lab scale process itself has certain limitations and requirements, and industrializing this process only introduces more.

#### Scientific and technical constraints

Along with lignin, the production of adipic acid requires genetically modified *Pseudomonas putida* to convert the lignin to muconic acid, oxygen and nutrients to keep the bacteria alive, and hydrogen to hydrogenate the muconic acid to adipic acid.

In the lab scale process, the bacteria required a minimum of 50% dissolved oxygen saturation<sup>1</sup> and an M9 media containing significant quantities of sulfate, phosphate, and sodium salts.<sup>2</sup> Since the first step of this process is funneling the compounds in lignin to muconate with bacteria, the living conditions of the bacteria are very important for this process to succeed. The life span of the bacteria and its ability to be recycled and reused will determine the amount of bacteria needed, and the frequency of replacement.

The amount of hydrogen required for hydrogenation of the muconic acid to adipic acid is based on stoichiometry. If too little hydrogen is supplied, the reaction cannot proceed and adipic acid will not be produced. To ensure the completion of the reaction, excess hydrogen will be supplied. This introduces the need for a recycle stream for the unused hydrogen.

#### Production constraints

To be on the same production level as the three largest petrochemical plants, 250,000 tons of adipic acid must be produced annually.<sup>3</sup> However, based on NREL's yields this would require more lignin than is currently available. The amount of lignin available to purchase from cellulosic ethanol plants in the U.S. is limited to 200,000 tons/year.<sup>4</sup> This may make it difficult to achieve the economies of scale that will allow the plant to be competitive.

The lignin must be in contact with the bacteria for 78.5 hours.<sup>1</sup> This prevents the implementation of a continuous process since a residence time of at least 3 days is required for the bioreactor.

#### Practical constraints

The bacteria require a large volume of nutrient solution, and according to NREL's experiments, the ratio of this volume to the amount of lignin fed is extremely large. This sets a size minimum on the bioreactor. However, commercial availability sets a size maximum on the bioreactor, and production must be adjusted and will be based on the largest bioreactor volume that can be obtained. While the bioreactor could be built onsite to achieve the necessary size, this may not be within monetary constraints.

Activated carbon was used by NREL to adsorb unwanted aromatics from the bioreactor outlet. An industrial process will require an impractical amount of activated carbon, but this step cannot be eliminated. The use of activated carbon industrially becomes more practical if it can be regenerated rather than replaced when it becomes exhausted.

A significant amount of ethanol is required in the hydrogenation step of producing adipic acid. Because the ethanol is not actually used up, a recycle can be implemented. This recycle is required to reduce variable costs and keep the process environmentally friendly.

#### Production and feedstock specification constraints

The majority of adipic acid is used to manufacture nylon-6,6. Synthesis of this polymer requires high purity adipic acid (at least 99.8%),<sup>2</sup> so in order for this process to be competitive, it must meet these purity standards. NREL reports achieving this purity in their laboratory process, so achieving this purity industrially will require following their materials and methods very closely.

The lignin feedstock must be pure so that when it is fed to the bioreactor it does not poison the bacteria or detrimentally alter their living conditions. If the lignin is obtained from a cellulosic ethanol plant that pretreats their corn stover feedstock and is directly fed to the bioreactor, it can be assumed that the lignin is not contaminated. However, if the cellulosic ethanol plant does not treat their corn stover to kill mold and other impurities, or if the lignin must be transported long distances and stored for long periods, it would be necessary to pretreat the lignin before feeding it to the bioreactor. This could be done with acid or heat.

#### Safety constraints

This process requires sulfuric acid to convert muconate to muconic acid. The sulfuric acid will be stored in a tank until it is added to the process. To maximize safety, the amount of acid stored at one time must be minimized and the material of the storage tank must be appropriate.

This process does not run at extreme conditions so if the conditions from NREL's process are maintained, the process does not present many risks.

#### Environmental constraints

This process requires filtering a muconic acid slurry, which results in a saltwater waste stream. Ideally, this waste stream could be recycled and the salts could be used as nutrients for the bacteria as previously mentioned. If a recycle of this waste cannot be implemented, it will need to be desalinated before being released. This may require the implementation of an ion exchange column.

Since this process is the environmentally friendly alternative to producing adipic acid the petrochemical way, the plant design should be as environmentally friendly as possible. Federal and state emissions regulations must be met and energy consumption minimized.

#### Economic constraints

This process needs to be profitable to compete with the petrochemical plants currently producing adipic acid. If it is not profitable, then it is not competitive and not worth pursuing. This will be a new chemical plant, so it must also meet a minimum profitability standard set by an investor.

The price of adipic acid should not exceed market prices. To be competitive with other sellers, it will need to be sold at close to market price. There is chance that it could be sold at a premium due to customer preference for environmentally friendly products, but this could not be significantly higher than that of conventionally made adipic acid. Lignin is available at a price of half its fuel value and the price of hydrogen is given in the problem statement as well.<sup>5</sup>

## Introduction

First-generation biofuels are made from the sugars and vegetable oils found in arable crops, which can be easily extracted using conventional technology. In comparison, second-generation biofuels are made from lignocellulosic biomass, agricultural residues or waste, which makes it harder to process for the extraction of the required fuel. The commercialization of this second-generation biofuels derived from lignocellulose has been the primary focus of recent government and private industry support in the biofuels area. Several cellulosic ethanol plants in the U.S. are beginning, or have recently begun, to produce fuel ethanol from lignocellulosic feedstocks such as corn stover, and production is expected to increase significantly over the next few years.<sup>6</sup>

In addition to ethanol, second-generation lignocellulosic ethanol plants make a byproduct consisting primarily of lignin as shown in Figure 1. Lignin is a heterogeneous mixture of largely-aromatic polymers that provides plant cell walls their structural strength and recalcitrance to biologic attack. The chemical industry has not been able to make money from lignin because a boiler to generate steam and electricity from lignin is expensive. This capital would be avoided if an alternative use for lignin is found. An economical projection estimated that lignin, as raw material, would be available at a price of half of its fuel value.<sup>7</sup> The National Renewable Energy Laboratory (NREL) is working under this premise to make lignin a profitable byproduct.

NREL has demonstrated an integrated process from corn stover-derived lignin to *cis,cis*-muconic acid, followed by high yield recovery and hydrogenation to adipic acid.<sup>1</sup> Adipic acid is the dicarboxylic acid produced industrially in the largest quantity and it is used primarily as a monomer to make nylon-6,6 used for fibers and engineering polymers.<sup>8</sup> NREL has accomplished this by genetically modifying *Pseudomonas putida* KT2440 (a bacterium) to funnel many lignin model compounds to *cis,cis*-muconate as shown in Figure 2.

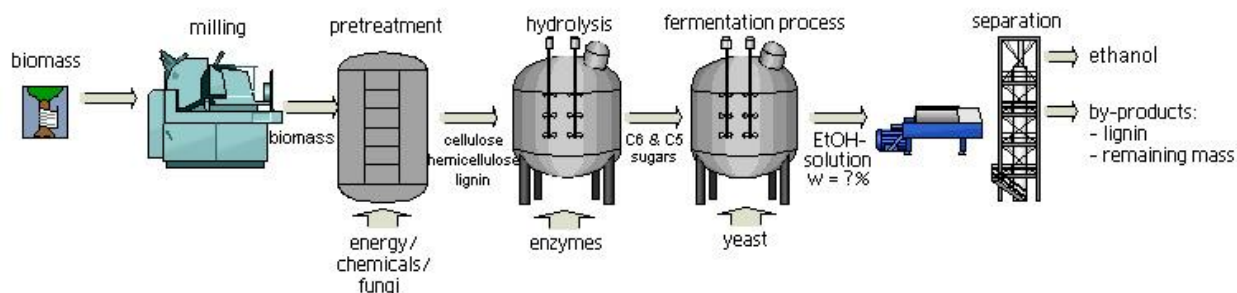


Figure 1. Typical second-generation lignocellulosic ethanol plant, where biomass usually refers to corn stover. Notice the byproducts, specifically lignin coming out of the separation unit (distillation tower). DuPont (2013).

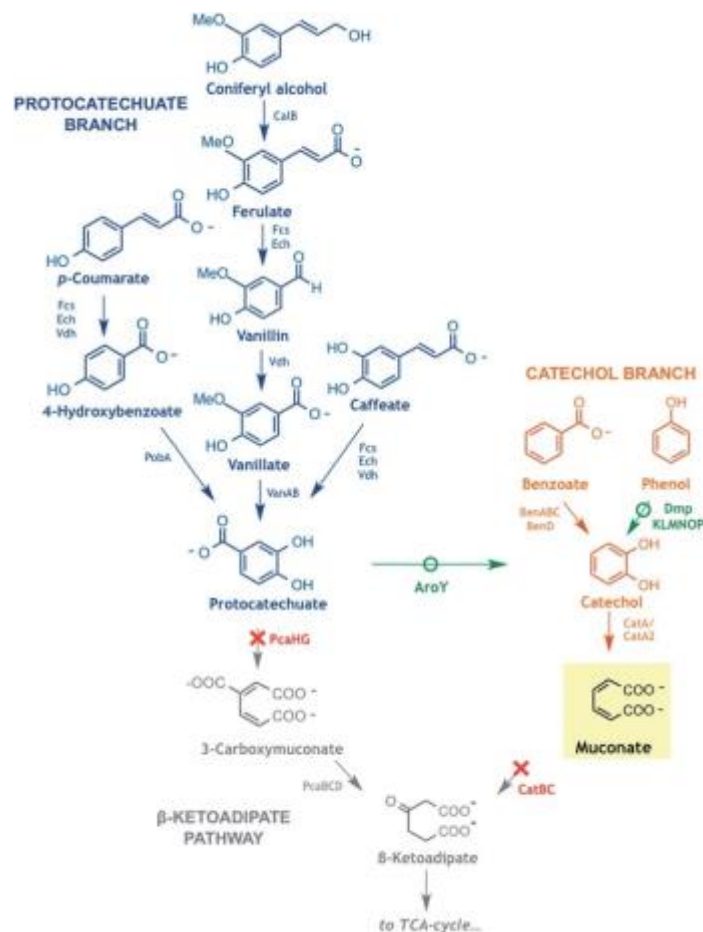


Figure 2. Biological funneling of lignin-derived aromatics to muconate. *P. putida* KT2440 was engineered to delete genes encoding PcaHG and CatBC (red crossed arrows) and insert genes encoding AroY and DmpKLMNOP (green circled arrows), enabling biological funneling of diverse lignin-derived monomers to muconate. Vardon, D.R. *et al.* (2015).

The introduction of NREL's biologically engineered microorganism, *P. putida* KT2440-CJ103, provides the missing piece for a vertically integrated scheme for the conversion of lignin to adipic acid for nylon-6,6 production. Starting with corn stover at a second-generation lignocellulosic ethanol plant to produce ethanol and lignin. Followed by lignin biological processing to produce adipic acid and its subsequent polymerization to nylon-6,6 as the final product.<sup>9</sup> Thus, the success of this outline depends on the biological conversion of lignin-derived compounds to muconate using NREL's engineered bacteria. Specifically, four lignin-derived aromatic compounds that have been identified as very promising due to high conversion yields, as shown in Figure 3, resulting in a final muconate titer of 13.5 g/L after 78.5 hours.

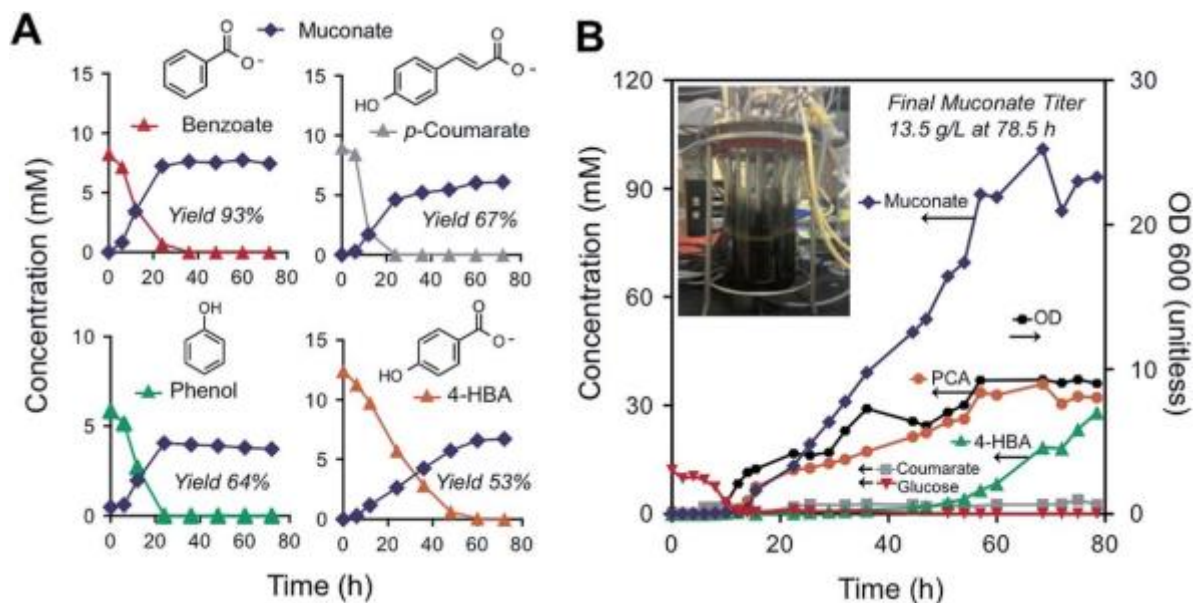


Figure 3. Biological conversion of lignin-derived aromatics to muconate. (A) Shake flask experiments using *P. putida* KT2440-CJ103 to convert benzoate, p-coumarate, phenol, and 4-hydroxybenzoate (4-HBA) to muconate. (B) DO-stat fed-batch cultivation of *P. putida* KT2440-CJ103 using glucose as a carbon source for the conversion of lignin to muconate. Horizontal arrows indicate corresponding axis for tracked compounds and optical density at 600 nm (OD 600). Vardon, D.R. *et al.* (2015).

Since 2015, NREL has further developed the technology by means of several modifications to their lignin to adipic acid process as shown in Figure 4. Among the most impressive improvements is the ability of the engineered bacteria, *P. putida* KT2440-CJ102, to take upon more lignin at once (process limited by contact area) for its conversion to muconate. Contact area availability restricts the amount of lignin that can be reacted to muconate per volume of broth (solution containing the bacteria). However, NREL has improved the originally reported value of roughly 20 g/L in 2015 to 160 g/L in 2016, and improvements to the process are expected to continue.<sup>2</sup> The engineered strain *P. putida* KT2440-CJ102 is identical to *P. putida* KT2440-CJ103 described in NREL's previous work, except that it lacks a phenol monooxygenase.

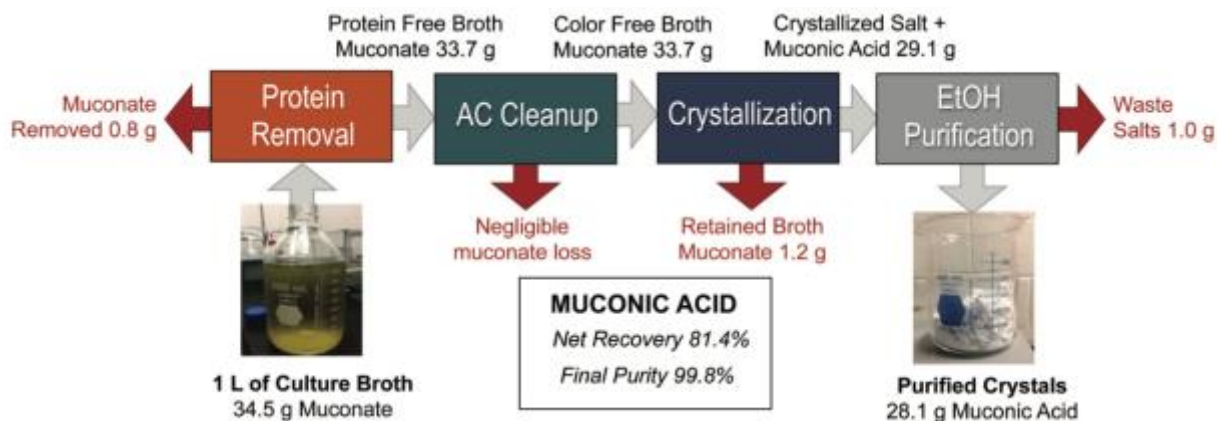


Figure 4. Separation and purification scheme to recover muconic acid from biological culture broth. Initially, proteins and bacteria were removed by microfiltration, followed by adsorption of non-target aromatic metabolites with 5 g/L of activated carbon. Muconic acid was crystallized by reducing the pH to 2 and temperature to 5 °C, and the resulting solids were recovered by vacuum filtration and dried in a vacuum oven. Recovered solids were dissolved in ethanol prior to a second stage of vacuum filtration to remove insoluble salts. For yield and purity analysis, ethanol was removed by rotary evaporation and muconic acid was dried for 48 hours in a vacuum oven. Vardon, D.R. *et al.* (2016).

Alternatively, adipic acid can be synthesized from the conventional petrochemical process.<sup>8</sup> This process is well developed, however the high cost of the raw material (cyclohexane) as well as the environmental impact (CO<sub>2</sub> and NO<sub>x</sub> gas emissions) leave room for improvement and present a business opportunity. The question then arises as to whether the NREL process, Vardon, D.R. *et al.* (2016), is competitive when scaled up from laboratory to industrial basis, or if it needs significant new inventions to be economically viable in replacing the conventional approach. This report addresses the question by investigating the conversion of lignin to adipic acid alternative via scaling up the process demonstrated by NREL (most recent results, year 2016). Thus, allowing PetroPalooza to identify limitations and opportunities of its implementation.

## Description of Base Case

A simplified version of the lignin to adipic acid process flowsheet can be seen in Figure 5.

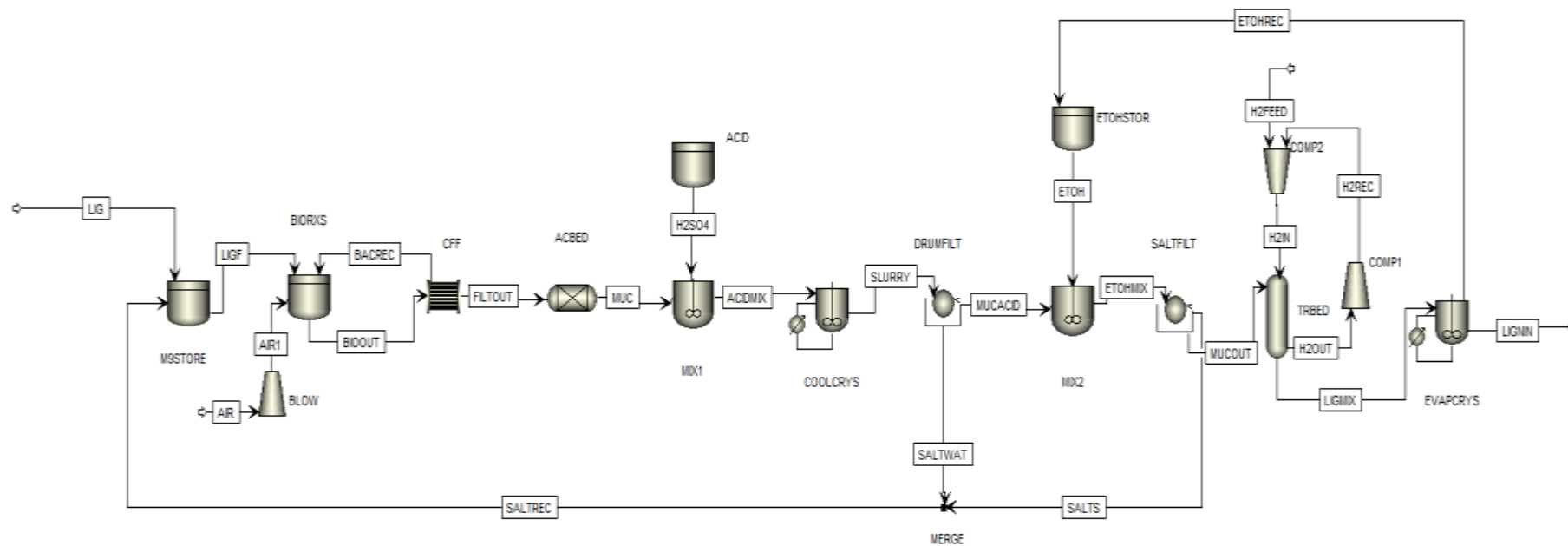


Figure 5. Simplified overall lignin to adipic acid process modelled in Aspen Plus.

## Bioreactor

From the second-generation lignocellulosic ethanol plant, dry or nearly dry lignin will be transported to the bioreactor using a conveyor belt or trucks depending upon the distance separating them. The bioreactor will allow engineered *Pseudomonas putida* KT2440-CJ102 to perform biological conversion of lignin-derived aromatic compounds to muconate.<sup>2</sup> The bioreactor relies on the engineered bacteria, *P. putida* KT2440-CJ102, in an M9 minimal medium to be fed to the bioreactor where it will mix with lignin and react for 72 hours. A total of 121470 L of the liquid medium containing the bacteria will be used per bioreactor (21.4 ton of lignin). The engineered bacteria will be obtained from NREL, where seed cultures are prepared in Luria-Bertani (LB) broth, centrifuged, and washed with excess M9 minimal medium. The M9 minimal medium provides the bacteria with the proper environment (e.g., salts, sugars, vitamins) necessary for survival. M9 minimal medium is composed of: 15 mM glucose, 13.56 g/L Na<sub>2</sub>HPO<sub>4</sub>, 6 g/L KH<sub>2</sub>PO<sub>4</sub>, 1 g/L NaCl, 2.25 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 2 mM MgSO<sub>4</sub>, 0.10 mM CaCl<sub>2</sub>, and 0.018 mM FeSO<sub>4</sub>. All M9 minimal medium components will be mixed in a tank that will feed the bioreactor.

Once everything has been fed to the bioreactor a temperature of 30 °C will be maintained by heating with an electrical heater or cooling (in case the reaction behaves exothermic, which has not been reported) by running cold water in the bioreactor's jacket as needed. An electrical heater was chosen because the energy input should be relatively low (even when electricity is used as the utility) in achieving a low temperature such as 30 °C. Also, this type of heating system can deliver heating with precision and promptitude. The pH of the medium will be automatically controlled and adjusted to 7. pH changes are only expected from the metabolic reactions produced from the bacteria. Hence, only slight adjustments are expected and this, just like the temperature, would be constantly monitored and adjusted as needed with H<sub>2</sub>SO<sub>4</sub> and NaOH for lowering and increasing the pH respectively. Filtered air will be constantly fed to the bioreactor through a blower to provide aeration for the aerobic *P. putida* KT2440-CJ102.<sup>2</sup> The air will be filtered using glass wool or a membrane. An impeller will be implemented in the bioreactor to give the engineered bacteria enough suspension in solution for optimum contact area with lignin. Baffles will be situated inside the bioreactor to eliminate vortex effects created by the impeller. In-situ measurements for temperature, pressure, pH, and dissolved oxygen will allow for control of the biological reaction. Figure 6 shows a diagram of the bioreactor and its components for the biological conversion of lignin to muconate.

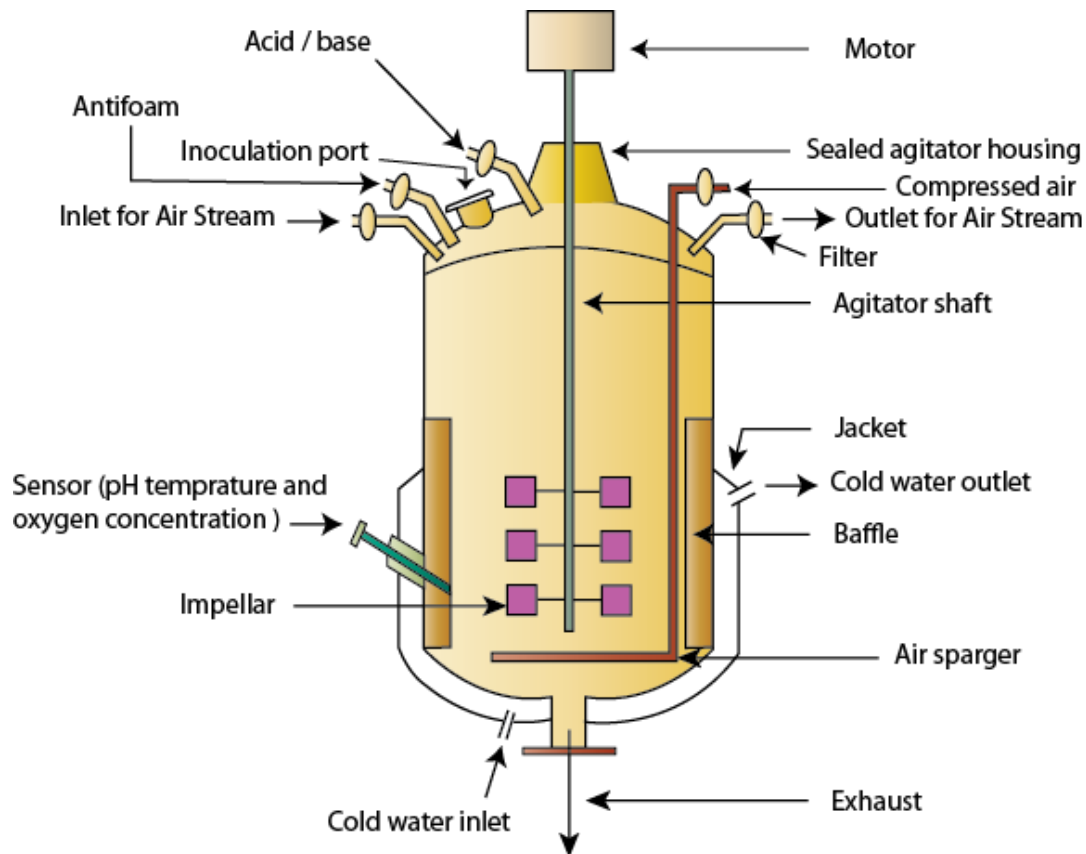


Figure 6. Stirred tank bioreactor for the conversion of lignin to muconate at 30 °C, 1 atm absolute, and pH 7. Reaction time of 72 hours and shell made of stainless steel (capacity for 170000 L and can withstand up to 50 psia) with a cooling jacket.<sup>10</sup> Air sparger to provide the engineered bacteria, *P. putida* KT2440-CJ102, with sufficient oxygen. Impeller to uniformly suspend the engineered bacteria and baffles to eliminate vortex effects. Electrical heater to provide heating to achieve operating conditions (30 °C). Sensors for temperature, pressure, pH, and dissolved oxygen. Image obtained from open literature.

The current design is based on three batch bioreactors, all identical to the one described in Figure 5, with operating schedules staggered (24 hours), so that the 72 hours (reaction time) can be reduced to 24 hours for the same production capacity of one bioreactor. This allows to size the rest of the units in the lignin to adipic acid chemical plant, for processing 21.4 ton of lignin in 24 hours. Thus, a continuous design is implemented after the initial batch bioreactor step, with allocation of time (24 hours) for each subsequent process, based on each unit operation requirements.

The continuous design starts with the implementation of a cross-flow filter directly at the effluent stream of the bioreactor. This unit accomplishes the separation of the engineered bacteria from solution by filtering parallel to the direction of the flow as shown in Figure 7. Thus, bacteria with a particle size in the range of 1 to 10  $\mu\text{m}$  cannot permeate through the cross-flow filter,<sup>11</sup> whereas smaller particles such as aqueous salts and sugars (M9 minimal medium), and organic compounds (muconate and lignin-derived compounds) will readily move across the

filter to the next unit (a packed bed column) where organic compounds (apart from muconate) will be separated out. Particle sizes for filtration considerations can be seen in Figure 8. Once the engineered bacteria have been separated from the bioreactor broth, it will be recycled back to the bioreactor to continue the biological conversion of lignin to muconate with a new lignin batch. Selective purging or addition of the bacteria would be needed to keep the population in balance, and can be determined by sampling and analyzing (in the laboratory) the recycle stream, before it reenters the bioreactor. Since the filtration occurs parallel to the flow, as opposed to perpendicular, the cross-flow filter should not become too overwhelmed/clogged, and cleaning or even replacing filters would not occur as often as with a membrane filtration design. A back-flow through the filter can be used to dislodge stuck particles when giving maintenance to the filter.

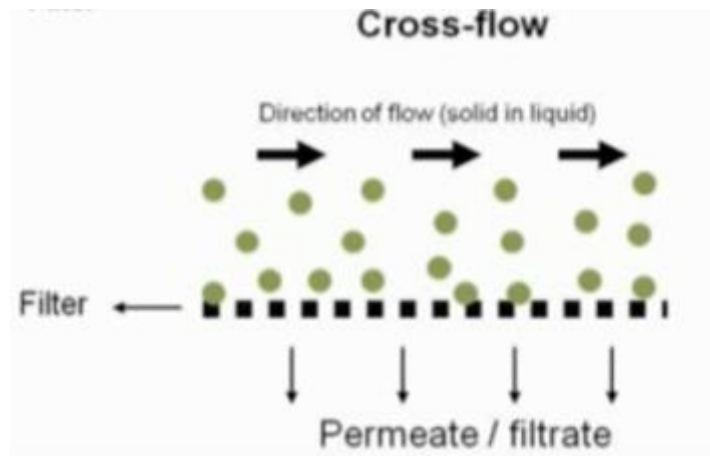


Figure 7. Cross-flow filter system showing parallel filtration action between the flow and filter. Gerardo, M. (2013).

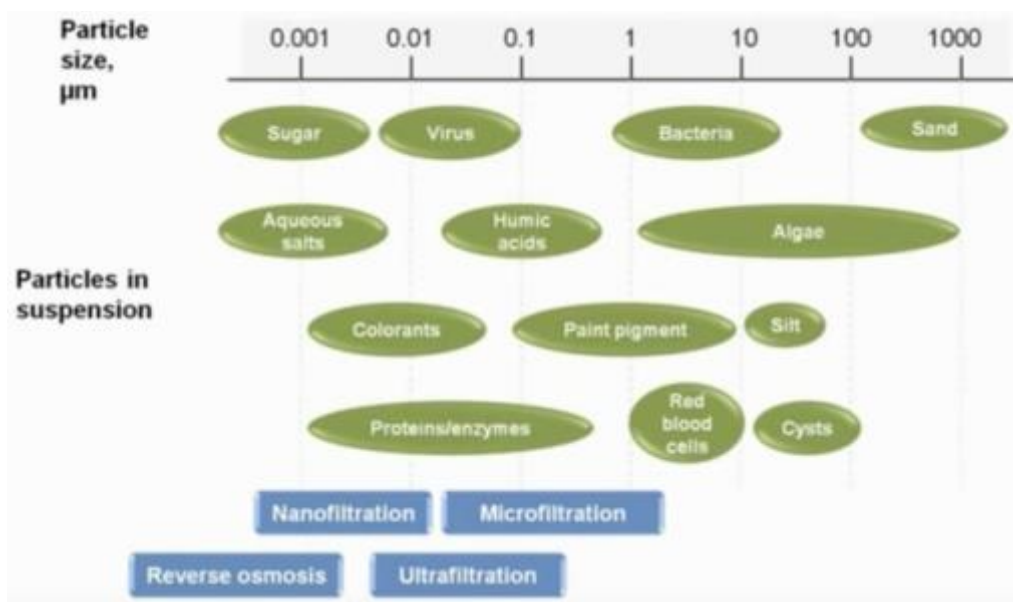


Figure 8. Particle size distribution for cross-flow filter considerations. Gerardo, M. (2013).

### Activated Carbon Packed Bed Reactor

After the bioreactor and subsequent filtration, muconate and various aromatic intermediates will be fed to an activated carbon packed bed column. The purpose of the activated carbon is to remove the aromatic intermediates that come out of the bioreactor with the muconate and any other impurities such as color compounds that may be present in the stream. The chemistry of this can be seen in Figure 9. NREL demonstrated effective purification of the muconate broth with 5 g of activated carbon per liter of broth.<sup>2</sup> Rather than using a packed bed column, however, they added the carbon to the solution and stirred it for one hour. Since it is more desirable to use a packed bed column for the industrial version of this process, the 5 g/L ratio was increased to 10 g/L for the calculations. This increase should account for any differences between adsorption with a batch reactor and adsorption with a packed bed reactor. A residence time of one hour is expected and muconate loss at this step is negligible.<sup>2</sup>

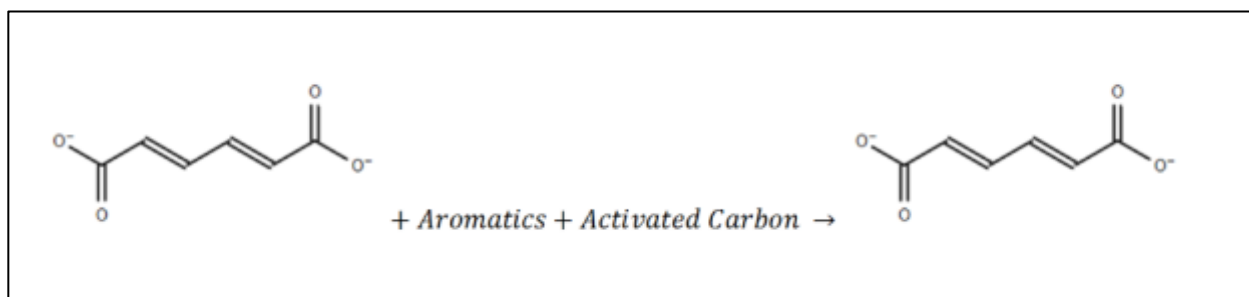


Figure 9. The muconate and aromatics enter the activated carbon packed bed, and only muconate exits the packed bed. The activated carbon adsorbs the undesirable aromatics.

As the activated carbon adsorbs the impurities, it will become exhausted. A majority of the muconate will remain in solution while unwanted aromatics such as protocatechuate and 4-hydroxybenzoate will adsorb to the activated carbon.<sup>1</sup> The effluent stream of this packed bed will contain muconate to be fed to a crystallizer where muconic acid will crystallize out of solution. However, in order to regulate the effluent stream and ensure the activated carbon is properly allowing aromatics to adsorb, a sensor using ultraviolet light will be implemented. If significant amounts (2-5%) of unwanted aromatics are detected in the effluent stream, an alarm will sound and the activated carbon will be replaced since it is likely exhausted.

Aromatics absorb ultraviolet (UV) light, so even very small amounts can be detected using UV absorption monitoring.<sup>12</sup> A UV absorption sensor can be placed on the outlet stream like in Figure 10. This allows for continuous monitoring and eliminates the need to take samples and test the composition manually.

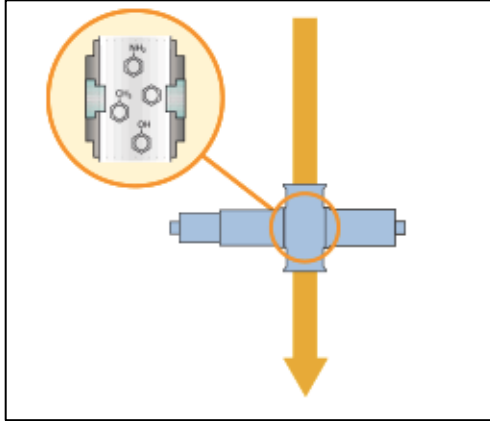


Figure 10. A UV absorption sensor that will detect unwanted aromatic compounds in the activated carbon packed bed effluent stream. Taken from Fischer, Paul (2017).

To keep the process as continuous as possible, two activated carbon packed bed columns will be rotated. When the first packed bed becomes exhausted, rather than waiting to dispose of and replace the activated carbon, the entire column will be removed and replaced with a second column that is already packed with fresh activated carbon. The exhausted activated carbon will be removed from the column and sent to an outside company that regenerates catalysts. This will be cheaper than buying fresh activated carbon whenever it becomes exhausted. Eventually, it may be economically useful for this plant to regenerate the activated carbon onsite rather than using an outside company.

Figure 11 shows a general design for the adsorption columns.<sup>13</sup> The muconate broth will enter at the top of the column and be distributed over the activated carbon. As it moves down the column, impurities will remain in the packed bed and a purified muconate broth will exit at the bottom. A support will be needed at the bottom of the packed bed to keep the activated carbon packed and in place.

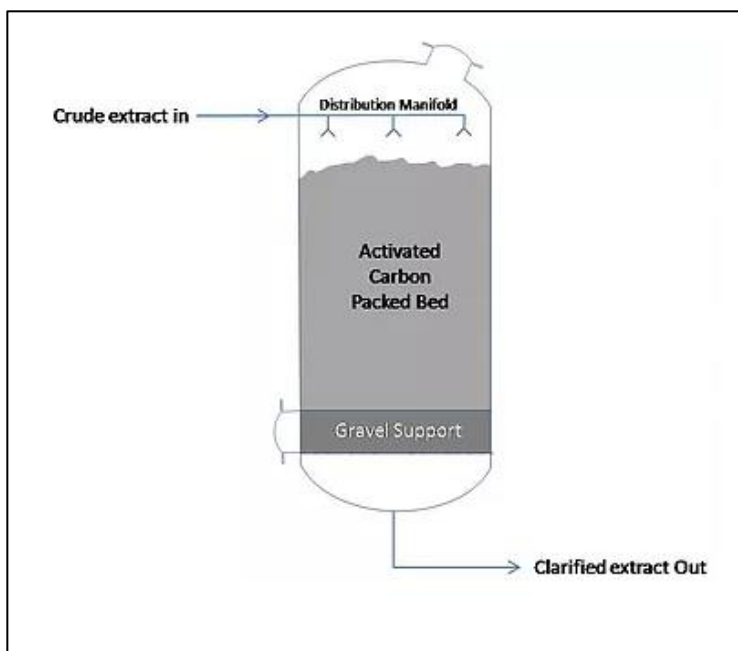


Figure 11. Packed bed adsorption column to retain undesirable aromatics before sending muconate into the crystallizer. Activated carbon used as the adsorbent medium. The muconate broth enters at the top (crude extract in) and the purified muconate broth exits at the bottom (clarified extract out). Taken from “Stevia Extraction Technology” (2017).

The purified muconate stream from the activated carbon packed bed reactor will then enter a mixing tank where it will be mixed with sulfuric acid and converted to muconic acid.

#### *Sulfuric Acid Storage Tank*

The sulfuric acid tank used, Figure 12, is designed specifically to handle very concentrated sulfuric acid. Since our design requires 98% sulfuric acid, which is roughly twice as heavy as water, typical materials are not strong enough and cannot be used. We determined that the SAFE-tank design was the best option for our system; this is a double walled tank composed of polyethylene so that if the first layer fails the second layer acts as secondary containment.<sup>14,15</sup> This is an optimum form of secondary containment as it does not come in contact with the air and will less likely come in contact with operators and maintenance crew. 316 stainless steel can also be used at this sulfuric acid concentration and will be utilized for bolts and fittings as well as in other unit operations down the line.<sup>14,15</sup> The tank will hold 2,080 liters of sulfuric acid. This size was determined based on monthly deliveries of sulfuric acid. Since the sulfuric acid we require is so concentrated and poses many hazards we wanted to minimize the amount of acid we had on hand at any given time.



Figure 12. SAFE-Tank design that is being utilized for sulfuric acid storage.<sup>14,15</sup>

### *Mixing Tank 1*

A 5,450 liter mixing tank made of 316 stainless steel will be used to initiate the reaction between muconate and sulfuric acid. The 316 stainless steel is required because it is compatible with 98% sulfuric acid without significant corrosion or other damage. Sulfuric acid is added until the solution reaches a pH of 2.<sup>1,2</sup> This is the required pH that allows for crystallization to occur. Since sulfuric acid reactions are extremely exothermic,<sup>14,15</sup> we will need to put a cooling jacket on the mixing tank. This jacket will allow us to regulate the temperature to keep it at a reasonable level and provide a safety measure in the event of a runaway reaction.

### *Cooling Crystallizer*

Once the muconate and sulfuric acid have combined, Figure 13, and adjusted to the appropriate pH, the mixture will go to the cooling crystallizer. The crystallizer will be 5,450 liters and made of 316 stainless steel. The solution will be cooled to a temperature of 5 °C (41°F), which is the temperature required for the crystallization of muconic acid.<sup>1,2</sup> Since our plant is small scale, a simple jacket scraping-cooling crystallizer should be enough.<sup>16</sup> The design of this type of crystallizer is very simple; the liquid enters and is agitated by a scraping blade. The entire reactor is enveloped in a cooling jacket which drops the temperature, allowing for crystallization. At the end a slurry of desired crystals and unreacted solution leaves the system. This set up is illustrated in Figure 14.

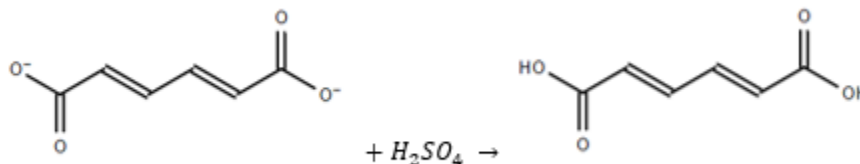


Figure 13. Chemical equation of the conversion of muconate into muconic acid.

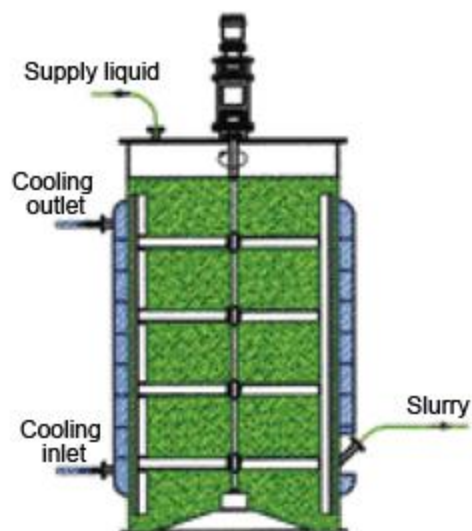


Figure 14. Basic Design of a jacket scraping-cooling crystallizer. Katsuragi, accessed April, 2017.

If this pilot plant were successful and it was decided to build a full scale plant, a different crystallizer design would be necessary to allow for adequate cooling. For example, rather than only a cooling jacket there would need to be some sort of cooling tube or another setup on the inside as well. This would allow for complete, efficient cooling of the entire solution.

The sulfuric acid is used as a reducing agent for muconate, which reacts into muconic acid. Since this reaction is temperature dependent, the bulk of this reaction will occur in the crystallizer where the muconic acid will crystallize out. However, it is possible that there will be some conversion in the preliminary step that is the mixing tank. As can be seen in the reaction in Figure 13, the hydrogens in sulfuric acid bond with the oxygen ions in muconate to form muconic acid. This reaction requires a pH of 2 and temperature of 5°C which is accomplished by both the mixing tank and the crystallizer. This reaction also produces sulfate ions (not pictured) from the sulfuric acid. Additionally, there are some salts and elemental impurities from the M9 media that will have made it through to this point but they are not known to interfere with the reaction so they are not pictured.

Based on laboratory experiments, we expect to get a 74% conversion of muconate to muconic acid.<sup>1</sup> This translates to a conversion of 56.51% of lignin to muconic acid.

#### *Rotary Drum Vacuum Filter (1)*

The slurry that leaves the cooling crystallizer then goes to the rotary drum vacuum filter, Figure 15. Here the excess solution is pulled from the muconic acid crystals. This solution contains water and elemental impurities from the salts used, including: sodium (13,400 ppm), sulfur (8,950 ppm), phosphorus (3,130 ppm), potassium (1,120 ppm) and nitrogen (147 ppm).<sup>6</sup> There is also trace amounts of iron (<0.2 ppm).<sup>6</sup> These impurities have been found to hinder the

production of nylon (synthesized from adipic acid) and has been deemed necessary. Additionally, iron and nitrogen are known poisons to the catalyst used in the trickled-bed, since not all of it will be removed through vacuum filtration, additional purifying will be necessary.

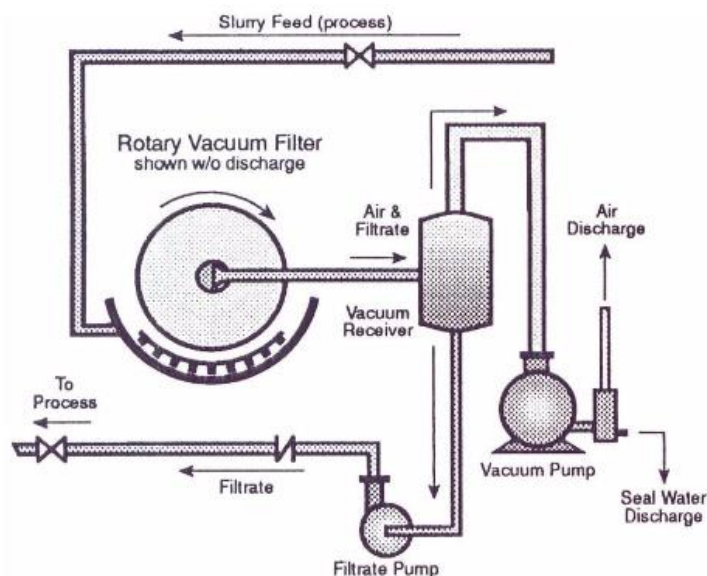


Figure 15. Design of a rotary drum vacuum filter.<sup>17</sup>

Under our current process design we are assuming that we will be able to reuse/regenerate all of the elemental impurities to produce the salts and nutrients required in the M9 nutrient media used for the bacteria in the bioreactor (M9 will be fully replaced with fresh M9 every year). Therefore, the solution pulled from the filter will be recycled back to the start of the process where it will be manipulated into the form we need.

At this point in the process, the muconic acid crystals are only  $97.71 \pm 0.07\%$  pure. This is below the required purity standard of 99.8% that is needed to use the adipic acid in polymer applications.<sup>2</sup> These impurities will be accounted for in the following operation (ethanol CSTR). Since the salty and elemental impurities are present not only in the liquid of the slurry but are also trapped within the crystals themselves, a second “purification” is inevitable.

Currently we are assuming that we will have 100% recovery of the muconic acid crystals from solution.

### *Ethanol Storage Tanks*

The ethanol storage tank is used to hold the ethanol used to solubilize the muconic acid. The purpose of solubilizing the ethanol is so it can more easily go through the catalytic hydrogenation reaction. These tanks will have proper pressure relief valves that will mitigate pressure build up and possible bursting.

Additionally, the ethanol storage will have secondary containment in the event of a rupture of the ethanol can be contained. Similar to Figure 16, these storage tanks will be made of fiberglass due to the corrosive properties of ethanol<sup>21</sup>. The tanks will be stored inside the battery limits, but not in close proximity to the plant itself. This is for the safety of the workers since the ethanol vapors are highly flammable and the excess of ethanol in one area could pose a hazard if an accidental spill occurs. It should be noted, that even will the significant amount of ethanol used in this process, the amount is still below the EPA regulated emissions amount for volatile organic compounds. This is further discussed in the Environmental Permitting section.



Figure 16. Stainless steel ethanol storage tank. Image obtained from open literature.

### *Continuous Stirred Tank Reactor*

The CSTR is fed ethanol from the ethanol storage tanks, in addition to the muconic acid slurry from Vacuum Filter I. This will need to have an inlet capable of feeding solids to the system, since the muconic acid are crystalline. The CSTR is made of stainless steel and has a jacket for cooling if necessary. Pressure manipulation is available, ranging from vacuum to high pressure. This can be seen in Figure 17. Two reactors will be present in our plant and will work in parallel to allow for all of the muconic acid slurry to move forward. Each tank is 50,000 liters in size. In the CSTR the ethanol is able to solubilize the muconic acid; however, the salts present in the solution from the first vacuum filter are not able to solubilize. Therefore, these salts remain out of solution while the muconic acid desired product is solubilized in the ethanol tanks.

After mixing with ethanol the solution will likely be cloudy due to the presence of the salts out of solution. The tanks are assumed to run under continuous processes from the vacuum filter so as to allow for recycle from the storage tanks and therefore minimal use of new ethanol. The only reaction occurring in this unit operation is the muconic acid solubilizing in the ethanol, there are no other outside reactions. Based off of data from NREL's publication, the amount of

ethanol necessary to solubilize the amount of muconic acid was calculated as approximately 10g/L.<sup>2</sup>

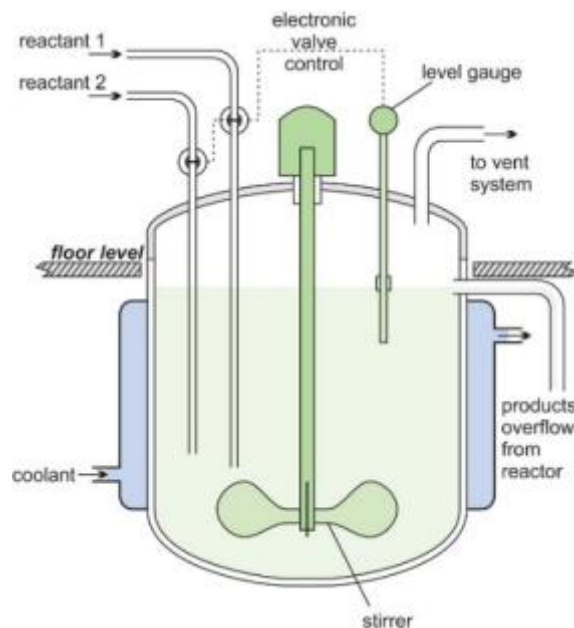


Figure 17. CSTR with jacket for cooling and pressure relief valves for pressure control. Image obtained from open literature.

#### *Rotary Drum Vacuum Filter (2)*

The solution leaving the CSTR needs to be filtered so the muconic acid can be isolated for further processing. Since the muconic acid is solubilized in the ethanol, the filtrate is the desired product from this unit operation. As described by NREL, the salts are not in solution and, therefore, when the vacuum filter is implemented the salts will be separated from the solubilized muconic acid in the ethanol solution. Some salts may not fully solubilize out of solution; however, this still allows for the proper purity to move forward in the process. This is a liquid slurry and the ethanol is volatile, potentially posing a problem.

The largest impurities in this solution are sulfur, sodium, and nitrogen as well as aluminum calcium, chloride, magnesium and silicon. These impurities are mostly in salt form. Some impurities were greatly reduced, but not to a large extent and these include nitrogen and iron. The dried muconic acid product after the ethanol dissolution and filtration showed a purity of 99.8% +/- 0.04%. The largest problem occurred with the reduction of Nitrogen and Iron with their levels still above Adipic acid polymer specifications. A rotary drum filter is put in place for this pilot plant as shown in Figure 18; however, other types of filters could be utilized as well, as later described in the Alternatives section.

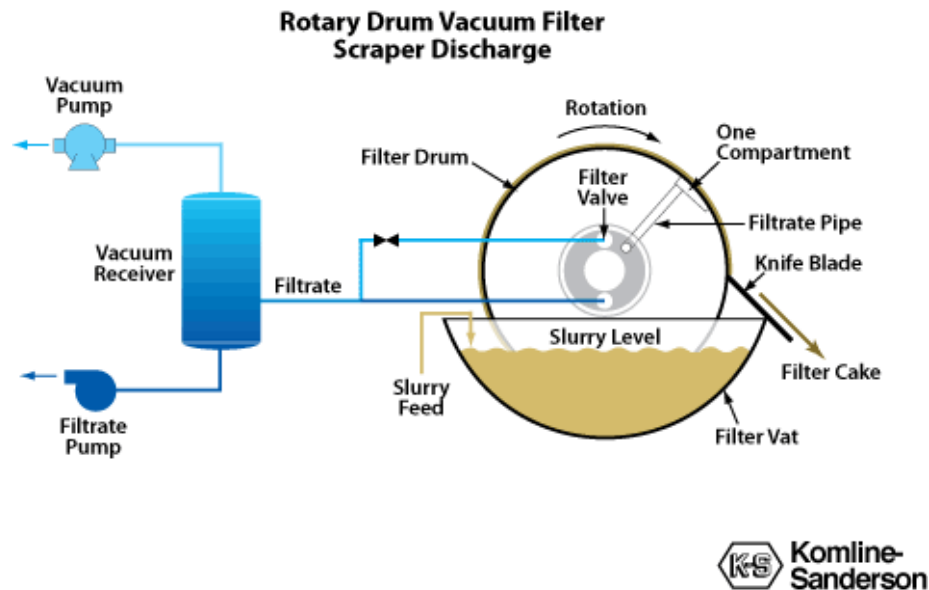


Figure 18. Rotary Drum Vacuum Filter.<sup>22</sup>

### *Trickle Bed Reactor*

From the ethanol-mixing tank, a solution of muconic acid in ethanol will be fed through a filter to the trickle bed reactor. The trickle bed reactor will allow the muconic acid to be hydrogenated to adipic acid through the use of a 1% palladium on carbon (Pd/C) catalyst. The trickle bed will be run at approximately 24°C. A muconic acid-ethanol solution will be fed through the trickle bed reactor. Hydrogen will also be fed through the trickle bed reactor, at a pressure of 24 bar (approximately 400psi). In order to get the hydrogen to a pressure of 400 psi, the hydrogen will be fed to the trickle bed reactor through a Sprague PowerStar 4 S010P4BS010 gas compressor. Based on the chemical equation shown in Figure 19, a flowrate of 198 L/hr of hydrogen is required in the trickle bed reactor to convert cis-cis-muconic acid to adipic acid. A second gas compressor at the outlet of the trickle bed reactor is used to recycle the hydrogen back to the first gas compressor. We assumed that the second gas compressor would be the same type (Sprague PowerStar 4 S010P4BS010) as the first gas compressor.

The trickle bed reactor is a combination of multiple components. The first component in the trickle bed reactor is a pressure-tested column that is packed with pellets of the Pd/C catalyst. The muconic acid-ethanol solution and the hydrogen gas will enter the top of the column, and flow (trickle) over the Pd/C pellets. The effluent of the trickle bed reactor column is a liquid gas mixture. This mixture is sent to a series of flash tanks. The first flash tank is at high pressure, and the second flash tank is at low pressure. These flash tanks are used to separate the liquid and the gas. The hydrogen gas from both flash tanks is then recycled back to the tower inlet via the second compressor. The majority of the recycled hydrogen comes from the first flash tank. About 11 tons of the liquid (adipic acid) is sent to the evaporative crystallizer per day. Figure 20 shows the set-up of the trickle bed reactor.

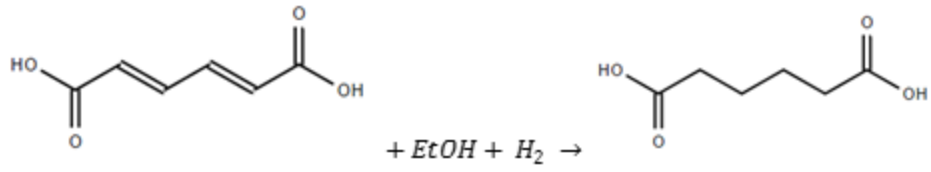


Figure 19. Hydrogenation of muconic acid to adipic acid.

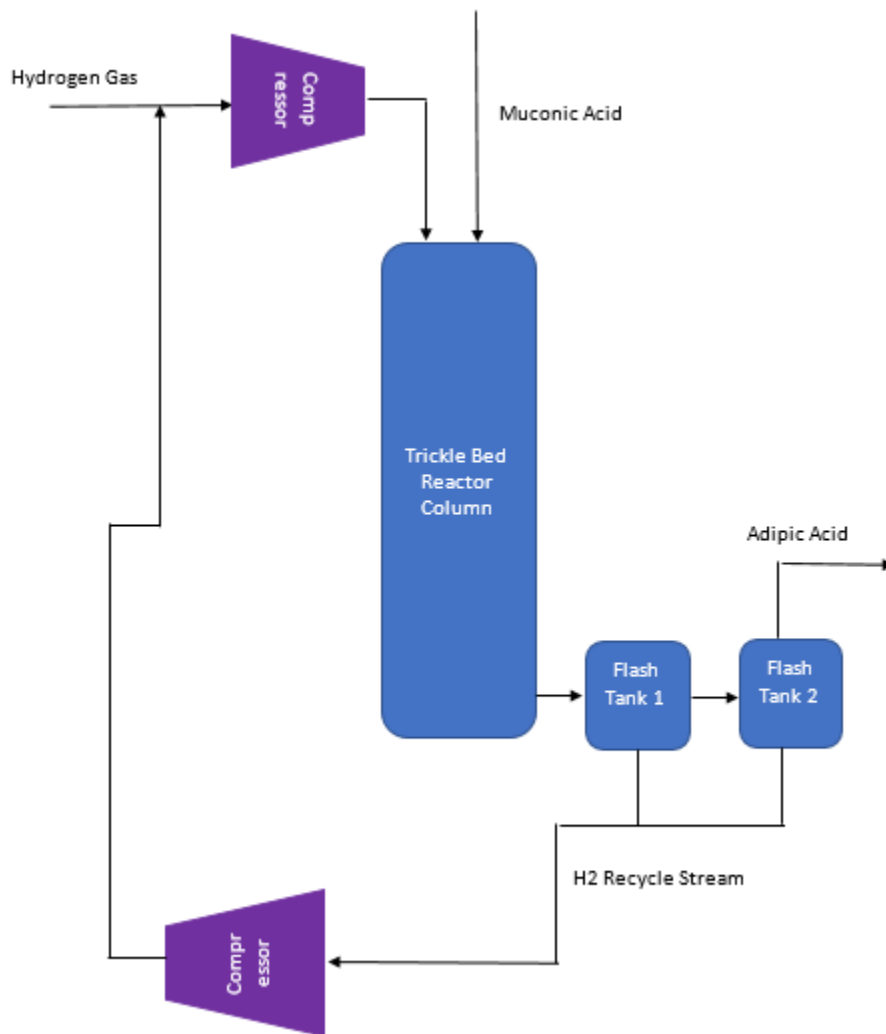


Figure 20. Trickle bed reactor and hydrogen compressor set-up.

The chemical equation in Figure 19 is not balanced. To produce one mole of adipic acid, two moles of hydrogen is needed for every one mole of muconic acid. Using stoichiometry, a flowrate of about 198 L/hr of hydrogen gas was calculated to convert about 11.66 tons/day of muconic acid into adipic acid. Using high and low pressures, the flash tanks in the trickle bed reactor separate the liquid phase from the gas phase; thus, the hydrogen gas is separated from the adipic acid solution. By using a catalyst, the hydrogen gas bonds with the muconic acid and breaks the double bonds to form adipic acid.

A 1% palladium on carbon catalyst was chosen for this process based on NREL's research. In NREL's first paper about converting lignin to adipic acid, Pd/C was compared to multiple catalysts at multiple weight percentages.<sup>1</sup> NREL found that Pd/C was the most active catalyst, have a selectivity to adipic acid of over 97%.<sup>1</sup> In NREL's second paper discussing lignin to adipic acid, they did a more in depth study of the catalyst. NREL compared catalyst activity, and the catalyst lifetime.<sup>2</sup> Based on the results of the second NREL paper, Pd/C was still the chosen catalyst for this process.

### *Evaporation Crystallizer*

As the last unit operation in this process, the evaporation crystallizer is used to separate the adipic acid from the ethanol in the liquid outlet stream from the trickle bed reactor. The crystallizer utilizes the large differences in physical properties to achieve separation. The boiling point of ethanol is 78°C,<sup>18</sup> whereas the boiling point of adipic acid is 265°C.<sup>19</sup> Since the boiling point of ethanol is significantly lower than that of adipic acid, this allows the heating of the mixture to a temperature high enough to evaporate all of the ethanol but not the adipic acid. This evaporated ethanol will then have to go through a cooling process and will be recycled back into the ethanol tank. A 1% loss of ethanol per year is assumed. The ethanol is only being used as a solubilizing agent and is not being used up. Theoretically, 100% recycle could be assumed; however, it is more realistic to assume that there is some ethanol loss during the process. It is not assumed to escape due to a leak, but with the adipic acid product. Also, a larger loss than probably realistic was assumed so that the total ethanol cost would be overestimated rather than underestimated. The adipic acid will remain in the crystallizer in its crystalline form and will need to be removed. Since adipic acid is our final product, it would leave the crystallizer as a slurry in ethanol where it would be dried and then enter a shipping tank or some other storage container to be shipped to customers where it will most likely be used for the manufacture of nylon-6,6.

Further studies will be required to determine the properties of the muconic acid when dissolved in ethanol. On its own, muconic acid has a melting point of 194°C,<sup>20</sup> which would suggest that it would not evaporate in the crystallizer. If this is the case, it can be concluded that unreacted muconic acid is the impurity in our adipic acid product. Knowing this information would allow us to determine how critical this impurity would be. However, if when solubilized in ethanol the muconic acid does evaporate from the crystallizer, it in theory would allow us another chance to react the unreacted material. NREL reports a 99.8% pure adipic acid product,<sup>2</sup> however, which is acceptable for sale and nylon-6,6 synthesis.

## Design Alternatives

### *Bioreactor*

The production of adipic acid from lignin is regulated by the ability of the engineered bacteria, *P. putida* KT2440-CJ102, to convert lignin to muconate (process limited by contact area). Currently, a value of 160 g/L (grams of lignin per liter of bioreactor broth) has been reported by NREL, Vardon, D.R. *et al.* (2016). Although, this value was considerably improved from previous work, roughly 20 g/L in 2015, 160 g/L is still low for a reasonable implementation of this process at an industrial scale (see Economics section). In order to make this process more economically attractive either, the amount of lignin per volume of bioreactor broth must increase or the reaction time (72 hours) must decrease. These two factors mainly depend on the engineered bacteria since other considerations such as biological reaction conditions (temperature, pressure, and medium) have been studied and optimized.<sup>1,2</sup> Thus, if significant improvements are made to the engineered bacteria in the near future, then the project economics would drastically improve and design alternatives such as making the entire process continuous to increase production could be considered. For instance, consider the case where the 160 g/L is tripled to 480 g/L. The impact of this change on the revenue based upon adipic acid production would be from \$7,432,000 to \$22,296,000 for the same size units. Cost would only increase by the extra amounts of raw materials, activated carbon for separation, and catalyst for hydrogenation. All the hardware will remain the same size (no cost) because the total volume processed per bioreactor does not change, only becomes redistributed. Specifically, the volume increased by the extra lignin gets decreased from the M9 minimal medium added to the bioreactor. Note that the amount of M9 medium is obtained from an inversely proportional function of the amount of lignin in the bioreactor (limiting factor based on the current limitations of the engineered bacteria to process lignin, 160 g/L). Hence, if the bacteria become more dependent on lignin and less on the M9 medium (160 g/L value increases), M9 per bioreactor decreases as lignin increases resulting in no net volume change.

Another important consideration is the sterilization of lignin to ensure no contamination in the bioreactor. A contaminant could jeopardize the lignin to adipic acid process, as the biological conversion of lignin to muconate is quite sensitive to disturbance, specially the engineered bacteria. The main contaminant would be mold formation if lignin is not reacted right after leaving the lignocellulosic ethanol plant. Thus, lignin storage or long distance transportation must account for a pretreatment process before the lignin gets fed into the bioreactor. The chemical plant for the lignin to adipic acid process presented in this report only utilizes close to 10% of the lignin produced by an average size lignocellulosic ethanol plant. Therefore, there is no need for the current design to transport lignin from other lignocellulosic ethanol plants (long distance transportation) or store it (available in excess). Furthermore, a pretreatment process for lignin was not part of the base case in the current design. If pretreatment is considered however, acid is recommended because the use of heat could result in the formation of endospores in the lignin.

According to NREL,<sup>1,2</sup> after the biological conversion of lignin to muconate a liquid product (no solids) is obtained. If this is not the case at an industrial scale, a separation unit would be required after the bioreactor and before the cross-flow filter. If there is sufficient

density difference between the bioreactor broth and the solids a separation that relies on gravity will be used. This unit could be a clarifier (solids denser) or a gravity filter using a mesh to retain the solids (bioreactor broth denser). If both densities are similar a more sophisticated method such as centrifugation will be required.

#### *Activated Carbon Packed Bed Reactor*

Activated carbon was chosen as an adsorbent due to its relatively low cost, origin from renewable resources, and effectiveness for removing impurities from aqueous media.<sup>2</sup> Oxygenated aromatics are easily adsorbed by activated carbon whereas aliphatic acids are not.<sup>1</sup> NREL demonstrated adsorption of most impurities with no loss of muconate by using activated carbon. This is extremely important as it is the muconate that is further converted into adipic acid. Muconate recovery and purity cannot be sacrificed.

While still using activated carbon, a few different methods for adsorption were explored. The original process designed by NREL did not use a packed bed column as mentioned before. They added activated carbon to the muconate broth in a batch reactor set-up and stirred the mixture for one hour.<sup>1</sup> Originally, it was thought that the industrial process could use this method as well. A batch reactor would be put in the same location as the current column, and the effluent from the bioreactor filters would enter. The appropriate amount of activated carbon would be added and the solution would be stirred until tests showed the absence of aromatics and impurities. The problem with this design is that it eliminates the possibility of a continuous process. The impure muconate stream would need to be stopped after every addition to the batch reactor, and the pure muconate stream would need to be filtered to remove the activated carbon. This design was rejected, and the packed bed column design was implemented. The packed bed column design offers a more continuous operation with less required labor.

Due to the replacing of the column after activated carbon exhaustion, the process will still need to be stopped periodically. In the future, if this process continues to be explored, it may be useful to place several columns in parallel so that the exhausted one can be replaced while the others are still in operation.

Another potential design to be explored in future work is the pulsed bed activated carbon process.<sup>13</sup> This system is comprised of a packed bed column with the periodic addition of fresh carbon and discarding of spent carbon. A general design can be seen in Figure 21. This was not explored due to time and monetary constraints.

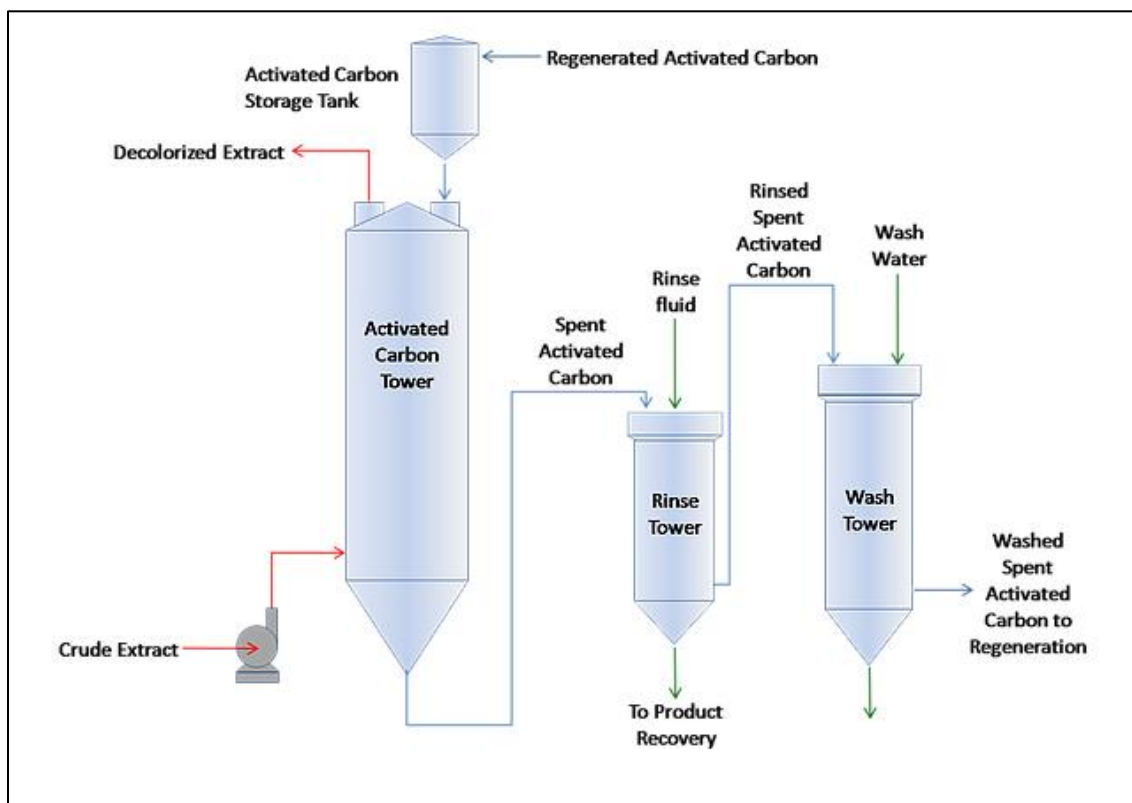


Figure 21. A general design of a pulsed bed activated carbon process where the impure solution enters at the bottom, is pumped up through the activated carbon bed, and exits at the top as a purified solution. Fresh carbon is added through the top as exhausted carbon is discharged at the bottom. The exhausted carbon is rinsed and sent to regeneration. Taken from “Stevia Extraction Technology” (2017).

It may also be desirable to implement a solvent extraction process to remove the bulk of the aromatics before sending the final impurities to an activated carbon packed bed. An experimental program to demonstrate the effectiveness of the solvent extraction of these particular aromatics would be required before implementation, though.

### *Cooling Crystallizer*

Initially the combination of the sulfuric acid and the cooling of the solution were both carried out within a crystallizer. However, with additional research this idea was rejected as it did not appear to be stable or reliable. If the acid was added directly to the crystallizer, thorough mixing could not be guaranteed and it would be difficult to control the pH of the solution. There was also the possibility that this could cause unnecessary damage to the crystallizer by adding the acid directly into it. The extra cost of paying for both a mixing tank and a crystallizer was deemed necessary in order to have a safe, functioning process.

An evaporative crystallizer was considered but dismissed because the reaction is dependent on temperature, specifically cold temperatures. Without further experimentation and studies, we did not feel that we could implement an evaporation crystallizer while still

maintaining the full extent of the reaction that is occurring. However, further studies may indicate that we indeed are able to use such a crystallizer in the future.

#### *Rotary Drum Vacuum Filter (1)*

A water spray that is applied to the drum may help increase the purity of the muconic acid in this step, however, a large portion of the impurities is due to the way the crystals are grown. Due to the way the crystals are formed, salty impurities are trapped within the crystals themselves as well as being present in the filtrate. Therefore a water spray would help to eliminate some of the impurities that are present at the surface of the crystals, however it would not eliminate our need for secondary purification.

#### *Ethanol Storage Tanks*

This volume of ethanol storage tanks possibly will not be necessary for use. This is due to the potential of our plant being in close proximity to the cellulosic ethanol plants producing our lignin feedstock. If the plant is next to the ethanol source, fewer storage tanks would be needed and would serve only as reserve storage if for some reason the ethanol plant were to shut down. If this is the case this would cut down on capital costs of the tanks, but we would need to include proper piping from the ethanol feed to our CSTR. The piping would need to have proper coating to ensure corrosion does not occur, and the ethanol may need to be pretreated to allow it to be at proper conditions for our plant to obtain the best purity of our product.

#### *Continuous Stirred Tank Reactor*

For the CSTR, an alternative is simply an agitated mixing tank, as this could give the proper agitation needed to solubilize the muconic acid in the ethanol and would be cheaper due to needing fewer units. A larger storage tank could be found so that only one would be necessary, eliminating some capital cost from our project. Batch reactors and plugged flow reactors were eliminated due to the nature of these reactors, and the fact that a residence time of 1 hours is needed.

#### *Rotary Drum Vacuum Filter (2)*

Alternative methods of filtration can be used in this process. Since the ethanol is volatile and could evaporate in the rotary filter, a physical mesh filter could be used. This would need to be of small enough mesh to allow only the muconic acid slurry to pass through, something of 100 nm mesh sizing. Studies on a small scale have shown micron syringe filters to work for this, and NREL used a 0.2 $\mu$ m PES membrane to filter their solution. This filter would need to be large scale to be implemented into our pilot plant design; however, this would lower overall capital cost.<sup>22</sup> Additionally, a belt filter could be used along with a wash system. This could be implemented on the industrial scale and would better allow for the filtering of the liquid ethanol solution.

### *Trickle Bed Reactor*

One potential alternative to a trickle bed reactor is a slurry reactor. In a trickle bed reactor the catalyst is fixed. In a slurry reactor, the catalyst particles are smaller and in motion within the reactor.<sup>23</sup> There are several potential benefits to a slurry reactor. Slurry reactors provide good temperature control, have a potentially high rate of reaction if the catalyst is highly reactive, have easy heat recovery, is adaptable to either batch or flow processing, and the catalyst can be readily removed and replaced if the working life is short.<sup>23</sup> There are also several disadvantages to slurry reactors. Slurry reactors are difficult to use to obtain high degrees of conversion, have difficulties with catalyst removal using a filter, and the high ratio of liquid to solid allows homogeneous side-reactions to become more important.<sup>23</sup> Although a slurry reactor has potential benefits, a trickle bed reactor was chosen for this process because a high conversion of muconic acid to adipic acid is desired, and slurry reactors do not obtain high degrees of conversion.

The hydrogenation of muconic acid to adipic acid requires a catalyst. Like NREL, this process currently uses a Pd/C catalyst to hydrogenate muconic acid to adipic acid.<sup>1,2</sup> However, other catalysts were considered for the hydrogenation of muconic acid. NREL tested a rhodium on carbon (Rh/C) catalyst for the hydrogenation of muconic acid, and report their results.<sup>2</sup> We also considered using a Rh/C catalyst, but we decided to use results from the initial NREL paper, and use a Pd/C catalyst because NREL never specifically says what catalyst they use in their second paper.<sup>1,2</sup>

In the future, different catalysts should be examined for use in the trickle bed reactor. NREL just tested different weight percents of Rh/C and Pd/C to hydrogenate muconic acid. However, if another catalyst can be found that is more active, and less expensive than either Rh/C or Pd/C, that catalyst will be ideal for this process. The use of a nickel catalyst should also be examined instead of a precious metal catalyst. In nickel catalysts compared to precious metal catalysts, the metal is less active, but it is also less expensive, so more of the catalyst can be used.

The operating conditions of the trickle bed reactor should also be explored further. NREL ran their catalysis at a pressure of 24 bar and a temperature of 24°C.<sup>1</sup> These operating conditions should be researched further to determine if they hydrogenate the optimum amount of muconic acid into adipic acid. Also, these conditions should be examined to determine if they work for an industrially scaled process, as opposed to a laboratory scaled process.

### *Evaporation Crystallizer*

A few alternative designs were considered for removing the ethanol from the adipic acid. NREL did not go into detail about the method they used to remove the ethanol, which left much room for investigation.

Since there is such a drastic difference in the boiling points of ethanol and adipic acid, a distillation column was considered. Since the melting point of adipic acid is very high, 151-154°C,<sup>6</sup> this tower would have to operate at very high temperatures to prevent the solidification of the

adipic acid which would not be achievable without pressurization of the column. This may not be a problem if enough solvent (ethanol) is present. Overall, a crystallizer proved more effective, though. With a crystallizer there is no reflux, so the liquid only needs to be boiled once, which is significantly more energy efficient. In addition, crystallizers are designed to produce large, bulky crystals, which makes separation convenient.<sup>24</sup> If the distillation column produced liquid adipic acid, with little to no ethanol impurities, though, it may be the better choice because it would eliminate the need for a filter and dryer after the crystallizer.

A flash drum was also considered as a reasonable option since the goal is to evaporate off the ethanol while leaving behind the adipic acid. If the flash drum is run under the right settings, the ethanol could be vaporized while the adipic acid remains in crystalline form, with each going to a heat exchanger once leaving the drum. Like the distillation column, this would be less energy efficient than a crystallizer because the flash has to be above the melting point of adipic acid. The capital cost, however, would be less.<sup>24</sup>

Overall, a crystallizer proved to be the best design. It tends to leave impurities in solution, which results in a purer product. The impurities would be recycled long with the ethanol, so they would need to be addressed at some point in the process. Crystallizers are designed specifically for crystallizing a desired product (adipic acid) out of solution (ethanol), so it can be safely concluded that a crystallizer is the best choice for this final step of the process.

## Permitting and Environmental Concerns

### *Environmental Concerns*

The materials used in this process generate some environmental concerns. According to the safety data sheet (SDS) for the M9 medium used to feed the bacteria, M9 is hazardous to aquatic life.<sup>25</sup> M9 is also not biodegradable.<sup>25</sup> The sulfuric acid that is used to crystallize the muconic acid in this process is also harmful to aquatic life.<sup>26</sup> However, unlike the M9 medium, sulfuric acid is biodegradable.<sup>26</sup> The ethanol that is used to dissolve the muconic acid is 95% biodegradable according to the SDS.<sup>18</sup> Ethanol is also harmful to aquatic life.<sup>18</sup> Finally, the final product of this process, adipic acid, is also harmful to aquatic life.<sup>19</sup> Adipic acid is only 83% biodegradable.<sup>19</sup> Due to the environmental concerns produced by the materials in this process, permitting needs to be done for this process, and its materials. All of the other materials in this process do not have any environmental concerns associated with them.

The manufacturing of organic chemical compounds is type K hazardous waste.<sup>27</sup> In this process, muconic acid and adipic acid are the organic chemical compounds produced. Salts with a concentration greater than 3% are considered P001 hazardous waste.<sup>27</sup> The M9 medium contains salts. However, the salts in the M9 medium do not exceed 3%.<sup>2</sup> Due to its corrosive nature, sulfuric acid is considered a type D002 hazardous waste.<sup>27</sup> Most of the potential hazardous wastes in this process are not normally produced as waste, except the waste stream of sulfuric acid, and other compounds, from the cooling crystallizer. Because of sulfuric acid in the waste stream of the cooling crystallizer, a hazardous waste permit needs to be obtained for this process.

### *Hazardous Waste Permitting*

Permitting is the main method of properly handling hazardous waste generation. Several steps must be taken in order to obtain a hazardous waste permit. First, the business looking to get a hazardous waste permit must hold a pre-application meeting with the public.<sup>28</sup> In this case, PetroPalooza would announce the pre-application to meeting via a sign on the facility property. PetroPalooza may also use the radio, television, internet, or newspaper to advertise the pre-application meeting. During the meeting, the business must present its plans to operate the facility, including the proposed processes and the waste it will handle.<sup>28</sup> At the pre-application meeting, PetroPalooza would explain the entire lignin to adipic acid process, and how M9, sulfuric acid, muconic acid, and adipic acid are hazardous waste. Then the public would be given an opportunity to ask questions and make suggestions.<sup>28</sup> Finally, the business can choose to incorporate the public's suggestions in the permit application, and the permitting agency will use the attendance list to set up a mailing list for the facility.<sup>28</sup>

The second step to getting a hazardous waste permit is to submit a hazardous waste permit.<sup>28</sup> The hazardous waste permit application comes in two parts: part A, and part B.<sup>28</sup> Part A of the application is EPA form 8700-23.<sup>28</sup> Part B of the application is a narrative form that describes how the facility will be designed, maintained, and controlled to protect the environment and public health.<sup>28</sup> Part B will also include how potential emergencies will be handled, how the facility will handle any potential environmental contamination, and how the

facility will clean up and close once it is no longer in operation.<sup>28</sup> In part B of the permit application, PetroPalooza would describe that everything potentially hazardous in this process is controlled by safety measures, and will be disposed of properly by using a hazardous waste disposal company. PetroPalooza will also generate as little hazardous waste as possible by recycling, and regenerating all possible materials.

Thirdly, to obtain a hazardous waste permit, the permitting agency receives and reviews the hazardous waste permit application.<sup>28</sup> Once the application is received, the permitting agency notifies everyone on the calling list, and makes a copy of the application available to the public area.<sup>28</sup> Meanwhile, the permitting agency also ensures that the applications contains all the required information.<sup>28</sup> Also during this time, the permitting agency evaluates the proposed design and operation of the facility, and determines if it can be built and operated safely.<sup>28</sup>

If the hazardous waste permit application is deficient in any aspect, the permitting agency will send a notice of deficiency (NOD) to the applicant.<sup>28</sup> The applicant will then revise the application, and send it back to the permitting agency.<sup>28</sup> This process can then be repeated if deficiencies continue to occur.<sup>28</sup> For example, if a permitting agency informed PetroPalooza that it was not doing enough to eliminate the waste of aromatic compounds, PetroPalooza would examine further options for eliminating aromatic compounds besides just activated carbon adsorption.

Once all revisions are complete, the permitting agency makes a preliminary decision about whether to issue or deny the hazardous waste permit.<sup>28</sup> If the application meets appropriate standards, the permitting agency issues a draft permit containing the conditions at which the facility can operate.<sup>28</sup> If the permitting agency decides that the application does not meet appropriate standards, then they deny the permit and prepare a “notice of intent to deny”.<sup>28</sup> Once a decision is made, the permitting agency gives notice to the public.<sup>28</sup> Once the announcement is made the public has 45 days to comment, and request a public hearing.<sup>28</sup>

Finally, the permitting agency makes a final decision whether to grant or deny the hazardous waste permit.<sup>28</sup> The agency issues a “response to public comments,” and specifies any changes from the draft permit.<sup>28</sup> Then the agency can grant or deny the final permit.<sup>28</sup> Once the final permit is issued the permitting agency continues to monitor the facility, and ensure that it is compliant with federal rules.<sup>28</sup> Because this process is a potential hazardous waste generator, PetroPalooza needs to go through the process detailed above to obtain a hazardous waste permit.

### *Air Quality Permitting*

Carbon dioxide is a green-house gas. In this system, CO<sub>2</sub> may be produced from the heating system, and from the bacteria in the bioreactor. For this project, the heating system was not investigated. While the heating system would most likely produce CO<sub>2</sub> and CO, the heating system was not investigated, so the carbon dioxide and carbon monoxide from the heating process was not considered. Carbon dioxide is also produced by most aerobic organisms, such as the aerobic bacteria used in the bioreactor for this process. However, the CO<sub>2</sub> from the bacteria is biomass-derived, and biomass-derived CO<sub>2</sub> is not normally considered as a contributor to global

warming. Therefore, an air emissions permit for the CO<sub>2</sub> produced by the bacteria in the bioreactor is not required.

Ethanol is a volatile organic compound. Because this process is storing ethanol in a liquid storage tank, an air quality permit may need to be obtained for the storage of ethanol.<sup>29</sup> In Iowa (EPA location 7), where this process is located, state and local authorities have the primary responsibility of Clean Air Act (CAA) permitting.<sup>30</sup> So PetroPalooza would need to go through the Iowa state authorities to obtain an air quality permit for the ethanol storage tank.

Because the ethanol tank may require an air quality permit, a best available control technology (BACT) analysis was performed on the ethanol tank (see Appendix). Four types of control technologies were examined for the BACT analysis on the ethanol storage tank. The first control technology examined was an internal floating roof and seal system. An activated carbon vapor recovery system was examined as the second control technology. Thirdly, a refrigerated vent condenser was examined as a control technology. Finally, thermal oxidation control was researched as a control technology. A BACT analysis was conducted on all of these control methods, and the optimum option was selected.

The thermal oxidation vapor control system was the most effective volatile organic compound (VOC) vapor control system. Thermal oxidation vapor control removes up to 98% of VOC vapors.<sup>31</sup> In this system, the ethanol storage tank emits about 0.16 tons/yr and 0.04 lb/yr of VOC vapor emissions.<sup>32</sup> Therefore, thermal oxidation control reduces ethanol vapor emissions by about 0.16 tons/yr and 0.039 lb/yr. The yearly cost of a thermal vapor control system was estimated to be about \$70.<sup>33</sup> Using Equation 1 and the estimated cost of thermal oxidation control per year, the average cost effectiveness of thermal oxidation vapor control was calculated as about \$910 per ton.<sup>34</sup>

$$(1) \text{ Average cost effectiveness} = \text{TAC}/(\text{baseline-control})$$

Where, TAC is the estimated yearly cost of the control system, baseline is the baseline emission rate, and control is the emission rate with the control method in place. Using Equation 2, the incremental cost effectiveness of thermal oxidation vapor control was estimated to be \$7896 per ton.<sup>34</sup>

$$(2) \text{ Incremental cost effectiveness} = (\text{TAC control-TAC next})/(\text{emission next-emission control})$$

Where, TAC control is the estimated yearly price of the control option currently being discussed, TAC next is the yearly estimated price of the control option discussed next, emission next is the estimated emissions of the control option discussed next, and emission control is the estimated emission of the control currently being discussed.

The second most effective emission control method for the ethanol storage tank is activated carbon vapor recovery. Activated carbon vapor recovery removes about 95% of VOC vapor emissions.<sup>31</sup> Based on the estimated emissions of the ethanol tank, activated carbon vapor recovery would reduce ethanol vapor emissions by about 0.15 tons/yr, and 0.038 lb/yr. The

yearly cost of activated carbon vapor recovery was estimated to be about \$32 per year. Using Equation 1 and the estimated cost of activated carbon vapor recovery, an average cost effectiveness of \$210 per ton was estimated. The incremental cost effectiveness of activated carbon vapor recovery was estimated using Equation 2, and found to be about -\$27300 per ton.

The third most effective ethanol emission control method was a refrigerated vent condenser. A refrigerated vent condenser removes about 90% of VOC vapor emissions.<sup>31</sup> A refrigerated vent condenser reduces ethanol emissions by about 0.14 tons/yr and 0.036 lb/hr. The estimated yearly cost of a refrigerated vent condenser is about \$250.<sup>35</sup> By using this information and Equation 1, the average cost effectiveness of a refrigerated vent condenser was estimated at about \$3906.25 per ton. The incremental cost effectiveness of a refrigerated vent condenser was calculated to be about -\$72115 per ton.

The final control method examined for ethanol emission control on the ethanol storage tank was an internal floating roof and seal system. The internal floating roof and seal system was the least effective control system for controlling ethanol emissions. An internal floating roof and seal system removes 69% to 98% of VOC vapor emissions.<sup>31</sup> Therefore, on average an internal floating roof and seal system only removes about 84% of VOC vapor emissions. Using this information, an internal floating roof and seal system only reduces ethanol vapor emissions by 0.13 tons/yr and 0.03 lb/hr. The annual cost of an internal floating roof and seal system is about \$1000.<sup>36</sup> Equation 1 was used to estimate the average cost effectiveness of an internal floating roof and seal system, and the average cost effectiveness of an internal floating roof and seal system was estimated to be \$7485 per ton. Because an internal floating roof and seal system was the last control technology examined to reduce ethanol vapor emissions, no internal cost effectiveness cost was calculated for an internal floating roof and seal system.

The results of BACT analysis were analyzed, and used to decide the best technology available to control ethanol emissions from the ethanol storage tank. A thermal oxidation vapor control system has the highest removal of VOC vapor emissions, but it has an average cost effectiveness of \$910 per year compared to an average cost effectiveness of activated carbon vapor recovery of \$210 per year. That equates to a difference in average cost effectiveness of \$700 per year for only a difference of 3% ethanol vapor emission removal. Therefore, activated carbon recovery was determined to be the best available control technology for ethanol vapor emissions.

Activated carbon vapor recovery is the best available control technology for the ethanol tank for several reasons. As mentioned above, activated carbon removal has a low yearly price of about \$32. It also has an average cost effectiveness of \$210 per year which is \$700 less than the second cheapest control method (thermal oxidation vapor control). Also, there is already activated carbon being used in this process, so there is no need to buy one more product to use in this process. Activated carbon vapor recovery does have one drawback concerning reducing ethanol vapor emissions. Activated carbon vapor recovery works well for nonpolar VOCs, and ethanol is polar.<sup>31</sup> Due to this fact, activated carbon vapor recovery may reduce ethanol vapor emissions by less. However, given the current information, activated carbon vapor recovery is still the best available control technology for reducing ethanol vapor emissions from the ethanol storage tank.

If this process produced enough yearly ethanol vapors (100 tons/yr), then it would require an air quality permit for the storage of ethanol. However, the process for producing adipic acid from lignin only emits 0.16 tons/yr of ethanol vapors. Therefore, unless more ethanol was used in this process, and more ethanol vapors were released (meeting the yearly limit), an air quality permit is not required for the ethanol vapor emissions from this process.

### *Environmental Comparison to Petrochemical Process*

Lignin to adipic acid produces hazardous waste and air emissions, but compared to the conventional petrochemical process, lignin to adipic acid produces significantly less environmental concerns. The conventional petrochemical process of producing adipic acid is typically done in two steps. First the oxidation of cyclohexane is used to produce cyclohexanone and cyclohexanol.<sup>37</sup> Next this ketone-alcohol mixture is oxidized with nitric acid to form adipic acid.<sup>37</sup> Nitric acid and water are removed from the adipic acid, and nitric acid is a hazardous waste for the conventional process.<sup>37</sup>

The conventional petrochemical process of producing adipic acid also produces more air emissions than the process that uses lignin to produce adipic acid. Carbon monoxide (CO) is produced in the first step of the conventional petrochemical process.<sup>37</sup> In the second step of the conventional petrochemical process, NO<sub>x</sub> gas is produced.<sup>37</sup> There are also particulate emissions from the drying, cooling, loading, and storage of the adipic acid.<sup>37</sup> The potential sources of air emissions from the process of converting lignin to adipic acid are CO<sub>2</sub> produced from the bacteria in the bioreactor, CO<sub>2</sub> produced from heat exchangers within the process, and ethanol vapors from the ethanol storage tank.

In the oxidation of cyclohexane, carbon monoxide, carbon dioxide, and other organic compounds are emitted.<sup>37</sup> At the end of the adipic acid manufacturing process, a waste stream from the oxidation of cyclohexane contains metals, residues from catalysts, and volatile and nonvolatile hydrocarbons (nonvolatile residue).<sup>37</sup> These two waste streams may be used as fuel for process heating units as a way to help reduce air emissions from the production of adipic acid.<sup>37</sup> A caustic soda solution can be used as a final purification method.<sup>37</sup> If this caustic soda solution is used for final purification, the spent caustic waste can be burned or sold as a byproduct.<sup>37</sup> While burning the nonvolatile residue helps eliminate some air emissions, burning the nonvolatile residue also emits cobalt and chromium, so the pollution is not completely eliminated.<sup>37</sup> Also, storing the nonvolatile residue in tanks emits caproic, valeric, butyric, and succinic acids.<sup>37</sup>

The oxidation of nitric acid mainly produces NO<sub>x</sub> as an air pollutant. The NO<sub>x</sub> can be stripped from the effluent of the nitric acid oxidation through a bleaching column.<sup>37</sup> From the bleaching column, NO<sub>x</sub>, carbon monoxide, carbon dioxide, and DBA are contained in the effluent gas stream. The gaseous effluent from the nitric acid oxidation and the bleaching column are then passed through an adsorption tower to recover most of the NO<sub>x</sub>.<sup>37</sup> However, the adsorption tower does not remove significant amounts of nitrous oxide (N<sub>2</sub>O).<sup>37</sup> Therefore, there are still air emissions even if the majority of the NO<sub>x</sub> is recovered.<sup>37</sup> Recovering the NO<sub>x</sub> also requires controls that adds cost to the process.

Controlling NO<sub>x</sub> reduction can be done using two methods. First extended absorption of the NO<sub>x</sub> can be done by increasing the volume of the absorber, extending the residence times, or providing sufficient cooling to remove the heat released from adsorbing NO<sub>x</sub>.<sup>37</sup> Thermal reduction can also be used to reduce NO<sub>x</sub> in the system.<sup>37</sup> Thermal reduction is the process of reacting NO<sub>x</sub> with excess fuel in a reducing atmosphere.<sup>37</sup> The cost effectiveness of extended absorption \$98 per ton.<sup>37</sup> Whereas, the cost effectiveness of thermal reductions is \$458 per ton.

Product drying, cooling, storage, and loading operations of adipic acid emit dust particulates.<sup>37</sup> Scrubbers and bag filters are commonly used to control particulate emissions from adipic acid.<sup>37</sup>

Compared to the conventional petrochemical process, converting lignin to adipic acid has some advantages and disadvantages. Converting lignin to adipic acid has less of an environmental impact than the conventional petrochemical process used to produce adipic acid. In the process of converting lignin to adipic acid, there are only a few sources of air emissions: CO<sub>2</sub> and CO from the heating system, CO<sub>2</sub> from the bacteria in the bioreactor, and ethanol vapor from the ethanol storage tank. In the conventional petrochemical process, there are several sources of air emissions. Carbon monoxide, carbon dioxide, NO<sub>x</sub>, DBA, metals, particulates, and N<sub>2</sub>O are all possible air emissions in the conventional petrochemical process.<sup>37</sup> Therefore, the conventional petrochemical process of producing adipic acid is less environmentally friendly, and would require more permitting, and equipment to reduce air emissions than the lignin to adipic acid process.

Hazardous waste is also an environmental concern that applies to both processes. The process of producing adipic acid from lignin handles M9 medium, sulfuric acid, muconic acid, and adipic acid. These materials are all potentially hazardous wastes. Because the amount of salts in the M9 medium is less than 3%, M9 is not considered a hazardous waste in this case. The conventional petrochemical process of producing adipic acid handles nitric acid, cyclohexane, cyclohexanol, cyclohexanone, and adipic acid. These are all, also, potentially hazardous wastes. The process of producing adipic acid from lignin has three potentially hazardous wastes, and the conventional petrochemical process of producing adipic acid has five potentially hazardous materials. Thus, more permitting and equipment needs to be used in the conventional petrochemical process in order to discard of hazardous waste compared to the process of producing adipic acid from lignin.

Finally, the cost effectiveness of control methods for each air emission can be compared for each process. To control air emissions from the ethanol storage tank in the lignin process, there are four possible solutions. First a thermal oxidation vapor control system could be used to reduce ethanol vapor emissions. Second, activated carbon vapor recovery could be used to reduce ethanol vapor emissions. Third, a refrigerated vent condenser could be used to reduce ethanol vapor emissions, and an internal floating roof and seal system could be used to reduce ethanol vapor emissions. Activated carbon vapor recovery was chosen as the best control system because it removes approximately the same amount of ethanol vapor and it has a low average cost effectiveness than thermal oxidation vapor control. Therefore, the average cost effectiveness of controlling ethanol vapor emissions was determined to be \$210 per ton. However, the average cost effectiveness of a thermal oxidation vapor control system, a refrigerated vent condenser, and

an internal floating roof and seal system were \$910 per ton, \$3906 per ton, and \$7485 per ton respectively. For control of NO<sub>x</sub> emissions in the conventional petrochemical process there were only two options: extended absorption, and thermal reduction. Extended absorption has a cost effectiveness of \$98 per ton, and thermal reduction has a cost effectiveness of \$458 per ton.<sup>37</sup> Both of these control methods have better cost effectiveness than the methods of control that were not chosen for the lignin process. However, only the extended absorption has a higher cost effectiveness than the activated carbon vapor recovery.

Based on environmental impacts, permitting, and average cost effectiveness of control, the process of producing adipic acid from lignin is the more environmentally friendly process. The process of converting lignin to adipic acid produces less air emissions, and less hazardous wastes. Using extended adsorption to control NO<sub>x</sub> emissions does have a lower cost effectiveness than using activated carbon vapor recovery to control ethanol vapor emissions, but NO<sub>x</sub> is not the air emission from the conventional petrochemical process. Ethanol is the only air emission for the lignin to adipic acid process. Therefore, more controls would be needed for the conventional petrochemical process. Thus, based on this information, the production of adipic acid from lignin is more environmentally friendly than the conventional petrochemical process.

## Safety and Risk Management

### *Chemical Concerns*

#### Sulfuric Acid

Sulfuric acid is very corrosive, especially at the concentration required for our process (98%). At this concentration, the pH of sulfuric acid is roughly 1.2, which is very acidic.<sup>26</sup> Due to its highly corrosive nature, typical structural materials will not be suitable for containment or piping purposes.<sup>14</sup> Therefore, we have decided to use a storage tank composed of polyethylene and 316 stainless steel will be used for bolts and unit operations that contain sulfuric acid; it has been proven that these materials are compatible with highly concentrated sulfuric acid, however, if the concentration were to ever drop lower (<93%) there is high possibility that the steel will be damaged.<sup>14</sup> Sulfuric acid is significantly heavier than water, roughly 2 times the weight of water to be exact; the polyethylene design accounts for this and is strong enough to hold it.<sup>14</sup> Further precautions may need to be implemented for the pipes and the unit operations down the line. For unit operations that involve the sulfuric acid, 316 stainless steel will be used; the pipes, and possibly the unit operations as well, will be coated with an oxidant resistant resin. This will be to support the structural integrity of these materials, as well prevent the production of hydrogen gas from the reaction between the metal and acid.

There are no chemicals used in our design that are incompatible with sulfuric acid. However, highly concentrated sulfuric acid is known to create aerosols, or vapors, when water is added to it.<sup>15</sup> The fluid that is moving the muconate through the system is M9 cell media, which is essentially water. This could potentially result in a severe explosion, therefore the acid mixing tank will need to be carefully monitored to assure that the acid is slowly being added to the muconate and not the other way around. This results in a more controlled reaction with less likelihood of a runaway reaction. A runaway reaction could result in extreme temperatures, which would damage the tank, and also extreme pressures which would result in an explosion.

Since sulfuric acid is corrosive, it presents the typical problems to humans and all life when they come in contact with it. When it comes in direct contact with the skin or eyes it will result in severe and when inhaled it severely damages the mucous membranes of the lungs as well in the throat.<sup>26</sup> Exposure can also result in inflammation, edema, headache, nausea and more.<sup>26</sup> The Internal Agency for Research on Cancer has also found that “occupational exposure to strong inorganic-acid mists containing sulfuric acid is carcinogenic to humans”.<sup>26</sup> Additional information on the effects of sulfuric acid can be found in the Safety Data Sheet. Sulfuric acid is even more of a risk than most strong acids in general because it produces highly exothermic reactions and therefore is capable of producing severe thermal burns on top of the already destructive chemical burn.<sup>15</sup> This also means it has a dehydrating effect when it touches things, particularly living things, which leads to even more complications in an already dire situation.<sup>15</sup>

In case of small sulfuric acid spills, absorbent materials will be kept on hand and close by. Possible absorbents may include: PIG® pads specific for corrosive materials (or other brand of absorbent pad), absorbent pillows or socks, vermiculite or sodium bicarbonate. Additional studies will need to be conducted to determine the most likely cause and location of a small spill

which better determine which type of absorbent and which form will be ideal for our plant. In the event that a large spill occurred, it is likely we would need to evacuate the plant and have it professionally cleaned. However, if this pilot plant were to be successful and expanded into a larger plant we could potentially hire a group of operators or specialists to undergo the appropriate respirator and HAZWOPER training so that we would have an on-site HAZMAT crew to handle such things.

When sulfuric acid is exposed to fire it produces other harmful chemicals like sulfur oxides and hydrogen sulfide. Sulfur oxides are not only air pollutants, but they also react to form sulfuric acid in the atmosphere which results in acid rain. Hydrogen sulfide is a very poisonous gas that results in fatality when inhaled. If a fire were to occur, water, alcohol-resistant foam or carbon dioxide can be used to extinguish it.<sup>26</sup>

### Hydrogen Gas

Hydrogen is an extremely flammable gas; it is also kept under pressure which increases the impact it would have if it were to catch fire. Due to its high flammability, we must keep all sparking and possible ignition sources away from the unit operations that contain hydrogen. Additionally, we will be required to regulate the temperature around the hydrogen operations and ensure that the ambient temperature does not exceed 52 °C (125°F) as heat alone is enough to trigger an explosion.<sup>38</sup>

All unit operations that hold hydrogen will have emergency pressure reliefs. Also, these unit operations will not be enclosed in a secondary structure to allow for adequate ventilation. Ventilation is important because hydrogen can easily displace the oxygen in the air which will result in asphyxiation for anyone in the area.<sup>38</sup> However, this does mean that in the case of hydrogen release, there is excessive hydrogen in the air which has the potential to result in a massive explosion if an ignition source is present. Hydrogen has flammability limits of 4% to 76%,<sup>38</sup> meaning that it does not require excessive amounts of hydrogen present to burn. Additionally, when released hydrogen will rapidly expand and can result in severe burns or frostbite.<sup>38</sup>

In the event that a spill should occur, the area will need to be evacuated immediately due to explosion and asphyxiation risks. Once evacuated, emergency personnel will need to be contacted to manage the leak. Since hydrogen is an asphyxiant, and therefore requires an air providing respirator when working in an environment, operators should not try to fix the situation unless properly trained and the leak can easily be fixed.

### Ethanol

Ethanol is an extremely flammable, volatile liquid. In order to best control the effects of it, we will keep the ethanol in properly enclosed tanks with pressure relief valves to prevent massive explosions. To help prevent any accidental ignition or explosions, we will ensure that there are no spark producing sources anywhere near operations that involve ethanol. Additionally we implement explosion-proof electrical, lighting and mechanical equipment in the area. Since the flashpoint of ethanol is 14°C (57.2 °F),<sup>18</sup> it is crucial that all ignition sources are removed

from the environment. There are no oxidizing or incompatible chemicals used in our process which decreases the risks associated with ethanol due to chemical reaction significantly.

The boiling point of ethanol is 78° (172 °F).<sup>18</sup> Although it is highly unlikely that the ambient temperature will ever reach this point, it is possible that direct sunlight could increase the temperature within the tank to excessively high levels. In order to determine how much of a threat this is, additional studies concerning the weather and sun patterns in the location will need to be conducted. However, ethanol has been used in industry for years and our plant is being built off an existing cellulosic ethanol plant so the possibility of boiling, which would lead to an explosion due to pressure build up, is highly unlikely. Also, we are building off of an existing cellulosic ethanol plant so the necessary precautions concerning ethanol storage should already be accounted for and explored.

Ethanol is a known carcinogen in addition to being generally toxic to living things.<sup>18</sup> Due to this, we would likely want to build these operations in some sort of secondary containment so that if something were to happen the ethanol would be contained and would not reach water sources or harm wildlife. It also causes irritation of the respiratory tract and the eyes.<sup>18</sup> Since precautions are being taken to avoid exposure and release, these issues would only become a concern in the event of an accident.

In the event of a spill, common absorbents such as PIG® pads for flammable liquids, vermiculite and absorbent pillows can be used. If the spill is small enough, only basic personal protective equipment would be required, however if it is larger a respirator would be needed to avoid the negative health effects the vapors of ethanol have. In the event that there were a small fire, water spray or alcohol-resistant foam can be used to extinguish it. However, due to the flammable nature of ethanol and its vapor, if the fire is not small and cannot be managed quickly and safely, evacuation would be necessary as it is very likely that an explosion will occur.

### Other

There are several other chemicals used in our process, however they have minimal concerns when it comes to the safety of the operations, the people and the environment. Lignin is the by-product of reacted corn stover; therefore it is an organic material that comes from nature and has no harmful effects. Like any powder, there may be slight respiratory irritation when inhaled but it should not result in any negative health effects.<sup>39</sup> More information can be found in the safety data sheet for lignin.

Activated carbon (charcoal) is being used to absorb some impurities in the solution after biological conversion. Activated charcoal is not hazardous and only produces a very small chance of flammable powder in operations that will not be conducted at our plant.<sup>40</sup> More information concerning the properties of activated carbon can be found in the safety data sheet.

Palladium, specifically palladium on carbon, is a non-regulated (transportation) chemical that does not present many hazards. It results in irritation of the eyes and skin when it comes in contact with them, however these have not been determined to become severe.<sup>41</sup> Also, there is a small chance that a flammable dust may form, however it is highly unlikely that this will occur

due to the way that the catalyst is being used in our process.<sup>41</sup> More information can be found in the safety data sheet.

The M9 media used to support bacteria life consists of the salts: ammonium sulfate, potassium phosphate monobasic, sodium chloride and sodium phosphate dibasic.<sup>2</sup> Out of all these salts, only sodium phosphate dibasic,<sup>43</sup> is actually classified as hazardous while the rest are not classified. All of these salts are safe to use and the only damage will occur if there is a spill and they reach the water systems as they will cause some harm to aquatic life. There is potential for dangerous reaction when these salts are combined with other chemicals, however they should not come into contact with any of these and therefore are determined to be safe throughout our operation. More information concerning these possible reactions and the exact toxicity to wildlife can be found in the safety data sheets.<sup>43-46</sup>

Adipic acid is classified as an environmentally hazardous substance.<sup>19</sup> It causes harmful effects to aquatic life and some bacteria, however effects on humans are currently minimal with only irritation of the eyes when it is contacted.<sup>19</sup> At its solubility point in water (23g/L at 25°C), the pH of the solution is 2.7.<sup>19</sup> This means that it is acidic and may possibly exhibit some properties characteristic of corrosive materials. It has a melting point of 151-154 °C (305-309 °F) which is what allows us to utilize evaporation crystallization to separate it from the ethanol.<sup>19</sup> We will likely implement some kind of secondary containment around the evaporation crystallizer so that in the event of a leak or spill, the adipic acid would not be introduced into the environment and cause problems.

Several of these chemicals have the potential to produce a combustible dust. However, under nearly all circumstances in our process they will be wetted so the likelihood of producing a combustible dust during typical operations is very small. We will be sure that proper handling techniques are implemented during periods of maintenance and whenever the materials are being changed (such as the activated carbon) to minimize the production of dust when these materials are not wetted.

All of the chemicals listed under this section can be put using typical fire extinguishing procedures (water spray, alcohol resistant foam, etc.) in the event of a fire. Since they do not pose extreme hazards, typical spill procedures can also be used. This includes absorbent materials in the event of a liquid spill and a broom and dust pan for solid spills.

### *Biological Concerns*

Our process also utilizes genetically modified bacteria (*Pseudomonas Putida* KT2440) to convert our raw lignin into muconate.<sup>1,2</sup> Since it is genetically modified, it is classified as a Biosafety Level 2 (BSL-2) which means that it poses a moderate hazard to surrounding personnel as well as the environment.<sup>47</sup> Due to this, all operators will be required to undergo special training in order to be allowed to work with the bacteria and restricted access will be required when the bacteria are being actively manipulated.<sup>47</sup> Further requirements specific to the handling of BSL-2 organisms can be found in the Center for Disease Control and Prevention's guide to biosafety.<sup>47</sup> Secondary containment will be required for all unit operations that involve

the bacteria in order to reduce the potential of introducing this foreign bacteria into the environment.

It should be noted that the bacteria being used in our system was created using scarless integration, which means that it will not be antibiotic resistant. This is important as we do not want to accidentally introduce a new super bug into the environment.

### *Unit Operation Concerns*

A thorough hazard and operability study (HAZOP) was conducted for the entire plant design. A complete description of all possible hazards for the units can be found in Appendix B, however some of the major issues for the bigger units will be discussed further here.

#### M9 Storage Tank

The biggest concern for the M9 storage tank is that it will overflow. This could be due to a number of things including an excessive of raw materials being pumped in or reverse flow into the tank due to a faulty pump or valve. The most concerning result of this would be the releasing of the salts, which have a negative impact on aquatic life, into the environment. In order to minimize the damage, we will place the storage tank in some kind of secondary containment so that the released liquid would not reach anything of importance.

#### Bioreactors

The most critical failures that could happen to the bioreactors that would result in the most destruction to the surroundings would be the bioreactors overflowing or the pressure becoming too high. The bioreactors could overflow if the feed pump for the M9 and lignin failed open or if backflow was introduced to the system. This overflowing of the bioreactor would result in an increase of pressure, however the more concerning increase of pressure would come from the air blower being stuck open and the relief valve stuck closed. Both of these scenarios would result in the release of contents, whether it comes from a steady overflow or a small explosion. This would result not only in the loss of M9 media, which poses problems for aquatic life, but it also results in the release of the genetically modified bacteria. More information concerning the actual effects of these can be found in the chemical and biological concerns sections.

#### Cross Flow Filter and Activated Carbon Bed

While both the cross flow filter and the activated carbon bed seem like simple, small units in our process, they are both critical to the process as they remove many impurities that what would otherwise cause significant problems for units and reactions down the line. One of the worst things that could happen to each of these would be either a plug somewhere in the outlet or an excess of inlet fluid. A plug in the outlet could result in excess pressure within the unit that could lead to damage in the structural integrity and, if extensive enough, could result in a release of contents. Additionally, the pumps that control this would be damaged and operations may have to be halted to fix this. An excess of inlet flow would result in improper filtration and could upset the filter, specifically the activated carbon in the packed bed. Both of these would

result in an excess of impurities throughout the operation which have an unknown effect on the rest of the system at this point.

### Sulfuric Acid Mixing Tank

A major concern for the sulfuric acid- muconate mixing tank would be the temperature becomes excessively high; since sulfuric acid typically results in exothermic reactions this is very real issue. The major result that comes from high temperature would be extreme thermal strain on the tank which could eventually lead to tank rupture. Tank rupture would result in the loss contents from the tank. This poses serious health and environmental risks. As described in the chemical concerns section, the sulfuric acid we are using is very concentrated and can corrode and react with metals as well as living tissues. Additional issues with the sulfuric acid itself can be found under the chemical concerns section.

### Crystallizer

While overflow is a concern for the cooling crystallizer as well, a bigger concern would be a malfunction of the heat exchanger, specifically one in which the heat exchanger is not able to reduce the temperature to the set point. Such a problem would arise if there were a leak in the heat exchanger or if the valve that controls the flow of cooling water was broken. The reaction requires a decreased a temperature in order to occur, or at least to occur completely. This means that while some of the sulfuric acid will have converted, a majority of it will not. Since unit operations following the cooling crystallizer are not built to handle strong acids this will result in the corrosion and severe damage of the drum filter 1 and possibly all of the ethanol operations. These damages would be very expensive and would likely result in the release of contents into the environment.

### Rotary Drum Vacuum Filters (1 and 2)

While there are some incidents that could occur that would result in physical and environmental damage, the more probable malfunctions of the drum vacuum filters would damage our production and the finances of the plant. All of these problems, which include an excess or lack of pressure or an improper speed of drum rotation, would all stem from mechanical issues. Since this form of filtration relies on the vacuum suction, a high pressure (lack of a vacuum) would result in a very wet mixture coming off the filter, meaning that we are not receiving pure crystals. If this is the first filter this may not be a huge issue since it goes through a second “purification” with the ethanol, however if this were to happen with the second filter we would be losing significant amounts of product in the waste. An extremely low pressure (extreme vacuum) could result in cavitation of the drum itself which would require maintenance of the unit and possible replacement. This creates a production burden, as we will not be able to run the process without either of these units, as well as a financial burden for the repair or replacements of the unit.

### Ethanol Mixing Tank (CSTR)

The worst thing that could happen concerning the ethanol CSTR would be overflow, either due to a feed pump malfunction or backflow. As stated in previous units this would result in release of reagents. This would result in significant air pollution as ethanol is a volatile organic compound. More information about ethanol and its effect on the air and environment can be found in the permitting and environmental concerns section.

### Trickle Bed Reactor

The trickle bed reactor runs at a high pressure (24 bar) and uses compressed hydrogen gas. The combination of strain due to high pressures and material strain due to the hydrogen make explosion a serious risk for this operation. An explosion, due to excessive pressure or material strain, would result not only in the loss of contents but would also create massive structural damage and may possibly end in a fire due to the extreme flammability of the reagents in use.

### Evaporation Crystallizer

A critical mishap that could occur with evaporation crystallizer would be extreme temperatures, either too hot or too cold. Depending on the severity of the low temperature, either the final product will not be separated from the ethanol or there could possibly damage to the unit operation itself. Though the loss of product would be detrimental to our finances, damage to the material of the crystallizer could result in the release products to the environment. This presents problems as ethanol is an air pollutant and adipic acid is environmentally hazardous. More concerning the actual hazards posed by the chemicals themselves can be found in the chemical hazards section.

An excessively high temperature in the evaporation crystallizer would likely result in thermal strain of the metal. If this becomes chronic it will weaken the metal to point where collapse or cracking could occur, in which case the release of product would also occur. Additionally, an increase in temperature would also result in an excess of ethanol vapor which would increase the pressure in the vessel and possibly result in an explosion. This would lead not only to the release of product to the environment but would also result in physical damage due to the power and the debris from the explosion.

## Economics

### *General Information and Approaches*

To be competitive, a lignin to adipic acid plant would have produce 250,000 tons of adipic acid per year. This is based on the capacities of current adipic acid producing petrochemical plants.<sup>3</sup> Using the yields that NREL obtained in the lab scale production of adipic acid from lignin, the amount of lignin required for a 250,000-ton adipic acid per year capacity was calculated to be approximately 584,000 tons of lignin per year. The lignin will come from cellulosic ethanol plants, and the three largest cellulosic ethanol plants in the US are only estimated to produce a total of approximately 200,000 tons of lignin per year as a byproduct.<sup>48</sup> This presents a major constraint. Rather than attempting to design a plant that will immediately compete with the petrochemical plants, a small pilot plant will be designed to determine if the process is technically and economically feasible. Lignin will be obtained from one cellulosic ethanol plant and the lignin to adipic acid plant will be built nearby.

The processing capacity of this plant is 7800 tons of lignin per year, or 21.4 tons/day. The sizes of the unit operations are based on this feed rate and the data given in, Vardon, D.R. *et al.* (2015) and Vardon, D.R. *et al.* (2016). All of the laboratory numbers were scaled up linearly based on this lignin feed rate. All costs were estimated and adjusted to today's date.

### *Major Equipment Cost*

The costs of the major equipment needed for this plant can be seen in Table 1.

Table 1. Purchased cost of each piece of major equipment needed for a new lignin to adipic acid plant.

Equipment Name	Size	Units	Number	Price per Unit	Total Price
M9 storage tank	375000.00	L	1	\$ 220,000.00	\$ 220,000.00
Bioreactors	170000.00	L	3	\$ 300,000.00	\$ 900,000.00
Blower	2.10	m <sup>3</sup> /s	3	\$ 80,000.00	\$ 240,000.00
Cross-flow filters	140000.00	L	2	\$ 35,000.00	\$ 70,000.00
AC Packed Bed Column	9000.00	L	2	\$ 1,000.00	\$ 2,000.00
Acid Storage Tank	550.00	gal	1	\$ 436.00	\$ 436.00
Mixing Tank 1	5450.00	L	1	\$ 25,000.00	\$ 25,000.00
Cooling Crystallizer	5450.00	L	1	\$ 168,500.00	\$ 168,500.00
Drum Vacuum Filter	15.00	m <sup>2</sup>	1	\$ 262,000.00	\$ 262,000.00
Ethanol Mixing Tank	50000.00	L	2	\$ 50,000.00	\$ 100,000.00
Filter	7.50	m <sup>2</sup>	1	\$ 60,000.00	\$ 60,000.00
Trickle Bed Reactor	45000.00	L	1	\$ 276,000.00	\$ 276,000.00
Hydrogen Compressor	400.00	psi	2	\$ 2,581.00	\$ 5,162.00
Evaporation Crystallizer	45000.00	L	1	\$ 311,800.00	\$ 311,800.00

*Total Fixed Capital Investment*

Summing the total prices of each piece of equipment results in a total ISBL FOB of \$2.6 million. Both delivery and OSBL were assumed to be 10% of ISBL FOB. Adding the delivery to the purchased cost results in a delivered ISBL of \$2.9 million. An installation factor of 5.04 was chosen.<sup>10</sup> Summing the delivered ISBL and OSBL and multiplying by the installation factor gives the installed and delivered fixed capital investment. These cost estimates for equipment, delivery and installation give an FCI of \$15.9 million dollars and can be seen in Table 2.

Table 2. ISBL, delivery, OSBL and FCI for a new lignin to adipic acid plant.

Total ISBL FOB	\$ 2,640,898.00
Delivery	\$ 264,089.80
Delivered ISBL	\$ 2,904,987.80
OSBL	\$ 264,089.80
FCI FOB	\$ 3,169,077.60
<b>Installed&amp;Delivered FCI</b>	<b>\$ 15,940,460.33</b>

*Operating Costs*

Based on this installed and delivered FCI, fixed costs were calculated and can be seen in Table 3. The total fixed cost per year was estimated to be approximately \$2.2 million per year.

Table 3. Annual fixed costs for a new lignin to adipic acid plant. These include utility, manpower, and additional operating costs.

<u>Fixed Cost</u>	<u>\$</u>	<u>Reference</u>
Labor	\$ 560,640.00	(2 operators at \$20/hr)
Laboratory	\$ 56,064.00	10% labor
Maintenance	\$ 637,618.41	4% FCI
Utilities	\$ 70,000.00	Cellulosic Ethanol Plant
Licensing & Bacteria	\$ 15,000.00	NREL
Taxes & Insurance	\$ 478,213.81	3% FCI
Overhead	\$ 376,296.72	30% labor, lab., main.
<b>Total</b>	<b>\$ 2,193,832.95</b>	<b>per year</b>

The estimated prices and required quantities of feeds were used to calculate the variable costs and can be seen in Table 4. The total variable cost per year was estimated to be approximately \$4.8 million per year. The majority of this variable cost comes from the M9 media required. This nutrient solution is expensive, and a large amount is required for the bacteria. When pricing the media, the individual components were first priced in an attempt to

decrease the cost by making it from scratch onsite. However, the costs of the individual components far exceeded the cost found for pre-made media. It is the sheer amount of M9 media required that results in such a high cost. Even if the cost of M9 was reduced by 50%, it would still account for almost 40% of the total variable costs. The catalyst costs were estimated by taking NREL's lab scale ratios (5 g/L muconate broth for activated carbon and 0.075 mg/mg muconic acid for Pd/C)<sup>1,2</sup> and scaling them up to industrial size.

Table 4. Annual variable costs for a new lignin to adipic acid plant. These include feedstocks and other raw material costs.

<b>Variable Cost</b>	<b>\$/yr</b>
Lignin	\$ 232,440.00
H2SO4	\$ 3,723.60
EtOH	\$ 16,699.10
Hydrogen	\$ 132,825.00
M9	\$ 3,660,000.00
Activated Carbon	\$ 97,800.00
Pd/C	\$ 691,200.00
<b>Total</b>	<b>\$ 4,834,687.70</b>

### *Cash Flow Analysis*

Using the above equipment, fixed and variable cost estimates, a cash flow was created assuming a 10-year lifespan and a start-up of 2 years. A tax rate of 35%, MACRS5 factors, and a discount rate of 10% were used throughout the calculations. The FCI was divided equally between years -2, -1 and 0. Adipic acid is projected to sell for \$1800/ton, which results in a revenue of \$7.4 million per year. A start-up cost of \$3.3 million is required in year one, and a working capital of \$2.7 million is required in year zero and recovered in year 10. The full cash flow analysis can be seen in the appendix. An edited cash flow analysis can be seen in Table 5.

Table 5. A cash flow analysis showing years -2, -1, 0, 1 and 10. Years 2 through 9 are eliminated but can be seen in the appendix.

Tax Rate	35%				
Year (for discounting)(year end)	-2	-1	0	1	10
FCI	\$ (5,313,486.78)	\$ (5,313,486.78)	\$ (5,313,486.78)		
WC			\$ (2,656,743.39)		\$ 2,656,743.39
MACRS5 Factors				0.2	
Depr Amount			\$ 2,125,394.71		
Depr Credit			\$ 743,888.15		
Revenue			\$ 7,431,912.00	\$ 7,431,912.00	
StartUp			\$ (3,328,408.64)		
Variable Costs			\$ (4,834,687.70)	\$ (4,834,687.70)	
Fixed Costs			\$ (2,193,832.95)	\$ (2,193,832.95)	
Total Expenses (including SU)			\$ (10,356,929.29)	\$ (7,028,520.65)	
Revenue - Expenses (including SU expenses)			\$ (2,925,017.29)	\$ 403,391.35	
Tax Liability on Above Item			\$ 1,023,756.05	\$ (141,186.97)	
Cash Flow	\$ (5,313,486.78)	\$ (5,313,486.78)	\$ (7,970,230.16)	\$ (1,157,373.09)	\$ 2,918,947.77
CumCF (PV0)	\$ (5,313,486.78)	\$ (10,626,973.55)	\$ (18,597,203.72)	\$ (19,754,576.81)	\$ (11,762,441.41)
DF10	1.21	1.1	1	0.909090909	0.385543289
PV10	\$ (6,429,319.00)	\$ (5,844,835.45)	\$ (7,970,230.16)	\$ (1,052,157.35)	\$ 1,125,380.72
cumPV10	\$ (6,429,319.00)	\$ (12,274,154.45)	\$ (20,244,384.62)	\$ (21,296,541.97)	\$ (16,699,653.25)

*NPV and IRR*

The NPV and IRR were calculated using the cash flow analysis. The NPV0, the net present value with no discount rate, is the value of the cumulative cash flow in year 10, and for this project is negative \$11.8 million. The NPV10, the net present value at a 10% discount rate, is the value of the cumulative cash flow in year 10 after applying a discount factor, and for this project in negative \$16.7 million. The IRR is -11% and these values are summarized in Table 6.

Table 6. The NPV0, NPV10 and IRR for a new lignin to adipic acid plant.

NPV0	\$ (11,762,441.41)
NPV10	\$ (16,699,653.25)
IRR	-11%

The NPV0 is negative \$11.8 million, and the NPV10 is negative \$16.7 million, so overall this process is not profitable. An internal rate of return (IRR) of -11% was obtained, and knowing that the minimum acceptable rate of return (MARR) is typically around 16% for medium risk projects, this is not an attractive business opportunity. Although this process is technically feasible, it is not economically feasible. Even if this process was scaled up to consume all of the lignin produced by the cellulosic ethanol plants, it would not be profitable due to the high fixed and capital costs. The necessary lignin processing capacity of the bacteria has not yet been reached. If NREL can increase the ratio of lignin to bacteria (and thus M9 media), the process could be profitable. This is further discussed below through sensitivities.

### Sensitivity Analysis

Because this process is not economically feasible, a sensitivity analysis was performed mainly to determine what aspects of the current process must be changed to make the process economically feasible. As can be seen in table 4, one of the most expensive aspects of this process is the M9 media. A very large amount of M9 media is required for the bacteria, and the ratio of lignin that can be fed to the bioreactor to volume of bacteria/M9 solution is very small (160 g/L). As can be seen in Table 7, if the lignin to bacteria ratio can be increased, the process becomes economically feasible.

Table 7. Sensitivity analysis for a new lignin to adipic acid plant. The parameters, change in values, and resulting NPVs and IRRs are shown along with the base case.

Parameter	Change	NPV0 (MM\$)	NPV10 (MM\$)	IRR
Base Case	No change	-11.8	-16.7	-11%
Lignin-Bacteria Ratio	Increased by factor of 3	71.5	34.5	34%
Lignin-Bacteria Ratio	Increased by factor of 2	29.9	8.9	17%
M9 amount	Decreased by 50% per year	0.1	-9.4	0%
M9 amount	Decreased by 75% per year	6	-5.7	4%
M9 amount	100% recycle over project life	9.6	-4.2	6%
Project Life	Increased to 20 years	-9	-16	-6%

A tornado chart (Figure 22) was created by changing the lignin-bacteria ratio, the price of lignin, the operating costs, the fixed capital investment (FCI), and the project life (years). It is apparent from both table 7 (above) and figure 5 (below) that increasing the lignin to bacteria ratio will allow this process to be profitable. Altering other variables still results in a negative NPV. The lignin to bacteria ratio can only be increased with further research by NREL or another laboratory. For this process, the ratio from Vardon, D.R., et al (2016) had to be used for all the industrial calculations because it is the only way lignin can be effectively converted to adipic acid.

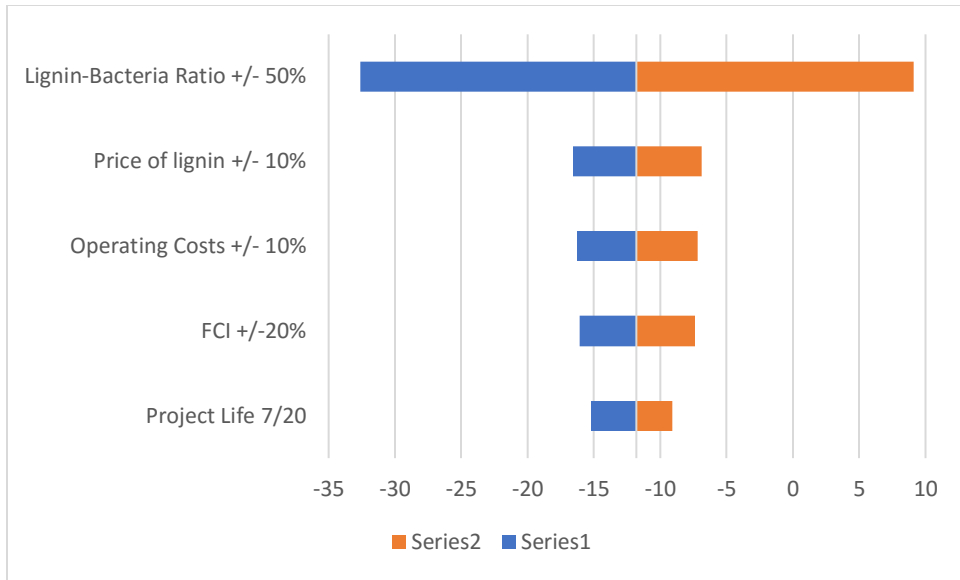


Figure 22. A tornado chart showing the effects of certain parameters on NPV. The base case NPV is -\$11.8 million. Project life is in years.

## Global Impacts

The implementation of an industrial scale lignin to adipic acid plant has both small and large scale impacts on the world around us. Here it will be discussed the contrast between the petrochemical process used to produce adipic acid, and the green, more eco-friendly way of utilizing lignin biomass to produce adipic acid.

### *Old Petrochemical Process*

Adipic acid is manufactured from cyclohexane in a series of two reactions. The first step, shown in Figure 23, the oxidation of cyclohexane and produces both cyclohexanone and cyclohexanol. This mixture is converted to adipic acid by oxidizing the cyclohexanol with nitric acid in the second reaction as shown in Figure 24. Then, the wet adipic acid crystals are separated from water and nitric acid. The product is dried and cooled before packaging and shipping. Dibasic acids are potentially recovered from the nitric acid solution as a byproduct.<sup>37</sup>

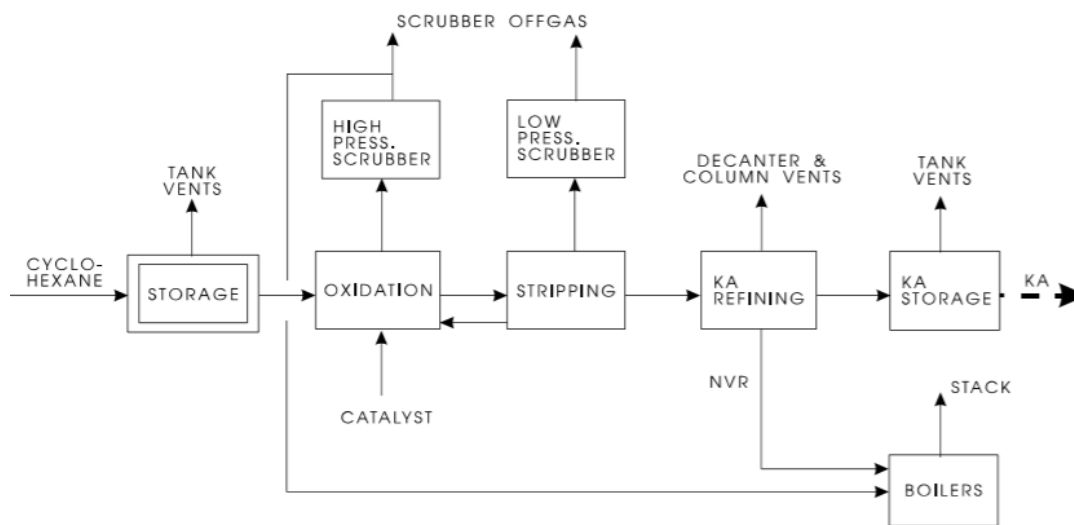


Figure 23. The first reaction in the oxidation of cyclohexanone to produce adipic acid.<sup>37</sup>

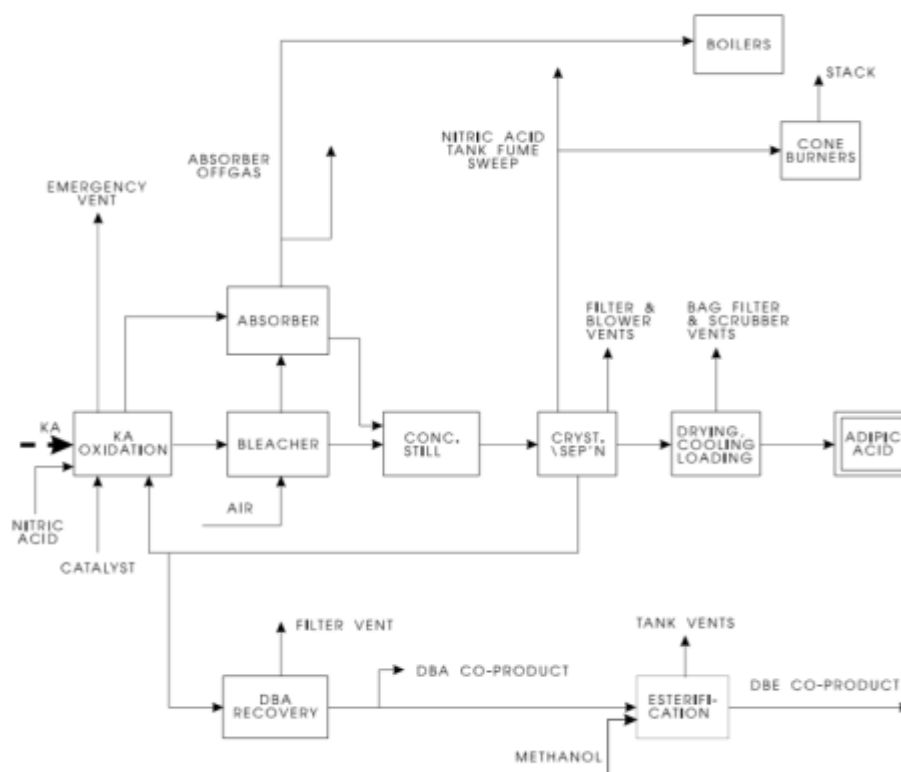


Figure 24. The second reaction in the oxidation of cyclohexanone to produce adipic acid

The liquid product contains primarily water, nitric acid and adipic acid, as well as significant quantities of NO<sub>x</sub>. The gaseous effluent from oxidation contains NO<sub>x</sub>, CO<sub>2</sub>, CO, and DBA. The gaseous effluent from both the bleaching column and the oxidation reactor are typically passed through an absorption tower to recover most of the NO<sub>x</sub>; however, this process does not significantly reduce the concentration of nitrous oxide (N<sub>2</sub>O) in the stream.<sup>37</sup>

The largest source of waste and emissions from this petrochemical process is a result of the oxidation of cyclohexane. This product will contain CO, CO<sub>2</sub>, and organic compounds and will also emit NO<sub>x</sub> gases throughout the entire process. In addition, the most concentrated waste stream, which comes from the final distillation column contain metals, residues from catalysts, and volatile and nonvolatile hydrocarbons. These waste and emissions pose a serious hazard to the environment. The greenhouse gases and carbon footprint for this process is immense and is continually dumping carbon into our atmosphere.<sup>37</sup>

**Nitrogen oxides** The use of an aqueous solution of nitric acid in the oxidation of the intermediates cyclohexanone and cyclohexanol to adipic acid results in the presence of significant quantities of oxides of nitrogen in the gaseous effluent from the oxidation process and subsequent bleaching, purification, and crystallization steps.<sup>37</sup>

### *New Biochemical Process*

Producing lignin through this series of biochemical reactions greatly eliminates harsh byproducts that the petrochemical processes have. This will reduce the amount of carbon produced from the system and also the hazardous gases like NO<sub>x</sub> and N<sub>2</sub>O and CO and CO<sub>2</sub>. Overall this is a very environmentally friendly process.<sup>37</sup> Lignin is utilized in a green way by harnessing the recalcitrant structure immediately after being produced from the cellulosic ethanol plant. The lignin is able to directly be biochemically altered and funneled into muconate which can easily be turned into muconic acid and hydrogenated into adipic acid.

This adipic acid is then able to be used to produce polyurethane, nylon, as well as bioplastics. This type of industry is on the rise, as nylon is used in synthetic fibers which will continue to be used. The biochemical way of processing this lignin would provide jobs in the near upcoming years since the lignin is able to be used immediately. In addition to this, the industrial production of adipic acid through clean, environmentally friendly processing paves the way for the globe to produce adipic acid in this sense. When this technology can be refined, harnessed, and perfected, adipic acid can be produced large scale and the petrochemical method will be obsolete.

## Conclusions and Recommendations

Currently, using lignin to produce adipic acid is not profitable, resulting in internal rate of return (IRR) values of -11% and -6% for ten and twenty years of production respectively. Nevertheless, using lignin to produce adipic acid is an attractive alternative to the conventional petrochemical process because lignin is an inexpensive feedstock. Additionally, this process is significantly more environmentally friendly (not a significant source of CO<sub>2</sub> and NO<sub>x</sub> gas emissions relative to the petrochemical approach) than the petrochemical one. However, a main flaw was uncovered when developing the process, and perhaps not surprisingly, it deals with the ability of the engineered bacteria, *Pseudomonas putida* KT2440-CJ102, to perform biological conversion of lignin-derived compounds to muconate (160 grams of lignin per liter of bioreactor broth). This is so critical because the entire process relies on this biological conversion, which occurs right at the start of the process resulting in bottlenecks at initial stages in the design. Thus, further research and advances in the technology developed by the National Renewable Energy Laboratory are required before a process that uses lignin to produce adipic acid can be implemented industrially.

In short, this report presents an alternative to the current process of producing adipic acid from the conventional petrochemical process. It also introduces the advantages and challenges of the biological approach, and suggests a base case as well as alternatives to implement the process at an industrial scale. Finally, the analysis presented in this report led PetroPalooza to conclude that using lignin to produce adipic acid is a process currently unable to compete with the well-established petrochemical approach. Even when a larger scale plant could be implemented for achieving economies of scale, the economical improvements would be insignificant due to the low amounts of lignin that can be processed by the bacteria, 160 g/L. That is where the key limitation of this biological approach resides.

Even when the process of using lignin to produce adipic acid should not be implemented right away, close attention must be given to any improvements of the technology developed by NREL specially the performance of the engineered bacteria. PetroPalooza found that subtle changes in the performance of *P. putida* KT2440-CJ102 can largely impact the economics of the process. Specifically, the amount of lignin that can be biologically converted to muconate per volume of bioreactor broth, currently 160 g/L. Thus, our recommendation is to wait and keep up with the research and advances in the technology, because using lignin to produce adipic acid has the potential to become economically profitable in the near future, representing direct competition to the conventional petrochemical process.

## **Future Work**

Based on the information provided in this report, PetroPalooza will explore more methods and specifications for the production of adipic acid. Firstly, the bioreactor poses many problems since it takes a considerable amount of lignin to convert into muconate. A lignin feed to bacteria ratio that is effective needs to be investigated, so capital cost isn't spent on the bacteria and the lignin feed. In addition to this, a severe amount of capital cost is coming from purchasing the M9 media necessary to feed the bacteria organisms. It should be investigated how necessary these vitamins and trace minerals are, and if there are alternatives for these nutrients.

The activated carbon used to adsorb the aromatics has proven to be successful, and we are not looking into the liquid liquid extraction as an alternative since we are able to get better purity otherwise. However, the activated carbon needs to be regenerated and this regeneration would be ideal if it were onsite and not needed to be shipped. We also will look into the use of the activated carbon to reduce the ethanol emissions since our plant utilizes an extreme amount of this volatile compound.

Possible use of heat exchangers with the crystallizer could be used to help with the temperature difference. The muconate needs to be at low temperature and pH, and thus a heat exchanger would help this temperature change occur if it is not included in the abilities of the crystallizer. For the CSTR, investigating the amount of ethanol used would be helpful to as to reduce our overall consumption of volatile, flammable compounds. Also looking at using a different solvent, most likely another alcohol, to solubilize the muconic acid. Lastly, the trickle bed reactor could potentially use a different catalyst that is more cost effective and able to convert to our desired product with better yield. Operating conditions of the trickle bed reactor can be investigated, right now they are running at 24 bar, but this could be investigated to see how purities change.

The largest concern for future work resides in the bioreactor. If the lignin to M9 media ratio can be reduced this will help the overall capital cost of the plant, which would make the production of adipic acid more profitable and a competitive process with the older petrochemical method.

## **Acknowledgements**

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## **Appendix A. Process Design Flowsheet**

More detailed flowsheet broken down into sections.

Figure A.1. The flowsheet of the first section of operation. The biological processes are shown here. The pink dotted line indicates a recycle stream; this stream will be discharging into the bioreactors. The blue dashed lines indicate units where multiple are being built, but only one is in operation at a time.

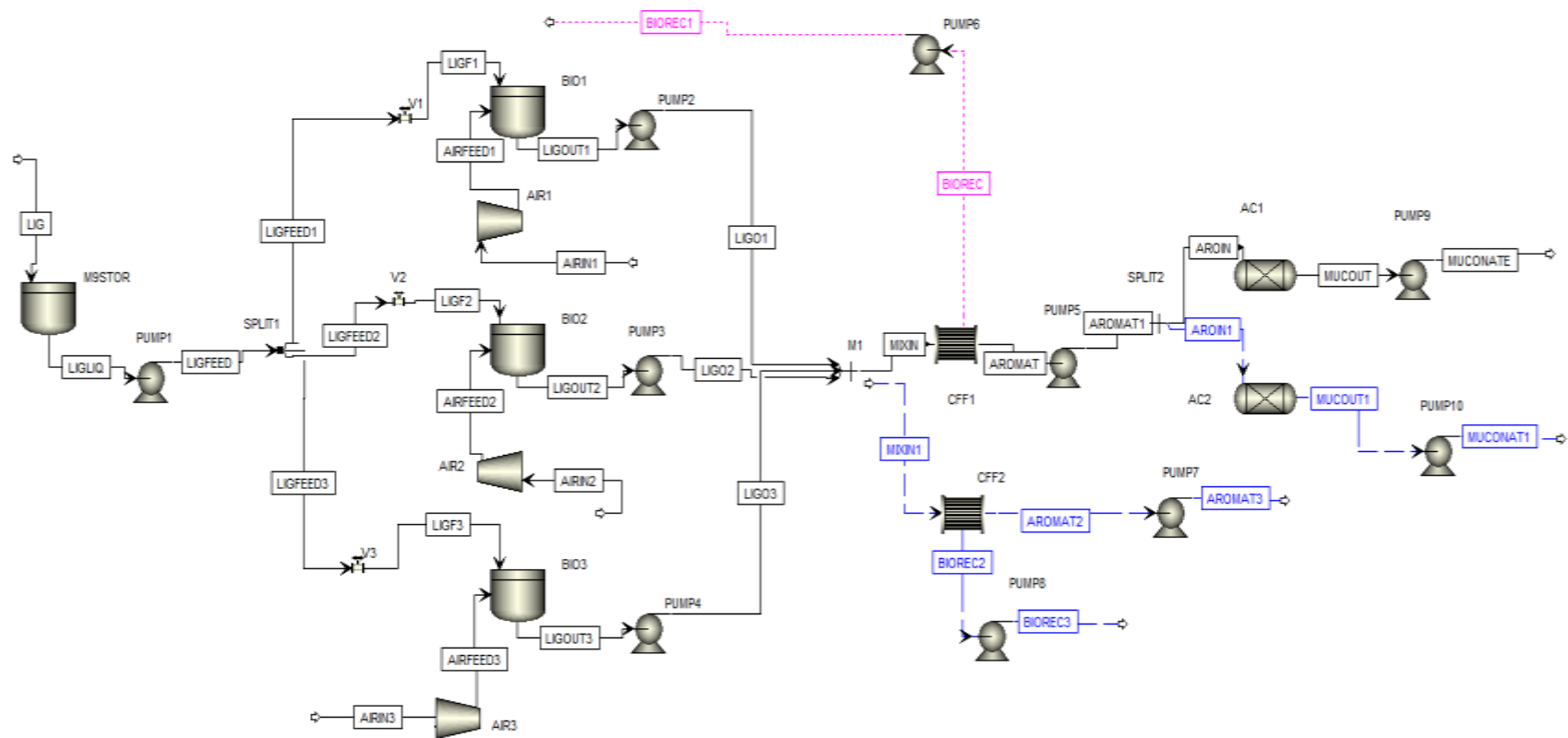


Figure A.2. Flowsheet of the section of the plant. Acidic operations occur here. The pink dotted line indicates a recycle stream which is being recycled back to the beginning of the plant.

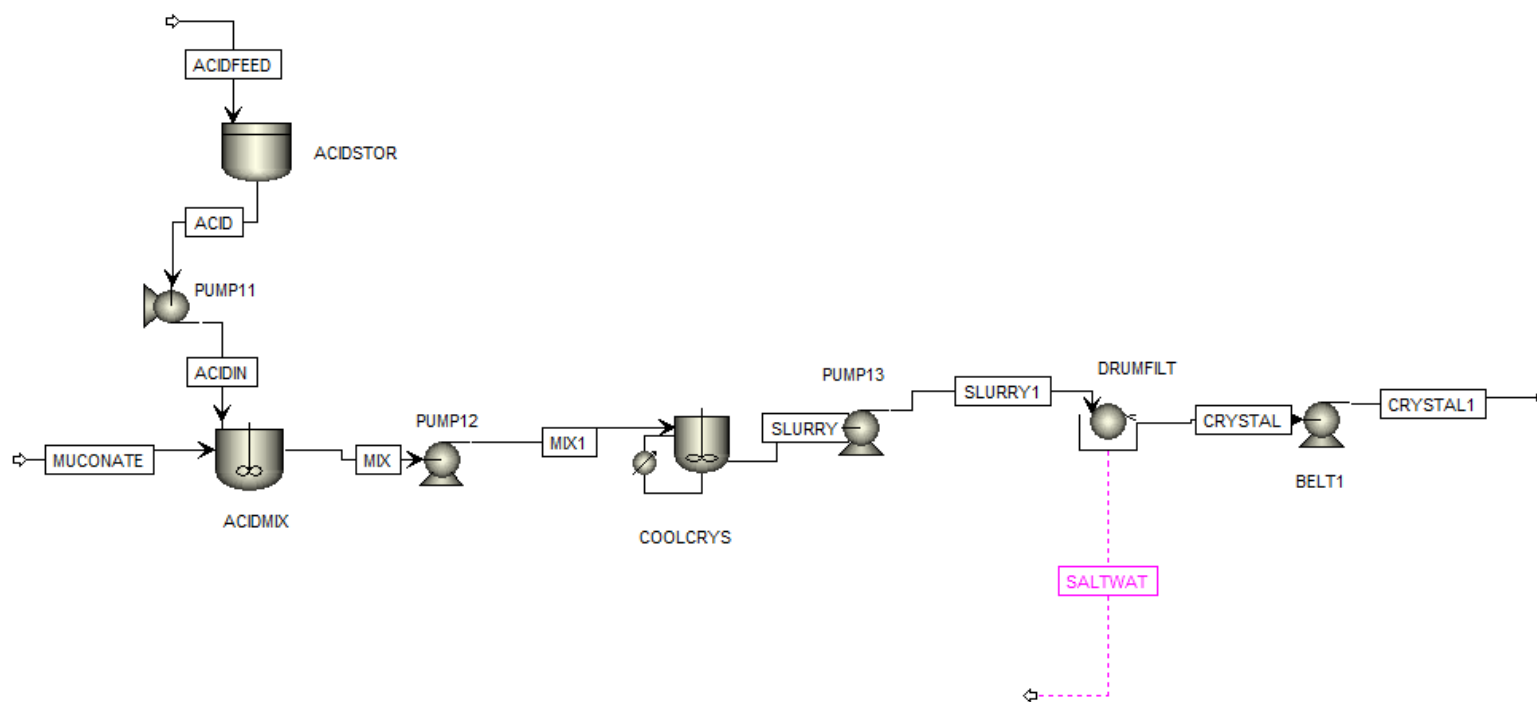
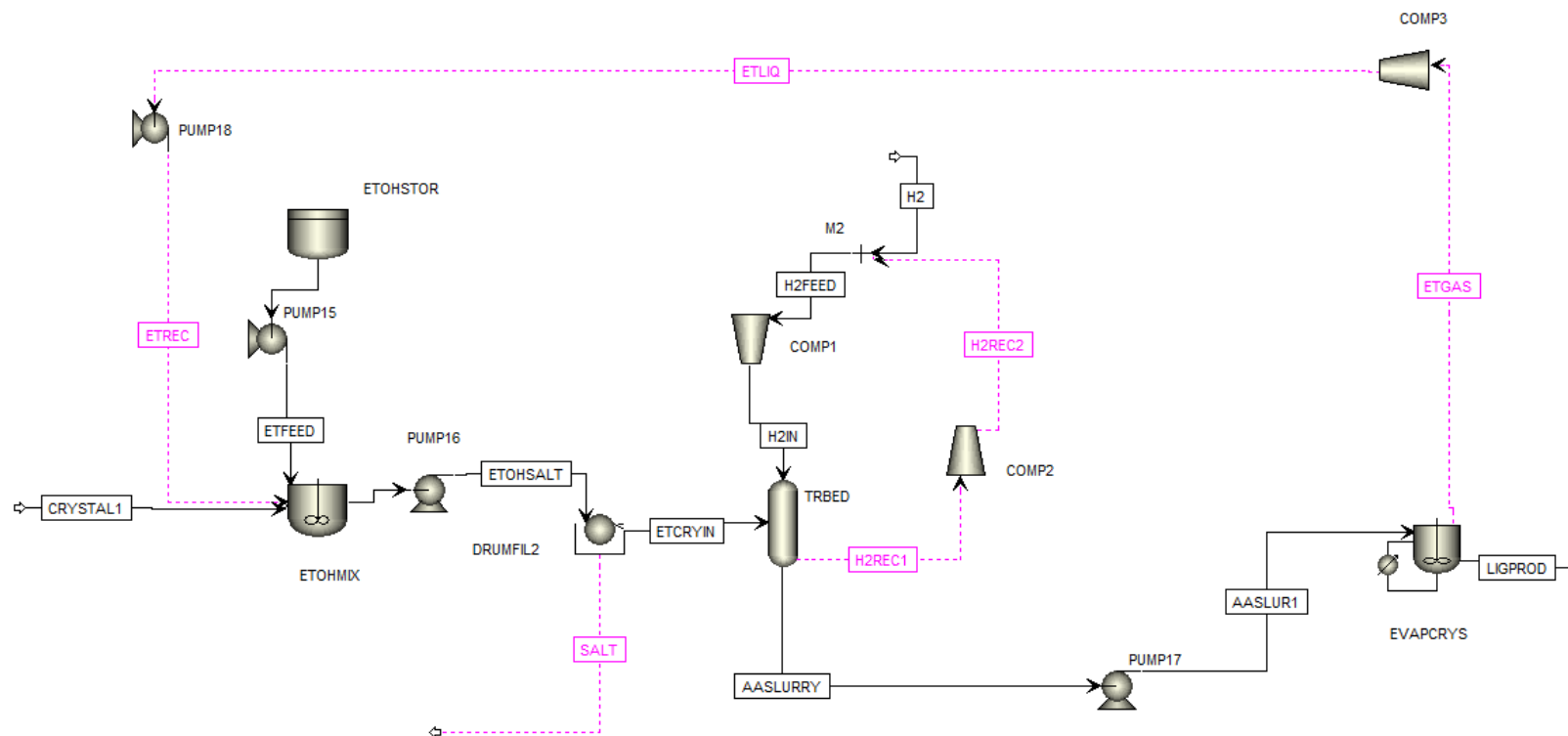


Figure A.3. The flowsheet for the third section of operation. The ethanol operations occur here. The pink dotted lines indicate recycle streams. The salt recycle stream, which does not picture its final destination, is being recycled to the beginning of the entire process.



## **Appendix B. Hazard and Operability Study (HAZOP) Table**

The following is a summarized table of the possible hazards and problems that could occur in our system and what the effects of those problems would be. Not included in this table are the alarms and controllers that would indicate that there is a problem.

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
M9 storage tank	<b>Level</b>			
	Less	Tank runs dry	Pump cavitates	Damage to pump
		Rupture discharge line	Reagent released	Potential contamination of environment
		Tank rupture	Reagent released	Potential contamination of environment
	More	Unload too much from tank truck	Tank overfills	Reagent released
		Reverse flow from process	Tank contamination from bioreactor Tank overfills	Possible reaction Reagent released
	<b>Composition</b>			
	Other than	Wrong reagent	Possible reaction	Possible tank failure
	As well as	Impurity in reagent	Upset in bioreactor	Death of the microorganisms in bioreactor
	<b>Pressure</b>			
	Less	Head loss	Reagent released	Potential contamination of environment
	More	Overfill tank	Reagent released	Potential contamination of environment
		Temperature of inlet is hotter than normal	Reagent released	Possible tank failure
		Volatile impurity in feed	Reagent released	Possible tank failure
<b>Temperature</b>				
Less	Temperature of inlet is colder than normal	Thermal stress on tank	Possible tank failure	
More	Temperature of inlet is hotter than normal	Thermal stress on tank	Possible tank failure	
Air blower	<b>Flow</b>			
	Less	Valve to bioreactor fails closed Line plugs	Deadhead blower Deadhead blower	Damage to blower Damage to blower
	More	Valve to bioreactor fails open	Upset in bioreactor	Reagent released
	No	Same as less		
	<b>Pressure</b>			
	More	Valve to bioreactor fail closed	Deadhead blower	Damage to blower
	Less	Valve to bioreactor fail open	Upset in bioreactor	Reagent released
<b>Temperature</b>				
More	Valve to bioreactor closed	Deadhead blower	Damage to blower	

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
Feed pump for M9 to bioreactor	<b>Flow</b>			
	Less	Valve from tank fails closed	Pump cavitates	Damage to pump
		Line plugs	Pump cavitates	Damage to pump
	More	Valve from tank fails open	Upset in bioreactor	Reagent released
	No Pressure	Valve to bioreactor closed	Deadhead pump	Damage to pump
	More	Valve to bioreactor fails closed	Deadhead pump	Damage to pump
	Less	Valve to bioreactor fails open	Pump cavitates	Damage to pump
Bioreactor	<b>Temperature</b>			
	More	Valve to bioreactor closed	Deadhead pump	Damage to pump
	<b>Level</b>			
	Less	Bioreactor runs dry	Pump cavitates	Damage to pump
		Not enough air in bioreactor	Air valve fails closed	Damage to blower
			Blower fails	Upset in bioreactor
		Rupture discharge line	Reagent released	Potential contamination of environment
		Bioreactor rupture	Reagent released	Potential contamination of environment
	More	Valve for pumping M9 fails open	Bioreactor overfills	Reagent released
		Valve for air blower fails open	Bioreactor overfills	Reagent released
		Reverse flow from process	Bioreactor overfills	Reagent released
	<b>Composition</b>			
	Other than	Wrong ratio in mixture	Possible side reactions	Possible bioreactor failure
	As well as	Impurity in bioreactor	Upset in bioreactor	Kill of the microorganisms in bioreactor
	<b>Pressure</b>			
Less	Head loss	Reagent released	Potential contamination of environment	
	Not enough air in bioreactor	Air valve fails closed	Bioreactor runs dry	
		Blower fails	Upset in bioreactor	
	Not enough M9 in bioreactor	M9 valve fails closed	Bioreactor runs dry	
		Pump fails	Upset in bioreactor	
More	Overfill bioreactor	Reagent released	Potential contamination of environment	
	Temperature of inlet is hotter than normal	Reagent released	Possible bioreactor failure	
	Valve for air blower fails open	Bioreactor overfills	Reagent released	
	Valve for pumping M9 fails open	Bioreactor overfills	Reagent released	

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
(Bioreactor cont.)	<b>Temperature</b>			
	Less	Temperature of inlet is colder than normal	Thermal stress on bioreactor Upset in bioreactor	Possible bioreactor failure No rxn
	More	Temperature of inlet is hotter than normal	Thermal stress on tank Exothermic rxn Exothermic rxn	Possible bioreactor failure Melting of bioreactor Melting of bioreactor
		Cooling system fails		
Discharge pump from bioreactor to cross-flow filter	<b>Flow</b>			
	Less	Valve from bioreactor fails closed Line plugs	Pump cavitates Pump cavitates	Damage to pump Damage to pump
	More	Valve from bioreactor fails open	Upset in filter	Improper filtration
	No	Valve to filter closed	Deadhead pump	Damage to pump
	<b>Pressure</b>			
	More	Valve to filter fails closed	Deadhead pump	Damage to pump
	Less	Valve to filter fails open	Pump cavitates	Damage to pump
<b>Temperature</b>				
More	Valve to filter closed	Deadhead pump	Damage to pump	
Cross-flow filter for microorganisms	<b>Flow</b>			
	Less	Line plugs Pump to filter valve fails closed	Pump cavitates Deadhead pump	Damage to pump Damage to pump
		Pump fails	Improper filtration	Damage to filter
	More	Pump to filter valve fails open	Improper filtration	Damage to filter
	No	Same as less		
	<b>Composition</b>			
	Other than As well as	Failure in bioreactor Impurity in bioreactor	Improper filtration Improper filtration	Damage to filter Damage to filter
	<b>Pressure</b>			
	More	Issue with pump or valve	Improper filtration	Damage to filter
	Less	Issue with pump or valve	Improper filtration	Damage to filter
	No	Lack of pressure gradient between inlet and outlet	Reverse flow from process	Bioreactor contamination from filter
	<b>Temperature</b>			
	Less	Temperature of inlet is colder than normal	Improper filtration	Damage to filter
More	Temperature of inlet is hotter than normal	Improper filtration	Damage to filter	

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
Feed pump for packed bed (AC)	<b>Flow</b>			
	Less	Flow from filter insufficient	Pump cavitates	Damage to pump
		Line plugs	Pump cavitates	Damage to pump
	More	Flow from filter is excessive	Upset in packed bed	Packed bed overfills
	<b>No</b>			
	Pressure	Lack of flow from filter	Deadhead pump	Damage to pump
	More	Issue with packed bed	Deadhead pump	Damage to pump
Less	Issue with packed bed	Pump cavitates	Damage to pump	
<b>Temperature</b>				
More	Line plugs	Deadhead pump	Damage to pump	
Packed bed reactor (AC)	<b>Flow</b>			
	<b>No</b>			
		Inlet valve closed	None	None
		Inlet clogged	None	None
		Outlet clogged	Packed bed overfills	Damage to packed bed
	More	Inlet flow increase	Packed bed overfills	Damage to packed bed
			Overflow	Damage to inlet pipe
	Less	Inlet clogged	None	
		Outlet clogged	Packed bed overfills	Damage to packed bed
	Reverse	Outlet valve closed		
		Outlet clogged		
	<b>Composition</b>			
	As well as	Impurity in inlet	Poisons AC	Replace AC
			Undesirable reaction	Damage to packed bed
	Other than	Wrong catalyst	Undesirable reaction	Damage to packed bed
		AC exhausted	No adsorption	
	<b>Temperature</b>			
	Less	Colder inlet temp	Deactivates AC	No/less adsorption
		Colder ambient temp	Deactivates AC	No/less adsorption
	More	Warmer inlet temp	Deactivates AC	No/less adsorption
	Warmer ambient temp	Deactivates AC	No/less adsorption	
	Exothermic reaction	Deactivates AC	No/less adsorption	
<b>Pressure</b>				
Less	Crack in column	Loss of AC	No/less adsorption	
	Outlet pipe detached	Loss of product/AC		
More	Outlet clogged	Packed bed overfills	Damage to packed bed	
	Outlet valve closed	Packed bed overfills	Damage to packed bed	

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence	
Sulfuric Acid Storage Tank	Level More	Truck pumps too much	Tank overflow	Reagent released	
		Process backflow	Tank overflow	Reagent released; possible damage to valves/pumps	
	Less	Tank runs dry	Cavitation	Pump damage	
		Tank rupture	Reagent released		
		Valve/Pump open	Cavitation		
	No Pressure	Same as less			
	More	Tank overflow	Tank rupture	reagent released	
		Increased temperature [extreme]	Possible tank rupture	reagent released	
	Less Composition	Tank rupture/leak	Reagent released		
	Other than	Wrong reagent	Possible reaction	Tank rupture	
		Wrong reagent	Highly volatile	Increased pressure	
As well as Temperature	Impurity	See other than			
More	Elevated temperature from inlet [truck]	Increased pressure	Thermal stress		
Less	External cold [extreme]	Possible freezing	Stress on tank		
Mixing Tank 1 (Acid+Muconate)	Level Less	Tank runs dry	cavitation	pump damage	
		Tank rupture	reagent released		
	More	Acid feed open or broken	tank overfills	reagents released; damage to pumps and valves	
		pH meter broken	tank overfills	reagents released; damage to pumps and valves	
		Reverse Flow from process	tank overfills	reagents released	
	No Composition	Same as less			
	Other than	Wrong reagent (from acid tank)	Possible undesired reaction	Tank rupture; Overheating	
	As well as	Impurity	side reactions	same as other than	
	[Lack of acid]	Part of [Less] (High pH)	Acid feed broken-closed (pH)ICA malfunctioning	reaction not initiated	waste of muconate feed
	[excess of acid]	Part of [More] (Low pH)	(pH)ICA malfunctioning	Excess of acid	corrosion of following unit ops
	Acid feed broken-open	Excess of acid	Tank overfills		

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
(Mixing Tank 1 cont.)	<b>Pressure</b>			
	More	Undesired reaction by-products	Gases released	Pressure release activates
	Less	Outlet pump running to high	Vacuum forms	Cavitation; Release of reagents
	<b>Temperature</b>			
	More	Acid inlet at elevated temperature	Produces more heat	Thermal stress on tank
	Less	Runaway reaction Tank exposed to extreme (cold) conditions Tank exposed to extreme (cold) conditions	Excess heat Premature crystallization Cracking/Damage to tank material	Tank rupture; Thermal Stress Clogging of outlet pipe; Formation on tank walls-Loss of product Possible release of reagents
Cooling Crystallizer	<b>Level</b>			
	Less	Inlet clogged/broken closed	Possible cavitation	Outlet pump damage
		Outlet valve broken open	Residence time of mix not long enough	Corrosion to piping and vacuum filter, Loss of product
	More	Feed broken open	Crystallizer overflow	Damage to equipment, possible reagent release
	No	Inlet clogged/broken closed	Possible cavitation	Outlet pump damage
	<b>Composition</b>			
	Other than	side reactions from mixing tank	Damage to crystallizer	
	<b>Temperature</b>			
	More	Heat exchanger for cooling jacket broken	Reaction does not "occur"	Unreacted acid may damage crystallizer
		Valve for cooling jacket broken-closed	Reaction does not "occur"	Unreacted acid may damage crystallizer
		Leak in cooling Jacket	Reaction does not "occur"	Coolant released to the environment
	Less	Valve for cooling jacket broken-open	Too cold for crystallizer	Possible cracking
	Temp. control broken, resulting in colder temps	Water freezes	Possible cracking, cannot remove materials	
<b>Pressure</b>				
More	Heat exchanger broken [high T]	Pressure in crystallizer increases	Stress to materials	
Less	Heat exchanger broken [Lower T]	Pressure decreases	Possible cavitation	
Drum Vacuum Filter 1	<b>Level</b>			
	More	Feed pump broken open	Tub overfills	Slurry released
	Less	Feed pump broken closed	No slurry	none
	<b>Pressure</b>			
Less	Vacuum pump malfunctioning	Possible cavitation	Damage to drum	

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
(Drum vacuum filter 1 cont.)	More Composition	Vacuum pump fails	Slurry not dried	Contaminates process down the line
	Other than Mechanical	Impurities	May end up in final crystals	none
	More	Rotates too fast	Not sufficient filtering time	Excess liquid present in crystals
	Less	Rotates too slow	Production slowdown	May lead to tub overflow
	No	Motor broken	No filtering	Tub overflow, Halt in production
CSTR	Level			
	More	Valve for pumping muconic acid fails open	CSTR overfills	EtOH and muconic acid released
		Valve for pumping EtOH fails open	CSTR overfills	
	Less	Valve for pumping muconic acid fails closed	Unit op runs dry	
		Valve for pumping EtOH fails closed	Unit op runs dry	
	Pressure			
	More	Overfill of CSTR- influent muconic acid valve fails open	muconic acid released	environmental damage
		Overfill of CSTR- influent EtOH valve fails open	EtOH released	environmental damage
	Less	loss of head to the CSTR due to pump failure	CSTR level too low- runs dry	damage to reactor
Temperature				
More	temperature of inlet hotter than desired	EtOH evaporates	muconic acid crystals in CSTR- plugs reactor and pressure buildup (causing potential failure)	
Less	temperature of inlet cooler than desired	purification not effective	salts and other impurities in product	
Drum Vacuum Filter 2	Level			
	More	feed line broken open	overflow of unit operation	muconic acid released to environment
	Less	feed line broken closed	no feed to filter- runs dry	damage to vacuum filter
	Pressure			
	Less	pump fails to pressure up	Tub overfills	Slurry released
	More	pump overpressures	No slurry	none
Composition				
Different	impurities in product	salts in final product- cannot make nylon 6,6		

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
(Drum vacuum filter 2 cont.)	<b>Mechanical</b>			
	More	rotates too fast	insufficient filtering	muconic acid not fully in EtOH
	Less	rotates too slow	slows production time	could overflow unit operation
	No	no rotation	no filtering	production stops
Trickle Bed Reactor	<b>Flow</b>			
	No	Hydrogen Inlet closed	Incorrect reaction	No/incorrect product
		Hydrogen Outlet closed	Pressure increases in reactor	Damage to reactor and surroundings
		Muconic Acid Inlet closed	Incorrect reaction	No/incorrect product
		Muconic Acid Outlet closed	Reactor overfills	Damage to reactor
	More	Hydrogen Inlet increases	Pressure increases in reactor	Damage to reactor and surroundings
			Incorrect reaction	No/incorrect product
		Muconic Acid Inlet increases	Reactor overfills	Damage to reactor
			Incorrect reaction	No/incorrect product
		Hydrogen Outlet decreases	Pressure increases in reactor	Damage to reactor and surroundings
			Incorrect reaction	No/incorrect product
		Muconic Acid Outlet decreases	Reactor overfills	Damage to reactor
			Incorrect reaction	No/incorrect product
	Less	Hydrogen Inlet decreases	Decreased reaction	Less product
		Muconic acid inlet decreases	Decreased reaction	Less product
		Hydrogen Outlet increases	Decreased reaction	Less product
		Muconic acid outlet decreases	Decreased reaction	Less product
	Reverse	Compressor reversed	Incorrect reaction	No/incorrect product
	<b>Composition</b>			
	As well as	impurities in muconic acid	Poison Catalyst	Replace catalyst
			Incorrect reaction	No/incorrect product
	Other than	Wrong catalyst	Incorrect reaction	No/incorrect product
				Damage to reactor
		Catalyst exhausted	No/incorrect reaction	No/incorrect product
	<b>Temperature</b>			
	More	Temperature increases	Catalyst deactivates	No/incorrect product
		Exothermic Reaction	Pressure increases in reactor	Damage to reactor and surroundings
Less	Temperature increases	Catalyst deactivates	No/incorrect product	
	Endothermic Reaction	Slows reaction	Less product	
<b>Pressure</b>				
Less	Compressor Output decreased	Implodes	Damage to reactor	
More	Compressor output increased	Explodes	Damage to reactor and surroundings	
<b>Level</b>				
No	Muconic Acid flow stopped	Incorrect reaction	No/incorrect product	
Less	Muconic Acid outlet increases	Less reaction	Less product	

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence			
(Trickle Bed Reactor cont.)	More	Muonic acid inlet decreases	Less reaction	Less product			
		Muonic Acid Inlet increases	Reactor overfills	Damage to reactor			
		Muonic Acid Outlet decreases	Reactor overfills	Damage to reactor			
	Time	More	Muonic Acid Outlet blocked	Less reaction	No/incorrect product		
			Muonic Acid Inlet blocked	Less reaction	No/incorrect product		
		Hydrogen Inlet blocked	Less reaction	No/incorrect product			
		Hydrogen Outlet blocked	Less reaction	No/incorrect product			
Reaction	More	Unexpected Reaction	Runaway Reaction	Damage to reactor and surroundings			
Hydrogen Compressors	Flow	No	Inlet closed	Pressure increase	Damage to compressor and surroundings		
	Outlet closed		Pressure increase	Damage to compressor and surroundings			
	Less	Improper function	Inlet blocked	Less hydrogen	Less product		
			Outlet blocked	Less hydrogen	Replace compressor		
			Inlet decreased	Less hydrogen	Less product		
			Outlet decreased	Less hydrogen	Less product		
			More	Inlet increased	Outlet increased	Less hydrogen	Less product
					Pressure increase	Damage to compressor and surroundings	
	Composition	As well as Temperature	Impurities in hydrogen	Improper compressor function	Damage to compressor		
						Outlet increased	Pressure increase
	More	Temperature increase	Pressure increase	Damage to compressor and surroundings			
	Less	Temperature decrease	Improper compressor function	Damage to compressor			
	Pressure	Less	Inlet blocked	Less flow	Damage to compressor		
				Outlet blocked	Less flow	Less product	
		Improper function	Less flow	Damage to compressor			
			Less flow	Less product			
			Less flow	Replace compressor			

Equipment reference and operating conditions	Deviations from operating conditions	What event could cause this deviation?	Consequences of this deviation on item of equipment under consideration	Additional implications of this consequence
Evaporation Crystallizer	<b>Flow</b>			
	No	Inlet valve closed	None	None
		Inlet clogged	None	None
		Outlet clogged	Crystallizer overfills	Damage to crystallizer
	More	Inlet flow increase	Crystallizer overfills Overflow	Damage to crystallizer Damage to inlet pipe
	Less	Inlet clogged	None	
		Outlet clogged	Crystallizer overfills	Damage to crystallizer
	Reverse	Outlet valve closed	Crystallizer overfills	Damage to crystallizer
		Outlet clogged	Crystallizer overfills	Damage to crystallizer
	<b>Composition</b>			
	As well as	Impurity in inlet	Undesirable reaction No crystallization	Damage to crystallizer Less pure product
	<b>Temperature</b>			
	Less	Colder inlet temp	No evaporation	No product
		Colder ambient temp	No evaporation	No product
		Crystallizer malfunction	No evaporation	No product
	More	Warmer inlet temp	No crystallization	No product
		Warmer ambient temp	No crystallization	No product
		Crystallizer malfunction	No crystallization	No product
	<b>Pressure</b>			
	Less	Crack in crystallizer	Leak	No/incorrect product
		Outlet pipe detached	Leak	No/incorrect product
	More	Outlet clogged	Crystallizer overfills	Damage to crystallizer
		Outlet valve closed	Crystallizer overfills	Damage to crystallizer
<b>Level</b>				
Less	Decrease inlet flow	None	Less product	
More	Increase inlet flow	Crystallizer overfills	Damage to crystallizer	

## **Appendix C. Other Tables**

The excel sheet included in the folder contains the full economic and BACT analysis performed.