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Dear Dr. Schlup,

We are pleased to present you with a full design report for producing 10,000 metric tons of maleic anhydride per year. Work on this project began in early October, with the selection of a process in which benzene will be oxidized to make our desired product.

This report includes the evaluation of two different designs. The first design is not profitable based on several metrics. Due to this, an alternative approach is presented and discussed in full. Sections of this report include our conclusions and recommendations, as well as a complete process description with a process flow diagram. In addition, we discuss the health, safety, and environmental hazards associated with this process. Several design specifications are included to make this design inherently safer. Finally, we include a full costing report of our process, as well as several profitability measures.

Our finalized process design is capable of producing maleic anhydride of 98% purity. We calculated this project to have a net present worth of $37 million. In addition, we calculated the return on investment to be 48%, making this project highly profitable.

Please feel free to contact us with any questions or concerns.

Best Regards,

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BASE CASE DESIGN FOR MALEIC ANHYDRIDE PROCESS

Submitted as a Part of Course Requirements in CHE 550, CHE 560, and CHE 570

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ABSTRACT

The purpose of this report is to design a process capable of producing 10,000 metric tons per year of maleic anhydride. Our marketing department has identified a need for this production, and believe it is an opportune time to enter the market. Our current plant has a suitable benzene coproduct stream capable of producing the desired amount of maleic anhydride. Because of this, our design is based on the oxidation of benzene to produce maleic anhydride.

In order to model our designs, we used Aspen Plus as a process simulator. In addition, we made sure to check the results given by the simulator with several correlations and sizing equations.

Our research led us to the development of two different process designs. Upon calculating the operating costs of our first distillation-based design, we found that this option would not be profitable. This led us to an alternate flash-based design approach. The second design proved to be profitable with a return on investment of 48%. Additional profitability measurements can be found in the report. This process was able to achieve a final purity of 98% which was given as a constraint for this project.

Also included in this report is an in depth discussion of the health and safety hazards involved with this process. Design specifications have been made to ensure that our process is inherently safer when handling toxic substances including benzene and maleic anhydride. We also discuss the environmental considerations for this process and the controls put in place for the main reactor.

We strongly recommend that our flash-based design be implemented for the production of maleic anhydride. It has proved to be safe economical investment as an addition to the existing plant.

INTRODUCTION AND PROBLEM STATEMENT

Our marketing department has identified a market opportunity for the production of 10,000 metric tons of maleic anhydride. For this base case design, we will utilize the catalytic oxidation of benzene to meet the production opportunity. The primary reason for selecting this reaction scheme among alternatives is that we seek to employ an existing benzene stream from the significant amount of by-product benzene generated by other processes in the plant. Details on three potential reaction schemes and their safety and environmental considerations are discussed under Reaction Schemes.

Maleic anhydride is a raw material utilized in the manufacture of copolymers, plasticizers, polyester resins, surface coatings, lubricant additives, agricultural chemicals, and 1,4-butanediol (BDO) [1]. In recent years, BDO is one of the world's fastest growing chemical markets, ensuring a long term need for increased maleic anhydride production. Originally in the 1930s, maleic anhydride was manufactured from benzene, but due to its hazardous nature was replaced with butane feeds in the 1980s [1]. This was accompanied with a new set of issues as a high enough conversion was unachievable without significant loss due to the low catalytic activity, spurring the generation of a new set of processes and catalysts. Fixed bed and fluidized bed processes were developed using vanadium-phosphorous oxide (VPO) catalysts; however, VPO is unstable and loses phosphorous over time at reaction temperatures, decreasing selectivity.

In 2000, 1359 k.t./yr of maleic anhydride was produced worldwide, 250 k.t. in the United States alone [1]. Over 50% was produced in a fixed bed process with a butane feed [1]. Approximately 63% of the production in the U.S. goes into the manufacture of unsaturated polyester resins and 11% into lube oil additives [1]. Overall, maleic anhydride market is expected to grow by modest rates in most of the world with vigorous growth in the Middle East and Southeast Asia [2]. The estimated total capital investment for a plant producing 60,000 metric tons per year is about $150 million dollars with a production cost of $830/m.t. of maleic anhydride with a purity of 99.8 wt% [3].

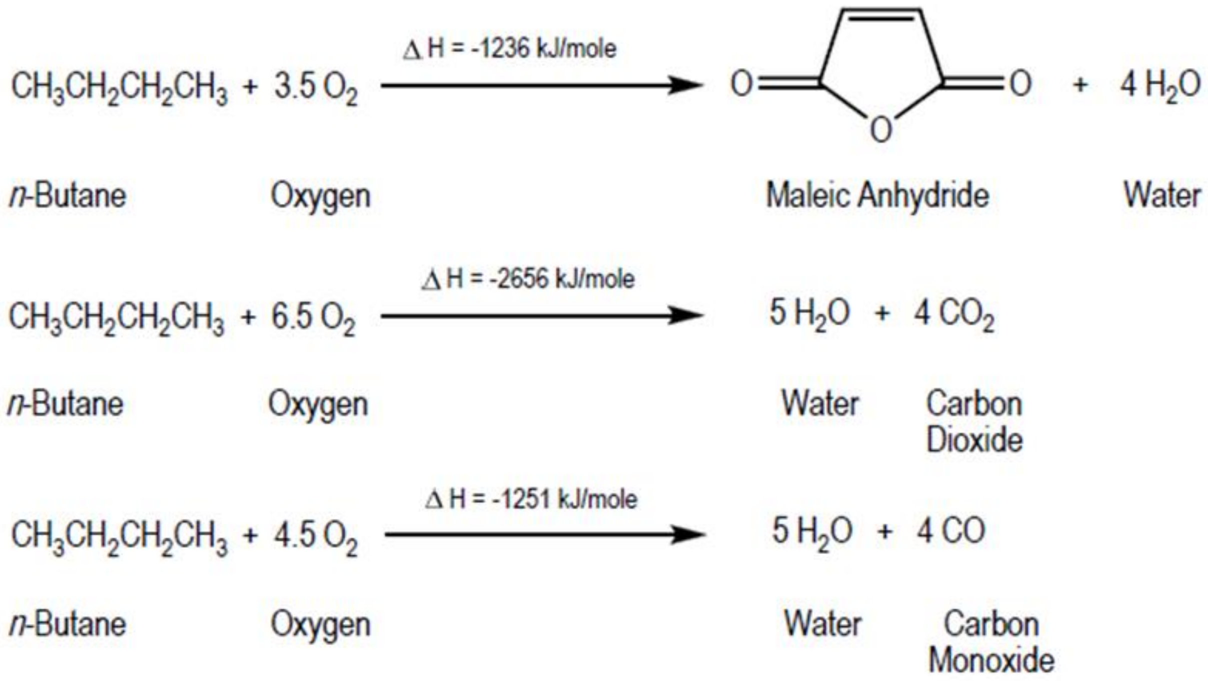
Reaction Schemes

To start, we examined five reaction schemes for the production of maleic anhydride: catalytic oxidation of n-butane, of benzene, and of 1-butanol. Other potential reactions include recent biobased chemicals including, but not limited to furan, furfural, 2,5-furandicarboxylic acid, and 5-(hydroxymethyl)furfural [4]. Due to the the large amount of research needed to implement these reaction schemes, they are considered to be beyond the scope of the project. To establish numerical comparisons of the reactions, we calculated the Effective Mass Yield (EMY), E-factor, Atom Economy (AE), and Mass Intensity (MI). These green engineering, alongside Gross Product Potential calculations, provide a basis for eliminating reaction pathways. The following subsections detail the alternatives investigated.

Catalytic Oxidation of n-Butane

This reaction uses a fixed bed, multi-tubular reactor with a vanadium phosphate catalyst on silica with a 65% maleic anhydride yield [5]. As the reaction scheme is highly exothermic, heat is removed with an exit gas stream [3]. The steam in this stream can be partially condensed to recycle some of the energy back to the plant. There are separation concerns with the large amount of water produced, as maleic anhydride does not separate easily from water based systems and, in the presence of high amounts of water, maleic anhydride decomposes into maleic acid and fumeric acid. However, this can be separated with a series of distillation columns.

Figure 1: The reaction scheme for the catalytic oxidation of n-butane [6]

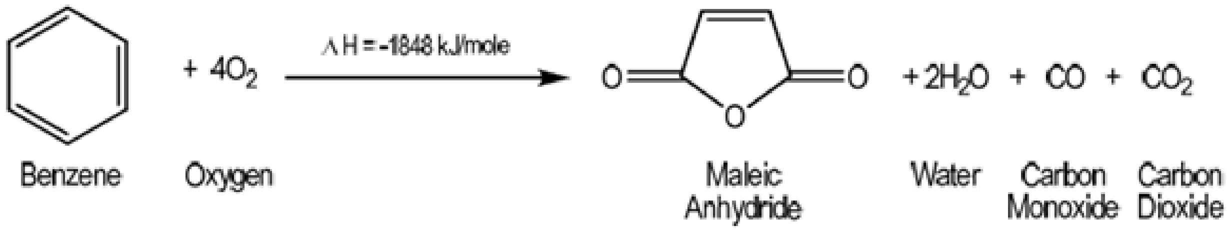


Catalytic Oxidation of Benzene

A benzene feed reaction utilizes a 30% vanadium pentoxide and 70% molybdenum trioxide which were common until 1980s [7]. Several other catalysts have also been used including vanadium phosphorous. Two major factors are considered deterrents from widespread industrial benzene use for the production of maleic anhydride: 1) its environmental and toxic hazards, and 2) its high cost [8]. The primary reaction is shown in

Figure **2** and side reactions will be discussed later. Maleic anhydride yield for the catalytic oxidation of benzene is 70% [7].

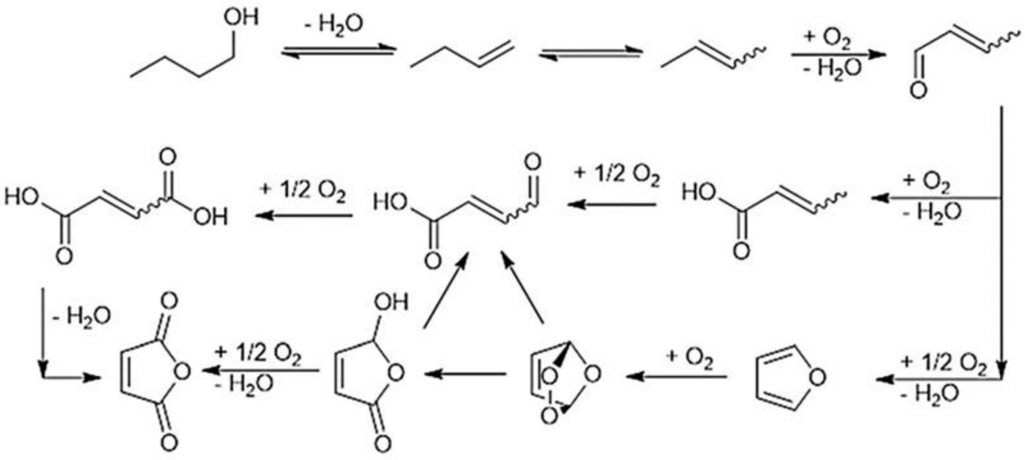
Figure 2: The reaction scheme for the catalytic oxidation of benzene [6]



Catalytic Oxidation of 1-Butanol

The reaction occurs in a continuous fluidized bed reactor using vanadyl pyrophosphate (VPP) as the catalyst [9]. The feed source is 1-butanol, which can be produced from biomass or fossil fuels, therefore this process can be considered renewable. There are some concerns about separation costs due to the large amounts of intermediates that must be sorted out towards the end of the process.

Figure 3: The reaction scheme for the catalytic oxidation of 1-butanol [9]



Green Engineering Metrics

The green metrics are defined as follows [10]:

$$Effective\ mass\ yield\ (\%) = \frac{Mass\ of\ products\ x\ 100}{Mass\ of\ non-benign\ reagents} \tag{1}$$

$$E\ Factor = \frac{Total\ waste\ (kg)}{kg\ product} \tag{2}$$

$$Atom\ Economy = \frac{MW\ Desired\ Products}{MW\ Reactants} \tag{3}$$

$$Mass\ Intensity\ (MI) = \frac{Total\ mass\ used\ in\ process\ or\ process\ step\ (kg)}{Mass\ of\ product\ (kg)} \tag{4}$$

Gross Profit Potential (GPP)

GPP is calculated using the monetary value of the chemicals and the molecular weight. The weights and market prices are tabulated below. All the dollar amounts are from or scaled to 2015 prices.

Table 1: Reaction metrics comparison [11], [12], [13]

Chemical	$/m.t.	Molecular Weight (g/mol)
Maleic Anhydride	1540	98.06
1-Butanol	550	74.12
Benzene	546	78.11
Butane	339	58.12
Water	0	18.02
Carbon Monoxide	0	28.01
Carbon Dioxide	0	44.01

For example, the GPP for maleic anhydride from benzene is estimated as follows:

$$\frac{\$1540}{m.t.} * \frac{98.06\frac{g}{mol}}{98.06\frac{g}{mol}} - \frac{\$546}{m.t.} * \frac{78.11\frac{g}{mol}}{98.06\frac{g}{mol}} = \$1105/m.t$$

Reaction Scheme Comparison and Selections

The green metrics and gross profit potential for the three reaction schemes have been compiled below. The highlighted numbers are the best performing in each category.

Table 2: Reaction metrics comparison

Carbon Source	**Yield (to maleic anhydride)**	**Effective Mass Yield**	**E-factor**	**Atom Economy**	**Mass Intensity**	**Gross Profit Potential**
n-butane	65%	109.7%	1.67	56.7%	2.67	$1339
Benzene	70%	87.8%	2.01	89.1%	1.87	$1105
1-butanol	39%	51.6%	0.93	57.6%	18.7	$1124
Good Value	High	High	Low	High	Low	High

Based on these calculations, 1-butanol was discontinued as a feed source due to the large amount of bioproducts and intermediates. If more importance was placed upon using a biobased approach, this process should be reevaluated. From a metrics perspective, n-butane oxidation is a good alternative to the handling of toxic and reactive benzene with a high gross product potential and yield to maleic anhydride. However, our company has significant amounts of by-product benzene for other processes that can be easily used in maleic anhydride production. Therefore, our process utilizes the production of maleic anhydride from the catalytic oxidation of benzene with atmospheric oxygen.

CONCLUSIONS

A design for the production of 10,000 metric tons/year of maleic anhydride from the catalytic oxidation of benzene with atmospheric oxygen is presented. For the flash-based process, the resulting product stream has a purity of 98% containing only quinone impurities. The return on investment of this project is 48%. The second method using an adsorption-distillation process has a product stream with 97% purity, however this design is unprofitable. For both processes, the packed bed reactor requires a high level of control to avoid sintering and a runaway reaction. Also, several health and safety concerns are noted with regards to handling of toxic and hazardous benzene and maleic anhydride have been addressed.

RECOMMENDATIONS

We strongly recommend the implementation of our flash-based process for the production of maleic anhydride. Resulting product stream is 10,000 metric tons/yr of 98% maleic anhydride purity with only quinone impurities. For a 15-year project life, net present worth of the project is $37 million with all capital investment in year 0. This project exceeds the necessary 30% return on investment achieving a return of 48% in year 3.

PROJECT PREMISES AND CONSTRAINTS

The process design and analysis follows from the assumption that benzene comes from an existing process in quantities necessary to meet the market opportunity for the production of 10,000 metric tons of maleic anhydride per year. Holding tanks are considered for storage of benzene between in-house processes. Benzene is toxic, flammable, and highly reactive, therefore eliciting special considerations in process design. We are not considering carbon emissions and cost of incineration of carbon dioxide byproduct. The cost analysis considers that the current amount of land is sufficient for the addition of this process.

The molybdenum-vanadium catalyst sinters at temperatures greater than 600°C, therefore the reactor must be designed to achieve the greatest conversion at temperatures less than 600°C and provide room for fluctuations [14]. The feed into the reactor is a 1.5 v/v% benzene in air with the assumption that air is 79 mol% nitrogen and 21 mol% oxygen [15].

A major concern for any design considering a benzene reaction is the amount of water produced. Firstly, water separations with an organic phase are difficult and require a lot of heat due to large heat capacities [16]. Secondly, maleic acid in the presence of water hydrolyzes to form maleic acid. At 0°C, hydrolysis occurs following first order kinetics at a rate of 34.3×10^{-4} s^{-1} [17]. However, the reaction proceeds quickly at temperatures above 150°C (within 10 minutes, maleic anhydride degrades to maleic acid) [18].

PROCESS FLOW DIAGRAM AND STREAM TABLE

We developed two processes for the catalytic oxidation of benzene to maleic anhydride. The difference between these two designs occurs at the separations process; one considers a series of flash drums followed by a single distillation column and the other an absorber followed by a series of distillation columns. The process flow diagram (PFD) for the absorber-distillation process with accompanying overall stream tables is shown below.

Since the above process is not profitable, we investigated further the secondary separations process utilizing a series of flash drums. The process flow diagram for this method is shown in Figure 4. This process achieves a 98% maleic anhydride purity with a feed flow rate of 24.28 kmol/hr benzene and a product flow rate of 12.52 kmol/hr. Further details of the process are discussed in the Process Description section.

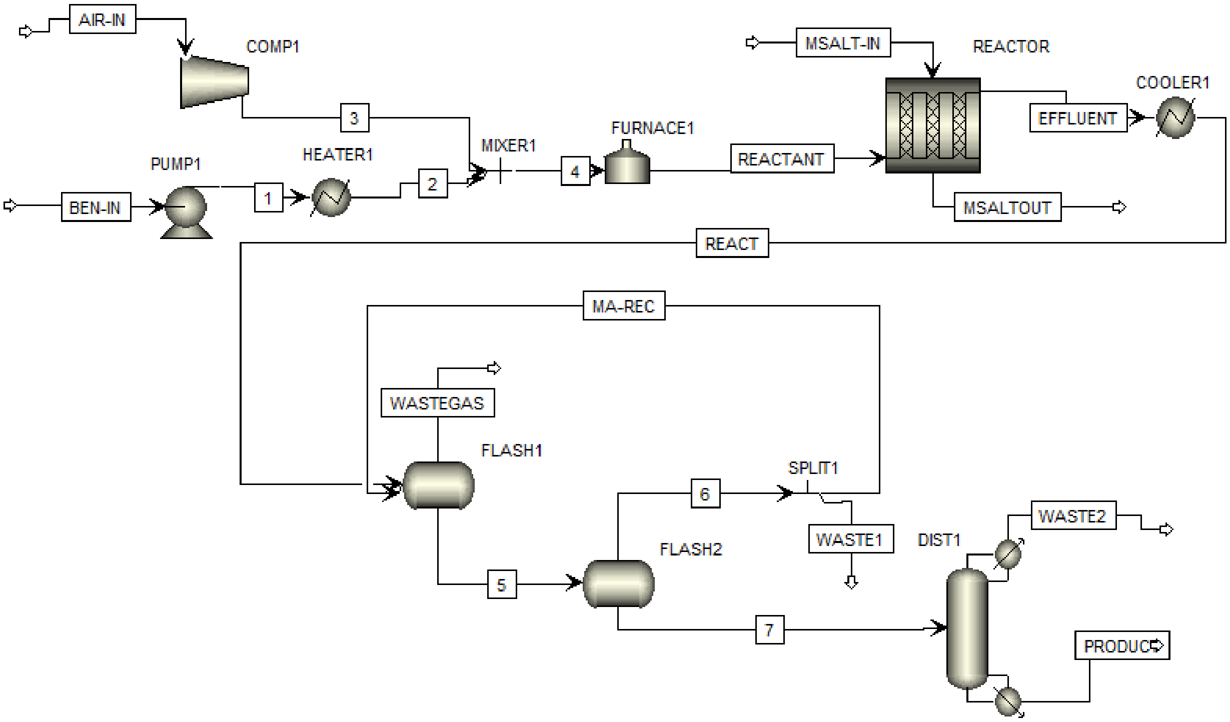


Figure 4: Flash-based separations process PFD.

Table 3: Basic overall stream table for the flash-based process.

	Streams					
Mole Flows (kmol/hr)	AIR-IN	BEN-IN	WASTE1	WASTE2	WASTEGAS	PRODUCT
Total	1594.14	24.28	1.14	1.09	1601.54	12.52
Maleic Anhydride	0.00	0.00	0.44	0.16	0.91	12.26
Benzene	0.00	24.28	0.00	0.00	0.12	0.00
Oxygen	334.77	0.00	0.00	0.00	197.53	0.00
Nitrogen	1259.37	0.00	0.00	0.00	1259.37	0.00
Carbon Dioxide	0.00	0.00	0.00	0.00	87.24	0.00
Quinone	0.00	0.00	0.02	0.03	0.14	0.27
Dibutyl Phthalate	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.68	0.90	56.25	0.00
Mole Fractions						
Maleic Anhydride	0.00	0.00	0.38	0.15	0.00	0.98
Benzene	0.00	1.00	0.00	0.00	0.00	0.00
Oxygen	0.21	0.00	0.00	0.00	0.12	0.00
Nitrogen	0.79	0.00	0.00	0.00	0.79	0.00
Carbon Dioxide	0.00	0.00	0.00	0.00	0.05	0.00
Quinone	0.00	0.00	0.02	0.02	0.00	0.02
Dibutyl Phthalate	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.60	0.83	0.04	0.00

The second process we investigated involved an absorber and two distillation columns in series. This process, shown below, achieves a 97% maleic anhydride purity with a feed flow rate of 23.93 kmol/hr benzene and a product flow rate of 12.83 kmol/hr. Further details of the process are discussed in the following section.

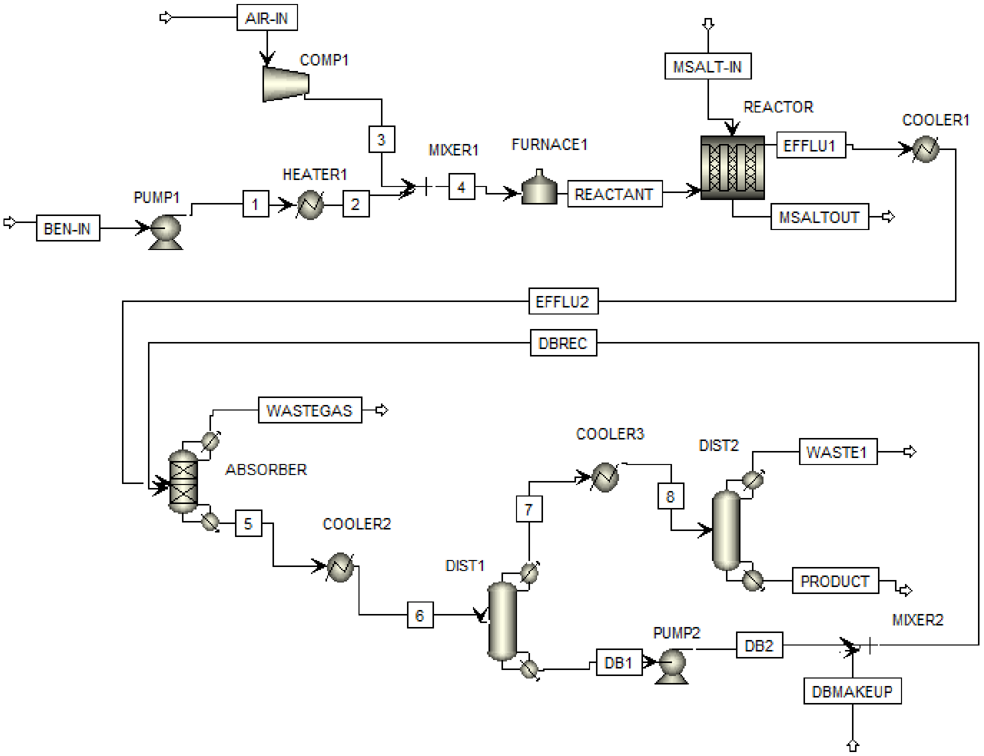


Figure 5: Absorber-distillation separations process PFD.

Table 4: Basic overall stream table for the absorber-distillation process.

	Streams					
Mole Flows (kmol/hr)	AIR-IN	BEN-IN	DBMAKEUP	WASTE1	WASTEGAS	PRODUCT
Total	1571.51	23.93	0.11	1.27	1579.34	12.83
Maleic Anhydride	0.00	0.00	0.00	1.11	0.00	12.46
Benzene	0.00	23.93	0.00	0.00	0.12	0.00
Oxygen	330.02	0.00	0.00	0.00	194.80	0.00
Nitrogen	1241.49	0.00	0.00	0.00	1241.49	0.00
Carbon Dioxide	0.00	0.00	0.00	0.00	85.94	0.00
Quinone	0.00	0.00	0.00	0.16	0.01	0.28
Dibutyl Phthalate	0.00	0.00	0.11	0.00	0.01	0.09
Water	0.00	0.00	0.00	0.00	56.98	0.00
Mole Fractions						
Maleic Anhydride	0.00	0.00	0.00	0.87	0.00	0.97
Benzene	0.00	1.00	0.00	0.00	0.00	0.00
Oxygen	0.21	0.00	0.00	0.00	0.12	0.00
Nitrogen	0.79	0.00	0.00	0.00	0.79	0.00
Carbon Dioxide	0.00	0.00	0.00	0.00	0.05	0.00
Quinone	0.00	0.00	0.00	0.12	0.00	0.02
Dibutyl Phthalate	0.00	0.00	1.00	0.00	0.00	0.01
Water	0.00	0.00	0.00	0.00	0.04	0.00

PROCESS DESCRIPTION

Process Description

Flash-Based Process

Benzene is taken from a storage tank and pumped to 2.35 kPa before being heated just above the boiling point. This stream is then mixed with compressed air and fed to a furnace to heat reactants to 460°C. Reactants enter a packed bed reactor temperature controlled by a co-current molten salt stream. Reactor effluent exits at 506°C and enters a cooler which drops the temperature to 60°C. Waste gas composing of nitrogen, oxygen, carbon dioxide, benzene, and most of the water is taken off at the first flash drum. As maleic anhydride reacts in excess water to become maleic acid, the second flash drum removes additional water in the vapor phase at 200°C. The vapor phase is sent to a splitter where 75% is recycled back to the first flash drum, and the other 25% is removed as waste. The remaining maleic anhydride, quinone, and water is sent to a distillation column where maleic anhydride leaves in the bottoms at 98% purity with quinone as the only significant impurity.

Absorption-Distillation Process

Up to and including the reactor, the absorption-distillation process is the same as the flash-based process. The reactor effluent is sent to a cooler that brings the temperature to 270°C. This stream enters the absorber and is scrubbed by dibutyl phthalate at a 50:1 ratio. Waste gas composed of carbon dioxide, nitrogen, oxygen, benzene, and water is taken off the top of the absorber. The scrubbed product is sent to a cooler which takes the temperature down to 194°C. The first distillation column separates the maleic anhydride product stream from the dibutyl phthalate recycle stream. A dibutyl phthalate recycle stream is pumped back to a pressure of 215 kPa and make up is added before returning to the absorber unit. The maleic anhydride product stream is cooled to 125°C and sent to a second distillation column to remove excess water and increase purity. The waste stream exits as the distillate and contains water, quinone, and some maleic anhydride. The bottoms product stream has 97% purity maleic anhydride with 2% quinone and less than 1% dibutyl phthalate.

Material Balances

Flash-Based Process

To check the accuracy of our simulation, we conducted simple mass balance calculations around major units. Individual component mass flows were added together at the inlet and outlet of each equipment of interest. Table 5 summarizes the overall mass flow data and detailed calculations can be found in Appendix 3: Material Balance Calculations.

Table 5: Mass flows around major units in the flash-based process

Unit	Mass In (kg/hr)	Mass Out (kg/hr)
Reactor	425834	425834
Flash 1	48080	48080
Flash 2	1495	1495
Distillation	1265	1265
Overall	425834	425834

Absorption-Distillation Process

A similar process was utilized to check the absorption-distillation design. Any number differences in Table 6 can be attributed to differences in rounding when summing streams.

Table 6: Mass flows around major units in the absorption-column process

Unit	Mass In (kg/hr)	Mass Out (kg/hr)
Reactor	47208	47208
Absorber	276691	276690
Distillation 1	230857	230857
Distillation 2	1404	1405
Overall	47237	47238

Energy Balances and Utility Requirements

Utilities are discussed in detail for each unit in the following section.

Equipment List, Unit Descriptions/Specifications

Flash-Based Process

COMP1

COMP1 is an air compressor that takes air at atmospheric conditions of 25°C and 101 kPa to 235 kPa. For the necessary flow rate of 9 m^3/s at these pressures, a large centrifugal compressor with an isentropic 75% efficiency is recommended from heuristics [19]. Mechanical efficiency is approximately 80% [20]. Aspen model uses an isentropic compressor to consider the thermodynamic and mechanical effects using the more rigorous ASME method [21]. Electrical duty on the compressor is 1747 kW.

PUMP1

PUMP1 draws benzene from the storage tank and pumps from atmospheric pressure to 235 kPa. This is a centrifugal pump, since according to heuristics, centrifugal pumps are the most common type of pump and cheapest [19]. Efficiency of the pump was taken to be 45% as given by heuristics for pumps with liquid flow rates of $6x10^{-3}$ m/s [19]. Driver efficiency for centrifugal pumps is approximately 80% [20]. Electrical duty on the pump is 0.22 kW.

HEATER1

HEATER1 heats benzene from 25°C to 115°C at 235 kPa, just above the boiling point at 100°C [22]. The utility for this heater is low pressure steam at 130 kg/hr with a heat duty of 0.28 GJ/hr.

MIXER1

MIXER1 combines air and benzene streams for a resulting stream at 117°C and 235 kPa. Since both streams are vapors and contact time before the reactor is large, streams are combined in-line without additional stirring.

FURNACE1

FURNACE1 is a natural gas fired furnace heating the reactant stream of 1900 kg/hr from 117°C to 460°C. Inlet temperature of the utility is 1000°C and outlet temperature is 400°C at 29750 kg/hr. Heat duty of the furnace is 17.85 GJ/hr.

REACTOR

The reactor is a packed bed reactor for the catalytic oxidation of benzene with atmospheric oxygen to produce maleic anhydride. See Appendix 5: Reactor for a description of the reactions. The reactor has 15,000 tubes of diameter 25 mm with a length of 3 m. Catalyst for this reaction is 70 mol% vanadium pentoxide and 30 mol% molybdenum oxide on inert support [23] [24]. Catalyst particle size is 5 mm in diameter. In order to avoid sintering of the catalyst, the reactor temperature must remain below 600°C [14].

As suggested by heuristics, the reactor uses a co-current cooling process [25]. The coolant fluid is a molten salt stream of 41.3 mol% sodium nitrate and 58.7 mol% sodium nitrite at a rate of 4999 kmol/hr. Molten salt compositions were chosen at the eutectic point at 230°C [26]. The coolant enters the reactor at 500°C and exits at 506°C and serving initially to heat reactants and then to cool the highly exothermic reaction.

Inlet temperature of the reactants is 460°C. Reactor effluent leaving is at 506°C with 99.5 mol% of the benzene reacting. The reactor gives a ratio of maleic anhydride product to benzene reactant of 0.61 on a molar basis. Pressure in the reactor drops from 235 kPa to 223 kPa. This pressure drop is minimal, because each tube can hold at maximum five catalyst particles in any cross section.

A simulation to model the reactor was developed in Polymath. This simulation was used to find the optimized inlet temperature of reactants and cooling fluid. Also, co-current and countercurrent cooling processes were analyzed. This was then compared to the Aspen simulation. Additional information about the reactor can be found in Appendix 5: Reactor.

COOLER1

COOLER1 cools reactor effluent from 506°C to 60°C at 215 kPa. Utility used is cooling water from 20°C to 25°C at a flow rate of 1.16 x 10^6 kg/hr. Heat duty of the cooler is -24.34 GJ/hr.

FLASH1

FLASH1 is a flash drum at 60°C and 215 kPa which removes most of the carbon dioxide, nitrogen, oxygen, benzene, and water from the product stream containing maleic anhydride, quinone, and residual water. The flash drum is vertical carbon steel drum with a volume of 6,900 m^3. This separation yields a liquid stream of 78 mol% maleic anhydride with water and quinone impurities.

A wide difference in bubble point and dew point is desirable for the maximum separation while allowing for control of the process. Pressure of the drum was determined using simple bubble point calculations to determine the maximum difference in bubble and dew point temperatures. At 215 kPa, the bubble point and dew point of the mixture was found to be -189°C and 103.59°C in an Aspen using SRK equilibrium method. At 101 kPa (atmospheric pressure), the bubble point and dew point of the mixture was found to be -196°C and 89°C. Therefore, the drum pressure is 215 kPa.

Temperature of a flash drum should ideally be between the boiling temperature of the most volatile liquid component and the least volatile vapor component. To determine the best temperature for the flash drum, the boiling temperature of pure water and carbon dioxide was found to be 122°C and -69°C [27] , [28].Thus, a reasonable initial guess of a temperature was

50°C. Stream table results for a flash drum at 50°C, 60°C, and 70°C are shown in Appendix Table 35. The flash drum at 60°C yields the greatest amount of maleic anhydride with the smallest amount of impurities at 14.2 kmol/hr maleic anhydride exiting in 18.2 kmol/hr total.

Required heat duty for this large flash drum is -0.14 GJ/hr. Cooling water is used as the utility of this drum at a rate of 6740 kg/hr.

FLASH2

FLASH2 is a second flash drum at 200°C and 215 kPa that removes excess water from the product stream. The drum is vertical and has a volume of 0.39 m^3. This separation yields a liquid phase of 91 mol% maleic anhydride containing water and quinone impurities. Gas phase contains 60 mol% water, 38 mol% maleic anhydride, and 2 mol% quinone.

A flash separation relies upon the difference in volatility of the components. First, bubble temperature and dew temperature of the mixture at 215 kPa was found using SRK equilibrium method in Aspen to be 165°C and 224°C. Initial temperature guess of 180°C yielded very little separation with most of the water and maleic anhydride present in the liquid stream as shown in Appendix Table 37. At a temperature of 220°C, very little separation occurred as well with most of the water and maleic anhydride present in the vapor stream. However, at 200°C, a purity of 91 mol% maleic anhydride was achieved in the liquid stream. Although, some maleic anhydride is lost in the vapor phase, over 50% of the water is removed. Without this flash drum, distillation is impossible due to the small difference in bubble and dew temperature.

Utility for this flash drum was costed as high pressure steam with an inlet temperature of 250°C and outlet temperature of 249°C at 572 psia. If using high pressure steam, for the required heat duty of 0.66 GJ/hr, the steam must flow at 380 kg/hr. However, we could potentially use the molten salt stream to heat this unit.

SPLIT1

From the Flash 2 unit, 1.74 kmol/hr maleic anhydride is lost in the vapor phase. This is 12% of the total maleic anhydride produced. In order to reduce the loss of maleic anhydride, the vapor stream is split and 75% is returned to FLASH1 in the maleic anhydride recycle. This leaves waste stream (WASTE1) to be 1.14 kmol/hr containing 60 mol% water, 38 mol% maleic anhydride, and 2 mol% quinone.

DIST1

DIST1 is a distillation column that removes excess water resulting in a maleic anhydride product stream of 98% purity with only quinone impurities. This is a packed column of 0.2 m diameter and 0.6 m height. For a column of less than 0.5 m, heuristics recommend a packed column [29]. In general, random packing columns are cheaper than structured packing although are generally less efficient, so a random packed column is used [30]. The column packing is Raschig metal rings of 15 mm diameter due to low cost and high packing factor of 170 [29].

The column has a partial condenser, kettle reboiler, and equivalent height of 4 stages. The reflux ratio is 4 and distillate to feed ratio is 0.08 on a molar basis. Feed is above stage 2. Utility for the partial condenser is cooling water at a rate of 12100 kg/hr. Heat duty of the partial condenser is -0.25 GJ/hr. Utility for the reboiler is high pressure steam at a rate of 220 kg/hr to provide a heat duty of 0.38 GJ/hr.

Absorption-Distillation Process

The column process uses the same design as the flash process aside from the separations units. Changes in process units are discussed below.

COMP1

Electrical duty of COMP1 is 1722 kW.

PUMP1

Electrical duty of PUMP1 is 0.22 kW.

HEATER1

Heat duty of HEATER1 is 0.19 GJ/hr. Low pressure steam is used as the utility at a flowrate of 87 kg/hr.

MIXER1

No changes.

FURNACE1

FURNACE1 uses fired natural gas at a rate of 29500 kg/hr to provide a heat duty of 17.69 GJ/hr.

REACTOR

No changes.

COOLER1

COOLER1 cools reactor effluent from 506°C to 270°C. Utility is cooling water at a rate of 597,800 kg/hr to provide a heat duty of -12.50 GJ/hr.

ABSORBER

ABSORBER is a packed column to separate gaseous waste consisting of carbon dioxide, oxygen, nitrogen, water, and benzene from product streams containing maleic anhydride, quinone, and stripping material. To achieve this separation, dibutyl phthalate is added as the stripping material at a 50:1 ratio to hydrocarbons. Column size is 2 ft in diameter and 5.2 ft in height. Packing is Pall Ring ceramic (50 mm). Various packings were analyzed as discussed in Appendix 6: Separations.

The column has 8 equivalent stages with a partial condenser and kettle reboiler. Reactor effluent enters the column above stage 9 and dibutyl phthalate recycle stream enters above stage 2. This design is typical in absorbers and allows for the greatest amount of contact with the dibutyl phthalate stripper [29]. The column has a reflux ratio of 1.75 and a distillate to feed mole ratio of 0.65.

The partial condenser uses refrigerated water to provide a heat duty of -132 GJ/hr. The kettle reboiler uses a natural gas fired heater at a rate of 235,800 kg/hr to provide a heat duty of 141 GJ/hr. The large utility requirements of the partial condenser and kettle reboiler are a significant part of the total operations cost for the column process.

This separation completely removes water, carbon dioxide, oxygen, nitrogen, and benzene. However, the resultant stream contains a large amount dibutyl phthalate (824 kmol/hr) mixed with the desirable product of maleic anhydride and quinone (totaling 15.26 kmol/hr).

COOLER2

COOLER2 cools the bottoms of the absorber from 362°C to 194°C. The utility of this cooler is cooling water with a flow rate of 4.3×10^6 kg/hr, providing a heat duty of -90 GJ/hr.

DIST1

DIST1 is a trayed distillation column to separate dibutyl phthalate from maleic anhydride product stream. Resulting product stream contains 96 mol% maleic anhydride and the recycle stream contains 99.8 mol% dibutyl phthalate. Column size is 4.7 ft in diameter with a height of 26 ft. Sieve trays are spaced 2 ft apart. Discussion about tray type and spacing can be found in Appendix 6: Separations.

The column consists of 2 stages with a partial condenser and kettle reboiler. The reflux ratio is 1.2 and the distillate to feed ratio is 0.017 on a molar basis. Feed enters above stage 2.

The condenser utility is chilled water at 73,200 kg/hr providing a heat duty of -1.53 GJ/hr. The kettle reboiler is heated by a natural gas fired heater at a rate of 117,900 kg/hr to provide a heat duty of 70.73 GJ/hr. Again, high utility costs contribute to large operational costs.

COOLER3

COOLER3 cools the maleic anhydride stream from DIST1 at 197°C to 125°C. The utility used is cooling water at a rate of 46,600 kg/hr providing a heat duty of -0.97 GJ/hr.

PUMP2

PUMP2 is a centrifugal pump which returns the dibutyl phthalate recycle to a pressure of 2.15 kPa. Pump efficiency is 0.7 and driver efficiency is 0.8 [19], [20]. Electrical duty is 18.94 kW.

DIST2

DIST2 is a packed distillation column to remove quinone impurities from the product stream. Resulting product stream contains 97 mol% maleic anhydride, 2 mol% quinone, and 1 mol% dibutyl phthalate. The waste stream (WASTE1) contains 87 mol% maleic anhydride, 12 mol% quinone, and less than 1 mol% of dibutyl phthalate and water combined. The waste stream contains 8 mol% of the maleic anhydride fed to the column. This column shows the trade-off between loss of maleic anhydride product and improvement in purity from 96 mol% to 97 mol%. Packing for the column is Rasching Metal rings (15 mm) due to high packing factor and low cost [30]. There is a partial condenser, kettle reboiler, and the equivalent of 8 stages with the feed entering above stage 2. The reflux ratio is 1 and the distillate to feed ratio is 0.09 on a molar basis. The condenser utilizes cooling water at a rate of 4430 kg/hr to provide a heat duty of -0.09 GJ/hr. The kettle reboiler utilizes high pressure steam at a rate of 220 kg/hr for a heat duty of 0.28 GJ/hr.

Other Important Factors

Environmental Problems and their solutions

It is difficult to place numbers to determine the environmental friendliness of a plant design. However, a few green metrics have been proposed and are discussed in. Additionally, environmental aspects of the adsorption-column process are compared to the flash process in the Introduction and Problem Statement. The following environmental concerns apply to both processes.

Handling of toxic materials such as benzene presents and environmental concern if leaks in the system occur. At a temperature of 50°C, benzene has an evaporation rate of $4.00\text{x}10^{-5}$ kg/s with an air velocity of 1 m/s [31]. To prevent vapor emissions, benzene is stored in a floating head tank, and the rest of the system is contained within a closed piping system [32]. Environmental concerns regarding benzene will arise due to piping leaks or uncompleted conversion in the reactor leading to the presence of benzene in waste streams. The Federal Water Pollution Control Act deems benzene a hazardous substance making any enclosure breaks into ground water or drinking water a serious environmental hazard [33]. The Maximum Contaminant Level (MCL) of benzene in drinking water is 0.005 mg/L as established by the Environmental Protection Agency in 2014 [34] [35].

Maleic anhydride is also identified as a hazard in the Clean Air Act and Clean Water Act [36], [33]. It is also known to known or suspected to cause serious health problems as discussed in the following section [36]. In the case of leaks, maleic anhydride will quickly hydrolyzes into maleic acid which may become violent [37]. Most vapors are heavier than air and will stay close to the ground [37]. Maleic anhydride, when exposed to carbon dioxide, rapidly biodegrades over 93% of the original mass [38]. In waste streams, it can be disposed of by controlled incineration to achieve complete oxidation to nontoxic products [39].

Gaseous waste products including carbon dioxide, oxygen, nitrogen, water, and small quantities of benzene are to be incinerated. Although incineration is not considered as part of this process, nitrous oxide (NO_x) emissions could be produced through incineration of oxygen and nitrogen at high temperatures [40] [41]. The current limits on NO_x, carbon monoxide, and ammonia emission are 2 ppm [42] [43]. Additionally, carbon dioxide emissions are regulated and total plant emissions would need to be considered in regards to carbon capture or carbon sequestration [44].

Safety and Health Concerns

There are several health and safety concerns associated with this process. There are significant hazards associated with benzene that will require constant monitoring and inherently safer design of equipment. Additional safety hazards and design choices are also discussed in the following sections.

Benzene Storage Tank

The benzene should be stored in a floating roof storage tank [32]. This will keep benzene emissions to a minimum. In addition, this tank will need to be insulated to keep benzene at optimal storage conditions. A major concern is keeping benzene above its freezing temperature of 42°F [32]. An insulated tank as well as internal heating coils are recommended for the floating roof storage tank to ensure that the benzene will not freeze in cold weather conditions.

For warmer conditions, benzene also needs to be kept in a dry, cool environment. Insulating the storage tank will aid in keeping the benzene at a moderate temperature. Because it is highly flammable, benzene vapors in elevated concentrations can be dangerous. The upper flammability limit (UFL) of benzene is 7.8% by volume [45]. The concentration of the ambient air around the storage tank should be monitored at all times to ensure that this limit is not reached.

In addition, concentrations of benzene should be monitored in the plant ambient environment for the safety of the employees. The time weighted average (TWA) for benzene exposure for an 8-hr work day is 1 ppm, and the short term exposure limit (STEL) is 5 ppm [46] [45]. Any exposure above these limits can be harmful to the employees at the plant.

Utilities

The utilities used for heating and cooling in this process are composed mostly of low hazard materials. The fired heater is the only piece of equipment that requires natural gas for heating. Other heat requirements are fulfilled using steam, cooling water, electric power, or a molten salt stream. This allows us to limit the minimum/maximum temperatures attained in this process, thus making it a safer environment.

Reactor Control

Another process that could present safety hazards is our reactor. In order to better control this process, we have designed a system for managing its operation. The full controls system can be seen in Process Controllability and Instrumentation. Most importantly, the reaction temperature needs to be controlled and maintained below 600°C [14]. At this temperature, the combustion reaction of benzene becomes a runaway reaction. In addition, sintering of the catalyst and the degradation of the main product maleic anhydride will occur [14]. Controlling these elevated temperatures requires a molten salt stream composed of 41.3 mol% sodium nitrate and 58.7 mol% sodium nitrite.

Additionally, it is important to keep the conversion of benzene as high as possible. For one, this ensures that we are making the maximum amount of maleic anhydride. Also, it ensures that there is a minimum amount of benzene in the process after the reactor. It is important to keep hazardous substances to a minimum anywhere throughout the process. In our process flow sheets, it can be seen that we achieve a conversion of benzene of 99.5% in the reactor. This minimizes the hazard of any benzene in the flash or distillation units following the main reaction.

Dibutyl Phthalate

The original proposed design for this project included a large stream of dibutyl phthalate. Dibutyl phthalate is toxic by both inhalation and ingestion. The threshold limit value (TLV) for an 8-hour work day is 5 mg/m^3 [47]. Our flash based process has eliminated the need for any dibutyl phthalate, making it an inherently safer design.

Maleic Anhydride

Our main product, maleic anhydride, also presents safety and health hazards. Maleic anhydride can react violently when exposed to large amounts of water, and produce some flammable and toxic vapors [48]. Maleic anhydride itself is also very toxic. It is both a respiratory and skin irritant, making it a hazard to employees handling the final product [48]. Any product handling performed by an employee needs to be done with proper protective clothing and breathing apparatus to prevent significant exposure.

Maleic anhydride also has a flash point of 102°C [48]. The environment in which the final product is handled or shipped needs to be kept below this temperature to reduce any flammability hazards.

Process Controllability and Instrumentation

The following considerations for the controls around the reactor is shown in the piping and instrumentation diagram (P&ID) in Figure 6 and described in the ensuing sections.

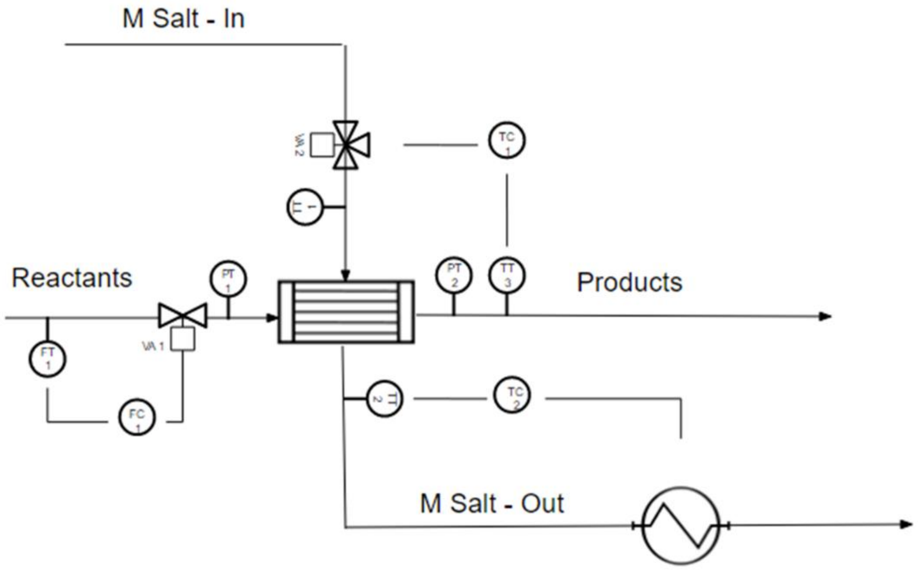


Figure 6: P&ID of the reactor.

A HAZOP Study was conducted to determine and evaluate hazards and establish a basis for necessary instrumentation and controls around the reactor.

Table 7: HAZOP study for the reactor.

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	Process Indications	Notes and Questions
Level					
Less	1. VA 1 closed or broken	Less residence time in the reactor	Maximum conversion is not reached	PT 1	At what low florwrate will Maleic Anhydride not be made?
	2. Inlet Pipe Ruptured	No flow	Potential Fire	FT 1, PT 1	What external events can cause rupture? Effect of released reactants on surroundings?
	3. Reactor has leak	Less residence time in the reactor	Damage to Pump	PT 2, TT 3	Estimate release quantity
More	4. VA 1 open or broken	Upset in reactor	Reagent released	PT 1	Possible problem in reactor
Pressure					
Less	5. Less flow of Benzene	Less residence time in the reactor	Maximum conversion is not reached	PT 1	At what low florwrate will Maleic Anhydride not be made?
	6. Less flow of Air	Less residence time in the reactor	Maximum conversion is not reached	PT 1	How much Benzene will not react?
	7. Inlet Pipe Ruptured	No flow	Potential Fire	FT 1, PT 1	What external events can cause rupture? Effect of released reactants on surroundings?
	8. Valve closed/broken	Less residence time in the reactor	Maximum conversion is not reached	PT 1	Possible problem in reactor
More	9. Pipe blockage	More pressure in reactor	Reactor failure	PT 1, PT 2 , FT 1	Reactor explosion
	10. FC 1 fails	More pressure in reactor	Reactor failure	PT 1, PT 2	Reactor explosion
	11. Temperature of inlet is hotter than normal	More pressure in reactor	Reactor failure	PT 1, PT 2	Reactor explosion
Composition					
Other than	12. Wrong concentration of reactants	Possible Reaction	Maximum conversion is not reached	PT 2, TT 3	How much side products are made?
Temperature					
Less	13. Temperature of the inlet is colder than normal	Possible Reaction	Maximum conversion is not reached	PT 2, TT 3	What temperature setting for the heater on the coolant?
	14. VA 1 closed/broke	Low flowrate of reactant	Maximum conversion is not reached	FT 1, PT 1, PT 2	FC 1 might be broke?
	15. TC 1 not functioning	Higher flowrate of coolant	Maximum conversion is not reached	VA 2	FT 1 might not be transmitting correctly
	16. Heater lowers temperature too low	Possible Reaction	Maximum conversion is not reached	TT 1, TC 2	What temperature setting for the heater on the coolant?
More	17. No/low flow of coolant	Sintering of cataylst	Runaway reaction	VA 2, TT 2, TT 3	Reaction will utlimately fail
	18. PT 1 failure	More pressure in reactor	Reactor failure	PT 1, PT 2	Reactor explosion
	19. VA 1 open/broke	More pressure in reactor	Reactor failure	PT 1, PT 2	Could cause large amounts of side
	20. Heater of coolant not working	Sintering of cataylst	Runaway reaction	TT 1, TT 3	Reaction will utlimately fail

The reactant flow (Reactants) is monitored by a flow transmitter (FT1). The transmitter relays a signal to the flow control (FC1). The flow control manages the flow valve (VA1) by opening/closing the valve to the required flow.

The pressure of the Reactants inlet stream is measured by a pressure transmitter (PT1). The pressure transmitter is to monitor the pressure inside the piping. The pressure transmitter will relay a signal to a pressure control (not on the P&ID) to shut down the system in case of pressure build-up.

To avoid catastrophe, such as a runaway reaction, sintering of the catalyst, breaking down of the maleic anhydride, a temperature transmitter (TT1) is placed immediately at the outlet of the reactor. In case the outlet (Product) is too hot, the temperature transmitter relays a signal to the temperature control (TC1). The temperature control manages a flow valve on the molten salt stream to the reactor. For example, the flow of the molten stream will increase to lower the temperature of the product stream.

The pressure of the outlet stream is also measured by a pressure transmitter (PT 2) to ensure the pipe does not burst due to excess pressure. The transmitter sends a signal to a pressure control (not on the P&ID) to shut down the system.

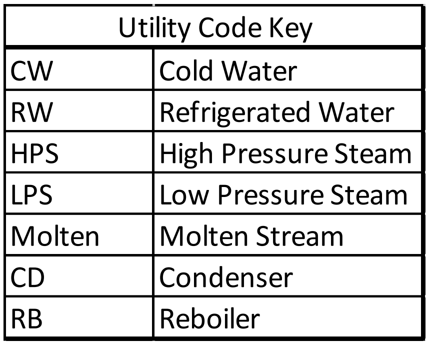
The coolant is monitored by a temperature transmitter before and after the reactor (TT1 and TT2, respectively). The temperature transmitter after the reactor communicates with temperature control (TC2). The temperature control manages the heater on the outlet coolant stream to the temperature required.

PROCESS ECONOMICS AND PROFITABILITY

Operating Costs

The utility costs of the two processes investigated are tabulated and discussed in their respective sections. The full operation costs are only calculated for the flash process as the utility cost alone exceeds the sales from maleic anhydride, therefore all economic analysis after this section will only include the flash-based process. Table 8 correlates the code in both of the utility tables to descriptions.

Table 8: Codes for utility table.



Utility Code Key	
CW	Cold Water
RW	Refrigerated Water
HPS	High Pressure Steam
LPS	Low Pressure Steam
Molten	Molten Stream
CD	Condenser
RB	Reboiler

Absorption-Distillation Process

Calculating the utilities required using both Aspen, and certain heuristics. Electric power was used as the utility for all pumps and compressors. For other utilities, we first used Aspen to calculate the heat duty for each piece of equipment. Based on that heat duty, as well as the temperature difference in the given stream, we employed heuristics to help us determine what utility to use. For example, we had several reboiler streams that required heating above 244 degrees C which is the maximum steam temperature [49]. Due to this we chose to use natural gas as the utility for these pieces of equipment. Then using the utility costs given in the design report, we were able to calculate the total cost of the utility per year based on 330 days/ year or 7920 hours/year.

Table 9: Utility costs for absorption-distillation process

Equipment	Utility	Amount		Cost of Utility		Total Cost (per year)
Air Compressor	Electirc	1722.11	kW	$ 0.06	/kWh	$ 818,346.67
Benzene Pump	Electric	0.21935	kW	$ 0.06	/kWh	$ 104.24
Benzene Heater	LPS	0.191264	GJ/hr	$ 13.28	/GJ	$ 20,116.69
Furnace	Natural Gas	17.6869	GJ/hr	$ 11.00	/GJ	$ 1,540,882.73
Product Cooler	CW	12.5021	GJ/hr	$ 0.35	/GJ	$ 35,051.89
Absorber RB	Natural Gas	141.494	GJ/hr	$ 11.00	/GJ	$ 12,326,957.28
Absorber CD	RW	131.726	GJ/hr	$ 4.43	/GJ	$ 4,621,685.75
Liquid Cooler	CW	90.0068	GJ/hr	$ 0.35	/GJ	$ 252,350.27
Distillation1 RB	Natural Gas	70.7254	GJ/hr	$ 11.00	/GJ	$ 6,161,596.85
Distillation1 CD	CW	1.53139	GJ/hr	$ 0.35	/GJ	$ 4,293.53
Recycle Pump	Electric	18.9384	kW	$ 0.06	/kWh	$ 8,999.53
Distillate Cooler	CW	0.974822	GJ/hr	$ 0.35	/GJ	$ 2,733.09
Distilation2 RB	Molten/HPS	0.380859	GJ/hr	$ 17.70	/GJ	$ 53,390.34
Distillation2 CD	CW	0.067916	GJ/hr	$ 0.35	/GJ	$ 190.42
					TOTAL	**$ 25,846,699.25**

As stated previously in the report, this process was found to not be profitable. The total sales from 10,000 metric tons of maleic anhydride equate to $15.4 million/year. According to the utilities calculation, this process will require over $25 million/year just for utilities, making this process not profitable. Due to this, further calculation for this design was deemed unnecessary for economic evaluation and this design was discontinued.

Flash-based Process

As it can be seen in Table 10, the utility costs for the flash-based process are significantly cheaper than that of the absorber-distillation process. The large decrease in utility costs stems from the limited use of natural gas as a utility. The process as a whole requires a smaller heat duties total (50.31 GJ/hr versus 473.56 GJ/hr) and on each of the units, therefore require mostly cooling water and steam as utilities. The utility cost is a strong sign that this process will be profitable. More profitability measurements are performed later in Economic Analysis.

Table 10: Utility costs for flash-based process.

Equipment	**Utility**	**Amount**		**Cost of Utility**		**Total Cost (per year)**
Air Compressor	Electirc	1746.9	kW	$ 0.06	/kWh	$ 830,126.88
Benzene Pump	Electric	0.22256	kW	$ 0.06	/kWh	$ 105.76
Benzene Heater	LPS	0.194061	GJ/hr	$ 13.28	/GJ	$ 20,410.87
Furnace	Natural Gas	17.9421	GJ/hr	$ 11.00	/GJ	$ 1,563,115.75
Product Cooler	CW	24.3416	GJ/hr	$ 0.35	/GJ	$ 68,246.06
Flash 1	CW	0.199936	GJ/hr	$ 0.35	/GJ	$ 560.56
Flash 2	Molten/HPS	0.687479	GJ/hr	$ 17.70	/GJ	$ 96,373.56
Distilation RB	Molten/HPS	0.395594	GJ/hr	$ 17.70	/GJ	$ 55,455.95
Distillation CD	CW	0.2622	GJ/hr	$ 0.35	/GJ	$ 735.12
					TOTAL	**$ 2,635,130.51**

In addition to utilities, the total production cost was calculated for the flash-based process. This calculation can be seen in Appendix 4: Economic Analysis and Calculations. The total production cost for the flash based process was found to be approximately $5.3 million/year [50]. Similar to the Fixed Capital Investment (FCI) estimation, we utilized several suggested factors by Peters et al. for each of the operating costs. For example, we did not factor in any research and development costs because this process is very well known and used in industry. In addition, we did not include depreciation in this calculation, as it will be considered in the profitability measurements.

Equipment Cost Summary

Using the process flow diagram for the flash-based process, each piece of equipment was costed in 2010 dollars. Two sources were used for finding the information necessary to cost the equipment. These sources can be seen in the Equation section of the above table. Any information on the heat duty or energy requirements were found in Aspen. Additionally, the heat transfer coefficients used to calculate heat transfer area were given to us as project specifications. Using various charts and sizing equations, each piece of equipment was costed, and then scaled up to the cost in 2010 using the 2010 CEP Index of 550.8 [51] [52]. The total equipment cost for this process was just below $2 million.

Table 11: Equipment cost for flash-based process.

Equipment	**Additional Info**	**Equipment Specs**	**Equation**	**Cost**	**CP Index**	**Equipment Cost in 2010 Dollars**
Storage Tank	Size based on ~1.5 times amount received	Floating roof, carbon steel, 125000 gal	C=375*$V^{0.51}$ (Seider et al.)	$ 149,000	394	$ 208,297
Benzene Pump	Size based on capacity = 30.75 L/min and 235 kPa	Stainless steel, centrifugal pump	Chart and Material Adjustment Factor (Peters et al, p. 519)	$ 2,880	390.4	$ 4,063
Benzene Evaporator	Q=57412.9 cal/sec from Aspen; U=100 W/(m^2K)	A=2.67 m^2, stainless steel, horizontal tube	C=3200*$A^{0.53}$ (Seider et al.); Material Adjustment Factor (Peters et al.)	$ 11,306	390.4	$ 15,951
Air Compressor	1673 hp from Aspen	Carbon steel, centrifugal compressor	C=$e^{(7.2223+0.8*\ln(hp))}$ (Seider et al.)	$ 519,280	394	$ 725,938
Reactants Fired Heater	Q=962012 cal/s from Aspen	Stainless steel, direct fired heater	Chart (Peters et al, p. 692)	$ 400,000	390.4	$ 564,344
Reactor	U=100 W/(m^2K)	Shell and Tubed Packed Bed, 15000 tubes at D=25 mm, L=3 m, A=7.362 m^2	Chart (Peters et al, p. 682)	$ 4,000	390.4	$ 5,643
Molten Salt Pump	Mass flow = 105 kg/s; 41.3 mol% nitrate; 58.7 mol% nitrite	Stainless steel, centrifugal pump	Chart andMaterial Adjustment Factor (Peters et al, p. 519)	$ 28,800	390.4	$ 40,633
Products Cooler	Q=1050000 cal/s from Aspen; U=100 W/(m^2K)	A=13 m^2, stainless steel tubes, shell and tube	Chart in (Peters et al, p. 682)	$ 10,500	390.4	$ 14,814
Flash Unit Series	Costed in Separations Appendix	3 flash units in series	Peters et al.	$ 234,000	390.4	$ 330,141
					TOTAL	**$ 1,909,825**

Fixed Capital Investment Summary

Based on the purchased equipment cost, the fixed capital investment could be calculated. A delivery cost of 10% of the equipment cost was assumed. Then, the direct and indirect cost could be calculated from the purchased delivered equipment cost [53]. Peters et al. offers suggested percentages to use for a fluids processing plant, but are often given as a range. Each of these ranges was evaluated for our specific process. For example, in calculating the service facilities, we chose to use a lower percentage because this is only an expansion project for a single product. Again, each cost was evaluated in a similar manner for our process. Following this, the FCI was costed at approximately $9.5 million and the Total Capital Investment (TCI) was found to be approximately $11.4 million. The working capital was assumed to be 15% of the TCI.

Costs	% of Delivered Eq. Cost	Justification	Cost
Direct Costs			
Purchased Equipment Delivered	100	Calculated Previously	$ 2,100,808
Purchased Equipment Installation	47	Installation varies from 25-55 %, higher for fluids plant	$ 987,380
Instramentation & Controls	36	This process will require a significant amount of control. Range from 8-50%	$ 756,291
Piping	68	Fluids processesing requires a larger amout of required piping. Max=80%	$ 1,428,549
Electrical Systems	11	Ranges 15-30%	$ 231,089
Buildings	6	This is the percent given for an expansion to an existing site	$ 126,048
Yard Improvements	10	ranges 10-20%	$ 210,081
Service Facilities	40	Ranges 30-80%, for single product, continuous process will be lower	$ 840,323
		Total	$ 6,680,570
Indirect Costs			
Engineering & Supervision	30	Approximately 30%	$ 630,242
Construction Expenses	41	Suggested percentage	$ 861,331
Legal Expenses	4	Mostly from equipment purchases, and environmental & safety complience	$ 84,032
Contractor's Fee	22	Suggested percentage	$ 462,178
Contingency	40	A value slightly smaller than suggested due to this only being an addition.	$ 840,323
		Total	$ 2,878,107
		Fixed Capital Investment	**$ 9,558,677**
		WC	**$ 1,869,719**
		Total Capital Investment	**$ 11,428,396**

Table 12: Fixed capital investment for flashed-based process.

Economic Analysis

The first profitability measurements calculated for the flash-based process are return on investment (ROI) and payback period (PBP). Both measurements were calculated in the third year of production, as it was assumed that the process would be at full capacity by this point. The table for calculating these measurements can also be found in Appendix B. Return on Investment is defined as:

$$ROI\ (year\ 3) = \frac{Annual\ Net\ Profit}{Total\ Capital\ Investment}$$

$$= \frac{(Sales - Costs - Depreciation)(1 - tax\ rate)}{Total\ Capital\ Investment}$$

For these calculations, a tax rate of 35% was assumed. The ROI was found to be 0.48 for this process. Additionally, the payback period was calculated in year 3; the equation is as follows:

$$PBP(year\ 3) = \frac{Total\ Depreciable\ Capital}{Annual\ Cash\ Flow} = \frac{TDC}{(S - C)(1 - t) + D}$$

The payback period was found to be 1.16 years. Both the ROI and PBR show that the flash-based process stands to be very profitable.

Profitability

Net Present Worth

The next profitability measure we performed was the net present worth. We calculated the net present worth (NPW) for two scenarios. One in which all the total investment is all payed at year 0, and the other when the total investment is done in several payments prior to the plant start up. Net present worth is defined as:

$$NPW = Present\ Worth\ of\ Cash\ Flows - Present\ Worth\ of\ Capital\ Investments$$

The calculations of NPW can be found in Appendix 4: Economic Analysis and Calculations, and can also be seen in the graphs below. Figure 7 is a cash flow diagram over the 15-year project life, showing the initial capital investment paid in year zero, and the profits made following that year.

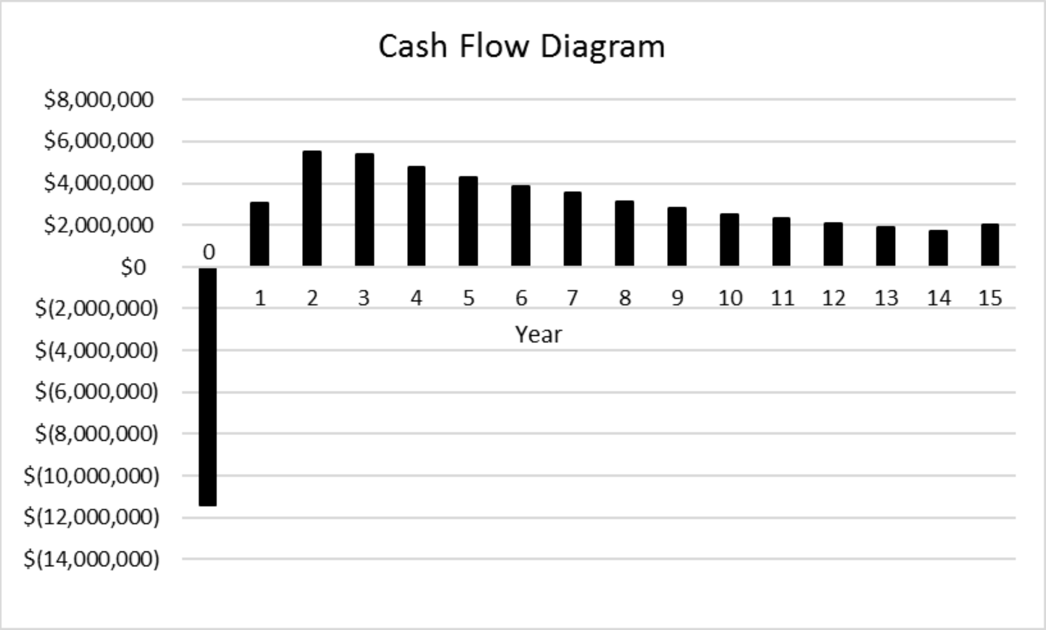


Figure 7: Annual cash flow diagram considering all investment at year zero.

Figure 8 shows the net present worth over the 15-year project life. This chart shows that the process will start to be profitable in year 3 following the start-up of the plant. The total NPW at the end of the 15-year period is approximately $37 million. This shows that the flash-based process stands to be extremely profitable.

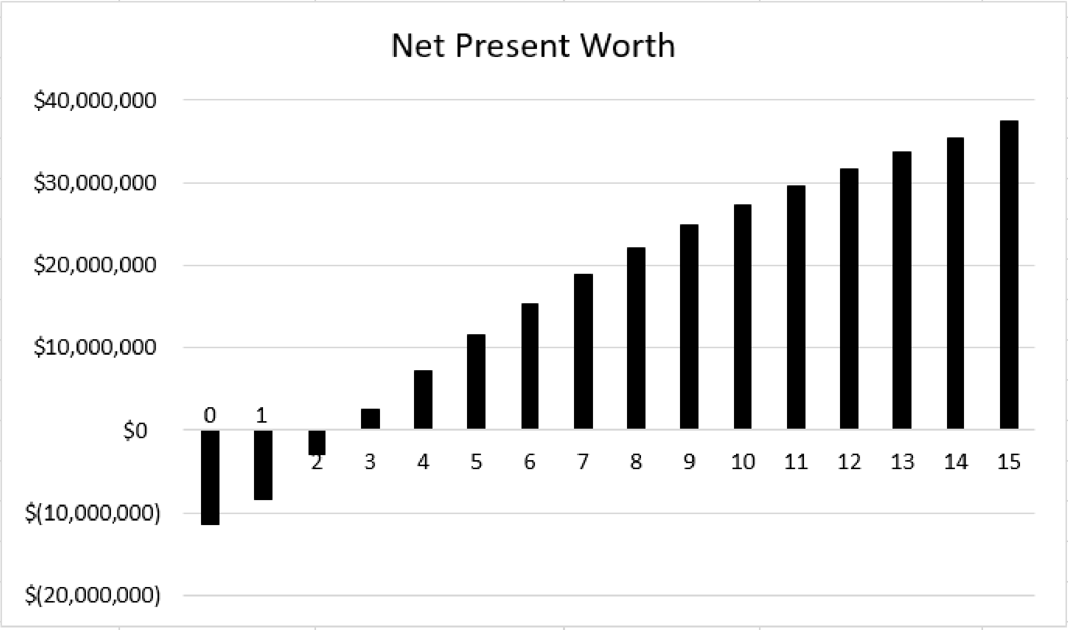


Figure 8: Annual net present worth considering all investment at year zero.

In contrast, we looked at the situation in which the total capital investment is made in a series of payments prior to start up. 70% would be paid two years before start-up, and the other 30% paid one year before start up. The corresponding charts (

Figure **9** and Figure 10) can be seen below for the annual cash flow and NPW. Both the cash flow diagram and net present worth chart have similar trends to that of the single total capital investment payment.

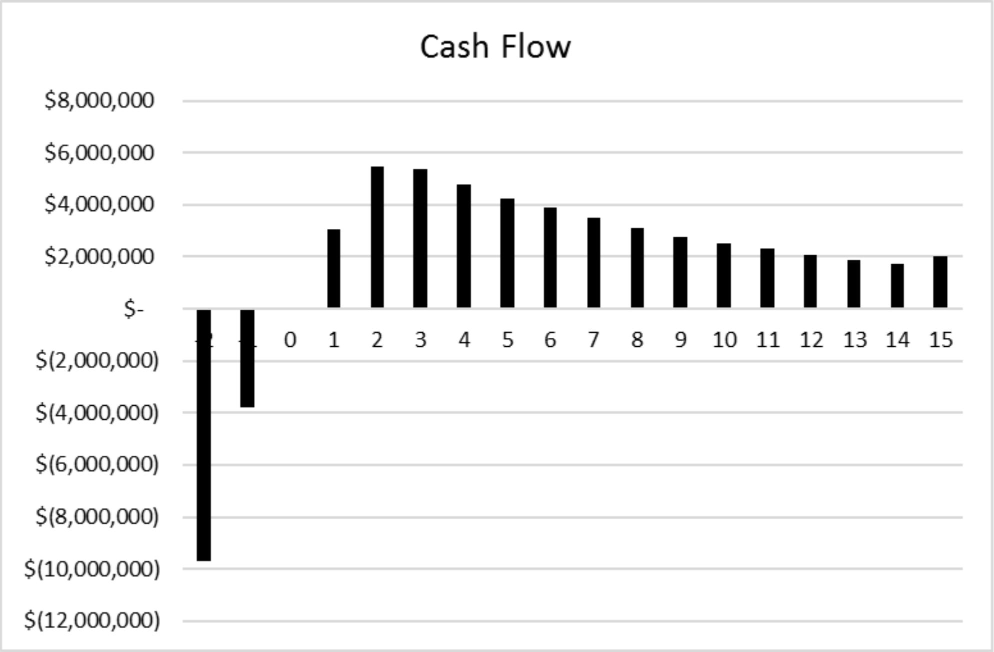


Figure 9: Annual cash flow diagram considering all investment two years before year zero.

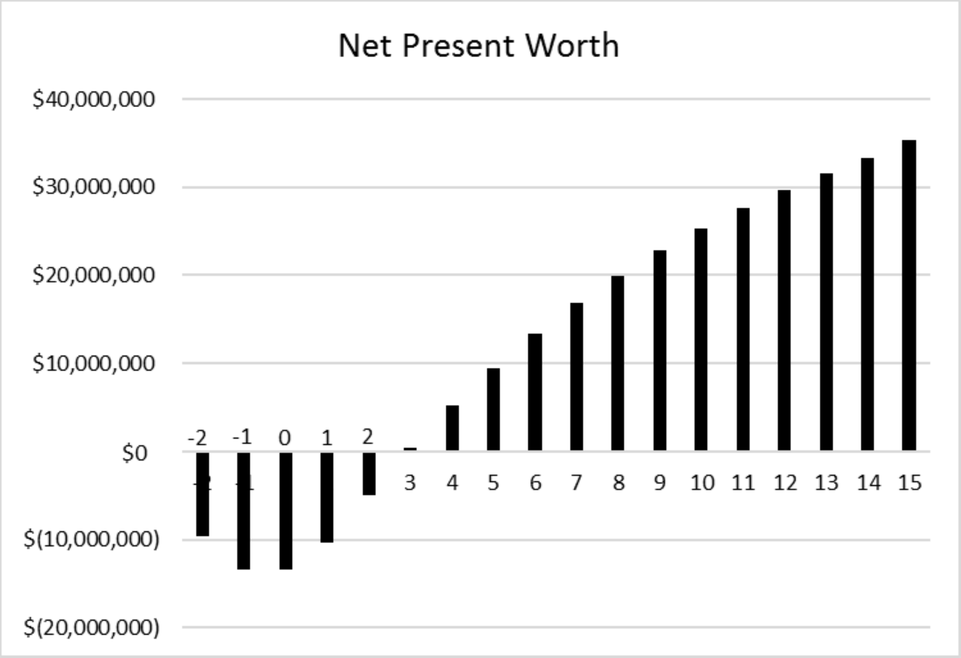


Figure 10: Annual net present worth considering all investment two years before year zero.

Figure 11 shows the net present worth of both scenarios compared to one another. It can be seen from this chart that the NPW at year 15 will be slightly lower at approximately $35 million. Both methods will be extremely profitable for this process.

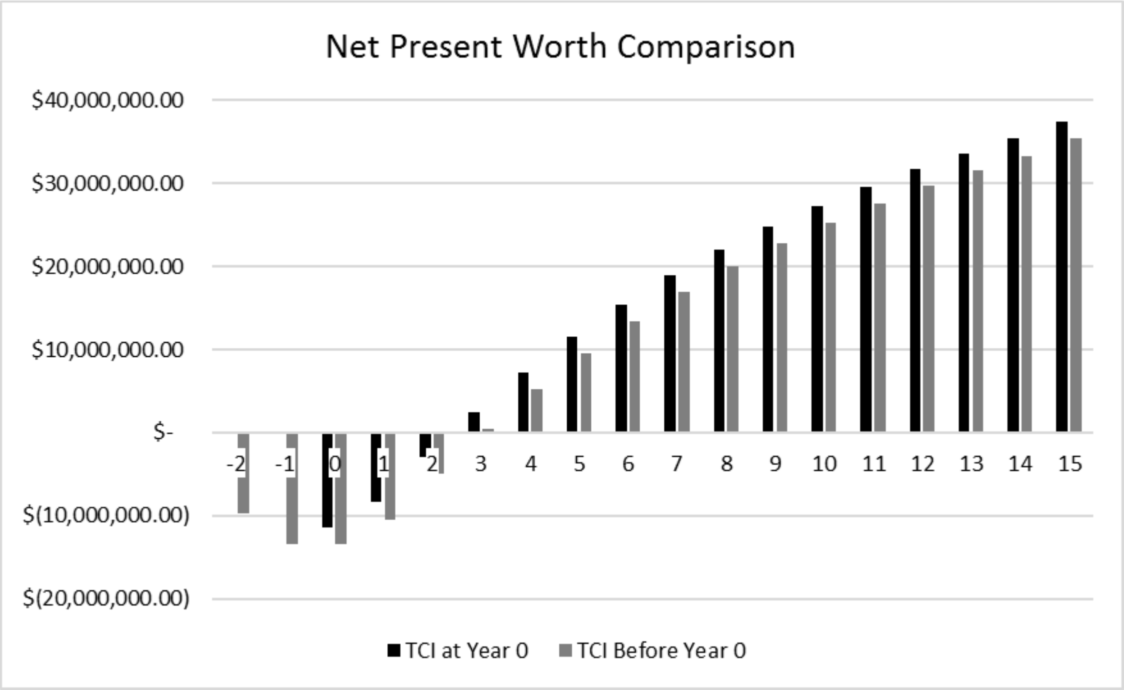


Figure 11: Comparison of annual net present worth considering all investment at year zero and two years before year zero.

Discounted Cash Flow Rate of Return

Finally, we calculated the discounted cash flow rate of return (DCFR). Due to the similarities in NPW regardless of year of investment, we only performed this calculation for the scenario in which all of the total capital investment is paid in year zero, prior to start up. The table below shows that for our presented process, the DCFR is 0.496 or 49.6%. This far exceeds the desired rate of return of 30%, thus making our recommended process a viable option.

Table 13: Discounted cash flow rate summary.

FCI	**Tax Rate**	**DCFR**
$ 9,558,676.52	0.35	0.496

Table 14: Discounted cash flow rate of return considering all capital investment at year zero.

Year	Annual Revenue	Annual Op. Expenses	Dep. Rate (%)	Depreciation	TCI	Recovery	PWF	Present Worth Cash Flows	Present Worth TCI
0					$ 11,428,396		1	$ -	$ 11,428,396
1	$ 7,700,000	$ 3,280,000	14.29	$ 1,365,935	$ -	$ -	0.668330454	$ 2,239,626.95	$ -
2	$ 13,860,000	$ 4,910,000	24.49	$ 2,340,920	$ -	$ -	0.446665596	$ 2,964,440.03	$ -
3	$ 15,400,000	$ 5,310,000	17.49	$ 1,671,813	$ -	$ -	0.29852022	$ 2,132,519.31	$ -
4	$ 15,400,000	$ 5,310,000	12.49	$ 1,193,879	$ -	$ -	0.199510154	$ 1,391,854.17	$ -
5	$ 15,400,000	$ 5,310,000	8.93	$ 853,590	$ -	$ -	0.133338712	$ 914,337.74	$ -
6	$ 15,400,000	$ 5,310,000	8.92	$ 852,634	$ -	$ -	0.089114322	$ 611,049.94	$ -
7	$ 15,400,000	$ 5,310,000	8.93	$ 853,590	$ -	$ -	0.059557815	$ 408,403.21	$ -
8	$ 15,400,000	$ 5,310,000	4.46	$ 426,317	$ -	$ -	0.039804302	$ 266,995.75	$ -
9	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.026602427	$ 174,472.02	$ -
10	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.017779212	$ 116,604.96	$ -
11	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.011882389	$ 77,930.65	$ -
12	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.007941362	$ 52,083.43	$ -
13	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.005307454	$ 34,808.94	$ -
14	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.003547133	$ 23,263.87	$ -
15	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ 1,869,719	0.002370657	$ 19,980.42	$ -
							SUM	$ 11,428,371.40	
							NPW	$ (24.26)	

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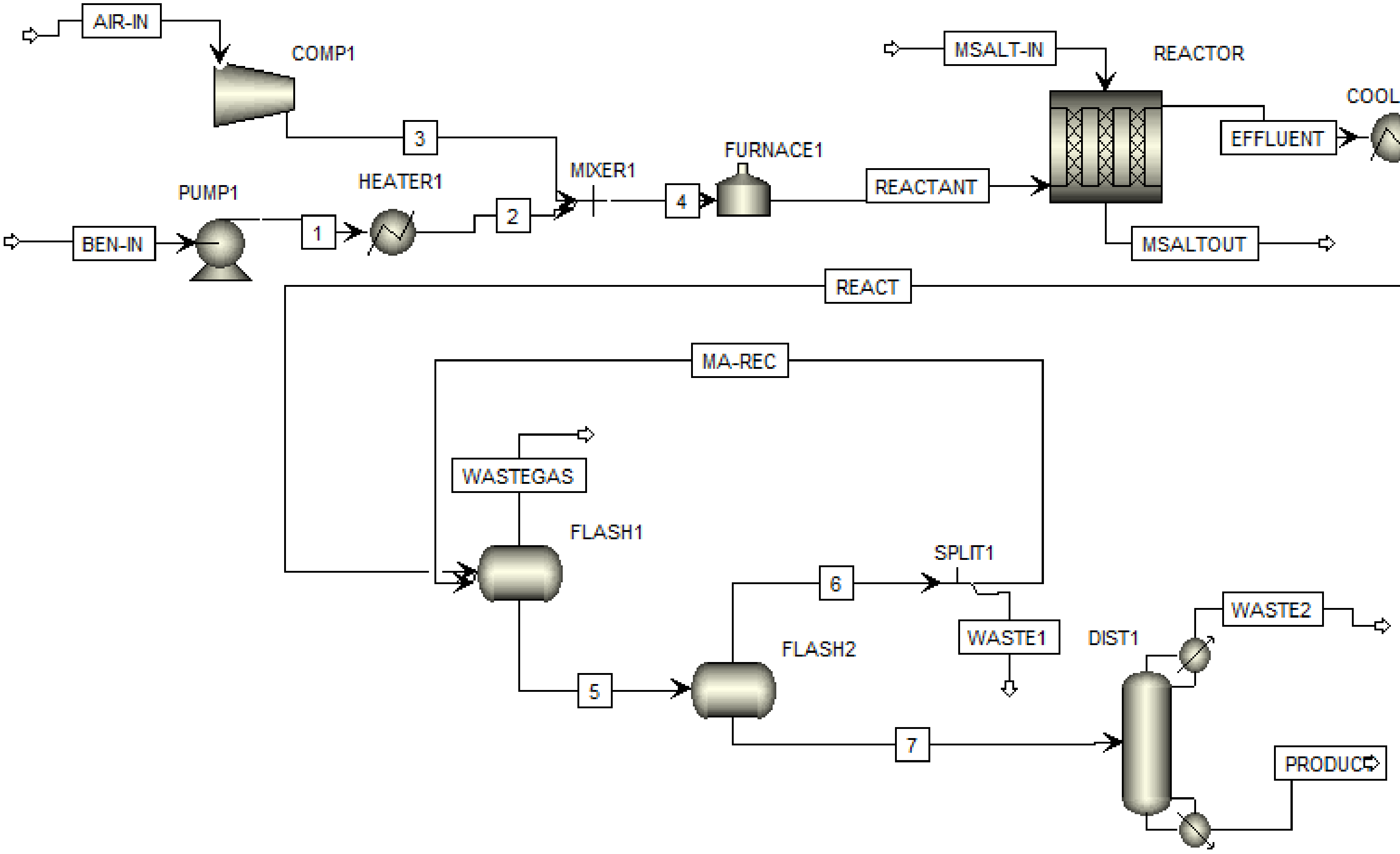
APPENDICES

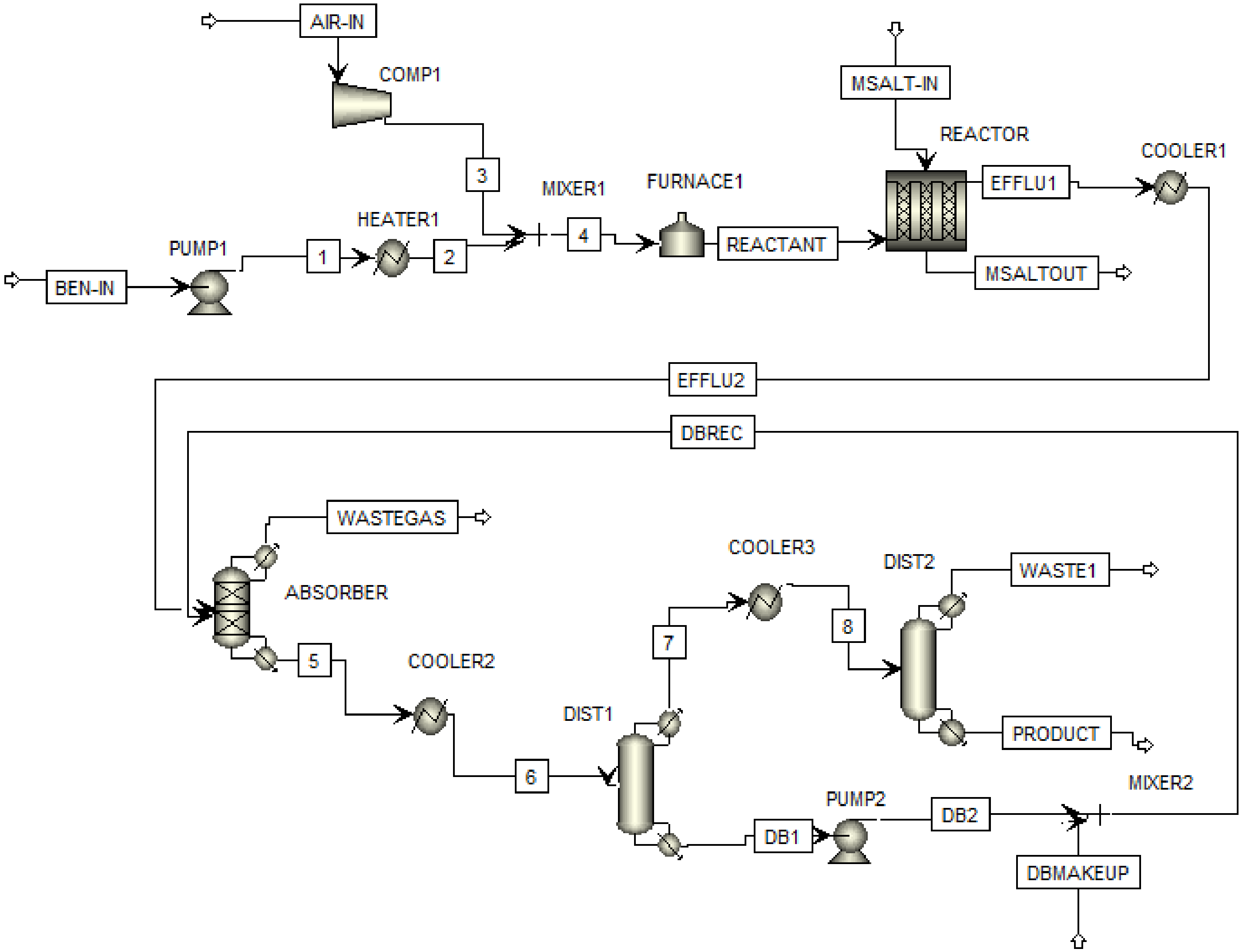
Appendix 1: Process Flow Diagrams

Flash-Based Process



Appendix Figure 1: Process flow diagram for the flash-based process.

Absorption-Distillation Process



Appendix Figure 2: Process flow diagram for the absorption-distillation process.

Appendix 2: Stream Tables

Flash-Based Process

Appendix Table 1: Complete stream table for the flash-based process (Part 1).

	Units	1	2	3	4	5	6	7	AIR-IN	BEN-IN	EFFLUENT	MA-REC
From		PUMP1	HEATER1	COMP1	MIXER1	FLASH1	FLASH2	FLASH2			REACTOR	SPLIT1
To		HEATER1	MIXER1	MIXER1	FURNACE1	FLASH2	SPLIT1	DIST1	COMP1	PUMP1	COOLER1	FLASH1
Phase		Liquid	Liquid	Vapor	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Vapor
Temperature	C	25	110	133	117	60	200	200	25	25	506	200
Pressure	bar	2.35	2.35	2.35	2.35	2.15	2.15	2.15	1.01	1.01	2.232	2.15
Mole Flows	kmol/hr	24.280	24.280	1594.140	1618.420	18.155	4.542	13.613	1594.140	24.280	1616.291	3.406
Maleic Anhydride	kmol/hr	0.000	0.000	0.000	0.000	14.157	1.741	12.416	0.000	0.000	13.759	1.305
Benzene	kmol/hr	24.280	24.280	0.000	24.280	0.001	0.001	0.000	0.000	24.280	0.116	0.000
Oxygen	kmol/hr	0.000	0.000	334.770	334.770	0.001	0.001	0.000	334.770	0.000	197.528	0.001
Nitrogen	kmol/hr	0.000	0.000	1259.370	1259.370	0.002	0.002	0.000	1259.370	0.000	1259.370	0.001
Carbon Dioxide	kmol/hr	0.000	0.000	0.000	0.000	0.007	0.006	0.000	0.000	0.000	87.238	0.005
Quinone	kmol/hr	0.000	0.000	0.000	0.000	0.379	0.087	0.292	0.000	0.000	0.452	0.065
Water	kmol/hr	0.000	0.000	0.000	0.000	3.610	2.704	0.905	0.000	0.000	57.829	2.028
Sodium Nitrate	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium Nitrite	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mole Fractions												
Maleic Anhydride		0.000	0.000	0.000	0.000	0.780	0.383	0.912	0.000	0.000	0.009	0.383
Benzene		1.000	1.000	0.000	0.015	0.000	0.000	0.000	0.000	1.000	0.000	0.000
Oxygen		0.000	0.000	0.210	0.207	0.000	0.000	0.000	0.210	0.000	0.122	0.000
Nitrogen		0.000	0.000	0.790	0.778	0.000	0.000	0.000	0.790	0.000	0.779	0.000
Carbon Dioxide		0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.054	0.001
Quinone		0.000	0.000	0.000	0.000	0.021	0.019	0.021	0.000	0.000	0.000	0.019
Water		0.000	0.000	0.000	0.000	0.199	0.595	0.066	0.000	0.000	0.036	0.595
Sodium Nitrate		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium Nitrite		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mass Flows	kg/hr	1897	1897	45992	47888	1495	229	1265	45992	1897	47888	172

Appendix Table 2: Complete stream table for the flash-based process (Part 2).

	Units	MSALT-IN	MSALTOUT	PRODUCT	REACT	REACTANT	WASTE1	WASTE2	WASTEGAS
From			REACTOR	DIST1	COOLER1	FURNACE1	SPLIT1	DIST1	FLASH1
To		REACTOR			FLASH1	REACTOR			
Phase		Liquid	Mixed	Liquid	Mixed	Vapor	Vapor	Vapor	Vapor
Temperature	C	500	506	232	60	460	200	173	60
Pressure	bar	3.6	3.6	2.15	2.15	2.35	2.15	2.15	2.15
Mole Flows	kmol/hr	4999.000	4999.000	12.524	1616.291	1618.420	1.135	1.089	1601.543
Maleic Anhydride	kmol/hr	0.000	0.000	12.258	13.759	0.000	0.435	0.158	0.907
Benzene	kmol/hr	0.000	0.000	0.000	0.116	24.280	0.000	0.000	0.116
Oxygen	kmol/hr	0.000	0.000	0.000	197.528	334.770	0.000	0.000	197.528
Nitrogen	kmol/hr	0.000	0.000	0.000	1259.370	1259.370	0.000	0.000	1259.370
Carbon Dioxide	kmol/hr	0.000	0.000	0.000	87.238	0.000	0.002	0.000	87.236
Quinone	kmol/hr	0.000	0.000	0.266	0.452	0.000	0.022	0.026	0.138
Water	kmol/hr	0.000	0.000	0.000	57.829	0.000	0.676	0.905	56.248
Sodium Nitrate	kmol/hr	2065.000	2065.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium Nitrite	kmol/hr	2934.000	2934.000	0.000	0.000	0.000	0.000	0.000	0.000
Mole Fractions									
Maleic Anhydride		0.000	0.000	0.979	0.009	0.000	0.383	0.145	0.001
Benzene		0.000	0.000	0.000	0.000	0.015	0.000	0.000	0.000
Oxygen		0.000	0.000	0.000	0.122	0.207	0.000	0.000	0.123
Nitrogen		0.000	0.000	0.000	0.779	0.778	0.000	0.000	0.786
Carbon Dioxide		0.000	0.000	0.000	0.054	0.000	0.001	0.000	0.054
Quinone		0.000	0.000	0.021	0.000	0.000	0.019	0.024	0.000
Water		0.000	0.000	0.000	0.036	0.000	0.595	0.831	0.035
Sodium Nitrate		0.413	0.413	0.000	0.000	0.000	0.000	0.000	0.000
Sodium Nitrite		0.587	0.587	0.000	0.000	0.000	0.000	0.000	0.000
Mass Flows	kg/hr	377946	377946	1231	47888	47888	57	35	46566

Absorption-Distillation Process

Appendix Table 3: Complete stream table for the absorption-distillation process (Part 1).

	Units	1	2	3	4	5	6	7	8	AIR-IN	BEN-IN
From		PUMP1	HEATER1	COMP1	MIXER1	ABSORBER	COOLER2	DIST1	COOLER3		
To		HEATER1	MIXER1	MIXER1	FURNACE1	COOLER2	DIST1	COOLER3	DIST2	COMP1	PUMP1
Phase		Liquid	Liquid	Vapor	Vapor	Liquid	Liquid	Vapor	Liquid	Vapor	Liquid
Temperature	C	25	85	133	115	362	194	197	125	25	25
Pressure	bar	2.35	2.35	2.35	2.35	2.15	2.15	0.82	0.82	1.01	1.01
Mole Flows	kmol/hr	23.930	23.930	1571.510	1595.440	839.251	839.251	14.099	14.099	1571.510	23.930
Maleic Anhydride	kmol/hr	0.000	0.000	0.000	0.000	14.798	14.798	13.565	13.565	0.000	0.000
Benzene	kmol/hr	23.930	23.930	0.000	23.930	0.000	0.000	0.000	0.000	0.000	23.930
Oxygen	kmol/hr	0.000	0.000	330.020	330.020	0.000	0.000	0.000	0.000	330.020	0.000
Nitrogen	kmol/hr	0.000	0.000	1241.490	1241.490	0.000	0.000	0.000	0.000	1241.490	0.000
Carbon Dioxide	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Quinone	kmol/hr	0.000	0.000	0.000	0.000	0.459	0.459	0.434	0.434	0.000	0.000
Dibutyl Phthalate	kmol/hr	0.000	0.000	0.000	0.000	823.992	823.992	0.097	0.097	0.000	0.000
Water	kmol/hr	0.000	0.000	0.000	0.000	0.003	0.003	0.003	0.003	0.000	0.000
Sodium Nitrate	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium Nitrite	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mole Fractions											
Maleic Anhydride		0.000	0.000	0.000	0.000	0.018	0.018	0.962	0.962	0.000	0.000
Benzene		1.000	1.000	0.000	0.015	0.000	0.000	0.000	0.000	0.000	1.000
Oxygen		0.000	0.000	0.210	0.207	0.000	0.000	0.000	0.000	0.210	0.000
Nitrogen		0.000	0.000	0.790	0.778	0.000	0.000	0.000	0.000	0.790	0.000
Carbon Dioxide		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Quinone		0.000	0.000	0.000	0.000	0.001	0.001	0.031	0.031	0.000	0.000
Dibutyl Phthalate		0.000	0.000	0.000	0.000	0.982	0.982	0.007	0.007	0.000	0.000
Water		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium Nitrate		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium Nitrite		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mass Flows	kg/hr	1869	1869	45339	47208	230857	230857	1404	1404	45339	1869

Appendix Table 4: Complete stream table for the absorption-distillation process (Part 2).

	Units	DB1	DB2	DBMAKEUP	DBREC	EFFLU1	EFFLU2	MSALT-IN	MSALTOUT	PRODUCT	REACTANT
From		DIST1	PUMP2		MIXER2	REACTOR	COOLER1		REACTOR	DIST2	FURNACE1
To		PUMP2	MIXER2	MIXER2	ABSORBER	COOLER1	ABSORBER	REACTOR			REACTOR
Phase		Liquid	Liquid	Liquid	Liquid	Vapor	Vapor	Liquid	Mixed	Liquid	Vapor
Temperature	C	326	326	325	326	506	270	500	506	197	460
Pressure	bar	0.82	2.15	2.15	2.15	2.232	2.15	3.6	3.6	0.82	2.35
Mole Flows	kmol/hr	825.152	825.152	0.105	825.257	1593.335	1593.335	4999.000	4999.000	12.830	1595.440
Maleic Anhydride	kmol/hr	1.233	1.233	0.000	1.233	13.566	13.566	0.000	0.000	12.459	0.000
Benzene	kmol/hr	0.000	0.000	0.000	0.000	0.118	0.118	0.000	0.000	0.000	23.930
Oxygen	kmol/hr	0.000	0.000	0.000	0.000	194.801	194.801	0.000	0.000	0.000	330.020
Nitrogen	kmol/hr	0.000	0.000	0.000	0.000	1241.490	1241.490	0.000	0.000	0.000	1241.490
Carbon Dioxide	kmol/hr	0.000	0.000	0.000	0.000	85.935	85.935	0.000	0.000	0.000	0.000
Quinone	kmol/hr	0.025	0.025	0.000	0.025	0.445	0.445	0.000	0.000	0.279	0.000
Dibutyl Phthalate	kmol/hr	823.895	823.895	0.105	824.000	0.000	0.000	0.000	0.000	0.092	0.000
Water	kmol/hr	0.000	0.000	0.000	0.000	56.979	56.979	0.000	0.000	0.000	0.000
Sodium Nitrate	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000	2065.000	2065.000	0.000	0.000
Sodium Nitrite	kmol/hr	0.000	0.000	0.000	0.000	0.000	0.000	2934.000	2934.000	0.000	0.000
Mole Fractions											
Maleic Anhydride		0.001	0.001	0.000	0.001	0.009	0.009	0.000	0.000	0.971	0.000
Benzene		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.015
Oxygen		0.000	0.000	0.000	0.000	0.122	0.122	0.000	0.000	0.000	0.207
Nitrogen		0.000	0.000	0.000	0.000	0.779	0.779	0.000	0.000	0.000	0.778
Carbon Dioxide		0.000	0.000	0.000	0.000	0.054	0.054	0.000	0.000	0.000	0.000
Quinone		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.000
Dibutyl Phthalate		0.998	0.998	1.000	0.998	0.000	0.000	0.000	0.000	0.007	0.000
Water		0.000	0.000	0.000	0.000	0.036	0.036	0.000	0.000	0.000	0.000
Sodium Nitrate		0.000	0.000	0.000	0.000	0.000	0.000	0.413	0.413	0.000	0.000
Sodium Nitrite		0.000	0.000	0.000	0.000	0.000	0.000	0.587	0.587	0.000	0.000
Mass Flows	kg/hr	229453	229453	29	229483	47208	47208	377946	377946	1278	47208

Appendix Table 5: Complete stream table for the absorption-distillation process (Part 3).

	Units	WASTE1	WASTEGAS
From		DIST2	ABSORBER
To			
Phase		Vapor	Vapor
Temperature	C	195	45
Pressure	bar	0.82	2.15
Mole Flows	kmol/hr	1.269	1579.340
Maleic Anhydride	kmol/hr	1.106	0.001
Benzene	kmol/hr	0.000	0.118
Oxygen	kmol/hr	0.000	194.801
Nitrogen	kmol/hr	0.000	1241.490
Carbon Dioxide	kmol/hr	0.000	85.935
Quinone	kmol/hr	0.155	0.011
Dibutyl Phthalate	kmol/hr	0.005	0.008
Water	kmol/hr	0.003	56.976
Sodium Nitrate	kmol/hr	0.000	0.000
Sodium Nitrite	kmol/hr	0.000	0.000
Mole Fractions			
Maleic Anhydride		0.872	0.000
Benzene		0.000	0.000
Oxygen		0.000	0.123
Nitrogen		0.000	0.786
Carbon Dioxide		0.000	0.054
Quinone		0.122	0.000
Dibutyl Phthalate		0.004	0.000
Water		0.002	0.036
Sodium Nitrate		0.000	0.000
Sodium Nitrite		0.000	0.000
Mass Flows	kg/hr	127	45833

Appendix 3: Material Balance Calculations

Material Balance Over Reactor

$$Mass\ In = Mass\ Out$$

$$M_B + M_{O2} + M_{N2} + M_{Salt} = M_B + M_{O2} + M_{N2} + M_{MA} + M_{CO2} + M_Q + M_{H2O} + M_{Salt}$$

$$\begin{aligned}1896.6 + 10712.2 + 35279.3 + 377946 \\ &= 9.06 + 6320.65 + 35279.3 + 1349.14 + 3839.31 + 48.85 + 1041.81 \\ &+ 377946\ \left(all\ in \frac{kg}{hr}\right)\end{aligned}$$

$$425834.2\ \left(\frac{kg}{hr}\right) = 425834.2\ \left(\frac{kg}{hr}\right)$$

Overall System Material Balance

$$M_{Bin} + M_{AirIn} + M_{SaltIn} = M_{SaltOut} + M_{Waste1} + M_{Waste2} + M_{WasteGas} + M_{Product}$$

$$M_{Bin} = 1896.6 \frac{kg}{hr}$$

$$M_{AirIn} = M_{O2} + M_{N2} = 10712.2 + 35279.3 = 45991.6 \frac{kg}{hr}$$

$$M_{SaltIn} = M_{SaltOut} = 377946\ kg/hr$$

$$\begin{aligned}M_{Waste1} &= M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O} \\ &= 42.67 + 0.01 + 0.008 + 0.01 + 0.07 + 2.36 + 12.18 = 57.31 \frac{kg}{hr}\end{aligned}$$

$$\begin{aligned}M_{Waste2} &= M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O} \\ &= 15.50 + 0.01 + 0.0008 + 0.00005 + 0.003 + 2.79 + 16.30 = 34.61 \frac{kg}{hr}\end{aligned}$$

$$\begin{aligned}M_{WasteGas} &= M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O} \\ &= 88.98 + 9.04 + 6320.64 + 35279.3 + 3839.24 + 14.96 + 1013.32 \\ &= 46565.5 \frac{kg}{hr}\end{aligned}$$

$$M_{Product} = M_{MA} + M_Q + M_{H2O} = 1201.99 + 28.74 + 0.01 = 1230.74 \frac{kg}{hr}$$

$$M_{Bin} + M_{AirIn} + M_{SaltIn} = M_{SaltOut} + M_{Waste1} + M_{Waste2} + M_{WasteGas} + M_{Product}$$

$$1896.6 + 45991.6 + 377946 = 377946 + 57.31 + 34.61 + 46565.5 + 1230.74$$

$$425834.2 \left(\frac{kg}{hr}\right) = 425834.2 \left(\frac{kg}{hr}\right)$$

Flash 1 Material Balance

$$M_{In} + M_{Recycle} = M_{WasteGas} + M_{Liq}$$

$$\begin{aligned}M_{In} &= M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O} \\ &= 1349.14 + 9.06 + 6320.65 + 35279.3 + 3839.31 + 48.85 + 1041.81 \\ &= 47888.2 \frac{kg}{hr}\end{aligned}$$

$$M_{Recycle} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 128.01 + 0.04 + 0.02 + 0.03 + 0.21 + 7.07 + 36.54 = 171.92 \frac{kg}{hr}$$

$$M_{WasteGas} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 88.98 + 9.04 + 6320.64 + 35279.3 + 3839.24 + 14.96 + 1013.32$$

$$= 46565.5 \frac{kg}{hr}$$

$$M_{Liq} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 1388.18 + 0.06 + 0.03 + 0.04 + 0.29 + 40.96 + 65.03 = 1494.58 \frac{kg}{hr}$$

$$M_{In} + M_{Recycle} = M_{WasteGas} + M_{Liq}$$

$$47888.2 + 171.92 = 46565.5 + 1494.58 = 48080.1 \left(\frac{kg}{hr}\right)$$

Flash 2 Material Balance

$$M_{In} = M_{Vap} + M_{Liq}$$

$$M_{In} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 1388.18 + 0.06 + 0.03 + 0.04 + 0.29 + 40.96 + 65.03 = 1494.58 \frac{kg}{hr}$$

$$M_{Vap} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 170.68 + 0.05 + 0.03 + 0.04 + 0.28 + 9.43 + 48.72 = 229.23 \frac{kg}{hr}$$

$$M_{Liq} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 1217.5 + 0.01 + 0.00008 + 0.00005 + 0.003 + 31.53 + 16.31$$

$$= 1265.35 \frac{kg}{hr}$$

$$M_{In} = M_{Vap} + M_{Liq}$$

$$1494.58 = 229.23 + 1265.35 = 1494.58 \frac{kg}{hr}$$

Distillation Column Material Balance

$$M_{In} = M_{Waste2} + M_{Product}$$

$$M_{In} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 1217.5 + 0.01 + 0.00008 + 0.00005 + 0.003 + 31.53 + 16.31$$

$$= 1265.35 \frac{kg}{hr}$$

$$M_{Waste2} = M_{MA} + M_B + M_{O2} + M_{N2} + M_{CO2} + M_Q + M_{H2O}$$

$$= 15.50 + 0.01 + 0.0008 + 0.00005 + 0.003 + 2.79 + 16.30 = 34.61 \frac{kg}{hr}$$

$$M_{Product} = M_{MA} + M_Q + M_{H2O} = 1201.99 + 28.73 + 0.0059 = 1230.74 \frac{kg}{hr}$$

$$M_{In} = M_{Waste2} + M_{Product}$$

$$1265.35 = 34.61 + 1230.74 = 1265.35\,\frac{kg}{hr}$$

Appendix 4: Economic Analysis and Calculations

Operating Costs

Appendix Table 6: Full tabulated calculations of operating costs for the flash-based process

Operating Cost	Factor	Rate		Cost per year		Total Cost
Benzene	From pre-existing process	24.28	kmol/hr	546	$/M.T.	$ -
Operating Labor	13000 total operator hours per year	3250	hours skilled	33.67	$/hour	$ 358,833
		9750	hours common	25.58	$/hour	
Operating Supervision	15% operating labor	`				$ 53,824.88
Utilities	Calculated to the right					$ 2,635,130.51
Maintenance and Repair	7% of FCI					$ 669,107.36
Operating Supplies	15% of maintenance and repairs					$ 100,366.10
Laboratory Charges	15% of operating labor					$ 53,824.88
Royalties	None					$ -
Catalyst	70% vanadium pentoxide, 30% molybdenum trioxide	17670	kg	10.32	$/kg	$ 182,354.40
				Variable Production Cost		**$ 4,053,440.62**
Taxes(property)	2% FCI					$ 191,173.53
Insurance	1% of FCI					$ 95,586.77
				Fixed Charges		**$ 286,760.30**
Plant Overhead Costs	60% of operating labor, supervision and maintenance					$ 649,058.84
Adminsitrative Costs	20% of operating labor					$ 71,766.50
Distribution and Marketing	5% of Total production cost					$ 250,000.00
Research & Development	None					$ -
				General Expenses		**$ 970,825.34**
				Total Product Costs (without depreciation) per year		**$ 5,311,026.25**

Profitability

Appendix Table 7: Full, tabulated annual profitability calculations for the flash-based process

	Year															
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**SUM**
Percent of Operating Time	50	90	100	100	100	100	100	100	100	100	100	100	100	100	100	
Product rate, 10^6 kg/year	5	9	10	10	10	10	10	10	10	10	10	10	10	10	10	144
Sales revenue ($1.54/kg) $10^6/yr	7.7	13.86	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4	221.76
Variable Costs, $\$10^6$/year	2.03	3.65	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05	58.37
Fixed Costs (without depreciation)	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	18.86
Total Costs (without depreciation)	3.28	4.91	5.31	5.31	5.31	5.31	5.31	5.31	5.31	5.31	5.31	5.31	5.31	5.31	5.31	77.23
Depreciation Rate % (7 yr MACRS)	14.29	24.49	17.49	12.49	8.93	8.92	8.93	4.46	0	0	0	0	0	0	0	100.00
Depreciation, $\$10^6$/year	1.37	2.34	1.67	1.19	0.85	0.85	0.85	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.56

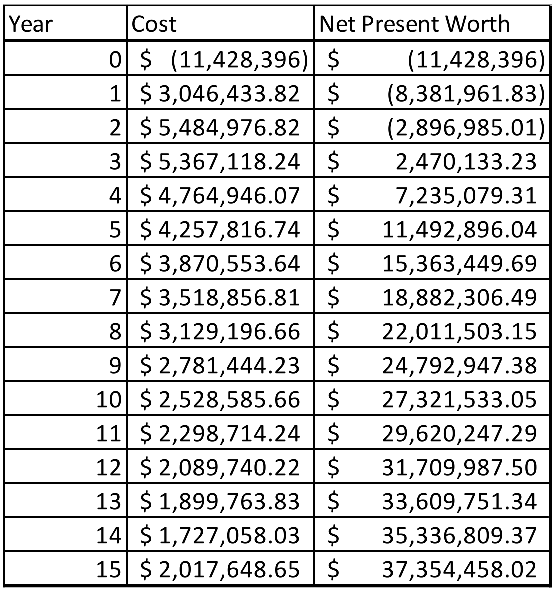
Variable Cost	**\$ 4,053,441**
Fixed Cost	**\$ 1,257,585.63**
FCI	**\$ 9,558,677**

Net Present Worth

Appendix Table 8: Annual present worth considering all investment at year zero.

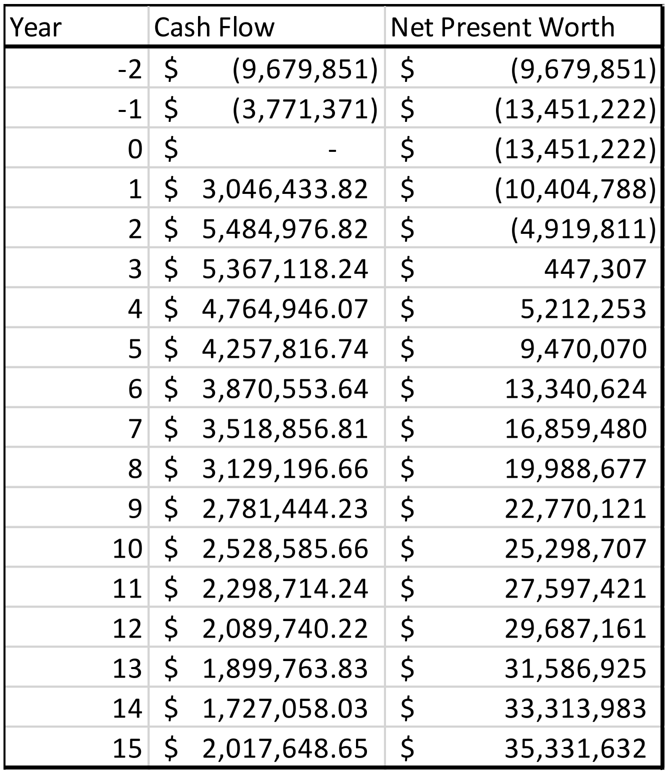
Year	Annual Revenue	Annual Op. Expenses	Dep. Rate (%)	Depreciation	TCI	Recovery	PWF	Present Worth Cash Flows	Present Worth TCI
0					$ 11,428,396		1	$ -	$ 11,428,396
1	$ 7,700,000	$ 3,280,000	14.29	$ 1,365,935	$ -	$ -	0.909090909	$ 3,046,433.82	$ -
2	$ 13,860,000	$ 4,910,000	24.49	$ 2,340,920	$ -	$ -	0.826446281	$ 5,484,976.82	$ -
3	$ 15,400,000	$ 5,310,000	17.49	$ 1,671,813	$ -	$ -	0.751314801	$ 5,367,118.24	$ -
4	$ 15,400,000	$ 5,310,000	12.49	$ 1,193,879	$ -	$ -	0.683013455	$ 4,764,946.07	$ -
5	$ 15,400,000	$ 5,310,000	8.93	$ 853,590	$ -	$ -	0.620921323	$ 4,257,816.74	$ -
6	$ 15,400,000	$ 5,310,000	8.92	$ 852,634	$ -	$ -	0.56447393	$ 3,870,553.64	$ -
7	$ 15,400,000	$ 5,310,000	8.93	$ 853,590	$ -	$ -	0.513158118	$ 3,518,856.81	$ -
8	$ 15,400,000	$ 5,310,000	4.46	$ 426,317	$ -	$ -	0.46650738	$ 3,129,196.66	$ -
9	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.424097618	$ 2,781,444.23	$ -
10	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.385543289	$ 2,528,585.66	$ -
11	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.350493899	$ 2,298,714.24	$ -
12	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.318630818	$ 2,089,740.22	$ -
13	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.28966438	$ 1,899,763.83	$ -
14	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.263331254	$ 1,727,058.03	$ -
15	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ 1,869,719	0.239392049	$ 2,017,648.65	$ -
							SUM	$ 48,782,853.68	
							NPW	$ 37,354,458.02	

Appendix Table 9: Net present worth considering all investment at year zero.



Year	Cost	Net Present Worth
0	$ (11,428,396)	$ (11,428,396)
1	$ 3,046,433.82	$ (8,381,961.83)
2	$ 5,484,976.82	$ (2,896,985.01)
3	$ 5,367,118.24	$ 2,470,133.23
4	$ 4,764,946.07	$ 7,235,079.31
5	$ 4,257,816.74	$ 11,492,896.04
6	$ 3,870,553.64	$ 15,363,449.69
7	$ 3,518,856.81	$ 18,882,306.49
8	$ 3,129,196.66	$ 22,011,503.15
9	$ 2,781,444.23	$ 24,792,947.38
10	$ 2,528,585.66	$ 27,321,533.05
11	$ 2,298,714.24	$ 29,620,247.29
12	$ 2,089,740.22	$ 31,709,987.50
13	$ 1,899,763.83	$ 33,609,751.34
14	$ 1,727,058.03	$ 35,336,809.37
15	$ 2,017,648.65	$ 37,354,458.02

Appendix Table 10: Net present worth considering all investment two years before year zero.



Year	Cash Flow	Net Present Worth
-2	$ (9,679,851)	$ (9,679,851)
-1	$ (3,771,371)	$ (13,451,222)
0	$ -	$ (13,451,222)
1	$ 3,046,433.82	$ (10,404,788)
2	$ 5,484,976.82	$ (4,919,811)
3	$ 5,367,118.24	$ 447,307
4	$ 4,764,946.07	$ 5,212,253
5	$ 4,257,816.74	$ 9,470,070
6	$ 3,870,553.64	$ 13,340,624
7	$ 3,518,856.81	$ 16,859,480
8	$ 3,129,196.66	$ 19,988,677
9	$ 2,781,444.23	$ 22,770,121
10	$ 2,528,585.66	$ 25,298,707
11	$ 2,298,714.24	$ 27,597,421
12	$ 2,089,740.22	$ 29,687,161
13	$ 1,899,763.83	$ 31,586,925
14	$ 1,727,058.03	$ 33,313,983
15	$ 2,017,648.65	$ 35,331,632

Appendix Table 11: Annual present worth considering all investment two years before year zero.

Year	Annual Revenue	Annual Op. Expenses	Dep. Rate (%)	Depreciation	TCI	Recovery	PWF	Present Worth Cash Flows	Present Worth TCI
-2					$7,999,877		1.21	$ -	$ 9,679,851
-1					$3,428,519		1.1	$ -	$ 3,771,371
0							1	$ -	$ -
1	$ 7,700,000	$ 3,280,000	14.29	$ 1,365,935	$ -	$ -	0.909090909	$ 3,046,433.82	$ -
2	$ 13,860,000	$ 4,910,000	24.49	$ 2,340,920	$ -	$ -	0.826446281	$ 5,484,976.82	$ -
3	$ 15,400,000	$ 5,310,000	17.49	$ 1,671,813	$ -	$ -	0.751314801	$ 5,367,118.24	$ -
4	$ 15,400,000	$ 5,310,000	12.49	$ 1,193,879	$ -	$ -	0.683013455	$ 4,764,946.07	$ -
5	$ 15,400,000	$ 5,310,000	8.93	$ 853,590	$ -	$ -	0.620921323	$ 4,257,816.74	$ -
6	$ 15,400,000	$ 5,310,000	8.92	$ 852,634	$ -	$ -	0.56447393	$ 3,870,553.64	$ -
7	$ 15,400,000	$ 5,310,000	8.93	$ 853,590	$ -	$ -	0.513158118	$ 3,518,856.81	$ -
8	$ 15,400,000	$ 5,310,000	4.46	$ 426,317	$ -	$ -	0.46650738	$ 3,129,196.66	$ -
9	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.424097618	$ 2,781,444.23	$ -
10	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.385543289	$ 2,528,585.66	$ -
11	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.350493899	$ 2,298,714.24	$ -
12	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.318630818	$ 2,089,740.22	$ -
13	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.28966438	$ 1,899,763.83	$ -
14	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ -	0.263331254	$ 1,727,058.03	$ -
15	$ 15,400,000	$ 5,310,000	0.00	$ -	$ -	$ 1,869,719	0.239392049	$ 2,017,648.65	$ -
							SUM	$ 48,782,853.68	
							NPW	$ 35,331,631.99	

Appendix 5: Reactor

Introduction

The purpose of the reactor design project is to react 1.5 vol% benzene with atmospheric air to produce 10,000 metric ton/yr of maleic anhydride. The kinetics for this reaction were given in the problem statement and can be found in the Equations section of this report. The reactor was specified as a packed bed reactor with either a co-current or counter-current cooling process, therefore the objective of this report is to determine the optimal heat exchanger design for the reactor. The catalyst for this reaction was specified as vanadium/molybdenum oxide on an inert support. A cooling process for the reactor was accomplished by circulating molten salt composed of 41.3 mol% sodium nitrate and 58.7 mol% sodium nitrite. In this report, the reaction was optimized using Polymath to achieve the highest conversion of maleic anhydride while keeping the temperature of the reactor below 600°C to avoid sintering of the catalyst [14]. The dimensions of the reactor are shown in the table below.

Appendix Table 12: Design specifications of the reactor.

Number of Tubes	Diameter of Tubes	Length of Reactor
15000	25 mm	3 m

Primary Reaction

$$C_6H_6 + 4.5O_2 \overset{k_1}{\rightarrow} C_4H_2O_3(maleic\ anhydride) + 2CO_2 + 2H_2O \tag{1}$$

Secondary Reactions

$$C_6H_6 + 7.5O_2 \overset{k_2}{\rightarrow} 6CO_2 + 3H_2O \tag{2}$$

$$C_4H_2O_3 + 3O_2 \overset{k_3}{\rightarrow} 4CO_2 + H_2O \tag{3}$$

$$C_6H_6 + 1.5O_2 \overset{k_4}{\rightarrow} C_6H_4O_2\ (quinone) + H_2O \tag{4}$$

Species

$$C_6H_6 = Species\ "A" \tag{5}$$

$$O_2 = Species\ "B" \tag{6}$$

$$C_4H_2O_3 = Species\ "C" \tag{7}$$

$$CO_2 = Species\ "D" \tag{8}$$

$$H_2O = Species\ "E" \tag{9}$$

$$C_6H_4O_2 = Species\ "F" \tag{10}$$

$$N_2 = Species\ "I" \tag{11}$$

Mole Balance

$$\frac{dF_A}{dW} = r_A\ ' \tag{12}$$

$$\frac{dF_B}{dW} = r_B\ ' \tag{13}$$

$$\frac{dF_C}{dW} = r_C\ ' \tag{14}$$

$$\frac{dF_D}{dW} = r_D\ ' \tag{15}$$

$$\frac{dF_E}{dW} = r_E\ ' \tag{16}$$

$$\frac{dF_F}{dW} = r_F\ ' \tag{17}$$

$$F_I = F_{I0} \tag{18}$$

Rates

$$r_A\ ' = r_{1A} + r_{2A} + r_{4A} \tag{19}$$

$$r_B\ ' = r_{1B} + r_{2B} + r_{3B} + r_{4B} \tag{20}$$

$$r_C\ ' = r_{1C} + r_{3C} \tag{21}$$

$$r_D\ ' = r_{1D} + r_{2D} + r_{3D} \tag{22}$$

$$r_E{}' = r_{1E} + r_{2E} + r_{3E} + r_{4E} \tag{23}$$

$$r_F{}' = r_{4F} \tag{24}$$

Rate Laws

$$r_{1A} = -k_1 C_A \tag{25}$$

$$r_{2A} = -k_2 C_A \tag{26}$$

$$r_{3C} = -k_3 C_C \tag{27}$$

$$r_{4A} = -k_4 C_A \tag{28}$$

Relative Rates

$$r_{1B} = 4.5 r_{1A} \tag{29}$$

$$r_{1C} = -r_{1A} \tag{30}$$

$$r_{1D} = -2 r_{1A} \tag{31}$$

$$r_{1E} = -2 r_{1A} \tag{32}$$

$$r_{2B} = 7.5 r_{2A} \tag{33}$$

$$r_{2D} = -6 r_{2A} \tag{34}$$

$$r_{2E} = -3 r_{2A} \tag{35}$$

$$r_{3B} = 3 r_{3C} \tag{36}$$

$$r_{3D} = -4 r_{3C} \tag{37}$$

$$r_{3E} = -r_{3C} \tag{38}$$

$$r_{4B} = 1.5 r_{4A} \tag{39}$$

$$r_{4F} = -r_{4A} \tag{40}$$

$$r_{4E} = -r_{4A} \tag{41}$$

Rate constants

$$k_1 = 7.7 \times 10^6 exp\left[\frac{-25{,}143}{RT}\right] * \frac{1}{\rho_c} \tag{42}$$

$$k_2 = 6.31 \times 10^7 exp\left[\frac{-29{,}850}{RT}\right] * \frac{1}{\rho_c} \tag{43}$$

$$k_3 = 2.33 \times 10^4 exp\left[\frac{-21{,}429}{RT}\right] * \frac{1}{\rho_c} \tag{44}$$

$$k_4 = 7.20 \times 10^5 exp\left[\frac{-27{,}149}{RT}\right] * \frac{1}{\rho_c} \tag{45}$$

The units of the activation energies are kcal/kmol, the units of concentration are kmol/(m^3s) (gas), and temperature is in Kelvin. Rate constants and kinetics were given by Dr. John Schlup.

Stoichiometry

$$C_A = C_{TO}\left(\frac{F_A}{F_T}\right)\left(\frac{T_O}{T}\right)\left(\frac{P}{P_0}\right) \tag{46}$$

$$C_B = C_{TO}\left(\frac{F_B}{F_T}\right)\left(\frac{T_O}{T}\right)\left(\frac{P}{P_0}\right) \tag{47}$$

$$C_C = C_{TO}\left(\frac{F_C}{F_T}\right)\left(\frac{T_O}{T}\right)\left(\frac{P}{P_0}\right) \tag{48}$$

$$C_D = C_{TO}\left(\frac{F_D}{F_T}\right)\left(\frac{T_O}{T}\right)\left(\frac{P}{P_0}\right) \tag{49}$$

$$C_E = C_{TO}\left(\frac{F_E}{F_T}\right)\left(\frac{T_O}{T}\right)\left(\frac{P}{P_0}\right) \tag{50}$$

$$C_F = C_{TO}\left(\frac{F_F}{F_T}\right)\left(\frac{T_O}{T}\right)\left(\frac{P}{P_0}\right) \tag{51}$$

$$C_I = C_{TO}\left(\frac{F_I}{F_T}\right)\left(\frac{T_O}{T}\right) \tag{52}$$

Flow Rates

$$F_T = F_A + F_B + F_C + F_D + F_E + F_F + F_I \tag{53}$$

$$F_{T0} = F_{A0} + F_{B0} + F_{C0} + F_{D0} + F_{E0} + F_{F0} + F_{I0} \tag{54}$$

Pressure Drop

$$\frac{dP}{dW} = -\frac{\alpha}{2}\left(\frac{T}{T_O}\right)\left(\frac{P_O}{P/P_0}\right)\left(\frac{F_T}{F_{TO}}\right) \tag{55}$$

$$\alpha = \frac{2\beta_0}{A_c \rho_c (1-\phi) P_0} \tag{56}$$

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right] \tag{57}$$

Where A_c , ρ_c , ϕ , G , ρ_0 , D_p , and μ are constants as defined in the Constants subsection.

General Energy Balance

$$\frac{dT}{dW} = \frac{(Ua)_{overall}(T_a - T) * \frac{1}{\rho_b} + (-r_{1A})(-\Delta H_{rx,1A}) + (-r_{2A})(-\Delta H_{rx,2A}) + (-r_{3C})(-\Delta H_{rx,3C}) + (-r_{4A})(-\Delta H_{rx,4A})}{F_A C_{P_A} + F_B C_{P_B} + F_C C_{P_C} + F_D C_{P_D} + F_E C_{P_E} + F_F C_{P_F} + F_I C_{P_I}} \tag{58}$$

Heat Exchanger

Co-current

$$\frac{dT_A}{dW} = \frac{(Ua)_{heat\ exchanger}(T - T_A)}{\dot{m}_{Coolant} C_{P_{Coolant}} \rho_b} \tag{59}$$

Counter-current

$$\frac{dT_A}{dW} = \frac{(Ua)_{heat\ exchanger}(T_A - T)}{\dot{m}_{Coolant} C_{P_{Coolant}} \rho_b} \tag{60}$$

Constants and Assumptions

The following constants were given in the problem statement:

$$(Ua)_{overall} = (Ua)_{heat\ exchanger} = 100\ W/m^2 C \tag{61}$$

$$D_p = 5\ mm \tag{62}$$

$$\rho_c = 1600\ kg/m^3 \tag{63}$$

$$void\ fraction\ (\varnothing) = 0.5 \tag{64}$$

$$\rho_b = \rho_c(1 - \varnothing) \tag{65}$$

The constants used when considering pressure drop and stoichiometry are defined as follows:

$$G = \rho_0 U \tag{66}$$

$$U = v_0/A_c \tag{67}$$

$$v_0 = 10.0055\, m^3/s \tag{68}$$

$$g_c = 1\text{(for metric units)} \tag{69}$$

$$\mu = 3.482 \times 10^{-5}\, kg/m \cdot s \tag{70}$$

$$A_c = 7.363\, m^2 \tag{71}$$

The viscosity, μ, is taken to be the viscosity of air at 750 K as the inlet is mostly air and the benzene has little effect on this constant. It is assumed that viscosity does not change significantly with temperature. The area of the reactor tubes is calculated from taking a bundle of 15000 tubes with a suggested diameter of 25 mm and length of 1.5-3 m found in patent literature [63] [64]. Patent literature shows that several different types of catalysts have been used including mixtures of molybedenum and vanadium oxide as used in this design [65]. Additional research would be needed to further analyze the ideal catalyst. The selected final length of the reactor tubes was calculated from the energy balance when considering the molten salt coolant stream.

Utilizing patent literature, a suggested initial temperature for the coolant (T_{A0}) and inlet (T_0) streams were found to be 500°C and 300-500°C respectively [7] [15]. These were used as starting points for a simulation study investigating the optimal temperature for reactor operation. Ideally, the pressure range of the reactor is between 1-3 bar absolute [66]. The inlet pressure, P_0, was taken as 235 kPa as provided by the problem statement and literature values [7] [15].

Molten salt coolants are commonly a mixture of nitrate and nitrite salts and applicable for temperatures in the range of 250°C to 550°C [67]. The coolant stream is a molten salt stream of 41.3% sodium nitrate and 58.7% sodium nitrate derived from the eutectic point at 230°C [26]. The flow rate was determined by considering the heat duty on the reboiler and doing an energy balance over the stream (reactor coolant heats a reboiler downstream). This gave a coolant flow rate of 2065 kmol/hr of sodium nitrate and 2934 kmol/hr of sodium nitrite leading to a total coolant mass flow rate of 105 kg/s. The heat capacity of the coolant is 1683.95 J/(kg K) as reported by the Royal Chemistry society [68].

The heats of reaction at a reference temperature were obtained from the heats of formation given by Knovel Critical Tables [16] and using the following equation:

$$\Delta H_{rx,i}(T_R) = \frac{d}{a} H^{\circ}_{D,f}(T_R) + \frac{c}{a} H^{\circ}_{C,f}(T_R) - \frac{b}{a} H^{\circ}_{B,f}(T_R) - \frac{a}{a} H^{\circ}_{A,f}(T_R) \tag{72}$$

Heat capacities were obtained from the following equation combined with literature values as show in Appendix Table 13:

$$C_{p,i} = a + bT + cT^2 + dT^3 + eT^4 \tag{73}$$

Appendix Table 13: Constants for heat capacities [16], [69], [70].

	Species	a	b	c	d	e
A	Benzene	-3.14E+01	4.75E-01	-3.11E-04	8.52E-08	-5.05E-12
B	Oxygen	2.98E+01	-9.49E-03	2.86E-05	9.87E-09	-5.67E-11
C	Maleic Anhydride	-7.20E+01	1.04E+00	-1.87E-03	1.65E-06	-5.56E-10
D	Carbon Dioxide	2.74E+01	4.23E-02	-1.96E-05	4.00E-09	-2.99E-13
E	Water	3.32E+01	-3.25E-03	1.74E-05	-5.98E-09	0.00E+00
F	Quinone	6.75E+01	-2.32E-01	2.23E-03	-4.44E-06	4.18E-09
I	Nitrogen	2.93E+01	-3.54E-03	1.01E-05	-4.31E-09	2.59E-13

Equations 72 and 73 are combined into Equation 74 below to find the heat of reactions for the energy balance.

$$\Delta H_{rx,i} = \Delta H_{rx,i}(T_R) - \int_{T_1}^{T_2} C_{pa}\,dT - 4.5 \int_{T_1}^{T_2} C_{pb}\,dT + \int_{T_1}^{T_2} C_{pc}\,dT + \int_{T_1}^{T_2} C_{pd}\,dT + 2 \int_{T_1}^{T_2} C_{pe}\,dT \tag{74}$$

The above equations were combined into a Polymath Code and run at various reactant and coolant inlet temperatures.

Simulation Study

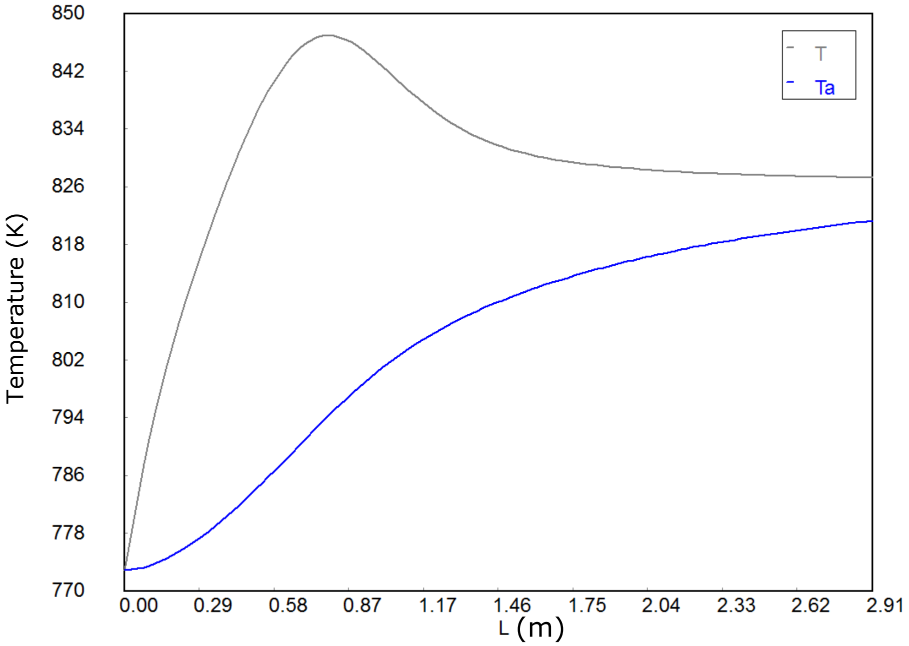
A reactor can be cooled via countercurrent and co-current heat transfer methods. However, co-current cooling is generally used to avoid hot spots and optimize conversion [25]. One method of measuring reaction selectivity is through conversion of benzene to maleic anhydride (assumed to be the only desirable product) as given in Equation 75. By applying the developed code for countercurrent and co-current systems, we confirmed that co-current cooling is preferred for optimal conversion as shown in Appendix Table 14.

$$Conversion = \frac{Flow\ rate\ of\ Maleic\ Anhdyride\ Product}{Flow\ rate\ of\ Benzene\ Product} \tag{75}$$

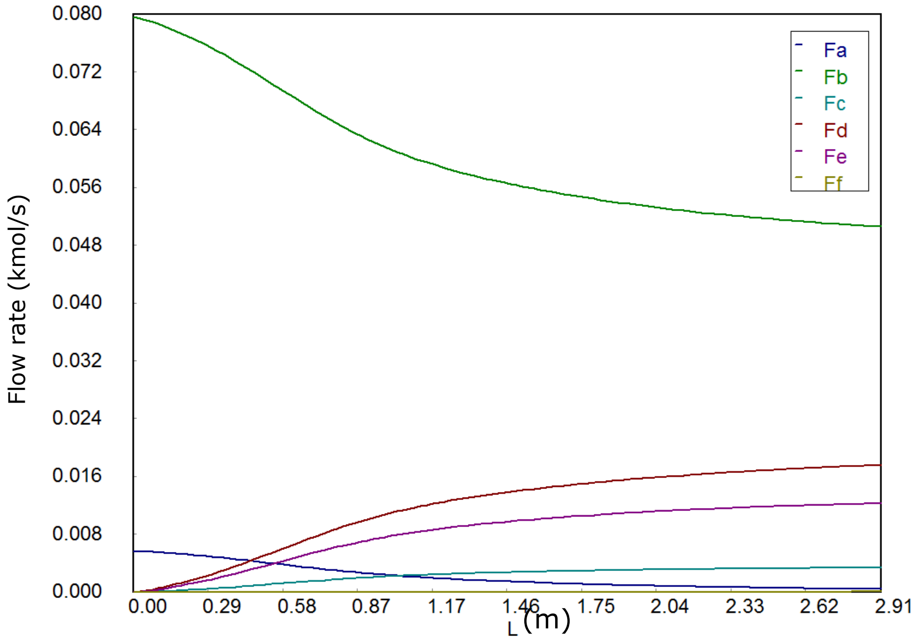
Appendix Table 14: Comparison of conversions of countercurrent vs. co-current at two different temperatures.

Reactants Inlet Temperature [C]	Coolant Inlet Temperature [C]	Counter Current Conversion	Co-Current Conversion
460	500	0.456	0.613
500	500	0.448	0.621

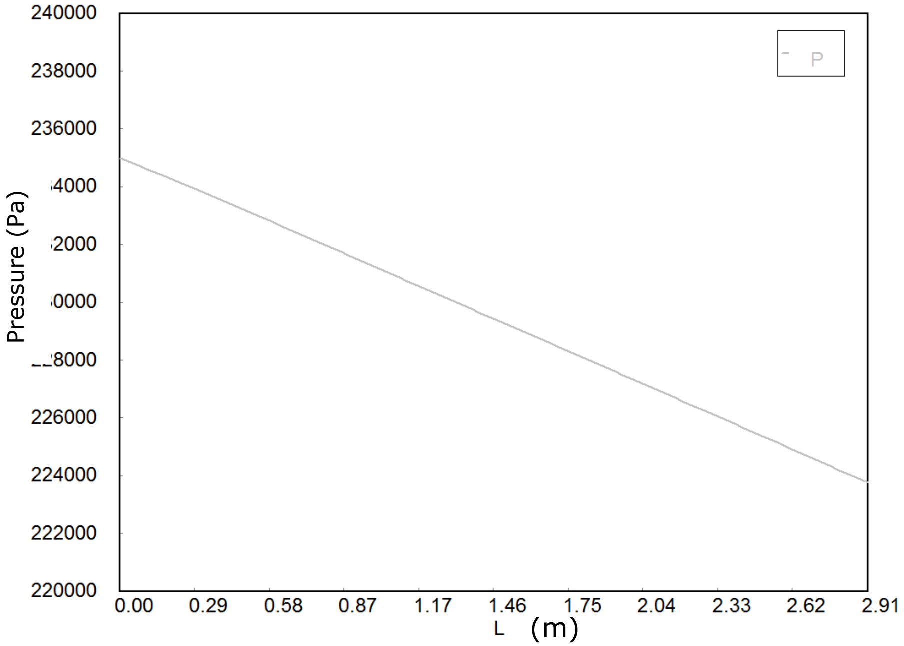
A comparison of flow rates, temperature profiles, and pressure drop for co-current and counter current designs are shown in the figures below. Reactant inlet temperature and coolant inlet temperature are both 500°C. The countercurrent reactor design has a longer reactor length as calculated from the energy balance. Thus, when considering conversion efficiency and reactor cost, a co-current design is preferred.



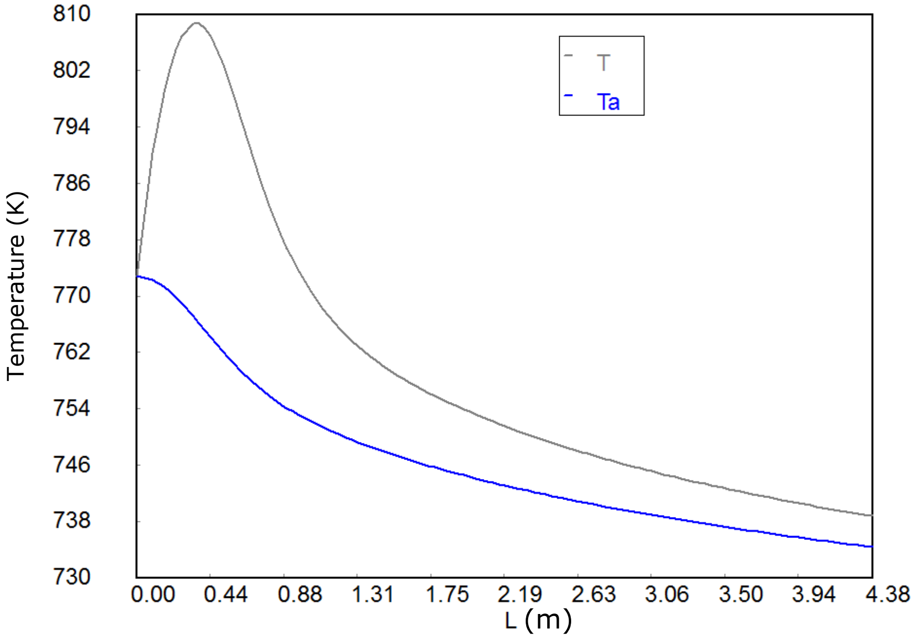
Appendix Figure 3: Temperature profile of a co-current reactor with an inlet reactant and coolant temperature of 500°C.



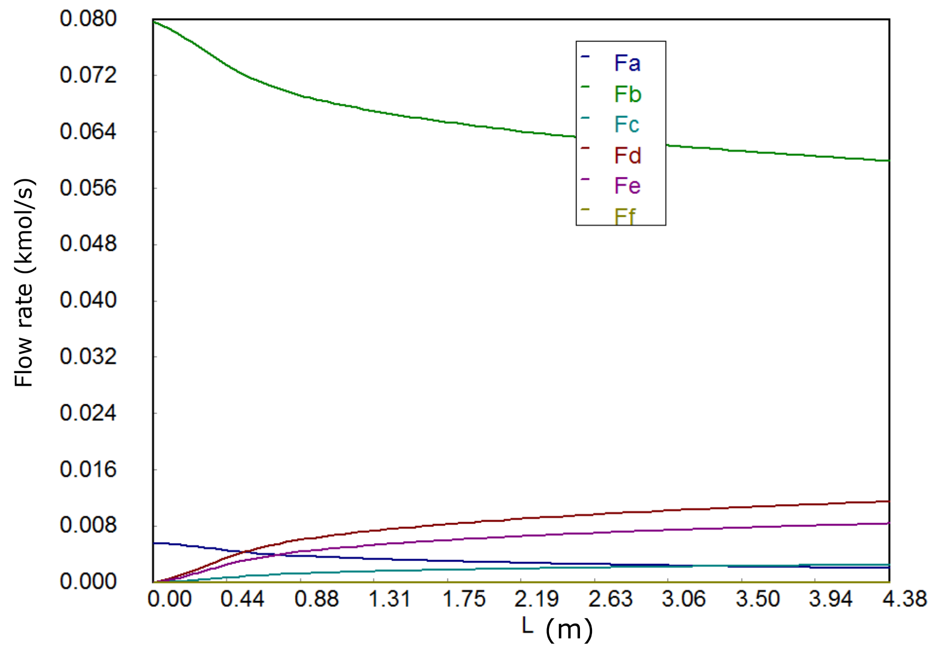
Appendix Figure 4: Flow profile of a co-current reactor with an inlet reactant and coolant temperature of 500°C.



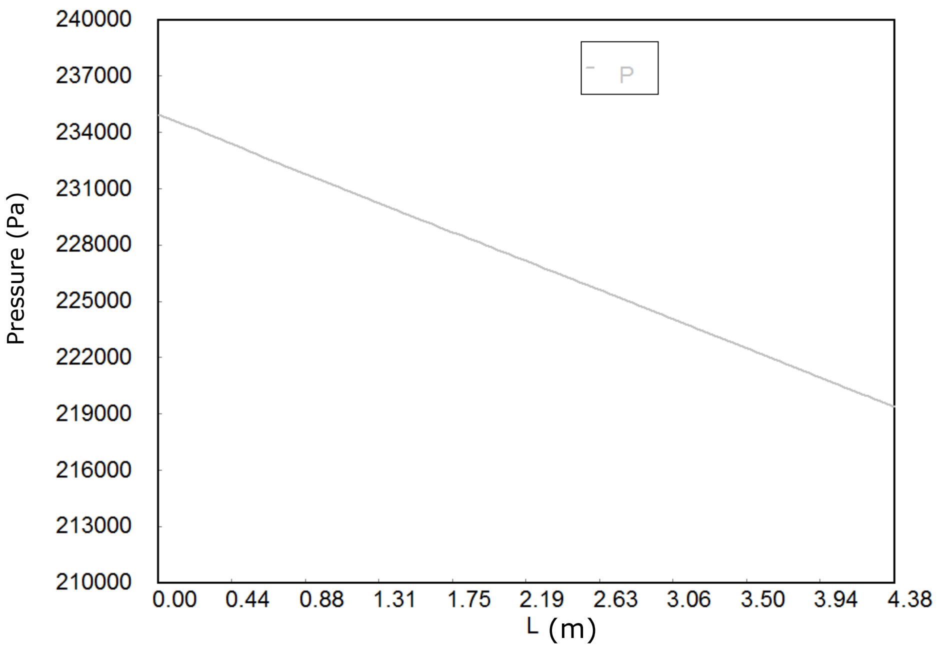
Appendix Figure 5: Pressure profile of a co-current reactor with an inlet reactant and coolant temperature of 500°C.



Appendix Figure 6: Temperature profile of a countercurrent reactor with an inlet reactant and coolant temperature of 500°C.



Appendix Figure 7: Flow profile of a countercurrent reactor with an inlet reactant and coolant temperature of 500°C.

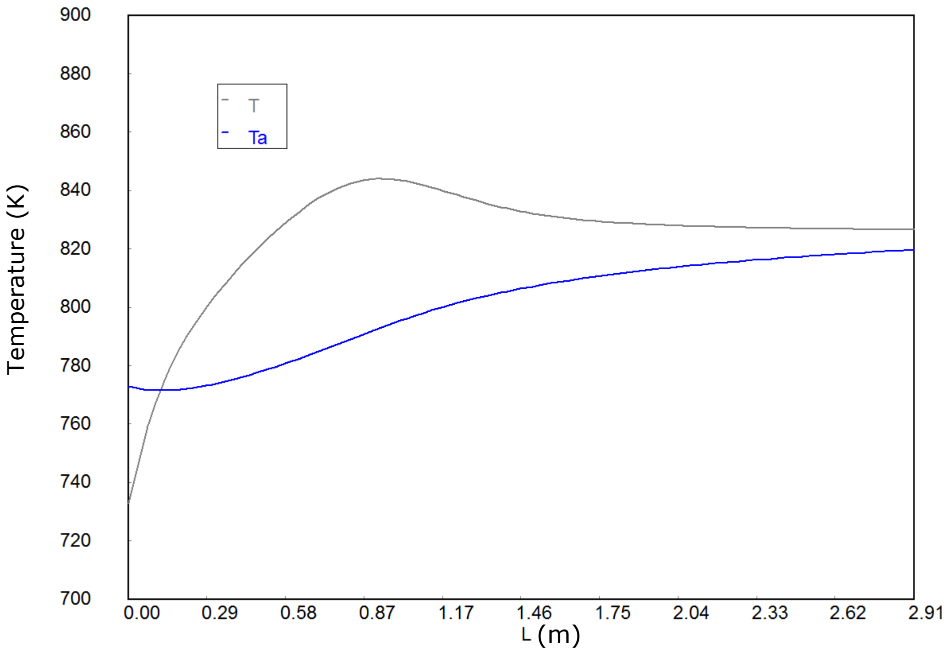


Appendix Figure 8: Pressure profile of a countercurrent reactor with an inlet reactant and coolant temperature of 500°C.

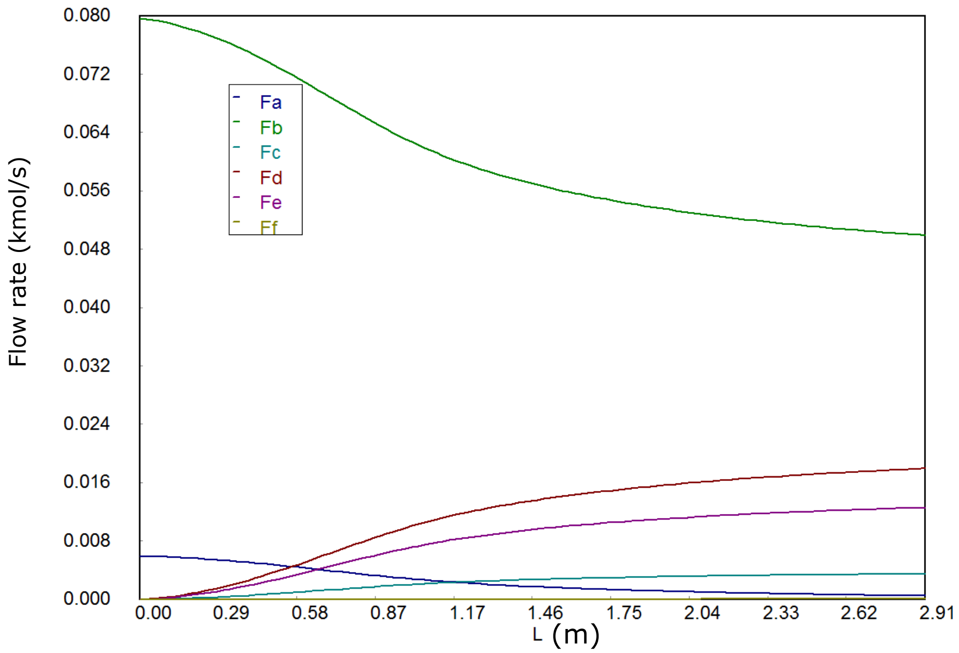
The co-current design was further optimized by varying molten salt coolant inlet temperature and reactant inlet temperature. Highest conversion was obtained at a reactant inlet temperature of 500°C and coolant inlet temperature of 500°C as shown in Table 3. A similar conversion rate was seen with a reactant inlet temperature of 460°C. Since a lower coolant heat is required to reach a similar conversion, a reactant temperature of 460°C with a coolant inlet temperature of 500°C was chosen as the optimal design. It should be noted that the coolant serves to heat the inlet reactant, cool the reactor product, and heat a downstream reboiler in this process. Reactor profiles for the optimized case are shown below.

Appendix Table 15: Co-current reactor conversion of coolant inlet temperature vs reactor inlet temperature.

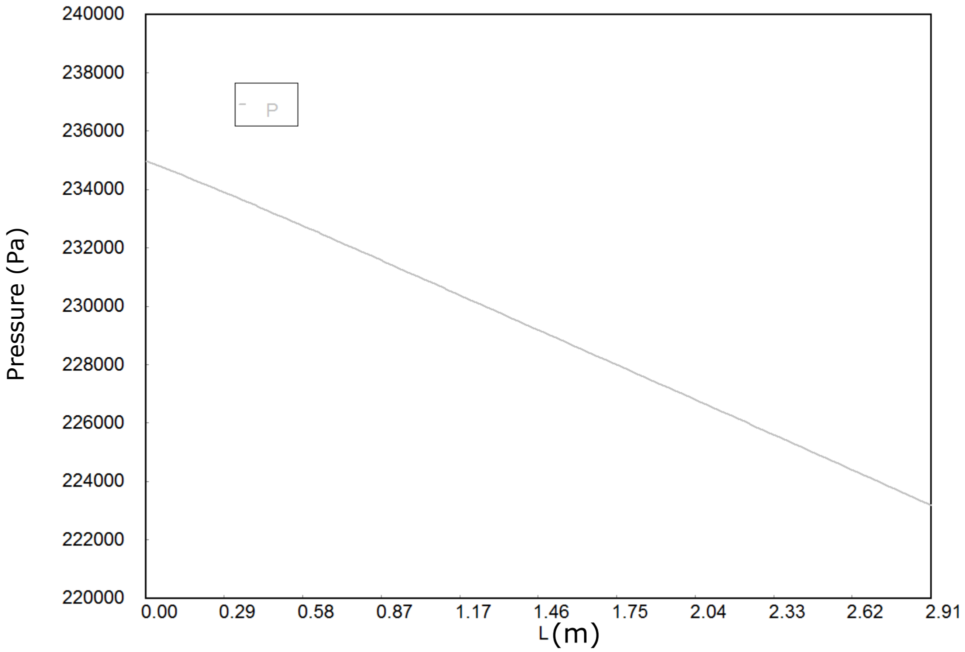
Co-Current Reactor Conversion						
		Reactant Inlet Temperature [C]				
		300	**400**	**460**	**500**	**550**
Coolant Inlet Temperature [C]	**400**	0.052	0.066	0.076	0.089	0.116
	450	0.175	0.216	0.249	0.346	0.417
	500	0.544	0.593	0.613	0.621	0.566
	550	0.454	0.434	0.419	0.404	-



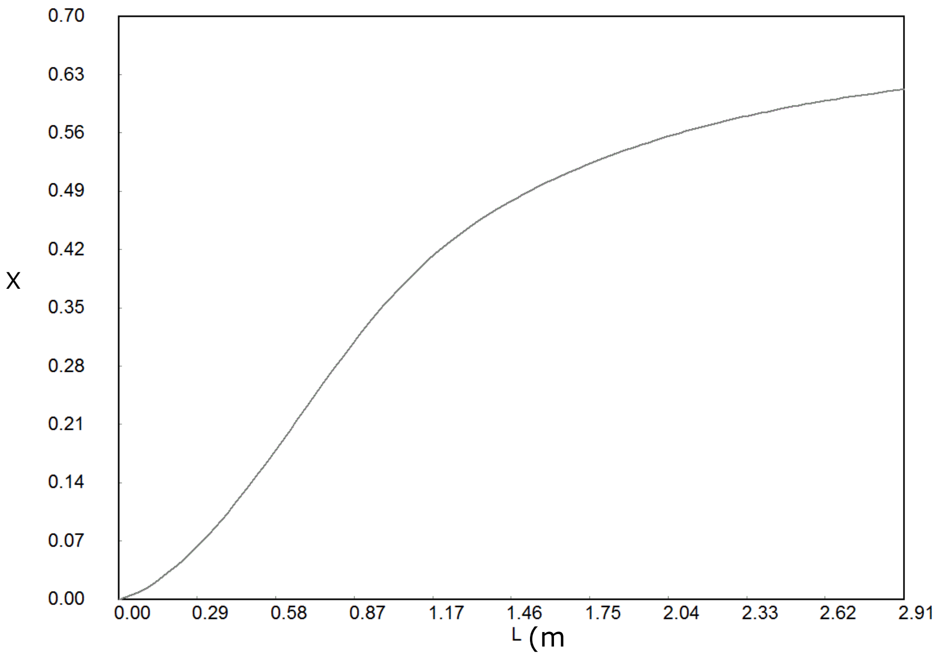
Appendix Figure 9: Temperature profile of the optimized co-current reactor.



Appendix Figure 10: Flow profile of optimized the co-current reactor.



Appendix Figure 11: Pressure profile of the optimized co-current reactor.



Appendix Figure 12: Conversion profile of the optimized co-current reactor.

Aspen and Polymath Simulation Comparison

Using the same design parameters, a model of the reactor was developed in Aspen. The Aspen model accounts for a designated pressure drop across the reactor. This pressure drop was obtained from the Polymath simulation. All other calculations were performed within the Apsen model. For the optimized co-current reactor design, Aspen and Polymath simulations have similar product stream compositions and temperatures as shown in Table 4.

Appendix Table 16: Reactor product stream table for Aspen and Polymath simulations.

	Flowrates (kmol/s)	
Component	Aspen	Polymath
Nitrogen	0.2999	0.2999
Oxygen	0.0470	0.0500
Carbon Dioxide	0.0208	0.0180
Benzene	0.0000	0.0005
Quinone	0.0001	0.0001
Water	0.0138	0.0126
Maleic Anhydride	0.0033	0.0035

Conclusion

To produce 10,000 metric tons of maleic anhydride, the ideal reactor design is a packed bed reactor with a co-current heat exchanger for the catalytic oxidation of benzene with atmospheric oxygen. The reactor has a length of 3 m with 15,000 25 mm diameter tubes. The catalyst selected is vanadium/molybdenum oxide on an inert support. Ideal inlet reactant temperature is 460°C with a coolant inlet temperature of 600°C and a pressure drop from 235 kPa to 219 kPa. This is a relatively insignificant pressure drop due to the small diameter of the tubes. With the current specifications, the diameter of the tube is only five catalyst particles (5 mm in diameter).

Polymath Code for PBR with Co-Current Heat Exchanger

```
d(Fa) / d(W) = ra #benzene
Fa(0) = 0.006 #kmol/s
d(Fb) / d(W) = rb #oxygen
Fb(0) = 0.0797140833
d(Fc) / d(W) = rc #maleic anhydride
Fc(0) = 0
d(Fd) / d(W) = rd #carbon dioxide
Fd(0) = 0
d(Fe) / d(W) = re #water
Fe(0) = 0
d(Ff) / d(W) = rf #quinone
Ff(0) = 0
Fi = 0.2998768333 #nitrogen

#rates
ra = r1a+r2a+r4a
rb = r1b+r2b+r3b+r4b
rc = r1c+r3c
rd = r1d+r2d+r3d
re = r1e+r2e+r3e+r4e
rf = r4f

#rate laws
r1a = -k1*(ct0*(Fa/Ft)*(T0/T)*(P/P0))
r2a = -k2*(ct0*(Fa/Ft)*(T0/T)*(P/P0))
r3c = -k3*(ct0*(Fc/Ft)*(T0/T)*(P/P0))
r4a = -k4*(ct0*(Fa/Ft)*(T0/T)*(P/P0))

#relative rates
r1b = 4.5*r1a
r1c = -r1a
r1d = -2*r1a
r1e = -2*r1a
r2b = 7.5*r2a
r2d = -6*r2a
r2e = -3*r2a
r3b = 3*r3c
r3d = -4*r3c
r3e = -r3c
r4b = 1.5*r4a
r4f = -r4a
r4e = -r4a

#rate constants
R = 1.9858775 #kcal/kmol.K
k1 = (7.7*10^6)*exp(-25143/R/T)/rhoc
k2 = (6.31*10^7)*exp(-29850/R/T)/rhoc
k3 = (2.33*10^4)*exp(-21429/R/T)/rhoc
k4 = (7.20*10^5)*exp(-27149/R/T)/rhoc

#stoich
#ca = ct0*(Fa/Ft)*(T0/T)*(P/P0)
#cb = ct0*(Fb/Ft)*(T0/T)*(P/P0)
#cc = ct0*(Fc/Ft)*(T0/T)*(P/P0)
#cd = ct0*(Fd/Ft)*(T0/T)*(P/P0)
```

```
#ce = ct0*(Fe/Ft)*(T0/T)*(P/P0)
#cf = ct0*(Ff/Ft)*(T0/T)*(P/P0)
#ci = ct0*(Fi/Ft)*(T0/T)*(P/P0)

Ft= Fa+Fb+Fc+Fd+Fe+Ff+Fi
Ft0 = 0.3853714722

#pressure drop (Ergun)
d(P) / d(W) = -alpha/2*(T/T0)*(P0/(P/P0))*(Ft/Ft0)
P(0) = 235000 #Pa
W(0) = 0
W(f) = 17149 #final weight of catalyst
alpha = 2*beta/(Ac*rhoc*(1-phi)*P0)
beta = G*(1-phi)/(rho*gc*Dp*phi^3)*((150*(1-phi)*mu)/Dp+1.75*G)
gc = 1 #metric
Dp = 0.005 #m
rhob = rhoc*(1-phi)
rhoc = 1600 #1600 kg/m3
phi = 0.5
#Ac = 4.908738521*10^-4 #diameter of 1 reactor tube (m^2)
Ac = 7.363107782
u = v0/Ac
G = rho*u
#G = 3.360722456
rho = 1.13966 #kg/m^3
v0 = 10.0055 #m^3/s
mu = 3.482 *10^(-5) #viscosity of air at 750K (kg/m.s)

#general energy balance
d(T) / d(W) = (100*a*(Ta-T)*(1/rhob)+(1000)*((-r1a)*(-dHrx1a)+(-r2a)*(-dHrx2a)+(-r3c)*(-
dHrx3c)+(-r4a)*(-dHrx4a)))/((1000)*(Fa*Cpa+Fb*Cpb+Fc*Cpc+Fd*Cpd+Fe*Cpe+Ff*Cpf+Fi*Cpi))
T(0) = 733 #Kelvin

#heat exchanger (co-curent)
d(Ta) / d(W) = 100*a*(T-Ta)/(rhob*105*1683.953)
Ta(0) = 773 #Kelvin
a = 160 #m^2/m^3
#coolant is mixture of sodium nitrate (41.3%) and sodium nitrite (58.7%)
#Cpco =  1683.953 #J/kg K
#mc = 105 #kg/s

#constants
R2=8.31447*10^3 #m^3.Pa/K/kmol
T0 = 733 #Kelvin (350-400 C inlet temp)
P0 = 235000 #Pa
ct0 = P0/R2/T0 #ideal gas law
#ct0 = 0.038559 kmol/m^3
#Uo = 100 #W/m2.C
#Uht = 60 #W/m2.C

#gas phase enthalpies at Tref (298 K)
#dHrx1aref = -1751860 #J/mol
#dHrx2aref = -3169390 #J/mol
#dHrx3cref = -1417530 #J/mol
#dHrx4aref = -509230 #J/mol

#enthalpies at T
dHrx1a = -1751860 + dCp1
```

```
dHrx2a = -1718410 + dCp2
dHrx3c = -1417530 + dCp3
dHrx4a = -509230 +dCp4

#change in heat capacities for each reaction, heat capacities in J/molK
dCp1= -1*dCpa-4.5*dCpb+dCpc+2*dCpd+2*dCpe
dCp2= -1*dCpa-7.5*dCpb+6*dCpd+3*dCpe
dCp3=-1*dCpc-3*dCpb+4*dCpd+dCpe
dCp4=-dCpa-1.5*dCpb+dCpf+dCpe

#heat capacities in J/mol K
Cpa = -31.368 + 0.4746*T + (-0.00031137)*(T^2) + 0.00000008524*(T^3) + (-
0.0000000000050524)*(T^4)
Cpb = 29.79023995 + (-0.009488538)*T + (0.0000285799)*(T^2) + 0.00000000987286*(T^3) + (-
0.0000000000566511)*(T^4)
Cpc = -72.015 + 1.0423*T + (-0.0018716)*(T^2) + 0.000001653*(T^3) + (-
0.00000000055647)*(T^4)
Cpd = 27.437 + 0.042315*T + (-0.000019555)*(T^2) + 0.000000003997*(T^3) + (-
0.00000000000029872)*(T^4)
Cpe = 33.17438187 + (-0.003246334)*T + (0.0000174365)*(T^2) + (-0.00000000597958)*(T^3)
Cpf = 67.50354799 + (-0.232224187)*T + (0.002229152)*(T^2) + (-0.00000444287)*(T^3) +
(0.00000000417641)*(T^4)
Cpi = 29.342 + (-0.0035395)*T + (0.000010076)*(T^2) + (-0.0000000043116)*(T^3) +
(0.00000000000025935)*(T^4)

#change in heat capacities in J/mol
dCpa = (-31.368*T + .2373*T^2 + (-1.04E-04)*(T^3) + (2.13E-08)*(T^4) + (-1.01E-12)*(T^5) -
9.14E+03)
dCpb = ((2.98E+01)*T + (-4.74E-03)*T^2 + (9.53E-06)*(T^3) + (2.47E-09)*(T^4) + (-1.13E-
11)*(T^5) - 8.70E+03)
dCpc = ((-7.20E+01)*T + (5.21E-01)*T^2 + (-6.24E-04)*(T^3) + (4.13E-07)*(T^4) + (-1.11E-
10)*(T^5) - 1.13E+04)
dCpd = ((2.74E+01)*T + (2.12E-02)*T^2 + (-6.52E-06)*(T^3) + (9.99E-10)*(T^4) + (-5.97E-
14)*(T^5) - 9.89E+03)
dCpe = ((3.32E+01)*T + (-1.62E-03)*T^2 + (5.81E-06)*(T^3) + (-1.49E-09)*(T^4)  - 9.88E+03)
dCpf = ((6.75E+01)*T + (-1.16E-01)*T^2 + (7.43E-04)*(T^3) + (-1.11E-06)*(T^4) + (8.35E-
10)*(T^5) - 2.27E+04)

ACONV=Fc/0.0057805556 #Fmaleic out/F benzene in

L=W/(rhoc*0.5*3.14*((.025)^2)*.25*15000)
```

POLYMATH Report No Title

Ordinary Differential Equations 28-Nov-2016

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	a	160.	160.	160.	160.
2	Ac	7.363108	7.363108	7.363108	7.363108
3	ACONV	0	0	0.61287	0.61287
4	alpha	5.077E-06	5.077E-06	5.077E-06	5.077E-06
5	beta	3513.965	3513.965	3513.965	3513.965
6	Cpa	181.3299	181.3299	196.1093	193.9943
7	Cpb	25.72505	19.30988	25.72505	20.58987
8	Cpc	176.765	176.765	185.9358	184.5671
9	Cpd	49.43512	49.43512	51.47711	51.17457
10	Cpe	37.8083	37.8083	39.26367	39.03005
11	Cpf	550.8778	550.8778	908.5877	839.8554
12	Cpi	30.53809	30.53809	31.07286	30.9877
13	ct0	0.0385593	0.0385593	0.0385593	0.0385593
14	dCp1	1.794E+04	1.794E+04	2.544E+04	2.403E+04
15	dCp2	6704.787	6704.787	1.318E+04	1.177E+04
16	dCp3	-1.124E+04	-1.227E+04	-1.124E+04	-1.226E+04
17	dCp4	4.942E+04	4.942E+04	1.085E+05	9.647E+04
18	dCpa	6.034E+04	6.034E+04	8.132E+04	7.792E+04
19	dCpb	1.267E+04	1.267E+04	1.522E+04	1.487E+04
20	dCpc	6.584E+04	6.584E+04	8.598E+04	8.275E+04
21	dCpd	1.929E+04	1.929E+04	2.491E+04	2.401E+04
22	dCpe	1.544E+04	1.544E+04	1.973E+04	1.905E+04
23	dCpf	1.133E+05	1.133E+05	1.929E+05	1.777E+05
24	dHrx1a	-1.734E+06	-1.734E+06	-1.726E+06	-1.728E+06
25	dHrx2a	-1.712E+06	-1.712E+06	-1.705E+06	-1.707E+06
26	dHrx3c	-1.429E+06	-1.43E+06	-1.429E+06	-1.43E+06
27	dHrx4a	-4.598E+05	-4.598E+05	-4.007E+05	-4.128E+05
28	Dp	0.005	0.005	0.005	0.005
29	Fa	0.006	0.0005376	0.006	0.0005376

30	Fb	0.0797141	0.0499784	0.0797141	0.0499784
31	Fc	0	0	0.0035427	0.0035427
32	Fd	0	0	0.0179993	0.0179993
33	Fe	0	0	0.0126431	0.0126431
34	Ff	0	0	0.0001007	0.0001007
35	Fi	0.2998768	0.2998768	0.2998768	0.2998768
36	Ft	0.3855909	0.3846787	0.3855909	0.3846787
37	Ft0	0.3853715	0.3853715	0.3853715	0.3853715
38	G	1.548649	1.548649	1.548649	1.548649
39	gc	1.	1.	1.	1.
40	k1	0.0001517	0.0001517	0.0014775	0.0010761
41	k2	4.899E-05	4.899E-05	0.0007308	0.0005016
42	k3	5.887E-06	5.887E-06	4.097E-05	3.127E-05
43	k4	3.575E-06	3.575E-06	4.176E-05	2.966E-05
44	L	0	0	2.912781	2.912781
45	mu	3.482E-05	3.482E-05	3.482E-05	3.482E-05
46	P	2.35E+05	2.232E+05	2.35E+05	2.232E+05
47	P0	2.35E+05	2.35E+05	2.35E+05	2.35E+05
48	phi	0.5	0.5	0.5	0.5
49	R	1.985878	1.985878	1.985878	1.985878
50	r1a	-9.101E-08	-4.527E-07	-4.883E-08	-4.883E-08
51	r1b	-4.095E-07	-2.037E-06	-2.197E-07	-2.197E-07
52	r1c	9.101E-08	4.883E-08	4.527E-07	4.883E-08
53	r1d	1.82E-07	9.766E-08	9.054E-07	9.766E-08
54	r1e	1.82E-07	9.766E-08	9.054E-07	9.766E-08
55	R2	8314.47	8314.47	8314.47	8314.47
56	r2a	-2.94E-08	-2.189E-07	-2.276E-08	-2.276E-08
57	r2b	-2.205E-07	-1.642E-06	-1.707E-07	-1.707E-07
58	r2d	1.764E-07	1.366E-07	1.313E-06	1.366E-07
59	r2e	8.819E-08	6.828E-08	6.566E-07	6.828E-08
60	r3b	0	-2.805E-08	0	-2.805E-08
61	r3c	0	-9.35E-09	0	-9.35E-09
62	r3d	0	0	3.74E-08	3.74E-08

63	r3e	0	0	9.35E-09	9.35E-09
64	r4a	-2.145E-09	-1.267E-08	-1.346E-09	-1.346E-09
65	r4b	-3.218E-09	-1.9E-08	-2.018E-09	-2.018E-09
66	r4e	2.145E-09	1.346E-09	1.267E-08	1.346E-09
67	r4f	2.145E-09	1.346E-09	1.267E-08	1.346E-09
68	ra	-1.225E-07	-6.84E-07	-7.293E-08	-7.293E-08
69	rb	-6.332E-07	-3.71E-06	-4.205E-07	-4.205E-07
70	rc	9.101E-08	3.948E-08	4.486E-07	3.948E-08
71	rd	3.584E-07	2.716E-07	2.236E-06	2.716E-07
72	re	2.723E-07	1.766E-07	1.579E-06	1.766E-07
73	rf	2.145E-09	1.346E-09	1.267E-08	1.346E-09
74	rho	1.13966	1.13966	1.13966	1.13966
75	rhob	800.	800.	800.	800.
76	rhoc	1600.	1600.	1600.	1600.
77	T	733.	733.	844.2637	826.7874
78	T0	733.	733.	733.	733.
79	Ta	773.	771.6729	819.8645	819.8645
80	u	1.358869	1.358869	1.358869	1.358869
81	v0	10.0055	10.0055	10.0055	10.0055
82	W	0	0	1.715E+04	1.715E+04

Differential equations

1 d(Fa)/d(W) = ra

benzene

2 d(Fb)/d(W) = rb

oxygen

3 d(Fc)/d(W) = rc

maleic anhydride

4 d(Fd)/d(W) = rd

carbon dioxide

5 d(Fe)/d(W) = re

water

6 d(Ff)/d(W) = rf

quinone

7 d(P)/d(W) = -alpha/2*(T/T0)*(P0/(P/P0))*(Ft/Ft0)

8 d(T)/d(W) = (100*a*(Ta-T)*(1/rhob)+(1000)*((-r1a)*(-dHrx1a)+(-r2a)*(-dHrx2a)+(-r3c)*(-dHrx3c)+(-r4a)*(-dHrx4a)))/((1000)*(Fa*Cpa+Fb*Cpb+Fc*Cpc+Fd*Cpd+Fe*Cpe+Ff*Cpf+Fi*Cpi))

9 d(Ta)/d(W) = 100*a*(T-Ta)/(rhob*105*1683.953)

Explicit equations

1 Fi = 0.2998768333

nitrogen

2 R = 1.9858775

kcal/kmol.K

3 Ft = Fa+Fb+Fc+Fd+Fe+Ff+Fi

4 R2 = 8.31447*10^3

m^3.Pa/K/kmol

5 rhoc = 1600

1600 kg/m3

6 P0 = 235000

Pa

7 k2 = (6.31*10^7)*exp(-29850/R/T)/rhoc

8 k3 = (2.33*10^4)*exp(-21429/R/T)/rhoc

9 k4 = (7.20*10^5)*exp(-27149/R/T)/rhoc

10 T0 = 733

Kelvin (350-400 C inlet temp)

11 ct0 = P0/R2/T0

ideal gas law

12 r4a = -k4*(ct0*(Fa/Ft)*(T0/T)*(P/P0))

13 r3c = -k3*(ct0*(Fc/Ft)*(T0/T)*(P/P0))

14 r4b = 1.5*r4a

15 k1 = (7.7*10^6)*exp(-25143/R/T)/rhoc

16 r1a = -k1*(ct0*(Fa/Ft)*(T0/T)*(P/P0))

17 r1b = 4.5*r1a

18 r1c = -r1a

19 r1d = -2*r1a

```
r2a = -k2*(ct0*(Fa/Ft)*(T0/T)*(P/P0))
ra = r1a+r2a+r4a
rc = r1c+r3c
r2b = 7.5*r2a
r2d = -6*r2a
r3d = -4*r3c
r4e = -r4a
r1e = -2*r1a
r2e = -3*r2a
r3b = 3*r3c
rd = r1d+r2d+r3d
Ft0 = 0.3853714722
r3e = -r3c
mu = 3.482 *10^(-5)
    viscosity of air at 750K (kg/m.s)
gc = 1
    metric
Dp = 0.005
    m
phi = 0.5
r4f = -r4a
rhob = rhoc*(1-phi)
Ac = 7.363107782
v0 = 10.0055
    m^3/s
u = v0/Ac
rho = 1.13966
    kg/m^3
G = rho*u
beta = G*(1-phi)/(rho*gc*Dp*phi^3)*((150*(1-phi)*mu)/Dp+1.75*G)
a = 160
    m^2/m^3
rb = r1b+r2b+r3b+r4b
```

```
rf = r4f
alpha = 2*beta/(Ac*rhoc*(1-phi)*P0)
re = r1e+r2e+r3e+r4e
dCpd = ((2.74E+01)*T + (2.12E-02)*T^2 + (-6.52E-06)*(T^3) + (9.99E-10)*(T^4) + (-5.97E-14)*(T^5) - 9.89E+03)
dCpa = (-31.368*T + .2373*T^2 + (-1.04E-04)*(T^3) + (2.13E-08)*(T^4) + (-1.01E-12)*(T^5) - 9.14E+03)
dCpe = ((3.32E+01)*T + (-1.62E-03)*T^2 + (5.81E-06)*(T^3) + (-1.49E-09)*(T^4) - 9.88E+03)
dCpb = ((2.98E+01)*T + (-4.74E-03)*T^2 + (9.53E-06)*(T^3) + (2.47E-09)*(T^4) + (-1.13E-11)*(T^5) - 8.70E+03)
dCpc = ((-7.20E+01)*T + (5.21E-01)*T^2 + (-6.24E-04)*(T^3) + (4.13E-07)*(T^4) + (-1.11E-10)*(T^5) - 1.13E+04)
dCp1 = -1*dCpa-4.5*dCpb+dCpc+2*dCpd+2*dCpe
dCp3 = -1*dCpc-3*dCpb+4*dCpd+dCpe
dCpf = ((6.75E+01)*T + (-1.16E-01)*T^2 + (7.43E-04)*(T^3) + (-1.11E-06)*(T^4) + (8.35E-10)*(T^5) - 2.27E+04)
Cpa = -31.368 + 0.4746*T + (-0.00031137)*(T^2) + 0.00000008524*(T^3) + (-0.0000000000050524)*(T^4)
Cpb = 29.79023995 + (-0.009488538)*T + (0.0000285799)*(T^2) + 0.00000000987286*(T^3) + (-0.0000000000566511)*(T^4)
Cpc = -72.015 + 1.0423*T + (-0.0018716)*(T^2) + 0.000001653*(T^3) + (-0.00000000055647)*(T^4)
Cpd = 27.437 + 0.042315*T + (-0.000019555)*(T^2) + 0.000000003997*(T^3) + (-0.00000000000029872)*(T^4)
Cpe = 33.17438187 + (-0.003246334)*T + (0.0000174365)*(T^2) + (-0.00000000597958)*(T^3)
Cpf = 67.50354799 + (-0.232224187)*T + (0.002229152)*(T^2) + (-0.00000444287)*(T^3) + (0.00000000417641)*(T^4)
Cpi = 29.342 + (-0.0035395)*T + (0.000010076)*(T^2) + (-0.0000000043116)*(T^3) + (0.0000000000025935)*(T^4)
dCp2 = -1*dCpa-7.5*dCpb+6*dCpd+3*dCpe
dCp4 = -dCpa-1.5*dCpb+dCpf+dCpe
dHrx1a = -1751860 + dCp1
dHrx2a = -1718410 + dCp2
dHrx3c = -1417530 + dCp3
```

70 dHrx4a = -509230 +dCp4

71 ACONV = Fc/0.0057805556

Fmaleic out/F benzene in

72 L = W/(rhoc*0.5*3.14*((.025)^2)*.25*15000)

General

Total number of equations	81
Number of differential equations	9
Number of explicit equations	72
Elapsed time	2.315 sec
Solution method	RKF_45
Step size guess. h	0.000001
Truncation error tolerance. eps	0.000001

Polymath Code for PBR with Countercurrent Heat Exchanger

```
d(Fa) / d(W) = ra #benzene
Fa(0) = 0.0057805556 #kmol/s
d(Fb) / d(W) = rb #oxygen
Fb(0) = 0.0797140833
d(Fc) / d(W) = rc #maleic anhydride
Fc(0) = 0
d(Fd) / d(W) = rd #carbon dioxide
Fd(0) = 0
d(Fe) / d(W) = re #water
Fe(0) = 0
d(Ff) / d(W) = rf #quinone
Ff(0) = 0
Fi = 0.2998768333 #nitrogen

#rates
ra = r1a+r2a+r4a
rb = r1b+r2b+r3b+r4b
rc = r1c+r3c
rd = r1d+r2d+r3d
re = r1e+r2e+r3e+r4e
rf = r4f

#rate laws
r1a = -k1*(ct0*(Fa/Ft)*(T0/T)*(P/P0))
r2a = -k2*(ct0*(Fa/Ft)*(T0/T)*(P/P0))
r3c = -k3*(ct0*(Fc/Ft)*(T0/T)*(P/P0))
r4a = -k4*(ct0*(Fa/Ft)*(T0/T)*(P/P0))

#relative rates
r1b = 4.5*r1a
r1c = -r1a
r1d = -2*r1a
r1e = -2*r1a
r2b = 7.5*r2a
r2d = -6*r2a
r2e = -3*r2a
r3b = 3*r3c
r3d = -4*r3c
r3e = -r3c
r4b = 1.5*r4a
r4f = -r4a
r4e = -r4a

#rate constants
R = 1.9858775 #kcal/kmol.K
k1 = (7.7*10^6)*exp(-25143/R/T)/rhoc
k2 = (6.31*10^7)*exp(-29850/R/T)/rhoc
k3 = (2.33*10^4)*exp(-21429/R/T)/rhoc
k4 = (7.20*10^5)*exp(-27149/R/T)/rhoc

#stoich
#ca = ct0*(Fa/Ft)*(T0/T)*(P/P0)
#cb = ct0*(Fb/Ft)*(T0/T)*(P/P0)
#cc = ct0*(Fc/Ft)*(T0/T)*(P/P0)
#cd = ct0*(Fd/Ft)*(T0/T)*(P/P0)
#ce = ct0*(Fe/Ft)*(T0/T)*(P/P0)
```

```
#cf = ct0*(Ff/Ft)*(T0/T)*(P/P0)
#ci = ct0*(Fi/Ft)*(T0/T)*(P/P0)

Ft= Fa+Fb+Fc+Fd+Fe+Ff+Fi
Ft0 = 0.3853714722

#pressure drop (Ergun)
d(P) / d(W) = -alpha/2*(T/T0)*(P0/(P/P0))*(Ft/Ft0)
P(0) = 235000 #Pa
W(0) = 0
W(f) = 25763 #final weight of catalyst
alpha = 2*beta/(Ac*rhoc*(1-phi)*P0)
beta = G*(1-phi)/(rho*gc*Dp*phi^3)*((150*(1-phi)*mu)/Dp+1.75*G)
gc = 1 #metric
Dp = 0.005 #m
rhob = rhoc*(1-phi)
rhoc = 1600 #1600 kg/m3
phi = 0.5
#Ac = 4.908738521*10^-4 #diameter of 1 reactor tube (m^2)
Ac = 7.363107782
u = v0/Ac
G = rho*u
#G = 3.360722456
rho = 1.13966 #kg/m^3
v0 = 10.0055 #m^3/s
mu = 3.482 *10^(-5) #viscosity of air at 750K (kg/m.s)

#general energy balance
d(T) / d(W) = (100*a*(Ta-T)*(1/rhob)+(1000)*((-r1a)*(-dHrx1a)+(-r2a)*(-dHrx2a)+(-r3c)*(-
dHrx3c)+(-r4a)*(-dHrx4a)))/((1000)*(Fa*Cpa+Fb*Cpb+Fc*Cpc+Fd*Cpd+Fe*Cpe+Ff*Cpf+Fi*Cpi))
T(0) = 773 #Kelvin

#heat exchanger (co-curent)
d(Ta) / d(W) = 100*a*(Ta-T)/(rhob*105*1683.953)
Ta(0) = 773 #Kelvin
a = 160 #m^2/m^3
#coolant is mixture of sodium nitrate (41.3%) and sodium nitrite (58.7%)
#Cpco =  1683.953 #J/kg K
#mc = 105 #kg/s

#constants
R2=8.31447*10^3 #m^3.Pa/K/kmol
T0 = 773 #Kelvin (350-400 C inlet temp)
P0 = 235000 #Pa
ct0 = P0/R2/T0 #ideal gas law
#ct0 = 0.038559 kmol/m^3
#Uo = 100 #W/m2.C
#Uht = 60 #W/m2.C

#gas phase enthalpies at Tref (298 K)
#dHrx1aref = -1751860 #J/mol
#dHrx2aref = -3169390 #J/mol
#dHrx3cref = -1417530 #J/mol
#dHrx4aref = -509230 #J/mol

#enthalpies at T
dHrx1a = -1751860 + dCp1
dHrx2a = -1718410 + dCp2
```

```
dHrx3c = -1417530 + dCp3
dHrx4a = -509230 +dCp4

#change in heat capacities for each reaction, heat capacities in J/molK
dCp1= -1*dCpa-4.5*dCpb+dCpc+2*dCpd+2*dCpe
dCp2= -1*dCpa-7.5*dCpb+6*dCpd+3*dCpe
dCp3=-1*dCpc-3*dCpb+4*dCpd+dCpe
dCp4=-dCpa-1.5*dCpb+dCpf+dCpe

#heat capacities in J/mol K
Cpa = -31.368 + 0.4746*T + (-0.00031137)*(T^2) + 0.00000008524*(T^3) + (-
0.0000000000050524)*(T^4)
Cpb = 29.79023995 + (-0.009488538)*T + (0.0000285799)*(T^2) + 0.00000000987286*(T^3) + (-
0.0000000000566511)*(T^4)
Cpc = -72.015 + 1.0423*T + (-0.0018716)*(T^2) + 0.000001653*(T^3) + (-
0.00000000055647)*(T^4)
Cpd = 27.437 + 0.042315*T + (-0.000019555)*(T^2) + 0.000000003997*(T^3) + (-
0.00000000000029872)*(T^4)
Cpe = 33.17438187 + (-0.003246334)*T + (0.0000174365)*(T^2) + (-0.00000000597958)*(T^3)
Cpf = 67.50354799 + (-0.232224187)*T + (0.002229152)*(T^2) + (-0.00000444287)*(T^3) +
(0.00000000417641)*(T^4)
Cpi = 29.342 + (-0.0035395)*T + (0.000010076)*(T^2) + (-0.0000000043116)*(T^3) +
(0.00000000000025935)*(T^4)

#change in heat capacities in J/mol
dCpa = (-31.368*T + .2373*T^2 + (-1.04E-04)*(T^3) + (2.13E-08)*(T^4) + (-1.01E-12)*(T^5) -
9.14E+03)
dCpb = ((2.98E+01)*T + (-4.74E-03)*T^2 + (9.53E-06)*(T^3) + (2.47E-09)*(T^4) + (-1.13E-
11)*(T^5) - 8.70E+03)
dCpc = ((-7.20E+01)*T + (5.21E-01)*T^2 + (-6.24E-04)*(T^3) + (4.13E-07)*(T^4) + (-1.11E-
10)*(T^5) - 1.13E+04)
dCpd = ((2.74E+01)*T + (2.12E-02)*T^2 + (-6.52E-06)*(T^3) + (9.99E-10)*(T^4) + (-5.97E-
14)*(T^5) - 9.89E+03)
dCpe = ((3.32E+01)*T + (-1.62E-03)*T^2 + (5.81E-06)*(T^3) + (-1.49E-09)*(T^4)  - 9.88E+03)
dCpf = ((6.75E+01)*T + (-1.16E-01)*T^2 + (7.43E-04)*(T^3) + (-1.11E-06)*(T^4) + (8.35E-
10)*(T^5) - 2.27E+04)

ACONV=Fc/0.0057805556 #Fmaleic out/F benzene in

L=W/(rhoc*0.5*3.14*((.025)^2)*.25*15000)
```

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	a	160.	160.	160.	160.
2	Ac	7.363108	7.363108	7.363108	7.363108
3	ACONV	0	0	0.4481345	0.4481345
4	alpha	5.077E-06	5.077E-06	5.077E-06	5.077E-06
5	beta	3513.965	3513.965	3513.965	3513.965
6	Cpa	187.0128	182.1864	191.7487	182.1864
7	Cpb	23.86633	21.78882	25.48168	25.48168
8	Cpc	180.1691	177.2678	183.1292	177.2678
9	Cpd	50.20133	49.54923	50.8574	49.54923
10	Cpe	38.32187	37.88244	38.79213	37.88244
11	Cpf	659.0096	565.4014	774.6568	565.4014
12	Cpi	30.72778	30.56551	30.90065	30.56551
13	ct0	0.036564	0.036564	0.036564	0.036564
14	dCp1	2.027E+04	1.826E+04	2.268E+04	1.826E+04
15	dCp2	8414.006	6919.448	1.05E+04	6919.448
16	dCp3	-1.185E+04	-1.218E+04	-1.134E+04	-1.134E+04
17	dCp4	6.626E+04	5.162E+04	8.531E+04	5.162E+04
18	dCpa	6.77E+04	6.14E+04	7.447E+04	6.14E+04
19	dCpb	1.367E+04	1.282E+04	1.449E+04	1.282E+04
20	dCpc	7.296E+04	6.687E+04	7.946E+04	6.687E+04
21	dCpd	2.129E+04	1.958E+04	2.31E+04	1.958E+04
22	dCpe	1.697E+04	1.566E+04	1.835E+04	1.566E+04
23	dCpf	1.375E+05	1.166E+05	1.632E+05	1.166E+05
24	dHrx1a	-1.732E+06	-1.734E+06	-1.729E+06	-1.734E+06
25	dHrx2a	-1.71E+06	-1.711E+06	-1.708E+06	-1.711E+06
26	dHrx3c	-1.429E+06	-1.43E+06	-1.429E+06	-1.429E+06
27	dHrx4a	-4.43E+05	-4.576E+05	-4.239E+05	-4.576E+05
28	Dp	0.005	0.005	0.005	0.005
29	Fa	0.0057806	0.0020612	0.0057806	0.0020612

30	Fb	0.0797141	0.0599926	0.0797141	0.0599926
31	Fc	0	0	0.0025905	0.0025905
32	Fd	0	0	0.0115521	0.0115521
33	Fe	0	0	0.0084335	0.0084335
34	Ff	0	0	6.7E-05	6.7E-05
35	Fi	0.2998768	0.2998768	0.2998768	0.2998768
36	Ft	0.3853715	0.3845737	0.3853715	0.3845737
37	Ft0	0.3853715	0.3853715	0.3853715	0.3853715
38	G	1.548649	1.548649	1.548649	1.548649
39	gc	1.	1.	1.	1.
40	k1	0.0003708	0.0001739	0.0007665	0.0001739
41	k2	0.0001416	5.761E-05	0.0003353	5.761E-05
42	k3	1.261E-05	6.613E-06	2.342E-05	6.613E-06
43	k4	9.385E-06	4.142E-06	2.056E-05	4.142E-06
44	L	0	0	4.375881	4.375881
45	mu	3.482E-05	3.482E-05	3.482E-05	3.482E-05
46	P	2.35E+05	2.194E+05	2.35E+05	2.194E+05
47	P0	2.35E+05	2.35E+05	2.35E+05	2.35E+05
48	phi	0.5	0.5	0.5	0.5
49	R	1.985878	1.985878	1.985878	1.985878
50	r1a	-2.033E-07	-3.433E-07	-3.328E-08	-3.328E-08
51	r1b	-9.151E-07	-1.545E-06	-1.498E-07	-1.498E-07
52	r1c	2.033E-07	3.328E-08	3.433E-07	3.328E-08
53	r1d	4.067E-07	6.656E-08	6.867E-07	6.656E-08
54	r1e	4.067E-07	6.656E-08	6.867E-07	6.656E-08
55	R2	8314.47	8314.47	8314.47	8314.47
56	r2a	-7.764E-08	-1.492E-07	-1.103E-08	-1.103E-08
57	r2b	-5.823E-07	-1.119E-06	-8.271E-08	-8.271E-08
58	r2d	4.659E-07	6.617E-08	8.95E-07	6.617E-08
59	r2e	2.329E-07	3.308E-08	4.475E-07	3.308E-08
60	r3b	0	-5.497E-09	0	-4.773E-09
61	r3c	0	-1.832E-09	0	-1.591E-09
62	r3d	0	0	7.329E-09	6.363E-09

63	r3e	0	0	1.832E-09	1.591E-09
64	r4a	-5.147E-09	-9.182E-09	-7.93E-10	-7.93E-10
65	r4b	-7.721E-09	-1.377E-08	-1.189E-09	-1.189E-09
66	r4e	5.147E-09	7.93E-10	9.182E-09	7.93E-10
67	r4f	5.147E-09	7.93E-10	9.182E-09	7.93E-10
68	ra	-2.861E-07	-5.017E-07	-4.51E-08	-4.51E-08
69	rb	-1.505E-06	-2.68E-06	-2.384E-07	-2.384E-07
70	rc	2.033E-07	3.169E-08	3.424E-07	3.169E-08
71	rd	8.726E-07	1.391E-07	1.585E-06	1.391E-07
72	re	6.448E-07	1.02E-07	1.144E-06	1.02E-07
73	rf	5.147E-09	7.93E-10	9.182E-09	7.93E-10
74	rho	1.13966	1.13966	1.13966	1.13966
75	rhob	800.	800.	800.	800.
76	rhoc	1600.	1600.	1600.	1600.
77	T	773.	738.8364	808.865	738.8364
78	T0	773.	773.	773.	773.
79	Ta	773.	734.4598	773.	734.4598
80	u	1.358869	1.358869	1.358869	1.358869
81	v0	10.0055	10.0055	10.0055	10.0055
82	W	0	0	2.576E+04	2.576E+04

Differential equations

1 d(Fa)/d(W) = ra

benzene

2 d(Fb)/d(W) = rb

oxygen

3 d(Fc)/d(W) = rc

maleic anhydride

4 d(Fd)/d(W) = rd

carbon dioxide

5 d(Fe)/d(W) = re

water

6 d(Ff)/d(W) = rf

quinone

7 d(P)/d(W) = -alpha/2*(T/T0)*(P0/(P/P0))*(Ft/Ft0)

8 d(T)/d(W) = (100*a*(Ta-T)*(1/rhob)+(1000)*((-r1a)*(-dHrx1a)+(-r2a)*(-dHrx2a)+(-r3c)*(-dHrx3c)+(-r4a)*(-dHrx4a)))/((1000)*(Fa*Cpa+Fb*Cpb+Fc*Cpc+Fd*Cpd+Fe*Cpe+Ff*Cpf+Fi*Cpi))

9 d(Ta)/d(W) = 100*a*(Ta-T)/(rhob*105*1683.953)

Explicit equations

1 Fi = 0.2998768333

nitrogen

2 R = 1.9858775

kcal/kmol.K

3 Ft = Fa+Fb+Fc+Fd+Fe+Ff+Fi

4 R2 = 8.31447*10^3

m^3.Pa/K/kmol

5 rhoc = 1600

1600 kg/m3

6 P0 = 235000

Pa

7 k2 = (6.31*10^7)*exp(-29850/R/T)/rhoc

8 k3 = (2.33*10^4)*exp(-21429/R/T)/rhoc

9 k4 = (7.20*10^5)*exp(-27149/R/T)/rhoc

10 T0 = 773

Kelvin (350-400 C inlet temp)

11 ct0 = P0/R2/T0

ideal gas law

12 r4a = -k4*(ct0*(Fa/Ft)*(T0/T)*(P/P0))

13 r3c = -k3*(ct0*(Fc/Ft)*(T0/T)*(P/P0))

14 r4b = 1.5*r4a

15 k1 = (7.7*10^6)*exp(-25143/R/T)/rhoc

16 r1a = -k1*(ct0*(Fa/Ft)*(T0/T)*(P/P0))

17 r1b = 4.5*r1a

18 r1c = -r1a

19 r1d = -2*r1a

```
r2a = -k2*(ct0*(Fa/Ft)*(T0/T)*(P/P0))
ra = r1a+r2a+r4a
rc = r1c+r3c
r2b = 7.5*r2a
r2d = -6*r2a
r3d = -4*r3c
r4e = -r4a
r1e = -2*r1a
r2e = -3*r2a
r3b = 3*r3c
rd = r1d+r2d+r3d
Ft0 = 0.3853714722
r3e = -r3c
mu = 3.482 *10^(-5)
   viscosity of air at 750K (kg/m.s)
gc = 1
   metric
Dp = 0.005
   m
phi = 0.5
r4f = -r4a
rhob = rhoc*(1-phi)
Ac = 7.363107782
v0 = 10.0055
   m^3/s
u = v0/Ac
rho = 1.13966
   kg/m^3
G = rho*u
beta = G*(1-phi)/(rho*gc*Dp*phi^3)*((150*(1-phi)*mu)/Dp+1.75*G)
a = 160
   m^2/m^3
rb = r1b+r2b+r3b+r4b
```

```
47 rf = r4f
48 alpha = 2*beta/(Ac*rhoc*(1-phi)*P0)
49 re = r1e+r2e+r3e+r4e
50 dCpd = ((2.74E+01)*T + (2.12E-02)*T^2 + (-6.52E-06)*(T^3) + (9.99E-10)*(T^4) + (-5.97E-14)*(T^5) - 9.89E+03)
51 dCpa = (-31.368*T + .2373*T^2 + (-1.04E-04)*(T^3) + (2.13E-08)*(T^4) + (-1.01E-12)*(T^5) - 9.14E+03)
52 dCpe = ((3.32E+01)*T + (-1.62E-03)*T^2 + (5.81E-06)*(T^3) + (-1.49E-09)*(T^4) - 9.88E+03)
53 dCpb = ((2.98E+01)*T + (-4.74E-03)*T^2 + (9.53E-06)*(T^3) + (2.47E-09)*(T^4) + (-1.13E-11)*(T^5) - 8.70E+03)
54 dCpc = ((-7.20E+01)*T + (5.21E-01)*T^2 + (-6.24E-04)*(T^3) + (4.13E-07)*(T^4) + (-1.11E-10)*(T^5) - 1.13E+04)
55 dCp1 = -1*dCpa-4.5*dCpb+dCpc+2*dCpd+2*dCpe
56 dCp3 = -1*dCpc-3*dCpb+4*dCpd+dCpe
57 dCpf = ((6.75E+01)*T + (-1.16E-01)*T^2 + (7.43E-04)*(T^3) + (-1.11E-06)*(T^4) + (8.35E-10)*(T^5) - 2.27E+04)
58 Cpa = -31.368 + 0.4746*T + (-0.00031137)*(T^2) + 0.00000008524*(T^3) + (-0.0000000000050524)*(T^4)
59 Cpb = 29.79023995 + (-0.009488538)*T + (0.0000285799)*(T^2) + 0.00000000987286*(T^3) + (-0.0000000000566511)*(T^4)
60 Cpc = -72.015 + 1.0423*T + (-0.0018716)*(T^2) + 0.000001653*(T^3) + (-0.00000000055647)*(T^4)
61 Cpd = 27.437 + 0.042315*T + (-0.000019555)*(T^2) + 0.000000003997*(T^3) + (-0.00000000000029872)*(T^4)
62 Cpe = 33.17438187 + (-0.003246334)*T + (0.0000174365)*(T^2) + (-0.00000000597958)*(T^3)
63 Cpf = 67.50354799 + (-0.232224187)*T + (0.002229152)*(T^2) + (-0.00000444287)*(T^3) + (0.00000000417641)*(T^4)
64 Cpi = 29.342 + (-0.0035395)*T + (0.000010076)*(T^2) + (-0.0000000043116)*(T^3) + (0.0000000000025935)*(T^4)
65 dCp2 = -1*dCpa-7.5*dCpb+6*dCpd+3*dCpe
66 dCp4 = -dCpa-1.5*dCpb+dCpf+dCpe
67 dHrx1a = -1751860 + dCp1
68 dHrx2a = -1718410 + dCp2
69 dHrx3c = -1417530 + dCp3
```

```
70 dHrx4a = -509230 +dCp4
71 ACONV = Fc/0.0057805556
   Fmaleic out/F benzene in
72 L = W/(rhoc*0.5*3.14*((.025)^2)*.25*15000)
```

General

Total number of equations	81
Number of differential equations	9
Number of explicit equations	72
Elapsed time	2.315 sec
Solution method	RKF_45
Step size guess. h	0.000001
Truncation error tolerance. eps	0.000001

Appendix 6: Separations

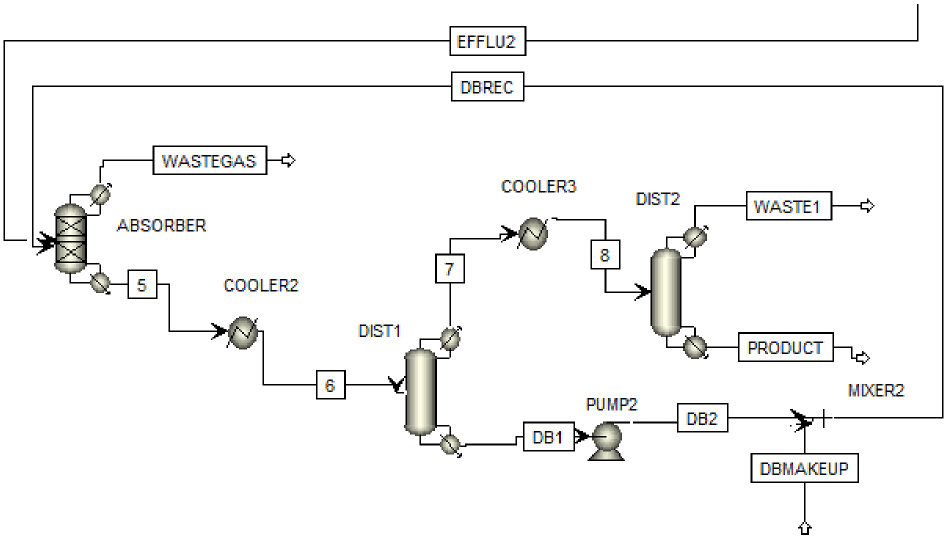
Introduction

This report includes a comparison between trayed and packed columns for the separations units in the production of maleic anhydride. The initial base case design considers the production of 10,000 metric tons per year of maleic anhydride by the catalytic oxidation of benzene. This design employs can employ one of two separations methods: a scrubber followed by a series of distillation columns, or a series of flash units followed by a distillation column.

Flash distillation units utilize one of the simplest separations processes. A liquid stream is partially vaporized in a flash drum at a particular temperature and pressure resulting in two phases: a vapor phase with the mover volatile components and a liquid phase with the less [71]. Distillation columns are essentially a series of flash drums that separate compounds via their relative volatilities [72]. The higher the relative volatility, the better the separations [73]. When the volatility differences between two or more species is small as to necessitate 100 or more stages for adequate separations, then "extractive distillation" is considered [74]. Absorption units are extractive distillation units where the feed is vapor and the stripping section of the column is not needed [75]. Generally, absorbers require a miscible mass separating agent (MSA) where the target species in the feed vapor dissolve in the absorbent, which is limited by the solubilities [74].

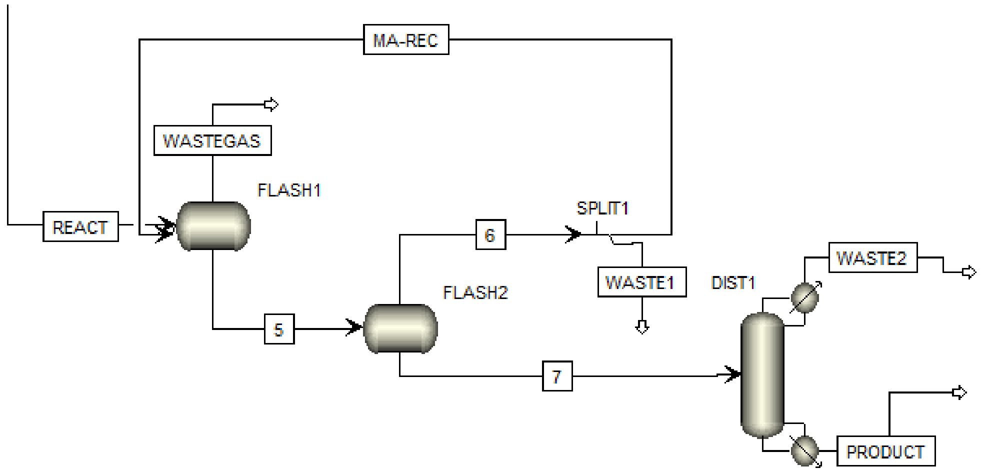
A major concern for any design considering a benzene reaction is the amount of water produced. Firstly, water separations with an organic phase are difficult and require a lot of heat due to large heat capacities [16]. Secondly, maleic acid in the presence of water hydrolyzes to form maleic acid. At 0°C, hydrolysis occurs following first order kinetics at a rate of $34.3\text{x}10^{-4}$ s^{-1} [17]. However, the reaction proceeds quickly at temperatures above 150°C (within 10 minutes, maleic anhydride degrades to maleic acid) [18].

For the design including an absorber, the general process is as follows: the absorber uses dibutyl phthalate as the MSA to remove maleic anhydride and quinone from oxidation reaction byproducts, nitrogen, carbon dioxide, oxygen, water, and benzene. The following distillation column then removes dibutyl phthalate from the maleic anhydride product stream. The process flow diagram (PFD) below shows the described absorber-distillation separations process. Detailed stream information can be found in Appendix 2: Stream Tables.



Appendix Figure 13: Absorber-based separations process PFD

A series of flash drums presents an alternative separation process with the first flash drum removing most of the carbon dioxide, excess oxygen, nitrogen, and water. The second flash drum removes more water and the distillation column separates the maleic anhydride product from water to achieve the target product purity. The separations process is shown in the PFD below with detailed stream information in Appendix 2: Stream Tables.



Appendix Figure 14: Flash-based separations process PFD

Models presented in this work use Soave-Redlich-Kwong (SRK) equilibrium method. Considered to be one of the most widely used Equation of State methods, SRK is suitable for hydrocarbon systems with pressures greater than 1 bar [76]. As suggested by Aspen, the NBS steam table is used as the free-water method as it provides greater accuracy and the SRK model is designed to utilize it [77]. SRK is also recommended for gas processing [77].

Conclusion

Two separations methods are viable: 1) an absorber followed by a distillation column, and 2) a series of flash units followed by a distillation column. For the first method, a packed absorber and trayed distillation column are optimal. For the second method, two flash units are needed followed by a small packed distillation column.

Absorber and Distillation Process

Column Selection

Common practice is to use packed columns if the diameter is less than 3 ft in diameter and 18 ft in height [51]. Applying this to the distillation column, a trayed column is the best option since packed column diameters were estimated to be greater than 5 ft. Sieve trays specifically would be best due to the lower cost and pressure drop.

For absorption, a packed column is preferred over distillation due to column dimensions. When determining a type of packing, a rough cost estimate was used to compare Pall ring (ceramic, 50 mm) to Gempak structured packing (metal, 2A 304T). A Gempak column would cost $246,600 compared to $66,500 for a Pall ring column with insignificant increase in efficiency (less than 0.01 mol% increase in maleic anhydride exiting).

Overall Column Process

The optimal design for column-based separations is a packed scrubber with ceramic 50 mm Pall rings followed by a two sieve tray distillation columns. The total equipment cost for this arrangement is $153,600. The stream table results for this design are shown in the table below.

Appendix Table 17: Streams for packed scrubber followed by a trayed distillation column.

	Distillate	Bottoms
Maleic Anhydride	0.9621	0.0015
Benzene	0.0000	0.0000
Oxygen	0.0000	0.0000
Nitrogen	0.0000	0.0000
Carbon Dioxide	0.0000	0.0000
Quinone	0.0308	0.0000
Dibutyl Phthalate	0.0069	0.9985
Water	0.0002	0.0000

After adding a second distillation column to increase the purity of maleic anhydride, we found that the purity increased approximately 1% with another $12,400 distillation column. The comparison of the product leaving in the distillate can be found in Appendix Table 18. The second distillation column has a reflux ratio of 1, distillate to feed ratio of 0.09, 6 trays, kettle reboiler, and a partial condenser. The feed enters on stage 2. Including this separation unit brings the total cost to $166,000 for the column-based separation process.

Appendix Table 18: Product exiting in distillate with one versus two distillation columns

Mole Fraction	Distillation Column 1 Product	Distillation Column 2 Product
Benzene	0.962	0.971
Oxygen	0.000	0.000
Nitrogen	0.000	0.000
Water	0.000	0.000
Maleic Anhydride	0.000	0.000
Carbon Dioxide	0.031	0.022
Quinone	0.007	0.007
Dibutyl Phthalate	0.000	0.000
Molar Flow Rate (kmol/hr)		
Benzene	13.57	12.46
Oxygen	0.00	0.00
Nitrogen	0.00	0.00
Water	0.00	0.00
Maleic Anhydride	0.00	0.00
Carbon Dioxide	0.43	0.28
Quinone	0.10	0.09
Dibutyl Phthalate	0.00	0.00

Flash Drum Process

An alternative approach to the absorber followed by distillation process was investigated. First, reactant gases are removed in a flash drum. Purification of the maleic anhydride stream via a column or series of flash drums was analyzed. In this process, no additional solvent such as dibutyl phthalate is necessary.

Comparison and Recommendations

Separation

A similar purity was seen between the column process and flash process from Aspen Simulations. The flash process has a maleic anhydride product flowrate of 12.97

kmol/hr (at 98% purity) compared to that of the column process at 12.83 kmol/hr (at 97% purity).

Cost Analysis

Further cost analysis should consider the difference in maleic anhydride production flowrates. Equipment costs for the flash drum method total $234,000 while for the column process total $123,700. Utility costs for a flash system in general are cheaper than that of the equivalent number of towers. From preliminary costing, the flash drum method appears to be more expensive in regards to equipment.

Environmental Factors

In general, removing additional solvents from a stream will decrease maintenance, potential hazards, and material waste. Environmental factors cannot easily be measured, however a few approaches have been suggested by Constable et al. [10]. Equation (76) was used to calculate mass intensity of the two streams.

$$Mass\ Intensity = \frac{Total\ mass\ used\ in\ process\ (kg)}{Mass\ of\ product\ (kg)} \tag{76}$$

Mass intensity of the column process is 193 whereas the mass intensity of the flash process is 40. Additionally, purification of the benzene from other gaseous products for recycle purposes could be accomplished through use of an additional flash unit.

Recommendations

Due to the previously discussed results comparing degree of separation, cost, and environmental factors, the flash process is preferred for the separation of products resulting from the catalytic oxidation of benzene with atmospheric oxygen.

Distillation Column Design Optimization

Each separation unit must first consider whether the estimated diameter is conducive to packing or trayed design. The following sections discuss the identification and subsequent optimization of the distillation column in step-by-step detail.

Trayed Distillation Column

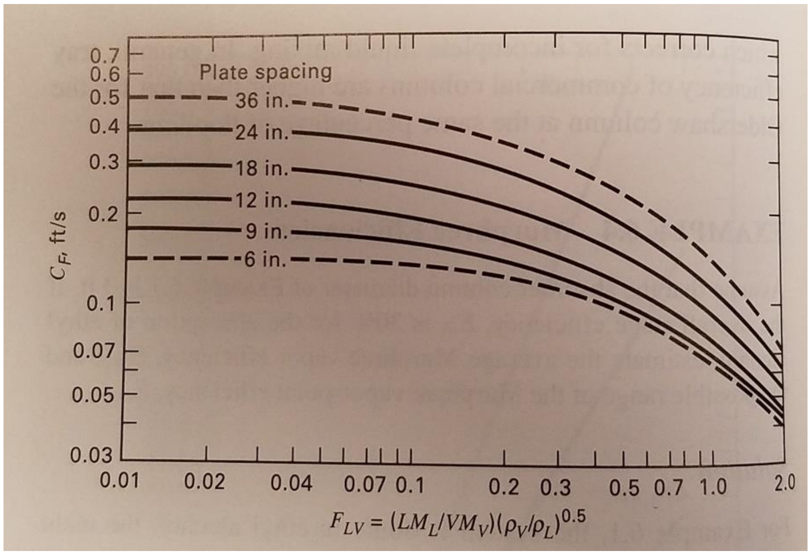
To begin designing a trayed distillation column, we used the design equations described in Seader et al. [78]. For these calculations, we needed to know the molar flow of the liquid and vapor in the distillation column with a kettle reboiler and total condenser. Using data from our base case process design in Aspen, we were able to determine the liquid and vapor flow rates, molecular weights, and densities.

Appendix Table 19: Aspen constants for trayed distillation.

Constants from Aspen		
V	14.10	kmol/hr
MW (V)	98.14	g/mol
Density(V)	0.00	kg/m^3
Temperature (V)	196.60	°C
L	825.18	kmol/hr
MW (L)	278.33	g/mol
Density (L)	0.80	kg/m^3
Temperature (L)	327.00	°C

These were determined using a simple distillation column with very few design specifications. We then used this data, with the design equations to calculate the diameter of the column. A major assumption made in doing these calculations was that the column has constant molar overflow (CMO). Thus, the liquid and vapor flowrates were assumed to be constant through the entire column. The equations used to calculate the diameter are as follows:

$$F_{LV} = \left(\frac{LM_L}{VM_V}\right)\left(\frac{\rho_G}{\rho_L}\right)^{\frac{1}{2}} \tag{77}$$



Appendix Figure 15: Entrainment flooding capacity in a trayed tower.

$$C = F_{ST} F_F F_{HA} C_F \tag{78}$$

$$F_F = F_{HA} = 1 \tag{79}$$

$$F_{ST} = \left(\frac{\sigma}{20}\right)^{0.2} \qquad \sigma = 15\ dyne/cm \tag{80}$$

$$U_F = C\left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{\frac{1}{2}} \tag{81}$$

$$\frac{A_D}{A} = 0.2 \quad , \quad F_{LV} \geq 1 \tag{82}$$

$$D_T = \left(\frac{4VM_V}{fU_F\pi\left(1 - \frac{A_D}{A}\right)\rho_V}\right) \tag{83}$$

From these calculations, we found the diameter of the column to be 4.8 feet. We were able to input diameter and height as a design specification into our Aspen simulation. In order to optimize the column, we then changed variables such as feed stage, tray type, number of stages, etc., and analyzed the outputs given in Aspen. The optimal results were as shown in Appendix Table 20.

Appendix Table 20: Trayed distillation design specifications.

Trayed Distillation Design Specifications		
Reflux Ratio	1.2	
Condensor	Partial	
Reboiler	Partial	
Tray Type	Sieve	
Tray Spacing	2	ft
Feed Stage	2	
# of Stages	4	
Diameter	4.83	ft
Height	18	ft
Distillate/Feed Ratio	0.0168	

The value for reflux ratio was initially assumed, and iterated to give the best separation. Since there were no issues with flooding in the column, sieve trays were chosen due to being cheap and having the smallest pressure drop [78]. The tray spacing was set as 2 ft according to heuristics [51]. Height was calculated using the number of trays and the tray spacing. We also included an additional 4 ft above the top tray for removal of entrained liquid, and 10 ft below the bottom tray for bottoms surge capacity [78].

The number of trays and stage of the feed were optimized. For the distillation column, the table below shows that only two trays are optimal; however, the difference is only a 0.05% increase in purity versus four trays.

Appendix Table 21: Tray optimization data from Aspen simulations.

	8 Trays		6 Trays		4 Trays		2 Trays	
Mole Fraction	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
Benzene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Oxygen	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nitrogen	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maleic Anhydride	0.962	0.002	0.962	0.002	0.962	0.002	0.967	0.002
Carbon Dioxide	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Quinone	0.027	0.000	0.027	0.000	0.027	0.000	0.026	0.000
Dibutyl Phthalate	0.011	0.998	0.011	0.998	0.011	0.998	0.007	0.998

The feed stage was found to be optimal at the second stage when considering a 2-trayed, 4-stage system. The difference in maleic purity decreases from 96.7% to 89.4% when fed on stage 3. The stream table at the end of the optimization of the trayed distillation column is shown in Appendix Table 23.

Appendix Table 22: Effect of feed stage on trayed distillation.

	Feed Stage 2		Feed Stage 3	
Mole Fraction	Top	Bottom	Top	Bottom
Benzene	3.96E-06	1.75E-10	3.87E-06	1.73E-09
Oxygen	1.74E-06	3.16E-14	1.74E-06	5.85E-12
Nitrogen	5.28E-06	4.83E-14	5.28E-06	1.15E-11
Water	0.0001934	8.66E-10	1.92E-04	2.01E-08
Maleic Anhydride	0.9668391	0.001534	0.894134	0.002777
Carbon Dioxide	4.80E-06	4.76E-13	4.80E-06	4.64E-11
Quinone	0.0261541	2.58E-05	0.024141	6.02E-05
Dibutyl Phthalate	0.0067977	0.99844	0.081517	0.997163

Appendix Table 23: Trayed distillation column stream table.

Trayed Distillation Column Stream Table				
Component		**Inlet**	**Distillate**	**Bottoms**
Total	kmol/hr	839.25	14.10	825.15
Benzene	kmol/hr	0.00	0.00	0.00
Oxygen	kmol/hr	0.00	0.00	0.00
Nitrogen	kmol/hr	0.00	0.00	0.00
Water	kmol/hr	0.00	0.00	0.00
Maleic Anhydride	kmol/hr	14.80	13.57	1.23
Carbon Dioxide	kmol/hr	0.00	0.00	0.00
Quinone	kmol/hr	0.46	0.43	0.02
Dibutyl Phthalate	kmol/hr	823.99	0.10	823.90

Packed Distillation Column

Flowrates for the column were initially found using the base case as described above. The constants and flow rates from Aspen are summarized in Appendix Table 24. Utilizing design equations, the estimated ideal number of stages was found to be 6 with a reflux ratio of 1.2 and distillate to feed ratio of 0.0182 [29].

Appendix Table 24: Aspen constants for trayed distillation.

Constants from Aspen		
V	14.10	kmol/hr
MW (V)	98.14	g/mol
Density(V)	0.00	kg/m^3
Temperature (V)	196.60	°C
L	825.18	kmol/hr
MW (L)	278.33	g/mol
Density (L)	0.80	kg/m^3
Temperature (L)	327.00	°C

The F_{LV} flow parameter was calculated as shown in Equation (84). Next, using a generalized pressure-drop correlation of Leva for packed columns, Y, as shown in Equation (85), was found. Rearranging this equation to Equation (86), the superficial velocity, u_v, was calculated. Flooding factor is generally taken to be between 0.5 to 0.7. Most commonly, flooding factor is considered to be 0.7 for packed columns. Using Equation (87), the superficial gas velocity at flooding was calculated. Finally, the diameter of the column was found using Equation (88).

$$X = \left(\frac{LM_L}{VM_V}\right)\left(\frac{\rho_V}{\rho_L}\right)^{0.5} = F_{LV} \tag{84}$$

$$Y = \frac{u_V^2 F_p}{g}\left(\frac{\rho_v}{\rho_L}\right) f\{\rho_L\} f\{u_L\} \tag{85}$$

$$u_V = \sqrt{\frac{Yg}{F_p}\left(\frac{\rho_L}{\rho_V}\right)\frac{1}{f\{\rho_L\}f\{u_L\}}} \tag{86}$$

$$u_{v,f} = u_v * f \tag{87}$$

$$D_T = \left(\frac{4VM_V}{fu_{f,v}\pi\rho_V}\right)^{0.5} \tag{88}$$

Packed height equivalent to a theoretical plate (HETP) was estimated. To find an estimate of height, this number was multiplied by the number of stages (6). For structured packing at low to moderate pressure with low viscosity liquids, Equation (89) yields HETP. For Pall rings and similar high-efficiency random packing with low-viscosity liquids, Equation (90) gives HETP.

$$HETP, ft = \frac{100}{a}, \frac{ft^2}{ft^3} + \frac{4}{12} \tag{89}$$

$$HETP, ft = 1.5 * D_p, in. \tag{90}$$

Liquid holdup, the cross sectional area occupied by the liquid in the pipe carrying the wet gas flow, was calculated using Equation (91). The liquid Reynold’s Number is given by Equation (92) and the liquid Froude Number by Equation (93). Ratio of specific hydraulic area of packing to specific surface area of packing is given in Equation (94) and Equation (95). From these calculations, it was determined that the liquid holdup had minimal reductions in the void fraction.

$$h_L = \left(12 \frac{N_{Fr_L}}{N_{Re_L}}\right)^{\frac{1}{3}} \left(\frac{a_h}{a}\right)^{\frac{2}{3}} \tag{91}$$

$$N_{Re_L} = \frac{u_L \rho_L}{a \mu_L} \tag{92}$$

$$N_{Fr_L} = \frac{u_L^2 a}{g} \tag{93}$$

$$\frac{a_h}{a} = C_h N_{Re_L}^{0.15} N_{Fr_L}^{0.1} \; for \; N_{Re_L} < 5 \tag{94}$$

$$\frac{a_h}{a} = 0.85 C_h N_{Re_L}^{0.25} N_{Fr_L}^{0.1} \; for \; N_{Re_L} \geq 5 \tag{95}$$

Height, diameter, and liquid holdup calculations were performed for a variety of different packing. To determine suitable packing, we used the heuristics summarized in

Appendix Table 25. Out of the fourteen packings examined shown in Appendix Table 26, the Pall Ring (ceramix, 50mm diameter) and Gempak structured packing (metal, A2 304T) were chosen because both are common packing that can be modelled in Aspen as a direct comparison and align with the heuristics in Appendix Table 25.

Appendix Table 25: Heuristics for column size and corresponding packing size [79].

Column Size	Packing Size
< 0.3 m (1 ft)	< 25 mm (1 in)
0.3-0.9 m (1 to 3 ft)	25-38 mm (1-1.5 in)
> 0.9 m (3 ft)	50-75 mm (2-3 in)

Appendix Table 26: Packed distillation column sizing estimates, packing characteristics courtesy of [78], [79].

Packed Distillation Column Sizing Estimates						
Packing	**Type**	**Material**	**Size (mm)**	**F_p**	**D_t (ft)**	**HETP (ft)**
Gempak	Structured	Metal	A2 T-304	15	6.15	1.96
Mellapak	Structured	Plastic	250 Y	20	6.61	1.65
Ralu Pak	Structured	Metal	YC - 250	20	6.61	1.65
Rachig Ring	Random	Carbon	25	180	11.45	0.49
Rachig Ring	Random	Ceramic	25	160	11.12	0.60
Rachig Ring	Random	Ceramic	15	540	15.07	0.35
Rachig Ring	Random	Metal	15	170	11.29	0.08
Pall Ring	Random	Ceramic	50	43	8.00	0.56
Pall Ring	Random	Metal	50	25	6.99	0.15
Pall Ring	Random	Plastic	50	26	7.06	0.26
Pall Ring	Random	Metal	25	56	8.55	0.07
Pall Ring	Random	Plastic	25	55	8.51	0.18
Hilflow Rings	Random	Plastic	90	9	5.41	0.16
Nor-Pak Rings	Random	Plastic	50	14	6.05	0.22

These two types of packing were simulated in Aspen. Stream table results are shown below in Appendix Table 27. Structured packing, such as Gempak, is known to have higher efficiency than rings but significantly higher cost [29] [80]. However, our simulation results do not indicate a significant increase in efficiency over the selected Pall rings.

Packed Distillation Stream Table						
Packing Type	Pall Ring			Gempak		
Packing Material	Ceramic			Metal		
Packing Size	50 mm			2A 304T		
HETP	2 in			24 in		
Diameter	6.5 ft			5.75 ft		
Feed Stage	3			3		
# of Stages	6			6		
Reflux Ratio	1.2			1.2		
Condensor	Total			Total		
Reboiler	Kettle			Kettle		
Distillate to Feed Ratio	0.0182			0.0182		
	Inlet	Bottoms	Distillate	Inlet	Bottoms	Distillate
Total (kmol/hr)	724.572	724.446	0.127	724.572	724.446	0.127
Benzene (kmol/hr)	0.000	0.000	0.001	0.000	0.000	0.001
Oxygen (kmol/hr)	0.000	0.000	0.000	0.000	0.000	0.000
Nitrogen (kmol/hr)	0.000	0.000	0.000	0.000	0.000	0.000
Maleic Anhydride (kmol/hr)	0.017	0.000	0.951	0.017	0.000	0.951
Carbon Dioxide (kmol/hr)	0.000	0.000	0.000	0.000	0.000	0.000
Quinone (kmol/hr)	0.000	0.000	0.024	0.000	0.000	0.024
Dibutyl Phthalate (kmol/hr)	0.982	1.000	0.009	0.982	1.000	0.009
Water (kmol/hr)	0.000	0.000	0.014	0.000	0.000	0.014

Appendix Table 27: Packed distillation stream table.

Absorber Design Optimization

Trayed Scrubber Design

In a similar manner to that of the trayed distillation column, we used the design equations to determine the diameter of a trayed scrubber [78]. The scrubber includes a partial condenser and kettle reboiler. The design equations are listed above. The only change made to these equations was that the foaming factor (F_f) was set to 0.75. This was given as a heuristic design specification for absorption columns.

Also similar to the trayed distillation column, we obtained information on the vapor and liquid flow rates using Aspen. The data is as shown in Appendix Table 28 below.

Appendix Table 28: Trayed scrubber constants from Aspen.

Constants from Aspen		
V	1579.4	kmol/hr
MW (V)	29.02	g/mol
Density(V)	1.41	kg/m^3
Temperature(V)	43.29	°C
L	839.28	kmol/hr
MW (L)	275.08	g/mol
Density (L)	742.98	kg/m^3
Temperature(L)	361.99	°C

With the design calculations, we found that the diameter of the trayed scrubber should be 10 feet. We set this as a design specification in Aspen and varied other parameters to achieve the best separation. The optimized column specifications are as shown in Appendix Table 29 below.

Appendix Table 29: Trayed scrubber design specifications.

Trayed Absorption Design Specifications		
Reflux Ratio	1.75	
Condensor	Partial	
Reboiler	Partial	
Tray Type	Sieve	
Tray Spacing	2	ft
Solvent Feed Stage	2	
Products Feed Stage	6	
# of Stages	7	
Diameter	10.78	ft
Height	24	
Distillate/Feed Ratio	0.653	

Sieve trays were chosen for this column because they are the cheapest and offer the lowest pressure drop [78]. Changing the tray type in Aspen did not seem to change the quality of the separation as shown in Appendix Table 30.

Appendix Table 30: Effects of number of trays on absorption column

	10 Trays		7 Trays		5 Trays	
Mole Fraction	Top	Bottom	Top	Bottom	Top	Bottom
Benzene	0.000	0.000	0.000	0.000	0.000	0.000
Oxygen	0.123	0.000	0.123	0.000	0.123	0.000
Nitrogen	0.786	0.000	0.786	0.000	0.786	0.000
Water	0.036	0.000	0.036	0.000	0.036	0.000
Maleic Anhydride	0.000	0.018	0.000	0.018	0.000	0.018
Carbon Dioxide	0.054	0.000	0.054	0.000	0.054	0.000
Quinone	0.000	0.001	0.000	0.001	0.000	0.000
Dibutyl Phthalate	0.000	0.982	0.000	0.982	0.000	0.982
Molar Flow Rate (kmol/hr)						
Benzene	0.118	0.000	0.118	0.000	0.117	0.001
Oxygen	194.801	0.000	194.801	0.000	194.801	0.000
Nitrogen	1241.490	0.000	1241.490	0.000	1241.490	0.000
Water	56.976	0.003	56.973	0.006	56.859	0.120
Maleic Anhydride	0.001	14.798	0.002	14.797	0.025	14.773
Carbon Dioxide	85.935	0.000	85.935	0.000	85.935	0.000
Quinone	0.011	0.459	0.013	0.457	0.094	0.376
Dibutyl Phthalate	0.008	823.992	0.009	823.991	0.019	823.981

Tray spacing was taken to be 2 ft according to the common standard. We found that the best separation occurred when the dibutyl phthalate stream entered at the top of the column, and the vapor products stream entered at the bottom. This set-up is typical for a trayed absorber. By lowering the temperature of the dibutyl phthalate stream to 50ºC, a better separation was achieved. Height was calculated using the number of trays and the tray spacing. We also included an addition 4 ft above the top tray for removal of entrained liquid, and 10 ft below the bottom tray for bottoms surge capacity [78].

Appendix Table 31: Trayed scrubber stream table.

Trayed Scrubber Stream Table					
Component		**Liquid In**	**Vapor In**	**Vapor out**	**Liquid Out**
Total	kmol/hr	825.26	1593.33	1579.34	839.25
Benzene	kmol/hr	0.00	0.12	0.12	0.00
Oxygen	kmol/hr	0.00	194.80	194.80	0.00
Nitrogen	kmol/hr	0.00	1241.49	1241.49	0.00
Water	kmol/hr	0.00	56.98	56.97	0.01
Maleic Anhydride	kmol/hr	1.23	13.57	0.00	14.80
Carbon Dioxide	kmol/hr	0.00	85.94	85.94	0.00
Quinone	kmol/hr	0.02	0.45	0.01	0.46
Dibutyl Phthalate	kmol/hr	824.00	0.00	0.01	823.99

Packed Scrubber Design

Parameters for the column design were taken from the base case scenario and are shown in Appendix Table 25. Through design equations, the estimated optimal number of stages was found to be 10, reflux ratio was 1.75, and distillate to feed ratio was 0.65. Diameter, height, and liquid holdup were calculated in the same manner as described above. Liquid holdup, again, had minimal effect on the void fraction.

Appendix Table 32: Packed scrubber constants from Aspen

Constants from Aspen		
V	1579.4	kmol/hr
MW (V)	29.02	g/mol
Density(V)	1.41	kg/m^3
Temperature(V)	43.29	°C
L	839.28	kmol/hr
MW (L)	275.08	g/mol
Density (L)	742.98	kg/m^3
Temperature(L)	361.99	°C

The packings considered are shown in Appendix Table 33. When applying the heuristics for column diameter relative to packing size, the packing chosen were Pall rings (ceramic, 50 mm) and Gempak structured packing (metal, 2A 304T) [29] [79].

Appendix Table 33: Packed scrubber column sizing estimates, packing characteristics courtesy of [78], [79].

Packed Absorber Column Sizing Estimates						
Packing	**Type**	**Material**	**Size (mm)**	**F_p**	**D_t (ft)**	**HETP (ft)**
Gempak	Structured	Metal	A2 T-304	15	2.45	1.96
Mellapak	Structured	Plastic	250 Y	20	2.64	1.65
Ralu Pak	Structured	Metal	YC - 250	20	2.64	1.65
Rachig Ring	Random	Carbon	25	180	4.57	0.49
Rachig Ring	Random	Ceramic	25	160	4.43	0.60
Rachig Ring	Random	Ceramic	15	540	6.01	0.35
Rachig Ring	Random	Metal	15	170	4.50	0.08
Pall Ring	Random	Ceramic	50	43	3.19	0.56
Pall Ring	Random	Metal	50	25	2.79	0.15
Pall Ring	Random	Plastic	50	26	2.82	0.26
Pall Ring	Random	Metal	25	56	3.41	0.07
Pall Ring	Random	Plastic	25	55	3.40	0.18
Hilflow Rings	Random	Plastic	90	9	2.16	0.16
Nor-Pak Rings	Random	Plastic	50	14	2.41	0.22

These two packings were then modeled in our Aspen simulation. Stream table results are shown in Appendix Table 34. Although structured packing is generally higher efficiency, a significant increase in efficiency from Pall Ring to Gempak packing was not seen.

Appendix Table 34: Packed scrubber stream table.

Packed Scrubber Stream Table								
Packing Type	Pall Ring				Gempak			
Packing Material	Ceramic				Metal			
Packing Size	50 mm				2A 304T			
HETP	0.65 ft				2 ft			
Diameter	3 ft				2.5 ft			
Solvent Feed Stage	2				2			
Product Feed Stage	9				9			
Reflux Ratio	1.75				1.75			
Condensor	Partial				Partial			
Reboiler	Kettle				Kettle			
Distillate to Feed Ratio	0.65				0.65			
	Dibutyl In	Reactor Effluent In	Liquid Out	Vapor Out	Liquid In	Vapor In	Liquid Out	Vapor Out
Total (kmol/hr)	825.26	1593.33	839.25	1579.34	825.26	1593.33	839.25	1579.34
Benzene (kmol/hr)	1.23	13.57	14.80	0.00	1.23	13.57	14.80	0.00
Oxygen (kmol/hr)	0.00	0.12	0.00	0.12	0.00	0.12	0.00	0.12
Nitrogen (kmol/hr)	0.00	194.80	0.00	194.80	0.00	194.80	0.00	194.80
Maleic Anhydride (kmol/hr)	0.00	1241.49	0.00	1241.49	0.00	1241.49	0.00	1241.49
Carbon Dioxide (kmol/hr)	0.00	85.94	0.00	85.94	0.00	85.94	0.00	85.94
Quinone (kmol/hr)	0.02	0.45	0.46	0.01	0.02	0.45	0.46	0.01
Dibutyl Phthalate (kmol/hr)	824.00	0.00	823.99	0.01	824.00	0.00	823.99	0.01
Water (kmol/hr)	0.00	56.98	0.00	56.98	0.00	56.98	0.00	56.98

Flash Drum Separations

Feed to the first flash drum for gas separation was the same as described above. At 215 kPa, pressure of the adsorption column, the bubble point and dew point of the mixture was found to be -189°C and 103.59°C in an Aspen using SRK equilibrium method. At 101 kPa (atmospheric pressure), the bubble point and dew point of the mixture was found to be -196°C and 89°C. The wider difference in bubble point and dew point temperatures was preferred for a better separation, so a pressure of 215 kPa was used.

To determine the best temperature for the flash drum, the boiling temperature of pure water and carbon dioxide was found to be 122°C and -69°C [27] [28].Thus, a reasonable initial guess of a temperature was 50°C. Changes in temperature were made until the maximum amount of maleic anhydride was in the liquid with the highest purity possible. A summary of tested temperatures and stream results are found in Appendix Table 35. The resulting conditions for the flash drum were 215 kPa at 60°C. Stream table results are shown below in

Appendix Table 36.

Appendix Table 35: First flash drum temperature optimization.

Streams							
Drum Temperature		50°C		60°C		70°C	
Mole Flows (kmol/hr)	REACT	5	WASTEGAS	5	WASTEGAS	5	WASTEGAS
Phase	Liquid	Liquid	Gas	Liquid	Gas	Liquid	Gas
Total	1616.291	19.950	1596.404	18.155	1601.543	13.833	1602.522
Maleic Anhydride	13.759	13.369	0.389	14.157	0.907	11.830	1.929
Benzene	0.116	0.001	0.115	0.001	0.116	0.000	0.116
Oxygen	197.528	0.001	197.527	0.001	197.528	0.001	197.527
Nitrogen	1259.370	0.001	1259.369	0.002	1259.370	0.001	1259.369
Carbon Dioxide	87.238	0.007	87.230	0.007	87.236	0.005	87.233
Quinone	0.452	0.376	0.076	0.379	0.138	0.250	0.202
Water	57.829	6.195	51.697	3.610	56.248	1.745	56.147

Appendix Table 36: First flash drum stream table.

	Mixture into Flash Unit	Recycle In	Liquid Out	Vapor Out
Total (kmol/hr)	1616.290	4.824	18.926	1602.190
Benzene (kmol/hr)	0.116	0.001	0.001	0.116
Oxygen (kmol/hr)	197.528	0.001	0.001	197.528
Nitrogen (kmol/hr)	1259.370	0.002	0.002	1259.370
Maleic Anhydride (kmol/hr)	13.759	1.845	14.702	0.905
Carbon Dioxide (kmol/hr)	87.238	0.007	0.007	87.238
Quinone (kmol/hr)	0.452	0.095	0.405	0.142
Dibutyl Phthalate (kmol/hr)	0.000	0.000	0.000	0.000
Water (kmol/hr)	57.829	2.871	3.809	56.892

Sizing of the flash drum was calculated as shown in Equation (96) [52]. Residence time suggested by Seider et al. is 10 minutes [52]. For a cylindrical drum, length to diameter ratio is commonly 3 [51]. Using Equation (97), the diameter of the drum was calculated. The drum was found to have a volume of 200900 ft^3 with a diameter of 44 ft (13.4 m) and length of 132 ft (40 m).

$$Volume = Feed\ Flowrate * 2 * \tau \tag{96}$$

$$D = \sqrt[3]{\frac{4 * Volume}{3 * \pi}} \tag{97}$$

Maleic Anhydride Purification

The largest source of impurity in the maleic anhydride stream is in the presence of water. In order to separate the water from the other hydrocarbons, first a column was examined. Pressure was assumed to be the same as the first flash drum at 215 kPa. Sizing of a trayed and packed column was performed as described previously. The feed flow rate to the column is relatively low at 15.7 L/min. Thus, when analyzing necessary column diameter for a packed or trayed column, a diameter less than 0.5 ft was obtained. In this design, the column contained 5 stages with a partial reboiler and partial condenser. Hence, separation was reanalyzed using a series of flash drums.

Initial temperature guess of 180°C yielded very little separation with most of the water and maleic anhydride present in the liquid stream as shown in Appendix Table 37. At a temperature of 220°C, very little separation occurred as well with most of the water and maleic anhydride present in the vapor stream. However, at 200°C, a purity of 91 mol% maleic anhydride was achieved in the liquid stream. Although, some maleic anhydride is lost in the vapor phase, over 50% of the water is removed. Without this flash drum, distillation is impossible due to the small difference in bubble and dew temperature.

Appendix Table 37: Second flash drum temperature optimization.

Streams							
Drum Temperature		180°C		200°C		220°C	
Mole Flows (kmol/hr)	5	6	7	6	7	6	7
Phase	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid
Total	16.329	1.613	14.716	3.904	12.425	10.803	5.526
Maleic Anhydride	12.845	0.314	12.531	1.498	11.346	7.529	5.315
Benzene	0.001	0.000	0.000	0.001	0.000	0.001	0.000
Oxygen	0.001	0.001	0.000	0.001	0.000	0.001	0.000
Nitrogen	0.001	0.001	0.000	0.001	0.000	0.001	0.000
Carbon Dioxide	0.006	0.006	0.000	0.006	0.000	0.006	0.000
Quinone	0.322	0.018	0.304	0.071	0.251	0.236	0.085
Water	3.154	1.273	1.881	2.327	0.827	3.028	0.126

Additional flash units were added to the system to maximize output purity. Following this criteria, three flash units were design in series at 200°C, 220°C, and 225°C. The third flash drum greatly reduced the amount of maleic anhydride in the liquid stream and improved purity by less than 0.5 mol%. Therefore, two flash drums total were chosen. To improve purity, a distillation column was added following the second flash drum. A potential recycle stream was suggested to refeed the vapor stream exiting the second flash drum to the first flash drum. When implemented in the Aspen Simulation, no significant change (less than 0.05 mol%) was seen in maleic anhydride purity of the product stream, but an increase in maleic anhydride flowrate was observed.

The distillation column removes excess water resulting in a maleic anhydride product stream of 98% purity with only quinone impurities. It is a packed column of 0.2 m diameter and 0.6 m height. For a column of less than 0.5 m, heuristics recommend a packed column [29]. In general, random packing columns are cheaper than structured packing although are generally less efficient, so a random packed column is used [30]. The column packing is Raschig metal rings of 15 mm diameter due to low cost and high packing factor of 170 [30]. The column has a partial condenser, kettle reboiler, and equivalent height of 4 stages. The reflux ratio is 4 and distillate to feed ratio is 0.08 on a molar basis. Feed is above stage 2. Streams are summarized in Appendix Table 38.

	Flash Unit 2		Distillation	
	Liquid Out	Vapor Out	Distillate	Bottoms
Total (kmol/hr)	14.101	4.824	1.128	12.973
Benzene (kmol/hr)	0.000	0.001	0.000	0.000
Oxygen (kmol/hr)	0.000	0.001	0.000	0.000
Nitrogen (kmol/hr)	0.000	0.002	0.000	0.000
Maleic Anhydride (kmol/hr)	12.854	1.848	0.158	12.696
Carbon Dioxide (kmol/hr)	0.000	0.007	0.000	0.000
Quinone (kmol/hr)	0.310	0.095	0.039	0.271
Dibutyl Phthalate (kmol/hr)	0.000	0.000	0.000	0.000
Water (kmol/hr)	0.937	2.871	0.931	0.006

Appendix Table 38: Maleic anhydride flash purification stream table.

Sizing calculations were performed as described above. The first flash drum is 14.3 m diameter with a length of 43 m and a total volume of 6,900 m^3. The second flash drum is 0.5 m in diameter, 1.7 m in length, and a total volume of 0.4 m^3. The distillation column diameter is 0.2 m, height is 0.6 m, and 6 stages with a partial condenser and total reboiler. The distillation column has Raschig metal rings of 15 mm, fitting the heuristics [79].

Costing

Trayed Columns

Costing of the trayed absorption and distillation columns were calculated in 2002 dollars. The trayed absorption column with five trays costs $177,400 (316 Stainless steel). For a trayed distillation column, the stainless steel column with 2 sieve trays costs $57,200.

Packed Absorber

To determine which packing would be best for our system, a simple cost estimate was found for the Pall Ring (50mm, ceramic) and Gempak (304 Stainless Steel) packed columns. 304 stainless steel is corrosion resistant to benzene, so this is the preferred packing material over the more expensive 316 stainless steel packing [81]. Equipment cost estimations (without instillation or shipping) are in 2002 dollars and should be taken with a ±20% consideration. An estimate cost for the Pall ring column (3 ft diameter, 6.5 ft packed height) was $66,500 ($60,000 for a 316 stainless steel column shell and $6,500 for packing) [82]. The Gempak column (2.5 ft diameter, 20 ft packed height) would approximately cost $246,600 ($240,000 for a 316 stainless steel column shell and $6,600 for packing) [51]. If the Gempak was made of 316 stainless steel instead of 304 stainless steel, the cost of packing would be approximately double [51]. By comparing packed volumes, the Pall Ring column is approximately half the size of the Gempak column. In general, random packing columns are cheaper than structured packing although are generally less efficient [78]. Therefore, our estimate that the Gempak column is more expensive than the Pall Ring column is reasonable.

Costing of Flash Drum Design

Costing of the flash drums was performed using methods presented by Peters et al. [51]. In 2002 dollars, the cost of the first larger drum was $220,000, the second, smaller drum is $2,000, and the distillation column is $12,000. The total cost of the flash drum separation process comes to $234,000.