

Acrylic Acid Production via the Catalytic Partial Oxidation of Propylene

Course: Chem Eng 4N04



Chemical
Engineering



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1 Introduction

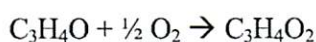
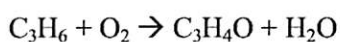
An extensive amount of chemicals in the polymer and textile industries rely on acrylic acid as a precursor [1]. It has an estimated annual production of 4.2 million metric tons, and its major uses are found in polymeric flocculants, dispersants, coatings, paints, and adhesives [2]. There are several methods used in the production of acrylic acid. In this report, the economics, operability as well as performance of a plant producing propylene via catalytic partial oxidation is examined. A detailed examination of initial capital costs as well as ongoing operational costs, yield a feasible and profitable plant. Due to the nature of this process and the tendency of the process to undergo a side reaction, the ideal operating window is determined and the reliability of the equipment present in assessed. Possible alternatives are examined proposed to the initial plant design in order to improve plant performance.

Safety considerations are also taken into account and proposed safety mechanisms are presented along with a HAZOP analysis and guidelines for start-up and shutdown of the plant as well as regeneration of a variety of columns and catalysts. Finally a troubleshooting case study is presented and solved using a systematic approach.

↖ good

2 Overview of Process

There are many different alternatives to producing acrylic acid industrially, and as a result, many patents exist for these different variations. However, the most common method is through the partial oxidation of propylene. The reaction is a two-step oxidation mechanism in which propylene is first oxidized to acrolein, and then to acrylic acid, each under separate catalyst and operating conditions [1]. The reactions are shown below:



There are also numerous side reactions that occur, resulting in the process setup consisting of two reactors at different conditions in order to maximize the formation of acrylic acid [1]. The most prevalent side reaction is the formation of acetic acid.

In order to operate a partial oxidation of a hydrocarbon safely, the composition of the feed stream must be carefully considered. With high compositions, the oxidation can produce large amounts of heat, making the reaction very dangerous. To overcome this, current designs in the industry use fluidized-bed reactors which provide isothermal conditions, allowing for stable operation [1]. Large amounts of steam are also supplied to the reactor for safety reasons. The PFD of the entire process can be found in Figure A1. The process is designed to operate for 8000 hours per year, producing 50,000 metric tons of 99.9% by mole acrylic acid [3]. Propylene, steam, and compressed air are combined into stream 4 and fed to the reactor initially. The reason air is combined with propylene and steam is to provide the oxygen necessary for oxidation, but also to minimize side reactions producing carbon dioxide, as feeding carbon dioxide will drive equilibrium side reactions in a favourable direction. Leaving the reactor is stream 6, which must be cooled promptly in order to avoid further oxidation reactions. To accomplish this, stream 6 is fed to a quench tower, T-1001, where it is cooled by a recycle stream of dilute aqueous acrylic acid. The cooled products are then sent to an off-gas absorber, T-1002, where additional recovery of acrylic acid, and the major by-product acetic acid is achieved. Deionized water is also sent to this tower. The vapour leaving this tower contains all of the un-reacted nitrogen, oxygen, carbon dioxide, water, and propylene from the reactor, as well as trace amounts of acetic acid and acrylic acid. This off-gas is discharged from the process as waste and sent to an incinerator. The bottoms product of this column is a dilute acrylic acid solution of which a portion is combined with the cooling recycle stream described previously, and the remainder being sent further into the process. Next, stream 9, the dilute aqueous acid solution, is fed to an acid extractor column, T-1003, to remove the acid fraction from the water. Many solvents can be used to accomplish this, so long as they have high solubility for acrylic acid and low solubility for water. The one most commonly used in the process is diisopropyl ether [3]. The reason a liquid-liquid extractor is used prior to purifying the acrylic acid is to achieve a greater difference in boiling points between the solvent and acrylic acid. The boiling point of water is 100°C, while the boiling point of acrylic acid is 141°C. To achieve a greater separation during purification, diisopropyl ether is used, having a boiling point of 69°C. To avoid large solvent feed costs, diisopropyl ether is recycled from a waste tower later in

the process. The bottoms product from the column, containing mostly water, is sent to a waste tower, T-1006, where perfect separation between water, diisopropyl ether, and acetic acid is achieved. The water from the waste tower contains trace amounts of acetic acid, and is sent to wastewater treatment, while the diisopropyl ether and acetic acid in the overhead are recycled back into the process. The top product from the extractor, containing diisopropyl ether and an acrylic acid solution, is sent to a solvent recovery tower, T-1004. The overhead product, containing mostly diisopropyl ether and some water is returned to the extractor, and the bottom product, containing mostly acrylic and acetic acid, is sent to an acid purification column, T-1005. The top product of this column is 95% by mol acetic acid, and the bottoms product is 99.9% by mole acrylic acid. The high concentrated acrylic acid solution is then cooled and sent to storage. There are several alternatives in the process, but they regard changing the raw material composition. Most commonly, substituted raw materials include the following processes:

1. Propane is catalytically oxydehydrogenated to form propylene.
2. Acrylic Acid produced via gas-derived acetylene complex
3. Acrylic Acid produced via dehydration of glycerol to acrolein , followed by oxidation
4. Acrylic acid via ethylene oxide carbonylation to β -propiolactone followed by catalytic conversion

2 effective alternatives to include to give reader place ~~with~~ relative to other common processes

3 Economics

3.1 Estimation of capital cost

The capital cost of the plant was calculated by following the cost estimation procedure outlined in the Chemical Engineering 4N04 course notes [4] supported by the Donald Woods booklet [5]. All of the equipment involved in the process was considered and is shown in Table 1.

Table 1: Summary of the equipment required in the production of acrylic acid

Equipment			
Off-Gas Absorber	Acid Condenser	Waste reflux pumps	Acid reflux pumps
Acid extractor	Waste Reboiler	Product pumps	Solvent HEX
Solvent Tower	Waste Condenser	CSTR Reactor	Acid feed pumps
Acid Tower	Product Cooler	Solvent Reboiler	Quench Cooler
Molten Salt Cooler	Quench Pumps	Acid Reboiler	

Each step involved in the final calculation of the total bare module cost is illustrated in Appendix B – Capital Cost. The first step required the calculation of the historical cost that lead to the cost of installation for each equipment (Table B1). The historical cost requires a capacity factor that converts the base case cost to the actual cost of the equipment. It is the factor that mostly affects the costing of the specific equipment. A list of the capacity factors is shown in Table B2 and its value is shown as “n” in Table B1. The second and third step required calculating the cost for pressure and materials and the cost for bare module piping. The results from the cost for pressure and materials and the cost for bare module piping are shown in Table B3 and Table B4. Both tables show that some of the equipment does not incur into any additional costing, this is because these specific equipment satisfied the base case. The summation of the cost for installation, cost for pressure and materials and cost for bare module piping results in the final bare module cost as shown by Table B5. The CSTR reactor was the only piece of equipment for which the capital cost was calculated through the use of an equation given directly from the process source:

$$\text{Cost of installed CSTR} = 2 \times 10^5 [\text{Area (m}^2\text{)}]^{0.5}$$

The capital cost of the entire plant resulted in a total of \$29.33M. However, these calculations cannot be considered fully accurate and it is advisable to take into account a percentage of uncertainty for the cost of each piece of equipment. This creates a low and high range of total bare module cost of \$22.8M and \$35.9M respectively, shown in Table B6.

Furthermore, an analysis of the bare module costs was made by breaking down the type of associated cost and each piece of equipment, depicted in Figure 1 and Figure 2 respectively.



Figure 1: Bare module associated costs breakdown

As clear from the pie chart, the installation costs represent over two thirds of the total cost, whereas the pressure and materials costing is approximately one third, leaving the piping cost to a negligible amount. This is because most of the equipment is not affected by piping, such as the tower equipment and some heat exchangers which also satisfy the pressure and materials base case (see Table B4).

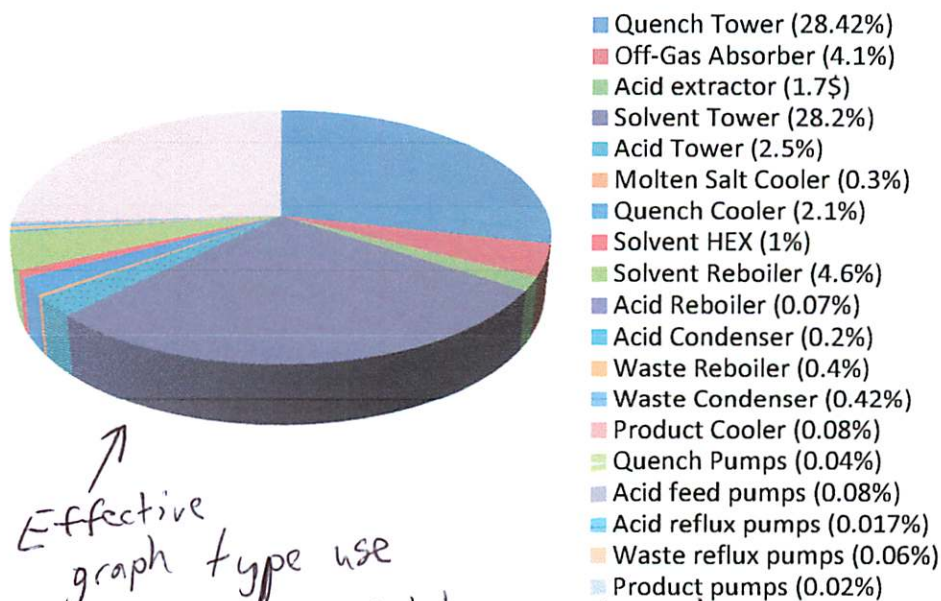


Figure 2: Equipment breakdown of the total cost

When considering each individual piece of equipment, Figure 2 gives a clear analysis of the total cost breakdown with the quench tower, solvent tower and CSTR reactor comprising almost 85% of the total cost. Only five other pieces of equipment are above the 1% boundary: the acid extractor, acid tower, quench cooler, and the solvent heat exchanger and reboiler. These pieces of equipment just mentioned are all directly or indirectly connected with each other and constitute the highest cost since they operate with high volumes of chemicals requiring extra power and size.

3.2 Estimation of Operating cost

The estimation of the operating cost required calculating the utilities and energy cost involved with the equipment and specifically the heat exchangers and pumps. These results can be seen in Table C1 and Table C2. The total operating cost added up to a total of \$32.2M as shown by Table C3.

3.3 Measures of profitability

Once the capital and operating costs were quantified, the revenue generated from the production of Acrylic Acid and Acetic Acid was calculated and shown in Table C4. Furthermore, with the acquired data ⁹ it was possible to calculate the net present value (NPV) and discounted cash flow rate of return (DCFRR) of the project. The 5- year NPV of the project was found to be approximately \$38.77M with a DCFRR of 41% whereas the 10- year NPV reached \$98.9M (Table C5). These numbers are extremely promising; however it is important to point out that these calculations did not take into account further expenses regarding the treatment and disposal of the chemicals and by-products, the cost of labour and the cost of land further reducing the net profits.

3.4 Sensitivity Analysis

In order to better assess the influence the price of the main revenue generator, acrylic acid, and the price of the main operating cost generator, propylene, have on the NPV of the project, a sensitivity analysis was produced and represented graphically as shown in Figure 3. The x-axis represents the variation in the acrylic acid price, whereas the shift is caused by the variation of the inlet propylene stream price ranging from 75% to 200%. The current base price of Acrylic Acid is approximately \$2200 per tonne. This implies that if that price stays constant, an increase of 25% in the price propylene will lead to essentially no profits and any further increases will incur into losses. However, the percentage increase in the price of acrylic acid has greater impact on NPV than the same percentage increase in the price of Propylene. Therefore, for this project to be non-profitable the percentage increase in price of propylene needs to be at least 25% higher than the percentage increase of acrylic acid. According to historical price data the price of acrylic acid has always been more volatile than the price of propylene further confirming the economic feasibility of the investment [6].

what is base price

of Propylene

(\$2200 ~~base~~?)

1.25 //



Easier for reader

if just given this number

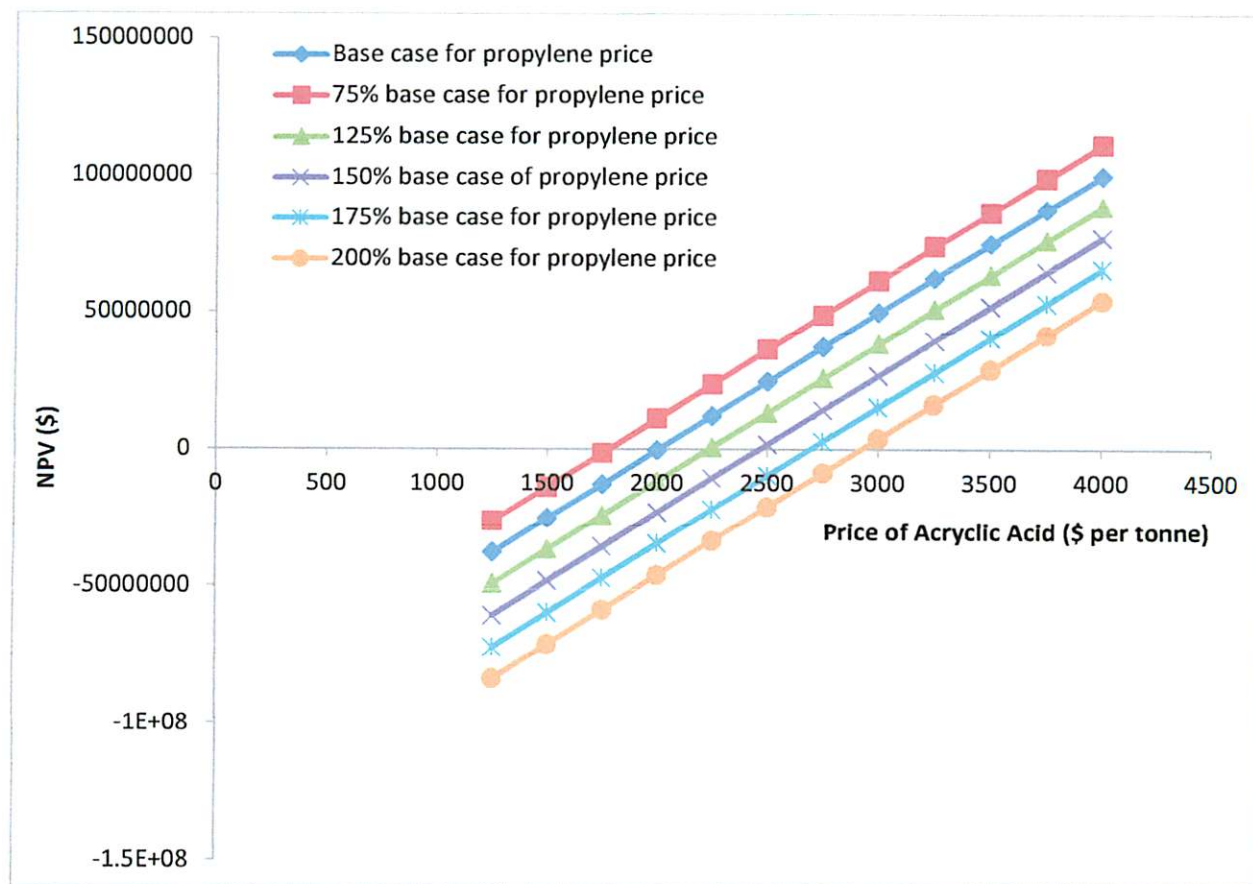


Figure 3: Sensitivity analysis performed on propylene

4 Operability

4.1 Operating Window

The two reactors in series determine the product purity that place stressors on the separation equipment downstream. In order to reduce the bi-product formation the reactors operate with different catalysts and at various temperatures. The two reactors can be seen in Figure A1, with the colour scheme indicating different reactor conditions. This is a method used to control the direction of partial oxidation to focus on: Propylene \rightarrow Acrolein \rightarrow Acrylic Acid. However, since the conditions at which this reaction takes place are strict this leaves a very narrow operating window that outputs an acceptable product. The main issue is that the possible

by-products (CO, CO₂, and C₂H₄O₂) are all thermodynamically favourable in comparison to the main product acrylic acid. The Gibbs free energy and Enthalpy of reaction for all four reaction schemes can be observed in Table 2.

Table 2: Thermodynamic constants of the reactor products and bi-products

Reactions	$\Delta_r G_{700}^o \left(\frac{kJ}{mol} \right)$	$\Delta_r \Delta H_{298}^o \left(\frac{kJ}{mol} \right)$
$C_3H_6(g) + 4.5O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$	-1942.089	-2058.43
$C_3H_6(g) + 3O_2(g) \rightarrow 3CO(g) + 3H_2O(l)$	-1276.765	-1209.48
$C_3H_6(g) + O_2(g) \rightarrow C_3H_4O_2(l) + H_2O(l)$	-550.2293	-404.21
$C_3H_6(g) + 4.5O_2(g) \rightarrow C_3H_4O(l) + 3H_2O(l)$	-338.7959	-426.24

In order to derive the operating window it was necessary to see how dependant the reaction conversion is on temperature. Figure 4 displays the relationship between the two variables. It is important to note that no reaction takes place in the first reactor below 300°C due to the fact that this is the limit at which the catalysts lower the activation energy. Figure 4 illuminates that fact that the largest conversion increase occurs in the temperature range from 300-400 °C.

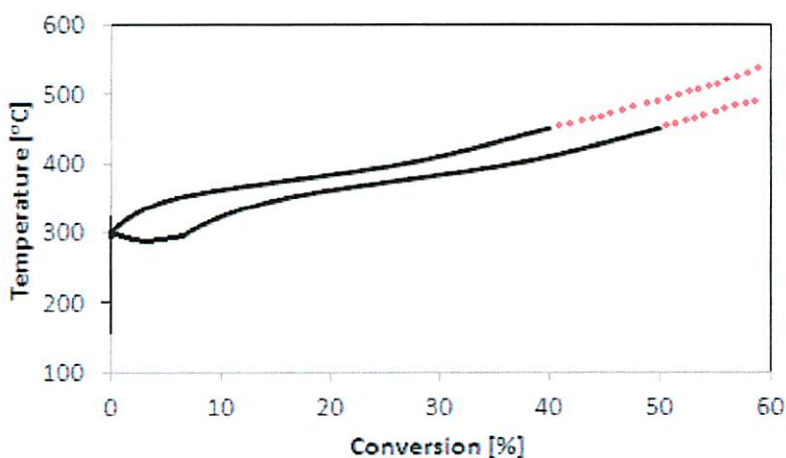


Figure 4: Relationship between the acrolein product conversion and the temperature of the reaction

The key limitation of the reactor is its ability to withdraw heat from the exothermic reaction occurring inside. The cooling loop can be observed in Figure A5 by the outlined blue section.

Therefore, the variables that affect this limitation are the temperature and flow rate of the cold water being fed to the heat exchanger and the flow rate of the HiTec Salt exchanger fluid. In addition, the partial pressure of propylene vs. oxygen ratio in the feed of the process is a very important factor. Any offset would greatly skew the final product; therefore, the feed stream has limitations in terms of composition. The desired feed ratio of propylene to oxygen is $170.0 \frac{\text{kmol}}{\text{h}} : 280.9 \frac{\text{kmol}}{\text{h}}$. Therefore, the optimal operating point for the reaction is propylene at a partial pressure of 60 kPa with the first and second reactors at 370 °C and 270 °C respectively. This was determined by using the first principles of the reaction to model the reaction rates of acrylic acid (R_1) and the by-products (R_2/R_3). The thermodynamic model and constants can be observed in Equation 1 and Table 3 respectively.

$$-r_i = k_{o,i} \exp \left[-\frac{E_i}{RT} \right] p_{\text{propylene}} \cdot p_{\text{oxygen}}$$

Equation 1: Thermodynamic model

Table 3: Constants for the formation of acrylic acid from propylene

Rxn. #	E_r $\frac{\text{kcal}}{\text{mol}}$	$K_{o,i}$ $\frac{\text{kmol}}{\text{m}^3}$
1	15000	159000
2	20000	883000
3	25000	181000000

The operating window was calculated from the thermodynamic model keeping the reaction rate of acrylic acid constant specifically at the optimum. However, from the calculations displayed in Table D.1, it can be noted that at higher temperature the reaction rate of the by-products increases drastically. Figure 5 displays the operating window of acrylic acid production.

Explain upper and lower bound curve in more detail

Also would aid to show how well your thermodynamic model (Eqn 1) models actual rxn scheme (show plot of model vs actual partial pressures)

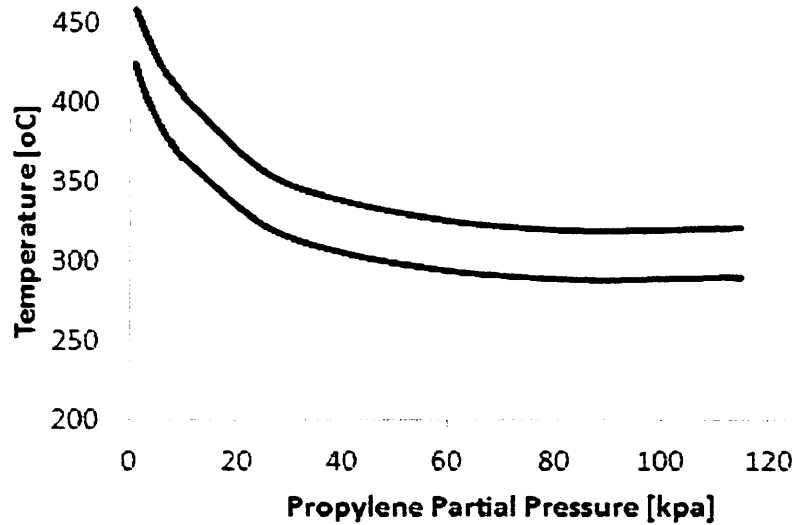


Figure 5: Operating window of acrylic acid production

4.2 Efficiency

From the thermodynamic models it can be noted that high product conversion surpassing 60% requires temperatures above 400°C. However, at high temperatures it is more thermodynamically favourable to create by-products via partial oxidation. Another trade-off is the fact that at a high partial pressure of propylene there is favourable conversion at low temperatures. However, the high concentration of propylene would dilute the O₂ concentration leading to weak partial oxidation and a reduced reaction rate. Furthermore, if there is a low propylene concentration then the exothermic reaction is less prominent since reaction rate decreases. This event is substituted by the fact that a larger volume of bi-products are being formed leading to poor final product quality. A final trade-off is that the optimal operating conditions that are aimed at lowering by-product formation *leave unreacted propylene in the final product stream* *good to realize*.

The solution that resolves the trade-offs involves focusing on balancing the reactant composition and temperature in the reactor by analyzing reaction kinetics and heat balances.

What are CV-MV pairing

Firstly, the composition of the reactor can be monitored and adjusted using process control methodologies specifically a feedback loop from the product stream. In addition, to ensure product runoff does not occur an industrial scale cooling tower would be implemented to ensure the cold water used for the heat exchanger was providing a necessary heat sink. Finally, the excess propylene in the product stream that would have been incinerated would be recycled through hollow fibre polymer membranes design to be selective to H_2O and CO_2 leaving propylene on the retentate side of the membrane. Using values the propylene is fed into a mixing stream before the reactor and the composition is analyzed so that the necessary control loop can adjust for the necessary disturbances to the feed stream. The schematic of the extra equipment implemented can be seen in Figure 6.

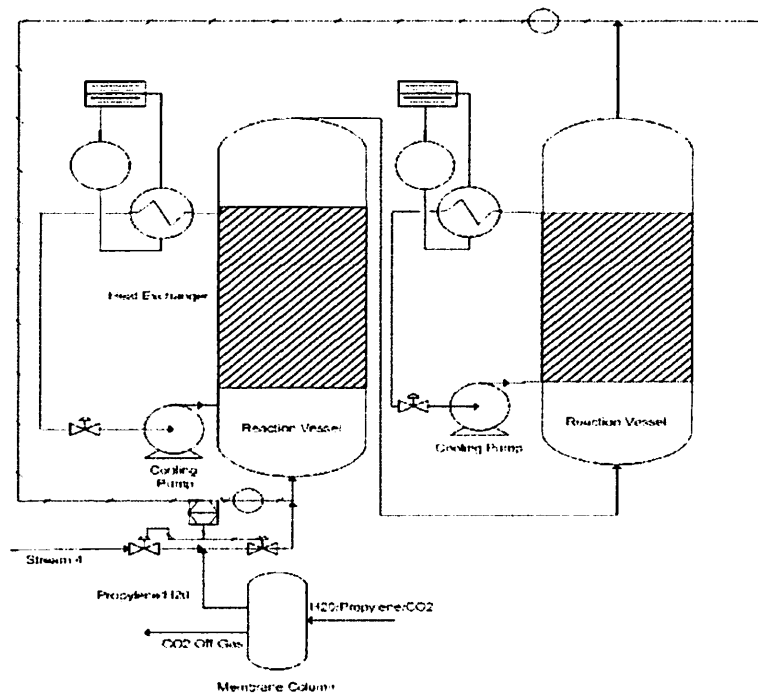


Figure 6: Control strategy, cooling towers, and membrane separation equipment schematic implementation

The solvent tower is the most energy intensive unit in the process, and thus it has the highest operating costs associated with it. With regards to efficiency, it was investigated if a

falling film evaporator could replace the solvent tower to lower operating costs. Calculations are provided in Appendix F - Sample Calculations, and the results can be seen in Table 4.

Table 4: Comparison of falling film evaporator to solvent tower

Equipment	Solvent Tower	Evaporator
Separation Energy Requirement	101,000 $\frac{MJ}{h}$	34755.398 $\frac{MJ}{h}$
Low Pressure Steam Flow Rate	48.5 $\frac{tonne}{h}$	16.398 $\frac{tonne}{h}$
Heat Transfer Area	891 m ²	306.6 m ²
Operating Costs	\$3,347,120/year	\$2,063,040/year

As seen in Table 4, the capital cost of the falling film evaporator is much lower than the current solvent tower, resulting in savings of \$1,284,080 per year. Less heat transfer area is required, but in order to operate at the same flow rate it is advised to size the evaporator at the same size as the solvent tower, resulting in very close capital costs between the two. Therefore, for just over a \$4 million dollar investment, the savings in operating cost can be dramatically lowered. The payback period of this investment is just over 4 years, and this is excluding the salvage value of the current solvent tower. It is therefore advised to go ahead with this investment, since the NPV will be well above zero over the long term.

4.3 Flexibility

In order to analyze the reactor scheme a single reactor model is used to determine the response of both reactors in series. The desired operating point for this system is a temperature of 310°C and propylene partial pressure of 60 kPa, which relays a single pass conversion of 88.5%. The uncertainties of the system include the heat transfer that can be provided by the heat exchanger loop and the vapour composition in the feed that may fluctuate due to the membrane separation equipment in practice that recycles the propylene. The disturbances in the reactor scheme deal with the feed composition and the ambient temperature affecting the cooling tower's

why are these uncertainties?

ability to act as a heat sink to the HiTec Salt in the heat exchanger loop. The process can be fairly flexible if two measures are taken: (1) Install valves and a composition analyzer after the mixing point and (2) Use an inline thermocouple that measures the temperature of the HiTec Salt to determine if enough heat exchange is being provided by the cooling tower water. Figure 7 illustrates the control scheme for the heat exchanger loop.

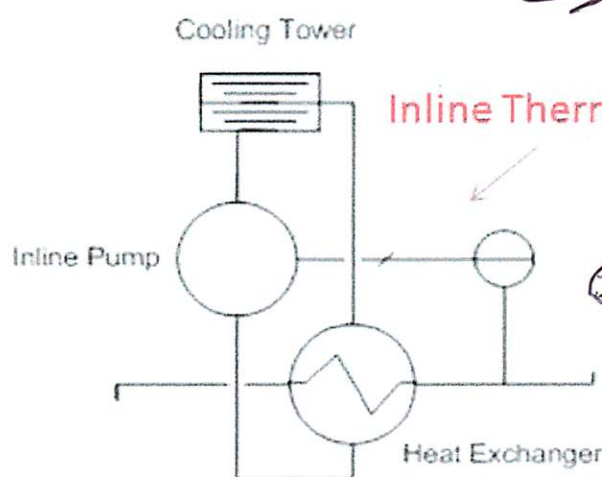


Figure 7: Control loop for reactor coolant heat exchanger

4.4 Reliability

In terms of reliability, due to the lack of operational data available from the process being analysed, some of the most recognized engineering reliability data databases were consulted and provided failure rates for most of the equipment involved such as the IAEA (International Atomic Energy Agency), HEI (Heat Exchange Institute) and OREDA (Offshore reliability data) [7]. The major equipment, such as the towers, was not considered due to the fact that their extremely high capital cost will not allow for any back up measures. On the other hand, the failure rates and reliability values of the sensors, heat exchangers and pumps are listed and shown in Appendix D – Operability & Reliability Data, Table D 2, Table D 3, Table D 4, respectively. Once the reliability was calculated from the failure rate, it was established that only a total reliability below 0.9 would require additional measures to increase the safety of the equipment. A 0.9 reliability value translated to approximately 11 years of mean time to

→ Explain in detail how it works

Figure clearer?

→ effective measure

translate reliability into a more reliable quantity to include to

failure (MTTF) which is the minimum safe time considered for this project. This case scenario was encountered in the case of the pumps equipment. The implementation of a parallel pump provided an increased reliability from 0.73 to 0.91 or from 3 to 11 years of MTTF Sample calculations involved with this procedure is shown in Appendix F - Sample Calculations. Out of all the types of pumps, the quench, acid feed and waste reflux pumps, are the ones that deal with highest volume of chemicals and are part of the mile stone steps of the process. For this reason they will be provided with parallel equipment with the appropriate hand and check valves as support. These implementations are graphically shown in Appendix A – Additional Figures: Figure A2, Figure A3, Figure A4.

4.5 Operating During Transitions

As mentioned previously, the acrylic acid production plant operates for 8000 hours per year, which translates into running the plant for 22 hours in a given day on average. This leaves very little time for transitions and thus careful planning of transient behaviour must be done in order to ensure that time, energy, and materials are not wasted. In a given year if the plant is running at full capacity, there is approximately 730 hours for start-ups, shut downs, regeneration and maintenance. There is no opportunity for blocked operation since the plant is running for such long periods of time and only one product is being produced.

4.5.1 Start up and Shutdown

The plant will be needed to be shut down whenever there is a failed unit, maintenance needs to be done, or regeneration must occur. The units most likely to fail have been identified as pumps and valves, and in the reliability section this problem was identified and a solution was implemented. With regards to maintenance, all of the towers including the reactor, off-gas absorber, acid extractor, acid tower and waste tower will require occasional maintenance. The quench tower, solvent tower, reboilers and the reactor will require regeneration of materials and

cleaning. The plant will be started up whenever the failed unit is replaced, the maintenance is finished, or the regeneration is complete.

The procedure that will be followed during shut down will be the material streams directed to the failed/maintained/regenerated unit will first be shut off. This will allow the material that is still in the unit or downstream of the unit to function at the desired set points and conditions, ensuring no product is wasted or at poor quality. Once the unit is emptied of material, the utility streams in the unit will be shut off, followed by shutting down of the actual unit. For units downstream in the process, the same procedure will be followed by subsequent units. It is very important to shut down the downstream units in the correct sequence, or else the product quality will not be as intended. For units upstream in the process there are two options. They will either need to be shut down as well at the same time as the unit being maintained, or they can continue to run and their flow directed to a backup unit or a storage tank. Since the columns in this process are extremely large and very expensive, it is not economically feasible to have backup towers. Instead, storage tanks will be implemented so that a portion of the plant can continue to run, and when the maintenance is complete the tank will be discharged back into the process.

Since the storage tanks will require a lot of floor space and a large investment, it is important to minimize both the amount of tanks as well as the size of the tanks. In order to minimize the amount of tanks, they will be placed strategically throughout the process. It was assumed that all units are equally likely to require maintenance, and thus the choice of where to place the tanks was independent of individual unit failure rates. In order to minimize the size of the tanks, the material streams entering each unit were examined, and the results are presented in Table 5.

such as... (give more description)

Table 5: material streams entering units of process

Equipment	Mass Flow Out ($\frac{\text{tonne}}{h}$)	Volume Flow Out ($\frac{m^3}{h}$)	Volume Flow Out in 730 hours (m^3)
Reactor	62.27	62.27	45457.1
Off-Gas Absorber	40.43	40.43	29513.9
Acid Extractor	163.87	163.87	119625.1
Acid Tower	6.63	6.63	4839.9
Waste Tower	157.24	157.24	114785.2
Solvent Tower	298.3	298.3	217759
Quench Tower	1957.27	1957.27	1428807.1

As seen in Table 5, the off-gas absorber and the acid tower have the lowest mass flow into the unit. It was assumed that the material streams had the density of pure water, and thus this mass flow rate was identical to the volume flow rate. In the worst case scenario, all 730 hours available for maintenance would be used on one unit, and thus each storage tank would need to be able to hold the volume that could accumulate in this time. The end result was that two storage tanks were implemented. This can be seen in Figure 8.

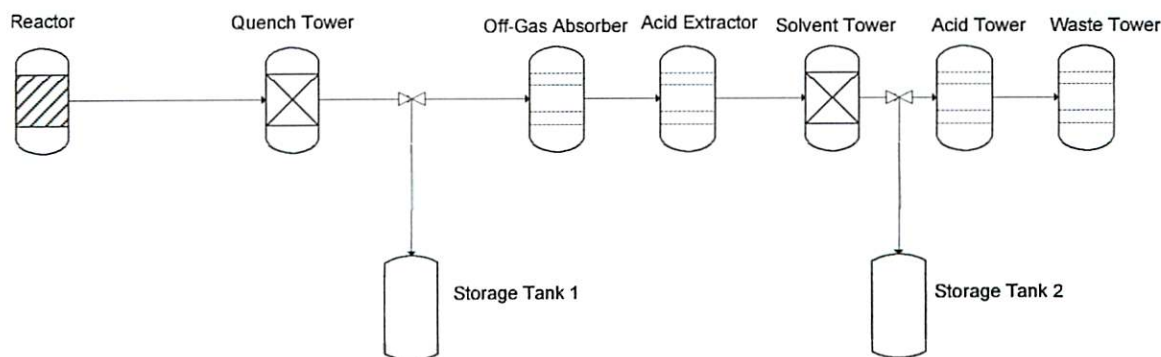


Figure 8: Storage tank implementation

As seen in Figure 8, the first tank was placed before the off-gas absorber. This allows the most important part of the plant, the reactor and quench tower, to continue to run in the case that any unit downstream requires maintenance. Since the reactor must be cooled right away, placing a

tank after the reactor is not possible. The second tank was placed after the solvent tower. This allows majority of the plant to run in the event that the acid tower or waste tower requires maintenance.

4.5.2 Regeneration

The next issue that rises after failed units and maintenance is the issue of regeneration within the plant. The reactor in the process is a fluidized bed with a catalyst also present. This means the reactor will need to be regularly regenerated and cleaned. Since this is a polymer process, the reboilers will also need to be cleaned since the surface will become coated *with* polymer. There are three reboilers in the process, namely the solvent tower reboiler, the acid tower reboiler, and the waste tower reboiler. The solvent tower reboiler and the waste tower reboiler contain mostly water, and thus will not need to be cleaned nearly as much as the acid tower reboiler which contains a significant amount of polymer. The quench tower and solvent tower also both contain high efficiency packing which will need to be replaced regularly. Since adding more storage tanks after these units in question is not economically feasible, the storage tank proposed in the previous section was moved to before the solvent tower instead of after it. In addition, since the reboilers are rather inexpensive compared to the cost of each unit, an additional acid reboiler was added in parallel. This allows the plant to continue to run while the acid reboiler is being cleaned. The proposed process can be seen in Figure 9.

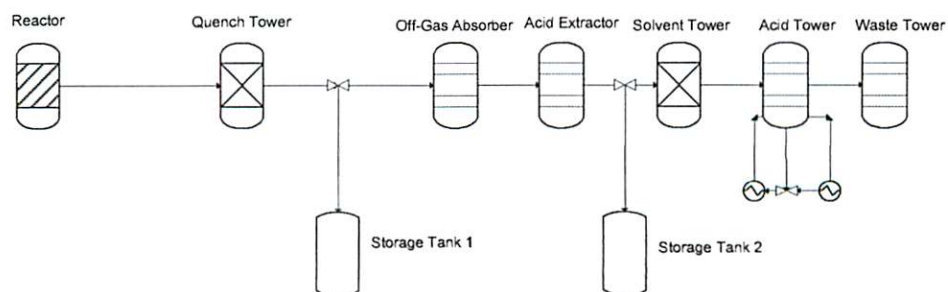


Figure 9: Modified storage tank configuration

As seen in Figure 9, having the second storage tank before the solvent tower allows the majority of the plant to continue to run while the solvent tower is being regenerated. Since this will occur much more often than the acid tower or waste tower requiring maintenance, it is much more economical to switch this position of the second tank.

4.5.3 Load Following

Detailed procedures have been outlined regarding the steps to take when specific units fail, require maintenance, or need to be regenerated and cleaned. With regards to the utility streams, it is also important to outline procedures and steps to be taken under the previously outlined circumstances. The utility streams present in the process are cooling water, refrigerated water, and low pressure steam, and can be seen in Table 6. The total utility streams required under transition periods are summarized in Table 7.

Table 6: Utility streams in process

Utility	Cw	Cw	Lps	Rw	Lps	Cw	Lps	Cw	Lps	cw
Flow (tonne/h)	1995	1682	48.5	5182	1.07	54.5	10.19	378	3.85	16.7

Table 7: Load following for various transition statuses

Status of Process Failure/Maintenance/Regeneration	Total Cw ($\frac{\text{tonne}}{h}$)	Total Lps ($\frac{\text{tonne}}{h}$)	Total Rw ($\frac{\text{tonne}}{h}$)
Full Operation	4126.4	63.61	5182
Reactor or Quench Tower F/M/R	0	0	0
Off-Gas Absorber or Acid Extractor F/M	3677	0	0
Solvent Tower, Acid Tower or Waste Tower F/M/R	3677	3.85	0

As seen in Table 7, when the reactor or quench tower requires maintenance or regeneration, no utility streams are required as the entire plant is shut down. If the off-gas absorber or acid

extractor failure or require maintenance, the reactor and quench tower are still run, and the flow is directed to the first storage tank. Therefore all the utility streams up until the off-gas absorber are still required. However, there will be an addition energy stream required to heat the material in the storage tank during start up when it is discharged back into the process. Alternatively the storage tank could be kept at a constant temperature during transitions, however since the duration of the maintenance is not known, this is not advised. If the solvent tower, acid tower, or waste tower require maintenance or regeneration, the off-gas absorber and the acid extractor are run in addition to the reactor and the quench tower, and thus all of the energy streams on these units are required. The second storage tank will also require additional energy to reheat the material before discharging it back into the process during start up.

4.6 Dynamic Performance

The most important pieces of equipment in the process have been identified as the reactor and the solvent tower. They both have extremely high operating and capitals costs, and are imperative for the quality of product produced. Therefore, the dynamic performance around these units must be closely monitored and controlled. Although there are a significant amount of controllers already present in the process diagram, it is proposed that two more be added in order to ensure the temperatures entering the reactor and the solvent tower are kept constant despite disturbances.

4.6.1 Important Disturbance Rejections

The most important disturbance rejection is the variation in the feed inlet temperatures. If the ambient air temperature is fluctuating, the streams entering the reactor must be monitored and controlled. It is proposed that a controller with a heat exchanger is added in order to account for these variations in temperatures prior to the streams entering the reactor. The proposed schematic can be seen in Figure 10.

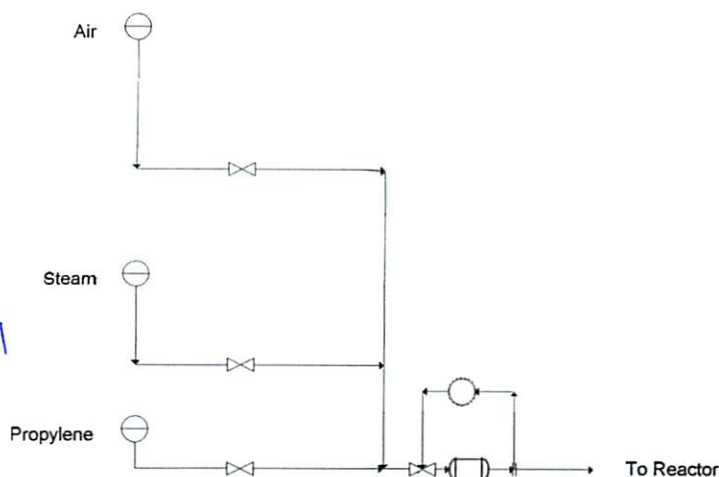


Figure 10: Feed temperature control system

As seen in Figure 10, for a low capital cost of an extra heat exchanger, as well as a low operating cost since the disturbances will typically not have extreme variation, the reactor inlet temperature can be controlled very easily.

The second disturbance that will be rejected is the feed temperature to the solvent tower. Control systems will be used to control both the temperature exiting the acid extractor, as well as the bottoms exiting the quench tower. Since both of these streams are the feed for the solvent tower, the amount of heating and cooling, respectively, will be monitored and controlled in order to ensure the solvent tower is running at its desired set point. In order to ensure a fast response, the piping to the controller will be shortened in order to allow a fast response to disturbances in the temperatures.

4.6.2 Recycle Streams

The off-gas absorber in the process produces an off-gas top product at approximately 48 °C. It is then sent to an incinerator where it is disposed of. The reactor product leaves the reactor at approximately 310 °C and must be cooled rapidly. Currently, this extremely hot stream is sent to a quench tower, which uses a significant amount of energy to cool the product. It is proposed

that using the relatively cooler off-gas in a shell and tube heat exchanger with the reactor product will dramatically lower capital costs. For a small initial investment of the heat exchanger, the operating costs of both the quench tower as well as the energy required to incinerate the off-gas will be lowered. The proposed heat exchanger can be seen in Figure 11.

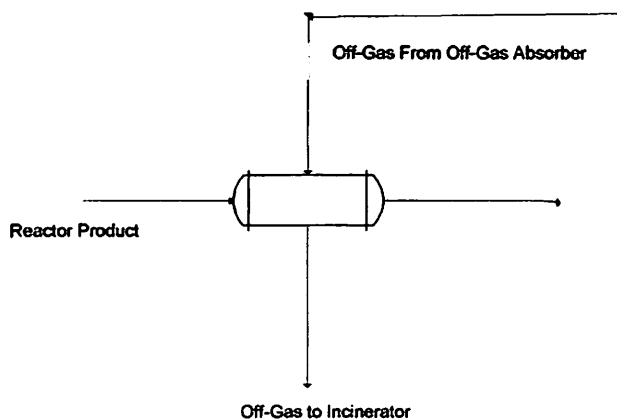


Figure 11: Alternative use for off-gas from absorber

It is hard to estimate the exact operating cost savings that will result from the implementation of the heat exchanger due to the complex composition of the off-gas. It is recommended that a small scale heat exchanger first be used in order to estimate how much heat can be removed from the exiting reactor stream, followed by scaling up to the size of the process if the result is feasible.

5 Safety Considerations

5.1 Six Levels of Safety

The reactor is the vessel of greatest concern for safety. A basic diagram of the reactor can be seen below in Figure 12. The reactor will be operating under the highest temperature and one of the highest pressures. As this is an exothermic reaction it is possible for the reactor to run-away if the temperature is not carefully maintained. In addition, operating outside ideal temperatures will favor the

production of by-products which are even more exothermic than the desired reaction. It is the most probable cause of an explosion as the reaction occurs in the gaseous phase and an increase in temperature will lead to an increase in pressure. Therefore, it is crucial that a systematic study regarding the safety issues of the reactor is performed. Potential causes of improper reactor temperature maintenance include a reduced cooling molten salt flow rate (e.g. cooling pump failure, pipe fouling, and pipe leak) or a decrease in heat exchanger efficiency. As several harmful by-products are often produced by the reaction it is essential that no leaks develop in the reactor.

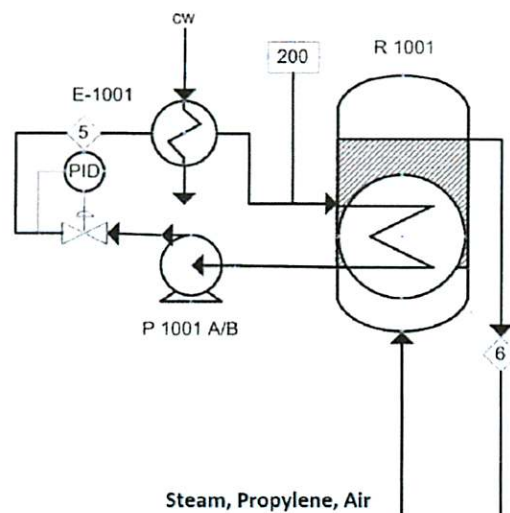


Figure 12: Basic flow diagram of the fluidized-bed catalytic reactor which converts propylene and oxygen into acrylic acid

A proposed control system can be seen in Figure 13. This system measures the temperature of the outlet stream and controls the flow of cooling water to the heat exchanger. Furthermore it is important to protect the pump (P1001 A/B) as failure of this pump would result in complete failure of the cooling system. Therefore an alarm has been attached to the flow sensor, if the flow drops below a value that would cause damage to the pump the alarm is sounded. Also the alarm can be set to sound if the flow rate of molten cooling fluid is such that insufficient heat removal is attained.

Also implemented are fail open and fail close systems shown in Figure 14 these redundancies act as a pseudo safety interlocking system. Although they do not shut down the reactor completely as

How do they
 I see (found it)

the cooling unit (heat exchanger and pump) is still operational, V3 closes the feed into the reactor thereby stopping the exothermic reaction. Meanwhile the cooling loop acts to reduce the temperature in the reactor, slowing the reaction of the remaining reactants inside. Once the reactor has been cooled to a safe temperature the cooling loop can then be overridden manually and shut off as well. This results in a complete shutdown of the reactor as is a true safety interlocking system.

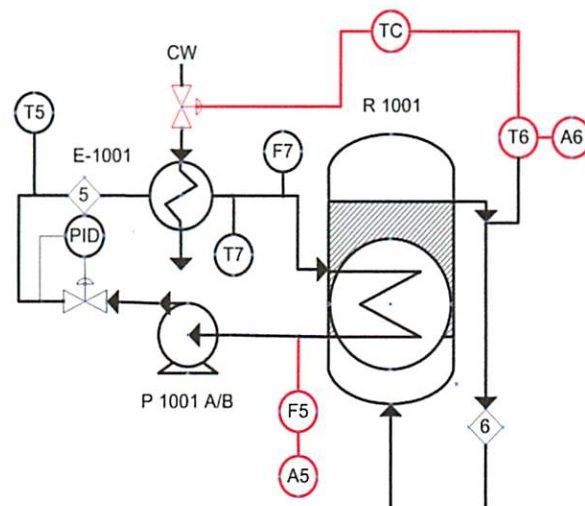


Figure 13: Basic process control system of the reactor along with appropriate alarms

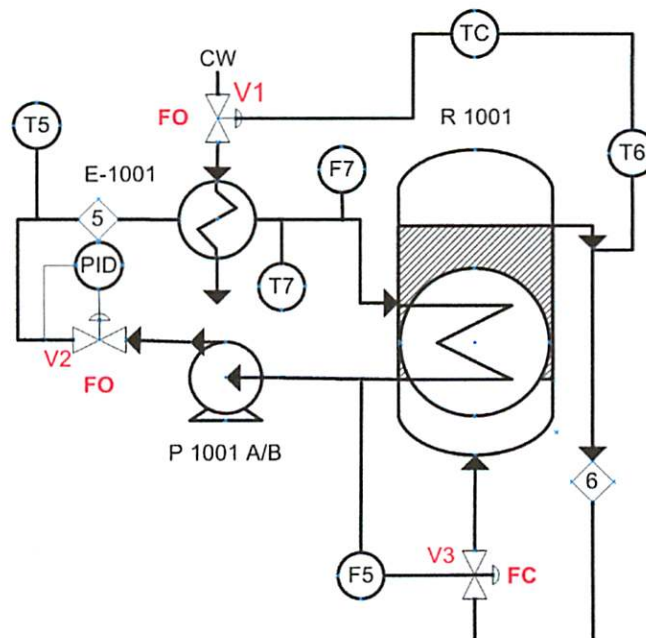


Figure 14: Proposed pseudo safety interlocking system

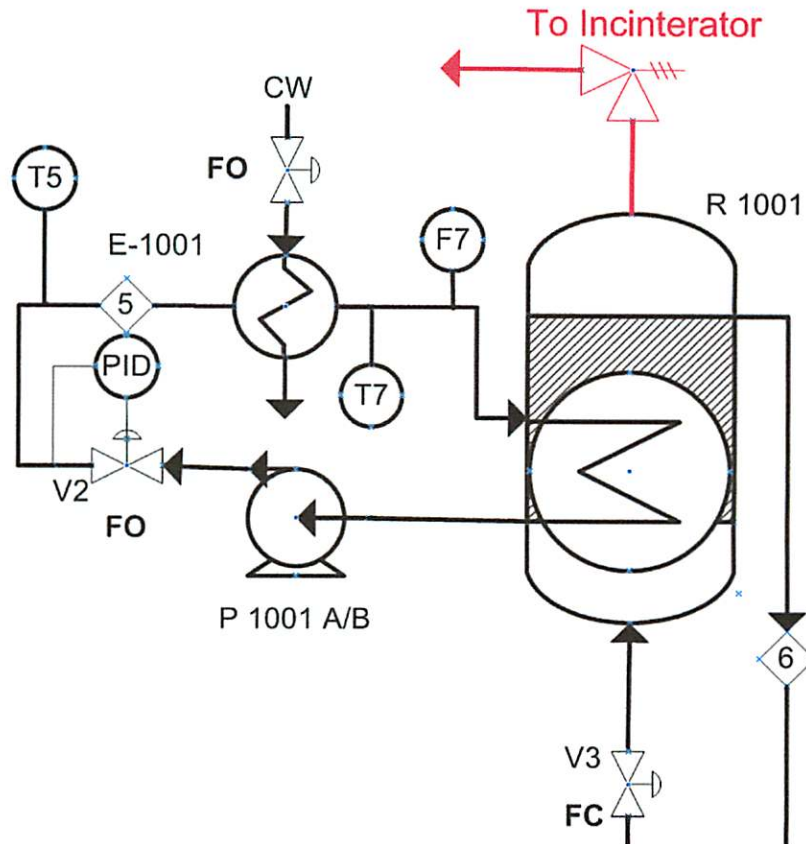


Figure 15: Relief and containment system.

describe in more detail - how it works - what does include (equipment)

As seen in Figure 15, a relief and containment system will be implemented so that the pressure inside the reactor will never exceed safety levels as the relief valve will open and divert reactor material towards the incinerator.

5.2 Emergency Evacuation & Fire Safety Protocol

It has been proposed that in case of a severe plant emergency that the plant workers will be evacuated as fast as possible through well-established safe exit routes. When designing the initial floor plan of the plant, safe fire routes will be incorporated into the design. For example, these routes will allow people to exit the plant away from high danger areas such as the reactor, liquid-liquid extraction column, and distillation columns. As all the chemical vapors are toxic in this process, full face-mask respirators will be accessible at all times to plant workers. Finally, in case of a fire, alcohol resistant foam

shall be used as some of the chemicals combusting possess an alcohol functional group as well as oxygenates.

6 Troubleshooting – Case Study

Define:

After initial plant start-up the acrylic acid purity remained very high for the first 4 months. However, after 4 months the acrylic acid purity in the outlet stream began to drift downwards.

What should be happening?

The acrylic acid in the outlet stream should be at 99.9% purity.

What is actually happening?

The acrylic acid purity in the outlet stream is at 95%.

Therefore, the deviation is?

The acrylic acid purity is 4.9% less pure than nominal.

Explore:

A series of hypothesis were developed and systematically analyzed to see if they could be the root cause of the observed problem. This process is summarized in Table 8.

Table 8: Summary of systematic troubleshooting approach to identify which formulated hypothesis is most correct, with D, N and S standing for “disprove”, “neutral to”, and “support” respectively

Working Hypotheses	Initial Evidence							
	A	B	C	D	E	F	G	H
Pump 1003 has slowly decreased in efficiency	N	D	D	N	S	S	S	N
Heat exchanger E1005 has decreased in efficiency	D	N	N	D	S	N	D	N
Heat exchanger E1007 has decreased in efficiency	D	S	S/N	D	S	N	N	N
The flow rate from pump 1002 has increased	N	S	N	N	D	N	N	N
The reactor has built up by-products on the interior	D	S	N	N	S	S	S	N
The L-L extraction column has begun to foul and decrease mixing efficiency	N	S	S	N	S	S	S	S

Initial Evidence:

- A) All temperatures appear to be normal based on past plant history
- B) The flow rate to the waste water treatment plant has increased
- C) The amount of acetic acid and acrylic acid in the waste water stream has increased
- D) The purity of acetic acid in the outlet stream is the same
- E) The flow rate of acetic acid in the outlet stream has decreased
- F) The flow rate entering the column separating acetic acid from acrylic acid has decreased
- G) The flow rate of the outlet acrylic acid stream has decreased
- H) The liquid-liquid extraction column is a perforated-plate type

Diagnostic Actions:

Check to see what type of fouling occurred on the plates. The fouling appeared to be sedimentation.

Do it:

The cause that ^{is} it most greatly supported is that the perforated plates (or sieve trays) liquid-liquid extraction have begun to foul. In perforated plate extraction towers, such as the one shown in Figure 16, a heavy liquid will flow through the downcomers from one tray to the next, while the lighter fluid travels up the perforated plate, coalesces, and jets up to the next plate. In our process, the heavy liquid is water and the light liquid is our solvent, diisopropyl ether. Clearly, if these perforated plates become fouled the efficiency of the liquid-liquid extraction column will be hindered. It explains why initially the plant was operating fine but then a slow decrease in plant performance was observed (as the fouling on the plates built-up). A potential solution would be to temporarily shut-down the plant and have the plates cleaned.

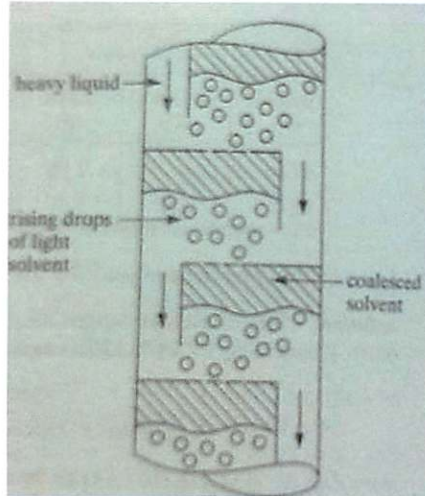


Figure 16: Cross-section of a typical perforated plate liquid-liquid extraction column. Picture courtesy of [8]

Evaluate:

Although the operating conditions of the plant will have been restored after the cleaning of the liquid-liquid extraction column, there is nothing to stop this fouling from re-occurring again. It was confirmed that the fouling sedimentation was due to the presence of propylene in the feed stream to the liquid-liquid extraction column. Once in the system propylene can easily react to form various other by-products by polymerizing, oxidizing, hydroformylating, oligomerizing, and hydrating. Thus, once in the system propylene can create by-products which will be hard to separate and will eventually build-up in the liquid-liquid extraction column as the solvent is continually recycled and not replaced.

There are two possible courses of action that may be taken to try and avoid future fouling of the liquid-liquid extraction column. The first option would be to get a larger scrubber that can remove more of the propylene and discharge it to the incinerator. However, this may have an initial high capital investment of purchasing and installing a new scrubber. The second option is to replace some of the solvent with fresh diisopropyl ether. This would allow the removal of 'dirty' solvent from the system. However, these may also be costly as a large volume of diisopropyl ether is required.

In the future, the plant operators will now know that the by-products formed from the initial reactions can still contribute significantly on plant performance. Therefore, proper and effective preventative measures should be put in place to alleviate the problems caused by the by-products.

7 HAZOP Workshop

A detailed HAZOP workshop can be found in Appendix E – HAZOP Workshop for the node shown in Figure 17.

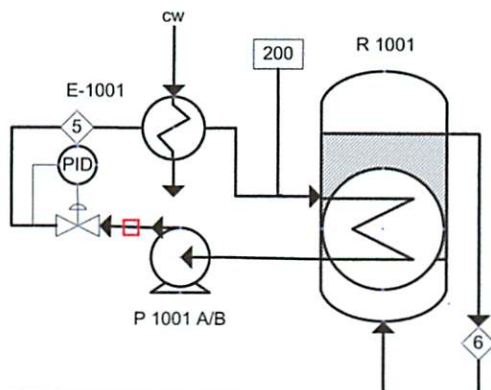


Figure 17: Location of node examined in the HAZOP analysis

8 Conclusion

From the data and analysis presented in this report it is economically feasible and very profitable to produce acrylic acid using catalytic partial oxidation, generating an estimated \$15 million in net profit, including operating expenditures without accounting for labour costs. This however requires a very large initial investment as capital costs are estimated to be approximately \$29million without land costs. The optimal operating window for this project is very narrow and stringent process control mechanisms should be put in place so as to prevent deviations in production. In order to improve the economics of the plant, alterations in the current plant design should be considered to include storage tanks and increased heat exchange integration.

Finally in the design of the plant the proposed control mechanisms are strongly recommended for implementation as safety measures. Additionally a careful planning of the plant layout should be undertaken so as to minimize evacuation time in the case of a failure as the nature of the chemicals used are very harsh and toxic.

good to include
summary of most important content found in body of report.

Figure A1: Complete PFD for the production of Acrylic Acid via catalytic partial oxidation of propylene adapted from [1]



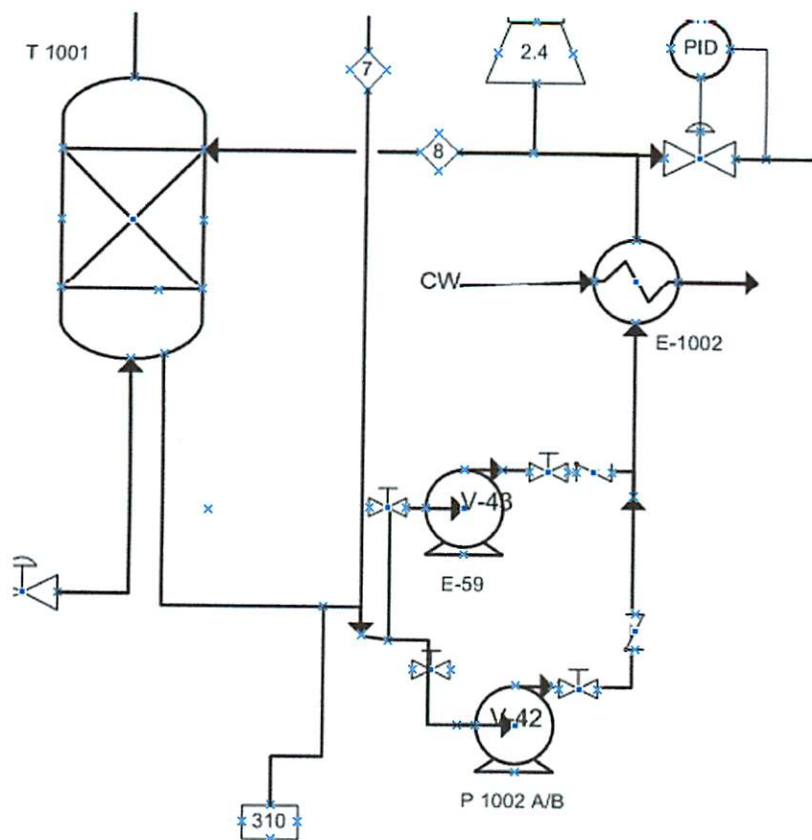


Figure A2: Parallel quench pumps implementation

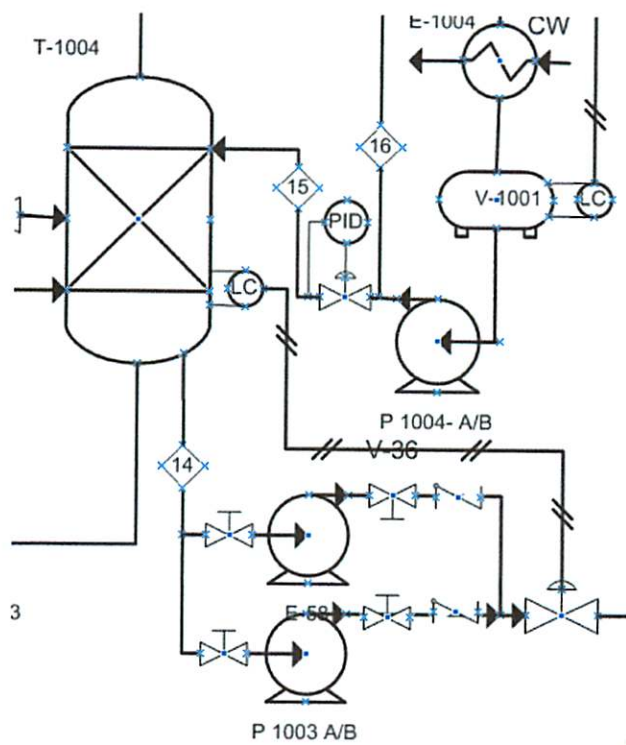


Figure A3: Parallel acid feed pumps implementation

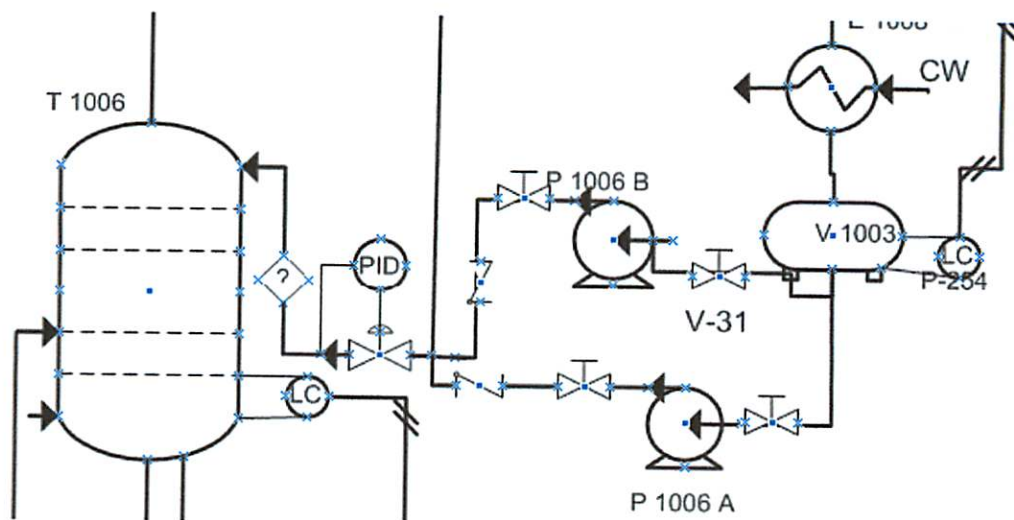


Figure A4: Parallel waste reflux pumps implementation

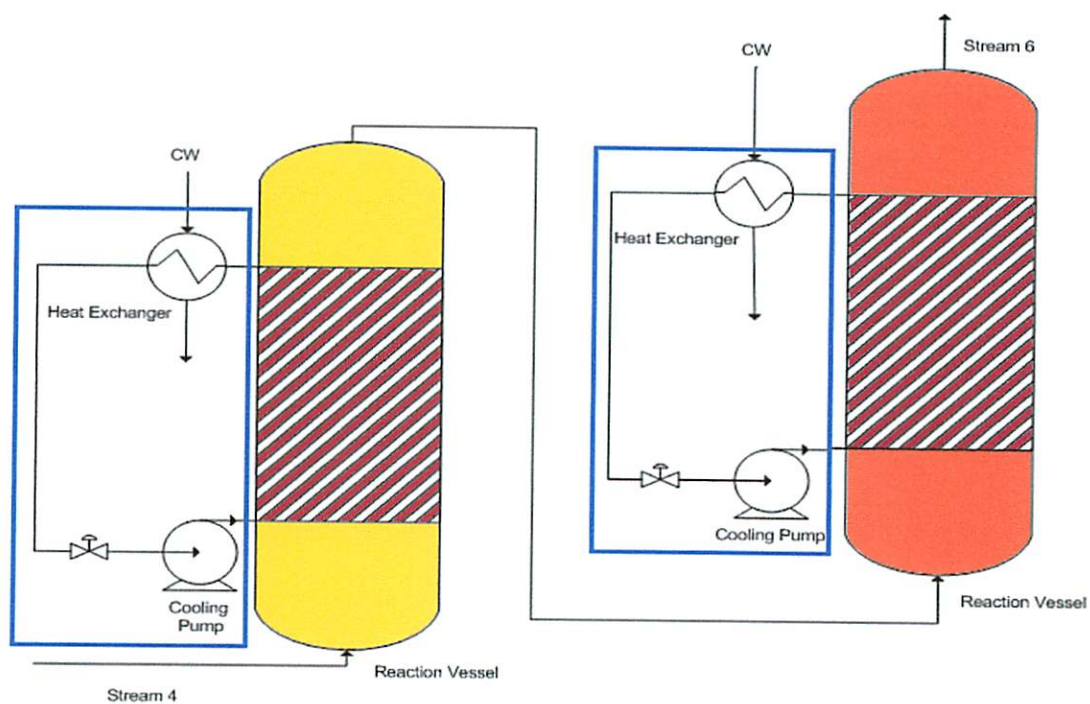


Figure A5: Illustration of the two fluidized bed reactors in series in the acrylic acid process

Appendix B – Capital Cost

Table B1: Summary table of historical cost per equipment and cost of installation

Equipment	Factor A	Factor B	Cost A (\$)	Cost B (\$)	n	Inflated cost (\$)	Fbm	Cost for Installation(\$)
Quench Tower	146.41	65.00	353053.54	170000.00	0.90	1270992.73	4.16	4016337.04
Off-Gas Absorber	72.00	100.00	53900.51	65000.00	0.57	194041.84	4.16	613172.21
Acid extractor	31.00	10.00	21253.08	8500.00	0.81	76511.09	4.16	241775.05
Solvent Tower	698.00	100.00	373579.67	65000.00	0.90	1344886.82	4.16	4249842.35
Acid Tower	93.00	100.00	62366.11	65000.00	0.57	224517.99	4.16	709476.84
Molten Salt Cooler	160.00	100.00	11169.02	8000.00	0.71	40208.48	3.14	86046.15
Quench Cooler	2550.00	100.00	79750.52	8000.00	0.71	287101.87	3.14	614397.99
Solvent HEX	891.00	100.00	37800.99	8000.00	0.71	136083.56	3.14	291218.82
Solvent Reboiler	7710.00	100.00	174943.82	8000.00	0.71	629797.74	3.14	1347767.16
Acid Reboiler	19.70	100.00	2524.42	8000.00	0.71	9087.90	3.14	19448.10
Acid Condenser	73.30	100.00	6416.73	8000.00	0.71	23100.23	3.14	49434.49
Waste Reboiler	187.00	100.00	12476.64	8000.00	0.71	44915.89	3.14	96120.01
Waste Condenser	210.00	100.00	13547.70	8000.00	0.71	48771.73	3.14	104371.51
Product Cooler	19.70	100.00	2524.42	8000.00	0.71	9087.90	3.14	19448.10
Quench Pumps	32.30	10.00	1017.31	750.00	0.26	3662.32	2.50	5493.48
Acid feed pumps	106.20	100.00	2052.41	2000.00	0.43	7388.67	2.50	11083.00
Acid reflux pumps	0.90	10.00	401.02	750.00	0.26	1443.67	2.50	2165.50
Waste reflux pumps	51.30	100.00	1501.00	2000.00	0.43	5403.60	2.50	8105.40
Product pumps	1.20	10.00	432.16	750.00	0.26	1555.79	2.50	2333.68
CSTR Reactor (equation)								7536577.47
Total								20024614.36

Table B2: Key capacity factor list required to calculate historical data

Equipment	Key Capacity factor	Donald Woods
Distillation Column / Absorption Column	Height – Diameter (m^2)	Pg. 212
Liquid- Liquid extractor	Length – Diameter	Pg. 218
Heat Exchanger	Surface Area (m^2)	Pg. 223
Pump	Power (hp)	Pg. 161
Compressor	Power drive (hp)	Pg. 157
Condenser	Water flow rate ($\frac{m^3}{min}$)	Pg.115
CSTR	Surface area (m^2)	Assumption
Boiler	Saturated steam capacity ($10^5 \frac{kg}{h}$)	Pg. 110
Cooling Tower	Water flow rate ($\frac{m^3}{min}$)	Pg. 115

Table B3: Summary table for cost for pressure and materials per equipment

Equipment	Fp	Fm	Materials	Cost for Pressure and Materials (\$)
Quench Tower	1.1	4	Stainless steel (316)	4321375.3
Off-Gas Absorber	1	4	Stainless steel (316)	582125.51
Acid extractor	1.1	4	Stainless steel (316)	260137.71
Solvent Tower	1	4	Stainless steel (316)	4034660.46
Acid Tower	1.1	1	Carbon Steel	22451.8
Molten Salt Cooler	1.1	1	Carbon Steel	4020.85
Quench Cooler	1	1	Carbon Steel	0
Solvent HEX	1	1	Carbon Steel	0
Solvent Reboiler	1	1	Carbon Steel	0
Acid Reboiler	1	1	Carbon steel	0
Acid Condenser	1.3	1	Carbon steel	6930.07
Waste Reboiler	1.3	1	Carbon steel	13474.77
Waste Condenser	1.3	1	Carbon steel	14631.52
Product Cooler	1.3	1	Carbon steel	2726.37
Quench Pumps	1.3	1.9	Carbon steel	5383.61
Acid feed pumps	1.36	1.9	Carbon steel	11703.65
Acid reflux pumps	1.36	1.9	Carbon steel	2286.77
Waste reflux pumps	1.36	1.9	Carbon steel	8559.3
Product pumps	1.36	1.9	Carbon steel	2464.37
Total				9292932.05

Table B4: Summary table for cost for bare module piping per equipment

Equipment	Piping factor	ϕ	Cost for bare module piping (\$)
Quench Tower	-	0.7	0
Off-Gas Absorber	-	0.7	0
Acid extractor	-	0.7	0
Solvent Tower	-	0.7	0
Acid Tower	0.46	0.7	0
Molten Salt Cooler	0.46	0.7	1294.71
Quench Cooler	0.46	0.7	0
Solvent HEX	0.46	0.7	0
Solvent Reboiler	0.46	0.7	0
Acid Reboiler	0.46	0.7	0
Acid Condenser	0.46	0.7	2231.48
Waste Reboiler	0.46	0.7	4338.88
Waste Condenser	0.46	0.7	4711.35
Product Cooler	0.3	0.7	877.89
Quench Pumps	0.3	0.7	1130.56
Acid feed pumps	0.3	0.7	2457.77
Acid reflux pumps	0.3	0.7	480.22
Waste reflux pumps	0.3	0.7	1797.45
Product pumps	0.21	0.7	517.52
Total			19837.83

Table B5: Summary table for each type of calculated cost and final total bare module cost per equipment

Equipment	Cost for Installation(\$)	Cost for Pressure and Materials (\$)	Cost for bare module piping (\$)	Total BM cost (\$)
Quench Tower	4016337.04	4321375.295	0	8337712.33
Off-Gas Absorber	613172.21	582125.5149	0	1195297.72
Acid extractor	241775.05	260137.7116	0	501912.76
Solvent Tower	4249842.35	4034660.463	0	8284502.82
Acid Tower	709476.84	22451.79861	0	731928.63
Molten Salt Cooler	86046.15	4020.848182	1294.713115	91361.71
Quench Cooler	614397.99	0	0	614397.99
Solvent HEX	291218.82	0	0	291218.82
Solvent Reboiler	1347767.16	0	0	1347767.16
Acid Reboiler	19448.10	0	0	19448.10
Acid Condenser	49434.49	6930.069092	2231.482247	58596.04
Waste Reboiler	96120.01	13474.77	4338.88	113933.65
Waste Condenser	104371.51	14631.52	4711.35	123714.38
Waste Reboiler	19448.10	2726.37	877.89	23052.37
Quench Pumps	5493.48	5383.61	1130.56	12007.65
Acid feed pumps	11083.00	11703.65	2457.77	25244.41
Acid reflux pumps	2165.50	2286.77	480.22	4932.49
Waste reflux pumps	8105.40	8559.30	1797.45	18462.15
Product pumps	2333.68	2464.37	517.52	5315.57
CSTR Reactor	7536577.47			7536577.47
Total	20024614.36	9292932.05	19837.83	29337384.24

Table B6: Table summary of the lower and upper limit ranges of the total bare module cost

Equipment	Total cost(\$)	BM	Uncertainty	Lower limit	Upper limit
Quench Tower	8337712.33		± 30%	5836398.63	10839026.03
Off-Gas Absorber	1195297.72		± 30%	836708.41	1553887.04
Acid extractor	501912.76		± 30%	351338.93	652486.59
Solvent Tower	8284502.82		± 30%	5799151.97	10769853.66
Acid Tower	731928.63		± 30%	512350.04	951507.23
Molten Salt Cooler	91361.71		± 40%	63953.2	118770.23
Quench Cooler	614397.99		± 40%	430078.6	798717.39
Solvent HEX	291218.82		± 40%	203853.17	378584.46
Solvent Reboiler	1347767.16		± 40%	943437.01	1752097.31
Acid Reboiler	19448.1		± 40%	13613.67	25282.54
Acid Condenser	58596.04		± 40%	41017.23	76174.86
Waste Reboiler	113933.65		± 40%	79753.56	148113.75
Waste Condenser	123714.38		± 40%	86600.06	160828.69
Product Cooler	23052.37		± 40%	16136.66	29968.08
Quench Pumps	12007.65		± 40%	8405.36	15609.95
Acid feed pumps	25244.41		± 40%	17671.09	32817.74
Acid reflux pumps	4932.49		± 40%	3452.74	6412.23
Waste reflux pumps	18462.15		± 40%	12923.5	24000.79
Product pumps	5315.57		± 40%	3720.9	6910.25
BM cost of CSTR reactor	7536577.47			7536577.47	7536577.47
Total	29337384.24			22797142.2	35877626.29

no error associated with CSTR cost?

Appendix C - Operating cost and Profitability

Table C1: Utility cost for the heat exchanger equipment

HEX Equipment	Duty (Mj/h)	Cooling water (tonne/h)	Utilities	
			Low pressure steam (tonne/h)	Refrigerated water (tonne/h)
Molten Salt Cooler	83400	1995	-	-
Quench Cooler	70300	1682	-	-
Solvent HEX	101000	-	-	5182
Solvent Reboiler	108300	-	48.5	-
Acid Reboiler	2230	1.07	-	-
Acid Condenser	2280	54.5	-	-
Waste Reboiler	21200	10.19	-	-
Waste Condenser	15800	378	-	-
Product Cooler	8000	16.7	-	--
Total	412510	4137.46	48.5	5182

Table C2: Utility costs for the pumping equipment

Pumps Equipment	Power Shaft (kW)
Quench Pumps	32.3
Acid feed pumps	106.2
Acid reflux pumps	51.3
Waste reflux pumps	1.2
Product pumps	9
Total	200

Table C3: Total operating cost for the plant

Utility	Price (\$)	Quantity	Total Cost	Total hours of operation in a year
Low pressure steam ($\frac{\text{tonne}}{\text{h}}$)	\$5.00	48.5	\$1,940,000.00	8000
Duty ($\frac{\text{MJ}}{\text{h}}$)	\$0.001 ⁱ	412510	\$3,300,080.00	
Electricity (kW)	\$0.05 ⁱⁱ	200	\$80,000.00	
Cooling water ($\frac{\text{tonne}}{\text{h}}$)	\$0.06 ⁱ	4137.46	\$1,985,980.80	
Refrigerated water ($\frac{\text{tonne}}{\text{h}}$)	\$0.60 ⁱ	5182	\$24,873,600.00	
Inlet steam ($\frac{\text{tonne}}{\text{h}}$)	\$5.00 ⁱ	17.88	\$715,200.00	
Inlet propylene ($\frac{\text{tonne}}{\text{h}}$)	\$1,065 ⁱⁱⁱ	5.38	\$45,837,600	
Diisopropyl ether ($\frac{\text{tonne}}{\text{h}}$)	\$12,000 ⁱⁱⁱ	118.2	1418400	
Deionized water ($\frac{\text{tonne}}{\text{h}}$)	\$1,000 ⁱⁱ	2.54	\$20,320,000	
Total			\$100,470,860.80	

i - price taken from: <http://www.che.cemr.wvu.edu/publications/projects/acrylic/acrylic-d.PDF>

ii - price taken from: http://www.hydro.mb.ca/regulatory_affairs/energy_rates/electricity/utility_rate_comp.shtml

iii - price taken from: <http://www.icispricing.com>

Table C4: Revenue from operation

Chemical	Price	Quantity ($\frac{\text{tonne}}{\text{h}}$)	Total Revenue	Total hours of operation in a year
Acrylic Acid	\$2,271 ⁱⁱⁱ	6.26	\$113,731,680.00	8000
Acetic Acid	\$500 ⁱⁱⁱ	0.35	\$1,400,000.00	
Total			\$115,131,680.00	

iii - price taken from: <http://www.icispricing.com>

Table C5: 5-year NPV for the plant, sample calculations shown in, Appendix F - Sample Calculations

NPV	Year 0	Year 1	Year 2	Year 3	Year 4	Year 5
Revenue	0	115131680	115131680	115131680	115131680	115131680
Expense s	0	100470860.8	100470860.8	100470860.8	100470860.8	100470860.8
Capital	29337384.24	0	0	0	0	0
Net Cash flow	-29337384.24	14660819.2	14660819.2	14660819.2	14660819.2	14660819.2
NPV	-29337384.24	14303238.24	13954378.77	13614028.07	13281978.61	12958027.91
Total NPV	38774267.37					

*Mandated discount rate in Ontario: 2.5% from: www.economica.ca/ew01_3p3.htm

Appendix D – Operability & Reliability Data

Table D 1: Reaction Rates of Bi-Products and Temperature Output at a Constant Acrylic Acid Production Rate
($2860 \frac{\text{kmol}}{\text{m}^3 \text{ reactor h}}$)

p , propylene (kpa)	p , oxygen (kpa)	$R_2 \left(\frac{\text{kmol}}{\text{m}^3 \text{ reactor h}} \right)$	$R_3 \left(\frac{\text{kmol}}{\text{m}^3 \text{ reactor h}} \right)$	Temp ($^{\circ}\text{C}$)
10	179	343	1517	384
25	164	260	873	340
40	149	230	680	321
59	130	212	577	310
75	114	204	535	305
90	99	201	521	303
115	74	204	537	305

Table D 2: Failure rates and reliability data for the flow instruments

FLOW INSTRUMENTS	Failure rate	MTTF (years)	R(year)	Repair Time	Reference
Temperature sensor	$6.14 \times 10^{-3}/\text{year}$	1.43×10^6	0.999999	3 hrs	IAEA
Pressure sensor	$7.63 \times 10^{-3}/\text{year}$	1.15×10^6	0.999999	2 hrs	IAEA
Flow sensor	$3.77 \times 10^{-2}/\text{year}$	2.33×10^6	0.999999	2 hrs	IAEA
Level sensor	$7.19 \times 10^{-2}/\text{year}$	1.22×10^6	0.999999	3 hrs	IAEA
Generic	$8.77 \times 10^{-3}/\text{year}$	1.00×10^6	0.999999	-	IAEA
Total			0.9999		

Table D 3: Failure rates and reliability data for the heat exchangers equipment

HEAT EXCHANGERS	Failure rate	MTTF(years)	R(year)	Reference
Tube leakage	$8.77 \times 10^{-4}/\text{year}$	1140×10^3	0.999123	HEI - OREDA
Tube rupture	$8.77 \times 10^{-6}/\text{year}$	1.14×10^5	0.999991	HEI
Shell leakage	$8.77 \times 10^{-5}/\text{year}$	1.14×10^4	0.999912	HEI
Shell rupture	$8.77 \times 10^{-7}/\text{year}$	1.14×10^6	0.999999	HEI
Erratic operation	$1.75 \times 10^{-2}/\text{year}$	57.1	0.982652	OREDA
Total			0.9823	

Table D 4: Failure rates and reliability data for the pumps equipment, sample calculations shown in, Appendix F - Sample Calculations

PUMPS	Failure rate	MTTF (years)	R(year)	Repair Time (hrs)	Reference
Failure to run	$3.5 \times 10^{-2}/\text{year}$	28.6	0.9656	15 hrs	IAEA
External leakage	$3.15 \times 10^{-1}/\text{year}$	3.17	0.7298	5 hrs	IAEA
Pump casing leakage	$2.6 \times 10^{-4}/\text{year}$	3.85×10^3	0.9999	41.6 hrs	OREDA
Failure to start	$2.5 \times 10^{-2}/\text{demand}$	-	-	12 hrs	OREDA
Support system	$1 \times 10^{-4}/\text{year}$	1.00×10^4	0.9999	-	OREDA
		Total	0.705		
		Total (parallel)	0.913		

Appendix E – HAZOP Workshop

Table E 1: HAZOP analysis for the point following the pump in the cooling unit of the reactor

Parameter:	Guide Word	Deviation	Cause	Consequence	Action
Flow Rate	Less	less than nominal cooling stream outlet flow rate	1. Fouling/blockage in heat exchanger E-1001	higher reactor temperature	clean/replace pipes
				Promote undesired secondary reactions	increase pump flow rate
				increased pressure in reactor vessel	open valve more
				damage cooling pipes inside reactor due to higher temperature and pressure build-up	increase steam flow rate
				damage reactor vessel itself	
			2. Non-operational valve (restricted flow)	higher reactor temperature	replace valve
				Promote undesired secondary reactions	increase pump flow rate
				increased pressure in reactor vessel	increase the steam flow rate
				damage cooling pipes inside reactor	
				damage reactor vessel itself	
			3. Non-operational Pump	higher reactor temperature	back-up pump
				Promote undesired secondary reactions	increase the steam flow rate
				increased pressure in reactor vessel	
				damage cooling pipes inside reactor	
				damage reactor vessel itself	
				damage to pump itself (cavitation)	
	More	more than nominal cooling stream outlet flow rate	1. Non-operational valve (fully open)	reduced rate of reaction in reactor vessel due to lower temperature	decrease pump flow rate
				reduced reactor efficiency	reduce cold water flow into heat exchanger

					higher percentage of residual reactants that will require downstream separation	decrease steam flow rate
			2. Pump operating at too high of rpm		reduced rate of reaction in reactor vessel due to lower temperature	reduce cold water flow into heat exchanger
					reduced reactor efficiency	decrease steam flow rate
					higher percentage of residual reactants that will require downstream separation	
	No	no cooling stream outlet flow	1. leak in pipe		higher reactor temperature	replace pipes
					Promote undesired secondary reactions	decrease steam flow rate
					increased pressure in reactor vessel	add a by-pass for a temporary solution
					damage cooling pipes inside reactor sue to higher temperature and pressure build-up	
					damage reactor vessel itself	
			2. Complete Valve or pipe obstruction		higher reactor temperature	clean/replace pipes
					Promote undesired secondary reactions	add a by-pass for a temporary solution
					increased pressure in reactor vessel	
					damage cooling pipes inside reactor sue to higher temperature and pressure build-up	
					damage reactor vessel itself	
			3. Pump failure		higher reactor temperature	back-up pump
					Promote undesired secondary reactions	
					increased pressure in reactor vessel	
					damage cooling pipes inside reactor sue to higher temperature and pressure build-up	
					damage reactor vessel itself	
Parameter:	Guide Word	Deviation	Cause	Consequence	Action	

Flow Rate	Less	less than nominal cooling stream outlet flow rate	1. Fouling/blockage in heat exchanger E-1001	higher reactor temperature	clean/replace pipes
				Promote undesired secondary reactions	increase pump flow rate
				increased pressure in reactor vessel	open valve more
				damage cooling pipes inside reactor sue to higher temperature and pressure build-up	increase steam flow rate
				damage reactor vessel itself	
			2. Non-operational valve (restricted flow)	higher reactor temperature	replace valve
				Promote undesired secondary reactions	increase pump flow rate
				increased pressure in reactor vessel	increase the steam flow rate
				damage cooling pipes inside reactor	
				damage reactor vessel itself	
			3. Non-operational Pump	higher reactor temperature	back-up pump
				Promote undesired secondary reactions	increase the steam flow rate
				increased pressure in reactor vessel	
				damage cooling pipes inside reactor	
				damage reactor vessel itself	
				damage to pump itself (cavitation)	
	More	more than nominal cooling stream outlet flow rate	1. Non-operational valve (fully open)	reduced rate of reaction in reactor vessel due to lower temperature	decrease pump flow rate
				reduced reactor efficiency	reduce cold water flow into heat exchanger
				higher percentage of residual reactants that will require downstream separation	decrease steam flow rate
			2. Pump operating at too high of rpm	reduced rate of reaction in reactor vessel due to lower temperature	reduce cold water flow into heat exchanger

					reduced reactor efficiency	decrease steam flow rate
					higher percentage of residual reactants that will require downstream separation	
No	no cooling stream outlet flow	1. leak in pipe			higher reactor temperature	replace pipes
					Promote undesired secondary reactions	decrease steam flow rate
					increased pressure in reactor vessel	add a by-pass for a temporary solution
					damage cooling pipes inside reactor sue to higher temperature and pressure build-up	
					damage reactor vessel itself	
		2. Complete Valve or pipe obstruction			higher reactor temperature	clean/replace pipes
					Promote undesired secondary reactions	add a temporary by-pass
					increased pressure in reactor vessel	
					damage cooling pipes inside reactor sue to higher temperature and pressure build-up	
					damage reactor vessel itself	
		3. Pump failure			higher reactor temperature	back-up pump
					Promote undesired secondary reactions	
					increased pressure in reactor vessel	
					damage cooling pipes inside reactor sue to higher temperature and pressure build-up	
					damage reactor vessel itself	

Appendix F - Sample Calculations

1 - 5- Year discounted cash flow rate of return calculation (DCFRR)

$$NPV = C_0 + \frac{C_1}{1+DCFRR} + \frac{C_2}{(1+DCFRR)^2} + \frac{C_3}{(1+DCFRR)^3} + \frac{C_4}{(1+DCFRR)^4} + \frac{C_5}{(1+DCFRR)^5} = 0$$

DCFRR = 41% Using solver on Excel

2 - Sample calculation for reliability for pumps

$$R_{\text{external leakage}} = \exp(-\lambda t) = \exp(-3.15e^{-1} 1) = 0.73$$

$$\begin{aligned} R_{\text{total}} &= (R_{\text{failure to run}}) \times (R_{\text{external leakage}}) \times (R_{\text{pump casing leakage}}) \times (R_{\text{support system}}) \\ &= 0.9656 \times 0.7298 \times 0.9999 \times 0.999 = 0.705 < 0.90 \end{aligned}$$

Requires additional safety measures – Parallel pump₂

$$R_{2\text{-parallel}} = 1 - (1 - R_1)(1 - R_2) = 1 - (1 - 0.705)^2 = 0.913$$

3 - Implementation of Falling Film Evaporator

Energy Requirements

Streams 13 and 15 enter the solvent tower, and streams 15+16 and stream 14 leave the column (stream 15 is recycled). Stream 15 leaves the column as a vapour, but is condensed and returned to the column as a liquid. The solvent tower will be replaced with an evaporator, and all streams will remain unchanged, leaving only the separation energy to change.

Energy Balance:

$$M_{13} \times H_{13} + M_{15} \times H_{15}^l + S \times H_S = M_{15} \times H_{15}^v + M_{16} \times H_{16} + M_{14} \times H_{14} + S \times h_s$$

Assumptions:

- 1) The heat capacity of stream 13 can be approximated as the heat capacity of pure liquid diisopropyl ether (81.67%) at 298.15 K.
- 2) The heat capacity of stream 14 can be approximated as the heat capacity of pure liquid acrylic acid (93.15%)
- 3) The heat capacity of stream 16 can be approximated as the heat capacity of pure vapour diisopropyl ether (86.75%) at 298.15 K.
- 4) The heat capacity of stream 15 can be approximated as the heat capacity of pure liquid diisopropyl ether going in, and pure vapour diisopropyl ether coming out (86.75%)
- 5) Low Pressure Steam is Supplied to provide the heat at 446 kPa (148 °C)

Mass Balance:

$$\begin{aligned} M_{14} &= M_{13} + M_{15} - (M_{15} + M_{16}) \\ &= 1591200 \frac{\text{mol}}{h} + 1705700 \frac{\text{mol}}{h} - \left(1705700 \frac{\text{mol}}{h} + 1498000 \frac{\text{mol}}{h} \right) = 93190 \frac{\text{mol}}{h} \end{aligned}$$

$$Cp_{13} = 0.2161 \frac{kJ}{mol \cdot K} \quad [9]$$

$$M_{13} = 1591200 \text{ mol/h}$$

$$Cp_{16} = 0.18255 \frac{kJ}{mol \cdot K} \quad [9]$$

$$M_{16} = 1498000 \text{ mol/h}$$

$$Cp_{15}^I = 0.2161 \frac{kJ}{mol \cdot K}$$

$$M_{15} = 1705700 \text{ mol/h}$$

$$Cp_{15}^V = 0.18255 \frac{kJ}{mol \cdot K}$$

$$M_{14} = 93190 \text{ mol/h}$$

$$Cp_{14} = 1.6828 + 6.9212e^{-2} \times T - 0.4475e^{-4} \times T^2 + 1.10186e^{-8} \times T^3 \frac{cal}{mol \cdot K} \quad [10]$$

$$H_{13} = \int_0^{40} Cp dT = \int_0^{40} 0.2161 dT = 0.2161 \times (40 - 0) = 8.644 \text{ kJ/mol}$$

$$H_{16} = \int_0^{90} Cp dT = \int_0^{90} 0.18255 dT = 0.18255 \times (90 - 0) = 16.4295 \text{ kJ/mol}$$

$$H_{15}^I = \int_0^{13} Cp dT = \int_0^{13} 0.2161 dT = 0.2161 \times (13 - 0) = 2.8093 \text{ kJ/mol}$$

$$H_{15}^V = \int_0^{90} Cp dT = \int_0^{90} 0.18255 dT = 0.18255 \times (90 - 0) = 16.4295 \text{ kJ/mol}$$

$$\begin{aligned} H_{14} &= \int_{273}^{363} Cp dT = \int_{273}^{363} (1.6828 + 6.9212e^{-2} \times T - 0.4475e^{-4} \times T^2 + 1.10186e^{-8} \times T^3) dT \\ &= \left(1.6828T + 6.9212e^{-2} \times \frac{T^2}{2} - 0.4475e^{-4} \times \frac{T^3}{3} + 1.10186e^{-8} \times \frac{T^4}{4} \right) \Big|_{273}^{363} \frac{cal}{mol} \\ &= \left(1.6828 \times 363 + 6.9212e^{-2} \times \frac{363^2}{2} - 0.4475e^{-4} \times \frac{363^3}{3} + 1.10186e^{-8} \times \frac{363^4}{4} \right) \\ &\quad - \left(1.6828 \times 273 + 6.9212e^{-2} \times \frac{273^2}{2} - 0.4475e^{-4} \times \frac{273^3}{3} + 1.10186e^{-8} \times \frac{273^4}{4} \right) \\ &= 1754.302 \frac{cal}{mol} = 7.343157 \frac{kJ}{mol} \end{aligned}$$

Energy Balance:

$$\begin{aligned} M_{13} \times H_{13} + M_{15} \times H_{15}^I + S \times H_S &= M_{15} \times H_{15}^V + M_{16} \times H_{16} + M_{14} \times H_{14} + S \times h_s \\ 1591200 \frac{mol}{h} \times \frac{8.655 kJ}{mol} + 1705700 \frac{mol}{h} \times 2.8093 \frac{kJ}{mol} + S \times \left(\frac{2743 kJ}{kg} \times \frac{1 kg}{1000 g} \times \frac{18 g}{mol} \right) \\ &= 1705700 \frac{mol}{h} \times 16.4295 \frac{kJ}{mol} + 1498000 \frac{mol}{h} \times 16.4295 \frac{kJ}{mol} + 93190 \frac{mol}{h} \\ &\quad \times 7.343157 \frac{kJ}{mol} + S \times (623.5 \text{ kJ/kg} \times \frac{1 kg}{1000 g} \times \frac{18 g}{mol}) \\ 13771836 \frac{kJ}{h} + 4791823.01 \frac{kJ}{h} + S \times \left(49.374 \frac{kJ}{mol} - 11.223 \frac{kJ}{mol} \right) \\ &= 28023798.15 \frac{kJ}{h} + 24611391 \frac{kJ}{h} + 683868.21 \frac{kJ}{h} \end{aligned}$$

$$38.151 \times S = 34755398.35 \frac{kJ}{h}$$

$$S = 910995.7367 \frac{mol}{h} \times \frac{18 g}{mol} \times \frac{1 kg}{1000 g} = 16397.923 \frac{kg}{h} = 16.398 \frac{tonne}{h}$$

$$q = S \times (H_S - h_s) = 16397.923 \frac{kg}{h} \times \left(2743 \frac{kJ}{kg} - 623.5 \frac{kJ}{kg} \right) = 34755398.35 \frac{kJ}{h} = 34755.398 \frac{MJ}{h}$$

Previous Heat Transfer Coefficient U Calculation:

Given [1]:

Duty = 101,000 MJ/h

Area = 891 m²

$$U = \frac{q}{A \times \Delta T} = 101,000 \frac{\text{MJ}}{\text{h}} \times 1000000 \frac{\text{J}}{\text{MJ}} \times \frac{1\text{h}}{3600\text{s}} \div (891 \text{ m}^2 \times (421\text{K} - 363\text{K})) = 542.89 \frac{\text{W}}{\text{m}^2 \cdot \text{K}}$$

Assume heat transfer coefficient is unchanged.

New Heat Transfer Area:

$$A = \frac{q}{U \times \Delta T} = 34755398.35 \frac{\text{kJ}}{\text{h}} \times 1000 \frac{\text{J}}{\text{kJ}} \times 1 \frac{\text{h}}{3600\text{s}} \div (542.89 \frac{\text{W}}{\text{m}^2 \cdot \text{K}} \times (421\text{K} - 363\text{K})) \\ = 306.6 \text{ m}^2$$

Operating Costs

Solvent Tower:

$$\text{Total Operating Costs} = P_{E-1003} + P_{E-1004} + P_{P-1003} + P_{P-1004}$$

Data [1,3]:

E-1003: 48500 kg/h low pressure steam

E-1004: 5182000 kg/h refrigerated water = 108,300 MJ/h = 108.3 GJ/h

P-1003: 0.9 kW

P-1004: 51.3 kW

Low Pressure Steam: \$5.00/1000kg

Refrigerated water: \$1.60/GJ

Electricity: \$0.05/kW h

Operating Hours: 8000h/year

Total Operating Cost

$$= \left(48500 \frac{\text{kg}}{\text{h}} \times \frac{\$5.00}{1000\text{kg}} + 108.3 \frac{\text{GJ}}{\text{h}} \times \frac{\$1.60}{\text{GJ}} + 0.9 \text{ kW} \times \frac{\$0.05}{\text{kW h}} + 51.3 \text{ kW} \times \frac{\$0.05}{\text{kW h}} \right) \times 8000 \frac{\text{h}}{\text{year}}$$

$$= \$3,347,120/\text{year}$$

Evaporator

Data:

Low pressure steam required by evaporator: 16398 kg/h

Since the two pumps and condenser will still be required,

$$\text{Total Operating Costs} = P_{\text{lps, evaporator}} + P_{E-1004} + P_{P-1003} + P_{P-1004}$$

$$= \left(16398 \frac{\text{kg}}{\text{h}} \times \frac{\$5.00}{1000\text{kg}} + 108.3 \frac{\text{GJ}}{\text{h}} \times \frac{\$1.60}{\text{GJ}} + 0.9 \text{ kW} \times \frac{\$0.05}{\text{kW h}} + 51.3 \text{ kW} \times \frac{\$0.05}{\text{kW h}} \right) \times 8000 \frac{\text{h}}{\text{year}}$$

$$= \$2,063,040/\text{year}$$

$$\text{Savings} = \frac{\$3,347,120}{\text{year}} - \frac{\$2,063,040}{\text{year}} = \$1,284,080/\text{year}$$

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