

HFE-143a Green Refrigerant Manufacture:

By

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Approved by:

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Abstract:

Delta Group was tasked with finding a large-scale production pathway for methyl trifluoromethyl ether (HFE-143a), due to increasing geopolitical concerns regarding hydrofluorocarbons and their effect on global warming. HFE-143a is a proposed replacement for R-134a, one of the most commonly used refrigerants currently, but has been poorly studied, especially in regards to the industrial scale. In this process, Delta Group elected to use a synthesis pathway consisting of two reactions in two separate reactors, using SF_4 , COF_2 , and CH_3OH to produce our compound. To purify the compounds used in this process, the group opted to use a distillation chain consisting of five towers to separate each component. The non-salable compounds and remaining reactants were recycled in the system, whereas the ether, HF, and SO_2 were sold. As many of these compounds are widely unstudied, accurate pricing information was unobtainable; therefore the team analyzed at what reagent purchasing price the process would remain profitable; in this case, the NPV would approach \$20 million at 20% interest after 30 years. Many of the chemicals used in this process have significant health and environmental safety hazards as well, so the team suggests further work before determining the advisability of this design.

Roles of Authors:

The works of Ryan Cartee and Elizabeth Lynn focused primarily on the compilation of the health and safety sections of the report, both in regards to human health and environmental health. Their work consisted of obtaining and collating information on widely unstudied chemicals into a presentable form, as well as filling out Public Health and Safety forms for “worst-case” scenarios. These worst case scenarios were central to Delta Group’s determination as to the weak points of our system, as well as what could be improved and what necessary hazards were.

The work of Kyle Hollingshead revolved primarily around the modeling of the reaction pathway. His work required gathering information on the chemical traits of the species used in our process, as many of them were unsuitably studied. Much of this information was modeled using group additivity methods, which were then entered into ASPEN Plus, a chemical process modeling software. Hollingshead’s work was crucial to the entire project, as his work determined temperatures, pressures, and quantities of each chemical in the main synthesis process.

The work of Matthew West was primarily on the economics of the process. Many of the optimizations (both presented and otherwise) came from West’s calculations. The most notable optimization is the switch from liquid nitrogen coolant to a propene refrigeration loop, saving approximately \$85 million per year in utilities costs. His work revolved mainly around the economic sustainability of the process.

The above roles are not meant to be exclusive . All of the authors worked together on many of the topics; it was not uncommon for one author to ask another for help regarding a specific task, especially if it was a new addition. For example, Cartee and Lynn both occasionally helped West find costing sources, and West did much of the work regarding the refrigeration loop. However, specializations naturally arose, and are outlined previously.



DELTA GROUP

Delta Group

HFE-143 Green Refrigerant Manufacture

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Presented by:
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Section 1: Introduction

The signatories of the Kyoto Protocol include most of the industrialized countries in the world, signaling a global legislative commitment to reduce emissions of greenhouse gases that contribute most to global warming. Major sources of chemical emissions that contribute greatly to global warming include compounds such as CFCs, HCFCs, and HFCs used as refrigerants in automobiles, residential and commercial refrigeration processes, unitary air conditioning, HVAC chillers, foam insulation, solvents for cleaning applications, aerosols, and fire protection (“Global”). Of these classes of compounds, CFCs and HCFCs have the additional negative characteristic of being classified as ozone depleting substances (ODPs) (Wachowski). As of 2000, the annual world uses of CFC-12, HCFC-22, and HFC-134a were 75Gg, 250Gg, and 100Gg, respectively (McCulloch). When disposed of, these compounds readily vaporize at ambient conditions and have large global warming potentials (GWPs) (Kumar). CFCs and HCFCs are already in various stages of being phased out of production under the Montreal Protocol’s Chlorofluorocarbons Phase-out Management Plan and will be completely banned from production by 2030. Currently, the Montreal Protocol’s latest revision (1999) has been signed by 153 countries (United Nations).

According to a May 2005 newsletter from the Mobile Air Conditioning Society (MACS), the production of R134a (HFC-134a) is limited to a handful of plants and supply has remained constant for more than a decade (“Assessing”). However, demand has continued to increase steadily as the number of related products like cars and home air conditioning systems has ballooned in developing countries such as Brazil, India, and China. The newsletter also states that efforts to increase supply have been sharply curtailed by speculation that the European Union will ban the production of R134a within the next few years, eliminating would-be investment in large new production plants to meet growing demand.

At odds with the increase in demand for R134a is its inclusion in the Kyoto Protocol’s comprehensive set of greenhouse gases slated for 5% reductions in emissions from their 1990 levels, along with carbon dioxide, methane, nitrous oxide, and other trace gases (“Global”). It is predicted that the impact of HFCs in terms of percentage contribution to total annual global warming will rise from 0.4% as of 1997 to 1.8% by 2030 (“Global”). As HFCs come to represent a bigger and bigger portion of global warming effects, it will be essential to address alternatives that can deliver results pursuant to the goals set forth by the Kyoto Protocol. The increasing world demand for more environmentally-friendly refrigerants, along with the obstacles that prevent supply increases in HFCs, signal a clear need for investment in large production plants capable of supplying refrigerants that will meet demand while decreasing greenhouse gas emissions.

To this end, Delta Group designed a pilot plant and investigated the production of a refrigerant with a lower impact on global warming. The compound is HFE-143, part of an emerging class of refrigerants with lower GWPs designed to replace older CFCs, HCFCs, and

HFCs in an effort to reduce greenhouse gas emissions while maintaining similar refrigerant properties (Tsai). The plant's annual capacity was determined at approximately 10,000 tonnes. Delta Group arrived at this production capacity by studying presently existing R134a production facilities and determining the amount of HFE-143 to produce that would provide equivalent cooling capacity to a R134a plant ("ICI").

The goal of the project was to build a plant producing HFE-143 at a price competitive with current market prices for R134a. Currently, there is not enough HFE-143 produced to provide an accurate selling price for comparison with R134a in the quantities produced in this plant design. For this reason, Delta Group assumed that HFE-143 would have to be sold at the same price per mass as R134a to be attractive to consumers. This assumption was a conservative one, since future government legislature may ban HFC-134a production or otherwise limit supply, or possibly subsidize HFE-143 because of its capacity to lower greenhouse gases.

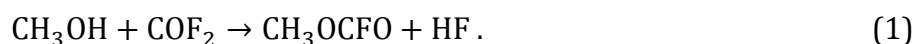
Section 2: Process Description, Rationale, and Optimization

2.1: Process Description

This process is composed of four major sections: A reactor section, containing Streams 1-12; a separation section, containing Streams 12-33; a propene (C₃H₆) refrigeration system, containing streams 34-57; and a steam heating line, containing streams 68-110. Cooling water is provided to the process as needed in streams 58-67 (see Figure 2.3).

Stream 1, containing methanol (CH₃OH) and carbonyl fluoride (COF₂), enters the process at an assumed temperature and pressure of 25 °C and 1.01 bar, and mixes with Stream 13, a methanol recycle stream with trace methyl fluoroformate (CH₃OCFO, hereafter described as formate), before passing into isentropic compressor C-101A/B (see Figure 2.4). The isentropic compressor C-101A/B increases the pressure of the combined stream to 1.22 bar in order to overcome equipment pressure drop across the reactor section of the process. The process material exits the compressor in Stream 2 at 39.9 °C and 1.22 bar, and enters shell-and-tube heat exchanger E-101, where it receives heat from condensing steam in Stream 69 before exiting the exchanger at 100.0 °C in Stream 3.

Stream 3 enters reactor R-101, where the two species react to produce the formate and hydrofluoric acid (HF) according to:



The reactor's temperature is maintained at 100.0 °C by adding heat from condensing steam in Stream 72. The effluent from the reactor leaves in Stream 4 containing methanol, the formate, and hydrofluoric acid (see Tables 2.5.1 – 2.5.11).

Meanwhile, sulfur tetrafluoride (SF₄) enters the process in Stream 5 at an assumed temperature and pressure of 25 °C and 1.01 bar and mixes with Stream 30, a recycle stream containing sulfur tetrafluoride and trace amounts of methyl-trifluoromethyl ether (CH₃OCF₃, hereafter described as ether). The combined stream is Stream 6, containing sulfur tetrafluoride. Stream 6 passes into isentropic compressor C-102A/B, which increases the pressure to 1.17 bar in Stream 7.

Stream 7 then mixes with Stream 4, the effluent from reactor R-101, and Stream 18, a recycle stream containing the formate, trace amounts of methanol, and trace amounts of hydrofluoric acid. The combined stream is Stream 8, which contains methanol, formate, hydrofluoric acid, and sulfur tetrafluoride. Stream 8 then enters floating-head

shell-and-tube heat exchanger E-102, where it receives heat from condensing steam in Stream 76 and leaves as Stream 9 at 175 °C and 1.01 bar.

Stream 9 enters reactor R-102, where the formate and the sulfur tetrafluoride react to form ether and sulfur dioxide (SO₂), according to:



Isothermal conditions are maintained within the reactor by exchanging heat with cooling water in Stream 63. The reactor's effluent, containing methanol, formate, hydrofluoric acid, sulfur dioxide, ether, and sulfur tetrafluoride, leaves in Stream 10 at 175 °C and 1.01 bar.

Stream 10 enters isentropic compressor C-103A/B, which raises its pressure to 1.56 bar in Stream 11. Stream 11 then enters heat exchanger E-103, where it exchanges heat with cooling water from Stream 65. The process material exits E-103 in Stream 12 at 48.0 °C and 1.35 bar.

Stream 12 feeds T-101, which is a 60-stage sieve tray distillation column. T-101 separates 99.9% of the methanol in Stream 12 from the rest of the process stream in the bottoms, while keeping 99.9% of the formate, which is the next heaviest component, in the distillate. The bottoms exit in Stream 13, which is recycled back to the first reactor as described previously. The distillate exits in Stream 14 and contains methanol, formate, hydrofluoric acid, sulfur dioxide, ether, and sulfur tetrafluoride. To achieve this separation, the column's reboiler E-104 must receive heat from condensing steam in Stream 80, and the column's condenser E-105 must exchange heat with propene (C₃H₆) refrigerant in Stream 35. To reduce fluctuation in the tower's steady state, the condensate first enters storage tank V-101 before either returning to the column as reflux or leaving as distillate.

Stream 14 exits T-101 and enters centrifugal pump P-101A/B, which raises its pressure to 1.32 bar in Stream 15. Stream 15 then enters heat exchanger E-106, where the process material receives heat from condensing steam in Stream 84 and exits E-106 in Stream 16 at 38.0 °C.

Stream 16 feeds T-102, which is a 24-stage sieve tray distillation column. T-102 separates 99.9% of the formate in Stream 16 from the rest of the process stream in the bottoms, while keeping 99.9% of the hydrofluoric acid, which is the next heaviest component, in the distillate. The bottoms exit in Stream 17 and are recycled back to the second reactor. To prevent backflow, this recycle stream first enters centrifugal pump P-107A/B, which increases the pressure of the recycled material. The material exits the pump in Stream 18, which has been described previously. The distillate exits T-102 in Stream 19 and contains formate, hydrogen fluoride, sulfur dioxide, ether, and sulfur tetrafluoride. To achieve this separation, the column's reboiler E-107 must receive heat from condensing steam in Stream 88 and the column's condenser E-108 must exchange heat with propene refrigerant in Stream 39. To reduce fluctuation in the tower's steady state, condensate first enters storage tank V-102 before either returning to the column as reflux or leaving as distillate.

Stream 19 exits T-102 and enters centrifugal pump P-102A/B which raises its pressure to 1.29 bar in Stream 20. Stream 20 then enters heat exchanger E-109, where the process material receives 219.4 kW of heat from 29.15 kmol/hr of condensing steam in Stream 92. The process material then exits E-109 in Stream 21 at 0.0 °C and 1.19 bar.

Stream 21 feeds T-103, which is an 18-stage sieve tray distillation column. T-103 separates 99.9% of the hydrogen fluoride in Stream 21 from the rest of the process stream in the bottoms, while keeping 99.9% of the sulfur dioxide, which is the next heaviest component, in the distillate. The bottoms exit in Stream 22 and are combined with liquid water from Stream 32 to form a saleable 70 wt% HF solution. This solution exits the process in Stream 33 at -8.9 °C and 1.01 bar. The distillate from T-103 exits in Stream 23 and contains hydrogen fluoride, sulfur dioxide, ether, and sulfur tetrafluoride. To achieve this separation, the column's reboiler E-110 must receive heat from condensing steam in Stream 96 and the column's condenser E-111 must exchange heat with propene refrigerant in Stream 43. To reduce fluctuation in the tower's steady state, condensate first enters storage tank V-103 before either returning to the column as reflux or leaving as distillate.

Stream 23 exits T-103 and enters centrifugal pump P-103A/B, which raises the process material's pressure to 1.42 bar in Stream 24. Stream 24 then enters heat exchanger E-112, where the process material receives heat from condensing steam in Stream 100 and exits in Stream 25 at -22.0 °C.

Stream 25 feeds T-104, which is a 41-stage sieve tray distillation column. T-104 separates 99.9% of the sulfur dioxide in Stream 25 from the rest of the process stream in the bottoms, while keeping 99.9% of the ether, which is the next heaviest component, in the distillate. The bottoms exit the tower and leave the process in Stream 26 at -8.3 °C and 1.13 bar. The distillate exits in Stream 27 and contains sulfur dioxide, ether, and sulfur tetrafluoride. To achieve this separation, the column's reboiler E-113 must receive heat from condensing steam in Stream 104 and the column's condenser E-114 must exchange heat with propene refrigerant in Stream 47. To reduce fluctuation in the tower's steady state, condensate first enters storage tank V-104 before either returning to the column as reflux or leaving as distillate.

Stream 27 exits T-104 and enters centrifugal pump P-104A/B, which raises its pressure to 1.28 bar in Stream 28.

Stream 28 feeds T-105, which is a 39-stage sieve tray distillation column. T-105 separates 99.9% of the ether in Stream 25 into the bottoms, while keeping 99.9% of the sulfur tetrafluoride, which is the final component, in the distillate. The bottoms exit T-105 and leave the process in Stream 29 at -23.5 °C and 1.06 bar. The distillate exits in Stream 30 and contains sulfur tetrafluoride and trace amounts of ether. To achieve this separation, the column's reboiler E-115 must receive heat from condensing steam in Stream 108 and the column's condenser E-116 must exchange heat with propene refrigerant in Stream 51. To reduce fluctuation in the tower's steady state, condensate first enters storage tank V-105 before either returning to the column as reflux or leaving as distillate. The distillate is then recycled, where it mixes with Stream 5 before the second reactor as described previously.

Cooling water enters the process in Streams 31 and 58 at a heuristic temperature of 30 °C and an assumed pressure of 1.01 bar. Some cooling water is split from Stream 31 into Stream 32, which then proceeds to mix with Stream 22 as described previously. The remainder of Stream 31's cooling water becomes Stream 61, which enters centrifugal pump P-106A/B. This pump increases the pressure of the cooling water to 1.36 bar in Stream 62. Stream 62 then splits into Streams 63 and 65. Stream 63 receives heat from reactor R-102, raising the temperature of the cooling water to 46.70 °C in Stream 64. Stream 65 receives heat from heat exchanger E-103, raising the temperature of the cooling water to 46.70 °C in Stream 66. Streams 64 and 66 are then mixed and exit the process in Stream 67.

Cryogenic and near-cryogenic cooling of distillation column condensers is provided by the propene refrigeration cycle, comprised of Streams 34-57. This cycle is diagrammed as a feed line, made up of Streams 34, 38, 42, 46, and 50; and a recycle line, made up of Streams 37, 41, 45, 49, and 53; with branches leaving the feed line to receive heat from the condensers. The feed line contains 807.5 kmol/hr of propene that is at -44.7 °C and 1.17 bar, and is 62% vapor. Stream 35 brings propene from the feed line to condenser E-105, where it receives heat. The propene is completely vaporized and its temperature is increased to -28.86 °C before it is returned to the recycle line by Stream 36. Stream 39 brings propene from the feed line to condenser E-108, where it receives heat. The propene is completely vaporized and its temperature is increased to -30.36 °C before it is returned to the recycle line by Stream 40. Stream 43 brings propene to condenser E-111, where it receives heat. The propene is completely vaporized and its temperature is increased to -36.46 °C before it is returned to the recycle line by Stream 44. Stream 47 brings propene to condenser E-114, where it receives heat. The propene is completely vaporized and its temperature is increased to -38.86 °C before it is returned to the recycle line by Stream 48. Finally, Stream 51 brings propene to condenser E-116, where it receives heat. The propene is completely vaporized before it is returned to the recycle line by Stream 52.

All of the propene recycle feeds are combined to form Stream 53, containing propene vapor at -35.21 °C and 1.17 bar. Stream 53 enters isentropic compressor C-104A/B, which compresses the propene to -4.8 °C and 3.27 bar in Stream 54. Stream 54 enters isentropic compressor C-105A/B, which compresses the propene to 39.3 °C and 9.11 bar in Stream 55. Stream 55 enters isentropic compressor C-106A/B, which compresses the propene to 91.4 °C and 25.43 bar in Stream 56. Stream 56 then enters heat exchanger E-117, where it exchanges heat with cooling water in Stream 59. The propene exits the heat exchanger having been completely condensed at 60.0 °C and 25.33 bar in Stream 57. Finally, the propene passes through an isenthalpic flash valve which drops the pressure back to 1.17 bar and returns the propene to Stream 34.

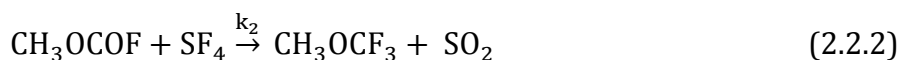
Cooling water for the propene refrigeration cycle enters the process in Stream 58, as described before, and enters centrifugal pump P-105A/B. P-105A/B increases the cooling water pressure to 1.36 bar in Stream 59. Stream 59 then enters heat exchanger E-117 where it receives heat from the condensing propene, raising its temperature to 46.7 °C. The cooling water then exits the process in Stream 60.

Heat is provided to the process by a moderate-pressure steam line, comprised of Streams 68-110, containing a total flow of 186.6 kmol/hr of saturated steam at 185.5 °C and 10.34 bar. The steam line is diagrammed similarly to the refrigeration loop, with a feed line (Streams 68, 71, 74, 78, 82, 86, 90, 94, 98, 102, and 106) and an exhaust line (Streams 70, 75, 79, 83, 87, 91, 95, 99, 103, 107, and 110), with branches leaving to provide heat to heaters and reboilers. All of the branches leave the feed line as saturated vapor at 185.5 °C and 10.34 bar, and return to the exhaust line as saturated liquid at about 181.7 °C and 10.24 bar.

The first branch carries steam in Stream 69 to heat exchanger E-101, where the steam exchanges heat with the process and leaves in Stream 70. The second branch carries steam in Stream 72 to reactor R-101, where the steam exchanges heat and leaves in Stream 73. The third branch carries steam in Stream 76 to heat exchanger E-102, where the steam exchanges heat and leaves in Stream 77. The fourth branch carries steam in Stream 80 to reboiler E-104, where the steam exchanges heat and leaves in Stream 81. The fifth branch carries steam in Stream 84 to heat exchanger E-106, where the steam exchanges heat and leaves in Stream 85. The sixth branch carries steam in Stream 88 to reboiler E-107, where the steam exchanges heat and leaves in Stream 89. The seventh branch carries steam in Stream 92 to heat exchanger E-109, where the steam exchanges heat and leaves in Stream 93. The eighth branch carries steam in Stream 96 to reboiler E-110, where the steam exchanges of heat and leaves in Stream 97. The ninth branch carries steam in Stream 100 to heat exchanger E-112, where the steam exchanges heat and leaves in Stream 101. The tenth branch carries steam in Stream 104 to reboiler E-113, where the steam exchanges heat and leaves in Stream 105. Finally, the eleventh branch carries steam in Stream 108 to reboiler E-115, where the steam exchanges heat and leaves in Stream 109. The condensed steam is combined in Stream 110 where it reaches a final state of 6% vapor at 181.7 °C and 10.24 bar, and leaves the process.

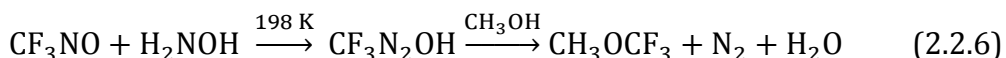
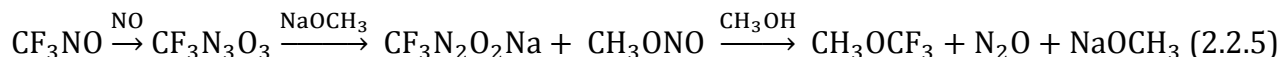
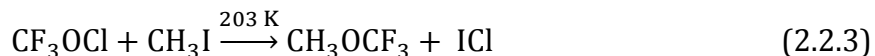
2.2: Rationale for Process Choice

The selected synthesis route for manufacturing HFE-143 is the industry standard. It is a two step reaction that takes place at atmospheric pressure with moderate heat (Aldrich):



In reaction 2.2.1, methanol is mixed with carbonyl fluoride to form hydrofluoric acid and methyl fluoroformate. Reaction 2.2.2 occurs with the addition of sulfur tetrafluoride, which reacts with methyl fluoroformate to produce HFE-143 and the sulfur dioxide byproduct. Reactions 2.2.1 and 2.2.2 occur in R-101 and R-102, respectively, as labeled on the PFD in Section 5.2. Aldrich et al. (1964) and Minkwitz et al. (1996) both state that with a two hour residence time, the HFE is produced with a 29% yield with respect to methanol.

Before selecting this synthesis route, four other reaction schemes were explored. The journal article containing the information regarding these other four reaction schemes was originally written in German. Due to time constraints and because our group was unable to translate German, limited information was available. These reactions are shown below.



Reaction 2.2.3 was seriously considered. It appeared to be a very easy reaction, as it occurs at 203 K, requires only two reagents, and produces only one unwanted byproduct (Minkwitz). It had a 50% yield after a relatively easy distillation to separate the components. Iodine monochloride is liquid from approximately 20 °C to 95 °C, at which the ether would completely vaporize. With respect to distillation, this would require a low heat duty and a reduced number of trays in the column. Of the alternatives, this reaction scheme showed the most promise, but it was passed over due to lack of information about specific process conditions.

Reaction 2.2.4 was reported to have an 80% yield with respect to CsOCF_3 , and therefore was also considered (Minkwitz). However, the reagents include a rare cesium salt. Cesium is a relatively expensive material, costing \$1267 for 10 grams as 99.9% pure Cs (“Cesium – Lump”) or \$3355 for 25 kg of reagent grade cesium carbonate (“Cesium carbonate”). The team decided that it would not be economically favorable to design a separation mechanism to recycle the cesium. The off-product was a methyl sulfate acid cesium salt. While there is a market for certain cesium salts, it is unlikely that this particular salt is in high demand. Thus, it would not be economically favorable to sell the cesium byproduct either. This possible synthesis route was eliminated because of economic constraints.

The methods shown in reactions 2.2.5 and 2.2.6 were skipped over due to lack of prevalent process information. Useful information, such as possible byproducts, operating conditions and residence time, was probably stated in the article but because of the language barrier, it was not easily accessed (Minkwitz). Both of these reactions seemed overly complicated, requiring significantly more separation steps. Reaction 2.2.6 had a 35% yield with respect to CF_3NO , but when compared to our chosen reaction scheme this difference in yield was deemed insignificant in relation to the amount of accessible information.

To determine the size of this HFE-143 production plant, the production rates of other refrigerant manufacturing plants were considered. Because this is a newer chemical, we originally decided to make a pilot plant with one tenth the capacity of a fully operational plant, so we divided the rate by ten. This left us with flow rates that were too small for

ASPEN Plus to accurately handle. Because of this, we set our design basis to 10,000 metric tons per year based on the ICI's HFC-134a plant in Runcorn, England ("ICI"). Our design is for a plant located in the southwestern United States. This location was chosen solely on the assumption of inexpensive land. Factors such as proximity to raw materials, labor costs, and utilities were not considered because their effects on the economics of our plant were assumed to be negligible ("Team meeting"). The purity of our final HFE product was a major factor in our design. Because the thermodynamic properties change with percent composition, the demand is for a pure refrigerant. Therefore, the market price increases as the product approaches purity. After five distillation stages, our plant produces 99.9% pure HFE-143a with traces of sulphur dioxide and sulphur tetrafluoride. Because the reaction has only a 29% yield, closed loop recycle streams were implemented to minimize required feed input, waste generation and to improve the atom economy of the process. The specifics of these recycle streams are shown on the PFD and stream table, in Sections 2.4 and 2.5.

After selecting the synthesis route and design basis, the team had to decide how to obtain the starting materials, methanol, carbonyl fluoride and sulfur tetrafluoride. Because methanol is abundant and inexpensive, we are purchasing it in bulk from QC Concepts for \$5.05 per gallon ("Methanol"). Onsite synthesis of sulfur tetrafluoride was investigated because the compound poses a severe environmental and safety risk ("Sulfur tetrafluoride"). Reducing the storage volume of this hazardous reactant would contribute to the minimization of the total risk associated with the plant. The SF₄ production rate would coincide with the required feed flow rate, eliminating the need for bulk storage. Three synthesis routes were studied during our process design. The first method utilizes elemental sulfur, chlorine gas, and uranium hexafluoride as starting materials (Asprey). The UF₆ readily fluorinates the sulfur producing gaseous SF₄ and SOF₂ byproducts with sulfur based yields of 69-78% and 3.5-6%, respectively. Mercury was used to remove the excess chlorine and no other gases were detected. These results were based on a bench scale experiment.

The other method, described in full by Tullock, et al., produced SF₄ from sulfur or sulfur chlorides reacting with sodium fluoride (Tullock). The reaction of sodium fluoride with sulfur dichloride in acetonitrile produced a 90% yield based on SCl₂ after a single distillation step to remove the more volatile sulfur monochloride. This separation would lead to the formation of a hazardous waste. The waste cannot be sold because there is nothing in the literature of sulfur monochloride that shows that there is a current market for it. The bottoms of this distillation also contain a 10% thionyl fluoride byproduct. To reduce the formation of thionyl fluoride, dry reactants are used and all moisture must be removed from the system. The remaining Cl₂ and SOF₂ can be removed by distillation as well, but because of the similar boiling points in the ternary mixture, some SF₄ product is lost. Currently, the loss of SF₄ is not quantitatively known. As stated in Section 6, future work includes a thermodynamic analysis of the ternary mixture. This enables us to determine the percent of SF₄ that distills with the byproducts, which allows for proper economic analysis.

Carbonyl fluoride is acutely toxic, making it a storage risk (“Carbonyl”). Three carbonyl fluoride synthesis routes were explored with the intent of onsite production. First a multiphoton decomposition of a CO₂ and SF₆ mixture at low pressure was considered (Malatesta). Because of the extreme conditions and low yield, this method was quickly disregarded. The second method proposed carbonyl fluoride synthesis by reacting carbon dioxide with fluorine gas with a tetragonal PbSnF₄ solid electrolyte cell as a fluoride ion conductor (Hasegawa). But in this experiment, the current density was too minute which resulted in zero COF₂ detection after three hours. Finally, a feasible option with 70-80% conversion is accomplished by adding liquefied phosgene to suspended sodium fluoride in acetonitrile (Fawcett). The product was condensed at solid carbon dioxide temperatures (-70 to -78 °C) which resulted in 95% carbonyl fluoride and 4-5% carbon dioxide with traces of phosgene and carbonyl chlorofluoride. However, this separation would require large, expensive cooling duties.

This information persuaded us to purchase SF₄ and COF₂ rather than manufacture them onsite. This is because onsite production does not decrease the total risk of the plant. Storing the necessary starting materials (Cl₂, SF₆, or phosgene) poses an equivalent threat as the reactants themselves. Therefore, to decrease the size and complexity of our facility, SF₄ and COF₂ are purchased from a commercial gas supplier. The price for SF₄ quoted by Custom Gas was \$16,500 for 40 kg while the price for COF₂ was not found (“Re: Re: Sulfur”). Neither SF₄ nor COF₂ are commercially produced on a large enough scale for us to buy them for our process at reasonable bulk prices. To properly analyze the economics of the plant, Delta Group assumed several different Investor Rate of Return (IRR) scenarios along with setting the selling price of HFE-143 equal to HFC-134a in order to calculate maximum allowable costs of the two starting materials annually. In this way, Delta Group established a worst-case scenario combined price for carbonyl fluoride and sulfur tetrafluoride that would provide a 25% IRR for investors over a 30 year plant life, as well as a combined price allowing for increased profits (“Re: Rationale”). This method of calculation provided an analog to a traditional sensitivity analysis, which couldn’t be fully investigated because of the lack of pricing data for some of the process materials.

Sulfur dioxide is created as an undesired byproduct of Reaction 2. It is a criteria pollutant of the Clean Air Act with strict emission regulations (Seinfeld). The first idea for SO₂ removal was by membrane absorption using hydrophobic microporous hollow fiber membrane modules (Nii). The high packing density demands large pressure drops, increasing the utility requirements. We then looked into the demand for the byproduct and discovered that the waste SO₂ has a current market value. Instead of paying to have the SO₂ waste hauled offsite, we decided to purify and sell our waste for reuse purposes. As seen in our PFD (Figure 2.4), the SO₂ is removed through distillation in T-104, with a 99.62% pure liquefied SO₂ stream leaving our process as stream 26. This is a beneficial process choice because it creates excess revenue by minimizing hazardous waste generation, eliminating the need for an absorption column, and producing a salable product.

To reduce or possibly eliminate hazardous hydrofluoric acid waste produced after the Reaction 2.2.1 in R-101, a method to produce salable sodium fluoride was considered. NaF

was obtained by adding aqueous NaOH to a purified HF stream. The resulting products were water and NaF. The water was then boiled off, leaving behind solid NaF. However, after investigating the markets for aqueous HF and NaF we found that it was more advantageous to sell our HF byproduct directly. This simplified our design by removing the additional reactor stage and heat duty for the water removal.

The five part separation train, T-101 through T-105, requires distillation at cryogenic temperatures with large cooling duties. Our original design implemented a liquid nitrogen cooling system. At one atmosphere, our operating condition, the temperature of liquid nitrogen is 77.36 K, and the lowest temperature needed for distillation is 242.15 K. Even though there is a large temperature difference between the N₂ and the process streams, to obtain the required cooling duty 5.676 million tons of N₂ per year are required. This results in \$83 million annually (“Cryogenics”). This is due to nitrogen’s low heat capacity. We considered onsite nitrogen liquefaction, but that increased the complexity and energy demand for the plant. In our optimized redesign, we incorporated a propene refrigeration cycle. The energy demands for this cooling method are significantly lower than for onsite liquefaction of nitrogen. Because the propene refrigeration cycle is a closed loop system, all of the propene is recycled, minimizing waste generation. A detailed economic comparison of the nitrogen cooling train and the propene refrigeration cycle are presented in Section 5, and the calculations in Appendix B.

2.3: Block Flow Diagram

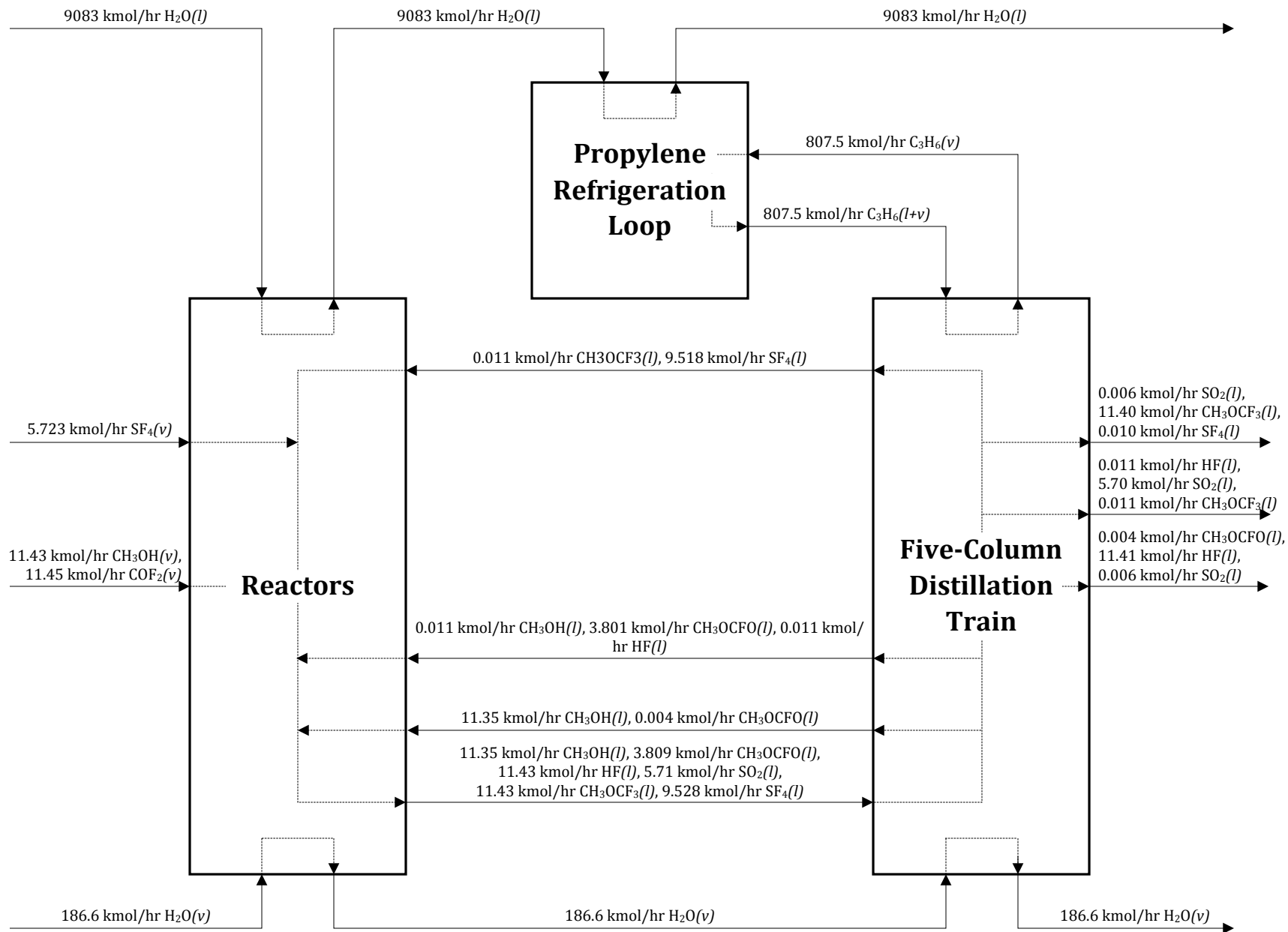
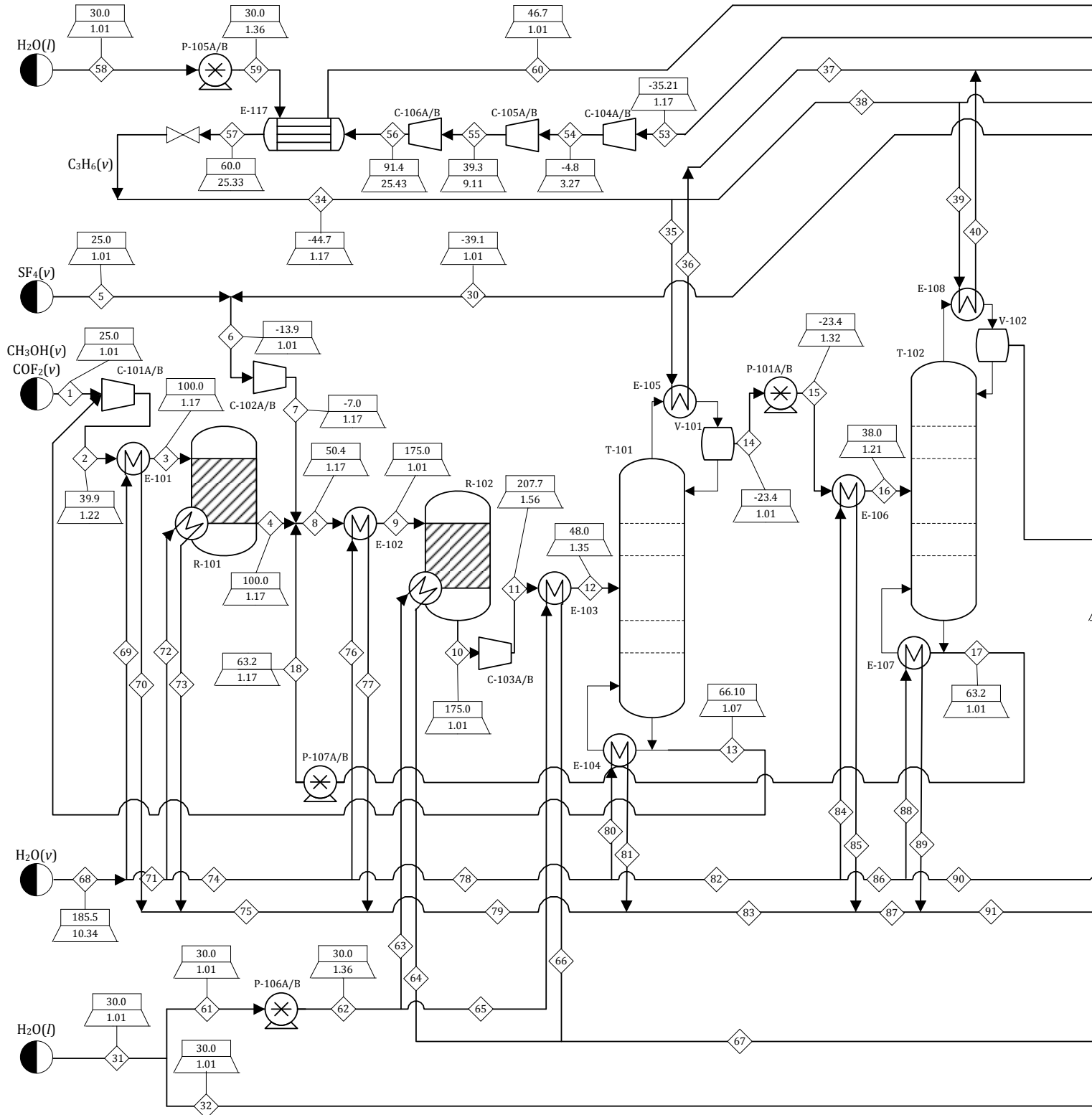


Figure 2.3.1: Block Flow Diagram for HFE-143 Synthesis

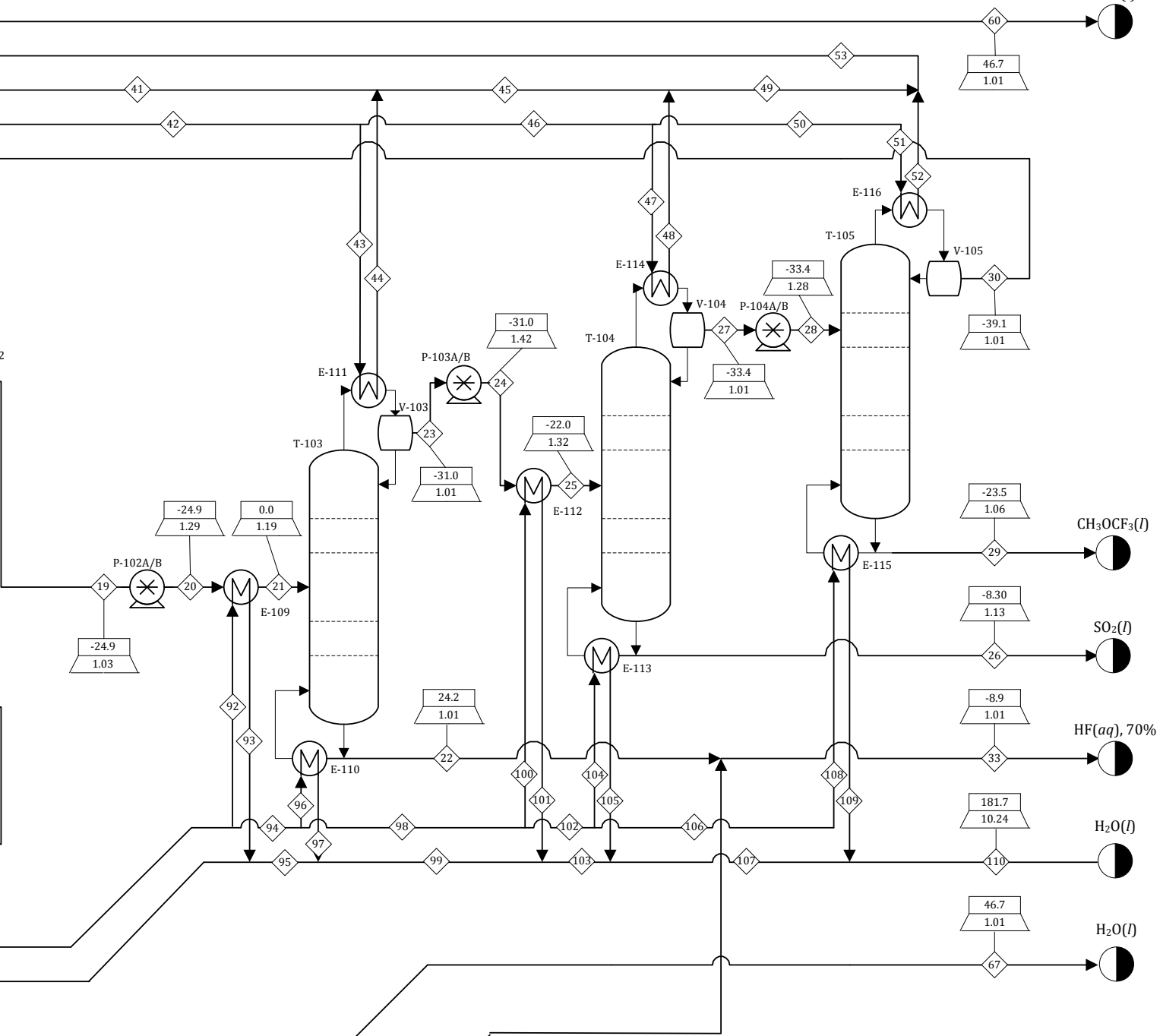
2.4: Process Flow Diagram

2.4: Process Flow Diagram

C-101A/B: Reactor Feed Compressor	R-101: Autoclave Reactor 1	C-102A/B: SF4 Feed Compressor	P-106A/B: CW Pump	E-102: Reactor 2 Preheater	R-102: Autoclave Reactor 2	C-105A/B: 2 nd Refrig Compressor	E-104: Column 1 Reboiler	T-101: Distillation Column 1	V-101: Column 1 Condensate Tank	E-101: Reactor 1 Preheater	P-105A/B: Refrig Loop CW Pump	E-117: Refrig Loop Heat Exchanger	P-107A/B: Centrifugal Pump	C-106A/B: 3 rd Refrig Compressor	C-103A/B: Effluent Compressor	E-103: Column 1 Precooler	C-104A/B: 1 st Refrig Compressor	E-105: Column 1 Condenser	P-101A/B: Centrifugal Pump	E-108: Column 1 Condenser	V-102: Column 1 Condensate Tank
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- E-106: Column 2 Preheater
- E-108: Column 2 Condenser
- P-102A/B: Centrifugal Pump
- T-103: Distillation Column 3
- E-110: Column 3 Reboiler
- P-103A/B: Centrifugal Pump
- T-104: Distillation Column 4
- E-114: Column 4 Condenser
- P-104A/B: Centrifugal Pump
- E-116: Column 5 Condenser
- V-105: Column 5 Condensate Tank
- E-107: Column 2 Reboiler
- T-102: Distillation Column 2
- V-102: Column 2 Condensate Tank
- E-109: Column 3 Preheater
- E-111: Column 3 Condenser
- V-103: Column 3 Condensate Tank
- E-112: Column 4 Preheater
- E-113: Column 4 Reboiler
- V-104: Column 4 Condensate Tank
- T-105: Distillation Column 5
- E-115: Column 5 Reboiler



HFE-143 Manufacture Pilot Plant	
Drawn By:	Date:
Checked By:	Date:
Approved By:	Date:
Drawing No.	Revision:

T [°C]
P [bar]

2.5: Stream Table

Table 2.5.1: Streams 1 – 10

Stream #	1	2	3	4	5	6	7	8	9	10
T (°C)	25.00	39.90	100.0	100.0	25.00	-13.90	-7.000	50.40	175.0	175.0
P (bar)	1.013	1.220	1.170	1.170	1.013	1.013	1.170	1.170	1.013	1.013
Vapor Frac	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.95	1.00	1.00
n (kmol/hr)	22.88	34.23	34.23	34.23	5.723	15.24	15.24	53.27	53.27	53.27
m (kg/hr)	1121.4	1485.1	1485.1	1485.1	618.42	1646.9	1646.9	3428.7	3428.7	3428.7
Mole Flow (kmol/hr)										
CH ₃ OH	11.45	22.79	22.79	11.36	-	-	-	11.36	11.36	11.36
CH ₃ OCFO	-	-	-	11.43	-	-	-	15.24	15.24	3.809
HF	-	-	-	11.43	-	-	-	11.43	11.43	11.43
SO ₂	-	-	-	-	-	-	-	-	-	5.71
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	11.43
SF ₄	-	-	-	-	5.723	15.24	15.24	15.24	15.24	9.528
COF ₂	11.43	11.43	11.43	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-	-	-
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

Table 2.5.2: Streams 11 – 20

Stream #	11	12	13	14	15	16	17	18	19	20
T (°C)	207.7	48.00	66.10	-23.40	-23.40	38.00	63.20	63.20	-24.90	-24.90
P (bar)	1.560	1.350	1.070	1.013	1.320	1.210	1.010	1.170	1.030	1.290
Vapor Frac	1.00	1.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
n (kmol/hr)	53.27	53.27	11.35	41.92	41.92	41.92	3.824	3.824	38.09	38.09
m (kg/hr)	3428.7	3428.7	363.96	3064.7	3064.7	3064.7	297.24	297.24	2767.5	2767.5
Mole Flow (kmol/hr)										
CH ₃ OH	11.36	11.36	11.35	0.011	0.011	0.011	0.011	0.011	-	-
CH ₃ OCFO	3.809	3.809	0.004	3.805	3.805	3.805	3.801	3.801	0.004	0.004
HF	11.43	11.43	-	11.43	11.43	11.43	0.011	0.011	11.42	11.42
SO ₂	5.71	5.71	-	5.71	5.71	5.71	-	-	5.71	5.71
CH ₃ OCF ₃	11.43	11.43	-	11.43	11.43	11.43	-	-	11.43	11.43
SF ₄	9.528	9.528	-	9.528	9.528	9.528	-	-	9.528	9.528
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-	-	-
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

Table 2.5.3: Streams 21 – 30

Stream #	21	22	23	24	25	26	27	28	29	30
T (°C)	0.000	24.20	-31.00	-31.00	-22.00	-8.300	-33.40	-33.40	-23.50	-39.10
P (bar)	1.190	1.010	1.010	1.420	1.320	1.130	1.010	1.280	1.060	1.010
Vapor Frac	0.82	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
n (kmol/hr)	38.09	11.42	26.67	26.67	26.67	5.725	20.95	20.95	11.42	9.530
m (kg/hr)	2767.5	228.97	2538.5	2538.5	2538.5	366.66	2171.9	2171.9	1142.2	1029.7
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	0.004	0.004	-	-	-	-	-	-	-	-
HF	11.42	11.41	0.011	0.011	0.011	0.011	-	-	-	-
SO ₂	5.71	0.006	5.71	5.71	5.71	5.70	0.006	0.006	0.006	-
CH ₃ OCF ₃	11.43	-	11.43	11.43	11.43	0.011	11.42	11.42	11.40	0.011
SF ₄	9.528	-	9.528	9.528	9.528	-	9.528	9.528	0.010	9.518
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-	-	-
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

Table 2.5.4: Streams 31 – 40

Stream #	31	32	33	34	35	36	37	38	39	40
T (°C)	30.00	30.00	-8.90	-44.70	-44.70	-28.86	-28.86	-44.70	-44.70	-30.36
P (bar)	1.010	1.010	1.010	1.170	1.170	1.170	1.170	1.170	1.170	1.170
Vapor Frac	0.00	0.00	0.00	0.62	0.62	1.00	1.00	0.62	0.62	1.00
n (kmol/hr)	396.5	5.430	16.85	807.5	222.6	222.6	222.6	584.9	141.6	141.6
m (kg/hr)	7142.9	97.823	326.79	80782	22273	22273	22273	58509	14163	14163
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	0.004	-	-	-	-	-	-	-
HF	-	-	11.41	-	-	-	-	-	-	-
SO ₂	-	-	0.006	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	396.49	5.430	5.430	-	-	-	-	-	-	-
C ₃ H ₆	-	-	-	807.5	222.6	222.6	222.6	584.9	141.6	141.6

Table 2.5.5: Streams 41 – 50

Stream #	41	42	43	44	45	46	47	48	49	50
T (°C)	-29.44	-44.70	-44.70	-36.46	-31.48	-44.70	-44.70	-38.86	-33.13	-44.70
P (bar)	1.170	1.170	1.170	1.170	1.170	1.170	1.170	1.170	1.170	1.170
Vapor Frac	1.00	0.62	0.62	1.00	1.00	0.62	0.62	1.00	1.00	0.62
n (kmol/hr)	364.2	443.3	149.4	149.4	513.6	293.9	147.7	147.7	661.3	146.2
m (kg/hr)	36436	44346	14949	14949	51385	29397	14775	14775	66160	14622
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	-	-	-	-	-	-	-	-
HF	-	-	-	-	-	-	-	-	-	-
SO ₂	-	-	-	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-	-	-
C ₃ H ₆	364.2	443.3	149.4	149.4	513.6	293.9	147.7	147.7	661.3	146.2

Table 2.5.6: Streams 51 – 60

Stream #	51	52	53	54	55	56	57	58	59	60
T (°C)	-44.70	-44.66	-35.21	-4.800	39.30	91.40	60.00	30.00	30.00	46.70
P (bar)	1.170	1.170	1.170	3.270	9.110	25.43	25.33	1.010	1.360	1.010
Vapor Frac	0.62	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00
n (kmol/hr)	146.1	146.1	807.5	807.5	807.5	807.5	807.5	7367	7367	7367
m (kg/hr)	14617	14617	80782	80782	80782	80782	80782	132751	132751	132751
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	-	-	-	-	-	-	-	-
HF	-	-	-	-	-	-	-	-	-	-
SO ₂	-	-	-	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	7367	7367	7367
C ₃ H ₆	146.1	146.1	807.5	807.5	807.5	807.5	807.5	-	-	-

Table 2.5.7: Streams 61 – 70

Stream #	61	62	63	64	65	66	67	68	69	70
T (°C)	30.00	30.00	30.00	46.70	30.00	46.70	46.70	185.5	185.5	181.3
P (bar)	1.010	1.360	1.360	1.010	1.360	1.010	1.010	10.34	10.34	10.24
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.95
n (kmol/hr)	1717	1717	1326	1326	391.1	391.1	1717	186.6	25.80	25.80
m (kg/hr)	30935	30935	23888	23888	7045.1	7045.1	30935	3361.7	464.79	464.79
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	-	-	-	-	-	-	-	-
HF	-	-	-	-	-	-	-	-	-	-
SO ₂	-	-	-	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	1717	1717	1326	1326	391.1	391.1	1717	186.6	25.80	25.80
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

Table 2.5.8: Streams 71 – 80

Stream #	71	72	73	74	75	76	77	78	79	80
T (°C)	185.5	185.5	181.3	185.5	181.7	185.5	181.3	185.5	181.7	185.5
P (bar)	10.34	10.34	10.24	10.34	10.34	10.34	10.24	10.34	10.34	10.34
Vapor Frac	1.00	1.00	0.06	1.00	0.65	1.00	0.07	1.00	0.49	1.00
n (kmol/hr)	160.8	13.30	13.30	147.5	39.10	15.28	15.28	132.2	54.38	1.530
m (kg/hr)	2896.9	239.61	239.61	2657.2	704.41	275.27	275.27	2382.0	979.68	27.563
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	-	-	-	-	-	-	-	-
HF	-	-	-	-	-	-	-	-	-	-
SO ₂	-	-	-	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	160.8	13.30	13.30	147.5	39.10	15.28	15.28	132.2	54.38	1.530
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

Table 2.5.9: Streams 81 – 90

Stream #	81	82	83	84	85	86	87	88	89	90
T (°C)	181.3	185.5	181.7	185.5	181.3	185.5	181.7	185.5	181.3	185.5
P (bar)	10.24	10.34	10.34	10.34	10.24	10.34	10.34	10.34	10.24	10.34
Vapor Frac	0.03	1.00	0.47	1.00	0.06	1.00	0.31	1.00	0.07	1.00
n (kmol/hr)	1.530	130.7	55.91	34.99	34.99	95.70	90.90	2.870	2.870	92.83
m (kg/hr)	27.563	2354.4	1007.2	630.36	630.36	1724.1	1637.6	51.704	51.704	1672.3
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	-	-	-	-	-	-	-	-
HF	-	-	-	-	-	-	-	-	-	-
SO ₂	-	-	-	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	1.530	130.7	55.91	34.99	34.99	95.70	90.90	2.870	2.870	92.83
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

Table 2.5.10: Streams 91 – 100

Stream #	91	92	93	94	95	96	97	98	99	100
T (°C)	181.7	185.5	181.3	185.5	181.7	185.5	132.4	185.5	181.7	185.5
P (bar)	10.34	10.34	10.24	10.34	10.34	10.34	10.237	10.34	10.34	10.34
Vapor Frac	0.31	1.00	0.29	1.00	0.30	1.00	0.00	1.00	0.29	1.00
n (kmol/hr)	93.77	29.15	29.15	63.68	122.9	5.400	5.400	58.28	128.3	16.76
m (kg/hr)	1689.3	525.15	525.15	1147.2	2214.4	97.283	97.283	1049.9	2311.7	301.94
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	-	-	-	-	-	-	-	-
HF	-	-	-	-	-	-	-	-	-	-
SO ₂	-	-	-	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	93.77	29.15	29.15	63.68	122.9	5.400	5.400	58.28	128.3	16.76
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

Table 2.5.11: Streams 101 – 110

Stream #	101	102	103	104	105	106	107	108	109	110
T (°C)	181.3	185.5	181.7	185.5	181.3	185.5	181.3	185.5	181.3	181.7
P (bar)	10.24	10.34	10.34	10.34	10.24	10.34	10.24	10.34	10.24	10.24
Vapor Frac	0.54	1.00	0.32	1.00	0.06	1.00	0.26	1.00	0.06	0.23
n (kmol/hr)	16.76	41.52	145.1	12.81	12.81	28.71	157.9	28.71	28.71	186.6
m (kg/hr)	301.94	747.98	2613.7	230.78	230.78	517.21	2844.4	517.21	517.21	3361.7
Mole Flow (kmol/hr)										
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ OCFO	-	-	-	-	-	-	-	-	-	-
HF	-	-	-	-	-	-	-	-	-	-
SO ₂	-	-	-	-	-	-	-	-	-	-
CH ₃ OCF ₃	-	-	-	-	-	-	-	-	-	-
SF ₄	-	-	-	-	-	-	-	-	-	-
COF ₂	-	-	-	-	-	-	-	-	-	-
H ₂ O	16.76	41.52	145.1	12.81	12.81	28.71	157.9	28.71	28.71	186.6
C ₃ H ₆	-	-	-	-	-	-	-	-	-	-

2.6: Equipment Tables

Table 2.6.1: Equipment Tables – Exchangers

Heat Exchangers	E-101	E-102	E-103	E-104	E-105	E-106	E-107	E-108	E-109
Type*	FLH	FLH	FLH	Reb	Cond	FLH	Reb	Cond	FLH
Surface Area (m ²)	2.25	2.68	6.49	0.13	10.88	2.12	0.24	7.95	1.59
Heat Duty (kW)	14.36	150.92	157.84	15.72	489.69	349.40	28.30	308.73	219.42
Shell (Cold)									
Inlet Stream #	2	8	65	N/A	35	15	N/A	39	20
Outlet Stream #	3	9	66	N/A	36	16	N/A	40	21
Inlet Temp (°C)	39.9	50.4	30.0	66.1	-44.7	-23.4	63.2	-44.7	-24.9
Outlet Temp (°C)	100.0	175.0	46.7	66.1	-44.5	38.0	63.2	-44.5	0.0
Pressure (bar)	1.22	1.17	1.36	1.07	1.17	1.32	1.01	1.17	1.29
Phase(s)	V	V & L	L	V & L	V & L	V & L	V & L	V & L	V & L
MOC	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS
Tube (Hot)									
Inlet Stream #	69	76	11	80	N/A	84	88	N/A	92
Outlet Stream #	70	77	12	81	N/A	85	89	N/A	93
Inlet Temp (°C)	185.5	185.5	207.7	185.5	-23.4	185.5	185.5	-24.9	185.5
Outlet Temp (°C)	185.5	185.5	48.0	185.5	-23.4	181.7	185.5	-24.9	181.7
Pressure (bar)	10.34	10.34	1.56	10.34	1.01	10.34	10.34	1.03	10.34
Phase(s)	V & L	V & L	V	V & L	V & L	V & L	V & L	V & L	V & L
MOC	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS
Heat Exchangers	E-110	E-111	E-112	E-113	E-114	E-115	E-116	E-117	
Type*	Reb	Cond	FLH	Reb	Cond	Reb	Cond	FLH	
Surface Area (m ²)	0.35	11.60	0.86	0.69	12.12	1.48	14.82		
Heat Duty (kW)	64.07	278.89	81.46	184.28	267.35	287.81	286.93	2556.71	
Shell (Cold)									
Inlet Stream #	N/A	43	24	N/A	47	N/A	51	59	
Outlet Stream #	N/A	44	25	N/A	48	N/A	52	60	
Inlet Temp (°C)	24.2	-44.7	-31.0	-8.3	-44.7	-23.5	-44.7	30.0	
Outlet Temp (°C)	24.2	-44.5	-22.0	-8.3	-44.5	-23.5	-44.5	46.7	
Pressure (bar)	10.34	1.01	10.34	10.34	1.01	10.34	1.01	25.43	
Phase(s)	V & L	V & L	V & L	V & L	V & L	V & L	V & L	V & L	
MOC	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	
Tube (Hot)									
Inlet Stream #	96	N/A	10	104	N/A	108	N/A	56	
Outlet Stream #	97	N/A	101	105	N/A	109	N/A	57	
Inlet Temp (°C)	185.5	-31.0	185.5	185.5	-33.4	185.5	-39.1	91.4	
Outlet Temp (°C)	185.5	-31.0	181.7	185.5	-33.4	185.5	-39.1	60.0	
Pressure (bar)	10.34	1.01	10.34	10.34	1.01	10.34	1.01	25.43	
Phase(s)	V & L	V & L	V & L	V & L	V & L	V & L	V & L	V & L	
MOC	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS	

*FLH = Floating Head Shell and Tube Heat Exchanger, Cond = Condenser, Reb = Reboiler

Table 2.6.2: Equipment Tables – Columns

Columns	T-101	T-102	T-103	T-104	T-105
Feed Stream	12	16	21	25	28
Bottoms Stream	13	17	22	26	29
Distillate Stream	14	19	23	27	30
Feed Flow (kmol/hr)	53.27	41.92	38.09	26.67	20.95
Bottoms Flow (kmol/hr)	11.35	3.82	11.42	5.73	11.42
Distillate Flow (kmol/hr)	41.92	38.09	26.67	20.95	9.53
Feed Temp (°C)	48.0	38.0	0.0	-22.0	-33.3
Bottoms Temp (°C)	66.1	63.2	24.2	-8.3	-23.5
Distillate Temp (°C)	-23.4	-24.9	-31	-33.4	-39.1
Number of Stages	60	24	18	41	39
Reflux Ratio	0.59	0.17	0.69	1.13	3.94
Tray Type	Sieve Trays	Sieve Trays	Sieve Trays	Sieve Trays	Sieve Trays
MOC	316 SS	316 SS	316 SS	316 SS	316 SS
Condenser Cooling (kW)	489.7	308.7	278.9	267.3	286.9
Reboiler Heating (kW)	15.7	28.3	64.1	184.3	287.8

Table 2.6.3: Equipment Tables – Pumps

Pumps	P-101A/B	P-102A/B	P-103A/B	P-104A/B
Flow Rate (m ³ /hr)	2.15	1.93	1.80	1.56
Head Developed (m)	2.22	1.28	2.98	1.98
Efficiency	0.16	0.14	0.13	0.10
Pressure Change (bar)	0.31	0.18	0.41	0.27
Power (W)	154.7	94.68	211.6	156.4
Pump Type*	Centri	Centri	Centri	Centri
MOC	316 SS	316 SS	316 SS	316 SS
Pumps	P-105A/B	P-106A/B	P-107A/B	
Flow Rate (m ³ /hr)	133.19	30.92	0.30	
Head Developed (m)	3.58	3.58	1.30	
Efficiency	0.73	0.57	0.36	
Pressure Change (bar)	0.35	0.35	0.16	
Power (W)	2154	663.6	5.20	
Pump Type*	Centri	Centri	Centri	
MOC	316 SS	316 SS	316 SS	

*Centri = Centrifugal

Table 2.6.4: Equipment Tables – Compressors

Compressors	C-101	C-102	C-103	C-104	C-105	C-106
Flow Rate (kmol/hr)	34.23	15.24	53.27	807.45	807.45	807.45
Outlet Pressure (bar)	1.22	1.17	1.56	3.27	9.11	25.43
Motor Efficiency	0.9	0.9	0.9	0.9	0.9	0.9
Pump Efficiency	0.75	0.75	0.75	0.75	0.75	0.75
Power (kW)	10.10	2.73	50.31	667.89	746.30	814.42
Type	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal
MOC	316 SS	316 SS	316 SS	316 SS	316 SS	316 SS

Table 2.6.5: Equipment Tables - Vessels

Vessels	V-101 A/B	V-102 A/B	V-103 A/B	V-104 A/B	V-105 A/B
Volume* (L)	113.9	75.5	101.8	110.3	91.7
Pressure (bar)	1.01	1.03	1.01	1.01	1.01
Temperature (°C)	-23.4	-24.9	-31.0	-33.4	-39.1
MOC	316 SS	316 SS	316 SS	316 SS	316 SS

*Based on assumed residence time of 2 minutes

Table 2.6.6: Equipment Tables -Reactors

Reactors	R-101	R-102
Inlet Flow (kmol/hr)	34.235	53.272
Outlet Flow (kmol/hr)	34.235	53.272
Temperature (°C)	100.0	175.0
Pressure (bar)	1.17	1.01
Volume (m ³)	2078.2	3893.9
Heat Duty (kW)	132.9	-416.0
MOC	316 SS (Glass Lined)	316 SS (Glass Lined)

2.7: Reagent, Utility, and Sales Tables

Table 2.7.1: Annual Reagents

Material	Units/Year	Unit	Cost/Unit	Annual Cost
Methanol	1.071 million	gallon	\$ 5.05	\$ 5,408,000.00
Carbonyl Fluoride	100.2 thousand	kmol	\$ 419.00	\$ 41,970,000.00
Sulfur Tetrafluoride	50.13 thousand	kmol	\$ 419.00	\$ 21,010,000.00
Water	302.7	ccf	\$ 1.63	\$ 493.50
TOTAL:				\$ 68,380,000.00

Table 2.7.2: Annual Utilities

Utility	Units/Year	Unit	Cost/Unit	Annual Cost
Electricity	20.12 million	kWh	\$ 0.03	\$ 588,700.00
Cooling Water	549.3 thousand	ccf	\$ 1.63	\$ 895,400.00
Steam @ 150 psig	29.44 thousand	tonne	\$ 10.50	\$ 309,200.00
Propene	2.178	tonne	\$ 132.00	\$ 287.50
TOTAL:				\$ 1,794,000.00

Table 2.7.3: Annual Sales

Product	Units/Year	Unit	Cost/Unit	Annual Sales
Hydrofluoric Acid (70%)	639.7 thousand	gallon	\$24.00	\$ 15,350,000.00
HFE-143 (99%)	22.03 million	pound	\$3.16	\$ 69,660,000.00
Sulfur Dioxide (99%)	7.055 million	pound	\$2.58	\$ 18,200,000.00
TOTAL:				\$ 103,200,000.00

Section 3: Equipment Description, Rationale, and Optimization

The goal in equipment selection for the process was to perform the required reactions necessary for product synthesis and achieve the desired product purity while minimizing waste and utilities. For purposes of safety and reliability, all process equipment was constructed of stainless steel 316 to resist corrosion. The equipment tables in Section 2.6 describe each piece of process equipment in more detail.

The most prominent section of the design process was the five distillation tower train (T-101, 102, 103, 104, & 105) used to separate the product, HFE-143, from the byproducts and unreacted starting materials. The distillation columns were made from stainless steel 316 to protect against the corrosive chemicals in the process such as HF and SF₄ (Turton). Distillation was chosen as the means of chemical separation for several reasons. Distillation towers are usually the most economical means of chemical separation (Turton). Data for boiling points and estimation methods for heats of vaporization and specific heats of the process chemicals were available, while other data for solubility and liquid-liquid behavior needed for liquid-liquid extraction were generally not available (see Appendix C). The crystallization temperatures for many of the process chemicals were extremely low, requiring significantly more energy for cooling than the chosen distillation process, which only required cooling sufficient to condense the compounds from the vapor phase ("Carbonyl", "HFE-7200", "Hydrogen", "Methyl alcohol", "Methyl formate", "Propylene MSDS", "Sulfur dioxide", "Sulfur tetrafluoride").

The reactor section housed two large reactors (R-101, 102) for each of the two steps required to produce HFE-143, SO₂, and HF (Aldrich). The reactors were built with stainless steel 316, as well as an inner glass lining for the first reactor, to protect them from the high volumes of corrosive chemicals at high temperatures moving continuously through the process. The pressures and temperatures of the two reactors were kept at approximately 1 bar and 100°C and 175°C to promote optimum conversion of the raw materials to HFE-143 (See Figure 2.4). A reactor residence time of two hours was implemented based on the literature (Aldrich). This led to reactor volumes of 2,078.2 m³ and 3,893.9 m³ for R-101 and R-102 (See Appendix A.5).

Heat exchangers were used throughout the process for a variety of purposes: as reboilers and condensers in each of the five distillation columns (E-104, 105, 107, 108, 110, 111, & 113-116), heating or cooling reactants before their entrance into the reactors (E-101 & 102), cooling reactor effluent (E-103), as part of the propene refrigeration cycle (E-117), and intercooling between each of the distillation towers except the last two (E-106, 109, & 112) (See Figure 2.4). In all, the process contained 17 heat exchangers. All heat exchangers were floating head shell and tube. This type of heat exchanger was chosen because it allowed pressure differentials within the tube side, which was necessary in most of the

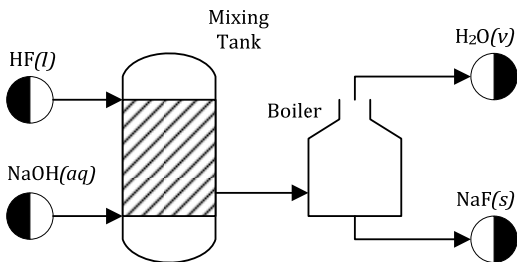


Figure 3.1: Original Boiler for NaF(s) Production

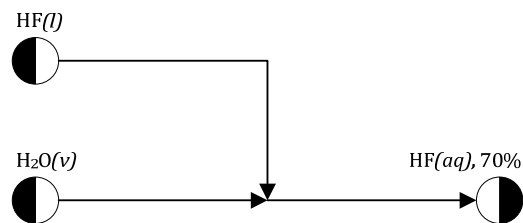


Figure 3.2: Final Design for HF(aq) Production

processes. In a few instances, there was no pressure differential in the tube side of the heat exchanger, but it was determined that it would be ultimately less expensive to have all the same type of exchanger so that the plant could have only one supplier to deal with for service and maintenance, as well as getting large order pricing from the supplier. An optimization analysis of the columns showed that heating and vaporizing the distillate before feeding it into the next tower saved energy and reduced utilities for all but the last tower (see Appendix A.2).

The compressors and pumps, as a group, served two main functions in the process. All seven pumps in the system (P-101, 102, 103, 104, 105, 106, & 107) functioned simply to move chemicals in the liquid phase through the process and overcome the pressure drops associated with the heat exchangers and distillation columns (see Appendix A.3). Centrifugal pumps were chosen because their costs were competitive with other pump types and they delivered a steady flow rate through the system (Seider).

Likewise, compressors C-101 A/B through C-103A/B served to push starting materials in the vapor phase through the reactors and overcome the pressure drops across the first several heat exchangers (E-101 through E-105). Compressors C-103 through C-106 served to compress a recycle stream of propene vapor to 25.33 bar before its entrance into E-117 as part of a refrigeration cycle used to condense the distillate from each tower (see Figure 2.4). This refrigeration cycle effectively served as a heat exchanger optimization of an earlier design in which liquid nitrogen was used at the coolant instead of liquid propene and the vaporized nitrogen leaving the process was simply released as waste. Changing the coolant from nitrogen to propene and implementing a refrigeration system to recycle it each led to large savings on raw materials costs and greatly reduced waste while increasing utilities costs only marginally (see Appendices A.6 & A.7). The compressors were centrifugal in order to ensure a steady flow through the process (Seider).

In the original design, there was a boiler that received the separated HF from stream 21 and reacted it with an inlet stream of aqueous NaOH, vaporizing the water and crystallizing out NaF that was then sold as a byproduct. This piece of equipment was later removed when it was realized that the HF could simply be diluted with used process cooling water into 70% aqueous hydrofluoric acid that could also be sold as a byproduct. Figures 3.1 and 3.2 (above) show the boiler idea and the optimized final design choice, respectively.

Section 4: Environment, Health, and Safety

4.1: Safety Issues

Delta Group's pilot plant design maintained a constant focus on achieving maximum safety in the process. From Table 4.1.1, it was clear that almost every chemical involved in the process was toxic, corrosive, possibly reactive, and hazardous to human health under the specified process conditions. For this reason, a Process Hazard Analysis (PHA) was performed to first group the various process stages into broader risk zones and then identify and control the foreseeable hazards associated with each zone. The PHA (see Appendix D) was undertaken by creatively proposing "what if" scenarios for likely process hazards and then devising control strategies to either mitigate or preemptively eliminate the negative consequences of various system failures.

Sulfur tetrafluoride (SF₄) was determined to be the most dangerous chemical in the process. Its Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) were both 0.1 ppm (see Table 4.1.2 for process chemical toxicity data), ten times lower than any other process chemical, and it had incompatibility with water (see Table 4.1.3 for general process chemical hazards). This meant that SF₄ was not only highly toxic, but there was a potential for violent reactions if it came in contact with the water vapor in air under ambient conditions. This was an especially high risk considering chemical storage, because if a storage container of SF₄ corroded, it would expose the chemical to ambient air and water vapor and could cause an explosion. Other process chemicals with high toxicities were sulfur dioxide and hydrofluoric acid. It is important to note that all process chemicals other than water existed as vapors at ambient conditions and were present in sufficient amounts to be lethal if leaked or otherwise released in the plant. This plant design would require a high degree of training and years of field experience for all operators working in it because of the high danger of the process chemicals. In addition, full body-covering PPE with ESD shoes and respirators would be required inside the plant at all times.

The PHA identified the liquid propene cooling system (Streams 34-57) as the most hazardous zone of the process. The direct causes of a cooling system failure were overpressuring of the liquid propene holding tank or lines leading to a leak, rupture, or explosion releasing flammable propene and displacing oxygen in the plant. This is a likely hazard because of the large amounts (807.5 kmol/hr) of propene used in the process and the high pressures in the storage tank and lines (up to 25.4 bar) after heat transfer from the reactors and condensers. The effects of a cooling system failure on the rest of the plant range from serious to catastrophic. A cooling system failure in either reactor could cause a

Table 4.1.1: Exposure Hazards and Responses for Process Chemicals^a

Compound	Hazard				Response			
	Skin	Eyes	Ingestion	Inhalation	Skin	Eyes	Ingestion	Inhalation
CH ₃ OH ^b	mild dryness	irritant	toxic	slight irritant, toxic	flush with water (15 min.)	flush with water (15 min.)	Induce vomiting	Administer oxygen
COF ₂ ^c	severe burns	severe burns	N/A	highly toxic	flush with water (15 min.)	flush with water (15 min.)	N/A	Administer oxygen
SF ₄ ^d	burns	burns	N/A	respiratory burns	flush with water (15 min.)	flush with water (15 min.)	N/A	Administer oxygen
H ₂ O	none	none	none	none	N/A	N/A	N/A	N/A
CH ₃ OCFO ^{e,f}	severe burns	severe burns	Unknown	Unknown	medical attention	medical attention	medical attention	medical attention
HF ^g	corrosive, burns	corrosive, burns	corrosive, burns	corrosive, burns	flush with water (15 min.)	flush with water (30 min.)	medical attention	medical attention
SO ₂ ^h	corrosive, burns	corrosive, burns	N/A	corrosive, irritant	flush with water (15 min.)	flush with water (15 min.)	N/A	medical attention
CH ₃ OCF ₃ ⁱ	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown	Administer oxygen
C ₃ H ₆ ^j	none	irritant	N/A	Irritant	flush with water (15 min.)	flush with water (15 min.)	medical attention	Administer oxygen

a: For more information on proper responses to various levels of exposure, see manufacturer's MSDS (ref. b-j)

b: MSDS for methanol, supplied by Methanex; c: MSDS for carbonyl fluoride, supplied by Air Liquide; d: MSDS for sulfur tetrafluoride, supplied by Matheson Tri-Gas, Inc.; e: Éditeur officiel du Québec (2009); f: Edwards and Maynard (2007); g: MSDS for hydrogen fluoride, supplied by BOC Gases; h: MSDS for sulfur dioxide, supplied by BOC Gases; i: No MSDS for HFE-143m was available. Approximate information was taken from the MSDS for HFE-7200, supplied by 3M; j: MSDS for propene, supplied by BMS, Inc.

rupture and/or explosion releasing scalding toxic chemical fumes at temperatures up to 175 °C into the plant and causing structural fires. In the distillation columns, a cooling system failure would prevent separation of chemicals from the process and allow corrosive chemicals into lines not built to withstand their presence, ultimately leading to leaks and ruptures in the process piping. Both scenarios would also release toxic fumes into the plant, since all of the process chemicals except water exist as vapors at standard temperatures and pressures. The final concern with the release of chemical fumes into the plant was their possible interaction with additional chemicals in storage containers resulting in interactions of chemicals under conditions not seen in the process itself.

Table 4.1.2: Toxicity Hazards and Limits for Process Chemicals

Compound	OSHA PEL [ppm]	ACGIH TLV [ppm]	LC ₅₀ [ppm/1hour] (rat)
CH ₃ OH ^a	200	200	16,000
COF ₂ ^b	2	Not Available	360
SF ₄ ^c	0.1	0.1	Not Available
H ₂ O	N/A	N/A	N/A
CH ₃ OCFO	Not Available	Not Available	Not Available
Hf ^d	3	3	1276
SO ₂ ^e	5	2	2520
CH ₃ OCF ₃ ^f	200	200	Not Available
C ₃ H ₆ ^g	N/A	N/A	Not Available

a: MSDS for methanol, supplied by Methanex

b: MSDS for carbonyl fluoride, supplied by Air Liquide

c: MSDS for sulfur tetrafluoride, supplied by Matheson Tri-Gas, Inc.

d: MSDS for hydrogen fluoride, supplied by BOC Gases

e: MSDS for sulfur dioxide, supplied by BOC Gases

HFE-7200, supplied by 3M

g: MSDS for propene, supplied by BMS, Inc.

In order to mitigate the hazards associated with a cooling system failure effectively, several measures were taken. All process equipment was designed using 316 stainless steel as the material of construction (MOC) in order to stop corrosive chemicals from corroding pipes they wouldn't normally flow through during a system failure. In addition, the first reactor was lined with glass to mitigate corrosion of the stainless steel by the carbonyl fluoride. A storage plan was selected that separated each process chemical into separate rooms with independent ventilation systems that circulated dehumidified air into the storage area. This would ensure there was no possible interaction between any chemicals outside of the process itself, reducing the risk of violent chemical interactions between incompatible compounds. Mass flow controllers, pressure regulators, and thermocouples were designed into the propene cooling lines throughout the process to monitor flow and react to any variations that could cause leaks or ruptures. A pressure regulator, thermocouples, and a scale were purchased for the liquid propene storage tank to monitor use, tank leakage, and varying temperatures throughout the year. Additionally, a backup generator was purchased to ensure this part of the process would continue to function during emergency power losses.

Table 4.1.3: General Chemical Hazards for Process Chemicals

Compound	Flammability	Reactivity	Incompatibilities	Special Hazard
CH ₃ OH ^a	Severe	Slight hazard	Strong oxidizing agents such as nitrates, perchlorates or sulfuric acid, some plastics and rubbers, and metallic aluminum	N/A
COF ₂ ^b	None	Medium	Alkalis, water, and most metals	N/A
SF ₄ ^c	None	Slight hazard	Water	N/A
H ₂ O	N/A	N/A	N/A	N/A
CH ₃ OCFO ^{d,e}	Not available	High	Not available	Nerve gas
HF ^f	None	Very high	Water, organic materials and metals	teratogenic, mutagenic, and reproductive effects
SO ₂ ^g	None	Slight hazard	Reacts violently with peroxides, chromates, bichromates, permanganates, chlorates, water, and oxygen difluoride	reproductive, mutagenic, tumorigenic, and respiratory effects
CH ₃ OCF ₃ ^h	None	None	Strong bases	N/A
C ₃ H ₆ ⁱ	Severe	Slight hazard	Oxidizing materials	N/A

a: MSDS for methanol, supplied by Methanex

b: MSDS for carbonyl fluoride, supplied by Air Liquide

c: MSDS for sulfur tetrafluoride, supplied by Matheson Tri-Gas, Inc.

d: Éditeur officiel du Québec (2009)

e: Edwards and Maynard (2007)

f: MSDS for hydrogen fluoride, supplied by BOC Gases

g: MSDS for sulfur dioxide, supplied by BOC Gases

h: No MSDS for HFE-143m was available. Approximate information was taken from the MSDS for HFE-7200, supplied by 3M

i: MSDS for propene, supplied by BMS, Inc.

4.2: Environmental Impact Statement

The Introduction, Section 1, draws attention to the environmental risk associated with greenhouse gasses. Three major end of life environmental hazard characteristics are the global warming potentials (GWP), atmospheric lifetimes (ATL), and the ozone depleting potentials (ODP). The values are presented in Table 4.2.1 for all process chemicals of which the data is published. The GWP is a simplified index to determine the compound's contribution to global warming. GWP is calculated based on the chemical's radiative properties and a carbon dioxide reference GWP equal to one. Publications commonly report the GWP for 20, 50, and 100 years. This is because the GWP is dependent on the ATL. The ATL is defined as the time necessary for the degradation of half of the sample in tropospheric conditions. Table 4.2.1 is incomplete because there is limited availability of the data. This could be caused by two reasons. One is that research in this area of environmental studies is relatively new and underdeveloped. The second reason for the lack of data could be because the chemicals are not of environmental concern based on these selected properties. After reviewing the data that is available, the conclusion can be

Table 4.2.1: Available Environmental Impact Data of Process Chemicals

Compound	GWP			ATL	ODP
	20 year	100 year	500 year		
CH ₃ OH		2.8 ^a		10-30 days ^b	
CH ₃ OCHO ^b				2 days	
SO ₂ ^b				relatively short	
CH ₃ OCF ₃ ^c	2200	656	202	5.7 years	

a. Forster, b. Seinfeld, c. Good

made that the process chemicals do not pose an immediate threat the environment based on their ATL and GWP.

Table 4.2.2 presents the environmental, health and safety information for all of the process chemicals. Information for methyl fluoroformate was unavailable, so we have substituted information for methyl formate, a structurally similar species. Methyl fluoroformate contains a fluorine atom instead of a hydrogen atom on the carbonyl carbon atom. Methyl formate is a highly toxic gas. Because of the hazards associated with fluorinated compounds, the addition of fluorine will likely make the chemical more toxic, reactive and dangerous. Before using methyl fluoroformate in any new processes or experiments, a comprehensive safety, environmental, and material compatibility study should be completed.

Also presented in Table 4.2.2 is relevant information on HFE-7200. Again, this is due to the lack of data on our final product, HFE-143a. The chemical formula for HFE-7200 is C₄F₉OC₂H₅. This HFE was selected because it resembles HFE-143a in the sense that all of its fluorines are on one side of the ether bond. When comparing HFE-7200 to HFE-143a it is important to note that HFE-7200 is a bigger molecule and exists in the liquid phase at standard temperature and pressure. This will cause differences in responses to the accidental release measures and other environmental and safety considerations.

For a majority of the process chemicals, the accidental release measures include isolating and ventilating the area before proceeding to contain leak or spill. During the clean up procedure, utilize all necessary personal protective equipment including respirators. In some cases, the toxic gases are denser than air; therefore it is important to prevent contamination to sewers, basements, workpits and other low areas.

Table 4.2.2: Environmental Considerations of Process Chemicals

Compound	Accidental Release Measures	Disposal Method	Degradation Byproducts	Incompatibilities	H ₂ O Solubility	Vapor Pressure	EPA Regulations
CH ₃ OH (l)	Ventilate and isolate area. Remove all sources of ignition. Contain liquid with non-sparking tools or absorb with inert material. Do not use combustible materials. Place in disposal container. ^a	Handled as hazardous waste and sent to a RCRA approved incinerator or disposed in a RCRA approved waste facility. ^a	CO ₂ and H ₂ O; CO ₂ , CO, and CH ₂ O when heated to decomposition. ^a	Strong oxidizing agents such as nitrates, perchlorates or sulfuric acid. Will attack some forms of plastics, rubber, and coatings. May react with metallic aluminum and generate hydrogen gas. ^a	Miscible. ^a	97 mm Hg (20 °C) ^a	CERCLA Hazardous Waste No. U154 ^b
COF ₂	Isolate and ventilate area. Prevent release to sewers, basements and work pits. Reduce vapor with water spray. Wash contaminated area with water. ^c	Waste gas flared through appropriate burner with flash back arrestor. Hazardous gases formed from combustion must be scrubbed before atmospheric discharge. ^c	None any worse than the compound itself. ^c	Reacts with most metals in the presence of water, releasing hydrogen gas and causing corrosion. Violent reactions with alkalis. ^c	Hydrolyzed ^d		
SF ₄	Isolate area and stay upwind. Spray water to reduce vapors without letting the water touch the material. Small spill: flood with water, Large spill: dike to prepare for later disposal. ^e		HF, SOF ₂ . Combustion products: acid halides, oxides of sulfur, fluorinated compounds. ^d	Contact with water or moist air may form flammable and/or toxic gases or vapors. ^e	Reacts violently. ^e	26.4 MPa (25 °C) ^d	TSCA Inventory Status, SARA Hazard Class: C, D ^e
CH ₃ OCHO ^f	Isolate area and remove all sources of ignition. Stay upwind and reduce vapors with water spray. Small spills: absorb with non-combustible material. Dispose of properly. Large spills: dike area for later disposal.		Combustion products: unknown	Acids, bases, oxidizing materials, combustible materials	30%	467.4 mm Hg (20 °C)	TSCA Inventory Status, SARA Hazard Class: A, D
SO ₂	Isolate area. If equipment leak, purge piping with inert gas before repairing. If container leak seek emergency assistance. See MSDS ^g	Return to authorized distributor in the shipping container, labeled with valve outlet plugs or caps secured. ^g	Leads to the formation of H ₂ SO ₄ in the atmosphere	Reacts violently with peroxides, chromates, dichromates, permanganates and oxygen difluoride. Forms sulfuric acid in water. Corrodes most metals. ^g	8.5 g/ 100 mL H ₂ O (25° C) ^d	49.1 psia ^g	NAAQS 1° Std: 0.03 ppm (annual arithmetic mean), 0.14 ppm (24 h); 2° Std 0.5 ppm (3 h). SARA Hazard Class: B, C, D, E ^h
CH ₃ OCF ₃ ⁱ	N/A	N/A	COF ₂ , SF ₄ , CF ₃ OC(O)H, CO ₂	N/A	N/A	N/A	N/A
HFE-7200 ^j	Isolate and ventilate area. Use inorganic absorbent material to contain spill. Work from the edges inward. Clean residue with soap and water. Dispose of absorbent and residue containing solution in a metal container.	Incinerate in industrial facility with combustible material. Facility must be able to treat halogenated materials.	HF, perfluorinated acid fluorides	Strong bases	Insoluble	109 mm Hg (25 °C)	
C ₃ H ₆ ^k	Shut off all ignition sources and ventilate. Wear PPE		CO, CO ₂	Oxidizers	22.05 cm ³ /100 ml	136.5 psig	
HF ^l	Evacuate area and use PPE. Purge with inert gas.	Return to supplier	Hydrogen and toxic fluoride compounds	Water, organic materials and metals.	Miscible	15.6 psia (STP)	SARA Hazard Class: A, B, C, D, E.

a. Methyl alcohol MSDS; b. Watts 1997; c. Carbonyl fluoride MSDS; d. Tsai 2005; e. Sulfur tetrafluoride MSDS, f. Methyl formate MSDS, g. Sulfur dioxide MSDS, h. Seinfeld 2006, i. Pacansky 1997, j. HFE-7200 MSDS, k. Propene MSDS, l. Hydrogen fluoride MSDS

To reduce the concentration of toxic fumes or vapors in the air, Delta Group suggests misting the process space with water (unless otherwise noted). However, some of the process chemicals are incompatible with water, so it is important not to let water contact the bulk material.

Because of the corrosive nature of the carbonyl fluoride reactant, the interior of the first reactor must be glassed lined. This is also true for the pipes, heat exchangers and all other upstream process equipment. This will prevent contact any contact with metals, greatly reducing the chance of a leak in the system.

It is also important to note that only one of the process chemicals is subject to polymerization upon disposal. Propene is very unstable and will violently polymerize or decompose under high temperatures or pressures ("Propylene"). The propene in our process is in a closed loop refrigeration cycle. Only a small percentage of the total propene used is lost annually, so the waste is insignificant.

Sulfur oxides are one of the six criteria pollutants regulated by the National Ambient Air Standards (NAAQS) as a part of the EPA's Clean Air Act (Seinfeld). The primary standard protects public health including sensitive populations such as children and the elderly. The secondary standard protects public welfare, considering visibility and damage to animals, agriculture and architecture. As shown in Table 4.2.2, the primary standard for sulfur dioxide is 0.03 ppm (annual arithmetic mean) and 0.14 ppm for 24 hours. The secondary standard is 0.5 ppm for 3 hours. The hourly standards are not to be exceeded more than once per year. It is also important to note the degradation byproducts of methanol contain carbon monoxide, another EPA criteria pollutant.

Anthropogenic emissions of sulfur dioxide acidify precipitation (Seinfeld). Sulfur dioxide hydrolyzes in water vapor equilibrating with the sulfite and bisulfite ions, the 6th oxidation state of sulfur, S(VI). Sulfuric acid is also formed by an oxidation process. Atmospheric oxygen, dihydrogen peroxide, or ozone, in concert with a number of natural occurring catalysts, oxidize S(IV) to S(VI) creating sulfuric acid. Sulfur dioxide reacts with hydroxyl radicals in the troposphere. The product, hydrogen sulfite, reacts with oxygen to form the hydroperoxyl radical and sulfur trioxide, which is also an EPA regulated Hazardous Air Pollutant. Sulfur dioxide also reacts with oxygen to form sulfur trioxide. However due to the lack of a natural catalyst, the rate of that reaction is slow. Sulfur trioxide in contact with water vapor in the air produces sulfuric acid as well. The presence of sulfuric acid drastically reduces the pH of the cloudwater. The pH of uncontaminated rain is 5.6. Deviation from neutral pH of 7 is because of carbon dioxide dissolution. The average pH of precipitation in the US in 2004 ranges from 4.3 to 6.6. Therefore the emission of sulfur dioxide can cause acidic deposition.

In our process, sulfur dioxide is isolated from the product stream through a series of distillation columns. As shown on the PFD in Section 2.4, the SO₂ leaves the system in stream 26 from the bottoms of column T-104. There is a market for the almost pure (99.6% by mole) liquefied sulfur dioxide, making our waste a salable product and

eliminating the need for disposal. Refer to the economic analysis in Section 5 for details regarding the sale of recycled sulfur dioxide. The final HFE product stream and the HF byproduct stream both contain 0.05 mole percent sulfur dioxide. None of the sulfur dioxide in our process is emitted to the atmosphere.

The EPA's Resource Conservation and Recovery Act (RCRA) considers a waste to be hazardous if it may cause an increase in mortality, serious irreversible or incapacitating reversible illness or if it poses a hazard to the health of humans or the environment when inappropriately handled (Watts). Wastes are deemed hazardous by meeting at least one of four characteristics: corrosivity, ignitability, reactivity, and toxicity. Every single process chemical used in our design meets at least one of these criteria. Companies that dispose of over 1000 kg per month of hazardous waste are considered a generator by the RCRA. This requires the company to file a Notification of Hazardous Wastes Activity form to receive an EPA identification number. Upon transportation for disposal, accumulated waste can only be stored for 90 days without a Treatment, Storage, and Disposal (TSD) permit. Small quantity generators produce 100-1000 kg per month of hazardous waste and are less strictly regulated. To dispose of hazardous waste the generator must complete a Uniform Hazardous Waste Manifest. The waste must be transported by a licensed hazardous waste transporter to a TSD facility. Because all of our byproducts and unreacted feed materials are either completely recycled or salable products, no hazardous waste is generated during HFE-143 manufacture. If there is suddenly no demand for hydrofluoric acid and/or sulfur dioxide, then it must be treated as hazardous waste and disposed of accordingly.

The EPA's Toxic Substances Control Act (TSCA) of 1976 imposes restrictions on the inventory list chemicals while also demanding adequate reporting, record-keeping, and testing requirements ("Summary"). A Significant New Use Notice (SNUN) must be filed with the EPA at least 90 days prior to the use of the listed substance. This can be accomplished by filling out a premanufacture notice (PMN). The TSCA also requires the EPA notification if information is obtained revealing that a compound is potentially dangerous to human health or to the environment and not currently on the inventory list. In our design, four of our process materials are on the TSCA Inventory, while the others are certainly dangerous to human health. The transportation of hazardous material is heavily regulated by the EPA. Relevant transportation information is presented in Table 4.2.3.

Methanol and hydrogen fluoride are both on the RCRA Hazardous Waste U List (Watts). This means that the compounds are only regulated as commercial products, not the byproducts of industrial operations. U List materials are classified as toxic.

There are five SARA Hazard Classes denoted with the letters "A" through "E" ("Protocol"). The "A" class represents a fire hazard and includes combustible, flammable liquids, oxidizers and pyrophoric substances. Methyl formate and hydrogen fluoride are class "A" hazards. Class "B" denotes that the compound is reactive. This includes unstable and water reactive chemicals along with organic peroxides which includes HF and SO₂. Hazard class "C" corresponds to a sudden release of pressure, which includes compressed gasses

Table 4.2.3: Process Chemical Transportation Information

Compound	Proper Shipping Name	ID No.	Hazard Class	Labeling Requirements
CH ₃ OH ^a	Methanol	UN1230	3, 6.1	
COF ₂ ^b	Carbonyl fluoride	UN2417	2	Toxic gas, corrosive
SF ₄ ^c	Sulfur tetrafluoride	UN2418	2.3	Toxic gas, corrosive
CH ₃ OCHO ^d	Methyl formate	UN1243	3	Flammable liquid
HF ^e	Hydrogen fluoride, Anhydrous	UN1052	8	Corrosive, poison, inhalation hazard
SO ₂ ^f	Sulfur dioxide	UN1079	2.3	Poison gas, corrosive

a. Methyl alcohol MSDS, b. Carbonyl fluoride MSDS, c. Sulfur tetrafluoride MSDS, d. Methyl formate MSDS, e. Hydrogen fluoride MSDS, f. Sulfur dioxide MSDS

and explosives. Sulfur tetrafluoride, hydrogen fluoride and sulfur dioxide fall under this category. Immediate or acute health hazards are a part of class “D.” This implies that the chemicals, as a result of short term exposure, cause a rapid, adverse effect to target organs. This includes highly toxic materials, corrosives, irritants, and sensitizers. Sulfur tetrafluoride, sulfur dioxide, hydrogen fluoride and methyl formate are class “D” hazards. Lastly, class “E” is the delayed or chronic health hazard class. Class “E” materials cause adverse effects on a target organ as a response to long term exposure. These materials are usually carcinogens. Sulfur dioxide and hydrogen fluoride are also included in this class. Hydrogen fluoride is listed on all five SARA hazard class lists.

Because of the potential to cause acidic rain and its appearance on four out of the five SARA Hazard Class lists, sulfur dioxide is considered the most environmentally perilous process chemical.

Section 5: Economic Analysis and Hazards

As the proposed design is based on relatively unstudied chemical species, Delta Group had to make several assumptions to perform an economic analysis. Delta Group's analysis assumed that the process byproducts were salable, since the process purified them to market quality. It was also assumed that the selling prices of these byproducts were stable and the increase in supply from due to this plant wouldn't significantly affect the global market for them. According to market data from the Chemical Marketing Reporter, the annual production of hydrofluoric acid in North America for 2002 was 434,000 tonnes ("Chemical"). For 2004, sulfur dioxide production in North America was 566,000 tonnes ("Chemical"). The annual production of hydrofluoric acid and sulfur dioxide in the plant design are approximately 2,000 tonnes and 3,200 tonnes, respectively. It is very likely that these quantities, representing such a small fraction of the market, will have little or no impact on market prices.

Delta Group also assumed a stable market price for the starting materials in the process that have accurate market prices – methanol, propene and water. As of 2001, the annual production of methanol was almost 1.8 billion gallons ("Chemical"). Propene production for 1999 was 36.4 million pounds ("Chemical"). The plant design required quantities of these products representing very small fractions of the total market, which made the assumption of pricing stability for these compounds fairly safe. The team assumed that the water purchased from Tucson Water Supply would be sufficiently pure to be used as both process water and cooling water.

Delta Group was unable to find reliable information for either carbonyl fluoride or sulfur tetrafluoride. The team did find information for sulfur tetrafluoride, but the price quoted by Custom Gas was \$16.5 thousand per 40 kg ("Re:Re: Sulfur"). At this price, the process was automatically economically unfavorable. The team then decided to design the plant regardless to determine at what maximum price carbonyl fluoride and sulfur tetrafluoride could be purchased and still produce an acceptable profit.

The first design done by Delta Group was using liquid nitrogen as a coolant. This case used pumps, compressors, distillation towers, heat exchangers, and autoclave reactors, all of which were costed using the equations found in Seider et al (2003). The bare module equipment cost for this design was found to be on the order of \$27 million. When pricing the utilities, it was found that the required liquid nitrogen would cost approximately \$85 million per year. Even though liquid nitrogen is relatively cheap at \$0.40 per liter, the amount required was found to be on the order of 18 tonnes per hour due to the relatively small heat duty provided by the liquid nitrogen ("Cryogenics"). At this point, the team decided that an alternative coolant was required (Appendix A.6).

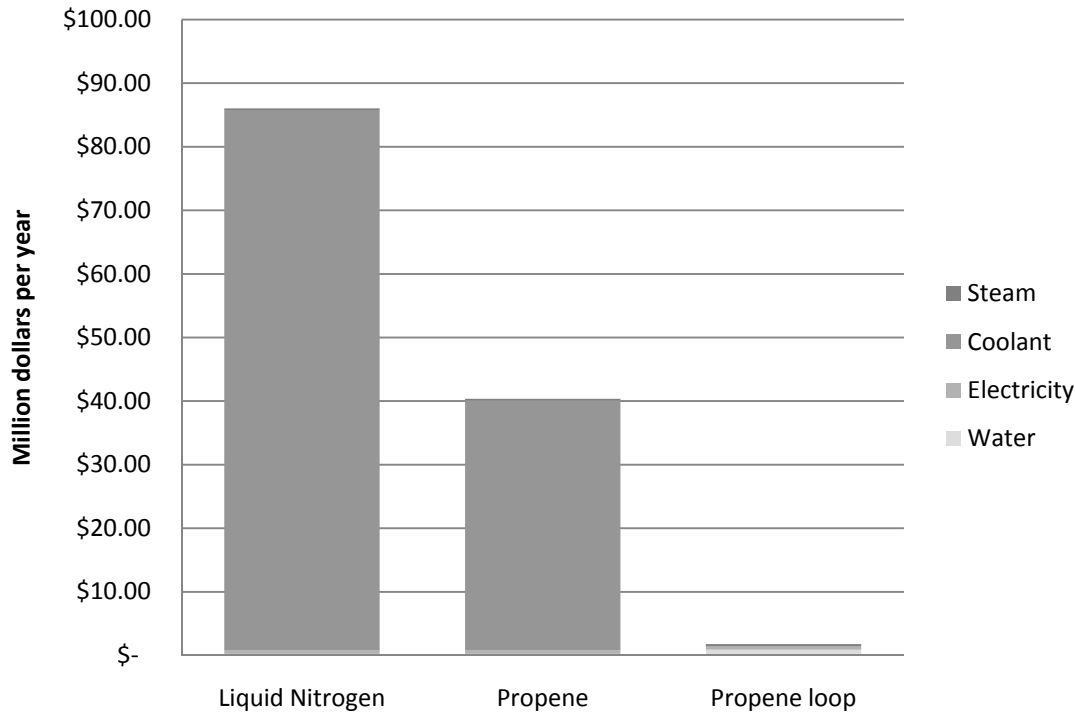


Figure 5.1: Utilities Cost Comparison

The second design used compressed propene as the coolant. The equipment between the liquid nitrogen case and the propene case wasn't found to change significantly, so there was no measurable difference in equipment price. The required amount of propene was significantly lower, and with its price at \$132 per tonne ("Propylene Prices"), the total required price per year was found to be approximately \$39.3 million per year (Appendix A.7). Even though this is a savings of approximately \$45 million per year from the previous design, the team decided that another optimization was needed, as this cost was still significantly larger than the cost of any of the other utilities, as shown in Figure 5.1.

The next optimization done by Delta Group was including a refrigeration loop in the process, which would serve to recycle the coolant. This loop added three compressors, a heat exchanger, and another pump, thereby increasing the bare module equipment cost to approximately \$37 million. The extra pumps and compressors also increased our electricity requirements, increasing the cost by about \$24 thousand per year, and the water required for the heat rejection medium was found to cost approximately \$740 thousand per year. However, this served to decrease our annual coolant cost to approximately \$300 per year. The team also changed from using cooling water to steam to heat the cryogenic streams in E-109 and E-112, which saved approximately another \$23 thousand dollars per year due to the increased amount of available heat from the steam (Figure 5.1).

As is shown by Figure 5.1, the most significant utility cost in this is the coolant. Even though Figure 5.2 shows an increased cost in equipment between the base cases and the optimized case, the change in the utilities was more than enough to overcome this increase.

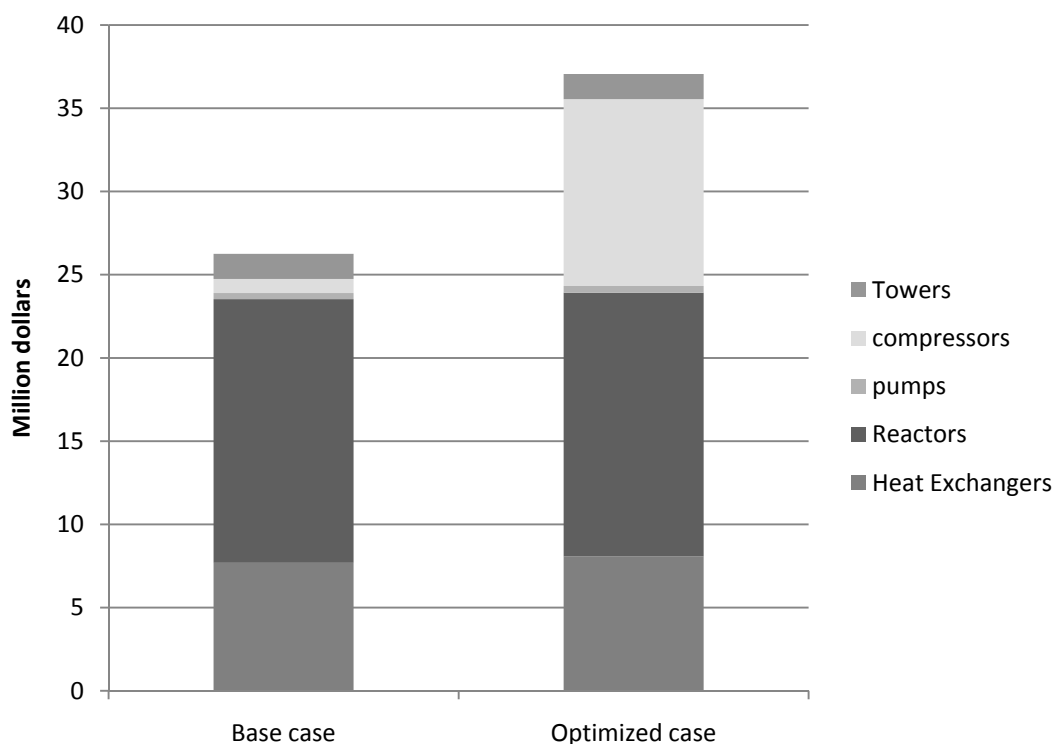


Figure 5.2: Equipment Cost Comparison

In order to maximize income, the team decided to sell both sulfur dioxide and hydrogen fluoride as well as our product HFE. The price of the sulfur dioxide was found to be \$2.58 per pound, as quoted by Advanced Specialty Gasses, giving a total amount of approximately \$18 million per year (“Re: Contact”). In order to sell the HF, the team decided to dissolve it in water and produce 70 wt% hydrofluoric acid. According to Spectrum Chemical, this product could be sold for \$24 per gallon, giving a total yearly price of approximately \$15 million per year (“Hydrofluoric Acid”). As no bulk price was found for the trifluoromethyl methyl ether, the team decided to create a selling price based off of R-134a, the HFC the ether is intended to replace. As informed by our mentor, trifluoromethyl methyl ether has a heat capacity almost identical to R-134a on a molar basis (Blowers). Converting this to a per mass basis, the team multiplied this ratio to the \$3.1 per pound of R-134a, as quoted by Lenz Distributing, Incorporated to get a price of \$3.16 per pound of ether (“R134a”). Based on this, the yearly income due to ether was found to be approximately \$70 million, giving a total yearly income of approximately \$103 million (Figure 5.3).

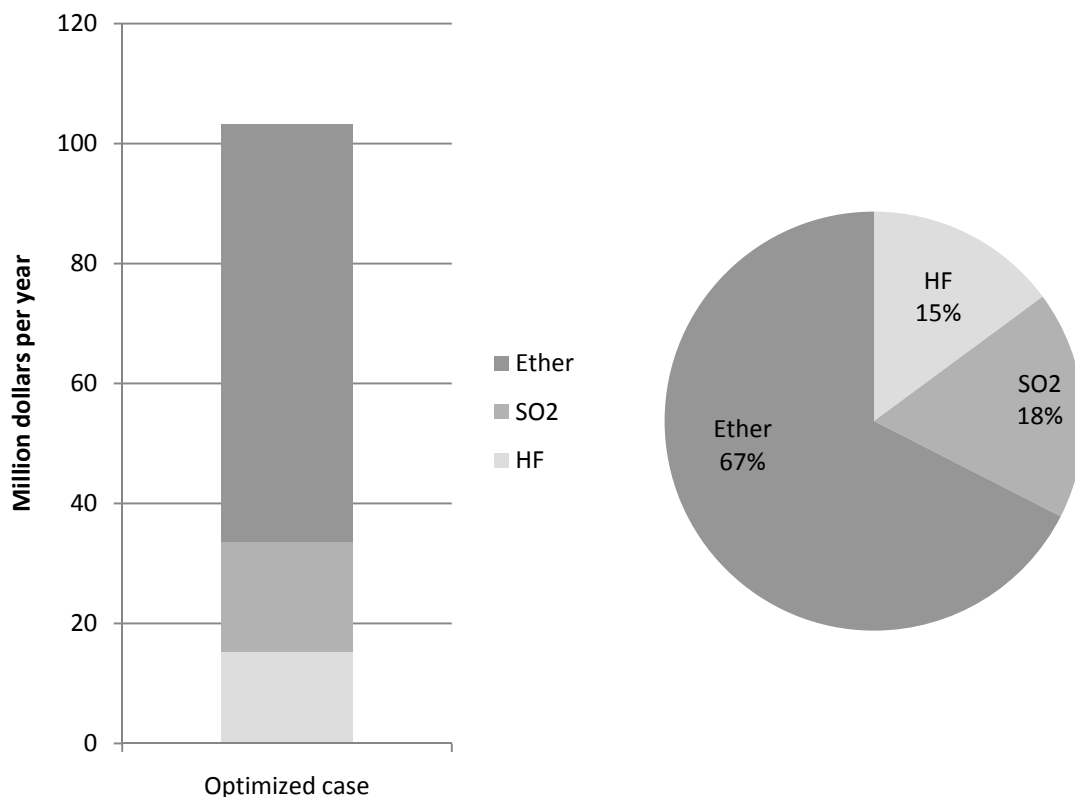


Figure 5.3: Product Value Comparison

From here the team used the economic calculations and cash flows based on the Guthrie method to determine Net Present Value (NPV), assuming that COF_2 and SF_4 could be purchased for a minimal amount compared to the rest of the materials. The team then set an IRR of 25% and determined what price the COF_2 and SF_4 combined could be purchased for (Appendix B.1). From this, it was found that the maximum price these materials could be purchased for was approximately \$5.23 thousand per tonne, assuming an identical price for both compounds, or approximately \$63 million for a year's supply of both materials combined.

With this price of reagents found, the NPV of the process could be found, based on multiple interest rates. With 0% interest, the process approaches \$440 million after 30 years, while at 10% and 20% it approaches \$92 million and \$16 million, respectively (Figure 5.4). An interesting note to this graph is that after approximately 20 years, the net present value asymptotically approaches the aforementioned numbers, due to the function of interest in the equation.

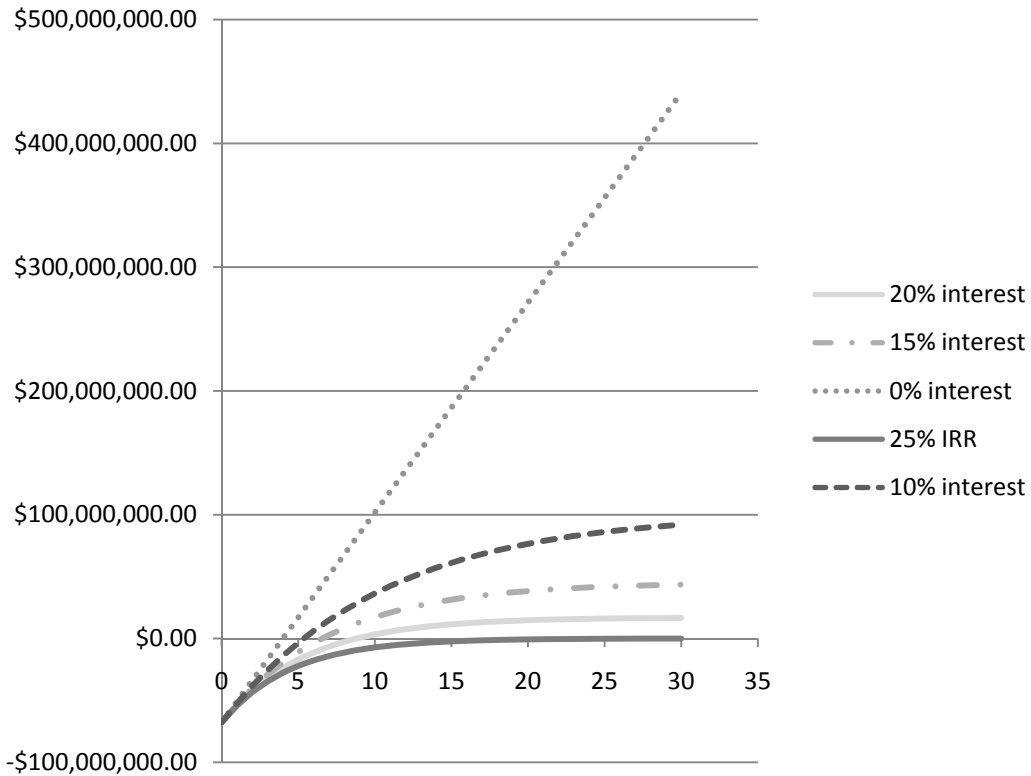


Figure 5.4: Net Present Value over life of plant

As is shown by Figure 5.5, the process depends very intensively on the cost of the COF_2 and SF_4 , as it makes up 92% of the reagent cost when determined via the above method. If the cost of these products was to increase beyond the determined threshold, the plant would immediately become unprofitable over the lifespan, and the IRR would be insufficient to justify the investment. Another economic hazard would be the price of the electricity; if the price of energy or water were to increase within the next 30 years due to any number of factors, not the least of which being a shortage of energy, our process would become significantly less profitable, as electricity currently amounts to 33% of our current utility costs, and water 50% (Figure 5.6).

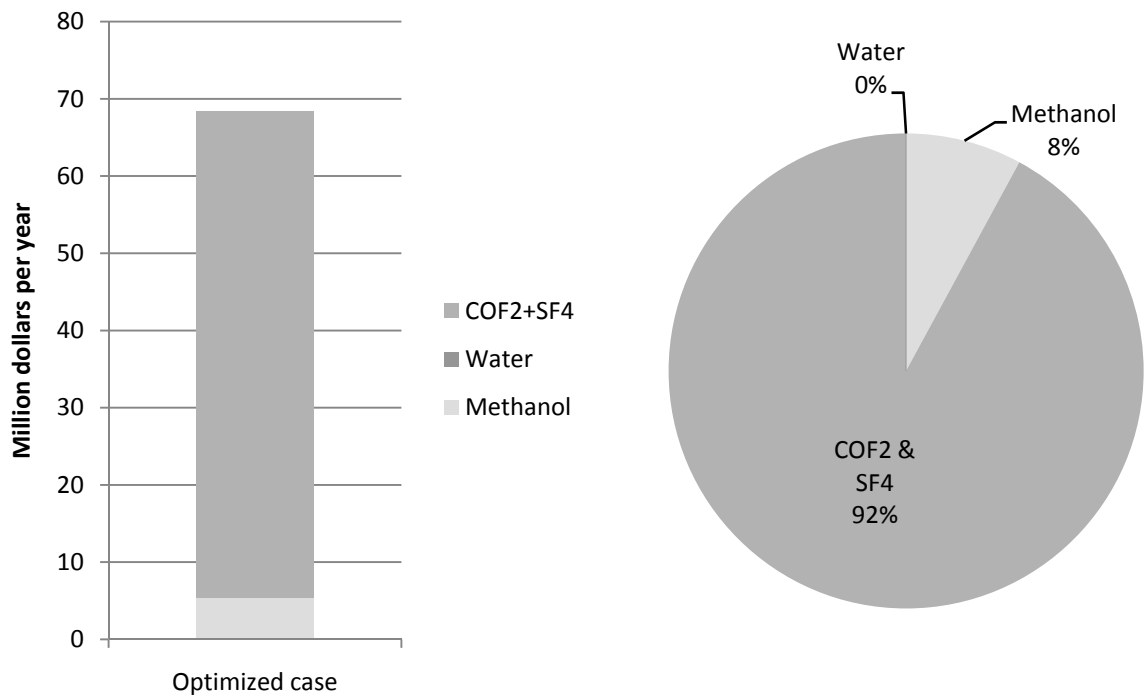


Figure 5.5: Reagent Cost Comparison

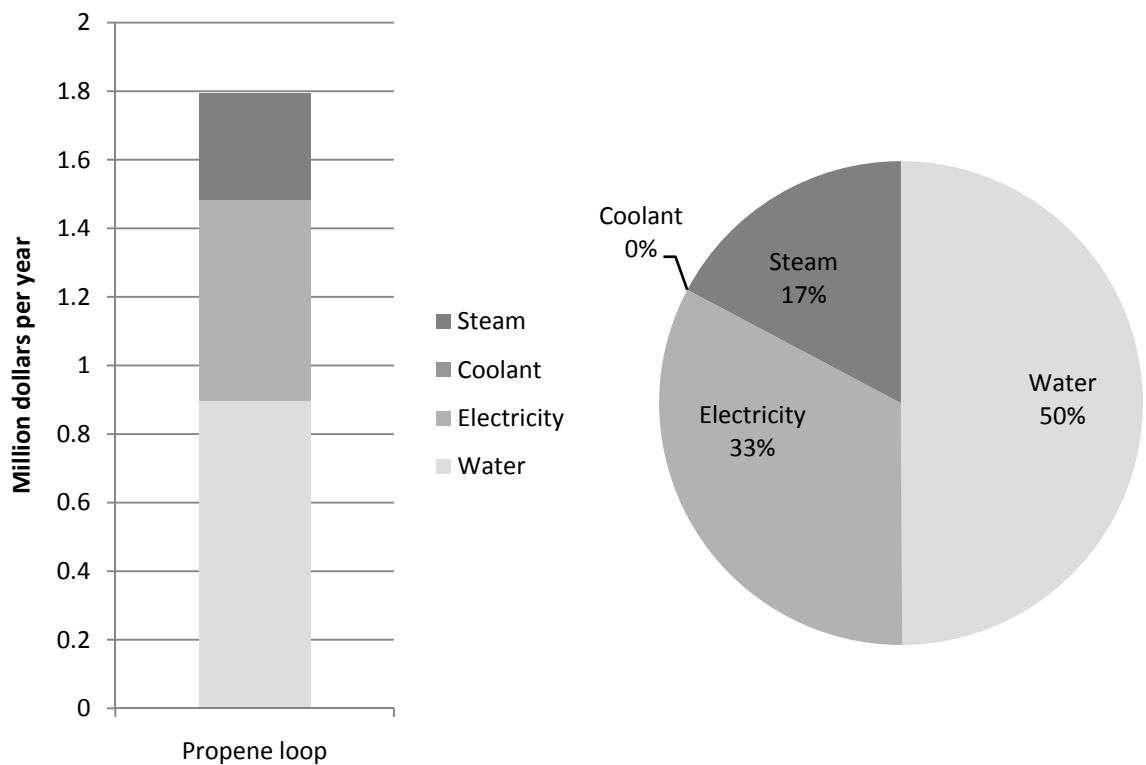


Figure 5.6: Optimized Utilities Comparison

As a sensitivity analysis, the team decided to see how the economics would change if the COF₂ and SF₄ could be purchased at a lower amount. The team decided to set this amount to be \$2.5 thousand per tonne for both compounds. From this new input, the team discovered that the NPV at 0% would reach approximately \$1.06 billion after 30 years. At 10% and 20% interest, the NPV would be approximately \$287 million and \$120 million, respectively, and the IRR would be approximately 56% (Figure 5.7). At this new price, the COF₂ and SF₄ would account for 85% of the reagents costs, which suggests that the economic hazards for this case would be very similar to those of the previous case (Figure 5.8).

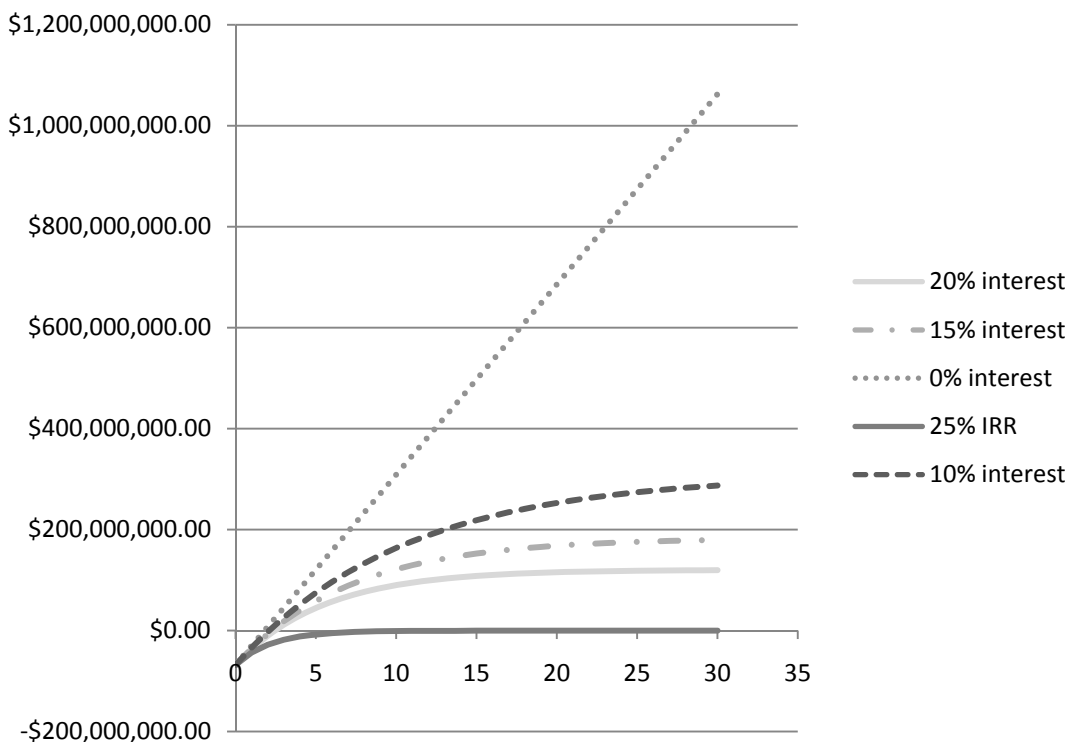


Figure 5.7: Net Present Value for theoretical case

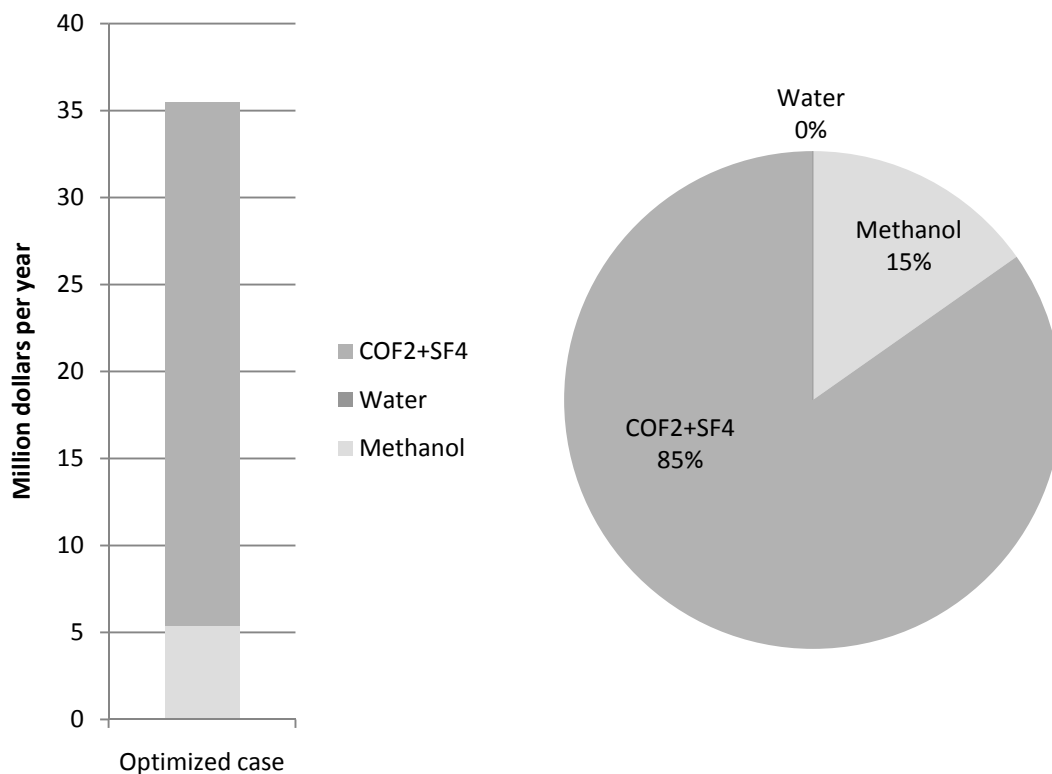


Figure 5.8: Reagent Cost Comparison for theoretical case

As discussed, this process is very economically unstable; the entire economic analysis is based upon the assumption that the COF₂ and SF₄ can be purchased at a price that would make this process economically feasible. However, if the Kyoto Protocol were to be signed by the United States, this HFE would be in a very high demand with a very stable market. This might allow the team to sell the ether at a price higher than shown in this analysis, which would significantly alleviate any fluctuations in reagent or utility prices. It should also be noted that the sale of the byproducts significantly increased the economic feasibility of this process, providing 33% of the total annual income; without this income the product sale price would be \$70 million dollars, while the total reagent costs would be approximately \$67 million.

Section 6: Conclusions & Recommendations

This process has the potential to be very profitable, but contains many economic hazards. The profitability of this process depends very strongly on the available purchase price of the carbonyl fluoride and sulfur tetrafluoride. If annual supply can be purchased for less than approximately \$63 million and all other factors remain constant, this process can be quite profitable, as shown in Section 5. However, as shown in Section 4, this process also has significant health and safety hazards. The team cannot give or deny a build recommendation without further information derived from an analysis of the process. This further work should investigate the cost of safety training and equipment for all personnel, the synthesis of the reagents on site, the inclusion of a cooling tower to reuse cooling water, alternative refrigerants, and determining the reaction kinetics of the process.

As the process contains many health hazards to the employees, the amount of safety training and safety equipment may impact the economics of the plant. It is recommended that all employees complete extensive training to fully understand where hazards may occur, what could happen if these hazards do occur, and how their personal safety equipment works.

The synthesis of reagents on site could impact the process considerably. On-site synthesis has the potential of increasing annual revenues if this synthesis is found to be cheaper than market value. Furthermore, as the reagents are hazardous, synthesizing them on-site would reduce the potential hazards of the system by reducing the amount of these chemicals present at any given time and by eliminating the risks encountered during transport.

As the annual cost of the cooling water in the optimized case was found to be half of the total price of utilities, the team would recommend the inclusion of a cooling tower to recycle the water and reduce annual costs. The cooling water sections of the process were designed so that the cooling tower would be a drop-in addition for future work. Work should also be done to determine whether the heating requirements in E-109, E-110, and E-112, and E-113 could be met with cooling water instead of steam, as with the recycle this might be cheaper. It could also be possible to recycle the condensed steam as cooling through this cooling tower as well, thereby further reducing the volume of water purchased from the city.

Investigation of alternative refrigerants in the refrigeration cycle is recommended. The current propene must be compressed up to a pressure of 25 bar in order for the water to be an acceptable heat rejection medium, which creates potential hazards. Furthermore, propene is a hydrocarbon, and is therefore combustible. If a leak were to occur, or oxygen

be introduced into the refrigeration loop somewhere, immediate response would be required by the employees to minimize the potential safety hazard. Other refrigerants might have a cheaper price, a higher heat capacity, and be less flammable, and therefore would be significant improvements over the current refrigerant.

The team heavily recommends further analysis of the kinetics of the two reactions to determine how the process could be further optimized by improving yields or increasing reaction rates. In many cases, turning one large reactor into multiple smaller reactors connected in series will result in a more efficient process; therefore, this analysis should be performed to see if the reactor costs can be minimized. With further knowledge of the kinetics of these reactions, it might also be possible to increase the yield of the trifluoromethyl methyl ether and other salable products, thereby increasing the annual income and decreasing the cost of the distillation towers by requiring fewer stages due to the increased inlet purity.

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Appendices

Appendix A: Process Calculations

A.1: Determining a Basis for Design

A.2: Usefulness of Intermediate Heaters

A.3: Determining Pump Requirements from Pressure Drop Heuristics

A.4: Stream Data from ASPEN Simulations

A.5: Equipment Data from ASPEN Simulations

A.6: Determining Required Nitrogen Flow Rates

A.7: Determining Required Propene Flow Rates

A.8: ASPEN Process Flowsheet

A.9: Aspen Process Stream Table (complete)

A.10: ASPEN Steam Line Flow Sheet

A.11: ASPEN Steam Line Stream Table (complete)

A.12: ASPEN Column Tray Details