Vinyl Chloride Production

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Introduction

The goal of this project is to design an environmentally friendly, safe, and economically profitable vinyl chloride production plant. Environmental friendliness requires that the design go beyond the minimum Environmental Protection Agency (EPA) compliance regulations while maintaining plant profitability. Plant safety includes addressing deviations from normal operation that may have adverse effects on employees or the surrounding community.

Process Design

Balanced Process Overview

The process chosen for vinyl chloride production is a combination of direct chlorination and oxychlorination called the balanced process. Direct chlorination by itself is a process that operates at lower temperatures and produces fewer by products when compared to oxychlorination. Oxychlorination is used in vinyl chloride production because it consumes the hydrochloric acid (HCl) generated by 1,2 dichloroethane (EDC) pyrolysis. This consumption of HCl is the main advantage of using the balanced process. Currently, nearly 95% of the world's supply is produced using this process, see Figure 1 for the balanced process PFD. The main reactions in the production of VCM are:

Direct chlorination	$CH_2CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$ (EDC)
Oxychlorination	$CH_2CH_2 + 2\ HCl + \frac{1}{2}\ O_2 \rightarrow ClCH_2CH_2Cl + H_2O$
EDC pyrolysis	$2\ ClCH_2CH_2Cl \rightarrow 2\ CH_2CHCl + 2\ HCl$
Overall reaction	$2\ CH_2CH_2 + Cl_2 + \frac{1}{2}\ O_2 \rightarrow 2\ CH_2CHCl + H_2O$

Process Outline

The five main processes used in the production of VCM are shown in Figure 1. The five processes include: direct chlorination of ethylene to form EDC, oxychlorination of ethylene to form EDC from recycled HCl and oxygen, purification of EDC, thermal cracking of EDC to form VCM and HCl, and purification of VCM. The reactors were modeled using kinetic data and theoretical design equations to determine specific design parameters. A Pro II simulation was performed on the entire process using various design parameters in order to develop the optimal design.

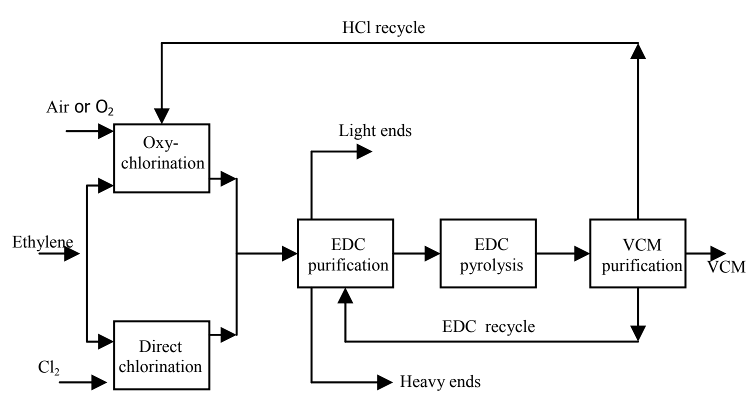

Figure 1: Vinyl Chloride Plant PFD

Direct Chlorination Design

Ethylene and chlorine combine in a homogeneous catalytic reaction to form EDC. Due to high selectivity, ferric chloride is the catalyst of choice for chlorination of the ethylene. Normally, the reaction rate is controlled by mass transfer, with absorption of ethylene as the limiting factor. Direct chlorination process equipment includes: a plug flow tubular reactor and a caustic scrubber. See Figure 2 for the direct chlorination P&ID.

Oxychlorination Design

The oxychlorination reactor is a PFTR with cupric chloride catalyst packed in the tubes while cooling water flows on the shell side for temperature control. Some oxychlorination processes utilize a fluidized bed reactor, but no heat recovery is possible with these reactors. An optimal temperature of 305 ^{o}C was determined by the reactor model. An increase in by-product formation is observed with increasing reactor temperature. This is due to an increase in oxidation of ethylene to carbon oxides and increased cracking of EDC. The oxychlorination design also contains a caustic scrubber to remove HCl and a flash to remove accumulation of light impurities. See Figure 3 for the oxychlorination P&ID.

EDC Purification

The EDC from direct chlorination, oxychlorination, and the recycle stream from the cracking step must be purified before pyrolysis. The EDC must be purified to 99.5 wt%. First, the combined EDC is washed with water in a wash tower. This is done to remove a majority of the water produced by the oxychlorination reaction. The EDC is then purified by two distillation columns. The first column, referred to as the lights column, removes water and low boiling point impurities. The bottoms from the lights column, which have lower volatility, are combined with the pyrolysis feed purge; these two streams combine to form the feed of the heavies column. The heavies column removes the higher boiling point impurities. The pure EDC composition is 99.3%, and is the overhead product of the heavies column. See Figure 4 for the EDC purification P&ID.

EDC Pyrolysis and Quench Design

Pyrolysis (thermal cracking) of EDC produces vinyl chloride. Pyrolysis of EDC is an endothermic reaction (ΔH=71KJ/mol) that is carried out in a furnace. The furnace consists of four main sections: a radiation section, a convection section, a shock section, and a stack. The heat required for endothermic reaction is supplied by combustion of fuel from the firebox burners. The fire box operates at 500 ^{o}C. The main reaction which yields VCM and HCl is a homogeneous, first order free-radical chain mechanism. See Figure 5 for the EDC pyrolysis P&ID.

Vinyl Chloride Purification

Two distillation columns are used to separate VCM from EDC, HCl and the remaining by-products. The first column, HCl column, distills the hydrogen chloride mixture to a pure overhead product. This HCl is recycled to the oxychlorination reactor. The bottoms product of the HCl column is fed to the second column, the VCM column. A VCM product of 99.9 wt% is produced as the overhead product of the VCM column. The bottoms of the VCM column are recycled to the lights column for re-purification. See Figure 6 for the VCM purification P&ID.

Heat Integration

The vinyl chloride plant process design includes a heat-integrated network. This network was designed using the pinch design method. Based on the stream data and the temperature targets that are required for the process a table cascade was constructed to find the minimum utilities. The pinch method resulted in a reduction of hot utility from 1247 to 903 MMBtu/hr and a corresponding reduction of cold utility from 652 MMBtu/hr to 308 MMBtu/hr.

Plant Location

The plant will be located in Taft, Louisiana. The decision making process utilized a factor rating maximization method. This method takes several attributes of a potential location into consideration when comparing it to other locations. These attributes or factors are ranked according to their importance to the success of the plant. These factors are all placed into the same scale so as to not distort the weight of a factor that inherently has larger values than others.

Market Analysis and Economics

Demand

The increase in demand for polyvinyl chloride (PVC) results in an increase in the demand for vinyl chloride monomer (VCM). By studying the demand over the past ten years, the future demand was estimated using a forecasting analysis method. The forecasting method uses three different fits to predict the future demand: a linear fit, an assumption of 5% increase per year, and an exponential fit. From an average of the three trends, it was found that the demand of the vinyl chloride monomer could be estimated to be approximately 4.1 billion pounds per year within the next three years, 6.4 billion pounds per year in five years, and 10.5 billion pounds per year in the next eight years. In order to be certain of the profitability of each plant capacity Monte Carlo simulations and a risk analysis were performed. A comparison of the net present worths (NPW's) will determine the optimal plant capacity.

Forecasting

The prices of raw materials and products were forecasted for the next 20 years, using historical price data from the past 20 years. A graph of the raw material and VCM prices for each year was created. The mean of this graph was extended in order to predict future prices. However, merely using the mean values of the plot is not sufficient, so the prices were estimated by generating random numbers of the mean and standard deviation.

Economic Analysis

The capacity of 6.4 billion pounds per year was chosen in order to meet the demand of VCM for the next five years. The total plant cost was approximated from the total capital investment, total product cost, and environmental cost. The capital investment from the total equipment cost was found using the "Ratio Factor" method described in Peters and Timmerhaus. However, these factors were catered specifically to the capacity of our plant. The production cost is the cost associated with plant operation. The environmental cost includes installing and running the vapor/liquid waste treatment and the waste water treatment. The total equipment cost for the capacity of 6.4 billlion pounds per year was found to be $14.5 million. The total production cost was found to be $1.6 billion per year. The net profit is $27.5 million per year. These values are only valid after the plant is operating at full capacity.

Risk Analysis

Three different plant capacities, 4.1 billion, 6.4 billion and 10.5 billion, were studied. The NPW's and profits were determined for each capacity. The plots of cumulative probability versus NPW were also used to determine the capacity that will give the highest NPW with the lowest risk. Nearly one thousand cases were evaluated, with each giving different prices of the raw materials and product. See Figure 2 for the risk curves.

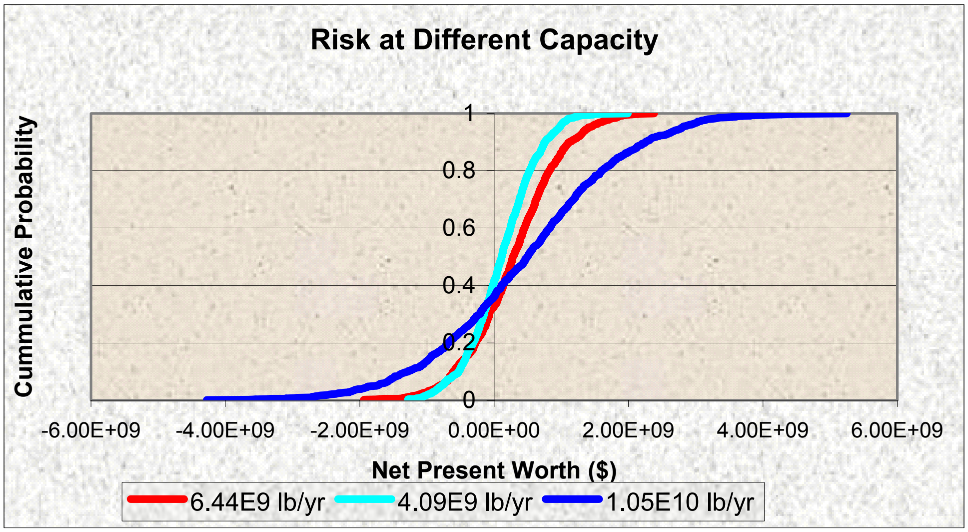

Figure 2: Graph of Risk vs. Probability

There is 41.7% chance of having a negative NPW for the 4.1 billion pound capacity. It has the highest probability for losing money of the three capacities investigated. The probability function has a short range, from –$1.5 billion NPW to $1.5 billion NPW. However, the probability is higher for having a negative NPW. Therefore, 4.1 billion lb/yr will not be used as the plant capacity.

The risk of losing money is 36% for the plant capacity of 10.5 billion pounds. There is an even distribution of NPW ranging from –$3.5 billion to $3.5 billion. There is a lot of risk associated with this capacity. There is a larger chance of having a very high profit; but at the same time, there is a 36% chance of losing money (up to -$3.5 billion).

The range of NPW for the plant capacity of 6.4 billion pounds is the same as the 4.1 billion pound capacity. However, there is a much higher probability of having a positive NPW. Analysis on this plant capacity shows that it has the lowest risk of losing money with 31%. Therefore, the 6.4 billion pounds is used as the plant capacity.

Waste Treatment

Two types of waste treatment are needed in order to treat all of the waste formed during the process, specifically, waste water treatment, and vapor/liquid waste treatment. Several treatment methods were studied in order to find the method that is best suited for this VCM plant. The system required for vapor/liquid treatment includes an incineration unit that consists of an incineration chamber, an absorption column, and a caustic scrubber. The system required for the waste water treatment is an activated carbon adsorption unit. Using these two treatment types eliminates 99.9% of all the potential waste being emitted into the environment. The total cost of both of these systems is $667,000. This cost includes the incineration unit, a water absorption column, a caustic scrubber, an activated carbon absorption column, and a carbon regeneration furnace.

The Environmental Impact Effect on Profit

Traditionally, cost optimization has been the most important aspect of plant design. However, due to an increase in environmental awareness, plant design should minimize or completely eliminate the production of waste material. Designing a plant with minimal environmental effects costs more money than merely designing a VCM plant with no regard for the environment. In order to study the effects of environmental impact on the profit, there must be a tool to quantify environmental impact. The Waste

Reduction Algorithm (WAR) algorithm is the tool employed to quantify the environmental impact. K.S. Telang of the University of Louisiana developed the WAR algorithm in 1998. A substantial amount of capital is needed in order to significantly reduce the amount of environmental impact. As can be seen in figure 3, significant reduction in environmental impact does not occur until the net profit is below zero.

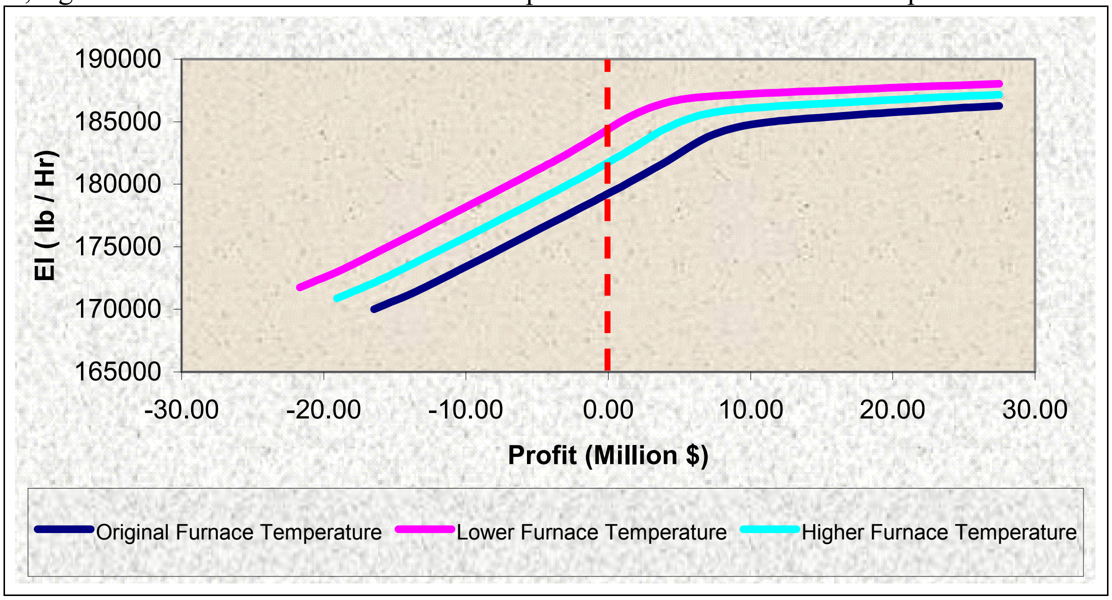

Figure 3: Environmental Impact vs. Profit

Conclusion

This project presents the design of a vinyl chloride plant with a capacity of 6.4 billion pounds per year located in Taft, LA. The capacity of the plant is based on comparing several different capacities' return on investment and net present worth. Applying different trends to the historical demand data allowed for the prediction of the capacities. The vinyl chloride product is 99.8 mol% pure, allowing for polymer feedstock applications. The total capital investment for the plant is $65.1 million. The plant produces a total net profit of $27.5 million per year. Extensive Monte Carlo simulations show that a 6.4 billion pound capacity has a 68% chance of having a positive net present value. A major focus of the design is to maximize safety and minimize environmental impact while maintaining profitability. The VCM plant produces a number of by-products resulting in eight waste streams. The Clean Air and Clean Water Acts, enforced by the Environmental Protection Agency, regulate the different waste streams. An integrated waste treatment system utilizing incineration, absorption, caustic scrubbing and activated carbon absorption is developed in order to avoid releasing any waste into the environment. The total capital investment of the waste treatment system is $667,000. The increase in environmental awareness increases the total equipment cost from $14.5 million to $15.2 million, and decreases the total net profit per year to $17 million.

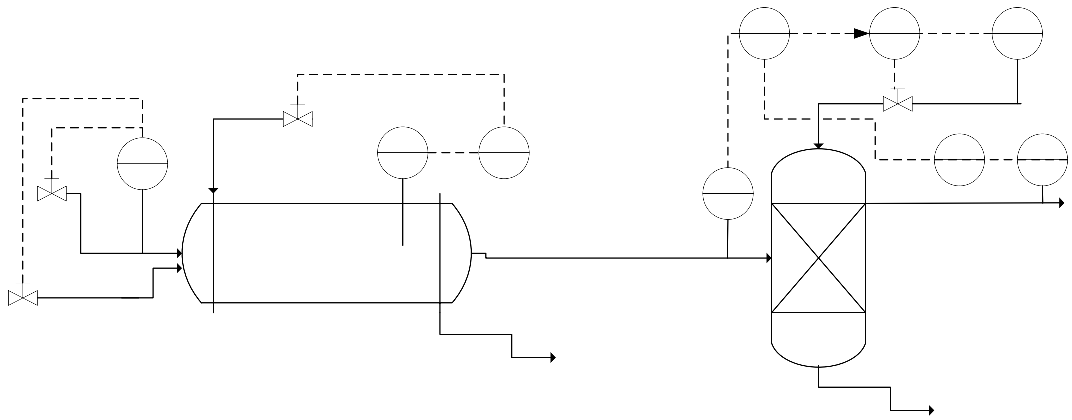

Figure 2: Direct Chlorination PFD

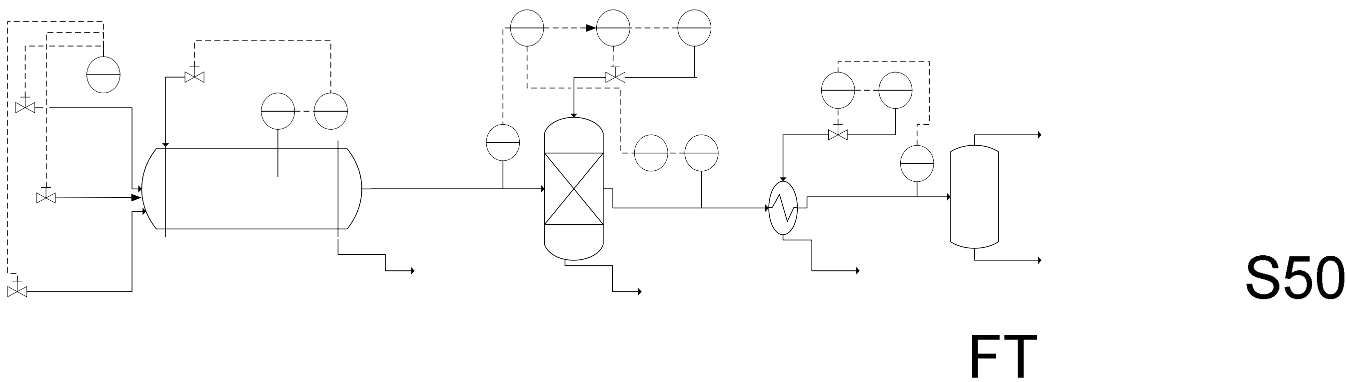

Figure 3: Oxychlorination Process PFD

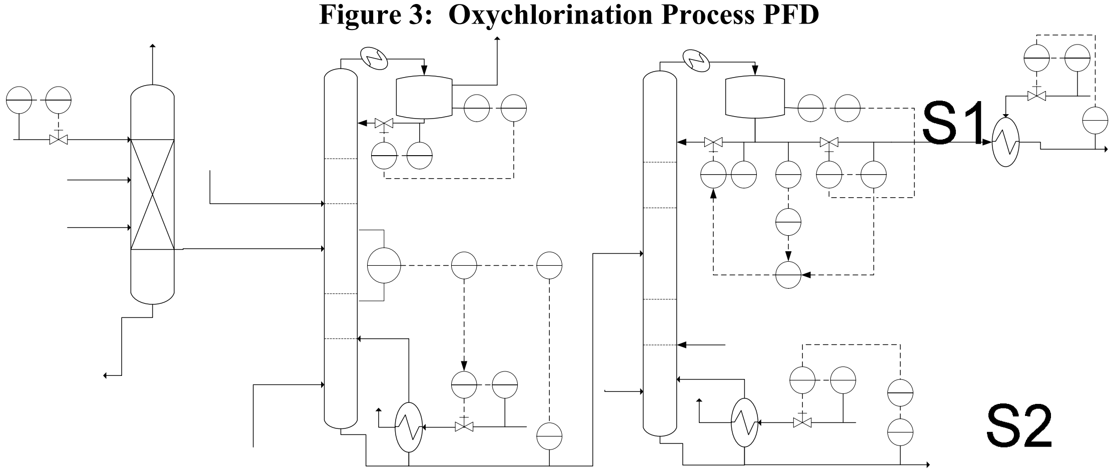

Figure 4: EDC Purification Section

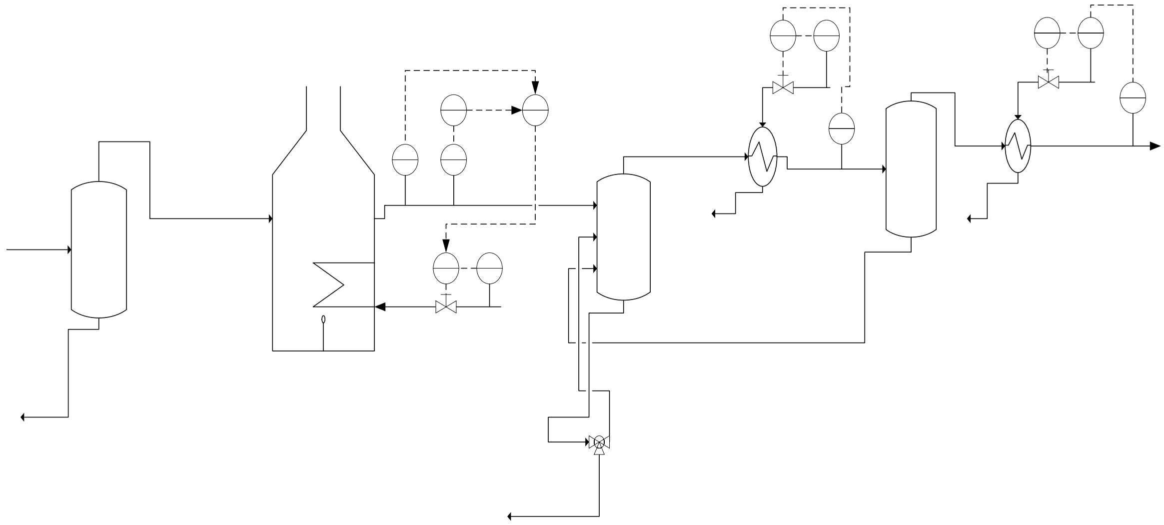

Figure 5: EDC Cracking and Quench Section

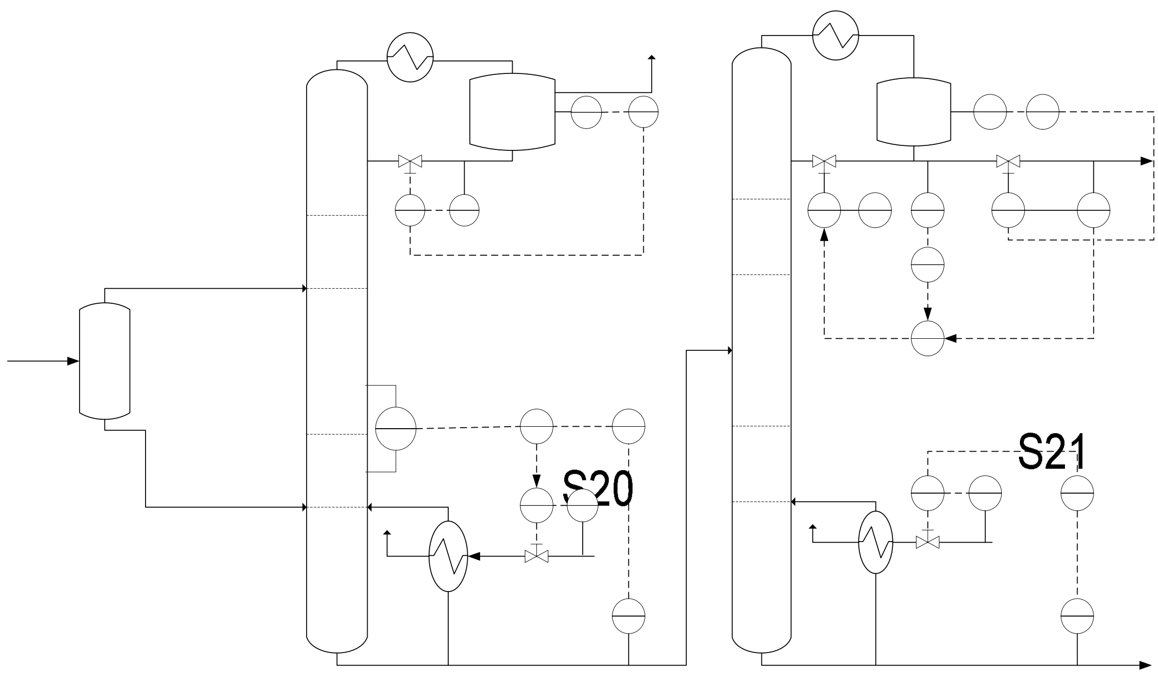

Figure 6: VCM Purification Section

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S49

Table A1. Stream Definitions for P&ID figures

Stream	Description	Stream	Description
S1	Ethylene	S37	HCl Feed to Oxy Reactor
S2	Chlorine	S38	NaCl Solution
S3	Ethylene	S39	Purified Water
S4	Oxygen	S40	Vapor Waste
S5	DC Reactor Effluent	S41	EDC Recycle
S6	Oxy Reactor Effluent	S42	Incinerator Flue gas
S7	DC Product	S43	Water
S8	Oxy Caustic Wash Effluent	S44	CO2 + Cl2 + Nox
S9	Oxy Caustic Wash Effluent	S45	Water & HCl
S10	Oxy Product	S46	Caustic Solution
S11	Vent	S47	Vapor Emissions
S12	Water	S48	NaCl Solution
S13	Water Wash Vent	S49	Furnace Feed Purge
S14	Water Decant	S50	Cooling Water
S15	EDC Purification Feed	S51	Cooling Water Return
S16	Light Ends	S52	Cooling Water
S17	EDC minus light ends	S53	Cooling Water Return
S18	Purified EDC	S54	Caustic Solution
S19	Heavy Ends	S55	NaCl Solution
S20	Purified EDC (vapor)	S56	Caustic Solution
S21	Cracking Furnace Feed	S57	NaCl Solution
S22	Furnace Effluent	S58	Cooling Water
S23	Furnace Effluent Quech	S59	Cooling Water Return
S24	Quench Bottoms	S60	Steam
S25	Quench Product	S61	Condensate
S26	Overhead Quench Product	S62	Furnace Fuel
S27	Quench Bottoms	S63	Cooling Water
S28	Quench Purge	S64	Cooling Water Return
S29	Quench Recycle	S65	Cooling Water
S30	VCM Purification Feed	S66	Cooling Water Return
S31	VCM Purification Feed (vapor)	S67	Steam
S32	VCM Purification Feed (liquid)	S68	Condensate
S33	HCl Recycle	S69	Steam
S34	VCM minus HCl	S70	Condensate
S35	VCM Prdouct	S71	Incinerator Fuel
S36	EDC Recycle		

Table A2. Equipment Definitions for P&ID figures

Tag Number	Equipment	Equipment Description
R-100	Direct Chlorination Reactor	PFTR, cooling fluid flowing shell side, ferric chloride catalyst
R-200	Oxychlorination Reactor	PFTR, cooling fluid flowing shell side, cupric chloride catalyst
F-100	EDC Cracking Furnace	furnace with tubes in radiation section
V-100	DC Caustic Scrubber	HCL is absorbed by NaOH, random packing used
V-101	Oxy Caustic Scrubber	HCL is absorbed by NaOH, random packing used
V-102	Oxy Flash	Used to separate light impurities for the system
V-103	Furnace Feed Flash	Vapor is charged to furnace, liquid recycled
V-104	Furnace Quench Flash 1	Quench Furnace effluent to prevent by product formation
V-105	Furnace Quench Flash 2	Quench Furnace effluent to prevent by product formation
V-106	HCl Column Feed Flash	Separates feed to liquid and vapor to utilize energy savings (3% reduction in reboiler duty)
V-107	Vent Flash	Used to recover EDC from waste streams
V-108	HCl Absorber	
V-109	Caustic Absorber	Absorbers Cl2
V-110	HCl Storage Tank	Stores the recycle HCl
V-111	Carbon Adsorption Column	Removes impurities from the water streams
V-112	Water Wash	Flash used to remove water generated by oxy, before the effluent is sent to the distillation columns. Removes water extractable impurities, i.e. chloral
T-100	Lights Column	17 theoretical trays, reflux ratio equal to 3, top tray pressure of 185 psig with a 22 psig pressure drop. Dia 6.5 ft H = 30ft
T-101	Heavies Column	30 theoretical trays, reflux ratio of 1, top tray pressure of 80 psig and has a 15 psig pressure drop.Dia 9 ft H = 56ft
T-102	HCl Column	42 trays and a top tray pressure of 135 psig with a column pressure drop of 10 psig. Dia 7.3 ft H = 80ft
T-103	VCM Column	20 trays, top tray pressure of 65 psig with a column pressure drop of 10 psig. Dia 6 ft H = 36ft
I-100	Waste Incinerator	Burns by products
E-100	Furnace Preheater	charge is heated to allow vapor feed to furnace, A = 2316 ft^2
E-101	Furnace Effluent Cooler 1	Quench Furnace effluent to prevent by product formation, A = 4411 ft^2
E-102	Furnace Effluent Cooler 2	Quench Furnace effluent to prevent by product formation, A = 5623 ft^2
E-104	Oxy Reactor Effluent Cooler	Cools reactors effluent, A = 728 ft^2