

Executive Summary

With increasing concern regarding the use of petrochemicals for the production of plastics and other commodity chemicals, the need for an alternative and renewable feedstock has become apparent. Most of the petrochemicals in plastic production are used to make ethylene via steam cracking. This ethylene can then go on to produce ethylene dichloride (EDC), which is a precursor to polyvinyl chloride (PVC). Another method for EDC production involves the dehydration of ethanol produced by fermentation or gasification of biomass to produce ethylene. This ethylene can then undergo the same reactions as ethylene formed from petrochemicals. This alternative route is a potential method for carbon sequestration as carbon from the atmosphere would ultimately end up in the plastics we use every day. This memo details the production of EDC from bio-ethanol with two methods: dehydration and then direct chlorination similar to current industrial processes and simultaneous dehydration over a dual catalyst bed. Included are the detailed designs, simulation results, economic analysis and safety considerations for each method.

The base case, which was modeled as a direct chlorination process, produces 1,373 tons of EDC per day by converting 1,000 tons of ethanol and 1,200 tons of chlorine gas via a series of direct chlorination reactions. The alternative case, which was modeled as a dual catalyst fluidized bed reactor, was found to produce 1,394 tons of EDC per day from 1,232 tons of liquid hydrogen chloride and 1,000 tons of ethanol.

It was determined that both processes are unprofitable with the current market prices. The current market prices of EDC and ethanol result in a 91 million dollar loss per year, for the direct chlorination process and a 15 million dollar loss per year for the dual catalyst process. However, this limited process does not represent the full potential of its economic feasibility. EDC is widely used as an intermediate product for the production of PVC and thus is an undesirable product in the market. Future research should be performed to obtain more accurate market prices of feedstocks. Also, analysis of the addition of a downstream vinyl chloride monomer (VCM), pyrolysis, unit after the processes explored in this report should be performed. The dual catalyst bed design had the advantage of performing both the dehydration and chlorination reactions in the same reactor. However, this process is still in the early development stage with little associated literature. In contrast, the dehydration and direct chlorination processes are both currently used industrially and thus are discussed thoroughly in literature. Therefore, the results of this report are likely much more accurate for the base case, the dehydration and chlorination process.

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2 Introduction

With increasing concern regarding the use of petrochemicals for the production of plastics and other commodity chemicals, the need for an alternative and renewable feedstock, such as bioethanol, has become apparent. The purpose of this project was to design a process capable of converting 1,000 tons/day of bioethanol into ethylene dichloride (EDC), which is an intermediate product used to manufacture vinyl chloride (VCM), a precursor for polyvinyl chloride (PVC). PVC is the third-most-widely produced synthetic polymer in the world, which makes alternative sources of the feedstocks required for its production relevant [1]. Using petroleum-based feedstocks to create PVC requires creating ethylene, a precursor to EDC, via the steam cracking of long-chain hydrocarbons; this cracking process is the world's second largest industrial chemical process and is one of the major emitters of greenhouse gases [2]. To address the need for producing EDC through renewable feedstocks, a base case process design was compared to an alternative design and the technical and economic feasibility of each design option were evaluated. Both options were based on commercially feasible methods of converting ethanol to ethylene, and ethylene into EDC.

The primary design objective for the project was to design a base case process for the production of ethylene from first-generation bioethanol and the conversion of the ethylene into polymer-grade EDC by a direct chlorination reaction. The process would feed in 87 mass percent ethanol at a rate of 1,000 tons of ethanol/day. A secondary design objective was in relation to the alternative design, which converted the bioethanol directly into EDC through the use of a dual-catalyst fluidized bed reactor. The final design object was to compare the economic profitability of each process using a 20-year rate of return model. Overall, the design objectives addressed the technical and financial needs that are typically associated with the commodity chemical industry and resulted in functional models and a thorough analysis of both the base case and the alternative case for producing EDC from first-generation bioethanol.

Due to the time constraints associated with the project timeline, the process of manufacturing first-generation bioethanol was not considered directly. Instead, it was assumed that bioethanol could be obtained for the production of EDC. A result of the time constraints was that the design stopped at ethylene dichloride instead of continuing to PVC; while the latter would have been more similar to the commodity chemical industry, stopping at EDC allowed the design to be achievable within the limited timeframe. Another deviation from the chemical industry was that environmental regulations weren't considered heavily in regards to waste treatment. Said regulations tend to be applicable to specific regions, so only the broadest concerns were addressed by the designs.

2.1 Design Objectives

A Design a base case process for the production of ethylene from first-generation bioethanol, and the conversion of ethylene into polymer-grade ethylene dichloride (>97%) by direct chlorination reaction. The process will feed 87 mass percent ethanol at a rate of 1,000 tons of ethanol/day.

(a) This design objective establishes a foundation process design and potential for

comparison. First generation bioethanol was chosen specifically due to current technologies and literature recommendations regarding the source of renewable ethanol feedstock; while second-generation bioethanol was considered, its commercial feasibility is low at present due to the high energy costs associated with the pretreatment [3]

B Design a process alternative that converts ethanol directly into EDC via a dual-catalyst bed reactor.

- (a) This objective is for an alternative process design that skips having ethylene as an intermediate. This is a relevant objective because it demonstrates the different methods by which EDC can be produced and provides design creativity through the use of fluidized beds, which is not used in the other possible designs.

C Compare the economic profitability of each process using a 20-year rate of return model.

- (a) Profitability is one of the primary tools for determining the viability of a process. As such, comparing the possible designs to a rate of return model over a 20-year period allows each design the potential to be economically viable. The 20-year range accounts for start-up and shut-down, which are among the most expensive processes that each design could experience. The results of the model will show which design is the most likely to be profitable and thus the better financial decision for the final design for potential stakeholders.

3 Background

One of the materials that makes modern life possible is PVC, which is created from VCM. It has a wide array of potential uses, such as packaging, piping, electrical wiring, and medical collection bags [4]. A result of its useful and versatile nature is that PVC is the third-most-widely produced synthetic polymer in the world, which makes alternative and renewable sources of the feedstock required for the production of PVC both relevant and necessary [1]. Producing PVC from petroleum, which is currently the most prevalent method, requires the production of several intermediate products, such as ethylene and EDC. Creating ethylene, which is a precursor to EDC, involves the steam cracking of long-chain hydrocarbons and is one of the world's largest industrial chemical processes and a significant emitter of greenhouse gases [2]. Pure EDC production is not common in the commodity chemical industry, thus the emissions that stem solely from EDC manufacturing are relatively unknown. However, the environmental impact of EDC's constituent products is reason enough to seriously consider using renewable feedstocks, such as first-generation bioethanol, for its industrial production.

With the current state of technology, the best choice of alternative feedstock is first-generation bioethanol. First-generation bioethanol is derived from the fermentation and subsequent distillation of starchy or sugary plants such as sugarcane, sugar beets, corn, and cassava [5]. This generation of ethanol can be used for chemical feedstock, such as for EDC, as well as for biodiesel. The technology required to produce bioethanol is well established, but it requires relatively high-quality feedstock to reduce the costs associated with pretreatment to be at all cost-competitive with petroleum products [5]. The quality of

the feedstock needed for first-generation bioethanol raises ethical dilemmas, primarily the debate of “food vs. fuel” and the implications of using both land and plants that could otherwise be used to feed the human population [6]. Second-generation bioethanol has been developed to try to circumvent the ethical issues surrounding the first-generation. This variety of bioethanol is derived from lignocellulosic biomass, which can be collected from food waste such as corn stover, wood chips, and other plant debris [5]. A result of the lower quality feedstock is that the pretreatment for second-generation bioethanol is harsh and expensive, and it has costs associated with transportation that isn’t typically relevant for first-generation bioethanol [7]. While first-generation bioethanol has the potential to be cost-competitive with petroleum, second-generation has yet to be on the same economic playing field as first-generation, let alone petroleum products [6]. As such, the only viable source of renewable feedstock for the production of EDC is from first-generation bioethanol.

Two design options were considered for producing EDC by first-generation bioethanol. The base case design produced EDC through direct chlorination, which first dehydrates the bioethanol into ethylene through an endothermic reaction and then converts the ethylene into EDC through an exothermic chlorination reaction [9, 10]. Producing EDC by direct chlorination isn’t unheard of commercially but it isn’t the primary method of production. The alternative case design produced EDC directly from ethanol through an oxychlorination reaction in a dual catalyst fluidized bed reactor [10]. The fluidized bed process has no evidence of being used on an industrial scale.

4 Initial Design Development and Designs

4.1 Key Assumptions

In order to start the design process for this project, assumptions about what the processes would be making had to be made. The initial design assumption was that the product EDC from the process was to be polymer grade. This assumption is reflected in the first design objective. Once the initial assumption was made, deviances arose, allowing for each process to become unique.

4.2 Alternative 1: Oxychlorination

This alternative uses oxychlorination to produce EDC; in this process, ethanol is dehydrated into ethylene which is separated from byproducts with flash and column distillation before being fed to the oxychlorination reactor. Unreacted ethanol is recycled to the first reactor. In the oxychlorination reactor, ethylene is reacted with HCl and air over the gamma-alumina catalyst, ($\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$) to produce EDC. The effluent is then flashed to recover unreacted ethylene and fed to distillation columns to separate the side products (Chloroethylene, Chloride, HCl, etc.)

4.3 Alternative 2: Direct Chlorination

This alternative uses direct chlorination instead of oxychlorinations to produce EDC. This process utilizes the same method for the conversion of ethanol and separation of ethylene

as Alternative 1. After ethylene is formed, it is mixed with a gaseous chlorine stream and fed to a bubble reactor over a ferric chloride (FeCl_3) catalyst. The reaction conditions are relatively low temperature and pressure (120°C and 2 bar), and the selectivity of the desired product is high at 98% [Ramesh, Monebelli]. Flash and distillation are again utilized to recycle ethylene and purify EDC.

4.4 Alternative 3: Dual Catalyst Bed

This alternative uses a dual catalyst fluidized bed to produce EDC directly from ethanol. This dual catalyst bed runs ethanol, HCl , and air over a zeolite catalyst (ZSM-5(50)) in the first bed and over the gamma-alumina catalyst in the second bed. The use of the dual-bed configuration overcomes some of the difficulties of making a truly bifunctional catalyst: achieving complete dehydration of ethanol and subsequently oxychlorination to EDC, while avoiding cracking of the product EDC to VCM on the acid sites. The highest selectivity for this process occurs at 300°C where EDC is produced at 87% and chloroethylene is produced at 15%. Flash and distillation are utilized after the reactor to separate EDC from the byproducts (Chloroethylene, Vinyl Chloride, Ethylene, Acetaldehyde, etc.).

4.5 Alternative 4: Direct Chlorination with no Ethanol Recycle

This alternative reaction series as Alternative 2. However, reactor 1 effluent is simply quenched to remove byproducts, and unreacted ethanol is not recycled. This separation is less energy intensive, but the overall conversion of ethanol is lower.

4.6 Decision Matrix

Initially, the team proposed four design opportunities: Direct chlorination with a recycle, Oxychlorination, Dual catalyst bed, and Direct chlorination without a recycle. These processes were scrutinized against different design criteria using a decision matrix which included: EDC purity based on literature sources for catalysts, feedstock prices, number of recycle streams, projected CAPEX and OPEX, and if the design was inherently safe. The price of feedstocks and if the design was inherently safe accounted for more weight than the other criteria due to a consensus from the team. This resulted in the direct chlorination process without the recycle stream coming in first; however, the processes were also informally rated based upon originality of the design. This informal criteria allowed the dual catalyst system to rise from fourth to second.

DECISION MATRIX - EDC Production							
	Criteria 1	Criteria 2	Criteria 3	Criteria 4	Criteria 5		
CRITERIA DESCRIPTION	EDC purity	Margin of outlet minus inlet	# Recycle stream(s)	Process/ Capital Costs	Inherently Safer Design		
Weight of Score (1-10)	8	5	3	5	9		
OPTIONS	Criteria 1 SCORES	Criteria 2 SCORES	Criteria 3 SCORES	Criteria 4 SCORES	Criteria 5 SCORES	TOTAL SCORE	Ranking
Oxychlorination	7	8	3	6	6	129	3
Direct Chlorination/ Quench	8	8	3	5	7	151	1
Dual Catalyst Fluidized Bed	6	8	2	7	7	122	4
Direct Chlorination/ Flash Separation	7	8	3	6	8	147	2

Figure 1: Formal decision matrix for evaluating probable design options.

The team was satisfied with the results of the decision matrix and was ready to proceed with designing the processes. Due to the complexity of the dual catalyst process, only two design alternatives were chosen. The design alternatives that were selected to be developed further were Alternatives Four and Three, which will henceforth be referred to as the Base Case and Alternative Case, respectively.

4.7 Conceptual Designs

Base Case: Direct Chlorination

The first step in converting ethanol to EDC is dehydration to ethylene. This reaction is endothermic and can be performed over many types of acidic catalysts, including oxides, zeolites, and heteropolyacids. The reaction can occur at temperatures between 300°F and 930°F depending on the type of catalyst used [11]. Selectivities can reach upwards of 99% and complete conversion of ethanol can be achieved with the zeolite catalysts [11]. The main side products for the dehydration of ethanol are diethyl ether (DEE), butylene, and acetaldehyde (ACA) [12]. Because this is a dehydration reaction, water will also be produced in large quantities. Detailed kinetics for this reaction over the γ -alumina catalyst are provided in the chemistry section.

After the reaction step, the ethylene must be separated from any unreacted ethanol and water produced by the dehydration reaction. This is a fairly simple separation with the boiling point of ethylene being -154.7°F [13] and water boiling at 212°F. Because ethylene is an intermediate in this process, it is not necessary to reach the 99.9% by mass purity polymer grade requirement for production of polyethylene [14]. Recycle of unreacted ethanol was initially considered, but with the high conversion of the reaction and azeotrope formed between water and ethanol it was quickly disregarded.

There are two methods for converting ethylene to EDC: direct chlorination and oxychlorination. Both are exothermic reactions, however oxychlorination requires higher reaction

temperatures 430-570°F and pressures 22-203 psi [15] while the direct chlorination reaction can be carried out at 70-300°F and 14-60 psi [3]. The industrial process of converting ethylene to VCM with EDC as an intermediate typically uses a balance of both of these processes by using oxychlorination to consume the HCl produced by the cracking of EDC. Since this process is not considering the production of VCM, the direct chlorination reaction was chosen because of the inherently safer conditions. Also, oxychlorination produces many more side products [15]. The direct chlorination occurs in a bubble reactor with suspended iron chloride catalyst [16] with the main byproduct being 1,1,2-trichloroethane (TCE) [Wachi]. Selectivities of the EDC product are cited as being as high as 99% and ethylene conversions of 97% are typical for industrial reactors [17].

The last step in this case is purification of the saturated vapor EDC product leaving the chlorination reactor. The byproducts that are being separated include the TCE and chlorinated side products of the first reaction: 1,2-dichlorobutane (DCB), and bis(chloroethyl) ether (DCEE). This separation is fairly simple with the EDC boiling point being 182°F [18] and TCE boiling at 237°F [19] with all other byproducts having higher boiling points. This separation should result in EDC of 97.5% by mass purity with the main byproduct being unreacted chlorine and HCl. The small amount of non condensables, mostly hydrogen and chlorine vapor, will also need to be removed from the product stream.

A block flow diagram of this process is shown below in Figure 2

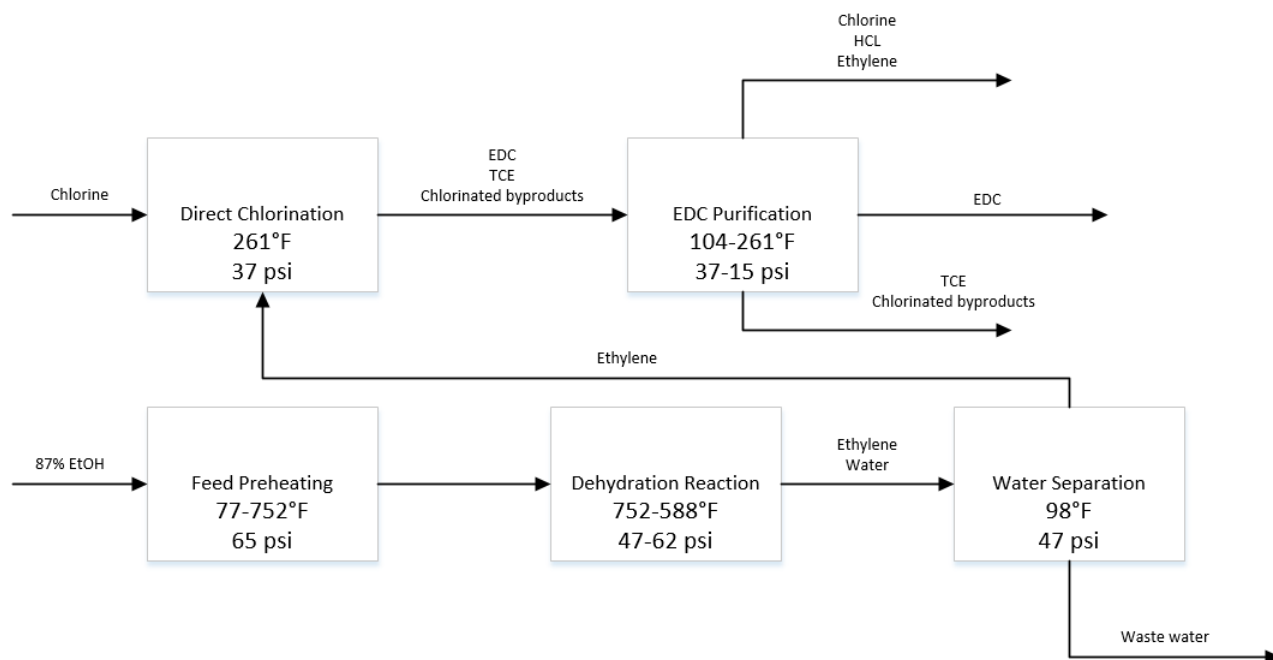


Figure 2: Block flow diagram for direct chlorination process

Alternative Case: Dual Catalyst Bed

In the dual catalyst design the dehydration reaction and chlorination reaction are combined into one reactor. This combination is done by having two catalysts present in the reactor

bed with all required reactants. The required reactants for this reaction are HCl, Air, and Ethanol, because this process utilized a oxychlorination reaction instead of direct chlorination [10]. The two catalysts used in this reactor are a proprietary zeolite catalyst ZSM-5 (50) to promote the dehydration of Ethanol and a gamma alumina/cupric chloride catalyst to promote oxychlorination [10]. The reactor is operated at 29 psi and 572 °F where it has the best conversion to EDC [10].

The inlet stream of Ethanol, Water, HCl, and Air must be compressed and heated to these conditions before entering the reactor. After the reactor there is a large amount of side products that must be separated from EDC to reach polymer grade purity. The major contaminants exiting the reactor are Ethyl-Chloride, Water, and Air. Separating EDC from Air is quite simple because Air condenses near -317 °F and EDC condenses near 182.2 -317 °F [20]. Separating Water from EDC is also relatively easy because these two compound form two liquid phases so their separation will be not extremely intensive [Aspen Plus®]. Separating ethyl-chloride from EDC is a more difficult separation because ethyl-chloride's boiling point is 54.14°F [21]. This separation will need to be run in a distillation column at about room temperature to ensure good separation.

All of the separated byproducts like Water and the chlorination by products will be mixed and sent to waste treatment where they will be combusted. Then the combustion products will be fed to caustic treatment to neutralize the remaining Chlorine [22]. The separated HCl and Air will be recycled back to the beginning of the process to reduce the amount required to be purchased. As simple overview of the process is shown in Figure 3.

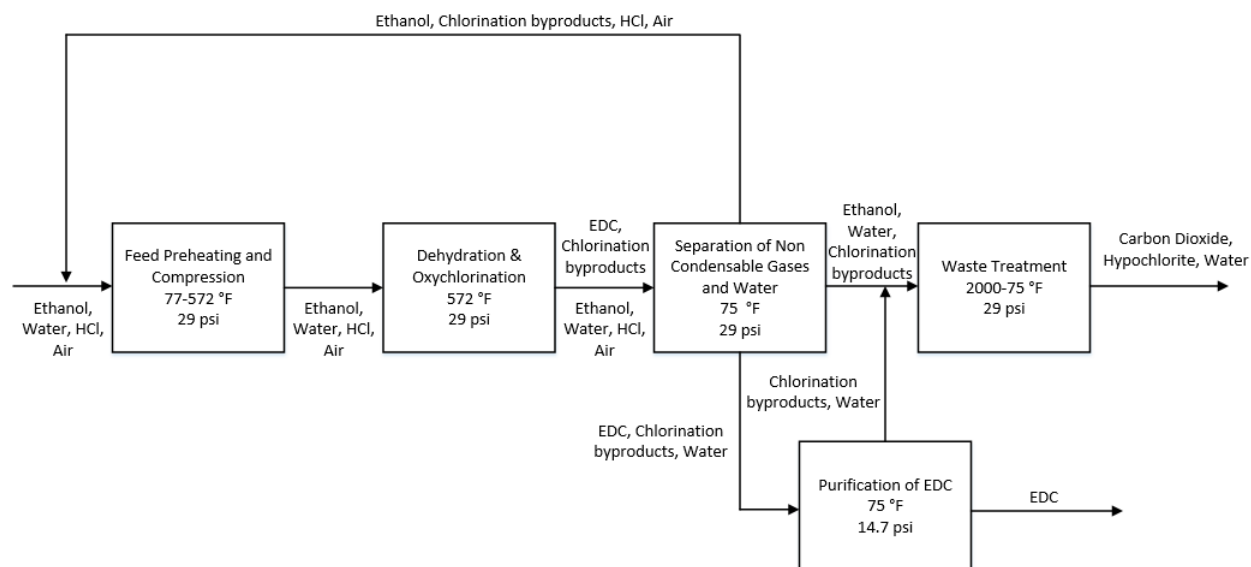


Figure 3: Block flow diagram for Dual Catalyst Process

5 Detailed Designs and Assessment: Direct Chlorination

The selected base case produces ethylene dichloride from ethanol through a direct chlorination reaction. The following sections detail the decisions and methods used to design the process.

5.1 Design Description and Justification

The 87% by weight ethanol feed to this process was selected as purification of ethanol to the azeotropic concentration is very energy intensive and since the process will be producing water, the higher water content does not appreciably affect the formation of ethylene [12]. Therefore the lower concentration will be cheaper to supply or produce if a bioethanol unit were added to this plant.

This feed is then sent to a pump to increase the pressure to 66 psi. While the dehydration reaction can be performed at lower pressures down to 14 psi [11], the pressure required for the subsequent reaction and separation steps is higher. Therefore higher feed pressure was chosen to allow for pressure drop through the remaining units and avoid expensive compression units downstream.

The ethanol is then sent to a feed/product heat exchanger that serves two purposes: to reduce the cooling water required for ethylene/water separation and to reduce the natural gas usage in the fired heater. After leaving this exchanger it is then sent to the fired heater where it is brought up to 752°F. This temperature allows for an acceptable reaction rate so that less catalyst can be used while also limiting the formation of ACA that occurs at higher temperatures over the γ -alumina catalyst [23].

The stream then enters the first adiabatic packed bed reactor in the reaction train. Because the reaction is endothermic the stream cools as it is reacted however the catalyst in each reactor is set so that the exiting temperature is always above 570°F to limit formation of DEE [23]. Between each reactor the stream is sent back to the fired heater to be heated back up to 752°F. Adiabatic reactors with interstage heating were chosen over isothermal reactors due to the high temperatures that the reaction occurs at. These temperatures would require that the reactor be placed directly in the fired heater and temperature control on this complex system would be difficult. Packed bed reactors were chosen over a fluidized bed reactor because the relatively long catalyst lifetime and lack of coke formation in this process [24]. Therefore, the added complexity of a fluidized bed reactor that heats and regenerates catalyst continuously is unnecessary.

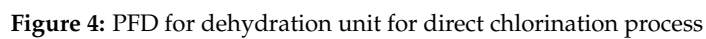
After leaving the last reactor and flowing through the feed/product heat exchanger, the stream enters the another heat exchanger where it is cooled with the waste water leaving the subsequent flash drum. This heat exchanger allows for reduced cooling water usage in the preflash heat exchanger that reduces the process stream temperature to 95°F. This temperature allows for use of cooling water at 85°C with a 10°F temperature of approach to reduce required heat exchanger area. This stream then enters an adiabatic flash where the ethylene exits as a vapor and the waste and majority of the unreacted ethanol remain in the liquid phase. Most of the DEE, ACA, and butylene exit with the ethylene vapor.

The ethylene is then sent to the chlorination reactor where it is mixed with chlorine. The

chlorine is assumed to be produced in an adjacent electrolysis unit or purchased from a supplier. These gasses enter the reactor riser where they dissolve in liquid EDC and react over the suspended iron chloride catalyst. Because this reaction is very exothermic, some of the liquid EDC vaporizes and is drawn off as product while the remaining EDC flows down the cooling arm of the reactor and exchanges heat with cooling water before flowing back up the riser. The advantage of using the bubble reactor is that it allows the heat of reaction to produce a relatively pure vapor product that reduces the utility required for the later purification step. During this reaction the butylene DEE will also be chlorinated to form DCB and DCEE [25].

The EDC purification takes place in a distillation column with a partial condenser to allow for unreacted chlorine and ethylene as well as produced HCl to leave uncondensed. The EDC leaves the top of the column at 97.5% mas purity with dissolved chlorine and HCl and chlorine being the largest contaminants. These contaminants are acceptable at these levels as the main use for EDC is production of VCM which produces HCl and some chlorine as byproducts [3]. The condenser operates at 100°F to allow for use of cooling water and the reboiler operates at 250°F and uses low pressure steam. Bottoms from the tower contain the TCE, DCB, and DCEE. The column contains 18 trays with the feed entering above the 14th stage and has a reflux ratio of 0.67. The PFD for this case is provided below in Figures 4 and 5

The non-condensable and liquid waste in the bottoms will be sent to the waste processing unit described in the safety and hazard analysis section.



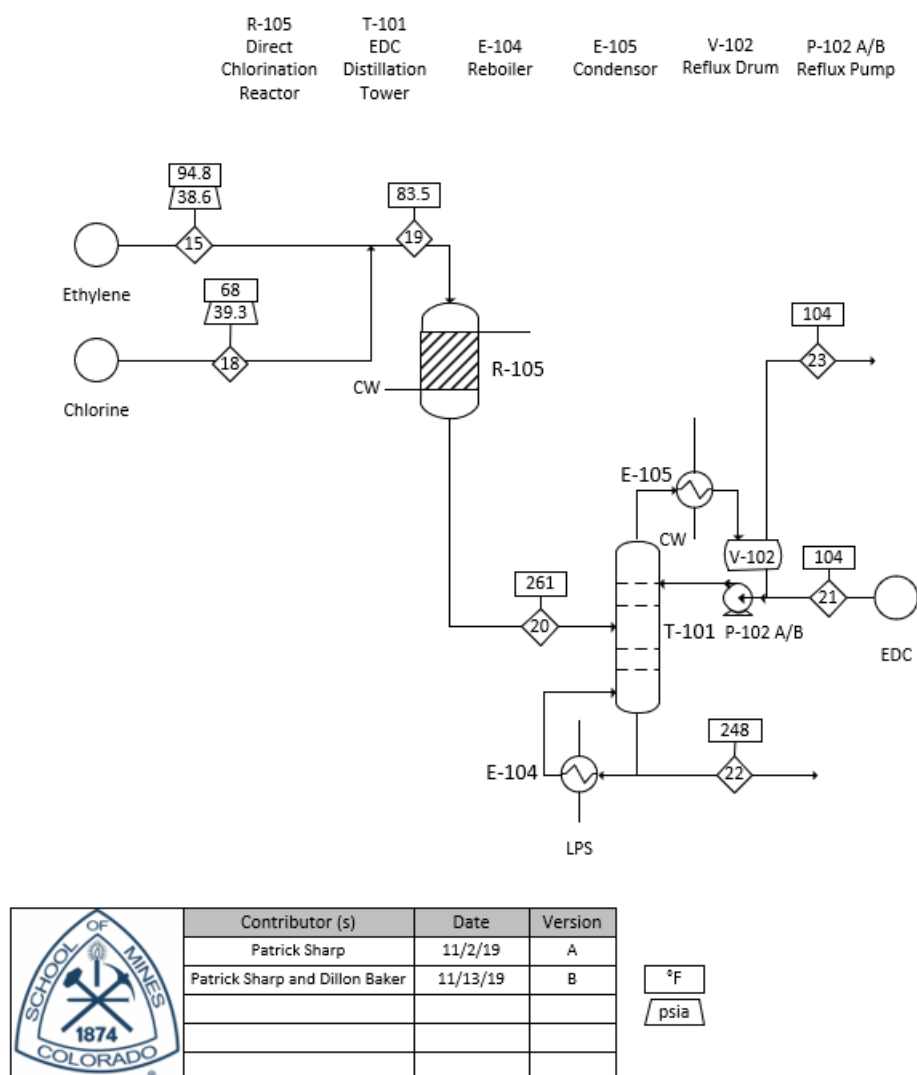


Figure 5: PFD for chlorination unit for direct chlorination process

5.2 Required Chemistry

The main reaction to produce ethylene from ethanol is endothermic and requires 702 Btu/lb_m of ethylene formed [12, 8]. A gamma alumina oxide ($\gamma\text{-Al}_2\text{O}_3$) has been chosen due to its textural properties, chemical and hydrothermal stability of the catalyst, lifespan, and selectivity for the desired product (98.8%) [24]. The temperature of the feed (752°F) balances the operating limits of the catalyst (up to 2100°F), the fact that ethylene conversion prevails at temperatures greater than 572°F, and suggested operating heuristics [24, 25, 26].

As seen in Figure 6, a mix of 87 wt% ethanol and water is fed to the reactor series, consisting of four adiabatic fixed bed reactors with interstage heating to supply the necessary energy for the desired reaction. At least nine side reactions have been reported in literature; however, this model focuses on the four that have the largest representation in product

streams and present the greatest concern for separation. Besides ethylene and water, the byproducts, on a mass percent basis, mainly consist of diethyl ether (DEE), acetaldehyde (ACA), butenes, and hydrogen gas, respectively. Formation of these byproducts is largely dependent on temperature with the ether forming at temperatures below 570°F and the aldehyde forming above 750°F.

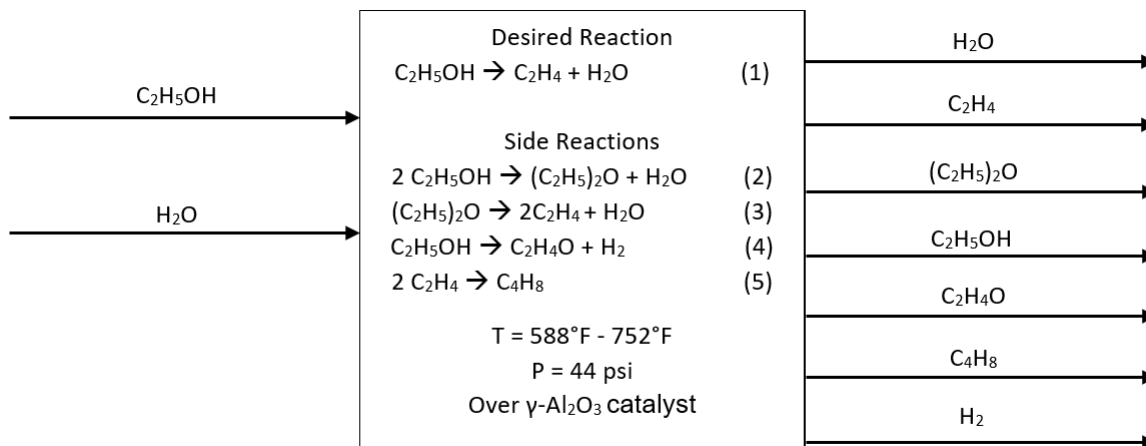


Figure 6: I/O Diagram of the dehydration reaction series over four adiabatic reactors. The products are listed in order of their representation in the final effluent stream: water, ethylene, ether, acetaldehyde, butenes, and hydrogen gas.

Major assumptions applied to the reaction model include a homogenous system and irreversible reactions. The kinetic parameters were calculated by using literature values at similar operating conditions, solving for the activation energy (E_a) and pre-exponential factor, then applying the constants to this system's operating conditions, as seen in Table 1:

Table 1: Kinetic parameters modeled in Aspen Plus

Reaction #	k (lbmol/lb _m -s)	E _a (Btu/lbmol)
1	5.41 E3	63.5
2	9.55 E4	43.4
3	2.79 E7	58
4	2.78 E5	59.5
5	1.45 E4	48.9

The second reaction in the process is the chlorination of ethylene to EDC. This reaction is exothermic with a heat of reaction of -7.74 E41 BTU/lbmol [27]. It is typically performed in a bubble reactor with ferric chloride (FeCl₃) catalyst. The bubble reactor utilizes the heat of reaction to vaporize the EDC, resulting in a high purity product. This reaction was modeled with the assumption that all the components are well mixed and the reactor is isothermal at the boiling point of EDC at the operating pressure of 39 psi. The feed temperature is 83.7°F, and the effluent temperature is 278°F. Figure 7 shows the feed components, the reactions that were modeled in Aspen Plus, and the effluent components.

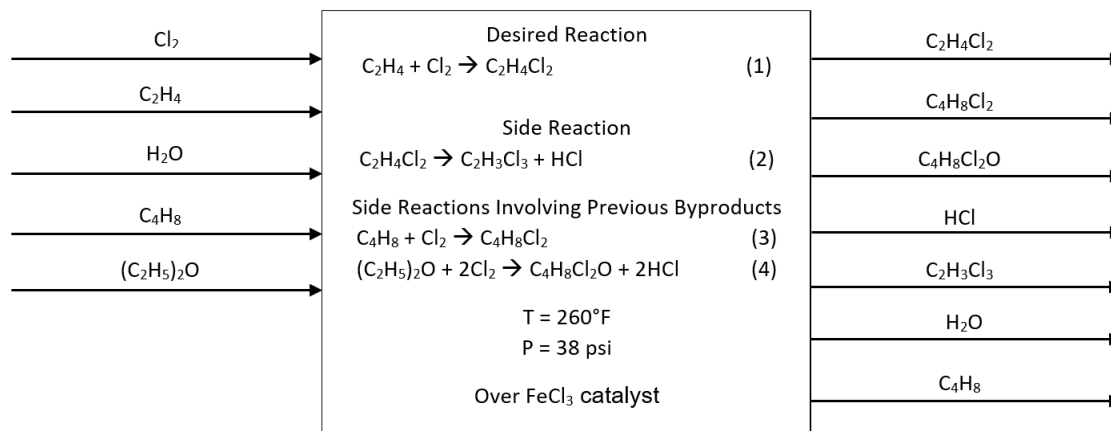


Figure 7: I/O Diagram of the direct chlorination reaction. The products are listed in order of their representation in the final effluent stream: ethylene dichloride, 1,2-dichlorobutane, dichloroethyl-ether, hydrogen chloride, trichloroethene, water, and butenes.

Literature values for kinetic parameters are either shrouded in proprietary information or not provided in published research. Aspen modeling of this reaction was based on literature values for fractional conversion at operating conditions.

Table 2: Reaction Conversion Paramaters Modeled in Aspen

Reaction #	Fractional Conversion	Conversion of Component
1	0.96	C ₂ H ₄
2	0.02	C ₂ H ₄
3	0.93	C ₄ H ₈
4	0.95	(C ₂ H ₅) ₂ O

5.3 Process Model Development

All modeling was done in Aspen Plus and the UNIFAC method was used globally throughout the process. This method was used because it takes into account the activity coefficients of the non-idealities associated with mixtures of ethanol water and EDC.

All heat exchangers were assumed to have a 10°F minimum temperature of approach and a pressure drop of 1.5 to 3 psi for each exchanger was assumed. The fixed bed reactors were also assumed to have a pressure drop of 5 psi per reactor and the bubble reactor had a pressure drop of 9 psi while the tower had a pressure drop of 0.1 psi per stage.

The outlet temperatures of the reactors were set to values above 570°F with a design spec that varied the weight of catalyst. The recovery of EDC in the product stream of the tower was set by varying the distillate to feed ratio and the mass purity of EDC was set by varying the reflux ratio.

Because of the complex heat and mass transfer within the chlorination reactor it was modeled isothermally and used selectivities and conversions from literature [27]. The flowsheet arrangement of the aspen model is shown in Appendix A.6 and stream tables are provided in Appendix A.3

5.4 Sizing and Costing Methods

All cost estimates were calculated using the estimated sizes along with parameters and equations from Appendix A in 'Analysis, Synthesis, and Design of Chemical Processes'. All units before the direct chlorination reactor should be made of carbon steel because of the low cost and that the components are not particularly corrosive or reactive to carbon steel. All other units need to be made of stainless steel due to the corrosive nature of HCl.

Heat Exchangers

All heat exchangers were sized using the LMTD method along with heuristics from chapter 11 in 'Analysis, Synthesis, and Design of Chemical Processes' and properties from Aspen Plus[®] simulations. The equation for the LMTD method can be seen in equation 1.

$$Q = UA\Delta T_{lm} \quad (1)$$

ΔT_{lm} is defined in equation 2.

$$\Delta T_{lm} = \frac{(T_{Hot,In} - T_{Cold,Out}) - (T_{Hot,Out} - T_{Cold,In})}{\ln\left(\frac{T_{Hot,In} - T_{Cold,Out}}{T_{Hot,Out} - T_{Cold,In}}\right)} \quad (2)$$

E-101 (Feed Pre-heater):

Heuristics used:

11.11.1 For conservative estimate set 10% design margin ($F = 0.9$)

11.11.6 Minimum temperature approach is 20°F for liquids

11.11.8 For condensers/evaporators U is 150 BTU/h °F ft²

Assumptions:

Partial evaporator

1-1 shell & tube heat exchanger

Information used:

Hot & cold stream temperatures: cold inlet at 66°F and outlet at 250°F, hot inlet at 664°F and outlet at 268°F

Duty (Q): 17,800,000 BTU/h

E-101 was priced as a fixed tube, shell and tube heat exchanger made of carbon steel.

E-102:

Heuristics used:

11.11.1 For conservative estimate set 10% design margin ($F = 0.9$)

11.11.6 Minimum temperature approach is 20°F for liquids

11.11.8 For condensers/evaporators U is 150 BTU/h °F ft²

Assumptions:

$U = 150$ BTU/h °F ft²

1-1 shell & tube heat exchanger

Information used:

Hot & cold stream temperatures: cold inlet at 95°F and outlet at 216°F, hot inlet at 268°F and outlet at 234°F

Duty (Q): 4,900,000 BTU/h

E-102 was priced as a fixed tube, shell and tube heat exchanger made of carbon steel.

E-103:

Heuristics used:

11.11.1 For conservative estimate set 10% design margin ($F = 0.9$)

11.11.7 Cooling water enters at 90°F and leaves at 115°F

11.11.8 For water to liquid exchangers, U is 150 BTU/h °F ft²

Assumptions:

$U = 150$ BTU/h °F ft²

1-1 shell & tube heat exchanger

Information used:

Stream temperatures: process inlet at 234°F and process outlet at 95°F

Duty (Q): 40,400,000 BTU/h

E-103 was priced as a fixed tube, shell and tube heat exchanger made of carbon steel.

E-104 (Reboiler):

Heuristics used:

11.11.1 For conservative estimate set 10% design margin ($F = 0.9$)

11.11.8 For a reboiler, U is 200 BTU/h °F ft²

Assumptions:

$U = 200$ BTU/h °F ft²

Low pressure steam enters at 320°F

Information used:

Stream temperature: enters and leaves at 248°F

Duty (Q): 9,370,000 BTU/h

E-104 was priced as a U-tube reboiler made of stainless steel.

E-105 (Tower Condenser):

Heuristics used:

11.11.1 For conservative estimate set 10% design margin ($F = 0.9$)

11.11.7 Cooling water enters at 90°F and leaves at 115°F

11.11.8 For condensers, U is 150 BTU/h °F ft²

Assumptions:

$$U = 150 \text{ BTU/h } ^\circ\text{F ft}^2$$

1-1 shell & tube heat exchanger

Information used:

Stream temperatures: Process inlet at 248°F and outlet at 104°F

Duty (Q): 33,200,000 BTU/h

E-105 was priced as fixed tube, shell and tube heat exchanger made of stainless steel.

Fired Heater

The fired heater was sized using the heat duty from the Aspen Plus® simulation. The area of each thermal section was calculated using equation 3 below.

$$A = \frac{Q}{q} \quad (3)$$

H-101

Heuristics used:

11.11.13 Radiant rate (q_{rad}) = 12,000 Btu/h ft² and convection rate (q_{conv}) = 4,000 Btu/h ft²

Assumptions:

The heat duty is split equally between the radiant and convective sections.

Information used:

Q = 70,400,000 BTU/h

H-101 was priced as a nonreactive fired heater made of stainless steel tubes.

Pumps

P-101 (Feed Pump):

Heuristics used:

11.8.1: Power for pumping liquids (kW) = Flow(gpm)*Δ P(psi)/1714/ε

Assumptions:

ε = 0.7

Information used:

Δ P = 51.4 psi

Flow = 202 gpm

P-101 was priced as a carbon steel centrifugal pump with an explosion proof drive.

P-102 (Reflux Pump):

Pump P-102 was sized based on the Bernoulli expression in equation 4

$$W = \frac{(\frac{\Delta P}{\rho} + \Delta z g) \dot{m}}{\eta} \quad (4)$$

Heuristics used:

11.9.4 Centrifugal pump efficiencies – use 50% for a small pump

Assumptions:

$$\eta = 0.5$$

Information used:

$$\Delta P = 10 \text{ psi}$$

$$\rho = 0.791 \text{ lb-mol/ft}^3$$

$$MW_{AVG} = 95.5 \text{ lb}_m/\text{lb-mol}$$

$$\Delta z = 46 \text{ ft}$$

$$\dot{m} = 23.94 \text{ lb}_m/\text{s}$$

P-102 was priced as a stainless steel centrifugal pump with an explosion proof drive.

Reactors

All of the dehydration reactors were sized based on catalyst loading weight. Using the catalyst density along with a void fraction, the volume of the packed bed was calculated as follows in equation 5.

$$V_{Bed} = \frac{\frac{m}{\rho}}{1 - \epsilon_{void}} \quad (5)$$

R-101 (Dehydration Reactor):

Heuristics used:

11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.17.1 The rate of reaction in every instance must be established in the laboratory, and the residence time or space velocity and product distribution eventually must be found from a pilot plant.

Assumptions:

Include 6.5 ft above & below the catalyst bed.

Void fraction of 0.3

Information used:

$$\text{Catalyst Weight} = 882 \text{ lb}_m$$

$$\rho_{cat} = 174.8 \text{ lb}_m/\text{ft}^3 \text{ (2.8 g/ml)}$$

R-101 was priced as a carbon steel vertical process vessel.

R-102 (Dehydration Reactor):

Heuristics used:

11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.17.1 The rate of reaction in every instance must be established in the laboratory, and the residence time or space velocity and product distribution eventually must be found from a pilot plant.

Assumptions:

Include 6.5 ft above & below the catalyst bed.

Void fraction of 0.3

Information used:

Catalyst Weight = 1,100 lb_m

$\rho_{cat} = 174.8 \text{ lb}_m/\text{ft}^3$ (2.8 g/ml)

R-102 was priced as a carbon steel vertical process vessel.

R-103 (Dehydration Reactor):

Heuristics used:

11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.17.1 The rate of reaction in every instance must be established in the laboratory, and the residence time or space velocity and product distribution eventually must be found from a pilot plant.

Assumptions:

Include 6.5 ft above & below the catalyst bed.

Void fraction of 0.3

Information used:

Catalyst Weight = 1,100 lb_m

$\rho_{cat} = 174.8 \text{ lb}_m/\text{ft}^3$ (2.8 g/ml)

R-103 was priced as a carbon steel vertical process vessel.

R-104 (Dehydration Reactor):

Heuristics used:

11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.17.1 The rate of reaction in every instance must be established in the laboratory, and the residence time or space velocity and product distribution eventually must be found from a pilot plant.

Assumptions:

Include 6.5 ft above & below the catalyst bed.

Void fraction of 0.3

Information used:

Catalyst Weight = 1,540 lb_m

$\rho_{cat} = 174.8 \text{ lb}_m/\text{ft}^3$ (2.8 g/ml)

R-104 was priced as a carbon steel vertical process vessel.

R-105 (Direct Chlorination Reactor):

The direct chlorination reaction was modeled using kinetics from Wachi [3]. The reactor was sized using the PFR design equation below and numerically integrating to find a solution.

$$\frac{dF_{EDC}}{dV} = r_{EDC} \quad (6)$$

Where F_A is the molar flow rate of EDC and r_A is the rate of reaction in respect to EDC.

The rate of reaction is defined as:

$$r_{EDC} = k_1[Cl_2][C_2H_4] - k_2[Cl_2]^2[C_2H_4] \quad (7)$$

Heuristics used:

11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.17.1 The rate of reaction in every instance must be established in the laboratory, and the residence time or space velocity and product distribution eventually must be found from a pilot plant.

Assumptions:

Ideal Gas

Information used:

Catalyst Weight = 3,310 lb_m

τ = 65 seconds

R-105 was priced as a stainless steel jacketed-nonagitated reactor.

Towers

The number of trays and reflux ratio was found in the Aspen Plus® simulation. The number of trays was then combined with heuristics to size the tower. The height was found from equation below:

$$H = (N_{Trays})(2ft) + 4ft + 6ft \quad (8)$$

T-101:

Heuristics used:

11.14.1 Tray efficiencies for distillation of light hydrocarbons and aqueous solutions are 60-90%

11.14.1 For reasons of accessibility, tray spacings are made 20-24 in. newline11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.13.13 For towers about 3ft dia., add 4 ft at the top for vapor disengagement, and 6 ft at the bottom for liquid level and reboiler return.

Information Used:

$N_{Trays} = 18$

T-101 was priced as a stainless steel vertical process vessel and T-101's trays were priced as stainless steel sieve trays.

Vessels

All process vessels were sized for being half full with liquid at a 5 minute hold-up time. All storage tanks were sized to allow 30 days of storage. Process Vessels were sized using equation 9.

$$\frac{1}{2}V = \frac{\dot{m}_{liq}t_{hold-up}}{\rho_{liq}} \quad (9)$$

Storage vessels were sized using equation 10.

$$V = \dot{V}t \quad (10)$$

V-101:

Heuristics used:

11.6.5 Holdup time is 5 min for half-full reflux drums and gas/liquid separators, 5–10 min for a product feeding another tower.

Information used:

$$\dot{m}_{liq} = 1,390 \text{ lb}_m/\text{min}$$

$$\rho_{liq} = 60.4 \text{ lb}_m/\text{ft}^3$$

$$t_{hold-up} = 5 \text{ min}$$

V-101 was priced as a vertical process vessel.

V-102

Heuristics used: 11.6.5 Holdup time is 5 min for half-full reflux drums and gas/liquid separators, 5–10 min for a product feeding another tower.

Information used:

$$\dot{m}_{liq} = 1,910 \text{ lb}_m/\text{min}$$

$$\rho_{liq} = 75.9 \text{ lb}_m/\text{ft}^3$$

$$t_{hold-up} = 5 \text{ min}$$

V-102 was priced as a horizontal process vessel.

V-103

Heuristics used:

11.7.4 Liquids subject to breathing losses may be stored in tanks with floating or expansion roofs for conservation.

11.7.6 Thirty-day capacity often is specified for raw materials and products.

Information used:

$\dot{V} = 39,000 \text{ ft}^3/\text{day}$
 $t = 30 \text{ days of storage}$

V-103 was priced as a floating roof storage tank.

V-104

Heuristics used: 11.7.6 Thirty-day capacity often is specified for raw materials and products.

Information used:

$\dot{V} = 36,200 \text{ ft}^3/\text{day}$
 $t = 30 \text{ days of storage}$

V-104 was priced as a fixed roof storage tank.

Unit Costs and Sizes

The total cost and capacity of each unit is summarized below in Table 3.

Table 3: Summary of Direct Chlorination Unit Costs

Equipment ID	Number of Units	Capacity	BM Cost (2001)	BM Cost (2018)
P-101	2	8.66 kW	\$40,600	\$61,600
P-101 Drive	2	8.66 kW	\$12,900	\$19,600
E-101	1	519 ft ²	\$74,300	\$113,000
H-101	1	70,400,000 BTU/h	\$2,960,000	\$4,510,000
R-101	1	30.9 ft ³	\$9,600	\$14,600
R-102	1	56.5 ft ³	\$12,800	\$19,500
R-103	1	56.5 ft ³	\$12,800	\$19,500
R-104	1	58.1 ft ³	\$13,000	\$19,700
V-101	1	230 ft ³	\$19,100	\$29,000
E-102	1	703 ft ³	\$80,600	\$123,000
E-103	1	3,810 ft ³	\$161,000	\$245,000
R-105	1	56.5 ft ³	\$13,100	\$20,000
T-101	1	8,680 ft ³	\$1,120,000	\$1,700,000
E-104	1	437 ft ²	\$150,000	\$228,000
E-105	1	4,190 ft ²	\$266,000	\$405,000
P-102	2	3.92 kW	\$29,800	\$45,300
P-102 Drive	2	3.92 kW	\$5,200	\$7,910
V-102	1	252 ft ³	\$36,400	\$55,300
V-103	3	391,000 ft ³	\$4,290,000	\$6,520,000
V-104	3	367,000 ft ³	\$3,510,000	\$5,340,000
T-101 Trays	18	189 ft ²	\$454,000	\$691,000
Total			\$13,300,000	\$20,200,000

5.5 Economic Analysis

The costs associated with utilities, labor, and feed streams were used to calculate internal rate of return (IRR or ROR) and net positive value (NPV), using a minimum ROR. The resulting selling price of EDC was also found and analyzed. The variations in the purchasing price of ethanol was examined in a sensitivity analysis, and Table 4 shows the lowest

price considered.

Table 4: Direct Chlorination Feedstock Costs

Species	\$/ton	Total Amount(ton/day)	Total Cost (\$/day)
Ethanol	\$351	1,000	(\$351,000)
Chlorine	\$100	1,200	(\$120,000)
Total	\$452	4,663	(\$471,000)

All utilities were priced using Aspen Plus[®] duties. The cost of cooling water was priced at \$0.0000107/lb_m, low pressure steam at \$0.000920/lb_m, natural gas at \$0.000860 /lb_m, and electricity at \$0.0859/kWh. The cost of utilities are summarized in Table 5 below. Cooling water is fed at 90°F and returned at 115°F. Low pressure steam is fed at 320°F and returned a saturated liquid. The cost of utilities factored into the cost of manufacturing, as shown in Appendix B.

Table 5: Direct Chlorination Utility Summary

Units	Type	Cost \$/hr	Cost \$/yr	Emissions Tons/yr
H-101A	Nat Gas	\$165.00	\$1,390,000	31800
H-101B	Nat Gas	\$26.30	\$222,000	5080
H-101C	Nat Gas	\$24.50	\$206,000	4730
H-101D	Nat Gas	\$19.30	\$163,000	3740
E-103	CW	\$16.10	\$136,000	0
P-101	Electricity	\$0.63	\$5,280	24
P-102	Electricity	\$0.18	\$1,540	7
R-105	CW	\$40.60	\$34,700	0
T-101	CW	\$13.20	\$112,000	0
T-101	LPSteam	\$9.59	\$80,700	6040
Total		\$315	\$2,650,000	51,400

Another one million dollars was added to the calculated utilities to account for waste treatment in the form of an incinerator and a caustic wash. The true cost of waste treatment would be narrowed down in further studies.

Labor was calculated using heuristics from from 'Analysis, Synthesis, and Design of Chemical Processes'. A table summarizing the labor cost can be seen below in Table 6. The costs associated with labor factored into the cost of manufacturing, as shown in Appendix B.

Table 6: Direct Chlorination Labor Summary

Type of Work	Annual Cost (2016 \$)	Annual Cost (2019 \$)
Operator Labor	\$1,290,000	\$1,380,000
Supervisory & Clerical Labor	\$232,000	\$249,000
Laboratory Charges	\$194,000	\$208,000
Total	\$1,720,000	\$1,840,000

The direct chlorination process used two different catalysts: gamma alumina oxide and ferric chloride. The gamma alumina oxide was used for the dehydration of ethanol into

ethylene and the ferric chloride was used for the direct chlorination of the ethylene. As shown in Table 6 below, the required amounts of each catalyst were similar but the costs associated with each were significantly different, with the gamma alumina oxide being much more expensive [28, 29]. The life cycles of the catalysts weren't the same, as mentioned in the table, which impacted the cost of manufacturing, and ultimately impacted the financial results and cash flows, although the costs of catalysts were essentially negligible compared to the costs of the feed streams.

Table 7: Catalyst Cost Summary

Catalyst	Required Amount (lb _m)	\$/lb _m	Cost	Replacement
γ-Al ₂ O ₃	3,750	\$41.00	\$154,000.00	every 2 years
FeCl ₃	3,310	\$0.15	\$497.00	every year

Using heuristics from the textbook, ROR and NPV were calculated, as shown in Appendix B. Overall, the costs associated with the feed streams made positive values difficult to calculate. To reach positive values for all of the terms, an assumption was made for the cost of chlorine gas in the feed stream. The assumption was made because of the high costs associated with chlorine gas. As such, an optimistically low purchase price, based on industrial contracts, was used in the calculations [30]. Another point of contention for the cost of the feed streams was the cost of ethanol. Even at historically low prices of ethanol, Because both designs used 87% where most prices quote fuel grade ethanol at nearly 100% concentration a lower price was assumed and the sensitivity to the price was analysed.

To accurately understand the effects of ethanol prices on the rate of return and the selling price of the produced EDC a sensitivity analysis was performed. Shown in Figure 8 below, each line represents a different purchase price of ethanol per gallon. The ethanol prices were adjusted from prices found for 95 mass percent ethanol; this was done by rounding down all of the prices by approximately 10¢/gal to account for the 87 mass percent ethanol modeled in the rest of the process [31]. The sensitivity analysis demonstrates how significantly the financial success of the direct chlorination process is reliant upon a low price of ethanol. In addition, the selling price of EDC proposed by the analysis is significantly higher than the price used in industry, which is closer to \$300/ton. The range of EDC prices that gave that the values found in Figure 8 can be found in Appendix B.

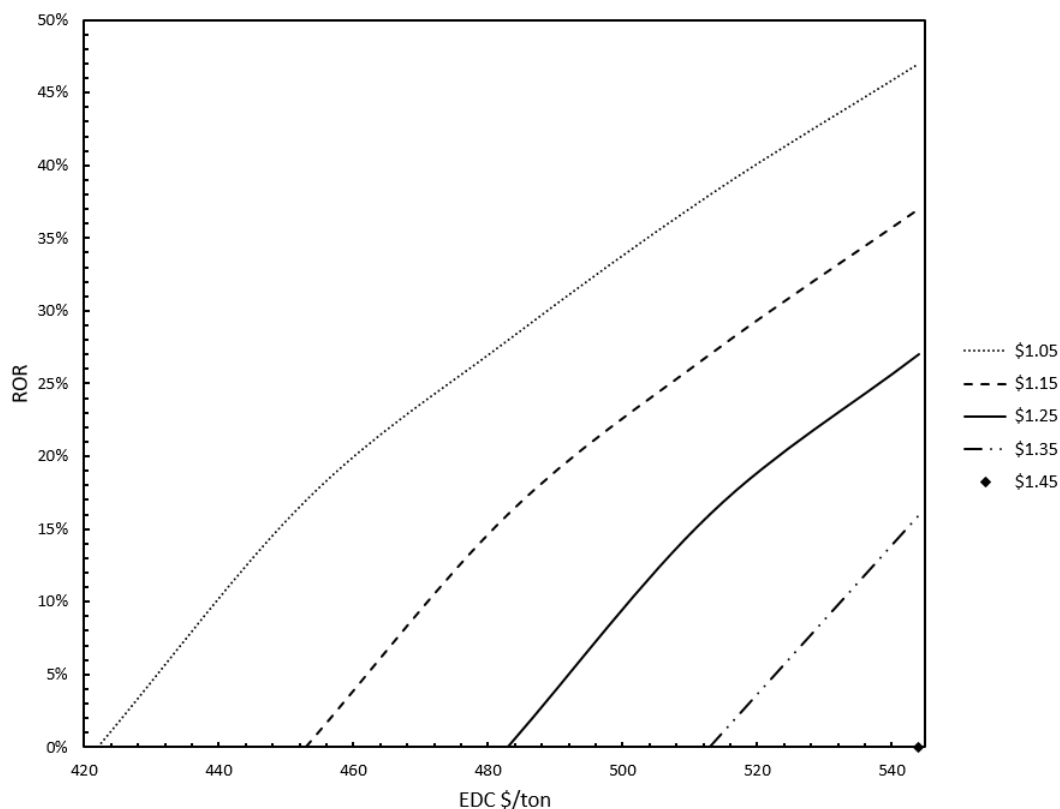


Figure 8: Sensitivity analysis of the rate of return for the direct chlorination process and the selling price of EDC to the purchase price of ethanol in dollars per gallon.

A loss forward tax credit was assumed that allowed 80% of the taxable income after other deductions were applied to be eliminated with the cumulative losses of previous years. Also, The remediation cost of the land was assumed to be covered by the sale of equipment and working capital resulting in a zero cash flow in the last year. The cash flow analysis is shown in Appendix B.

6 Detailed Designs and Assessment: Dual Catalyst Bed

The selected alternative case produces ethylene dichloride directly from ethanol through a dual catalyst fluidized bed reactor. The following sections detail the decisions and methods used to design this process.

6.1 Detailed Design Description & Justification

The second alternative that was explored was the conversion of ethanol straight to EDC in one reactor. The reaction in which ethanol is converted to dichloroethane using HCl is called oxychlorination. The reactants in this process are hydrogen chloride, ethanol, and air which in the final design are mixed together in the Mixing vessel (V-101) shown in the PFD below. The ethanol, hydrogen chloride, and air are combined with the mole percents of 0.14, 0.32, and 0.54 respectively to match the optimal mixture from literature [10]. After mixing

the process stream is evaporated in (E-101) to ensure that the stream can be compressed. The exiting temperature of the process stream from E-101 is approximately 107°F. Then the stream is compressed to 29.7 psia in (C-101) to ensure that the recommended reactor pressure is reached. The exiting temperature of C-101 is approximately

After being compressed to 29.7 psia the process stream is heated up to the reactor operating temperature in a fired heater (H-101) [10]. The process stream exiting the heater is at about 572°F and 29 psia, this stream then enters the dual bed reactor. In this study the reactor was treated as an isothermal reactor. The reason the reactor was treated as isothermal is because modeling the temperature change due to all nine reactions that take place in the reactor required the kinetics of each reaction to be known when they were not. Exiting the reactor is a mixture of Hydrogen Chloride (HCl), Ethanol, Vinyl Chloride monomer (VMC), Air, Chloroethane (EMC), Ethylene Dichloride (EDC), Hydrogen Gas, Acetaldehyde (ACA), Diethylether (DEE), Water, and Ethylene. This mixture was then used as the heating stream for E-101, and then is cooled further to approximately 120°F in E-102 before being fed to a flash separator.

In the first flash separator (V-102) most of the EDC, EMC, DEE, Water, Ethanol, and ACA are in the liquid stream. The vapor stream exiting V-102 is comprised of mostly HCl, Ethanol, Air, and Hydrogen Gas with moderate quantities of EDC and Water. The operating temperature of V-120 was determined using aspen sensitivity analysis to look for the best separation and recovery. The operating temperature of each flash separation was found to be 41°F. The liquid stream exiting V-102 goes into a decanter (D-101) which separates the EDC from the water since these two compounds form two liquid phases at 41°F and 29 psi. The vapor stream coming out of V-102 are fed into another flash separator (V-103).

The purpose of V-103 is to increase the recovery of all the EDC produced. The same sensitivity analysis that used to determine the operating temperature of V-102 was used to determine the operating temperature of V-103. V-103's operating temperature was determined to be 41°F and 29.7 psi as well. Exiting V-103 in the vapor phase is comprised of HCl, Ethanol, Air, and Hydrogen Gas and the liquid phase contains EDC and Water with some Ethanol. The vapor stream exiting the V-103 is recycled back to the mixing vessel to try and decrease the amount of HCl that must be bought. The liquid stream exiting V-103 enters a decanter (D-102) which separates the water liquid phase from the EDC liquid phase 41°F and 29 psi. The water phase exiting both D-101 and D-103 contain mostly water with some ethanol, DEE, ACA, and trace EDC. The EDC phase exiting both decanters are made of EDC and EMC with traces of Ethanol.

The two EDC streams exiting the decanters are mixed together and fed into a distillation tower T-101 which is meant to increase the purity of the product stream to about 99.9% mol EDC. The best separation for EMC and EDC occurred at approximately atmospheric pressure where the azeotrope between the compounds is below the entering composition. The bottoms of T-101 is the product stream which is then sent to storage in tank V-106. The tops of T-101 is comprised of mostly ethanol and EMC condensed at about 58°F and atmospheric pressure then mixed with the two water streams exiting the decanter and then sent to waste treatment. The waste treatment of this water stream involves incineration followed by caustic treatment to ensure that all of the chlorine is converted into Sodium hypochlorite (NaClO), which can be sold as bleach [22]. The final process flow diagram is

shown below as Figure 9.

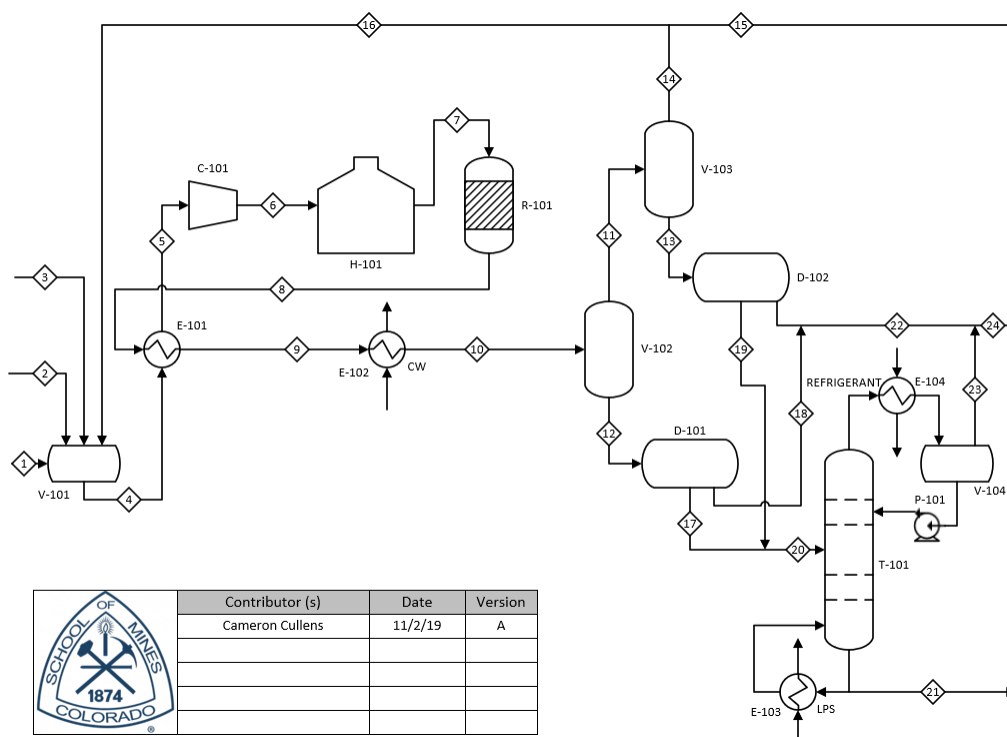


Figure 9: Final Process Flow Diagram for Dual Catalyst Process

6.2 Required Chemistry

Reactor (R-101) is a two different beds in the same reactor. The configuration of these two beds is a fluidized bed and packed bed. These two beds both dehydrate ethanol into ethylene and then chlorinate the ethylene to EDC in one reactor. Since there are many catalysts and reactants that are not usual in each others presence in this configuration there are a large amount of side products and reactions in the reactor. This configuration promotes the nine reactions shown below in Figure 10 [10].

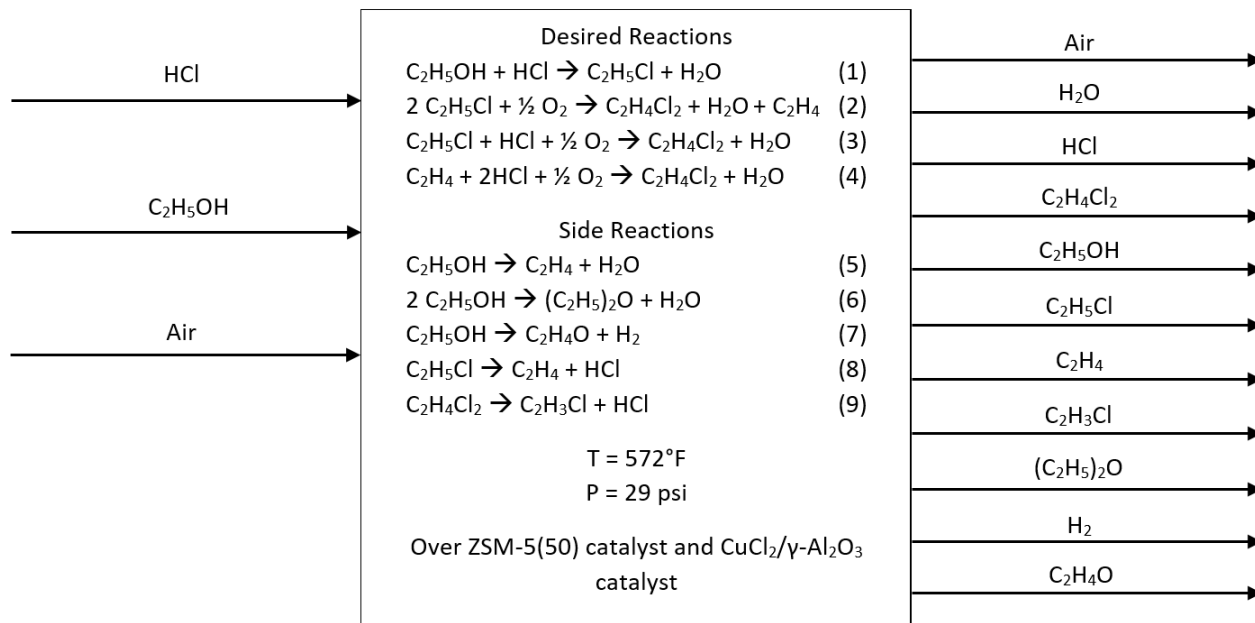


Figure 10: IO Diagram for Dual Catalyst Reactor

Since the this reactor has proprietary catalysts involved reliable kinetics for these reactions could not be found. So instead of modeling this reactor in Aspen[®] it was modeled using an extent of reaction method. The extent of reactions for each of these reactions were determined using Solver in excel by setting the target of the summation of the extent equal to the literature values exiting based on conversion and selectivity. The result of this analysis is shown below in Table 8

Table 8: Extent of Reactions for Dual Catalyst Reactor

Reaction Number	Extent of Reaction (lbmol/hr)
1	1537
2	0.02514
3	26.94
4	50.75
5	32.37
6	1213
7	19.02
8	0.6339
9	13.22

As state before the required catalysts to reach the above listed extents are ZSM-5(50) in a pack bed configuration and a fluidized gamma-alumina/cupric chloride [10]. The ZSM-5 (50) is estimated to need replacing approximately every other year [10]. Where as the gamma-alumina/cupric chloride will be regenerated continuously in a cyclone. Eventually the all of the gamma-alumina/cupric chloride will need to be replaced which will be done by producing it on site instead of purchasing more gamma-alumina [10].

6.3 Process Model Development

The method used to generate the model in Aspen Plus[®] was UNIFAC because it incorporates activities which is important to any separation involving ethanol and water. The dual catalyst reactor was modeled in Excel on a molar extent basis because the kinetic data for the reaction was proprietary. The extent of reactions for all nine reactions were determined using the literature conversions [10]. The total summation of the squared errors between conversion based model and the extent based model was approximately 0.0038 which is small enough to accept this solution.

Once the extents were calculated in Excel they were transferred to an RSTOICH reactor in Aspen[®]. The other notable part of the simulation that relied heavily on hand calculations was T-101, Aspen[®] would strip out errors when a RADFRAC was run in the system. So to circumvent the usage of a RADFRAC a DISTWU was modeled and then was sized up using the heuristics found in 'Analysis, Synthesis, and Design of Chemical Processes'.

The final notable modeling changes were the efficiency changes made to the preheating and compressing system. Originally the compressor was after the fired heater, but compressing a hot gas requires more energy than compressing a cool gas. So the order of these two units was switched and an evaporator was placed before C-101. This evaporator uses the exiting stream of the reactor to heat evaporate the feed, the addition of this evaporator reduced both the electricity required to operate the compressor and the amount of cooling water required in E-102. Another efficiency improvement caused by this reordering was a reduction in the natural gas required to heat the feed up to the reactor operating temperature. Since the compression also increases the temperature of the stream heading to H-101 which means the energy required to heat the process stream up decreased significantly.

6.4 Sizing and Costing Methods

All sizing for the decanters, flash vessels, reflux drums, heat exchangers, compressors, and fired heater were done in Aspen Plus[®] for this design. The results of the Aspen Plus[®] sizings were compared to hand sizing and were consistent. The sizing for the reactor (R-101), reflux pump (P-101), Storage Tanks, and distillation column (T-101) were done by hand using heuristics from Analysis, Synthesis, and Design of Chemical Processes.

The Reactor (R-101) was sized using the heuristics, assumptions, equations, and information listed below

Heuristics:

11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.17.1 The rate of reaction in every instance must be established in the laboratory, and the residence time or space velocity and product distribution eventually must be found from a pilot plant.

Equations:

$$V_{bed} = \frac{\dot{v}_{in}}{\tau}$$

Information:

Resonance Time: $11550 \frac{1}{hr}$ [7]

Flow Rate In: $8629390 \frac{ft^3}{hr}$

Pump (P-101) was sized based on the Bernoulli expression in equation 4 and the heuristics, assumptions, and information listed below.

Heuristics:

11.9.4 Centrifugal pump efficiencies – use 50% for a small pump

11.13.5 Economical optimum reflux ratio is in the range of 1.2 to 1.5 times the minimum reflux ratio, R .

Assumptions:

$$\eta = 0.5$$

Information:

$$\rho = 28.26 \text{ kg/ft}^3$$

$$\Delta z = 73.8 \text{ ft}$$

$$\dot{V} = 0.919 \frac{ft^3}{s}$$

The Storage Tanks V-104 and V-105 was sized using the heuristics, assumptions, equations, and below

Equations:

$$V = \dot{V}t \quad (11)$$

V-105

Heuristics used:

11.7.4 Liquids subject to breathing losses may be stored in tanks with floating or expansion roofs for conservation.

11.7.6 Thirty-day capacity often is specified for raw materials and products.

Information used:

$$\dot{V} = 39,000 \text{ ft}^3/\text{day}$$

$$t = 30 \text{ days of storage}$$

V-106

Heuristics used: 11.7.6 Thirty-day capacity often is specified for raw materials and products.

Information used:

$$\dot{V} = 38,000 \text{ ft}^3/\text{day}$$

$$t = 30 \text{ days of storage}$$

To size T-101 the minimum number of trays was found in the Aspen Plus® simulation. Then using the heuristics, assumptions, equations, and information listed below the tower was sized.

Equations:

$$N_{Trays} = \frac{2(N_{min})}{\eta}$$

$$H = (N_{Trays})(2ft) + 4ft + 6ft$$

Heuristics:

11.14.1 Tray efficiencies for distillation of light hydrocarbons and aqueous solutions are 60-90%

11.14.1 For reasons of accessibility, tray spacings are made 20-24 in (0.5-0.6 m). new-line11.6.4 Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.

11.13.13 For towers about 3ft dia., add 4 ft at the top for vapor disengagement, and 6 ft at the bottom for liquid level and reboiler return.

11.13.6 The economically optimum number of theoretical trays is near twice the minimum value N

Information:

$N_{min} = 7.1$

After every unit was sized and the sizings were in line with the estimates for a process of this size each unit was priced using heuristics from Analysis, Synthesis, and Design of Chemical Processes. The results of this analysis are shown below in Table 9

Table 9: Dual Catalyst Bare Module Cost Summary

Units	Number of Units	Capacity	BM Cost (2001 \$)	BM Cost (2018 \$)
V-101	1	1,210 ft^3	\$92,800	\$ 169,000
C-101 Drive	1	4,920 kW	\$266,000	\$ 484,000
C-101	1	4,820 kW	\$4,680,000	\$ 8,540,000
H-101	1	13,100 kW	\$2,710,000	\$ 4,940,000
R-101	1	1,090 ft^3	\$162,000	\$ 296,000
V-102	1	808 ft^3	\$126,000	\$ 230,000
V-103	1	944 ft^3	\$151,000	\$ 276,000
D-101	1	295 ft^3	\$57,700	\$ 105,000
D-102	1	101 ft^3	\$26,800	\$ 48,900
T-101	1	5,680 ft^3	\$683,000	\$ 1,250,000
E-102	1	7,450 ft^2	\$627,000	\$ 1,140,000
E-103	1	2,330 ft^2	\$300,000	\$ 548,000
E-104	1	11,430 ft^2	\$747,000	\$ 1,363,000
E-101	1	1,270 ft^2	\$173,000	\$ 315,000
V-104	1	295 ft^3	\$48,700	\$ 88,900
P-101 Drive	1	8.19 kW	\$6,100	\$ 11,100
P-101	1	8.19 kW	\$51,200	\$ 93,500
V-105	3	391,000 ft^3	\$4,290,000	\$ 6,520,000
V-106	3	383,000 ft^3	\$3,590,000	\$ 6,540,000
T-101 Trays	32	78.5 ft^2	\$273,000	\$ 497,000
Total			\$19,100,000	\$33,500,000

Further detailed description of each unit can be found in Appendix A.4

6.5 Economic Analysis

The costs associated with utilities, labor, and feed streams were used to calculate internal rate of return (IRR or ROR) and net positive value (NPV), using a minimum ROR. The

resulting selling price of EDC was also found and analyzed. The fluctuation of ethanol purchase prices was examined in a sensitivity analysis, and Table 10 shows the lowest price considered.

Table 10: Dual Catalyst Feedstock Costs

Species	\$/ton	Total Amount (ton/day)	Total Cost (\$/day)
Ethanol	\$351	1,000	(\$351,000)
HCl	\$67	1,232	(\$82,500)
Air	\$0	2431	(\$0)
Total	\$418	4,663	(\$434,000)

All utilities were priced using Aspen Plus[®] duties. The cost of cooling water was priced at \$0.0000107/lb_m, low pressure steam at \$0.000920/lb_m, natural gas at \$0.000860 /lb_m, and electricity at \$0.0859/kWh. The cost of utilities are summarized in Table 5 below. Cooling water is fed at 90°F and returned at 115°F. Low pressure steam is fed at 320°F and returned a saturated liquid. The cost of utilities factored into the cost of manufacturing, as shown in Appendix B.

Table 11: Dual Catalyst Utility Summary

Units	Type	Cost \$/hr	Cost \$/yr	Emissions Tons/yr
H-101	Nat Gas	\$181.90	\$1,532,000	281
E-102	CW	\$13.20	\$112,000	0
E-103	Refrigerant	\$60.50	\$510,000	123
E-104	LPS	\$52.30	\$440,000	180
P-101	Electricity	\$7.35	\$62,000	2.8
C-101	Electricity	\$418.70	\$3,530,000	162
Total		\$734.00	\$6,180,000.00	751

Another one million dollars was added to the calculated utilities to account for the cost of waste treatment. This value would be narrowed down to a closer estimate if the team had more time to study this design. Labor was calculated using heuristics from from Analysis, Synthesis, and Design of Chemical Processes. The reactor in this process has a fluidized bed component which means that there is one particulate unit that was factored into the labor calculation. The yearly cost calculation also factored in two weeks of down time for maintenance and repairs.

Labor was calculated using heuristics from from 'Analysis, Synthesis, and Design of Chemical Processes'. A table summarizing the labor cost can be seen below in Table 12. The costs associated with labor factored into the cost of manufacturing, as shown in Appendix B.

Table 12: Dual Catalyst Labor Summary

Type of Work	Annual Cost (2016 \$)	Annual Cost (2019 \$)
Operator Labor	\$2,140,000	\$2,300,000
Supervisory & Clerical Labor	\$385,000	\$413,000
Laboratory Charges	\$321,000	\$344,000
Total	\$2,850,000	\$3,050,000

The dual catalyst process used three different catalysts across two reactor beds: gamma alumina oxide, cupric chloride, and a zeolite catalyst. As shown in Table 13 below, the required amounts of each catalyst ranged from approximately 1,000 lb_m for the most expensive catalyst to 48,000 lb_m for a much less costly catalyst. The life cycles of the catalysts weren't the same, as mentioned in the table, which impacted the cost of manufacturing, and ultimately impacted the financial results and cash flows.

Table 13: Catalyst Cost Summary

Catalyst	Required Amount (lb _m)	\$/lb _m	Cost	Replacement
γ-Al ₂ O ₃	8,500	\$41.00	\$349,000.00	every 2 years
CuCl ₂	851	\$243	\$206,000	every 2 years
ZSM-5 (50)	47,700	\$83.60	\$4,000,000	every year

Using heuristics from the textbook, ROR and NPV were calculated, as shown in Appendix B. Overall, the costs associated with the feed streams made positive values difficult to calculate. Gulf Coast industrial prices were applied to the hydrochloric acid and air was assumed to be fed from the atmosphere, making the feedstock costs somewhat reasonable. A point of contention for the cost of the feed streams was the cost of ethanol. Even at historically low prices of ethanol, Because we are using 87% where most prices quote fuel grade ethanol at nearly 100% concentration a lower price was assumed and the sensitivity to the price was analysed

To accurately understand the effects of ethanol prices on the rate of return and the selling price of the produced EDC a sensitivity analysis was performed. Shown in Figure 11. below, each line represents a different purchase price of ethanol per gallon. The ethanol prices were adjusted from prices found for 95 mass percent ethanol; this was done by rounding down all of the prices by approximately 10¢/gal to account for the 85 mass percent ethanol modeled in the rest of the process [31]. The sensitivity analysis demonstrates how significantly the financial success of the direct chlorination process is reliant upon a low price of ethanol. In addition, the selling price of EDC proposed by the analysis is significantly higher than the price used in industry, which is closer to \$300/ton.

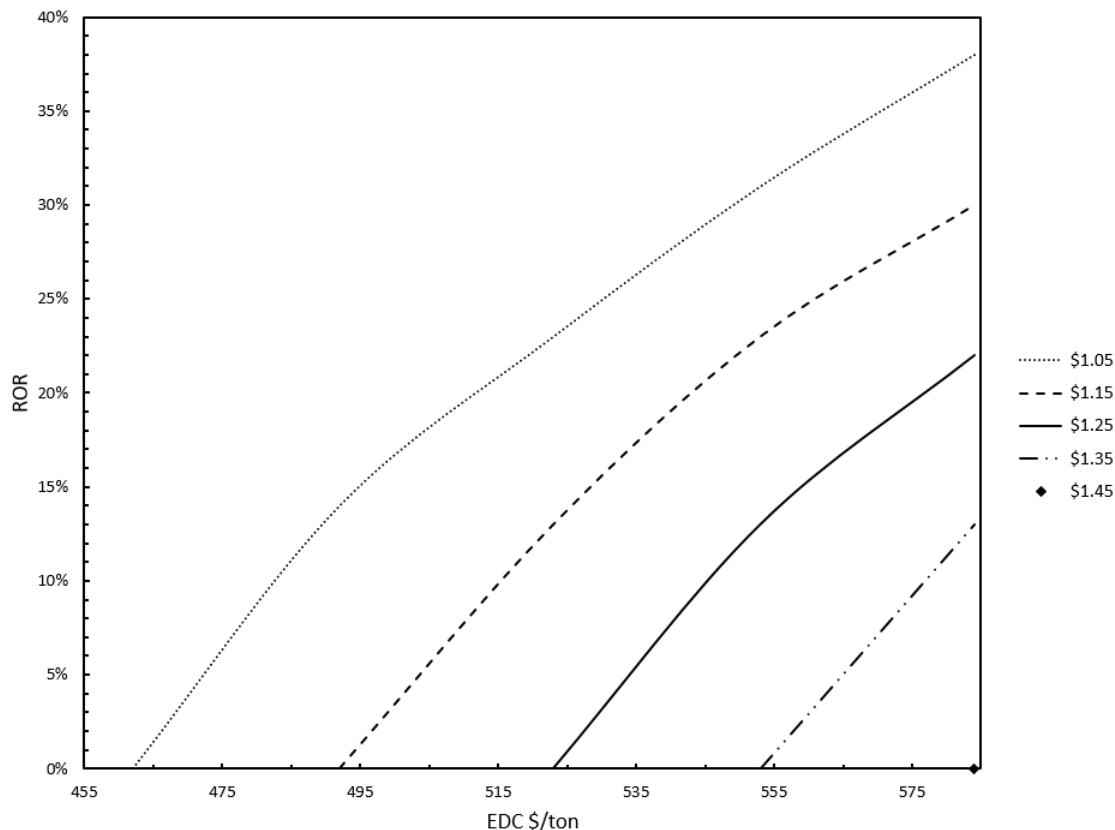


Figure 11: Sensitivity analysis of the rate of return for the dual catalyst process and the selling price of EDC to the purchase price of ethanol in dollars per gallon.

A loss forward tax credit was assumed that allowed 80% of the taxable income after other deductions were applied to be eliminated with the cumulative losses of previous years. Also, The remediation cost of the land was assumed to be covered by the sale of equipment and working capital resulting in a zero cash flow in the last year. The cash flow analysis is shown in Appendix B.

7 Safety and Preliminary Hazard Analysis

7.1 Base Case: Direct Chlorination

Safety of the workforce and community around is of the utmost importance. Safety data sheets have been attached (Appendix F) for the main compounds used and produced in this process to assure proper handling and treatment. Waste treatment recommendations by the Environmental Protection Agency (EPA) have been noted and considered in the design. All employees working in the plant will require adequate training and will be required to wear personal protective equipment (PPE) everywhere.

Feedstock and Product Concerns

Ethanol is highly flammable both as a liquid and a vapor. This requires strict handling and precaution to avoid a flash fire during the dehydration reaction. Ethanol can also cause

irritation to the eyes, skin and damage to organs. All handling of ethanol requires proper PPE and ventilation to avoid these risks.

Chlorine is an oxidizer and can explode under pressure when heated. Chlorine is also fatal when inhaled. These risks make chlorine one of the more dangerous compounds in the plant. To make sure little chlorine is leftover, excess ethylene is feed into the direct chlorination reactor. The chlorine feed will have adequate controls and alarms to avoid injury or death to the surrounding area. All workers in the immediate area will require proper PPE, including respiratory gear.

Ethylene is an extremely flammable gas and can also cause frostbite if it comes in contact with skin. The high risk of explosions with ethylene are of the largest concern with this gas. explosion proof equipment has been recommend and all personal around the ethylene production will need to be very cautious and aware.

EDC is toxic if inhaled and can also be absorbed through the skin and causes damage to central nervous system, liver, kidney, and adrenal gland. EDC is also highly flammable. Storage and production of EDC will require proper alarms and controls to avoid injury or death.

Process Concerns

The dehydration reactors' main risk is a flash fire of the ethanol. Since the reaction is endothermic, a runaway reaction would not occur. loss of containment can be another cause of concern and should be monitored closely.

The direct chlorination reactor was determined to be the most dangerous unit in the plant. This high risk is mainly due to the nature of the exothermic reaction. If proper temperature regulation is not implemented or running the reaction could 'runaway' and cause high pressure in the reactor leading to a possible explosion and loss of containment. A P&ID along with a HAZOP has been constructed for this unit. The P&ID can be seen in Figure 12. The level controller is used to control the liquid EDC level. If the liquid level gets too high, the liquid will be sent to a tank to be reacted later. A temperature controller was implemented to avoid a runaway reaction. The temperature controller will modify the cooling water flow and if the temperature gets too high, it stop the reaction by cutting the feed. A pressure controller was added to avoid over pressurizing the vessel and causing an explosion. The flow controller will control the feed ratio to avoid having too much chlorine or ethylene in the product stream.

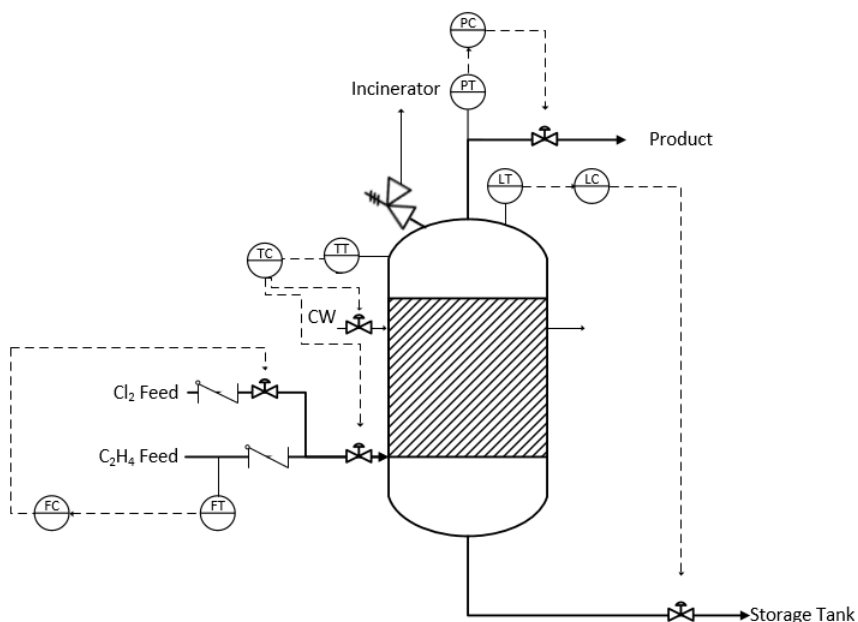


Figure 12: P&ID of the Direct Chlorination Reactor

The last area of concern is the distillation tower. Proper control of the steam feed is required to avoid over pressurizing the vessel.

Waste Treatment

EPA, States and local air pollution control agencies are becoming increasingly aware of the presence of contaminants in the air that are toxic at given concentrations. Many waste products are formed or feed during the production of EDC [32]. Waste products like EDC and excess chlorine can be very harmful to the environment as well as to human health. Because of this, these toxic compounds must be limited and if possible eliminated. To reduce our footprint of pollutants, waste treatment of our waste streams was considered. The recommended plan for waste treatment is to send the streams to an incinerator running at about 2,160 °F, followed by an absorption column using water as the solvent, and finishing at another absorption tower using NaOH as the solvent [33]. The incinerator will create chlorooxides, H₂O, HCl, Cl₂ and CO₂. These chlorooxides are unstable and break down into more H₂O, and HCl. The column that uses water as a solvent and removes HCl and H₂O from the stream. The NaOH absorber removes the Cl₂ and forms a solution of sodium chloride and sodium hypochlorite, which could be considered for selling down the line to a bleach production company [22].

7.2 Alternative Case: Dual Catalyst Bed

Process Concerns

The Dual-catalyst process has been designed to be inherently safe. The primary hazardous units in this process are the reactor and the distillation tower. Like the reactor in the

base case, a HAZOP analysis should be run in order to prepare for how the system could deviate from the design intent. The same nodes of the reactor should be analyzed as in the base case: the feed, the reactor itself, and the reactor product. An analysis of these nodes would encompass the whole reactor block creating a safer environment for the operators.

Chemical Compound Concerns

The chemicals in use and produced in the alternative case should be handled with extreme caution. The MSDS rates HCl as extreme when it comes to physical contact with the material [34]. The other materials such as ethanol, ethylene chloride, and EDC are all considered highly flammable materials to be kept in tightly sealed containers. EDC and ethylene chloride are both toxic if ingested/inhaled. In order to minimize risk for the operators of the process, a safety analysis should be done detailing the entrance and exit of the process, where the operators are at the most risk of exposure to these chemicals.

Catalyst Concerns

This process requires the use of two catalysts: a zeolite catalyst, ZSM-5(50), and cupric chloride catalyst on a γ -alumina support. Both catalysts can be harmful if ingested, however, neither catalyst causes major damage if handled with care [35, 36].

8 Results and Discussion

The design described above for the base case can turn 1,000 tons of ethanol and 1,200 tons of chlorine gas into 1,373 tons of polymer grade EDC a day. Using this production level, the estimated prices for capital, labor, and utilities and the market prices of each reactant and product were calculated and analyzed with a 20 year economic model to see how profitable this design was. An example of this 20 year economic model can be seen in Appendix B. This 20 year analysis for the Direct Chlorination was run for different prices of both ethanol and EDC. The results of this analysis shows strong dependence between net present value and these prices. This shows that this economic of the design is quite dependent upon the prices. Furthermore, the range of prices for EDC that showed any significant positive NPV are significantly above the market estimated prices. These results may be due to the inaccuracies in the design process, but it is more likely that this process is not economical in society in its current form. The best way to improve the economic feasibility of this project is to continue this process to produce vinyl chloride, or produce the EDC from the current market feed-stock, which is produced from ethane in oil and gas processes.

The alternate case turns 1,000 tons of ethanol into 1,394 tons of polymer grade EDC. It differs from the base case in that instead of consuming 1,200 tons of chlorine gas it consumes 1,232 tons of hydrogen chloride. The same 20 year economic analysis was run on this case for varying prices of ethanol and EDC and an example of that analysis is shown in Appendix B. The results of this analysis were similar to the results for the base case. The net present value of the production of EDC using the dual catalyst configuration is significantly negative when the estimated market prices for the ethanol and EDC are used. In order to achieve a positive NPV the price of EDC must be significantly higher than the highest recorded EDC price. The 20 year economic analysis also showed that economic revenue of this design is extremely sensitive to the pricing of ethanol. Overall,

this process is extremely financially risky and requires unrealistic product prices to be profitable. This result may be due to the lack of information about this process due to the reactor and catalysts being proprietary and thus held behind pay walls. There are few ways that this process could be modified so that it would have the potential to generate significant revenue without requiring proprietary information. Primarily, this would involve continuing the production of EDC all the way to VMC, because most market estimates show that the price of VMC is almost twice as high as EDC [37]. To ensure that the addition of VMC would increase the processes profitability it would require a full process to be designed and costed.

9 Conclusion

With both economic analysis requiring altered prices from their current market value to generate positive rates of return, this process is not considered to be currently profitable by itself. Future research should be conducted to gain better estimates of these prices. While both of these processes may be unprofitable on their own, further analysis of designs that crack the EDC produced by these methods to VCM may make this the overall process ofitable. The reasoning behind this is that EDC is not in high demandd, as most VCM plants only produce it as an intermediate; VCM has as a selling price of 700 to 900\$/ton with only EDC as a chemical feed [37]. This is a sharp contrast to both the researched selling price of EDC and the selling price generated by either deign model. As such, the addition of a VCM unit would also allow for balanced process in which oxychlorination and direct chlorination are used. This would also produce HCl and reduce the cost associated with its purchase. This balanced process is already well-established and would only require addition of an ethanol dehydration unit. Compared to the direct chlorination model, the dual catalyst bed technology has the advantage of only using one reactor to do both the dehydration and oxychlorination. However, this method is still in the early stages of development and does not have much literature regarding it. Therefore, much of the analysis of this process was based on only a few sources and any information not in these sources had to be assumed, which resulted in errors. This is in stark contrast with the direct chlorination process for which there is extensive literature and industrial sized facilities to compare to. Therefore, any of the above mentioned recommendations for future research be done on the direct chlorination base case.

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Appendix A (Technical Appendices)

Appendix A.1 Nomenclature

EDC: ethylene dichloride
PVC: polyvinyl Chloride
VCM: vinyl chloride monomer
DEE: diethyl ether
ACA: acetaldehyde
TCE: trichloroethane
DCB: 1,2-dichlorobutane
DCEE: bis(chloroethyl) ether
EB: ethylbenzene
EO: ethylene oxide
EG: ethylene glycol
U: Overall heat transfer coefficient (BTU/ h °F ft²)
 ΔT_{lm} : Log mean temperature difference (°F)
Q: Duty (BTU/h)
A: Area (ft²)
q : Heat flux (BTU/h ft²)
P: Pressure (psi)
 ϵ and η : Pump Efficiency
W: Power/Work (kW)
 ρ : Density (lb_m/ft³ or lbmol/ft³)
MW: Molecular Weight (lb_m/lbmol)
z: Altitude (ft)
 \dot{m} : Mass flow rate (lb_m/s)
 ϵ_{void} : Void Fraction
 τ : Residence Time (s)
t: Time (s or min)
V: Volume (ft³)
 \dot{V} : Volumetric flow rate (ft³/day)
EMC: Chloroethane
EPA: Environmental Protection Agency

PPE: Personal Protective Equipment

PFD: Process Flow Diagram

BFD: Block Flow Diagram

HAZOP: Hazardous Operations

P&ID: Piping and Instrumentation Diagram

SDS: Safety Data Sheets

NPV: Net Present Value

Appendix A.2 Diagrams and Models

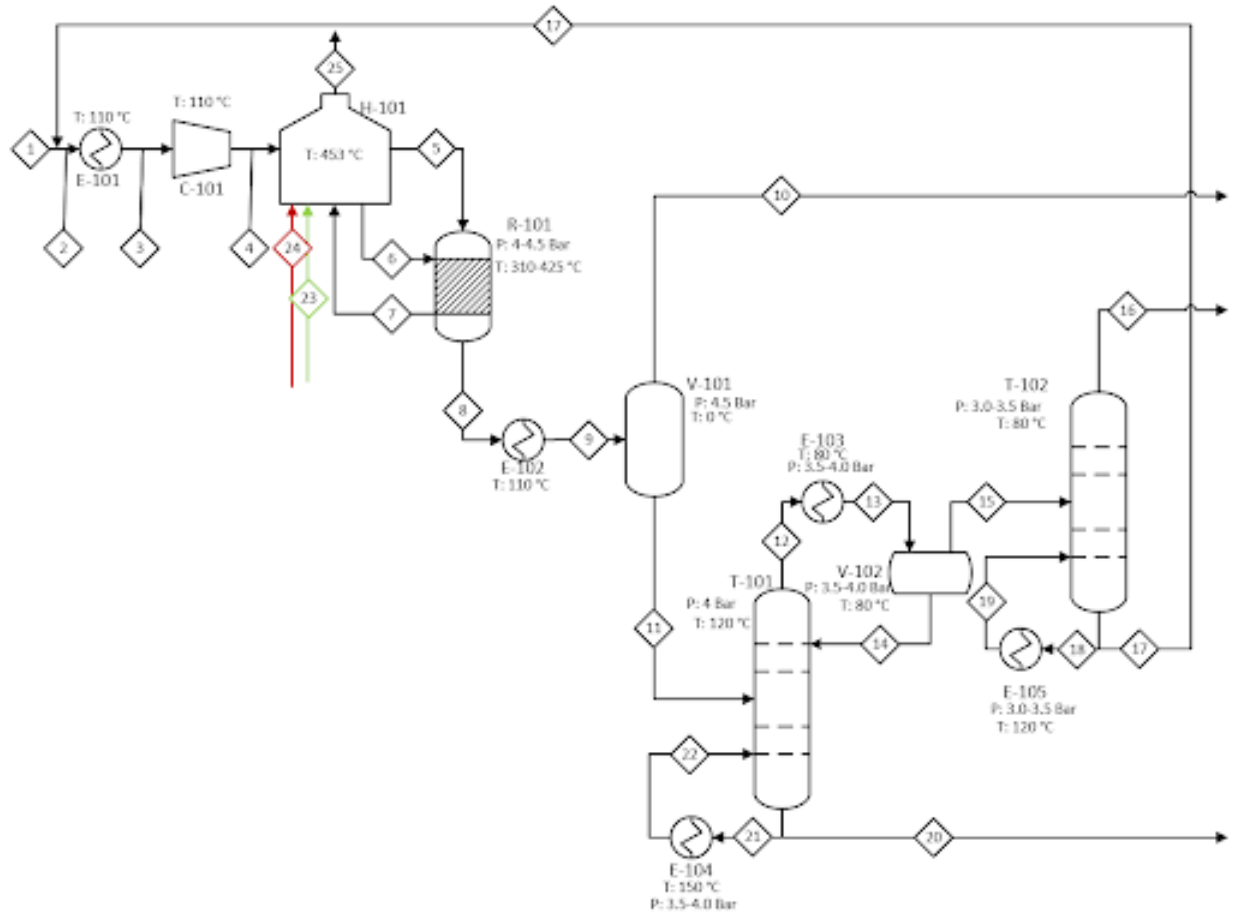


Figure 13: Preliminary Dehydration Unit for the Oxychlorination Alternative

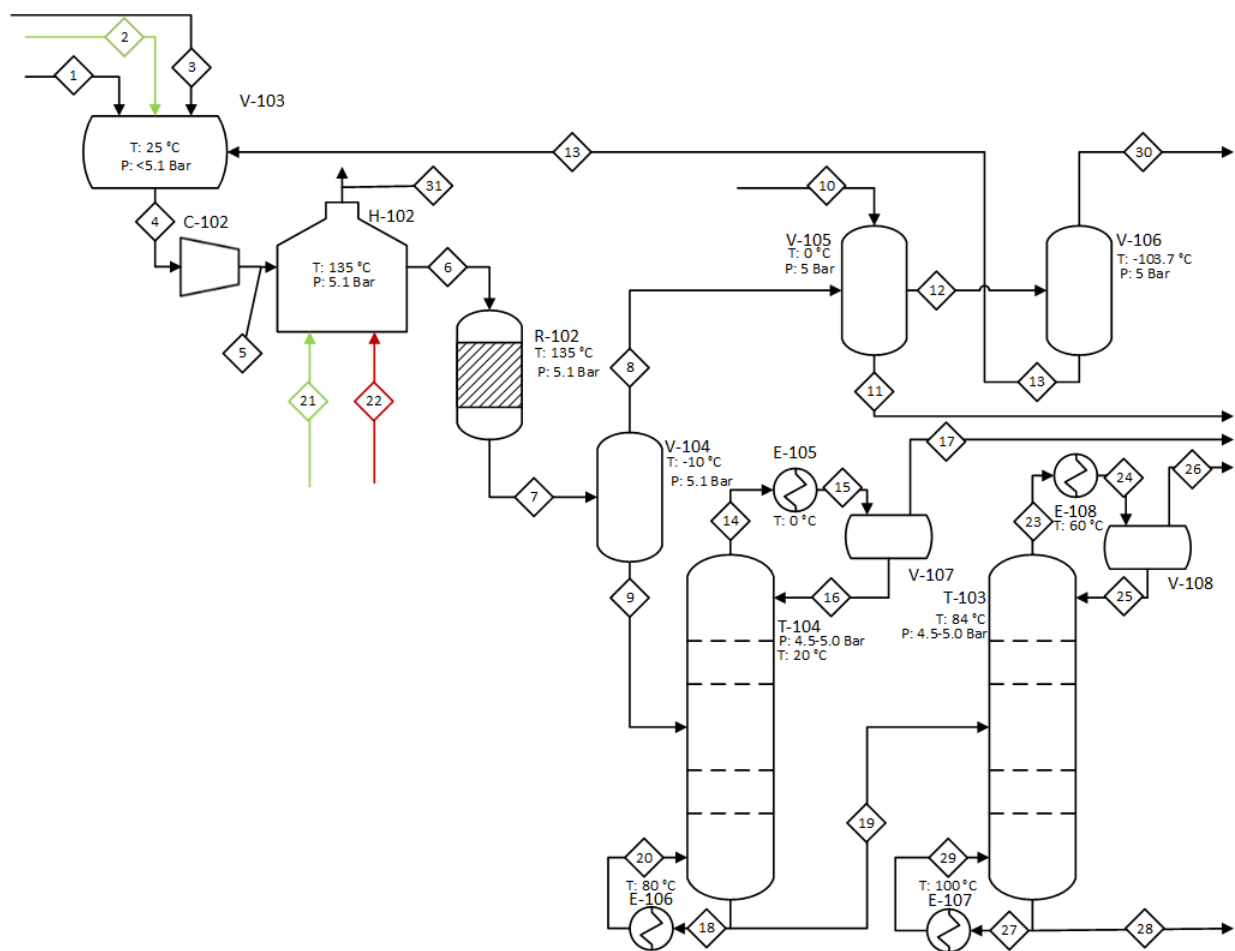


Figure 14: Preliminary EDC Unit for the Oxychlorination Alternative

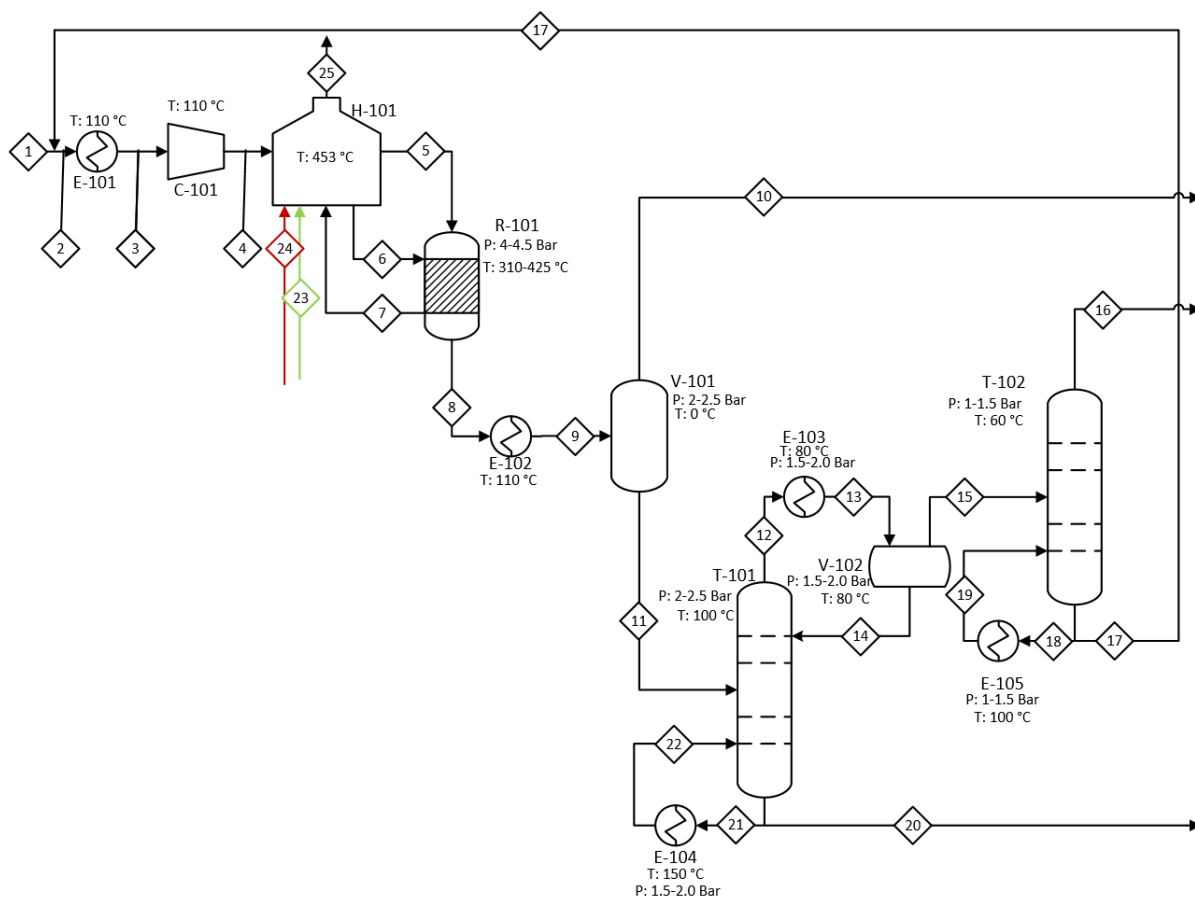


Figure 15: Preliminary Dehydration Unit for the Direct Chlorination with an Ethanol Recycle Alternative

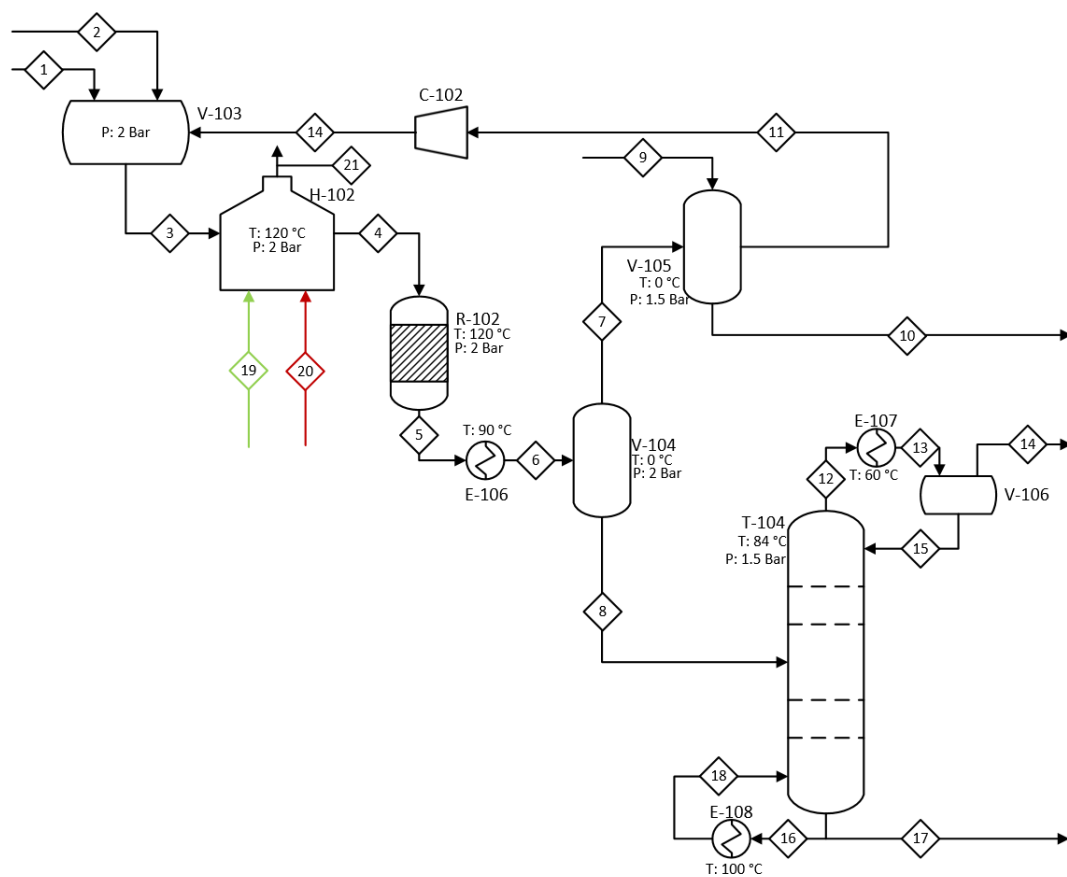


Figure 16: Preliminary EDC Unit for the Direct Chlorination with an Ethanol Recycle Alternative

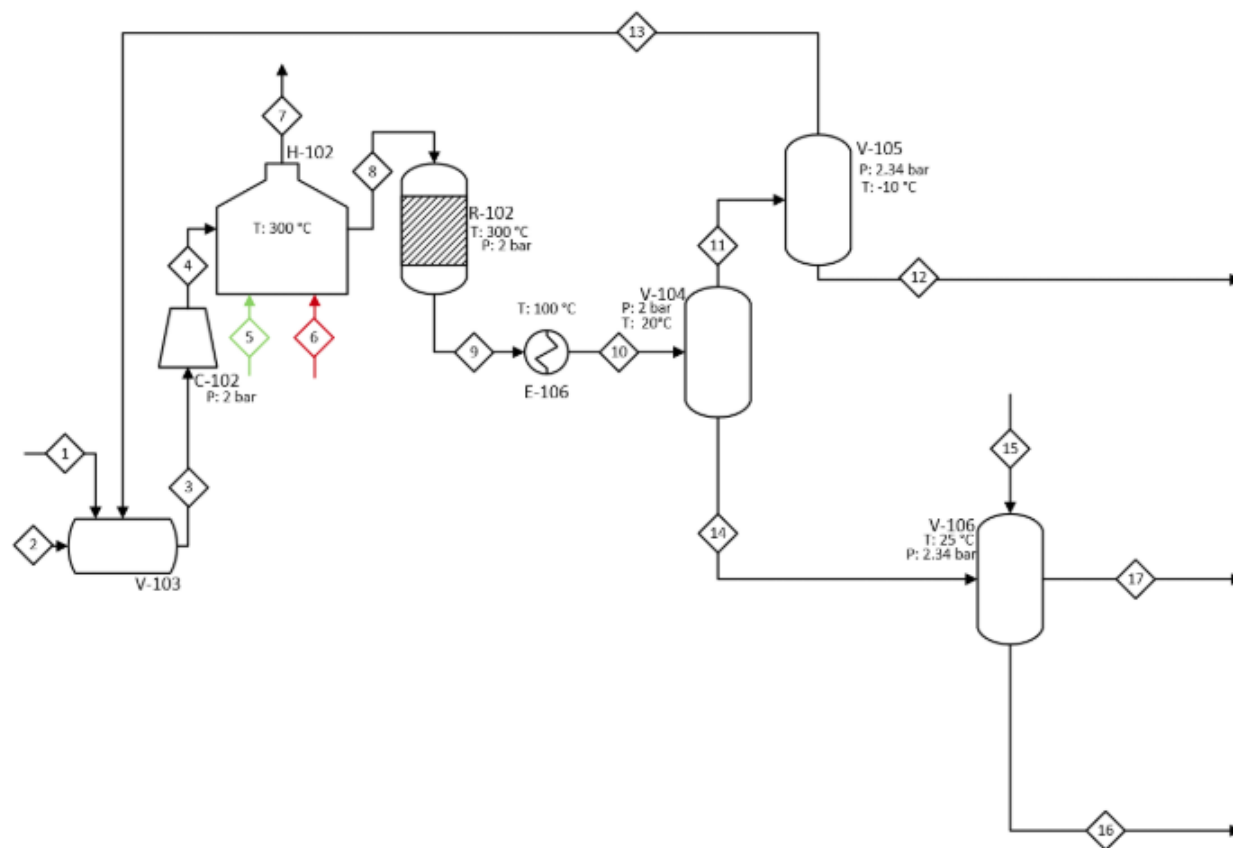


Figure 17: Preliminary EDC Unit for the Dual Catalyst Fluidized Reaction Alternative

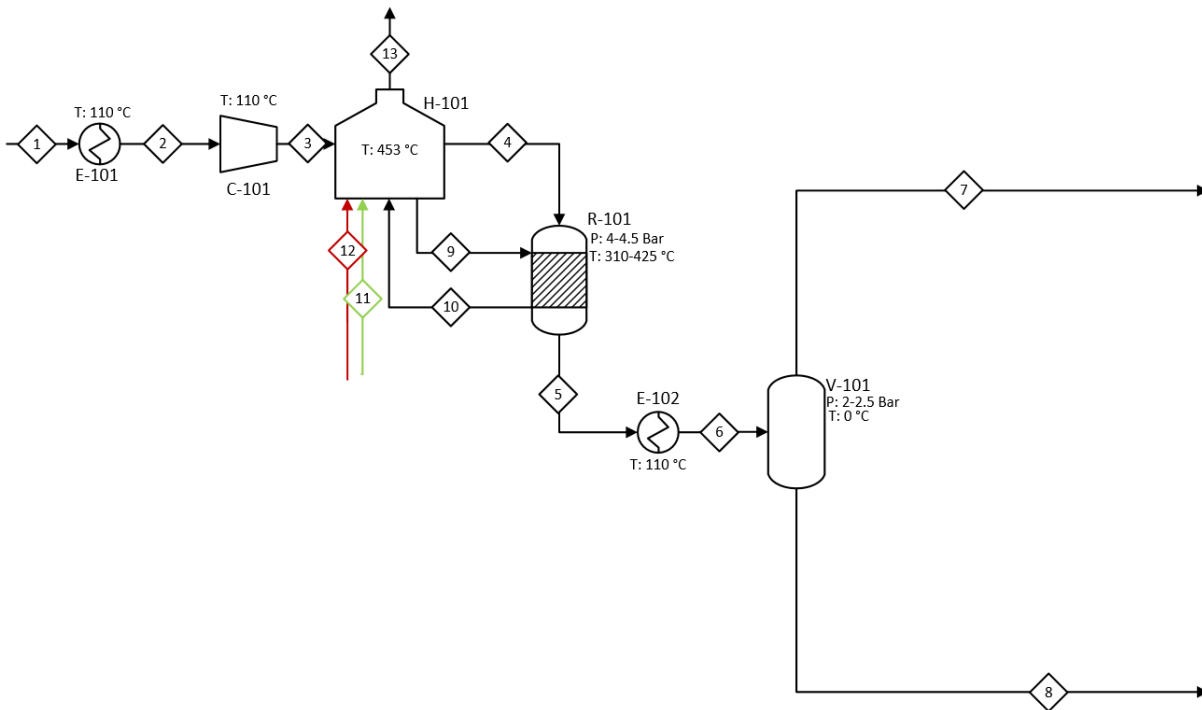


Figure 18: Preliminary Dehydration Unit for the Direct Chlorination without an Ethanol Recycle Alternative

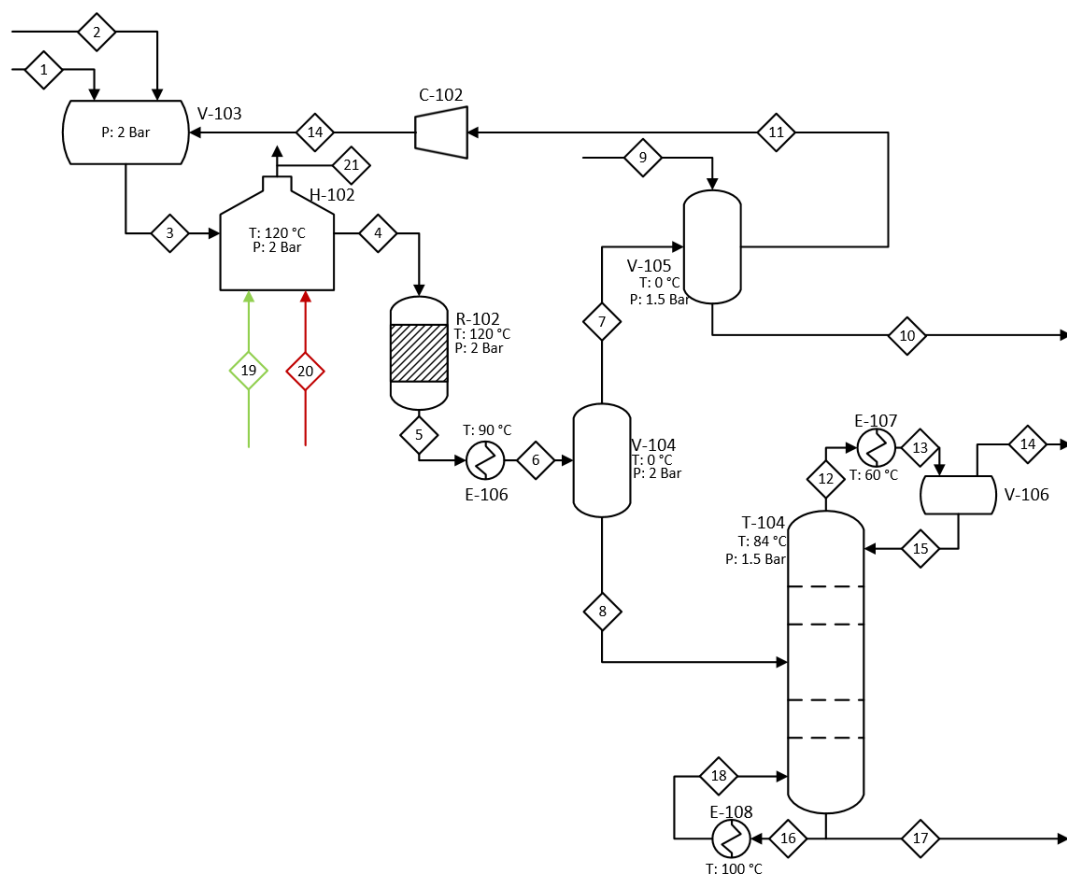


Figure 19: Preliminary EDC Unit for the Direct Chlorination without an Ethanol Recycle Alternative

Appendix A.3 Stream Tables

Base Case: Direct Chlorination

Table 14: Stream Summaries of the Base Case: Direct Chlorination

Stream Number	1	2	3	4	5	6
Temperature (°F)	77	77	250	752	588	752
Pressure (psia)	14.7	66.1	64.7	61.8	60.3	57.4
Vapor Fraction	0	0	0.190	1	1	1
Mass Flow (lb _m /hr)	83,300	83,300	83,300	83,300	83,300	83,300
Mole flow (lbmol/hr)	2,180	2,180	2,180	2,180	2,740	2,780
Component Flowrates (lbmol/hr)						
C ₂ H ₅ OH	1,570	1,570	1,570	1,570	185	185
H ₂ O	601	601	601	601	1,580	1,580
C ₂ H ₄	0	0	0	0	558	558
(C ₂ H ₅) ₂ O	0	0	0	0	411	411
C ₂ H ₄ O	0	0	0	0	1.97	1.97
H ₂	0	0	0	0	1.97	1.97
Cl ₂	0	0	0	0	0	0
C ₂ H ₄ Cl ₂	0	0	0	0	0	0
HCl	0	0	0	0	0	0
C ₂ H ₃ Cl ₃	0	0	0	0	0	0
C ₂ H ₈ Cl ₂	0	0	0	0	0	0
C ₄ H ₈ Cl ₂ O	0	0	0	0	0	0
C ₂ H ₈	0	0	0	0	3.69	3.69

Stream Number	7	8	9	10	11	12
Temperature (°F)	598	752	630	752	682	268
Pressure (psia)	56.0	53.1	51.6	48.7	47.3	41.5
Vapor Fraction	1	1	1	1	1	1
Mass Flow (lb _m /hr)	83,300	83,300	83,300	83,300	83,300	83,300
Mole flow (lbmol/hr)	3,060	3,060	3,330	3,330	3,520	3,520
Component Flowrates (lbmol/hr)						
C ₂ H ₅ OH	117	117	83.2	83.2	55.7	55.7
H ₂ O	1,780	1,780	1,940	1,940	2,080	2,080
C ₂ H ₄	870	870	1,110	1,110	1,240	1,240
(C ₂ H ₅) ₂ O	277	277	150	150	37.49	37.5
C ₂ H ₄ O	2.36	2.36	2.72	2.72	3.29	3.29
H ₂	2.36	2.36	2.72	2.72	3.29	3.29
Cl ₂	0	0	0	0	0	0
C ₂ H ₄ Cl ₂	0	0	0	0	0	0
HCl	0	0	0	0	0	0
C ₂ H ₃ Cl ₃	0	0	0	0	0	0
C ₂ H ₈ Cl ₂	0	0	0	0	0	0
C ₄ H ₈ Cl ₂ O	0	0	0	0	0	0
C ₂ H ₈	15.1	15.1	38.9	38.9	99.2	99.2

Stream Number	13	14	15	16	17	18
Temperature (°F)	234	95.2	94.8	94.8	216	68
Pressure (psia)	40.0	40.0	38.6	38.6	37.1	39.3
Vapor Fraction	0.940	0.402	1	0	0.00438	1
Mass Flow (lb _m /hr)	83,300	83,300	43,700	39,600	39,600	100,500
Mole flow (lbmol/hr)	3,520	3,520	1,420	2,100	2,100	1,410
Component Flowrates (lbmol/hr)						
C ₂ H ₅ OH	55.7	55.7	9.81	45.9	45.9	0
H ₂ O	2,080	2,080	30.1	2,050	2,050	0
C ₂ H ₄	1,240	1,240	1,240	5.28	5.28	0
(C ₂ H ₅) ₂ O	37.5	37.5	36.1	1.42	1.42	0
C ₂ H ₄ O	3.29	3.29	2.34	0.95	0.95	0
H ₂	3.29	3.29	3.29	6.74E-08	6.74E-08	0
Cl ₂	0	0	0	0	0	1,411
C ₂ H ₄ Cl ₂	0	0	0	0	0	0
HCl	0	0	0	0	0	0
C ₂ H ₃ Cl ₃	0	0	0	0	0	0
C ₂ H ₈ Cl ₂	0	0	0	0	0	0
C ₄ H ₈ Cl ₂ O	0	0	0	0	0	0
C ₂ H ₈	99.2	99.2	99.0	0.230	0.230	0

Stream Number	19	20	21	22	23
Temperature (°F)	83.5	261	104	248	104
Pressure (psia)	38.6	37.1	14.5	16.2	14.5
Vapor Fraction	1	1	0	0	1
Mass Flow (lb _m /hr)	144,200	144,200	113,800	20,200	10,190
Mole flow (lbmol/hr)	2,830	1,520	1,200	176.3	152.2
Component Flowrates (lbmol/hr)					
C ₂ H ₅ OH	9.8	9.8	8.70	6.24E-06	1.12
H ₂ O	30.1	30.1	19.2	4.51E-09	10.9
C ₂ H ₄	1,236	24.7	5.44	4.85E-09	19.3
(C ₂ H ₅) ₂ O	36.1	1.80	1.20	2.18E-07	0.61
C ₂ H ₄ O	2.34	2.34	1.87	2.32E-06	0.472
H ₂	3.29	3.29	2.75E-07	1.36E-18	3.29
Cl ₂	1,410	14.11	7.10	9.86E-08	7.01
C ₂ H ₄ Cl ₂	0	1,190	1,130	28.6	30.7
HCl	0	93	17.6	2.89E-09	76
C ₂ H ₃ Cl ₃	0	24.7	2.19	22.5	0.0193
C ₂ H ₈ Cl ₂	0	92.0	1.11	90.9	0.0079
C ₄ H ₈ Cl ₂ O	0	34.3	4.41E-11	34.3	2.34E-14
C ₂ H ₈	99.0	6.93	3.75	1.61E-07	3.17

Alternative Case: Dual Cat

Table 15: Dual Cat Stream Summaries

Stream Number	1	2	3	4	5	6
Temperature (°F)	77	77	77	44.9	107	246
Pressure (psia)	14.5	14.5	14.5	14.5	14.5	29
Vapor Fraction	0	1	1	0.828	1	1
Mass Flows (lb _m /h)	95,800	148,000	203,000	447,000	447,000	447,000
Mole Flows (lbmol/h)	2,500	4,070	7,000	13,600	13,600	13,600
Component Flow Rates (lbmol/h)						
C ₂ H ₅ OH	1,810	0	0	1,810	1,810	1,810
HCl	0	4,070	0	4,070	4,070	4,070
O ₂	0	0	1,460	1,460	1,460	1,460
C ₂ H ₄	0	0	0	0	0	0
C ₂ H ₅ Cl	0	0	0	0	0	0
C ₂ H ₄ Cl ₂	0	0	0	0	0	0
(C ₂ H ₅) ₂ O	0	0	0	0	0	0
C ₂ H ₃ Cl (VCM)	0	0	0	0	0	0
H ₂	0	0	0	0	0	0
H ₂ O	691	0	0	691	691	691
N ₂	0	0	5,470	5,470	5,470	5,470
Ar	0	0	65.2	65.2	65.2	65.2
C ₂ H ₄ O	0	0	0	0	0	0

Stream Number	7	8	9	10	11	12
Temperature (°F)	572	572	181	50	41	41
Pressure (psia)	29	29	29	29	29	29
Vapor Fraction	1	0.997	0.695	1	0	0
Mass Flows (lb _m /h)	447,000	447,000	447,000	257,000	190,000	13,800
Mole Flows (lbmol/h)	13,000	13,000	13,000	8,030	4,970	185
Component Flow Rates (lbmol/h)						
C ₂ H ₅ OH	270	270	270	21	249	15.8
HCl	1,340	1,340	1,340	1,260	78.4	6.95
O ₂	834	834	834	823	11.2	1.04
C ₂ H ₄	33.1	33.1	33.1	32.5	0.515	0.0813
C ₂ H ₅ Cl	259	259	259	190	69.6	20.1
C ₂ H ₄ Cl ₂	1,230	1,230	1,230	138	1,090	110
(C ₂ H ₅) ₂ O	0.634	0.634	0.634	0.464	0.169	0.0598
C ₂ H ₃ Cl (VCM)	19	19	19	16.1	2.96	0.784
H ₂	0.449	0.449	0.449	0.449	1.28E-09	2.67E-11
H ₂ O	3,470	3,470	3,470	33.7	3,440	28.2
N ₂	5,470	5,470	5,470	5,450	25.3	2.6
Ar	65.2	65.2	65.2	64.6	0.577	0.0705
C ₂ H ₄ O	0.449	0.449	0.449	0.227	0.222	0.0449

Stream Number	13	14	15	16	17	18
Temperature (°F)	0	0	0	41	41	41
Pressure (psia)	29	29	29	29	29	29
Vapor Fraction	1	1	0.928	0	0	0
Mass Flows (lb _m /h)	243,000	183,000	60,700	115,000	74,800	13,100
Mole Flows (lbmol/h)	7,840	6,350	1,490	1,250	3,710	156
Component Flow Rates (lbmol/h)						
C ₂ H ₅ OH	5.15	0	5.15	50.2	199	12
HCl	1,250	0	1,250	24	54.4	5.97
O ₂	822	822	0	4.14	7.09	0.925
C ₂ H ₄	32.5	0	32.5	0.467	0.0486	0.0802
C ₂ H ₅ Cl	169	0	169	66.9	2.68	20
C ₂ H ₄ Cl ₂	28.8	0	28.8	1080	11.7	109
(C ₂ H ₅) ₂ O	0.404	0.404	0	0.14	0.0293	0.0577
C ₂ H ₃ Cl (VCM)	15.3	15.3	0	2.65	0.312	0.772
H ₂	0.449	0.449	0	4.67E-10	8.13E-10	2.37E-11
H ₂ O	5.49	5.49	0	19.7	3420	4.15
N ₂	5,450	5,450	0	9.75	15.5	2.32
Ar	64.6	64.6	0	0.258	0.32	0.0641
C ₂ H ₄ O	0.182	0.182	0	0.135	0.0869	0.0423

Stream Number	19	20	21	22	23
Temperature (°F)	40.7	183	41	58.4	32.7
Pressure (psia)	29	14.7	29	14.7	14.7
Vapor Fraction	0	0	0	0	0.0191
Mass Flows (lb _m /h)	126,000	117,000	688	9,250	84,700
Mole Flows (lbmol/h)	1,360	1,180	29.6	178	3,920
Component Flow Rates (lbmol/h)					
C ₂ H ₅ OH	62.2	0.0622	3.75	62.2	265
HCl	0	0	0.982	0	55.4
O ₂	0	0	0.118	0	7.21
C ₂ H ₄	0	0	0.00111	0	0.0498
C ₂ H ₅ Cl	86.9	7.070E-07	0.131	86.9	89.7
C ₂ H ₄ Cl ₂	1,190	1,180	0.25	1.19	13.1
(C ₂ H ₅) ₂ O	0.198	7.72E-10	0.00213	0.198	0.229
C ₂ H ₃ Cl (VCM)	3.42	7.37E-11	0.0124	3.42	3.75
H ₂	0	0	3E-12	0	8.16E-10
H ₂ O	23.8	3.82E-09	24	23.8	3,470
N ₂	0	0	0.28	0	15.8
Ar	0	0	0.0064	0	0.326
C ₂ H ₄ O	0	0	0.00267	0	0.0895

Appendix A.4 Equipment Tables

Base Case Equipment Tables:

Table 16: Equipment Summaries for the Base Case: Direct Chlorination

Heat Exchangers	
E-101	E-104
A = 519 ft ²	A = 437 ft ²
1-2 exchanger, floating head, carbon steel	1-2 exchanger, floating head, stainless steel
Stream 2 in tubes	Process stream in tubes
Q = 17,800,000 BTU/h	Q = 9,370,000 BTU/h
Maximum pressure rating of 70 psia	Maximum pressure rating of 20 psia
E-102	E-105
A = 703 ft ²	A = 4,190 ft ²
1-2 exchanger, floating head, carbon steel	1-2 exchanger, floating head, stainless steel
Stream 16 in tubes	Process stream in shell
Q = 4,900,000 BTU/h	Q = 33,200,000 BTU/h
Maximum pressure rating of 45 psia	Maximum pressure rating of 20 psia
E-103	
A = 3,810 ft ²	
1-2 exchanger, floating head, carbon steel	
Process stream in shell	
Q = 40,400,000 BTU/h	
Maximum pressure rating of 45 psia	
Fired Heater	
H-101	
Required heat load = 70,400,000 BTU/h	
Design (maximum) heat load = 88,200,000 BTU/h	
Tubes = Stainless steel	
80% thermal efficiency	
Maximum pressure rating of 70 psia	
A _{rad} = 2,930 ft ²	
A _{conv} = 8,800 ft ²	

Pumps	
P-101 A/B	P-102 A/B
Centrifugal/explosion proof drive	Centrifugal/explosion proof drive
Carbon steel	Stainless steel
Actual power = 8.66 kW	Actual power = 3.92 kW
Efficiency 70%	Efficiency 70%
Reactors	
R-101	R-104
Carbon steel, γ -Al ₂ O ₃ catalyst (882 lb _m)	Carbon steel, γ -Al ₂ O ₃ catalyst (882 lb _m)
V = 30.9 ft ³	V = 58.1 ft ³
4.5 ft long, 1.5 ft diameter	5.5 ft long, 2 ft diameter
Maximum pressure rating of 65 psia	Maximum pressure rating of 65 psia
Maximum allowable catalyst temperature = 932°F	Maximum allowable catalyst temperature = 932°F
R-102	R-105
Carbon steel, γ -Al ₂ O ₃ catalyst (1,100 lb _m)	Stainless steel, FeCl ₃ catalyst
V = 56.5 ft ³	V = 56.5 ft ³
5 ft long, 2 ft diameter	8 ft long, 3 ft diameter
Maximum pressure rating of 65 psia	Maximum pressure rating of 45 psia
Maximum allowable catalyst temperature = 932°F	Maximum allowable catalyst temperature = 572°F
R-103	
Carbon steel, γ -Al ₂ O ₃ catalyst (1,100 lb _m)	
V = 56.5 ft ³	
5 ft long, 2 ft diameter	
Maximum pressure rating of 65 psia	
Maximum allowable catalyst temperature = 932°F	
Towers	
T-101	
Stainless steel	
18 ss sieve trays plus reboiler and total condenser	
75% efficient trays	
Feed on tray 14	
Reflux ratio = 0.668	
0.61 ft tray spacing	
Column height = 46 ft	
Diameter = 15.5 ft	
Maximum pressure rating of 20 psia	

Vessels	
V-101	V-103
Carbon steel	Floating roof tank
Vertical	3 tanks for ethanol storage
17.5 ft long, 6 ft diameter	96 ft tall, 72 ft diameter
V = 230 ft ³	V = 391,000 ft ³
Maximum operating pressure = 45 psia	Maximum operating pressure = 20 psia
V-102	V-104
Stainless steel	Fixed roof tank
Horizontal	3 tanks for EDC storage
15.5 ft long, 5.5 ft diameter	94 ft tall, 72 ft diameter
V = 252 ft ³	V = 367,000 ft ³
Maximum operating pressure = 20 psia	Maximum operating pressure = 20 psia

Table 17: Equipment Summaries for the Alternate Case: Direct Dual Catalyst

Heat Exchangers	
E-101	E-103
A = 1,270 ft ²	A = 2,330 ft ²
1-2 exchanger, floating head, stainless steel	1-2 exchanger, floating head, stainless steel
Stream 8 in tubes	Process stream in tubes
Q = 17,800,000 BTU/h	Q = 26,000,000 BTU/h
Maximum pressure rating of 20 psia	Maximum pressure rating of 35 psia
E-102	E-104
A = 7,450 ft ²	A = 11,430 ft ²
1-2 exchanger, floating head, stainless steel	1-2 exchanger, floating head, stainless steel
Process Stream in tubes	Process stream in tubes
Q = 59,000,000 BTU/h	Q = 20,900,000 BTU/h
Maximum pressure rating of 35 psia	Maximum pressure rating of 35 psia
Fired Heater	
H-101	
Required heat load = 40,600,000	
Design (maximum) heat load = 58,400,000 BTU/h	
Tubes = Stainless steel	
80% thermal efficiency	
Maximum pressure rating of 35 psia	
Pumps	
P-101 A/B	
Centrifugal/explosion proof drive	
Stainless Steel	
Actual power = 8.20 kW	
Efficiency 70%	

Towers	
T-101	
Stainless steel	
32 ss sieve trays plus reboiler and total condenser	
60% efficient trays	
Feed above Tray 23	
Reflux ratio = 6.65	
2 ft tray spacing	
Column height = 72 ft	
Diameter = 10 ft	
Maximum pressure rating of 20 psia	
Vessels	
V-101	D-102
Stainless Steel	Stainless Steel
Horizontal	Horizontal
24 ft long, 8 ft diameter	10.5 ft long, 3.5 ft diameter
V = 1,210 ft ³	V = 101 ft ³
Maximum operating pressure = 35 psia	Maximum operating pressure = 35 psia
V-102	V-104
Stainless Steel	Stainless Steel
Vertical	Horizontal
21 ft tall, 7 ft diameter	15 ft long, 5 ft diameter
V = 808 ft ³	V = 295 ft ³
Maximum operating pressure = 35 psia	Maximum operating pressure = 35 psia
V-103	V-105
Stainless steel	Floating roof tank
Vertical	3 tanks for ethanol storage
22.5 ft long, 7.5 ft diameter	96 ft tall, 72 ft diameter
V = 994 ft ³	V = 391,000 ft ³
Maximum operating pressure = 35 psia	Maximum operating pressure = 20 psia
D-101	V-106
Stainless Steel	Fixed roof tank
Horizontal	3 tanks for EDC storage
15 ft long, 5 ft diameter	95.5 ft tall, 71.5 ft diameter
V = 295 ft ³	V = 383,000 ft ³
Maximum operating pressure = 35 psia	Maximum operating pressure = 20 psia
Compressors and Drivers	
C-101	CD-101
Stainless Steel	Electric/explosion proof
W = 4680 kW	W = 4,780 kW
Efficiency 72%	98% Efficiency

Reactors
R-101
Stainless steel, γ -Al ₂ O ₃ /CuCl ₂ catalyst (850,000 lbm) and ZSM-5 (50) (48,000 lbm)
V = 1,090 ft ³
41.9 ft long, 5.75 ft diameter
Maximum pressure rating of 45 psia
Maximum allowable catalyst temperature = 932°F

Appendix A.5 Sizing Methods and Sample Calculations

Heat Exchangers:

The first step to sizing a heat exchanger is to calculate the log mean temperature difference. This is for a condenser using cooling water. The process inlet is at 248°F and leaves at 104°F. Cooling water enters at 90°F and leaves at 115°F.

$$\Delta T_{lm} = \frac{(T_{Hot,In} - T_{Cold,Out}) - (T_{Hot,Out} - T_{Cold,In})}{\ln\left(\frac{T_{Hot,In} - T_{Cold,Out}}{T_{Hot,Out} - T_{Cold,In}}\right)}$$

$$\Delta T_{lm} = \frac{(248F - 115F) - (104F - 90F)}{\ln\left(\frac{248F - 115F}{104F - 90F}\right)} = 52.86^\circ F$$

Using $U = 150 \text{ BTU/h}^\circ F \text{ ft}^2$ and $Q = 33,200,000 \text{ BTU/h}$ the following equation can be solved for A:

$$Q = U A \Delta T_{lm}$$

$$A = \frac{Q}{U \Delta T_{lm}}$$

$$A = \frac{33,200,000 \text{ BTU/h}}{(150 \text{ BTU/h}^\circ F \text{ ft}^2)(52.86^\circ F)} = 4,190 \text{ ft}^2$$

Fired Heater:

Using the fired duty of $Q = 70,400,000 \text{ BTU/h}$ and heat fluxes of $q_{rad} = 12,000 \text{ Btu/h ft}^2$ and $q_{conv} = 4,000 \text{ Btu/h ft}^2$

splitting the duty for each section the radiant area is calculated as follows:

$$A_{rad} = \frac{Q}{q_{rad}}$$

$$A_{rad} = \frac{(0.5)(70,400,000 \text{ BTU/h})}{12,000 \text{ BTU/h ft}^2} = 2,930 \text{ ft}^2$$

The convection rate is calculated by:

$$A_{conv} = \frac{Q}{q_{conv}}$$

$$A_{rad} = \frac{(0.5)(70,400,000 \text{ BTU/h})}{4,000 \text{ BTU/h ft}^2} = 8,800 \text{ ft}^2$$

Pumps:

The feed pump power was calculated by the following equation:

$$P = \dot{V} \Delta P / 1714 / \epsilon$$

$$P = (202)(66.1 - 14.7) / 1714 / (0.7) = 8.65 \text{ kW}$$

The reflux pump was calculated using the following equation:

$$P = \frac{\left(\frac{(\Delta P / \rho + \Delta z g) \dot{m}}{\eta} \right)}{0.5}$$

$$P = \frac{\left(\frac{(10 \text{ psi})(6.89 \text{ kPa/psi})}{(75.54 \text{ lbm/ft}^3)(0.45359 \text{ kg/lbm})(1 \text{ ft}^3/0.02831 \text{ m}^3)} + (46 \text{ ft})(0.3048 \text{ m/ft})(32.17 \text{ ft/s}^2) \right)(23.94 \text{ lbm/s})(0.45359 \text{ kg/lbm})}{0.5}$$

$$P = 3.92 \text{ kW}$$

Reactors:

The dehydration reactors are sized using the following equation:

$$V_{Bed} = \frac{\frac{W}{\rho}}{1-\epsilon_{void}}$$

$$V_{Bed} = \frac{\frac{882lb_m}{174.8lb_m/ft^3}}{1-0.3} = 7.21 \text{ ft}^3$$

Considering a 3:1 Length to diameter ratio:

$$D = \left(\frac{4V_{Bed}}{3\pi}\right)^{1/3} = 1.5 \text{ ft}$$

$$H = 3D + 13ft = 17.5 \text{ ft}$$

$$V = \frac{\pi}{4}D^2H = 30.9 \text{ ft}^3$$

Towers:

The height was calculated as follows:

$$H = (N_{Trays})(2ft) + 4ft + 6ft$$

$$H = (18)(2ft) + 4ft + 6ft = 46 \text{ ft}$$

Using a 3:1 height to diameter ratio:

$$D = \frac{H}{3} = 15.33$$

The diameter is then rounded up to 15.5 ft as you should round to the nearest 6 inches.

Vessels:

Process vessels are sized as being half full with liquid at a 5 minute hold-up time.

$$\frac{1}{2}V = \frac{\dot{m}_{liq}t_{hold-up}}{\rho_{liq}}$$

using a mass flow of $\dot{m}_{liq} = 1390 \text{ lb}_m/\text{min}$ and a density of $60.4 \text{ lb}_m/\text{ft}^3$

$$V = \frac{2(1390lb_m/min)(5min)}{60.4lb_m/ft^3} = 230 \text{ ft}^3$$

Storage tanks were sized for 30-day capacity using the following equation:

$$V_{Total} = \dot{V}t$$

Using a flow rate of $\dot{V} = 36,200 \text{ ft}^3/\text{day}$

$$V_{Total} = (36,200ft^3/day)(30days) = 1,086,000ft^3$$

Sizing for 3 tanks:

$$V_{Tank} = \frac{V_{Total}}{3} = 362,000 \text{ ft}^3$$

Using a 3:4 length to diameter ratio:

$$D = \left(\frac{3V_{Tank}}{\pi}\right)^{1/3} = 70.2 \text{ ft}$$

The diameter is then rounded up to 70.5 ft.

$$H = \frac{4}{3}D = 94 \text{ ft}$$

Appendix A.6 Aspen Flowsheets

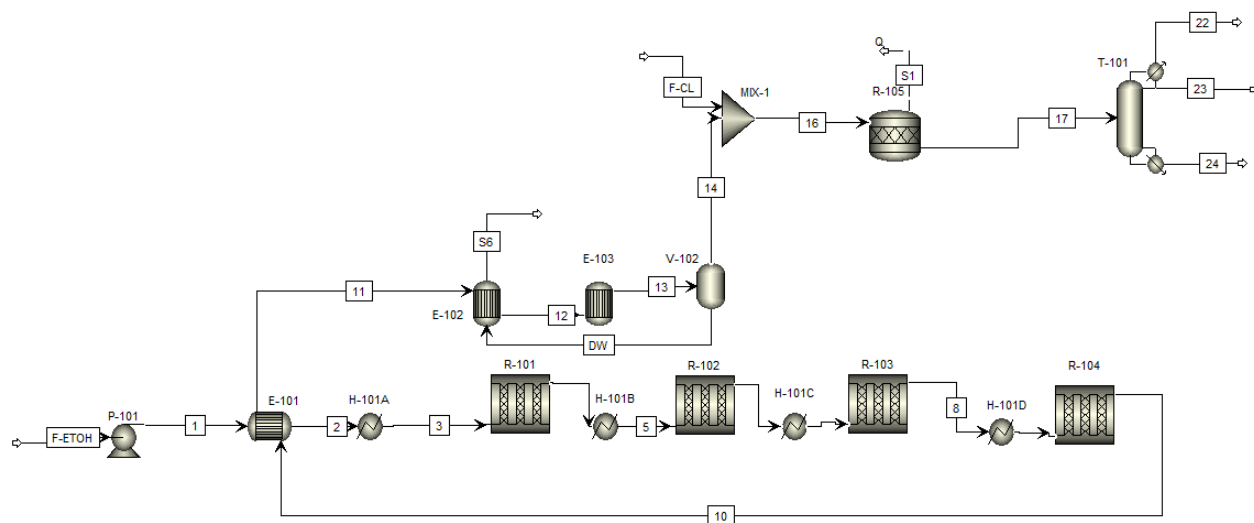


Figure 20: Flowsheet for the direct chlorination process

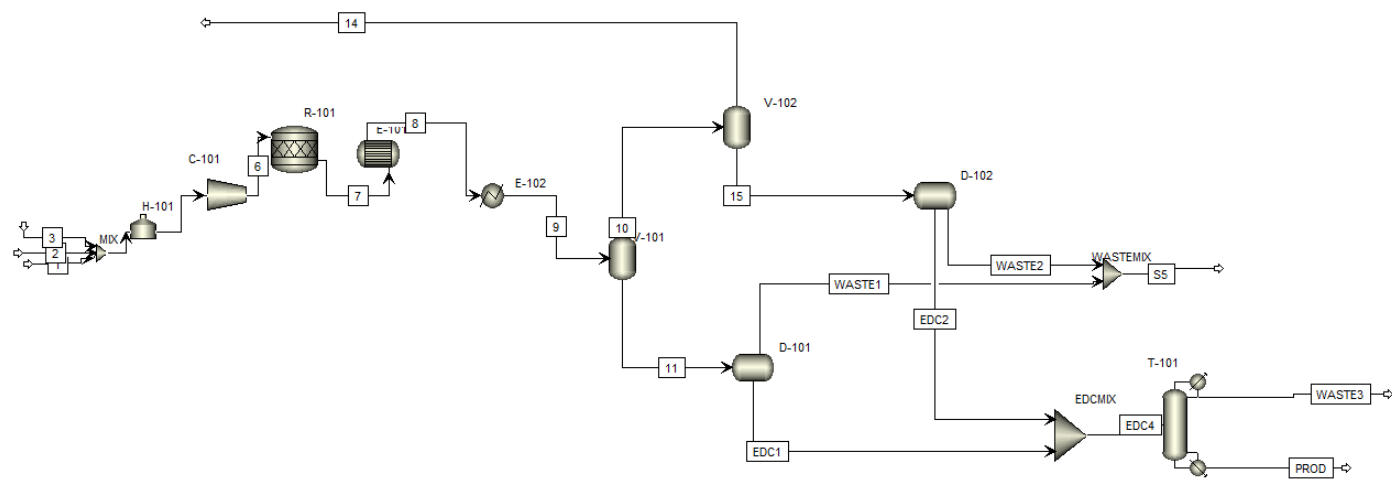


Figure 21: Flowsheet for the Dual Catalyst process

Appendix B (Economic Appendices)

End of Year	0	1	2	3	4	5	6	7
Sales Revenue				217	217	217	217	217
Cost of Manufacturing				(199)	(199)	(199)	(199)	(199)
Fixed Capital	(10.17)	(15.26)	(8.48)					
Land	(6.50)							
Working Capital			(49.74)					
BTCF	(16.67)	(15.26)	(58.22)	17.89	18.04	17.89	18.04	17.89
Depreciation (10 yr MACRS)				(3.39)	(6.10)	(4.88)	(3.91)	(3.13)
Taxable income before loss fwd	(16.67)	(15.26)	(58.22)	14.50	11.94	13.01	14.14	14.76
80% limit on loss fwd				(11.60)	(9.55)	(10.41)	(11.31)	(11.81)
Loss fwd		(16.67)	(31.93)	(90.15)	(78.55)	(69.00)	(58.59)	(47.28)
Allowable loss fwd				(11.60)	(9.55)	(10.41)	(11.31)	(11.81)
Taxable income				2.90	2.39	2.60	2.83	2.95
Tax				(0.75)	(0.62)	(0.68)	(0.74)	(0.77)
ATCF	(16.67)	(15.26)	(58.22)	17.14	17.42	17.21	17.31	17.12
IRR:	16%							
NPV:	\$195							
Minimum ROR:	1%							
Tax rate:	26.0%							
Depreciation Rate (MACRS):	10.00%	18.00%	14.40%	11.52%	9.22%	7.37%	6.55%	6.55%
FCI dist	30.0%	45.0%	25.0%					
Working Capital % COM	25.0%							

Figure 22: Cash flows for Direct Chlorination, years 0-7, values in millions of USD.

End of Year	8	9	10	11	12	13	14	15
Sales Revenue	217	217	217	217	217	217	217	217
Cost of Manufacturing	(199)	(199)	(199)	(199)	(199)	(199)	(199)	(199)
Fixed Capital								
Land								
Working Capital								
BTCF	18.04	17.89	18.04	17.89	18.04	17.89	18.04	17.89
Depreciation (10 yr MACRS)	(2.50)	(2.22)	(2.22)	(2.22)	(2.22)	(1.11)	0.00	0.00
Taxable income before loss fwd	15.54	15.67	15.82	15.67	15.82	16.78	18.04	17.89
80% limit on loss fwd	(12.44)	(12.54)	(12.66)	0.00	0.00	0.00	0.00	0.00
Loss fwd	(35.47)	(23.03)	(10.50)	0.00	0.00	0.00	0.00	0.00
Allowable loss fwd	(12.44)	(12.54)	(10.50)	0.00	0.00	0.00	0.00	0.00
Taxable income	3.11	3.13	5.33	15.67	15.82	16.78	18.04	17.89
Tax	(0.81)	(0.81)	(1.38)	(4.07)	(4.11)	(4.36)	(4.69)	(4.65)
ATCF	17.24	17.08	16.66	13.82	13.93	13.53	13.35	13.24
IRR:		16%						
NPV:		\$195						
Minimum ROR:		1%						
Tax rate:								
Depreciation Rate (MACRS):	9	10	11					
	6.56%	6.55%	3.28%					

Figure 23: Cash flows for Direct Chlorination, years 8-15, values in millions of USD.

End of Year	16	17	18	19	20	21	22	23
Sales Revenue	217	217	217	217	217	217	217	0.00
Cost of Manufacturing	(199)	(199)	(199)	(199)	(199)	(199)	(199)	0.00
Fixed Capital								0.00
Land								0.00
Working Capital								0.00
BTCF	18.04	17.89	18.04	17.89	18.04	17.89	18.04	0.00
Depreciation (10 yr MACRS)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Taxable income before loss fwd	18.04	17.89	18.04	17.89	18.04	17.89	18.04	0.00
80% limit on loss fwd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Loss fwd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Allowable loss fwd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Taxable income	18.04	17.89	18.04	17.89	18.04	17.89	18.04	0.00
Tax	(4.69)	(4.65)	(4.69)	(4.65)	(4.69)	(4.65)	(4.69)	0.00
ATCF	13.35	13.24	13.35	13.24	13.35	13.24	13.35	0.00
IRR:		16%						
NPV:		\$ 195						
Minimum ROR:		1%						

Figure 24: Cash flows for Direct Chlorination, years 16-23, values in millions of USD.

		EDC Price (\$/Ton)				
		422	453	483	513	544
Ethanol Price (\$/Gallon)	\$ 1.05	0%	17%	28%	38%	47%
	\$ 1.15	-%	0%	16%	27%	37%
	\$ 1.25	-%	-%	0%	16%	27%
	\$ 1.35	-%	-%	-%	0%	16%
	\$ 1.45	-%	-%	-%	-%	0%

Figure 25: Tabulated ROR Sensitivity Analysis for Direct Chlorination, comparing ethanol feed cost to EDC selling price.

		EDC Price (\$/Ton)				
		422	453	483	513	544
Ethanol Price (\$/Gallon)	\$ 1.05	-\$38	\$219	\$475	\$731	\$987
	\$ 1.15	-\$263	-\$37	\$219	\$475	\$731
	\$ 1.25	-\$519	-\$262	-\$38	\$218	\$475
	\$ 1.35	-\$775	-\$519	-\$263	-\$38	\$218
	\$ 1.45	-\$1,030	-\$775	-\$519	-\$263	-\$38

Figure 26: Tabulated NPV Sensitivity Analysis for Direct Chlorination, comparing ethanol feed cost to EDC selling price. NPV values are in millions\$

End of Year	0	1	2	3	4	5	6	7
Sales Revenue	\$ -	\$ -	\$ -	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241
Cost of Manufacturing	\$ -	\$ -	\$ -	\$ (217)	\$ (216)	\$ (217)	\$ (216)	\$ (217)
Fixed Capital	\$ (17)	\$ (25)	\$ (14)	\$ -	\$ -	\$ -	\$ -	\$ -
Land	\$ (6.5)	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Working Capital	\$ -	\$ -	\$ (54)	\$ -	\$ -	\$ -	\$ -	\$ -
BTCF	\$ (23)	\$ (25)	\$ (68)	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24
Depreciation (10 yr MACRS)	\$ -	\$ -	\$ -	\$ (5.6)	\$ (10)	\$ (8)	\$ (6.5)	\$ (5.2)
Taxable income before loss fwd	\$ (23)	\$ (25)	\$ (68)	\$ 18	\$ 14	\$ 16	\$ 18	\$ 19
80% limit on loss fwd	\$ -	\$ -	\$ -	\$ (14.7)	\$ (11.5)	\$ (12.7)	\$ (14.4)	\$ (15.0)
Loss fwd	\$ -	\$ (23.4)	\$ (48.7)	\$ (117)	\$ (102)	\$ (90.8)	\$ (78.1)	\$ (63.7)
Allowable loss fwd	\$ -	\$ -	\$ -	\$ (14.7)	\$ (11.5)	\$ (12.7)	\$ (14.4)	\$ (15.0)
Taxable income	\$ -	\$ -	\$ -	\$ 3.7	\$ 2.9	\$ 3.2	\$ 3.6	\$ 3.8
Tax	\$ -	\$ -	\$ -	\$ (0.95)	\$ (0.75)	\$ (0.82)	\$ (0.94)	\$ (0.98)
ATCF	\$ (23.4)	\$ (25.3)	\$ (68.3)	\$ 23.0	\$ 23.7	\$ 23.1	\$ 23.6	\$ 23.0

IRR: 16%
NPV: \$258
Minimum ROR: 1%

Tax rate: 26.00%
1 2 3 4 5 6 7 8
Depreciation Rate (MACRS): 10.00% 18.00% 14.40% 11.52% 9.22% 7.37% 6.55% 6.55%
1 2 3
FCI dist 30.00% 45.00% 25.00%
Working Capital % COM 25.00%

Figure 27: Cash flows for Dual Catalyst, years 0-7, values in millions of USD.

End of Year	8	9	10	11	12	13	14	15
Sales Revenue	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241
Cost of Manufacturing	\$ (216)	\$ (217)	\$ (216)	\$ (217)	\$ (216)	\$ (217)	\$ (216)	\$ (217)
Fixed Capital	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Land	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Working Capital	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
BTCF	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24
Depreciation (10 yr MACRS)	\$ (4.1)	\$ (3.7)	\$ (3.7)	\$ (3.7)	\$ (3.7)	\$ (1.8)	\$ -	\$ -
Taxable income before loss fwd	\$ 20	\$ 20	\$ 21	\$ 20	\$ 21	\$ 22	\$ 24	\$ 24
80% limit on loss fwd	\$ (16.3)	\$ (16.2)	\$ (16.7)	\$ -	\$ -	\$ -	\$ -	\$ -
Loss fwd	\$ (48.7)	\$ (32.4)	\$ (16.2)	\$ -	\$ -	\$ -	\$ -	\$ -
Allowable loss fwd	\$ (16.3)	\$ (16.2)	\$ (16.2)	\$ -	\$ -	\$ -	\$ -	\$ -
Taxable income	\$ 4.1	\$ 4.1	\$ 4.6	\$ 20.3	\$ 20.8	\$ 22.1	\$ 24.5	\$ 23.9
Tax	\$ (1.06)	\$ (1.05)	\$ (1.20)	\$ (5.27)	\$ (5.41)	\$ (5.75)	\$ (6.37)	\$ (6.22)
ATCF	\$ 23.4	\$ 22.9	\$ 23.3	\$ 18.7	\$ 19.1	\$ 18.2	\$ 18.1	\$ 17.7

IRR: 16%
NPV: \$258
Minimum ROR: 1%

Tax rate: 26.00%
9 10 11
Depreciation Rate (MACRS): 6.56% 6.55% 3.28%

Figure 28: Cash flows for Dual Catalyst, years 8-15, values in millions of USD.

End of Year	16	17	18	19	20	21	22	23
Sales Revenue	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241	\$ 241	\$ -
Cost of Manufacturing	\$ (216)	\$ (217)	\$ (216)	\$ (217)	\$ (216)	\$ (217)	\$ (216)	\$ -
Fixed Capital	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Land	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Working Capital	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
BTCF	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ -
Depreciation (10 yr MACRS)	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Taxable income before loss fwd	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ 24	\$ -
80% limit on loss fwd	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Loss fwd	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Allowable loss fwd	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Taxable income	\$ 24.5	\$ 23.9	\$ 24.5	\$ 23.9	\$ 24.5	\$ 23.9	\$ 24.5	\$ -
Tax	\$ (6.37)	\$ (6.22)	\$ (6.37)	\$ (6.22)	\$ (6.37)	\$ (6.22)	\$ (6.37)	\$ -
ATCF	\$ 18.1	\$ 17.7	\$ 18.1	\$ 17.7	\$ 18.1	\$ 17.7	\$ 18.1	\$ -

IRR: 16%
NPV: \$258
Minimum ROR: 1%

Tax rate: 26.00%

Figure 29: Cash flows for Dual Catalyst, years 16-23, values in millions of USD.

		EDC Price (\$/Ton)				
		462	492	523	553	584
Ethanol Price (\$/Gallon)	\$ 1.05	0%	14%	23%	31%	38%
	\$ 1.15	-%	0%	13%	23%	30%
	\$ 1.25	-%	-%	0%	13%	22%
	\$ 1.35	-%	-%	-%	0%	13%
	\$ 1.45	-%	-%	-%	-%	0%

Figure 30: Tabulated ROR Sensitivity Analysis for the Dual Catalyst Process, comparing ethanol feed cost to EDC selling price.

		EDC Price (\$/Ton)				
		422	453	483	513	544
Ethanol Price (\$/Gallon)	\$ 1.05	-\$38	\$219	\$475	\$731	\$987
	\$ 1.15	-\$263	-\$37	\$219	\$475	\$731
	\$ 1.25	-\$519	-\$262	-\$38	\$218	\$475
	\$ 1.35	-\$775	-\$519	-\$263	-\$38	\$218
	\$ 1.45	-\$1,030	-\$775	-\$519	-\$263	-\$38

Figure 31: Tabulated NPV Sensitivity Analysis for the Dual Catalyst Process, comparing ethanol feed cost to EDC selling price. NPV values are in millions\$

Appendix C (HAZOP Analysis and Results)

HAZOP for R-105 in the Direct Chlorination Process - CBE Senior Design

Colorado School of Mines

Project: Renewable Feedstocks - Production of Ethylene Dichloride

Team: Dillion Baker, Cameron Cullens, Sarah Elrod, Matthew Hartzoge, Kelsev Hoon, and Patrick Sharp

Date: 11/23/2019

ID	Node	Keyword	Guideword	Potential Cause(s)	(1 low, 10 high) Freq	Consequence(s)	(1 low, 10 high) Hazard	(1-100) Risk	Recommended Action(s)
1.101	Reactor Feed	Temperature	High	E-102 and/or E-103 failed/ is malfunctioning	2	Potential runaway reaction due to the reaction's exothermic nature	7	14	Addition of a temperature sensor on reactor that controls a valve on the cooling water line for easier control of flow rate. Have temperature controller in place to shut off feed if temperature is over threshold
1.102	Reactor Feed	Temperature	High	E-102 and/or E-103 failed/ is malfunctioning	2	Potentially reach a new operating temperature and achieve a new steady-state	4	8	Addition of a temperature sensor on reactor that controls a valve on the cooling water line for easier control of flow rate. Have temperature controller in place to shut off feed if temperature is over threshold
1.103	Reactor Feed	Temperature	Low	E-102 and/or E-103 failed/ is malfunctioning	2	May cause the reactor to reach a different equilibrium from the expected equilibrium	4	8	Temperature controller increases overall feed flowrate
1.104	Reactor Feed	Temperature	Low	E-102 and/or E-103 failed/ is malfunctioning	2	Reaction ends	4	8	Temporary shutdown, introduce liquid EDC to restart the reaction
1.201	Reactor Feed	Pressure	High	Upstream malfunction, likely due to issues with the fired heater or dehydration reactor	2	Damage to reactor: pressurize the vessel with risk of explosion	10	20	PSV on reactor vessel, pressure controller that can shut off the feed, temperature controller throttle the feed
1.202	Reactor Feed	Pressure	Low	Leak in the reactor	1	Release of Chlorine gas to the environment: Risk and hazardous to the workers' health and wellbeing	9	9	Shut it down and patch the leak, increase the operating temperature by decreasing the flow of cooling water
1.301	Reactor Feed	Flow	High	Upstream overproduction	3	Decrease in conversion	3	9	Throttle the feed with the temperature controller
1.303	Reactor Feed	Flow	Low	Upstream underproduction	3	Excess chlorine in product stream that would end up in the incinerator	1	3	Feed ratio controller that throttles the Cl2 with input of ethylene
1.304	Reactor Feed	Flow	Reverse	Depressurization upstream	1	Excessive damage due to chlorine, causing a breach of containment and environmental hazards	8	8	Shut off the feed with the pressure controller
1.401	Reactor Feed	Composition	Other than	Upstream ethylene flashtank, V101, ineffective	2	Impurities in product streams, increase in incinerator load	2	4	Shut off feed, fix the issues upstream

ID	Node	Keyword	Guideword	Potential Cause(s)	(1 low, 10 high) Freq	Consequence(s)	(1 low, 10 high) Hazard	(1-100) Risk	Recommended Action(s)
2.101	Reactor	Operating Temperature	High	Not enough coolant flowing through the jacket	4	Reactor may runaway as an exothermic reaction. May also pressurize the unit past its design specifications	10	40	Use temperature sensor to adjust coolant flowrate and throttle inlet feed
2.102	Reactor	Operating Temperature	Low	Too much coolant flowing through the jacket	4	Reaction would run too slowly	3	12	Use temperature sensor to adjust coolant flowrate (increase coolant)
2.201	Reactor	Operating Pressure	High	Upstream overproduction/overpressure	1	Overpressurization of reaction vessel, potential explosion	10	10	Implement a pressure sensor at the feed gas inlet, install a PSV, install a pressure gauge
2.202	Reactor	Operating Pressure	High	Vapor product valve fails (shut, obstructed, mechanical failure)	2	Overpressurization of reaction vessel, potential explosion	10	20	Implement a pressure sensor at the feed gas inlet, install a PSV, install a pressure gauge, fix the valve
2.203	Reactor	Operating Pressure	Low	Upstream underproduction	2	Low conversion, low reaction temperature	3	6	Use temperature controller to decrease the flowrate of coolant
2.204	Reactor	Operating Pressure	Low	There is a leak in the reactor	2	Release of chlorine to environment	8	16	Shut off the feed with the pressure controller, fix the leak
2.301	Reactor	Liquid Level	High	Low operating temperature, not enough heat of reaction	4	Liquid in product stream	3	12	Level transmitter and flowrate controller to decrease feed in
2.302	Reactor	Liquid Level	Low	High operating temperature	4	Potential runaway reaction, kill the reaction, vaporize the remaining liquid and overpressurize the reactor vessel	9	36	Level transmitter and flowrate controller to decrease feed in, feed in stored EDC, temperature controller decrease the operating temperature
2.303	Reactor	Liquid Level	None	High operating temperature	4	Potential runaway reaction, kill the reaction, vaporize the remaining liquid and overpressurize the reactor vessel	10	40	Level transmitter and flowrate controller to decrease feed in, feed in stored EDC, temperature controller decrease the operating temperature

ID	Node	Keyword	Guideword	Potential Cause(s)	(1 low, 10 high) Freq	Consequence(s)	(1 low, 10 high) Hazard	(1-100) Risk	Recommended Action(s)
3.101	Reactor Vapor Product	Temperature	High	High operating temperature	4	Damage to subsequent vessels	6	24	Temperature controller to decrease the operating temperature
3.102	Reactor Vapor Product	Temperature	Low	Low operating temperature	4	Crappy separations later on	4	16	Temperature controller to increase the operating temperature
3.201	Reactor Vapor Product	Pressure	High	High operating temperature	4	Damage to subsequent vessels	5	20	PSV or temperature controller to decrease the operating temperature
3.202	Reactor Vapor Product	Pressure	Low	Low operating temperature	4	Crappy separations later on	4	16	PSV or temperature controller to increase the operating temperature
3.301	Reactor Vapor Product	Composition	Other than	Impurities in product stream	2	More difficult separations later on	3	6	Increase the reaction temperature
3.401	Reactor Vapor Product	Phase Fraction	Less Than 1	If the reactor temperature or pressure is too low there could be accumulation of liquid to the point where there would be overflow to the vapor product exit	1	The 2-phase fluid could damage the subsequent vessels	4	4	Liquid level sensors, temperature controller to adjust operating temperature

Appendix D (Societal Analysis of Design Recommendations)

Certain societal effects will arise from the establishment of either of these plants in the United States. Most of these effects will be directly controlled by the efficiency and operation of the plant, but others will come from society's perspective on the plant.

The operational effects will have little impact on society unless something occurs that was not a part of the design intent. The main impact would come from a loss of containment of any vapor from the process. All of the chemical compounds used in this process are extremely hazardous to the population and should not be allowed to escape. There are many places within the process where any of the following chemicals are a vapor: chlorine, EDC, ethanol, or hydrochloric acid. All of these vapors are more dense than air and will settle near the ground before either condensing, or dissipating. There are treatment procedures for if these problems arise and most involve a professional treatment team.

The main perspectives that society will have on the new plant are what it is making and what it uses for fuel. The plant is currently modeled using first generation feedstocks, this means that food that is generally prepared for human consumption will be the primary feedstock for the production of ethanol. However, like the ethanol used for gasoline, there are specific food plots that are used only for this purpose. Society will not understand this and they will likely rally behind the fact that the new plant is taking away food for the human population just to make more plastic. Unlike the operational effects, this issue will be hard to combat if it escalates beyond a small populace. In order to combat this, the plant will have to be initially advertised as a green process. Another option is to move to second generation feedstocks, which means that the fuel used to generate the ethanol will come from either woody crops, agricultural residues, or non-food energy crops. The use of second generation feedstocks would allow the plant to run out of the scope of general populace's eye, therefore reducing the societal impact.

Appendix E (Description of Individual Contributions of Team Members)

Dillon Baker

A master of Aspen and economics, Dillon took point on doing the modeling for direct chlorination. He also used his knowledge of Engineering Economics to keep the cash flow tables in line. A brilliant beast to the end - Dillon worked late hours to help develop accurate results for deliverables.

Cameron Cullens

Another master of Aspen and economics, Cameron took point on doing the modeling for the dual catalyst. This reactor design also required hand calculations for several units due to their unique nature and the inherent limitations of Aspen. Using Engineering Economics, he made sure that the economic analysis for both designs was correct. He used his people skills to acquire crucial information that made the entire economic analysis possible.

Sarah Elrod

Sarah is also known as Hawk Eye for her oversight on group progress and completion of tasks. Her effective research skills provided answers to the team regarding prices and procedures. She held the team held together at the seams when we were ready to fall to bits. Other times she would have the team splitting at different seams with her awful puns (which are obviously the best kind).

Matthew Hartzoge

With his talent for formatting, Matthew used his skills throughout the semester by making sure that the presentations and progress reports looked professional and displayed all the necessary information. He also thoroughly researched the safety concerns related to the dual catalyst and the societal implications of both designs.

Kelsey Hoon

As the resident Excel goddess, Kelsey ensured that all of the economic calculations were logical, live, and correct. She also used her knowledge of Engineering Economics to keep the cash flow tables free of errors. Throughout the design process, she made sure that the group maintained communication, served as a sounding board during process modeling, and signed up for all of the meetings and presentations.

Patrick Sharp

The master of Overleaf formatting, Aspen manipulation, and Visio, Patrick used his many skills to make sure that the team was able to use any sort of graphics or table in a coherent manner. He also corroborated the direct chlorination sizing with thorough hand calculations. With his long-lasting patience and attention to detail, the team was able to analyze and write the report.

Appendix F (Safety Data Sheets)