

Epichlorohydrin Production

A Process Designed with Dow Chemical

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Executive Summary

The objective of this project was to design a profitable chemical plant capable of producing 100,000 metric tons per operating year of epichlorohydrin. The primary starting reactant, glycerol was specified to be the byproduct of the industrial biodiesel production process. To reach the set operating battery limit of 100,000 metric tons of epichlorohydrin per year, 106,490 metric tons of glycerol, 80,000 metric tons of HCl, 72,000 metric tons of NaOH, and 2,160 metric tons of hexanoic acid are needed, along with other utility streams like high pressure saturated steam, cooling water and cooling brine. This resulted in an overall conversion of glycerol to epichlorohydrin of 93.9%, according to the final mass balance using results from the cumulative Aspen Plus process simulation. This epichlorohydrin production process was simulated in multiple softwares; a combination of spreadsheet softwares (Google Sheets and Microsoft Excel), MATLAB coded solutions, and the aforementioned simulation software Aspen Plus.

The process begins with raw glycerol purification via flash drum which was designed for the purification of crude glycerol into a more concentrated stream which was sent to a hydrochlorination constant-stirred tank reactor and plug flow reactor in series to produce monochlorohydrins and di-chlorohydrins which completely converted all the fed hydrochloric acid reactant. The DCH product was refined using a purification distillation column in which product was sent downstream to be phase separated by means of a decanter. Sodium hydroxide was added to one of the liquid phases, and then mixed with the other liquid phase in a small plug flow reactor. This product was sent down stream to a reactive distillation column to simultaneously be reacted and separated into epichlorohydrin. The epichlorohydrin product was then distilled using two distillation columns in series to hit the desired purity and battery limit.

With a unit selling price of \$3300/metric ton of the epichlorohydrin product, the market standard spot price for epichlorohydrin, the following economic results were obtained. Equipment costs were determined through a variety of available industry-trusted resources. The internal rate of return (IRR) was calculated to be 20.6%, with a return on investment (ROI) of 15.3% and a total payback period of 6.5 years. For this economic scenario a total fixed capital investment (FCI) of \$325 million is required, with a yearly operational cost of \$142 million. Cumulatively speaking, this process achieved profit in 2030, 7 years after the beginning of construction. The US Gulf Coast was chosen due to its low tax rate, low land-cost, accessibility to material transportation by land or barge, and the accessibility of auxiliary industrial services.

1 Background

1.1 Project Description and Scope

A five-page document in which the general information of this project was provided. The most notable portion of this document which will be referred to as the prompt, was several consecutive lines of chemical reactions. It was immediately evident that this project would be centered around the reactors in which these reactions took place, but was not initially clear on what other unit operations would take place. There were no process flow diagrams provided of the scheme, or any straightforward general recommendations on the project. It was thus concluded that a process would have to be built from the ground up and that the liaison of this project, Dr. Bruce Hook, would serve as a mentor towards ensuring that this process was in-line with actual, realistic practices. The process described in this prompt was Epichlorohydrin (ECH) production at a scale of 100,000 metric tons per year. Dr. Bruce Hook, of Dow Chemical, has years of experience in researching and developing such technologies made evident through the plethora of patents that were listed on the last page of this prompt because many had his name listed under the inventors category. It was learned that Dr. Hook had previous associations with Dr. Alan Weimer, who is the lead faculty member for this course and through that relationship, graciously agreed to help students of Dr. Weimer's course in developing critical engineering skills.

1.2 Process Description and Technology Background

Based on the criteria described in the prompt, it was evident that a process would be designed that operates similarly to other large-scale manufacturing facilities. Most manufacturing facilities are located near the gulf coast, more specifically in Texas and Louisiana. A quick look at google maps will reveal the logic behind this with naval loading docks in which ships have access to take and deliver large amounts of product. It was foreseen that this would be extremely beneficial for this process, and so a Gulf coast location was selected. Establishing that the process would have essentially no limitations in terms of transporting goods and materials was important to ensure that the annual operation period of 8,000 hours was fulfilled on a consistent basis. The location establishment also ensured that labor shortages would be considered negligible as geography along the coast of Texas and Louisiana is reasonably populated.

The traditional route for large scale epichlorohydrin synthesis involves the chlorination of propylene to allyl chloride (alternative processes start at this step), followed by reaction with hypochlorous acid to two intermediate compounds: α,γ -DCH (1,3-dichlorohydrin) and β -DCH (2,3-dichlorohydrin). These are then reacted with a base, typically sodium hydroxide, to produce the final epichlorohydrin. This process route was historically used due to the low purchasing cost of the starting materials propylene and chlorine gas. However, as the world moves towards being less dependent on global oil production, a process that circumvents use of petroleum products becomes increasingly valuable.

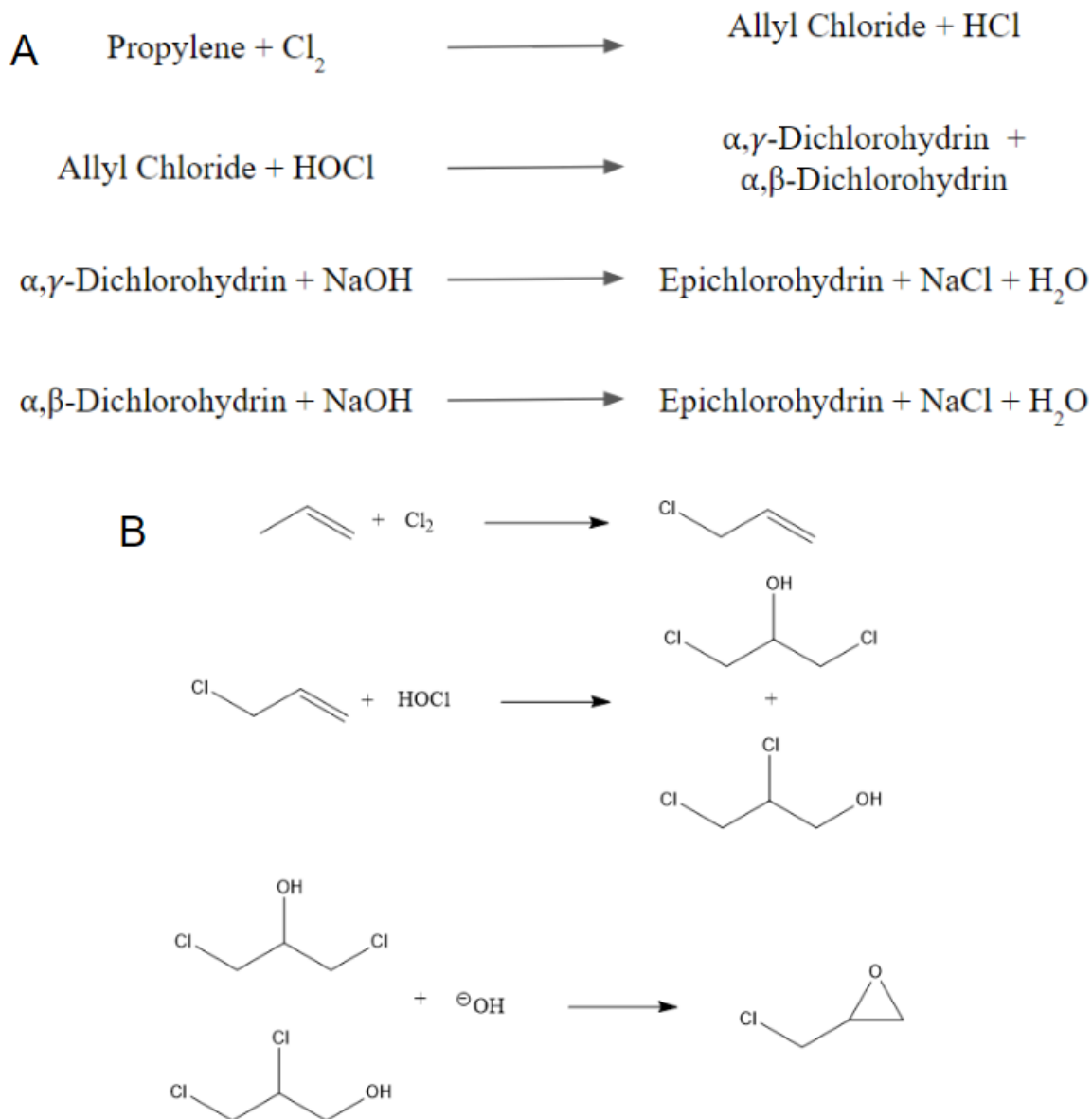


Figure 1.2.1: Epichlorohydrin reaction sequence from propylene; (A) Reactions with Names, (B) Reactions with Chemistry. Propylene is chlorinated to allyl chloride, then reacted with hypochlorous acid (often Cl₂ gas dissolved in water) to the corresponding α,γ -DCH and α,β -DCH. This is then reacted with a base to produce epichlorohydrin. (Note: some reaction byproducts not shown e.g. water, HCl, NaCl).

Research by Dow Chemical [P.2, P.3, P.6] revealed a process for producing epichlorohydrin using glycerol instead of propylene as a feedstock. In the first reaction sequence, glycerol is reacted with hydrochloric acid in the presence of a carboxylic acid catalyst, producing the first two intermediate compounds: α -MCH (3-chloropropanediol) and β -MCH (2-chloropropanediol). These two isomers react with a second equivalent of hydrochloric acid producing the previously mentioned intermediate compounds: α,γ -DCH and α,β -DCH. The second reaction sequence is similar to the process above, with both isomers of DCH being

reacted with sodium hydroxide, closing the epoxide ring and producing epichlorohydrin. The reaction scheme provided by Santasaria et. al. [1.2.1] gives:

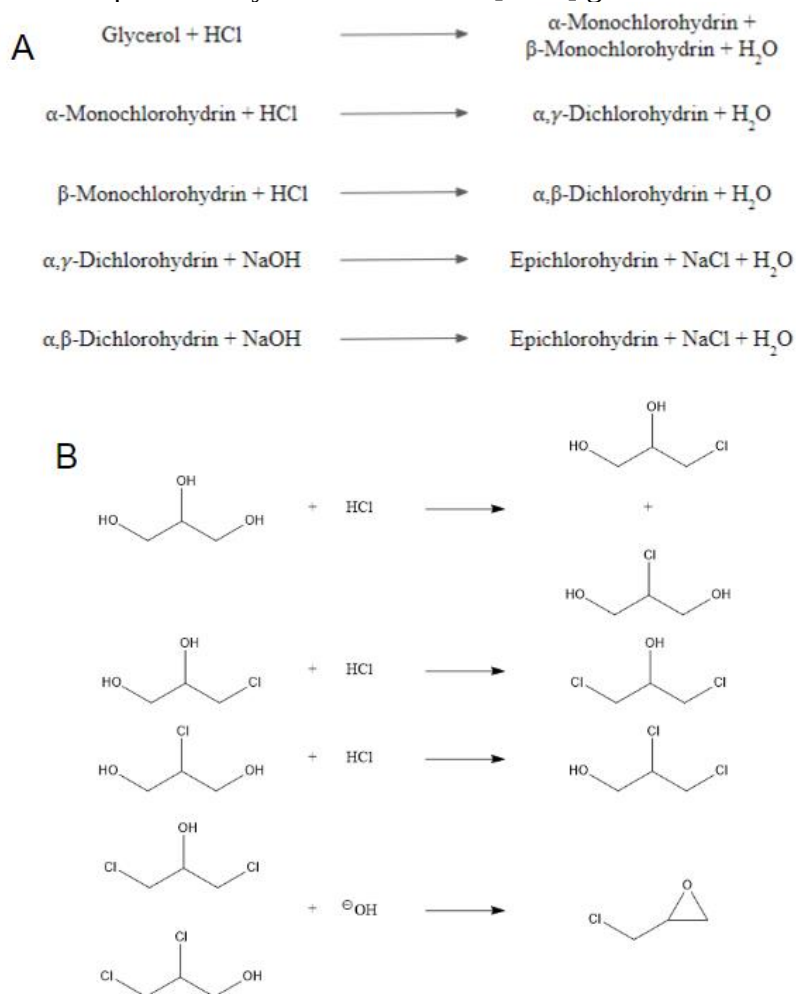


Figure 1.2.2: Epichlorohydrin reaction from glycerol; (A) Reactions with Names, (B) Reactions with Molecules. Glycerol reacts with hydrochloric acid to produce a mixture of α -MCH and β -MCH. Each of these isomers reacts again with hydrochloric acid to α,γ -DCH and α,β -DCH respectively. This is then reacted with a base to produce epichlorohydrin. (Note: some reaction byproducts not shown e.g. water, HCl, NaCl). [1.2.1].

Another important consideration in the design of this process is the potential for hydrolysis of the epichlorohydrin product. As described by Tolli et. al, [1.2.2], epichlorohydrin can react with water to a three step hydrolysis pathway shown below, ultimately returning the starting material glycerol. An important note about the hydrolysis reactions is the effect of pH on reaction rates. In strongly acidic or alkaline conditions the hydrolysis reactions are catalyzed. As a result, it must be ensured that any formed ECH is contacted as little as possible with the sodium hydroxide used in the second reaction sequence.

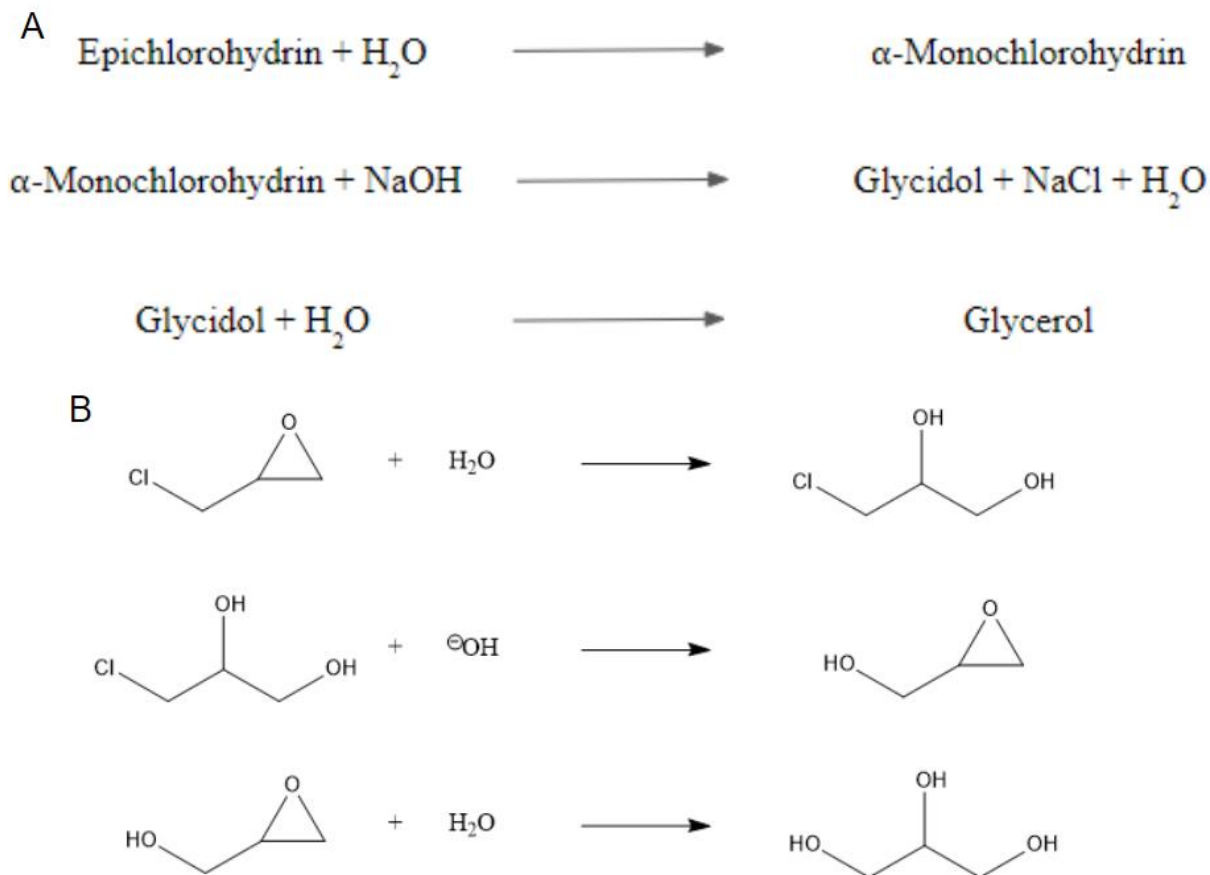


Figure 1.2.3: Epichlorohydrin hydrolysis reaction sequence; (A) Reactions with Names, (B) Reactions with Molecules. Epichlorohydrin reacts with water to open the epoxide ring to α -MCH. α -MCH then reacts with a base present producing glycidol. Finally, the glycidol reacts with water to again open the epoxide ring, producing the starting material glycerol [2]. Note: shown above is the simplified hydrolysis sequence. Tolli et. al. provides a complex full hydrolysis reaction scheme.

Yet another consideration that was pertinent to this process was the azeotropes between the compounds. The intermediate compounds α,γ -DCH and α,β -DCH experience an azeotrope with water. As these compounds are produced from a mixture of water and HCl, this introduces HCl to the azeotrope necessitating ternary considerations. Additionally the product epichlorohydrin also experiences an azeotrope with water. These azeotropes were utilized in the purification of these compounds, but also necessitated special equipment selections discussed later in this report.

With the advent of government subsidized biodiesel in the early 2000s, the price of glycerol feedstocks plummeted, increasing the viability of this alternative process. An additional innovation with this plant is the use of anhydrous hydrochloric acid rather than aqueous. The rationale behind this is the existence of anhydrous hydrochloric acid as a byproduct from several other industrial processes. This will further lower the price of one of the main feedstocks for the process, increasing the potential profit.

1.3 Project Impact

This project specifies a production rate of epichlorohydrin of 100,000 metric tons per year. From market research in the infancy of this project, a product purity of 99.97% was determined to be the industry standard. Given by Global Epichlorohydrin Market Analysis [1.3.1], in the year 2021 approximately 2,000,000 metric tons of epichlorohydrin were produced globally. This figure is expected to grow up to 3,200,000 metric tons by the year 2030.

One major impact of this project is based on the location of construction, the US Gulf Coast, specifically Texas. As given by [1.3.1], the largest regional market of epichlorohydrin is the Asia Pacific region, accounting for more than 50% of the market. The U.S. accounts for a much lower share, only 17%. Addition of the project looks to increase this figure to up to 21% when operating at full capacity.

This project operates on a “green” process, focusing on maximizing the sustainability and environmental factors. Additionally, this process aims to operate using mainly byproducts from other processes as the reactants for this process. Producing epichlorohydrin from glycerol as opposed to propylene is not only more economically feasible but also more economically friendly. However, this process produces chlorinated organics and potential VOCs. As a result, careful consideration must be taken in regards to the waste water output from the plant. This concern is compounded when the plant is next to a body of water, and very strict measures must be taken to ensure compliance with local and federal regulations.

This plant can be compared to several other glycerol to epichlorohydrin (GTE) plants constructed. In 2012, Solvay commissioned a new GTE plant in Thailand operating at 100,000 metric tons per year [1.3.2]. Additionally in 2022, Meghmani Finechem, announced plans for the construction of a 50,000 metric ton per year epichlorohydrin plant in India. Currently, all of India’s epichlorohydrin was obtained from import, and thus an incentive is in place in terms of sustainability and economics to produce at least a portion of the nation’s consumption autonomously [1.3.3]. Compared to these two plants, the design and specifications of this plant are both realistic and impactful in terms of capacity and impact. One of the largest weaknesses of this project is the economic robustness. In other words, the profitability is very sensitive to increases in cost of starting materials, utilities, and labor. With the current ideal economic setup, this process would be a good investment. However if the starting materials were to increase in price from the demand of other GTE processes, or if the worker wages were made to significantly increase due to worker demands, the economic viability of this process is affected significantly.

1.4 Project Timeline

The timeline for this project was centered around the amount of available resources as well as the personnel. This project had three people in charge with the help of a liaison, a professor, and professor emeritus. To establish a timeline, goals had to be set that determine what can and should be accomplished through the allotted time period. In analyzing the potential scope of this equipment, it was projected that 3 reactors would need to be designed with 3 subsequent columns (This turned out to be an underestimate of what was actually required to be designed). What was more clear was how this process was divided into two basic reaction schemes as provided by the prompt which in this report are referred to as the DCH and ECH Reaction Schemes which occur in chronological order. It was approximated that each scheme would take about the same amount of time, and that the two halves of the timeline should be centered around these two schemes in a symmetrical manner. It was projected that there would

additional tasks to perform, and so these were fitted on both sides of these schemes such that the overall plan for our timeline is shown as follows:

Table 1.4.1: Overall Timeline of Project

Start Date	End Date	Event Description
01-24-2023	N/A	Project initiation
01-25	02-01	Market research
02-02	02-06	DCH scheme development
02-07	02-14	DCH Reactor design
02-15	02-24	DCH Column design
02-25	03-03	ECH scheme improvement
03-04	03-10	ECH reactor design
03-11	03-18	ECH column design
03-19	03-26	ECH scheme improvement
03-27	04-10	Overall process improvement
04-11	04-25	Second oral presentation
04-26	05-04	Written report writing
05-05	N/A	Final oral presentation
05-05-2023	N/A	Project completion

Previous experience was gained with a project similar to this one, methanol production, in which a written report had to be compiled on a due date; there was a sense of familiarity with how long these tasks listed in Table 1.4.1 were actually going to take. Each of these timelines listed reflects a certain amount of leeway granted in anticipation of setbacks. So the project was deemed completable barring major setbacks.

These goals reflected a certain amount of specificity desired in designing equipment. Equipment could not be specified to the maximum extent and so compromises needed to be made in terms of advancement. The basic criteria for all equipment was that everything should be given physical sizing and a physical description. Additionally, every piece of equipment implemented should come with a reasonable amount of explanation as to why that unit was selected. In selecting the amount of specificity, foresight was required as to what would impact the economic outlook the most, that is what was financially important. Sizing was one thing already mentioned but anything requiring continuous material feeds should be given an adequate amount of consideration. Additionally, things that require safety concerns should be considered

to avoid any unnecessary hazards, that is equipment can not be implemented that is considered dangerous. It was decided that MATLAB files should be created for reactor designs that reflect the internal behavior to a respectable extent, as it was foreseen that software simulation would be much more difficult to design in this regard. Columns were elected to be sized, but it was agreed upon to shy away from intensive design of the internals especially considering that size specifications of these columns could very well change over time. It was envisioned that additional equipment would have to be installed such as heat exchangers or pumps, and that these should not be given an extraordinary amount of attention due to how late they would be implemented in the overall timeline.

1.5 Resourced Patents

Several patents were provided in the project prompt that reference technologies and concepts explored pertaining to epichlorohydrin production. Some of these patents were contributed to by the liaison of this project, Dr. Bruce, and his peers at Dow Chemical while others were contributed by neighboring companies such as Solvay Chemicals. Patents referenced throughout this text were given distinct notations of the form [P.#] and the citations for these patents can be found in their own references section (PATENT CITATIONS). A brief table detailing these patents is provided below:

Table 1.5.1: Patent citation notation

Notation	Number	Name
[P.1]	US 8,338,627 B2	Process for producing epoxides
[P.2]	US 7,910,781 B2	Process for the conversion of a crude glycerol, crude mixtures of naturally derived multihydroxylated aliphatic hydrocarbonsoresters thereof to a chlorohydrin.
[P.3]	US 8,586,802 B2	Multi-stage process and apparatus for recovering dchlorohydrins.
[P.4]	EP 1 752 435 B1	Process for producing epichlorohydrin.
[P.5]	US 7,906,690 B2	Batch, semi-continuous or continuous hydrochlorination of glycerin with reduced volatile chlorinated hydrocarbon by-products and chloracetone levels.
[P.6]	US 8,541,632 B2	Process and apparatus for producing chlorohydrin.
[P.7]	US 9,422,256 B2	Continuous process for producing epichlorohydrin from glycerol.
[P.8]	US 8,420,870 B2	Process and apparatus for recovery of dichlorohydrins via codistillation.
[P.9]	US 8,664,453 B2	Process and apparatus for azeotropic recovery of dichlorohydrins.

2 Material Balances

Based on the criteria described in the Background section, it was evident that a process would be designed that operates similarly to other large-scale manufacturing facilities. Most manufacturing facilities are located near the gulf coast, more specifically in Texas and Louisiana. A quick look at google maps will reveal the logic behind this with naval loading docks in which ships have access to take and deliver large amounts of product. It was foreseen that this would be extremely beneficial for this process, and so a Gulf coast location was selected. Establishing that the process would have essentially no limitations in terms of transporting goods and materials was important to ensure that the annual operation period of 8,000 hours was fulfilled on a consistent basis. The location establishment also ensured that labor shortages would be considered negligible as geography along the coast of Texas and Louisiana is reasonably populated.

The material balance over the whole process system was mathematically modeled in Google Sheets (a spreadsheet software). This spreadsheet initially served as a method of roughly calculating the input of reactants required to reach the battery limit of 100,000 metric tons of ECH produced in an 8,000 hour operation year. This original estimation used many assumptions to approximate the extent that reaction that occurred in the various reaction units with respect to glycerol and MCH in the first reaction sequence, then in respect to DCH and ECH in the second reaction sequence. The material balance spreadsheet had these assumptions changed when reaction extents were calculated in Aspen Plus or via MATLAB coded solutions. The initial scale estimations were most important when simulating or mathematically modeling the separation units of this process, moreover, MATLAB coded solutions which were used to find the required sizes of reactors used a combination of outputs from the material balance spreadsheet and from Aspen Plus to ensure realistic reactor sizes.

The material balance originally began with a basis of one kilogram of crude glycerol feed, assumed to have ten percent of water impurity (by mass) which was reacted with stoichiometric amounts of other reactants and an arbitrary initial catalyst amount of ten percent by mole. Subsequent calculations (done mostly on a molar basis) were done as this basis of feed moved through the process units. By dividing the final produced mass of ECH in that “first pass” of feed by the mass of the 100,000 metric ton battery limit yielded a scale-up factor by which the original basis could be multiplied by to reach an estimation of the feed required per year. The “first pass” calculations did not include recycle considerations that were present in our theoretical design, so stream splitting assumptions were applied to some streams, which were wasted otherwise, and the recycled amounts were added to the inlet streams of specific units. For example, in our final design, to keep the hexanoic acid catalyst from leaving the process as waste, the DCH purifying distillation column bottoms stream is almost wholly recycled back to CSTR where hexanoic acid presence facilitates the hydrochlorination reactions. This was at first approximated by making a flash assumption to model the separation of species in that distillation column, then arbitrarily selecting that 80% of the bottoms stream to be added to the feed basis at the inlet of the CSTR in the next iteration. Another important recycle consideration was that in the decantation step before ECH production, the aqueous phase products were recycled and added to the feed of the distillation column. The separation due to decantation was assumed to be an equilibrium flash separation where the azeotropic mass fractions of water and DCH were distributed in the respective aqueous and organic phases [4.3.2]. Additions of these recycles and the use of multiple iterations decreased the mass scale-up factor, however the decrease became

less substantial the more iterations that were calculated. This same scale-up method was applied to the feed flows in the final cumulative Aspen Plus simulation to achieve the battery limit.

Table 2.1: Material Balance Spreadsheet Reactor Conversion Assumptions:

Reactor	Conversion Assumption	Species Conversion Was Based on
CSTR	80% converted	Glycerol
PFR	95% converted	Glycerol
ECH Reactor	95% converted	DCH

As the project progressed, the initial material balances which were changed to better reflect reality, however as the cumulative Aspen Plus simulation was completed, the mass balance that follows from Aspen's calculations became more pertinent. An important measurement that was tracked across both material balances was the percentage yield of ECH produced based on the fed glycerol. On the spreadsheet material balances, the calculated ECH percent yield from glycerol was 82.1%. While the Aspen Plus simulation estimated an ECH yield from glycerol of 91.3%. The main cause of discrepancy between the percent yield of ECH from glycerol was the additional recycles and separation equipment that were added to the Aspen Plus simulation, but that the material balance spreadsheet neglected. The final estimation of feed scale from the spreadsheet material balance was very close to what was required to reach the battery limit, an decrease of about 6% was applied to the Aspen Plus simulation feed rate of glycerol to reach 100,000 metric tons of ECH produced in 8000 hours, at the target purity of 99.97% ECH.

Table 2.2: Material Balance Spreadsheet and Cumulative Aspen Plus Simulation Comparison:

Simulation	Glycerol Feed Rate (kg/hr)	Glycerol Feed Rate (mt/yr)	ECH Production Rate (kg/hr)	ECH Production (mt/yr)	Overall Yield of ECH from Glycerol
Material Balance Spreadsheet	15,025	120,198	12,500	100,000	0.821
Aspen Plus Cumulative	14,050	112,403	12,832	102,656	0.913

3 Dichlorohydrin (DCH) Reaction Scheme - Development

3.1 DCH Scheme Startup Considerations

With the information provided by the project prompt, there was a reasonably clear idea on what needed to be executed for the 1st reaction scheme. It was known that a stirred reactor would be required for mixing the two-phase reactants and that a following reactor would be needed for conversion of those reactants. There were presumably several species in the product stream coming off these reactors, and so a subsequent column would be needed to isolate the

desired species, DCH from the column. A general schematic of this reaction was created and is shown below in Figure 3.1.1:

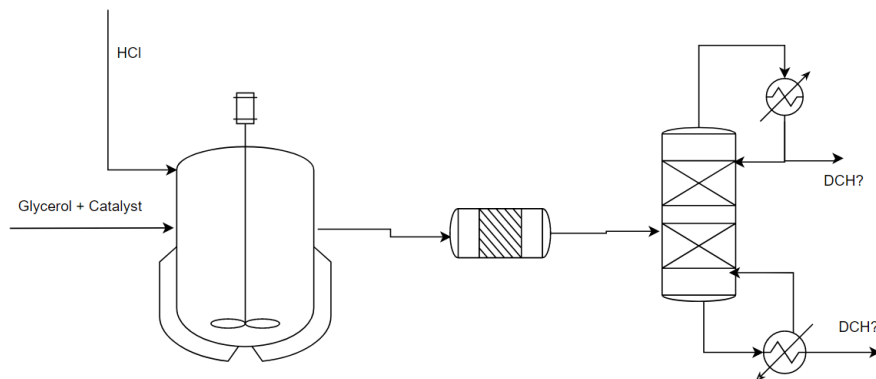


Figure 3.1.1: Initial perception of DCH reaction scheme.

It was unclear whether a recycle stream would be implemented as this would be dependent on the performance of the column which as stated from the prompt, was a challenge to design since there was a ternary azeotrope that needed to be considered amongst three of the most prominent species (HCl-Water-DCH). Going into the design of this scheme, it was desired and anticipated that the bottom stream coming out the column would be recycled back into the first reactor from initial research towards the boiling points of all the species involved (Table 3.1.1):

Table 3.1.1: Boiling points of relevant species [3.1.4]

Species	Boiling Point (°C)
HCl	-85.05
H ₂ O	100
DCH	175
MCH	213
Glycerol	290

From Table 3.1.1, it would appear that DCH would be a product of the bottoms streams and thus the distillate stream should be recycled back to the reactor. Upon further investigation, the binary azeotrope compositions suggest that it is actually the other way around in that DCH will get boiled off Table 3.1.2. It was thus elected to seek a catalyst that would be present in the recycle stream and thus be less volatile than the binary azeotrope solutions.

Table 3.1.2: Boiling points compared of species and binary azeotropes [3.1.4]

Species	Boiling Point (°C)
HCl	-85.05

H ₂ O(87%)-DCH(13%)	99.4
H ₂ O	100
DCH(33%)-H ₂ O(53%)-HCl(14%)	106
H ₂ O(79.8%)-HCl(20.2%)	108
DCH	175
MCH	213
Glycerol	290

Criteria for the catalyst included being a carboxylic acid, having a higher boiling point, and being cheap. The the three most notable catalysts found through research that are in line with these criteria are shown below in Table (3.1.3):

Table 3.1.3: Potential catalyst properties [7.3.2]

Species	Boiling Point (°C)	Price (\$/kg)
Acetic Acid	118	0.45 - 0.85
Hexanoic Acid	205	4.00 - 5.50
Malonic Acid	136	1.35 - 7.34

Using Table (3.1.3), hexanoic acid catalyst was selected because the boiling point was the highest and the price was not outrageous (relative to all catalysts). Observing the azeotrope boiling points, the expected maximum temperature used in the column would be around 110-120 °C so it would make sense to use malonic acid rather than hexanoic acid. The latter was selected due to the difference in reactivity which was not a straightforward comparison. From literature available, acetic acid was used as a baseline for both of these catalysts and it was found, through comparing results from two experiments, that malonic acid is significantly less reactive than hexanoic (Table 3.1.4).

Table 3.1.4: Left: Acetic acid and malonic acid comparison from [3.1.5], Right: Acetic acid and hexanoic acid comparison [P.2]

Catalyst	Reaction Rate Constant: Glycerol to α -MCH	Reaction Rate Constant: α -MCH to α,γ -DCH	Catalyst	α,γ -DCH Selectivity	α,β -DCH Selectivity
Acetic Acid	3.46E4	1.57E3	Acetic Acid	90.55	1.93

Malonic Acid	1.32E4	1.78E3
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Hexanoic Acid	90.67	1.91
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With a relatively non-volatile catalyst going into the column, it was expected that the bottoms stream would be recycled and that the distillate stream would contain the DCH product and thus be sent for downstream processing. Recycling the catalyst was considered an ideal scenario for this scheme, since it would not be consumed during reaction and thus could be used repeatedly. It was not expected that a perfect distillation would occur and that there would be some impurities in this recycle stream which would result in long term accumulation of species in this loop. This had to be accounted for and so a purge splitter had to be implemented on the recycled stream. Thus, building off the PFD of Figure (3.1.2), the perceived reaction scheme is shown below:

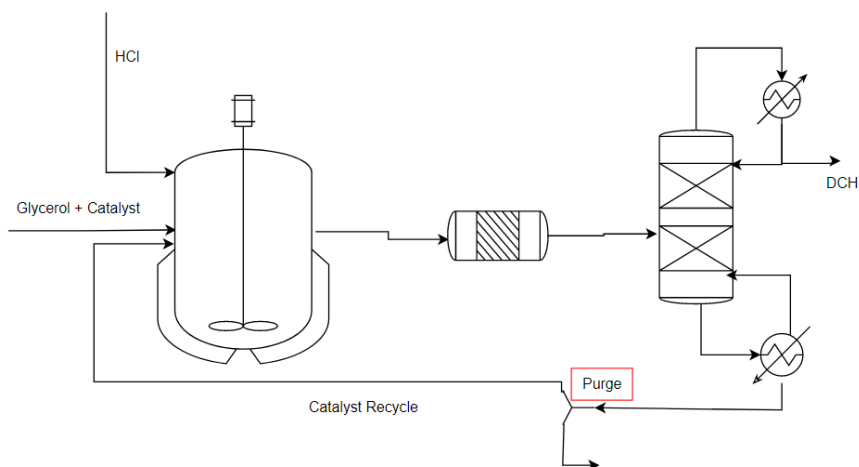


Figure 3.1.2: Adjusted perception of DCH reaction scheme

The reactions themselves were simplified based on deductions made through reading available literature. Sources available point to the reactions of Glycerol to the MCH isomers and the MCH isomers to the DCH isomers being reversible, yet none of these sources or any of the like provided reversible reaction rate parameters for kinetic calculations. These sources simply notated these reactions with singular rates implying that the reverse reactions for each of these schemes was negligible compared to the forward. So, in light of this, the reaction rates for Glycerol to the MCH isomers and the MCH isomers to the DCH isomers were modeled as irreversible. There was also literature suggesting that an additional reversible reaction occurs between α -MCH and α,β -DCH, but no rates were found for this and so the reaction was neglected. Below is a diagram depicting the simplification and adjusted notation for this reaction scheme (Figure 3.1.3):

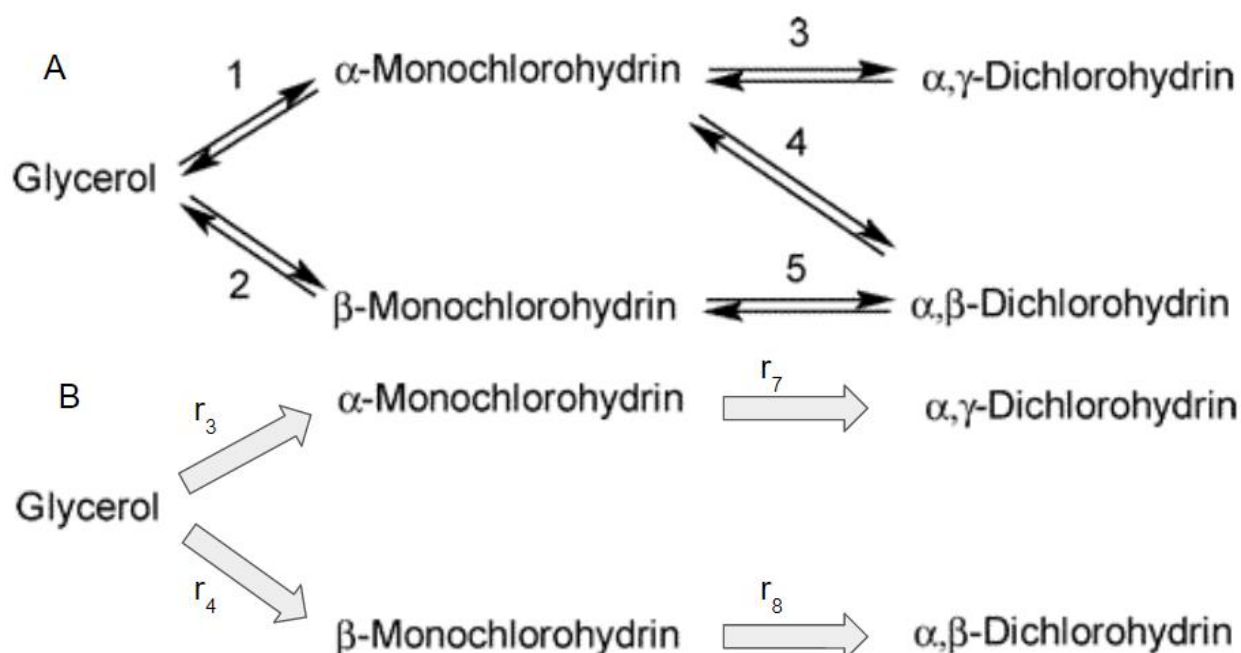


Figure 3.1.3: (A) Expected DCH reaction scheme, (B) Simplified DCH reaction scheme

What was considered after the reactions themselves were how the species would be fed towards the process. From market research, there were two primary modes of glycerol, one being a crude-grade with a significant amount of impurities (namely water) at a lower cost or a technical grade which has higher purity but at a higher cost. Selecting the crude-grade, without any further investigation, was thought to be the best choice but this would have required additional design of a preceding separation chain to achieve purity for reaction. It was decided that the best course of action would be to model downstream processing, beginning with the first reactor, to have a technical level feed of glycerol and if time permitted depending on the progress that was made in other aspects of the project, design the prior separation chain so that a crude-glycerol feedstock could be purchased. This approach was deemed reasonable because a high level of purity would likely have to be fed towards the reactor anyways as it was suspected at this time that additional impurities would impede the reaction kinetics.

The next big question was how to feed the hydrogen chloride, that is to feed it as a gas or as a liquid. Since HCl has a very low boiling point, the liquid HCl would have to be in the aqueous form which was suspected to interfere with the kinetics of the reaction for the same reason as crude glycerol would. It was thus confirmed that HCl would have to be fed in the gaseous form.

3.2 Hydrochlorination CSTR

Knowing the reaction scheme (Figure 3.1.3), the glycerol needed to be reacted in the presence of a catalyst with hydrogen chloride gas to MCH and subsequent DCH isomers. The most important initial consideration was the two-phase presence in this reactor which suggested that it needed significant mixing.. It was not feasible to convert the hydrogen chloride gas into a liquid phase before by means of condensation as this would have required a high-powered compressor or significant cooling due to HCl's very low boiling point. A compressor would have been extremely expensive and a subcooled stream would have put the overall reaction solution at

a temperature lower than necessary for reaction activation. Thus, a two-phase reactor had to be considered in which adequate, continuous mixing was provided towards the solution. A continuous-stirred tank reactor was elected to be used as this would fulfill these criteria. Heat transfer considerations were neglected up to the selection of this reactor because no prior information was obtained that suggested this reaction was extremely exothermic, or carried any significant safety hazards. Whether the reactor was mass transfer or reaction limited was unclear at this point, but it was clear that the mass transfer would be more difficult to model than the reaction rates. The reaction rates were found in literature from Medina et al and were with an apparatus quite similar to the one intended to be designed [3.2.2]. It was decided at this point that the reactor would be modeled solely with respect to the reaction rates, and if successful in a reasonable timeline, then with mass transfer considerations. Listed below are the reaction rates, parameters, and variables derived from Medina et al which are in accordance with the literature notation as well as the notation used in Figure 3.1.3 and Equations 3.2.1 - 3.2.4 [3.2.3]

$$r_3 = \frac{k'_3 C_{GLY} C_{HCl}^2 \left(\frac{C_{0,CAT}}{C_W + K' C_{GLY} + K'' C_\alpha} + K' \right)}{\frac{C_{0,CAT}}{C_W + K' C_{GLY} + K'' C_\alpha} + \alpha_{3HCl} C_{HCl} + \alpha_W C_W} \quad (3.2.1)$$

$$r_4 = \frac{k'_4 C_{GLY} C_{HCl}^2 \left(\frac{C_{0,CAT}}{C_W + K' C_{GLY} + K'' C_\alpha} + K' \right)}{\frac{C_{0,CAT}}{C_W + K' C_{GLY} + K'' C_\alpha} + \alpha_{3HCl} C_{HCl} + \alpha_W C_W} \quad (3.2.2)$$

$$r_7 = \frac{k'_7 C_\alpha C_{HCl}^2 \left(\frac{C_{0,CAT}}{C_W + K' C_{GLY} + K'' C_\alpha} \right)}{\frac{C_{0,CAT} C_W}{C_W + K' C_{GLY} + K'' C_\alpha} + \alpha_{7HCl} C_{HCl}} \quad (3.2.3)$$

$$r_8 = \frac{k'_8 C_\alpha C_{HCl}^2 \left(\frac{C_{0,CAT}}{C_W + K' C_{GLY} + K'' C_\alpha} \right)}{\frac{C_{0,CAT} C_W}{C_W + K' C_{GLY} + K'' C_\alpha} + \alpha_{7HCl} C_{HCl}} \quad (3.2.4)$$

Table 3.2.1: Hydrochlorination Reaction Kinetic Constants [3.2.3]

Parameter	Value	Units	Notes
$k_{m,3}$	2.40947	$m^3/mol\cdot min$	Pre-exponential factor, Glycerol to α -MCH
$E_{a,3}$	96.7595	kJ/mol	Activation Energy, Glycerol to α -MCH
$k_{m,4}$	0.101	$m^3/mol\cdot min$	Pre-exponential factor, Glycerol to β -MCH

$E_{a,4}$	116.789	kJ/mol	Activation Energy, Glycerol to β -MCH
$k_{m,7}$	0.1785	m ³ /mol-min	Pre-exponential factor, α -MCH to α,γ -DCH
$E_{a,7}$	54.0706	kJ/mol	Activation Energy, α -MCH to α,γ -DCH
$k_{m,8}$	0.1785	m ³ /mol-min	Pre-exponential factor, β -MCH to
$E_{a,8}$	95.1516	kJ/mol	Activation Energy, β -MCH to α,β -DCH
α_{3HCl}	1098.42	Unitless	Activity Coefficient of HCl, Glycerol to α -MCH and β -MCH
α_w	1256.71	Unitless	Activity Coefficient of Water, All Reactions (3, 4, 7, 8)
α_{7HCl}	3988.72	Unitless	Activity Coefficient of HCl, α -MCH and β -MCH to α,γ -DCH and α,β -DCH
κ_m'	0.00043	Unitless	Non-catalyst Reaction Constant
K'	4.2522	Unitless	1st Equilibrium Esterification Constant
K''	2.239	Unitless	2st Equilibrium Esterification Constant

Table 3.2.2: Hydrochlorination Reaction Variables [3.2.3]

Variable	Units	Notes
C_{GLY}	mol/m ³	Concentration of Glycerol
C_{HCl}	mol/m ³	Concentration of HCl
$C_{0,cat}$	mol/m ³	Concentration of Catalyst
C_w	mol/m ³	Concentration of Water
C_α	mol/m ³	Concentration of α -MCH

Modeling this reactor was expected to be done through a differential equations solver due to the simultaneity of the series reactions in this scheme. MATLAB was thus selected for use in which code was developed to model the reaction rates in the CSTR as a function of the changing concentrations which were a function of the initial feed rates. The paper reference mentioned that the heat transfer of this reaction scheme was considerably exothermic, but that the dissolution of the HCl gas was by far the most exothermic step. It was noted that their reactor design was carried out under isothermal conditions to derive temperature dependencies for the arrhenius equations of their reaction rates. Since this paper was the most likewise to this intended design, it was elected to model these reactions as isothermal in the MATLAB code. Figures of Medina et

al suggested negative first order, 2nd-order polynomial, and positive linear behavior for the reactant (Glycerol), intermediate product (MCH), and finalized product (DCH), respectively (Source). This behavior, with the assumptions that were in-place for the MATLAB code, was expected to be replicated to a reasonable extent in the program's results. Once these reactions were replicated after about two weeks of work, it was decided that mass-transfer considerations should be pursued for additional modeling considerations.

Reactors can be modeled as user-defined subroutines in simulation software such as Aspen Plus, but after information from Dr. David Clough that such methods are time-intensive, it was elected to stick to MATLAB modeling for both the reactions and mass transfer. Because the mass transfer, that is the dissolution of HCl gas into the liquid glycerol/catalyst, allows for the reactions to occur in the liquid phase, the mass transfer and reaction kinetics were modeled simultaneously through an iterative approach. Over a fraction of the residence time for a batch of feed into this reactor, a determined amount of mass transfer would occur and based on that mass transfer, the reactions would occur. The behavior of the following fraction of residence time would be determined from what occurred in this residence time portion, hence the iterative description. This iteration train would carry for the entirety of the residence time to model the behavior of a batch of reactants. The actual behavior of the reactor would be the sum of these batches, corresponding to a continuous process. Modeling over a residence time that resembled a batch would provide insight into the behavior along that residence time which would lead to deductions about how the reactor should be designed particular interest in the volume

Mass transfer considerations are dependent on the apparatus of use. A gas-inducing impeller design was elected for usage since this has the ability to recycle gas that is undissolved in its first passage through the liquid. If the rate of dissolution were to proportionately slow down, gas would not readily accumulate in the headspace as it would rather be cycled back down through the impeller rod due to a higher pressure gradient. This would increase the margin for error in comparison to non-recycling systems such as a direct bubbling feed. This is because if gas were to accumulate in the headspace, the pressure would accumulate which would push gas through the inducer at a higher rate. A gas inducing impeller apparatus was found through literature which uses a six-bladed impeller with evenly dispersed holes along the blade such that gas is pushed through the impeller rod and out through the blade holes as shown below:

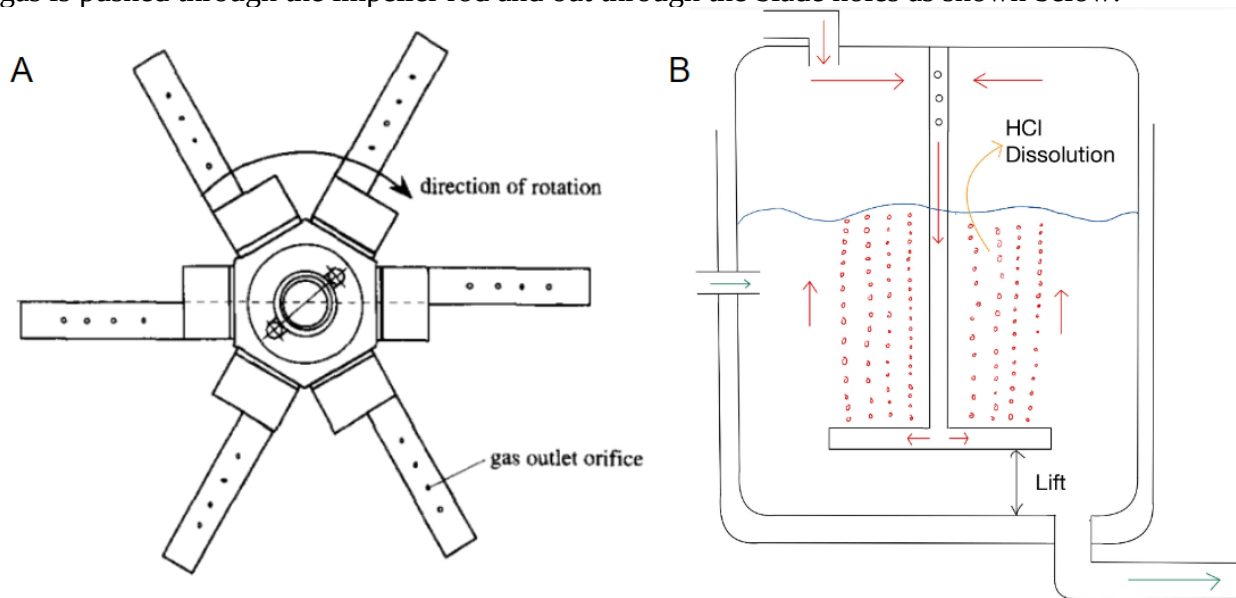


Figure 3.2.1: (A) Gas-inducing impeller apparatus [3.2.2], (B) Impeller's function in CSTR

From the referenced literature, Forrester et al describe a power number of 3.2 was used for this impeller which was based upon an oxygen-water system [3.2.2]. Since oxygen is similar in molecular weight to hydrogen chloride, the power number was kept the same for these calculations. There were other parameters that were mentioned by Forrester et al in perception to their apparatus that were kept near the same but not quite identical. Since literature performed their research in a lab their apparatus was at a much smaller scale and dimensional parameters are in terms of ratios rather than absolute values. The difference is listed below in Table 3.2.3:

Table 3.2.3: Comparison of Medina et. al. and Selected CSTR parameters. [3.2.3]

Parameter	Medina et al. Value	Selected Value
$\frac{\text{Impeller Diameter}}{\text{Vessel Diameter}}$	0.342	0.4
Impeller Frequency (RPS), N	4-8	1.5
Superficial Gas Velocity (m/s), μ_L	0 - (4.4E-3)	5.0E-5
$\frac{\text{Impeller Height}}{\text{Vessel Height}}$	0.5	0.1
Impeller Power Number, N_p	3.2	3.2
$\frac{\text{Vessel Height}}{\text{Vessel Diameter}}$	1	1.5

The dissolution mass transfer of the CSTR was modeled as a function of species concentrations, gas/ungassed powers, and viscosities of the solution. The following correlations were used for the mass transfer coefficient, k_{La} , of the solution for gas-to-liquid mass transfer (Equations 3.2.5 through 3.2.8) [3.2.5]:

$$k_L a = k \left(\frac{P_G}{V_L} \right)^\alpha \mu_L^\beta \quad (3.2.5)$$

$$\frac{P_G}{P_L} = 0.1 N_a^{-0.25} \left(\frac{D_I}{V_L} \right)^{-0.25} \left(\frac{N^2 D_I^4}{g H_I V_L^{2/3}} \right)^{-0.2} \quad (3.2.6)$$

$$P_L = N_p \rho_L N^3 D_I^5 \quad (3.2.7)$$

$$N_a = \frac{Q_{HCl}}{N D_I^3} \quad (3.2.8)$$

Note that nomenclature not directly listed can be found at the end of Section 3 (DCH Reaction Scheme). This equation (3.2.5) uses the assumption that liquids are non-coalescing which is a valid assumption for this experiment because of the low-frequency impeller. Coefficients were provided through Medina et al but these were not made clear because several of them were combined. Also, because of the expected difference in superficial gas velocities between those of Medina et al and this design, all the coefficients for the $k_L a$ term, k , α , and β , were gathered from Perry's handbook based on aqueous stirred vessels. These coefficients are shown below in Table 3.2.4:

Table 3.2.4: Mass Transfer Coefficients ($k_L a$ equation) [3.2.5]

Coefficient	Value
k	2.6E-3
α	0.8
β	0.2

The resulting $k_L a$ combined with the concentration gradient of HCl present in the liquid, a function of the saturation point of HCl, results in the following equation describing the driving force of the HCl mass transfer in the liquid phase (Equation 3.2.9):

$$N_{HCl} = k_L a (C_s - C_{HCl}) \quad (3.2.9)$$

This driving force results in the number of moles per volume-time that transfer from the liquid phase to the gas phases and which are present for reaction which determines the concentration term of HCl in the reaction rates (Equations 3.2.1 - 3.2.4). The pressure difference between the headspace of gas in the top of the reactor and inside the rotating impeller blades serves as the physical driving force for gas such that the amount of gas bubbled through the liquid is a function of what pressure the gas is fed into the reactor. A high pressure system would have required an upstream compressor which would be expensive and was thus elected to not be used. So instead only a slightly higher than atmospheric pressure (1.5 atm) was used for the gas feed to neglect a compressor system and was a safe assumption when considering an externally supplier of this gas for the economics. With the selected pressure, MATLAB simulations were run to see what volumes produced the most ideal disappearance of HCl and appearance of other species.

The inletting flow rates into the reactor were first determined by mass balance approximations and then improved to more accurate values based on what was needed for the aspen simulation. A CSTR has diminishing-returns in terms of volume to conversion, such that conversion of the main reactant reaches a point where any further conversion would require a significantly greater reactor volume. It was expected that conversion of 60 - 80% glycerol would be achieved in this reactor from Medina et al [3.2.4]. In toggling the volume of the reactor, the

ratio of dimensions such as height and diameter had to be determined. A critical criteria used for this was considering how gas bubbles are more likely to dissolve with longer distances to travel in liquid which meant that having a proportionately taller reactor would prove advantageous. A height:diameter ratio of 1.5 was selected to allow for better theoretical mass transfer, although this travel distance was not accounted for in the mass transfer of the MATLAB code. With these dimensions, the reactor volume was toggled to see what gave the appropriate conversion and it was found that the best results were obtained at around 18 m^3 (Figure 3.2.2).

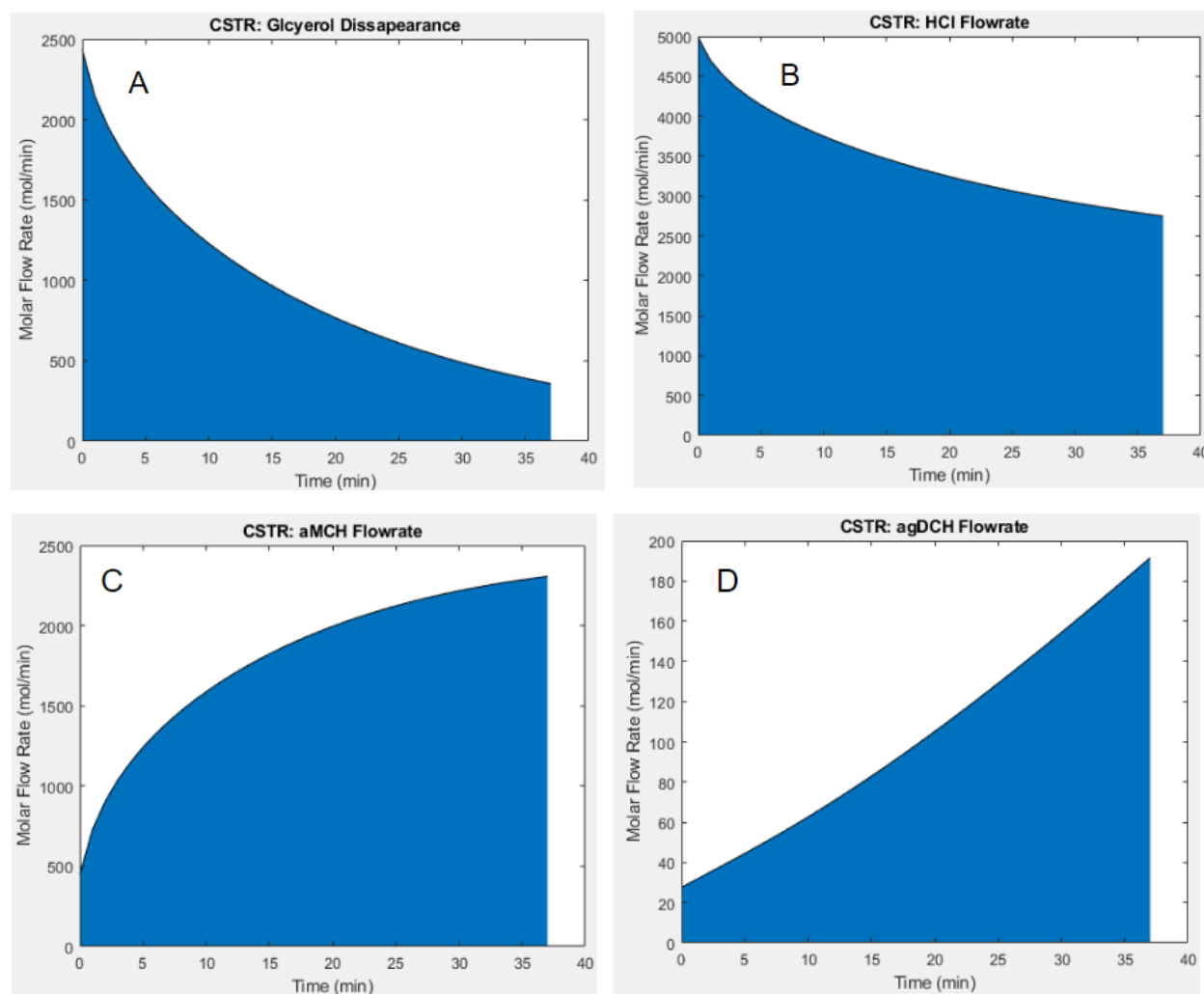


Figure 3.2.2: Hydrochlorination CSTR (A) Glycerol disappearance, (B) HCl disappearance, (C) α -MCH appearance and disappearance, (D) α,γ -DCH appearance along residence time for 18 m^3 design

These residence times correspond well to what was expected from Medina et al. which was a quickly decreasing reactant (Glycerol), moderately fast appearing intermediate (α -MCH), and a slowly appearing product (α,γ -DCH) over a residence time of similar magnitude (Figure 3.2.3). To reiterate, Medina et al used a different apparatus consisting of an argon inert to carry the HCl gas and an acetic acid catalyst at slightly different weights.

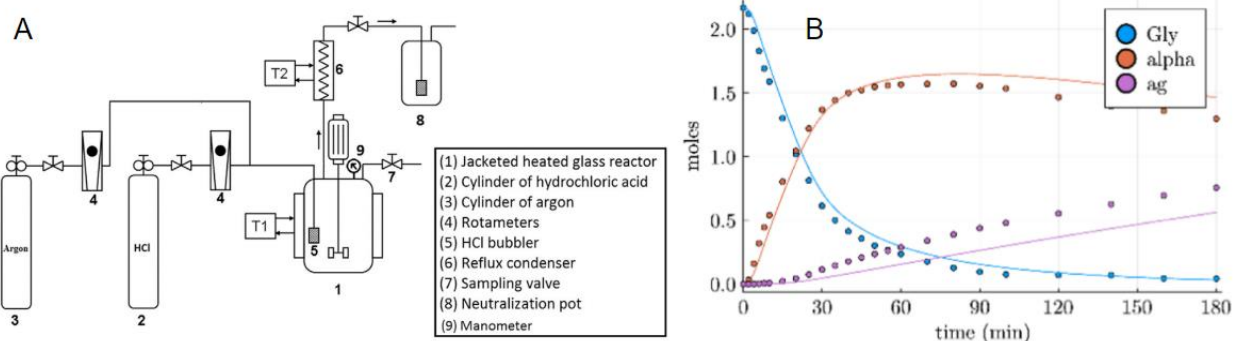


Figure 3.2.3: Medina et al's (A) testing apparatus, (B) Reaction results with 6% mass acetic acid catalyst, reactor temperature of 105 °C (Isothermal), reactor pressure of 1 atm where blue, orange, and purple data correspond to glycerol, α -MCH, and α,γ -DCH presences, respectively [3.2.1][3.2.3].

In analyzing the heat transfer of the CSTR, energy balances were implemented to model the temperature along a residence time. These implementations would not account for the overall behavior of the reactor as the heats of reaction differ along the residence time due to the difference in heats of individual reactions between the MCH and DCH appearance reactions, as well as the dissolution of HCl (Table 3.2.5):

Table 3.2.5: Heats of reactions/dissolutions for DCH scheme

	Heat of Reaction/Heat of Dissolution (kJ/mol)
Glycerol to α -MCH	-49
Glycerol to β -MCH	-41.5
α -MCH to α,γ -DCH	91
β -MCH to α,β -DCH	94.9
HCl Dissolution	-74.8

These values were calculated by summing the heat of formations for each of the components listed in the stoichiometric reactions. No consideration was given towards temperature normalization (from 80 °C to ambient conditions) of the heats of reactions as there is insufficient literature available on the heat capacity constants to perform such integrals. It is observed from Table 3.2.5 that the first stage of the reactions along a residence time would lead to the greatest increase in temperature as all of these contributions are exothermic while the following contributions are all endothermic, such that amount of coolant would need to be largely tailored to what is occurring at the beginning of the residence time. The temperature behavior in the CSTR was thus monitored along the residence time and so a differential energy balance was implemented that accounts for the temperature change over time. Balances were

implemented for heating contributions which were a function of the heats listed in Table 3.2.5, and the cooling contributions which were a function of the amount and type of coolant fed into the vessel's jacket. Below are the different energy balances for the heating and cooling contributions (Equations 3.2.10 and 3.2.11, respectively), as well as the parameters of the cooling utility (Table 3.2.6).

$$\frac{dT_H}{dt} = \frac{\sum_i r_i H_{rxn,i}}{\sum_i C_{p,i} F_i} \quad (3.2.10)$$

$$\frac{dT_C}{dt} = \frac{UA(T_R - T_C)}{\sum_c C_{p,c} F_c} \quad (3.2.11)$$

Table 3.2.6: CSTR Cooling Utilities Properties

Parameter	Value	Units
Type	Cooling Water	
Heat Capacity, C_p	75.6	J/mol-K
Overall Heat Transfer Coefficient, U	1000	mol
Temperature, T_C	20	°C

Cooling water was selected as the utility for this apparatus because cooling water is one of the most readily available utilities with a low price. Also considering that the differences in heats of reactions were not significant since having a large reactor would in itself allow for more endothermic reactions to occur. A bigger reactor would be harder to cool from a dimensional standpoint but it is also important to consider what is being cooled. This volumetric impedance is mitigated by the taller structure which was selected based upon the need for bubble travel, so these go hand-in-hand and it seems likely that even taller height:diameter ratios should be explored to approach the maximum pressure rating. It is also notable that a cooling of the recycle stream was implemented into the process as a later adjustment for a second line of heat mitigation.

In applying these energy balances to the isothermal setup in MATLAB, the temperature along the residence time was monitored to determine what amount of cooling water would be needed to keep the temperature near isothermal. The starting temperature was modeled at 80°C since this was found to be a combination of the best performing temperature and the most safe temperature as there would be an increased chance of inadequate cooling with a temperature in the northern part of the recommended 80-110°C range [3.2.3]. With these conditions, the results for a flow rate of 1382.4 kg/min of water at 20°C were as follows (Figure 3.2.4):

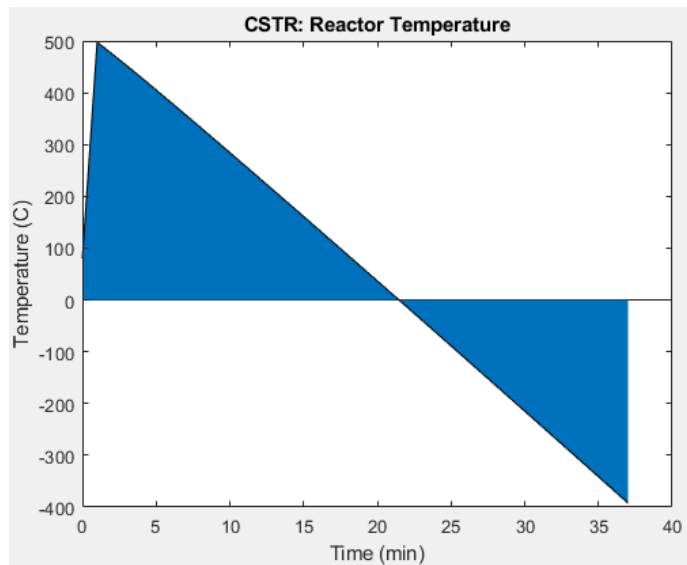


Figure 3.2.4: Hydrochlorination CSTR Temperature profile along residence time for batch of feed

It is observed in Figure (3.2.4) that the temperature initially rises but then steadily declines as the reactions proceed, as predicted from the values in Table (3.2.5). This amount of cooling is what results in an average value around the designated temperature of 80°C. Figure 3.2.4 depicts a single batch over a residence time where realistically the reactor temperature would be a compilation of batches with an even dispersion of conversions. This is why the value shoots up and then falls down and why the amount of coolant was not toggled to get the behavior at 80°C but rather to an average value of 80°C.

Aspen simulations were run in which conversion of MCH and DCH was achieved a lot faster than what is shown through MATLAB (Figure 3.2.4). It was initially attempted, once agreed upon to not design a user-defined subroutine for a reactor, that the reactor should be operated with an ideal head space to accommodate a two-phase consideration. This, after many attempts, proved successful in producing expected results. The inputs were used as shown below in Figure 3.2.5:

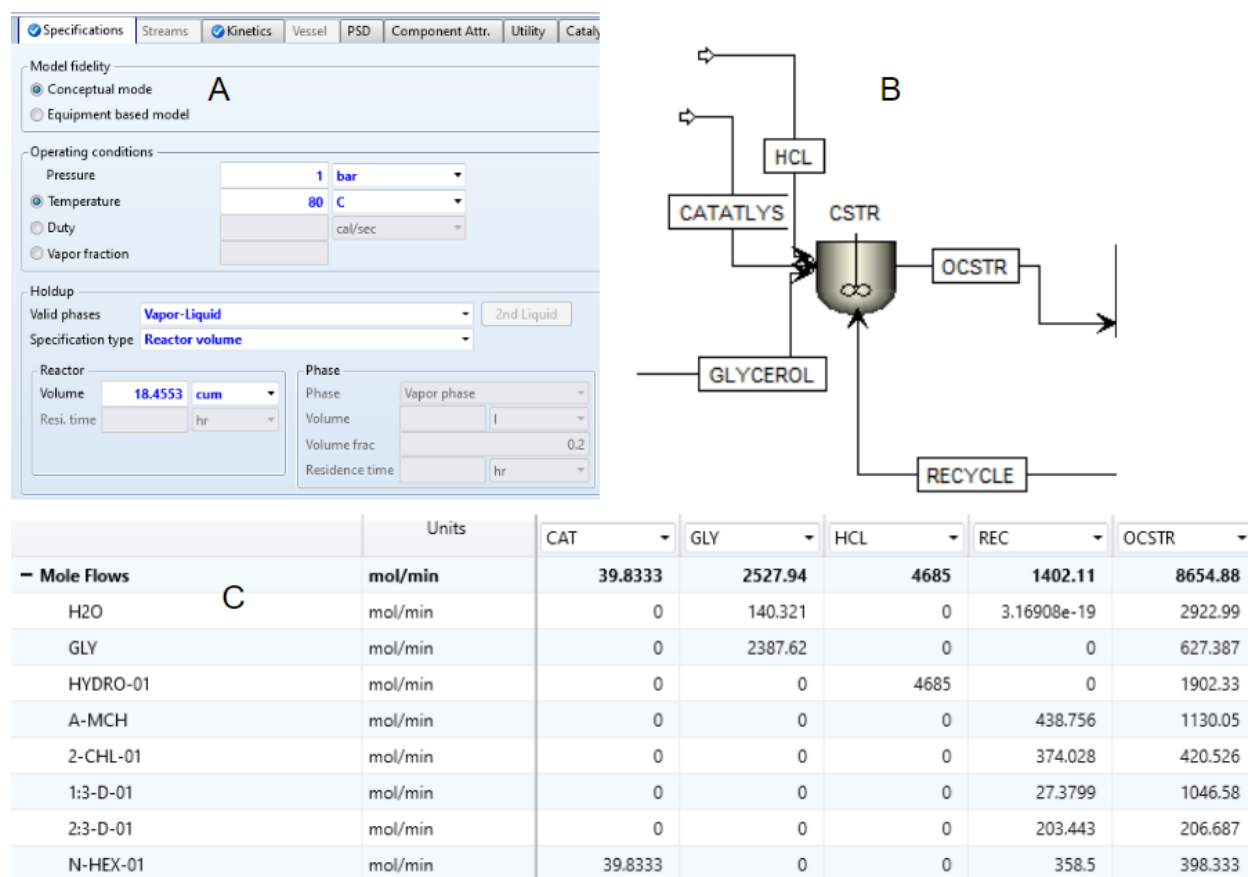


Figure 3.2.5: ASPEN Plus Hydrochlorination CSTR (A) Inputs, (B) Schematic design, (C) Stream results (Stream notation included in part (B))

Lower conversion of glycerol was achieved in Aspen's CSTR (0.737 vs 0.853) with a similar volume (18.45 vs 20 m³) than the MATLAB code but the behavior in kinetics was similar in terms of selectivity. A slightly lower catalyst was used for the Aspen CSTR, ~5%, wt. as opposed to MATLAB, ~7%. The amount of catalyst feedstock in ASPEN was primarily through the recycle stream (REC) since no catalyst gets consumed through reaction and very little boils out of the downstream DCH purification column.

What was lastly designed with this reactor was the material of construction. Acidic gas was going to be present in the reactor and thus the material of construction choice for this reactor was extremely important to avoid any long-term corrosion effects. An alloy was presumably the best selection but after initial research it was found that a coated material such as glass-lined stainless steel would best accommodate this system and reduce any long-term corrosion.

3.3 Hydrochlorination PFR

The CSTR, as per Figure (3.2.2), would have required a very large volume to achieve high conversion, and thus a PFR was used to complete the reaction sequence. An adequate CSTR volume was selected so that the entirety of the mass transfer occurred from the gaseous HCl phase into the liquid phase. The resulting mixture of the PFR was assumed to be entirely liquid not only because of the high conversion (85.3% conversion of glycerol per Figure 2.2.2) but also

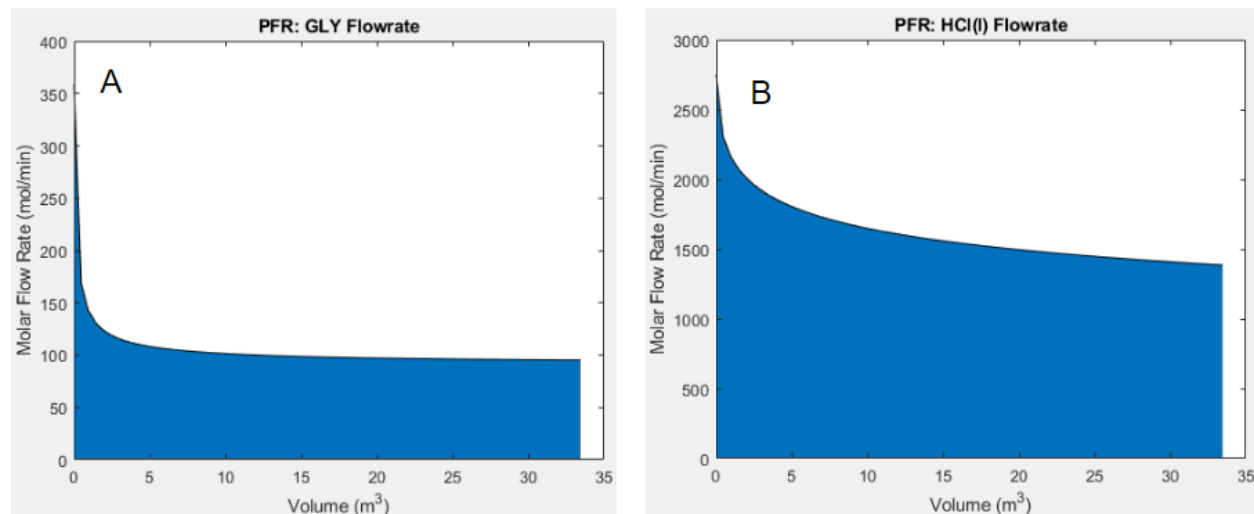
because the impeller of the CSTR was placed above the outletting flow (Figure 3.2.1). So the first big difference between the CSTR and the PFR is the amount of phases present and the second is the heat transfer. As per Table 3.2.5, the most exothermic contribution, the HCl dissolution, is a non-factor in this reactor and the two exothermic reactions occur less in this reactor such that the overall reaction scheme was thought to be exothermic. Thus, an adiabatic design was selected to where no cooling utility was necessary so that the system was insulated. Carrying forward the isothermal assumption from the CSTR, the temperature of the inletting feed was kept at 80 °C. If any sort of heat transfer were to be considered it would be in the form of heating to keep the reactor at a high enough temperature for the reactions to occur.

The goal of this reactor was to get near complete conversion of the Glycerol and near complete conversion of the reactive MCH isomer, α -MCH. This is theoretically feasible considering the absence of a volume-conversion constraint, but less likely due to the highly endothermic nature of the reaction coupled with activation energies such that reactions would be thermally limited. MATLAB models were performed with the outlets of the CSTR simulation serving as the inlet for this unit. The same kinetics, shown in Equations (3.2.1) - (3.2.4) with the parameters and variables, Tables (3.2.1) and (3.2.2), respectively, were used for these models. The goal of these simulations was to identify which volume would be appropriate for reasonable conversion. A fixed length:diameter ratio was predetermined to be 8 such that the volume could be iterated over using the following material balance:

$$\frac{dF_i}{dV} = r_i \quad (3.3.1)$$

$$F_i = \int_{V_i}^{V_f} r_i dV \quad (3.3.2)$$

Another notable difference, as inferred by Equation (3.3.2), is that this reactor's behavior was iterated with respect to volume rather than residence time. While the CSTR was modeled isothermally such that the temperature in the kinetic terms were kept constant, the temperature in these kinetic terms was allowed to vary as the reaction was proceeding in the same accordance as temperature was, that is with volume. The results for this model are shown below for a selected **34 m³ reactor** (Figure 3.3.1):



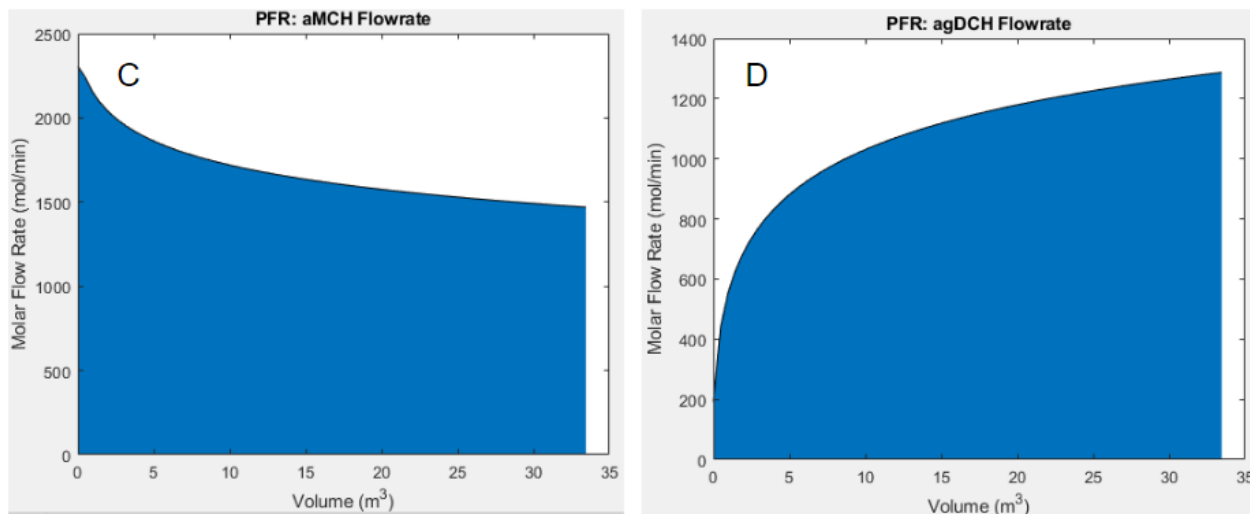


Figure 3.3.1: Hydrochlorination PFR species behavior along reactor length of (A) Glycerol, (B) HCl (Liquid form), (C) α -MCH, and (D) α,γ -DCH for 34 m³ volume.

As observed, these results show promising but concerning behavior which was found to be due to the temperature drop which is shown by the following result (Figure 3.3.2):

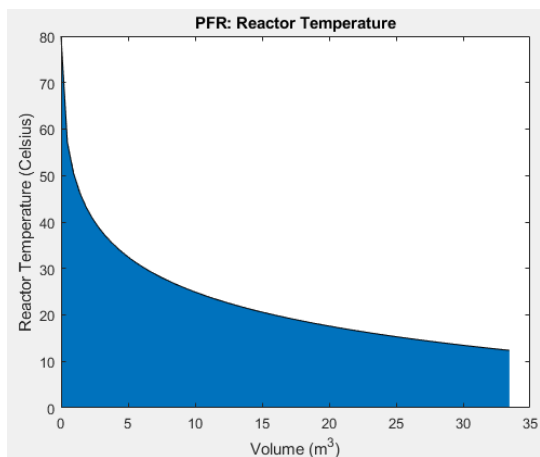


Figure 3.3.2: Hydrochlorination PFR temperature along reactor length

The very endothermic nature of these reactions suggests that heating needed to be implemented and was done so by considering the reactor isothermal in the simulation. As a disclaimer, utility was not actually designed to keep the reaction at or near its inlet temperature of 80 °C but the following results still serve as a useful guide as to what would happen if appropriate heating were provided to the same-sized reactor.

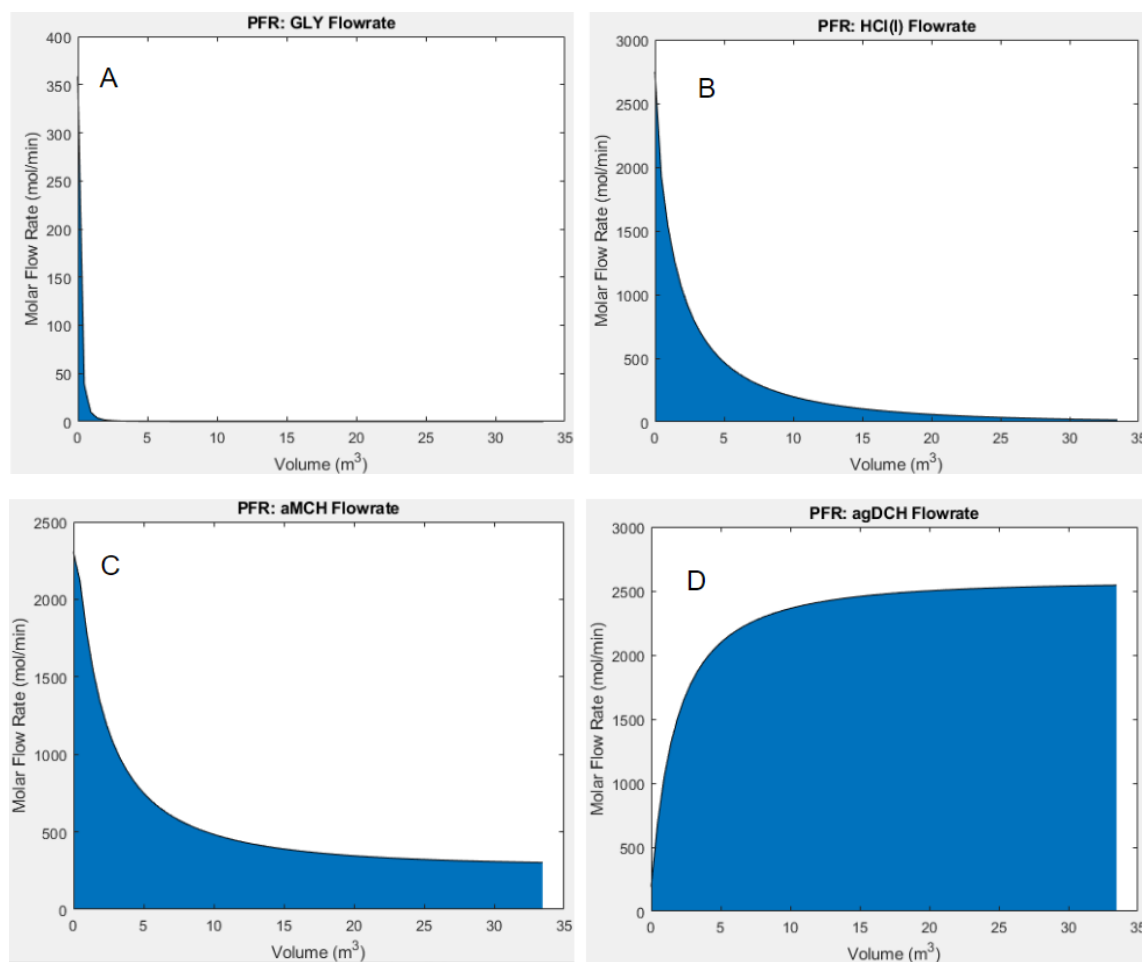


Figure 3.3.3: Isothermal Case: PFR Species behavior along volume length of (A) Glycerol, (B) HCl (Liquid form), (C) α -MCH, and (D) α,γ -DCH for 34 m³ reactor.

In comparing the two sets of graphs (Figure 3.3.1 and 3.3.3) it is apparent that a temperature decrease along the reactor significantly hampers the reactions of MCH to DCH. It was thus concluded that a heating utility should be implemented on the PFR to achieve desired conversion. Carrying this over to the aspen simulation, it was observed that a temperature rise takes place despite a similar conversion in the prior CSTR (similar feed):

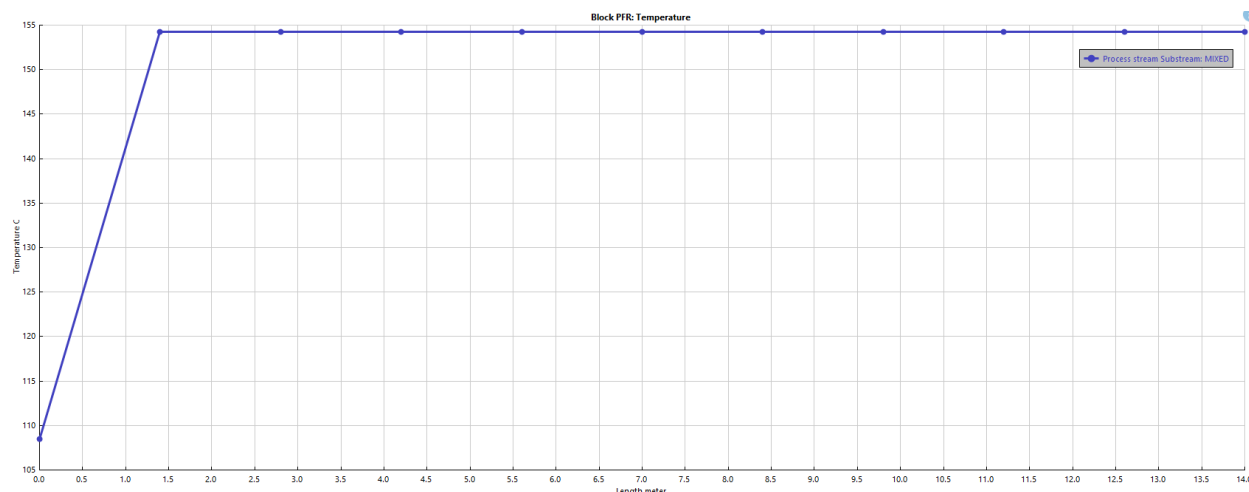


Figure 3.3.4: Aspen Plus Hydrochlorination PFR Temperature Profile (34 m³ reactor)

The temperature unexplainably shot up and conversion was readily achieved with the reactor identical volume (Figure 3.3.4). This temperature spike was challenging to identify because heat transfer was not considered in setting up this reactor nor were heats of reactions even provided. What is even more perplexing is how the temperature at the beginning of the reactor is ~110 °C when the process stream going into this PFR is 80 °C. A provided hypothesis on this behavior is that Aspen is considering HCl dissolution in the PFR, that is any conversion in the PFR is associated with mass transfer of HCl which is the most exothermic step in this reaction scheme. Unfortunately, this hypothesis is doubtful since the reactor was specified as having a singular liquid phase.

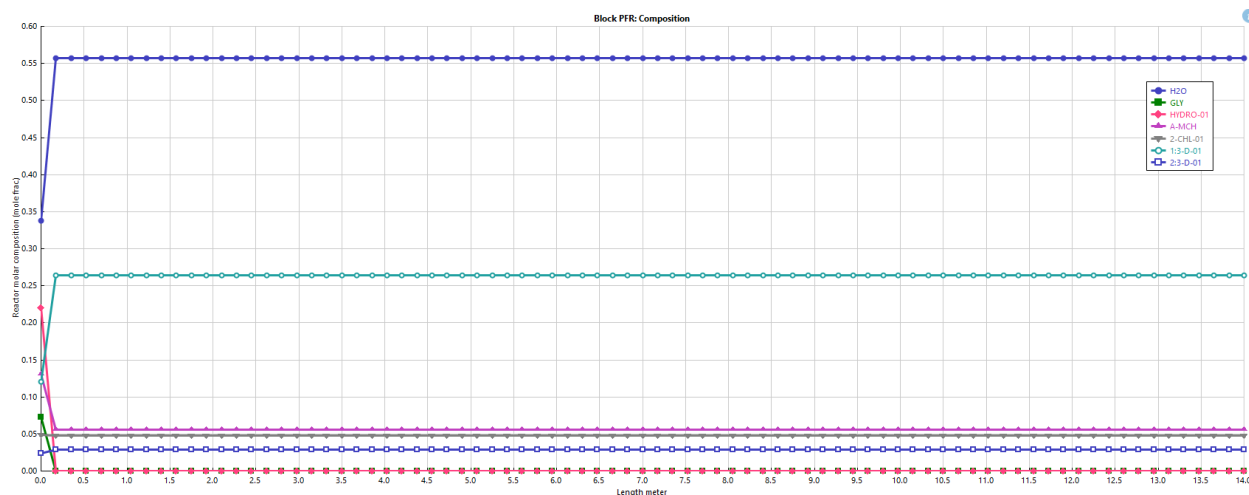


Figure 3.3.5: Aspen Plus Hydrochlorination PFR molar composition profile along reactor length - in accordance with Temperature profile of Figure 3.3.2

The reactions expectedly occur quickly at this high temperature to where the majority of the reactor volume is unnecessary. Still this reactor completes conversion and so the results were used to carry forward the simulation. It was understood going into this project that Aspen Plus has a large amount of error with non user-defined reactors and that reactors should be backwards

modified to achieve an expected performance. So while the MATLAB would be used for better approximation of PFR performance, a different model is used to achieve conversion for the sake of understanding every unit in a cumulative manner. The amount of volume required to achieve conversion was drastically less in the Aspen Simulation, and so the following specifications were used to produce the following results:

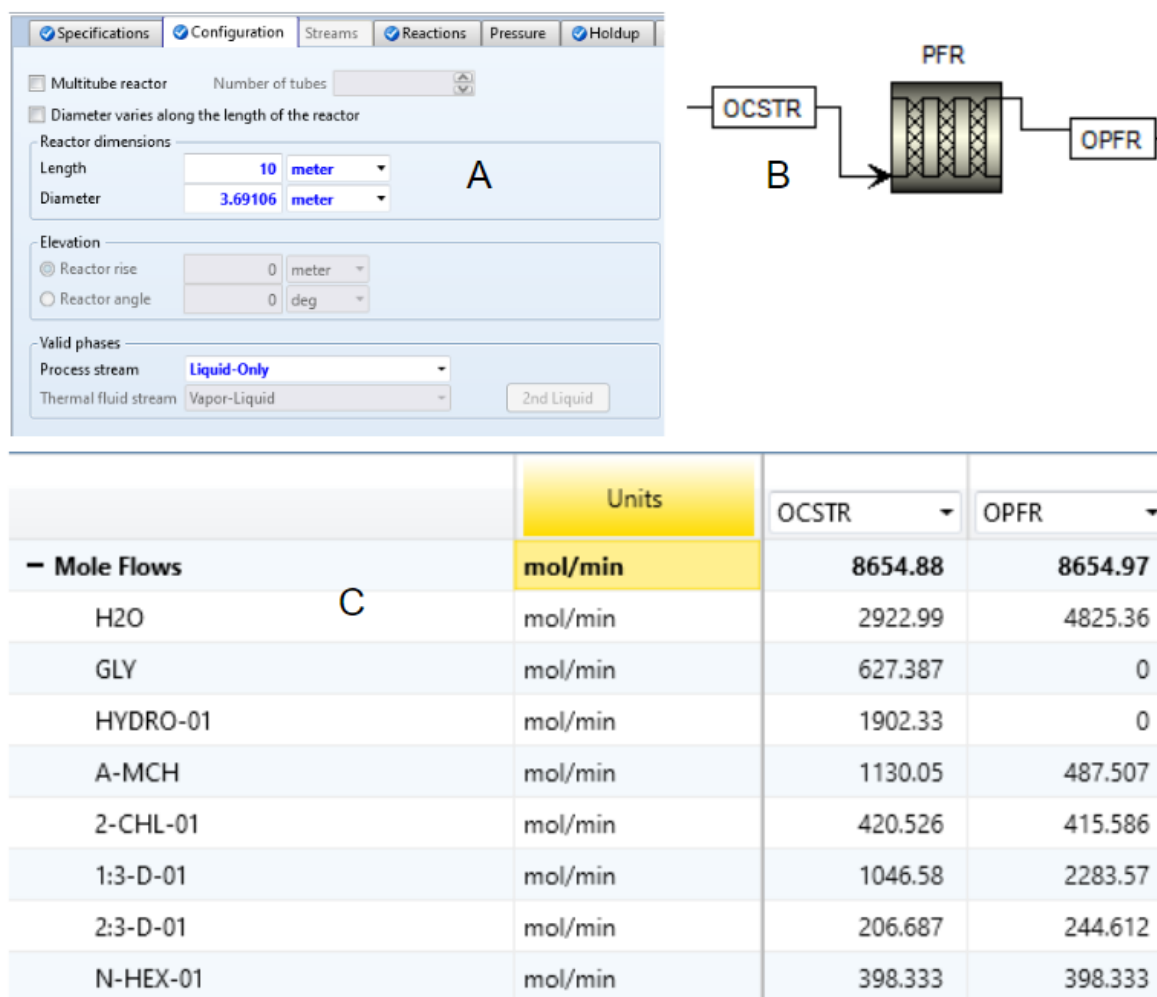


Figure 3.3.6: Hydrochlorination PFR Aspen Plus (A)Inputs, (B) Schematic, and (C) Stream Results

The volume dimensions did not have a noticeable impact on the unexplainable temperature rise and so these were implemented arbitrarily into the cumulative Aspen Plus file.

Table 3.3.1: Hydrochlorination CSTR and PFR Nomenclature

Variable/Parameter Notation	Value (N/A for Variable)	Units	Notes
α	0.8	Unitless	mass transfer coefficient 1

β	0.2	Unitless	mass transfer coefficient 2
C_{HCl}	N/A	mol/m ³	Concentration of HCl in liquid phase
$C_{\text{p},i}$	N/A	mol/m ³	Heat capacity of component i
C_s	6.31E3	mol/m ³	Saturation concentration of HCl in glycerol solution
D_I	1.34	m	Impeller diameter (length)
F_i	N/A	mol/min	Molar flow rate of species i
g	9.81	m/s ²	gravitational acceleration
H_I	0.505	m	height of impeller of bottom of reactor
$H_{\text{rxm},i}$	N/A	kJ/mol	Heat of reaction of reaction i
k	2.6E-3	Unitless	mass transfer coefficient 3
$k_L a$	N/A	unitless	mass transfer coefficient
N	1.5	rps	Impeller frequency
N_a	N/A	Unitiess	Aeration Number
N_p	3.2	Unitless	Power number
ρ_L	N/A	kg/m ³	Density of liquid solution
P_G	N/A	W/s	Gassed power- power required to stir liquid with bubbles present
P_L	N/A	W/s	Ungassed power- power required to stir liquid without bubbles present

Q_{HCl}	N/A	m^3/min	Volumetric flow rate of HCl gas into liquid solution
r_i	N/A	$\text{mol}/\text{m}^3\text{-min}$	Reaction rate of reaction i
t	N/A	min	Time (interval)
T_c	20	$^{\circ}\text{C}$	Coolant Temperature
T_R	N/A	$^{\circ}\text{C}$	Temperature of solution
V_L	N/A	m^3	Liquid volume
μ_L	5.0E-5	m/s	Superficial gas velocity

3.4 DCH Purification Distillation Column

After DCH is produced in the CSTR and PFR reaction units, it was desired that DCH be isolated from other partially hydrochlorinated MCH species, catalyst, and water. The design of this distillation column relied heavily on usage of Aspen Plus because the ternary azeotrope between water, DCH, and HCl disallowed use of the Fenske-Underwood-Gilliland mathematical modeling method (the FUG method). Selection of catalyst and operation temperature were also key considerations in the design of this distillation column.

The first attempted method of designing specifications for this distillation column was the Fenske-Underwood-Gilliland method, which mathematically estimates parameters like reflux ratio and number of equilibrium trays required for a given separation based on temperature-specific partition coefficients (also called K-values) at the inlet and both outlet conditions of the column. Calculations first begin with gathering those partition coefficients, which was done in the Aspen Plus properties environment where stream flow rate, composition and temperature and pressure were specified based on the feed conditions at the inlet of the column. These partition coefficients were applied to the material balance as a rough estimation of how the components would separate if the separation was assumed to be a temperature flash. However these partition coefficients were not suitable for usage in the FUG method because the azeotrope between water and DCH caused the partition coefficients for both isomers of DCH (α,γ -DCH and α,β -DCH) to be much lower than expected. Because DCH and water experience an azeotrope, setting the column operation conditions so that water exits out of the top of the column should carry an azeotropic amount of DCH also out of the top of the distillation column, but the partition coefficients, which is a ratio of fraction of species present in the gas phase over fraction of species present in the liquid phase at equilibrium, did not reflect this.

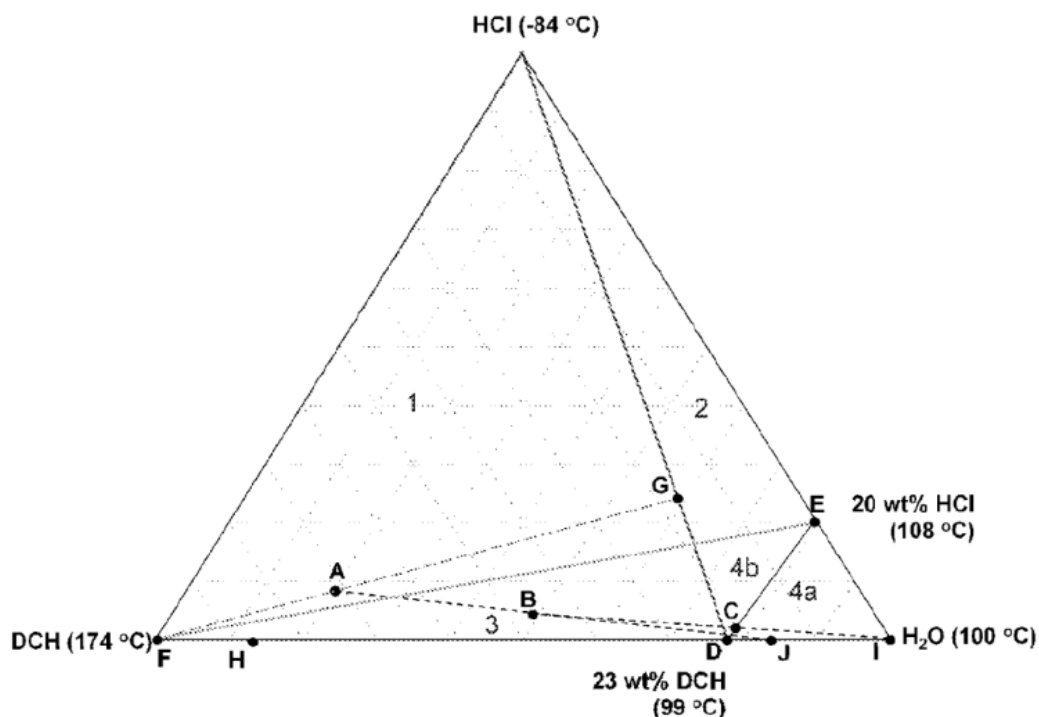


Figure 3.4.1: Ternary Azeotropic Interactions Between DCH, Water, and HCl [4.3.2]. This figure illustrates the azeotropic compositions, by weight, as well as the boiling points of the individual components at that azeotropic composition. The axes of this ternary diagram are the weight percent of the respective components. The DCH axis starts at 0% at the corner labeled with H₂O, and is 100% at the corner labeled DCH. Similarly, the left axis is the HCl composition axis (composition increases from the DCH corner to the HCl corner) and the right axis is the H₂O composition axis (composition increases from the HCl corner to the H₂O corner).

Therefore, it was advantageous to model this distillation column fully in Aspen Plus, which also uses a variation of the Fenske-Underwood method to estimate minimum stage number, reflux ratio, and other parameters, but can iteratively calculate partition coefficients at any condition in the column. It was discovered that only some fluid packages in Aspen Plus recognize a given azeotrope, so this distillation column was simulated using the NRTL fluid package after verifying that the Aspen Plus simulation recognized an azeotropic interaction between DCH, water, and HCl.

Table 3.4.1: DCH Purification Column Parameters

Parameter	Value	Units
Column Operating Pressure	0.0215	Bar
Reboiler Temperature	108.981	°C

Condenser Temperature	12.759	°C
Number of Equilibrium Stages	24	unitless
Feed Stage	13	unitless
Reflux Ratio	0.6	unitless
Distillate to Feed Ratio	0.82	unitless

Simulation of the DCH purification distillation column began with a shortcut column model in its own simulation environment using the inlet flows that resulted from the MATLAB coded simulation of the hydrochlorination PFR. Certain shortcut column specifications, like number of equilibrium stages, reflux ratio, and distillate to feed ratio, were then applied to a RadFrac unit with a decanter in the cumulative Aspen Plus simulation. Table (3.4.1) describes the final designed parameters of the RadFrac unit in the cumulative Aspen Plus simulation, which were determined via guess and check to reach separation behavior expected. These expectations came from discussion of separation fundamentals with Dr. Hook, as well as the reported separation that the research group he took part in (Hook et. al [P.3]).

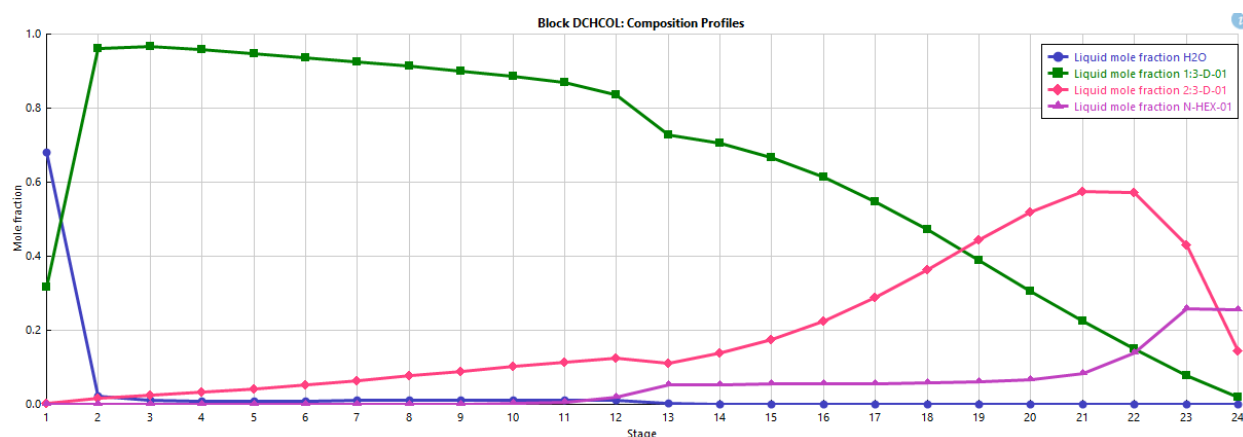


Figure 3.4.2: Molar Composition of Species in DCH Purification Column. This Aspen Plus generated figure describes the composition (by mole) of each component in the DCH purification distillation column on every equilibrium stage of the unit. The distillate stream exiting the column has the same composition as on stage 1 (on the y-axis), while the bottoms stream exiting the column has the same composition as on stage 24 (at the far right of the figure).

Given the separation that was conducted on the lab scale by Hook et. al [P.3], the separation achieved in the cumulative Aspen Plus file, and the operation of units downstream, changes were made to the stream flow rates. Most notably, research group Hook et. al achieved a similar composition of α,γ -DCH and water out of their two-column separation process due to the ternary azeotrope between DCH, water, and HCl [P.3], however because the Aspen Plus simulation had no feed of HCl entering this distillation column the binary azeotrope that DCH

experiences with water caused the DCH composition to be higher overall. It was desired to remove HCl from the process stream via reaction in the hydrochlorination PFR in order to minimize HCl composition in this distillation column in order to avoid the ternary azeotrope in favor of the binary azeotrope in which there is a higher azeotropic composition of DCH (see figure 3.4.1). Researchers Hook et. al in their lab-scale dual-column separation reported significant amounts of α,β -DCH exiting in the distillate stream, up to 14% (by weight) [P.3], however the Aspen Plus simulation calculated almost no α,β -DCH in the distillate stream. Due to this discrepancy, to make the Aspen Plus simulation better reflect the real separation, a stream of α,β -DCH was mixed into the organic stream products of the decanter to make up for the loss of this key reactant needed to produce ECH downstream.

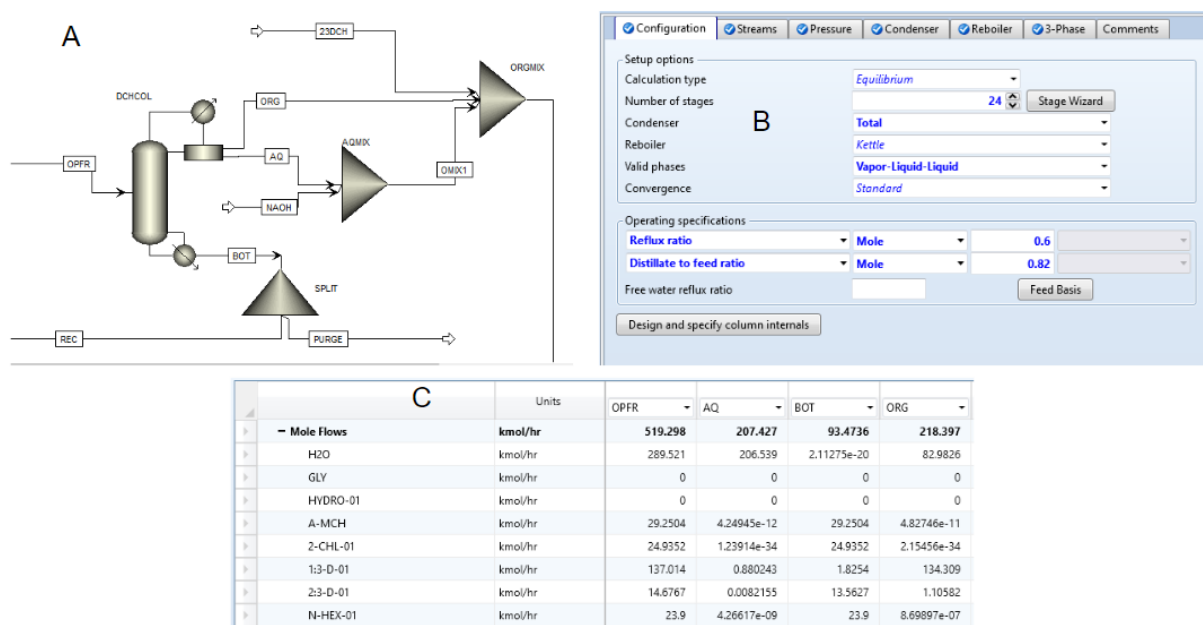


Figure 3.4.3: DCH Purification Column Aspen Plus Simulation Inputs and Stream Outputs. (A) shows how the streams enter and exit equipment around the DCH purification column. (B) shows the inputs used in the Aspen Plus simulation for the RadFrac with a decanter unit. (C) shows the molar flow rates of species and total streams, labeled with stream names.

The distillate and bottoms outlet streams were manipulated using mixers in order to prepare these streams for their destinations downstream and upstream, respectively. It was known that downstream from this purification column would be the dehydrochlorination mixing plug flow reactor (mixing PFR) and that the bottoms stream should be recycled back to the inlet of the hydrochlorination CSTR in order to preserve the catalyst and lessen the need to reintroduce it. In regards to the aqueous distillate stream, it was desired to mix this stream with the aqueous sodium hydroxide (NaOH) stream, so that the water produced in the hydrochlorination reactors could be utilized instead of adding more water to this process. While in the final design of the downstream mixing PFR made use of impinging jets that mix the organic distillate stream with the caustic-containing aqueous distillate stream within the mixing PFR, Aspen Plus was not able to accommodate this, so the streams were mixed in order to be sent to the mixing PFR in the simulation. The recovery of both DCH isomers in the organic

phase distillate stream was **89.2%**. in the For the bottoms product of the distillation column, because it contained α -MCH, which could be hydrochlorinated further into DCH after recycling, and the hexanoic acid catalyst. Hexanoic acid was specifically selected from amongst other researched carboxylic acid catalysts because of its higher boiling point which allows hexanoic acid to be recovered from DCH purification instead of sent downstream like the carboxylic acids with lower boiling points. However, a purge stream off of this recycle would still need to be implemented in the real process in order to disallow the accumulation of β -MCH, which cannot effectively be hydrochlorinated into DCH. This purge does cause a loss of catalyst in the process, however replacing the small purged amount of the more expensive hexanoic acid periodically is much more cost effective than replacing large amounts of cheaper, lower boiling point carboxylic acids like acetic acid.

Table 3.4.2: DCH Purification Column Sizing and Materials

Parameter	Value	Units
Column Height	7.3152	m
Column Diameter	1.46304	m
Tray Height/Diameter Ratio	0.9	Unitless
Number of Equilibrium Stages	24	Unitless
Maximum Pressure Rating	1035	kPa
Packing Material	Porcelan	Unitless
Construction Material	Nickel Alloy	Unitless

3.5 DCH Design Setbacks

Several setbacks occurred during the design of the first reaction sequence. First of which are the azeotrope considerations within Aspen Plus for the DCH purification column. In order to achieve the expected behavior of α,γ -DCH and water, the NRTL fluids package was used. However while α,γ -DCH showed correct VLE behavior, α,β -DCH was not achieving the separation that is expected. As a result, a all α,β -DCH that is formed that would be expected to be recovered nearly completely in the distillate is instead lost in the bottoms as waste. To remedy this, a comparable amount of α,β -DCH is added to the Aspen Simulation, mixing with the organic output from the column and sent downstream to the second reaction sequence.

One notable setback that was encountered in developing the reaction scheme was that the material balance calculations, which had minimal consideration of the recycle stream, were not changed in the Aspen simulation when the recycle stream was considered. This resulted in the amount of catalysts being drastically higher than necessary (~45% weight rather than ~10% weight) and significantly altered the performance of the reactors and first DCH column. This was not found until down the line in the design process but was promptly fixed by dropping the amount of catalyst fed into the CSTR and proportionately toggling the amount of HCl feed. Furthermore, the distillate to feed ratio of the DCH column was slightly increased so that an easier separation, that is one with less of the least volatile component, could occur. Column performance drastically increased from 93% to 98% and the overall yield of glycerol to ECH increased as well. The downstream processes were not altered in performance by much as the change in catalyst was counterbalanced. This mistake was a result of working with multiple different platforms at the same time. While this variety gave more insight into how the process should behave, there was a greater tendency to make a mistake when a drastic change was implemented into a singular platform. It was found later that this had a substantial impact on economic outputs as the cumulative cash flow reached a positive value two whole years earlier than previously thought.

4 Epichlorohydrin (ECH) Reaction Scheme - Development

4.1 ECH Scheme Startup Considerations

With the information provided by the project prompt, more information was required for the ECH reactions. Reactions were provided for the production of epichlorohydrin, as well as the epichlorohydrin hydrolysis side reactions. Reaction schemes and kinetics were obtained from Tolli et. al [4.1.2]. Tolli et. al. provides a complex hydrolysis reaction scheme compared to the project description, including reverse reactions and additional compounds.

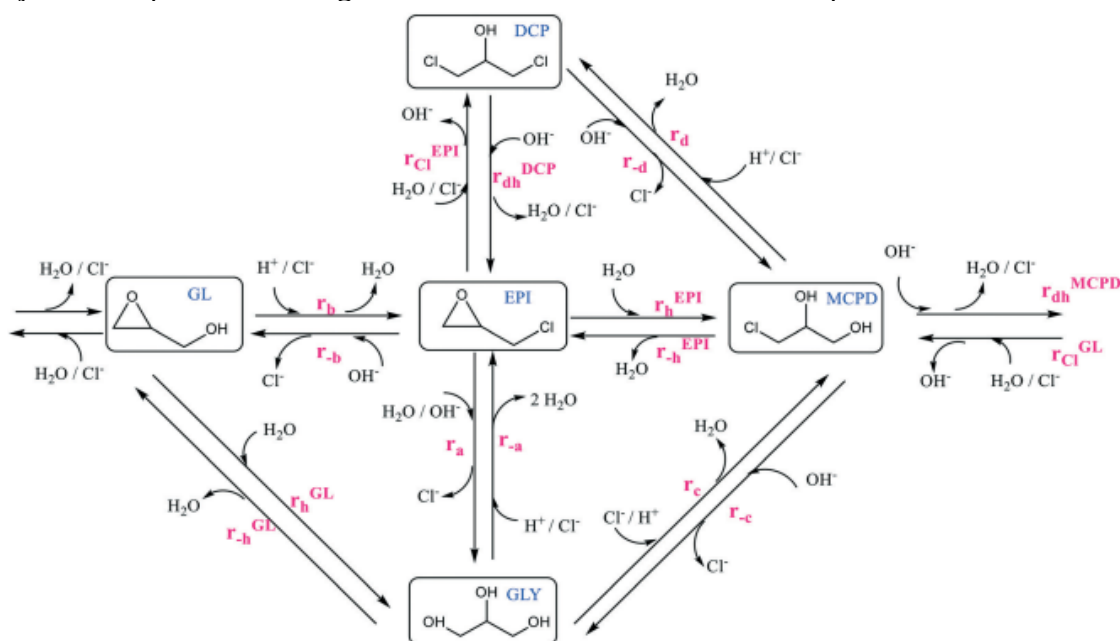


Figure 4.1.1: Provided by Tolli et. al. [4.1.2], shown is the full epichlorohydrin hydrolysis reaction sequence. Included is the reaction of α,γ -DCH to ECH. This scheme shows many more

possible reactions than were considered during this project. Reactions were simplified to the scheme shown below, as well as adding a reaction for α,β -DCH to ECH.

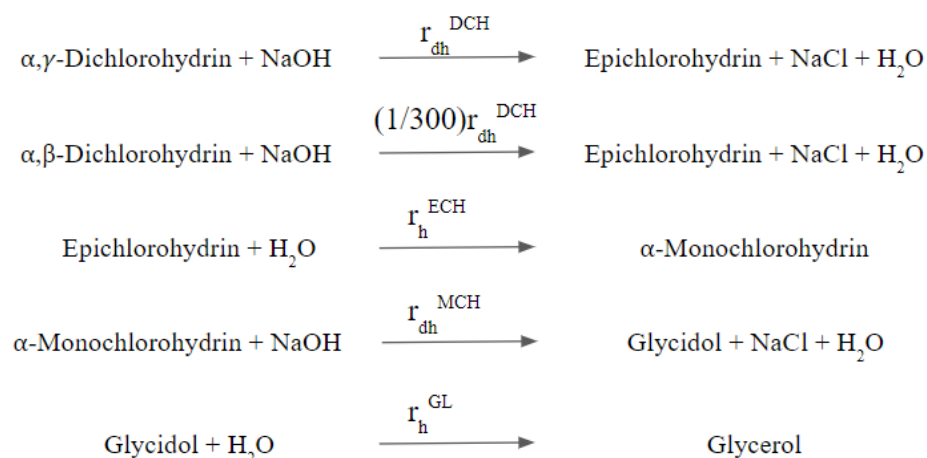


Figure 4.1.2: Reaction scheme from Tolli et. al. simplified to sequence specified in project description. Reaction rates correspond to rates in the paper. It is important to note that reaction rates for α,β -DCH are not provided. As a result, the kinetics used for α,β -DCH are the α,γ -DCH kinetics divided by a factor of 300, roughly matching the approximate reaction rate difference as given by Santacesaria et. al. [4.1.1]. Epichlorohydrin is hydrolyzed to α -MCH, which then undergoes dehydrochlorination to glycidol. Finally the glycidol is hydrolyzed to glycerol.

The reaction rate terms gleaned from Santacesaria et. al. [4.1.1] in Figure (4.1.2) come in two different forms: hydrolysis reactions and dehydrochlorination reactions. The dehydrochlorination terms are fairly standard, with only one kinetic constant and concentrations of the two reactants in the reaction. The hydrolysis reactions however take a different form, each containing an: alkaline, acidic, and neutral terms, in addition to the reactant concentrations. Full reaction rate equations are shown below in Equations (4.2.7) through (4.2.11).

An additional consideration that needed for this reaction sequence was the biphasic liquid behavior. The DCH being reacted does not readily mix with the aqueous sodium hydroxide also being fed. To ensure contact between the two for reaction, as well as to maintain a constituent pH and temperature, mixing apparatus must be used. A CSTR would be quite the poor reactor choice for this situation for conversion purposes. As a result, a PFR with mixing apparatus was chosen for use. Described more in depth below, the mixing PFR utilizes a pair of impingement jets for each inlet stream, in combination with a static mixing structure within to ensure mixing throughout the entire length. With α,γ -DCH shown to react nearly instantaneously, the PFR volume is optimized around getting complete conversion of α,γ -DCH to ECH.

Flowing out of the mixing PFR, a large majority of the ECH has been produced, however the α,β -DCH will not have been reacted to any significant amount. Leaving this α,β -DCH unreacted would result in a significant overall yield loss for the process, but extending the PFR volume significantly would make the formed ECH available for hydrolysis. In order to get reaction of α,β -DCH while minimizing the hydrolysis, a reactive distillation column is chosen for use. The reactive distillation column will allow the remaining α,β -DCH to react while providing continuous separation of the ECH, aided by

the ECH water azeotrope. ECH and water experience an azeotrope at approximately 89°C. If the reactive distillation column is kept at a high enough temperature and fed with sufficient amounts of water, the ECH will be successfully stripped and sent to the distillate of the column. Shown below is a summary of boiling points of relevant compounds within the reactive distillation column, including the ECH water azeotrope.

Table 4.1.1: Boiling points of relevant species

Species	Boiling Point (°C)
H ₂ O (26wt%) - ECH (74wt%)	88.5
H ₂ O	100
ECH	117
Glycidol	167
DCH	175
MCH	213
Glycerol	290

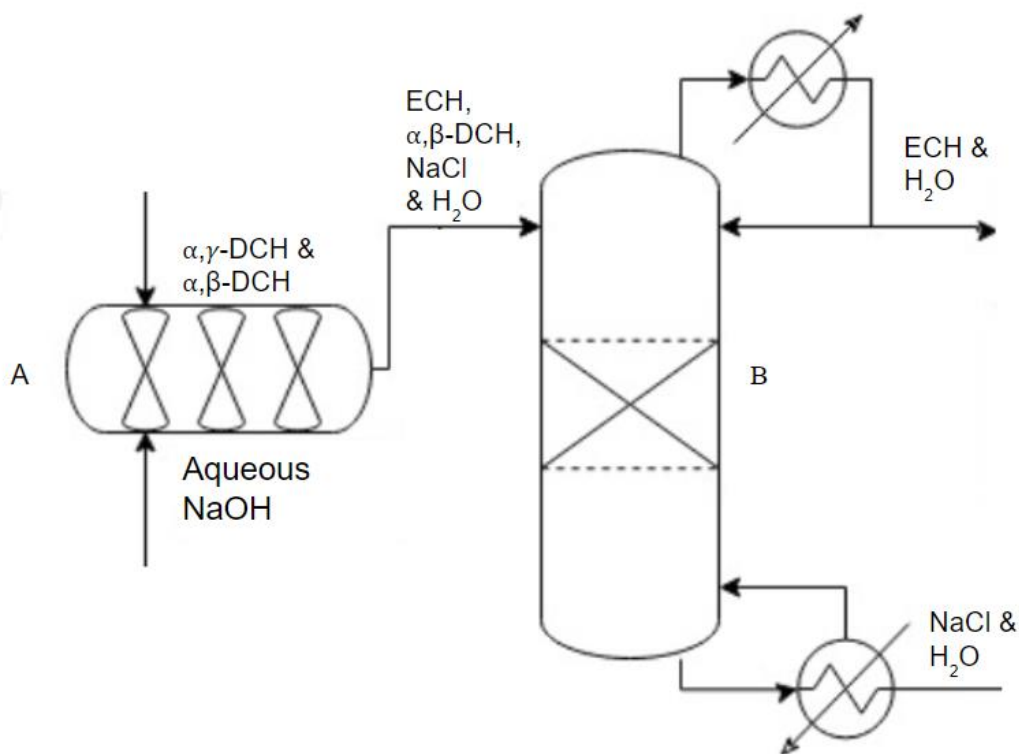


Figure 4.1.2: ECH Scheme PFD 1. α,γ -DCH & α,β -DCH along with aqueous sodium hydroxide is pumped into the mixing PFR (A). Output from this reactor is a mixture of ECH (produced from α,γ -DCH reacting quickly), α,β -DCH (that has yet to react), along with water and NaCl. This stream flows into the reactive distillation column (B) at a high feed stage to maximize reaction and stripping area. The distillate output from the column is a nearly azeotropic mixture of ECH and water. The bottoms output from the column is a waste water stream of NaCl and water, along with trace heavy organics.

With this preliminary PFR for the ECH scheme, near complete conversion to the final product is achieved. However, the purity requirement has not been met. There is still a large amount of water in the stream, along with the heavy hydrolysis products. The first attempt to hit purity requirements was done with a distillation column directly after the distillate output of the reactive distillation column. However, due to the azeotropic nature of the ECH water mixture that was utilized in separating in the reactive distillation column, achieving purity requirements through distillation alone was decided to be non feasible.

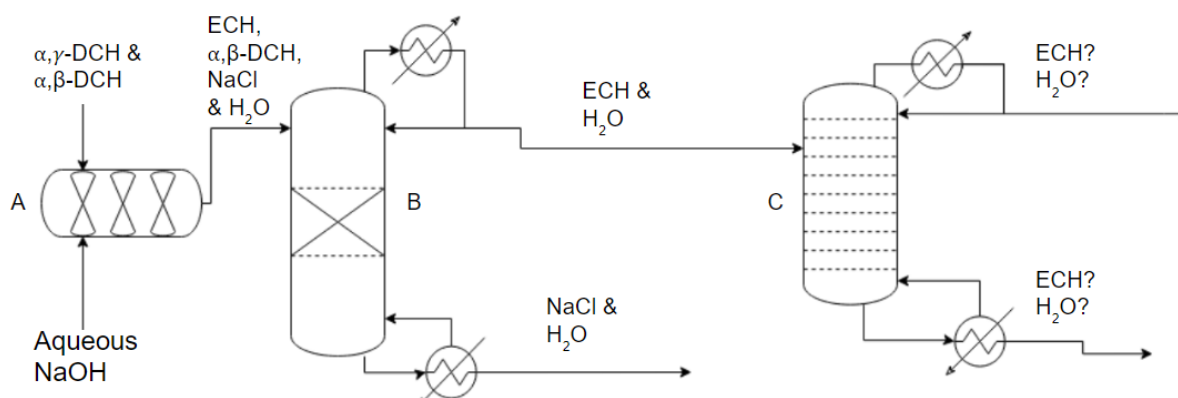


Figure 4.1.3: ECH Scheme PFD 2. Identical to the previous figure are the mixing PFR (A) and the reactive distillation column (B). Separation of ECH and water by distillation was problematic due to the azeotrope between the two components, necessitating another design.

Epichlorohydrin being an organic is only sparingly soluble in water, especially at lower temperatures. If the ECH and water mixture were to be cooled and undergo phase separation, this affords the opportunity to remove a vast majority of the water from the stream, effectively removing it from the azeotrope, greatly simplifying the purification process. Shown below in Figure (4.1.4) is the resulting process, which was used as the framework for designing the rest of the process.

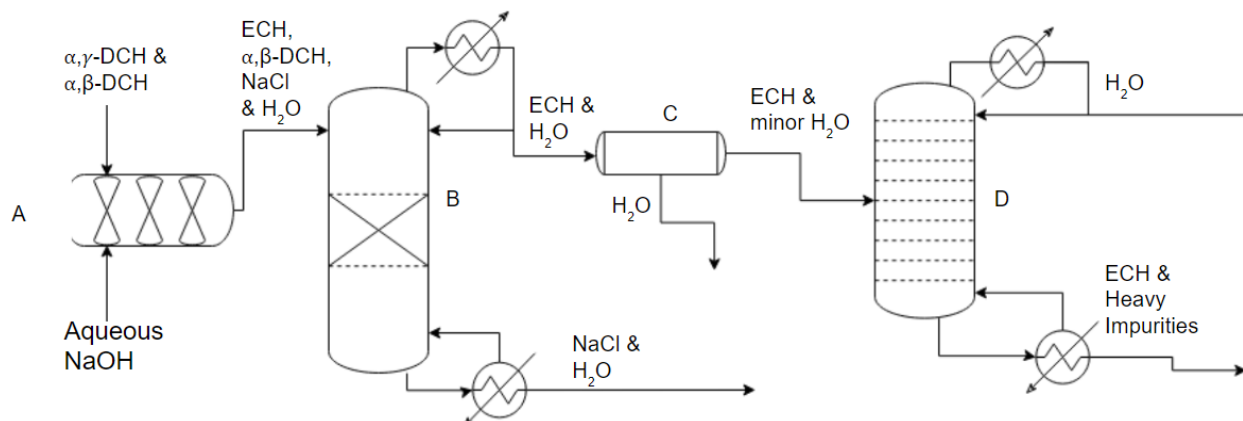


Figure 4.1.4: ECH Scheme PFD 3. The mixing PFR (A) is identical to the previous two figures. The reactive distillation column (B) has been modified using a decanter (C) on the distillate. This decanter will separate a majority of the water present in this stream, outputting a concentrated ECH stream with only minor water impurities, as well as a mixed aqueous stream. The organic decanter output is then set to a distillation column where the rest of the water will be removed, producing a bottoms stream nearly completely ECH with heavy organic impurities as well as a waste water distillate stream.

4.2 Dehydrochlorination Mixing PFR

Understanding the chemical reactions that were to take place to convert our DCH intermediate products into our final ECH product, we began to investigate reactor configurations that have been successful in the past. The most pertinent resource at the beginning of this investigation was patents filed by Dow Chemical researchers, which described the scheme of reactors that used a DCH-rich stream as a feed that was converted to ECH [P.1]. The patent and academic resources available, along with the advice of Dr. Hook, suggested that the reaction of α,γ -DCH with caustic soda happens near-instantaneously in practice, while α,β -DCH reacting with caustic soda happens about 300 times slower, but the ECH that results from both of these reactions can be easily hydrolyzed by water and hydroxide ions into unwanted side-products (Figure 1.2.3). To maximize ECH production while minimizing the production of side-products, ECH should not be allowed to interact with water or hydroxide ions. Fortunately, the purified DCH stream consisted mostly of DCH, water, and impurities, separated into two immiscible liquid phases where the aqueous phase contains most of the water in that stream, and both DCH isomers are contained in the organic phase. Research on the specific kinetics of this conversion from DCH to ECH showed that all the reactions, the reaction of interest and the undesired hydrolysis reactions occur in the aqueous solution when DCH is available. Because an aqueous stream containing sodium hydroxide must be added to the reactor, it was decided that the separated aqueous phase could be added to the new caustic soda aqueous stream to allow for a larger phase volume for reaction to occur. Researchers at Dow Chemical mentioned the potential use of different mixing equipment in a small plug flow reactor unit to react the fast-reacting α,γ -DCH with caustic soda followed by another unit where α,β -DCH is given more residence time over which it can react with caustic soda [P.1].

$$\frac{dC_{ECH}}{dt} = -r_h^{ECH} - r_{Cl}^{ECH} + r_{dh}^{DCH} \quad (4.2.1)$$

$$\frac{dC_{GL}}{dt} = -r_h^{GL} - r_{Cl}^{GL} + r_{dh}^{MCH} \quad (4.2.2)$$

$$\frac{dC_{DCH}}{dt} = r_h^{ECH} - r_{dh}^{MCH} \quad (4.2.3)$$

$$\frac{dC_{MCH}}{dt} = r_{Cl}^{GL} + r_h^{ECH} - r_{dh}^{MCH} \quad (4.2.4)$$

$$\frac{dC_{GLY}}{dt} = r_h^{GL} \quad (4.2.5)$$

$$\frac{dC_{H_2O}}{dt} = -r_h^{GL} - r_h^{ECH} + r_{dh}^{DCH} + r_{dh}^{MCH} - (k_{Cl,GL}^{neutral} \cdot C_{GL} + k_{Cl,ECH}^{neutral} \cdot C_{ECH}) \cdot C_{H_2O} C_{Cl} \quad (4.2.6)$$

$$r_h^{ECH} = (k_{h,ECH}^{base} C_{OH^-} + k_{h,ECH}^{neutral} + k_{h,ECH}^{acid} C_{H^+}) \cdot C_{ECH} C_{H_2O} \quad (4.2.7)$$

$$r_{Cl}^{ECH} = k_{Cl,ECH}^{neutral} C_{H_2O} C_{Cl^-} C_{ECH} + k_{h,ECH}^{acid} C_{H^+} C_{Cl^-} C_{ECH} \quad (4.2.8)$$

$$r_{dh}^{DCH} = k_{h,ECH}^{base} C_{OH^-} C_{DCH} \quad (4.2.9)$$

$$r_h^{GL} = (k_{h,GL}^{base} C_{OH^-} + k_{h,GL}^{neutral} + k_{h,GL}^{acid} C_{H^+}) \cdot C_{GL} C_{H_2O} \quad (4.2.10)$$

$$r_{Cl}^{GL} = k_{Cl,GL}^{neutral} C_{H_2O} C_{Cl^-} C_{GL} + k_{h,GL}^{acid} C_{H^+} C_{Cl^-} C_{GL} \quad (4.2.11)$$

$$r_{dh}^{MCH} = k_{dh,MCH}^{base} C_{OH^-} C_{MCH} \quad (4.2.12)$$

$$r_{dh}^{DCH} = C_{DCH} \quad (4.2.13)$$

$$k_{rxn,i}^{cond} = k_{m,rxn,i}^{cond} \exp\left(\frac{E_{cond,rxn,i}}{RT}\right) \quad (4.2.14)$$

Table 4.2.1: ECH Production Reaction Kinetic Parameters

Parameter	Value	Units	Notes
T	40	°C	The isothermal operation temperature of the reactor, all kinetic constants are calculated via the Arrhenius Equation (eq 4.2.14). Activation energies and pre-exponential factors from Tolli et. al. [1.2.2]
R	8.314	J/mol-K	Gas constant, used to calculate kinetic constants via the Arrhenius Equation (eq 4.2.14)
$k_{h,ECH}^{acid}$	6.23E-05	L ² /mol ² -s	Kinetic constant, ECH hydrolysis due to H ⁺
$E_{acid,h,ECH}$	7.5*10 ⁴	J/mol-K	Activation Energy, ECH hydrolysis due to H ⁺
$k_{m,h,ECH}^{acid}$	2.02*10 ⁸	L ² /mol ² -s	Pre-exponential factor, ECH hydrolysis due

			to H ⁺
$k_{h,ECH}^{neutral}$	1.94E-07	L ² /mol ² -s	Kinetic constant, ECH hydrolysis due to H ₂ O
$E_{neutral,h,ECH}$	4.9*10 ⁴	J/mol-K	Activation Energy, ECH hydrolysis due to H ₂ O
$k_{m,h,EC}^{neutral}$ _H	28.9	L ² /mol ² -s	Pre-exponential factor, ECH hydrolysis due to H ₂ O
$k_{h,ECH}^{base}$	1.10E-05	L ² /mol ² -s	Kinetic constant, ECH hydrolysis due to OH ⁻
$E_{base,h,ECH}$	8.8*10 ⁴	J/mol-K	Activation Energy, ECH hydrolysis due to OH ⁻
$k_{m,h,ECH}^{base}$	5.24*10 ⁹	L ² /mol ² -s	Pre-exponential factor, ECH hydrolysis due to OH ⁻
$k_{Cl,ECH}^{acid}$	1.37E-02	L/mol-s	Kinetic constant, ECH chlorination in acidic conditions
$E_{acid,Cl,ECH}$	6.7*10 ⁴	J/mol-K	Activation Energy, ECH chlorination in acidic conditions
$k_{m,Cl,ECH}^{acid}$	2.05*10 ⁹	L/mol-s	Pre-exponential factor, ECH chlorination in acidic conditions
$k_{Cl,ECH}^{neutral}$	4.87E-07	L ² /mol ² -s	Kinetic constant, ECH chlorination in neutral conditions
$E_{neutral,Cl,ECH}$	4.8*10 ⁴	J/mol-K	Activation Energy, ECH chlorination in neutral conditions
$k_{m,Cl,EC}^{neutral}$ _H	49.5	L ² /mol ² -s	Pre-exponential factor, ECH chlorination in neutral conditions
$k_{h,GL}^{base}$	1.06E-05	L ² /mol ² -s	Kinetic constant, glycidol hydrolysis due to H ⁺
$E_{base,h,GL}$	6.3*10 ⁴	J/mol-K	Activation Energy, glycidol hydrolysis due to H ⁺
$k_{m,h,GL}^{base}$	3.42*10 ⁵	L ² /mol ² -s	Pre-exponential factor, glycidol hydrolysis due to H ⁺
$k_{h,GL}^{neutral}$	3.98E-08	L ² /mol ² -s	Kinetic constant, glycidol hydrolysis due to

			H ₂ O
$E_{\text{neutral,h,GL}}$	6.5×10^4	J/mol-K	Activation Energy, glycidol hydrolysis due to H ₂ O
$k_{\text{m,h,GL}}^{\text{neutral}}$	2.77×10^3	L ² /mol ² -s	Pre-exponential factor, glycidol hydrolysis due to H ₂ O
$k_{\text{h,GL}}^{\text{acid}}$	1.44×10^0	L ² /mol ² -s	Kinetic constant, glycidol hydrolysis due to OH ⁻
$E_{\text{acid,h,GL}}$	6.6×10^4	J/mol-K	Activation Energy, glycidol hydrolysis due to OH ⁻
$k_{\text{m,h,GL}}^{\text{acid}}$	1.47×10^{11}	L ² /mol ² -s	Pre-exponential factor, glycidol chlorination in acidic conditions
$k_{\text{Cl,GL}}^{\text{acid}}$	5.00×10^{-2}	L/mol-s	Kinetic constant, glycidol chlorination in acidic conditions
$E_{\text{acid,Cl,GL}}$	5.7×10^4	J/mol-K	Activation Energy, glycidol chlorination in acidic conditions
$k_{\text{m,Cl,GL}}^{\text{acid}}$	1.61×10^8	L/mol-s	Pre-exponential factor, glycidol chlorination in acidic conditions
$k_{\text{Cl,GL}}^{\text{neutral}}$	5.64×10^{-9}	L ² /mol ² -s	Kinetic constant, glycidol chlorination in neutral conditions
$E_{\text{neutral,Cl,GL}}$	7.0×10^4	J/mol-K	Activation Energy, glycidol chlorination in neutral conditions
$k_{\text{m,Cl,GL}}^{\text{neutral}}$	2.68×10^3	L ² /mol ² -s	Pre-exponential factor, glycidol chlorination in neutral conditions
$k_{\text{dh,MCH}}^{\text{base}}$	1.06×10^{-1}	L/mol-s	Kinetic constant, MCH dehydrohalogenation in basic conditions
$E_{\text{base,dh,MCH}}$	1.2×10^5	J/mol-K	Activation Energy, MCH dehydrohalogenation in basic conditions
$k_{\text{m,dh,MCH}}^{\text{base}}$	1.10×10^{19}	L/mol-s	Pre-exponential factor, MCH dehydrohalogenation in basic conditions

Table 4.2.2: ECH Production Reaction Kinetic Variables

Variable	Units	Notes
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r_h^i	mol/L-sec	Rate of hydrolysis of component i
r_{Cl}^i	mol/L-sec	Rate of chlorination of component i
r_{dh}^i	mol/L-sec	Rate of dehydrohalogenation of component i
C_{ECH}	mol/L	Concentration of epichlorohydrin in the aqueous phase
C_{GL}	mol/L	Concentration of glycidol in the aqueous phase
C_{DCH}	mol/L	Concentration of dichlorohydrin in the aqueous phase
C_{MCH}	mol/L	Concentration of monochlorohydrin in the aqueous phase
C_{GLY}	mol/L	Concentration of glycerol in the aqueous phase
C_{H^+}	mol/L	Concentration of hydrogen ions in the aqueous phase
C_{H_2O}	mol/L	Concentration of water in the aqueous phase
C_{Cl^-}	mol/L	Concentration of chloride ions in the aqueous phase
$k_{rxn,i}^{cond}$	mol/L-s	Kinetic constant of the reaction whose subscript denotes the reaction (rxn) and component (i) and the superscript denotes the condition (cond); an “m” in the subscript denotes that variable as the pre-exponential factor in the Arrhenius Equation (eq 4.2.14)
$E_{rxn,i}^{cond}$	kJ/mol	Activation energy of the reaction whose subscript denotes the reaction (rxn) and component (i) and the superscript denotes the condition (cond)

Further research into turbulent liquid flow mass transfer, and the mixing operations that facilitate this, yielded that to minimize the residence time in a plug flow reactor (which would require maximized mass transfer rate of DCH from the organic to the aqueous phase for ECH conversion), impingement jet mixing and static mixing should be used in combination. Dow Chemical researchers Fan et. al reported that a constant power to mass ratio of 3 watts per kilogram yielded strong conversion of DCH to ECH in their lab-scale reaction apparatus [P.1]. Starting with an academic resource that Fan et. al cite as supplementary, research yielded a theoretical method of calculating mass transfer between the two phases due to impingement jet mixing [4.2.1]. The method used the aforementioned power to mass ratio to calculate the approximate surface area of organic phase droplets which would disperse into the aqueous phase using other parameters like reactor dimensions, viscosities, densities, and flow rates of the different phases. These parameters were used to model an inelastic collision between the organic and aqueous liquid streams from which the mass transfer results followed. A Fickian diffusion model was applied alongside the impingement jet mixing modeling method to mathematically model the mass transfer that would occur between the two phases.

$$\lambda = \left(\frac{v^3}{\epsilon}\right)^{1/4} \quad (4.2.15)$$

$$u_{aq} = \sqrt{\frac{2\epsilon(m_{org}+m_{aq})}{\frac{m_{aq}^2}{m_{org}}+m_{aq}}} \quad (4.2.16)$$

$$u_{org} = \frac{m_{aq}u_{aq}}{m_{org}} \quad (4.2.17)$$

$$d_{jet,aq} = 2\sqrt{\frac{\dot{V}_{aq}}{u_{aq}\pi}} \quad (4.2.18)$$

$$V_{col} = L_{col}A_c = d_{jet,aq}^3 \quad (4.2.19)$$

$$L_{jet} = 3d_{jet,aq} \quad (4.2.20)$$

$$t_m = \frac{L_{col}}{u_{film}} = \frac{L_{col}}{0.3u_{aq}} \quad (4.2.21)$$

$$n_{drop} = \frac{\dot{V}_{org}}{V_{drop}} \quad (4.2.22)$$

$$A_{MT} = n_{drop}A_{drop} = n_{drop}\left(4\pi\left(\frac{d_{drop}}{2}\right)^2\right) \quad (4.2.23)$$

$$J_{DCH,col} = D_{DCH}\left(\frac{C_{DCH,org}-C_{DCH,aq}}{\lambda}\right) \quad (4.2.24)$$

$$N_{DCH,col} = J_{DCH,col}A_{MT}t_m \quad (4.2.25)$$

$$u_{film} = 0.3u_{aq} \quad (4.2.26)$$

Notably, the mode of mass transfer for this MATLAB model in both the collision and static mixing regimes was assumed to be Fickian diffusion, where the concentration gradient acts as a driving force of mass transfer flux through an area. In the collision regime, the characteristic length over which the chemical species must diffuse was the Kolmogorov length (Equation 4.2.24), which represents the smallest eddy dimension in turbulent flow regimes [4.2.1] (clearly the impingement jets cause turbulence in the collision regime). In the static mixing regime where fluid flow is assumed to be more laminar, the characteristic length that chemical species must diffuse over was determined to be the radius of the droplets. This was the application of the assumption that these droplets could be treated as pockets of fluid where all the diffusing particles exist as point sources in the center of the droplet. In both the static mixing and collision regimes, molar flows of species in the aqueous and organic phases were affected by mass transfer, in order for the original inlet flow to be adjusted to reflect the species added to that particular phase, the molar Fickian flux of species was multiplied by the area over which mass transfer occurred (the surface area of the droplets) and by the residence time (Equations 4.2.25 and 4.2.28. In the case of the collision regime, the residence time was defined as t_m , which was the time that micromixing was needed to occur, while in the static mixing regime, the molar mass transfer was iterated upon per second, so t_{it} was only one second in every iteration (Equation 4.2.27).

$$J_{i,stat} = D_i \frac{\Delta C_i}{0.5d_{drop}} \quad (4.2.27)$$

$$N_{i,stat} = J_{i,stat} A_{MT} t_{it} \quad (4.2.28)$$

Table 4.2.3: Micromixing Mass Transfer Parameters

Variable	Value	Units	Notes
λ	$5.91 \cdot 10^{-5}$	m	Kolmogorov length, the theoretical smallest dimension of an eddy in turbulent flow.
ν	$3.32 \cdot 10^{-6}$	m ² /s	Kinematic viscosity of liquid film, calculated by averaging kinematic viscosity of all species present based on mole fraction.
ϵ	0.3	W/kg	Power dissipated per mass, a measure of the power input into a mixing system.
u_{aq}	2.25	m/s	Superficial velocity of the aqueous stream out of the impinging jet.
u_{film}	0.675	m/s	Superficial velocity of liquid film after impingement jet mixing inelastic collision.
m_{aq}	4.53	kg/s	Mass flow rate of the aqueous stream.
m_{org}	3.82	kg/s	Mass flow rate of the organic stream.
$d_{jet,aq}$	0.0506	m	Diameter of aqueous stream impingement jet.
$\dot{V}_{aq}$	0.2716	m ³ /min	Volumetric flow rate of aqueous stream.
$\dot{V}_{org}$	0.1925	m ³ /min	Volumetric flow rate of organic stream.
V_{col}	$1.30 \cdot 10^{-4}$	m ³	Volume of the collision regime of the PFR.
L_{col}	$1.99 \cdot 10^{-4}$	m	Length of the collision regime of the PFR.
A_c	0.6521	m ²	Cross-sectional area of the PFR.
L_{jet}	0.1519	m	Length of impingement jet, equal for both the aqueous and organic jets.
t_m	6.51	s	Time required for micromixing to occur.
n_{drop}	$5.45 \cdot 10^8$	number (of drops)	Number of organic phase droplets formed in the collision regime of the PFR.
V_{drop}	$5.88 \cdot 10^{-12}$	m ³	Volume of a single organic phase droplet.

A_{drop}	1.58×10^{-7}	m^2	Surface Area of a single organic phase droplet.
d_{drop}	200×10^{-6}	m	Diameter of a single organic phase droplet.
A_{MT}	85.9	m^2	Area over which mass transfer occurs, the plane through which particles travel, which is equal to the total surface area of the droplets.
D_{DCH}	4.8×10^{-9}	m^2/s	Diffusivity coefficient of DCH in the aqueous phase, which was assumed to be equal to the diffusivity coefficient of ethanol in water [4.2.2].
$J_{\text{DCH,col}}$	0.282	$\text{mol}/\text{m}^2\text{-s}$	Molar flux of DCH from the organic phase droplets to the continuous aqueous phase in the collision regime of the PFR.
$C_{\text{DCH,org}}$	3.47×10^3	mol/m^3	Concentration of DCH in the organic phase droplets (in the collision regime of the PFR).
$C_{\text{DCH,aq}}$	0	mol/m^3	Concentration of DCH in the continuous aqueous phase (in the collision regime of the PFR).
$N_{\text{DCH,col}}$	157.8	mol	Moles of DCH that transferred from the organic phase droplets to the continuous aqueous phase in the collision regime of the PFR.
t_{it}	1	s	Time step per iteration of MATLAB coded solution.

Table 4.2.4: Micromixing Mass Transfer Variables

Variable	Units	Notes
$J_{i,\text{stat}}$	$\text{mol}/\text{m}^2\text{-s}$	Molar flux of species i from organic phase droplets to the continuous aqueous phase in the static mixing regime of the PFR, DCH, ECH, and α -MCH were considered to undergo mass transfer.
D_i	m^2/s	Diffusivity coefficient of species i in the continuous aqueous phase, it was assumed that DCH, ECH, and α -MCH all had diffusivity coefficients equal to ethanol diffusing in water [4.2.2].
ΔC_i	mol/m^3	Concentration difference of species i between the organic phase droplets and continuous aqueous phase, positive values indicate a higher concentration in the organic phase droplets (in the static mixing regime of the PFR).

$N_{i,stat}$	mol	Moles of species i transferred from the organic phase droplets to the continuous aqueous phase.
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To model and size this mixing plug flow reactor, a MATLAB coded solution was used to iteratively solve multiple ordinary differential equations simultaneously which described the change in composition of the reacting fluid (in mass flow rates) as that fluid traveled down the length of the plug flow reactor (see Figure 4.2.2 and 4.2.3). Given the intricacies of the mass transfer and the limited reaction kinetics information available, assumptions about the behavior in this reactor were made. It was assumed that there would be a region of the reactor (the collision regime) where impingement mixing and mass transfer occurs, but no chemical reaction, and a region where static mixing, mass transfer, and reaction all occur (see Figure 4.2.1). No chemical reaction was assumed to occur in the collision regime because the species would flow into the other regime too quickly to allow reaction. Another assumption was that the collision regime volume was equal to the diameter of the aqueous jet raised to the third power, which was consistent with literature calculations [4.2.1].

It was also assumed that the reaction of α,γ -DCH with hydroxide ion to produce ECH happened instantly, as this reaction would only be limited by the mass transfer of α,γ -DCH from the organic phase to the reacting aqueous phase. However, other kinetics, which described the hydrolysis reactions of ECH (Equations 4.2.7 and 4.2.8), were mathematically described by an academic group of researchers [4.1.2]. The reaction of α,β -DCH was neglected in this reactor because the mixing plug flow reactor must be quite small, with a very low residence time. It was later discovered that the low concentration of α,β -DCH in the organic phase was not a significant enough driving force for appreciable amounts of α,β -DCH to reach to the aqueous phase where reaction occurred. The assumption was also made that fluid flow was ideal, so that fluid velocity in the reactor was constant.

In the static mixing regime, it was assumed that the usage of a static mixer would disallow for droplets to coalesce or break, so the interfacial surface area between the organic and aqueous phases was constant there. Also, in order to determine the PFR diameter, clearly the impinging jets must not touch, but because they protrude into the reactor from either side, it was assumed that the jet lengths multiplied by an arbitrary factor of six would be sufficient. The impinging jets used experimentally by researchers Mahajan and Kirwan [4.2.1] had a length to diameter ratio of three, so this was adopted in the MATLAB model (Equation 4.2.20). The MATLAB file coded solution iterated species material balances over the coordinate of plug flow reactor length (which is directly proportional to residence time when fluid velocity is fixed, which it was assumed to be) and took into account the mass transfer between phases of ECH and α,γ -DCH, as well as the aforementioned reaction kinetics. Researchers Mahajan and Kirwan [4.2.1] noted that 30% of the aqueous jet velocity was equal to the total fluid film velocity after impingement, due to the inelastic collision that took place (Equation 4.2.26). The diffusivities of pertinent species were assumed to be the same, and lacking species specific information, it was assumed that their diffusivities would be equal to the diffusivity of ethanol in water, which is a well-researched parameter [4.2.2]. The formed droplet diameters were most desirably at a maximum size of 200 microns [P.1] or smaller, which was achieved using a power to mass ratio of 0.3 watts per kilogram, so it was assumed that this was the size of droplets formed in the collision regime. It was also assumed that as the droplets of organic phase dispersed in aqueous

phase would not coalesce or break in the static mixing regime (constant droplet surface area) due to the presence of a helical static mixer which would impart some uniform power to mass as the fluid film flows past it.

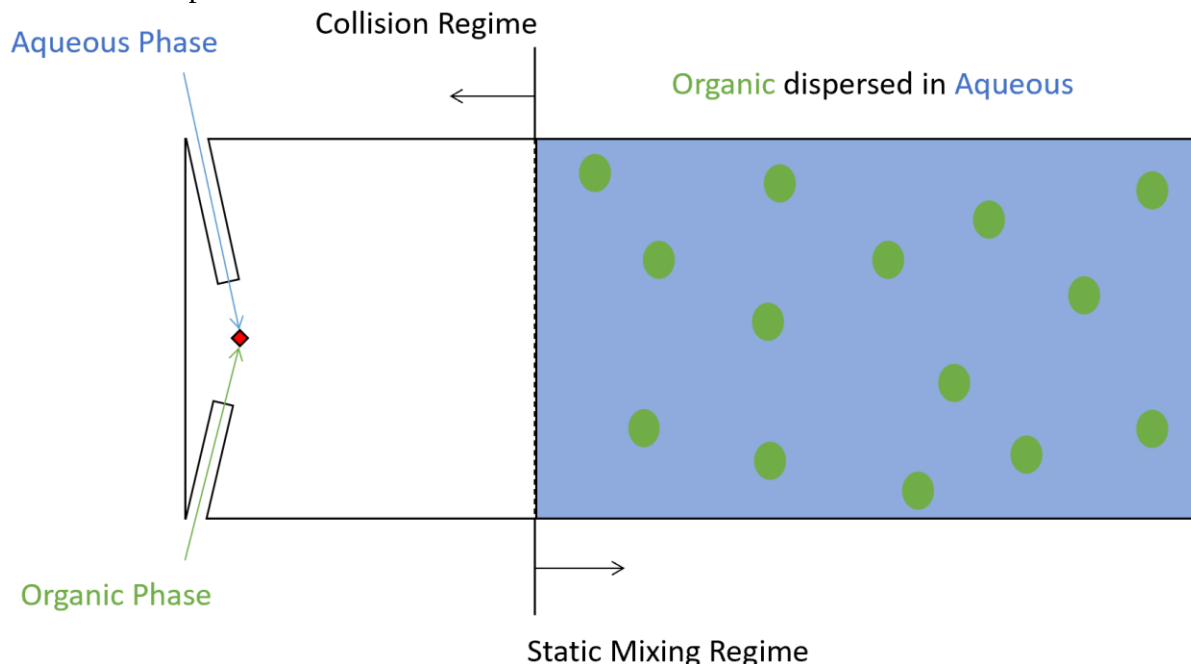


Figure 4.2.1: Dehydrochlorination Mixing PFR Diagram. On the left, in the collision regime of the PFR, impingement jets set at an 100 degree angle of collision shoot both organic and aqueous phases together where they experience an inelastic collision so that droplets of the organic phase become dispersed in the aqueous phase via micromixing. Droplet formation occurs in the collision regime and these droplets persist in the static mixing regime with the implementation of a helical static mixer.

Comparison of MATLAB coded simulation results with an Aspen Plus simulation of only the mixing plug flow reactor, with both simulations using the same feed, kinetic, and operating conditions, showed similar behavior. Initially, results showed that most ECH that formed immediately hydrolyzed, however careful incremented decrease of the operating temperature yielded results consistent with the experimental results of Dow Chemical patents as well as the cumulative and mixing PFR specific Aspen Plus simulations. Another key consideration was the mass transfer of ECH from the aqueous to the organic phase, which was driven by concentration gradient and minimized contact time between a large amount of ECH and its hydrolysis agents in the aqueous phase. The Aspen Plus simulation was used as a check for the behavior observed in the MATLAB coded model of the mixing PFR, but because the behaviors in both were very similar when the same feed rates were applied, no adjustments to the MATLAB solution were made based on Aspen Plus results.

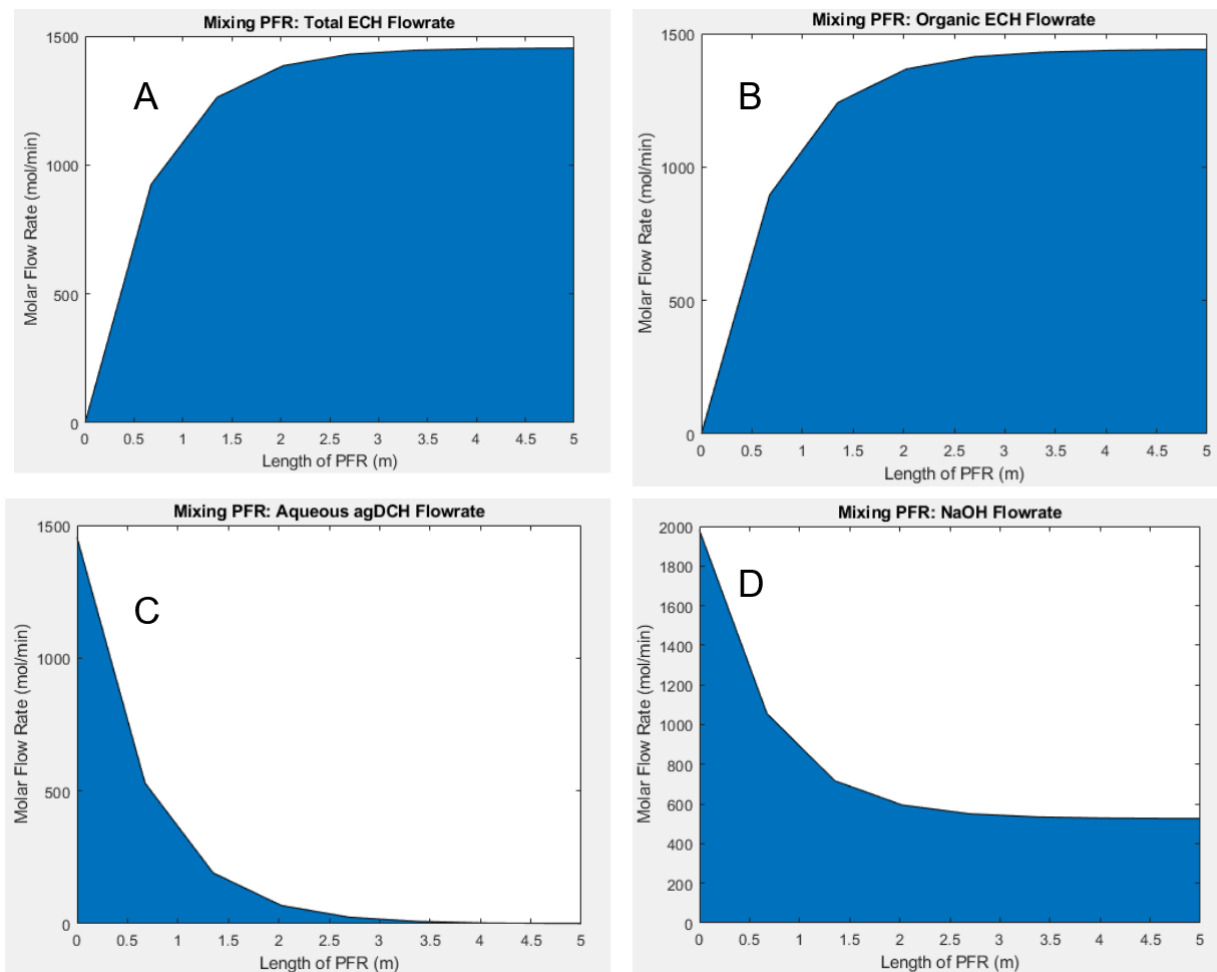


Figure 4.2.2: Mixing PFR MATLAB Coded Simulation Reactant and Product Mass Flow Rates. (A) describes the sum of the molar flow rates of ECH in both the organic and aqueous phases as the fluid travels along the length of the mixing PFR. (B) describes the molar flow rate of ECH only in the organic phase as the fluid travels along the length of the mixing PFR. (C) describes the molar flow rate of α,γ -DCH in the aqueous phase as the fluid travels along the length of the mixing PFR. (D) describes the molar flow of caustic soda in the aqueous phase as the fluid travels along the length of the mixing PFR.

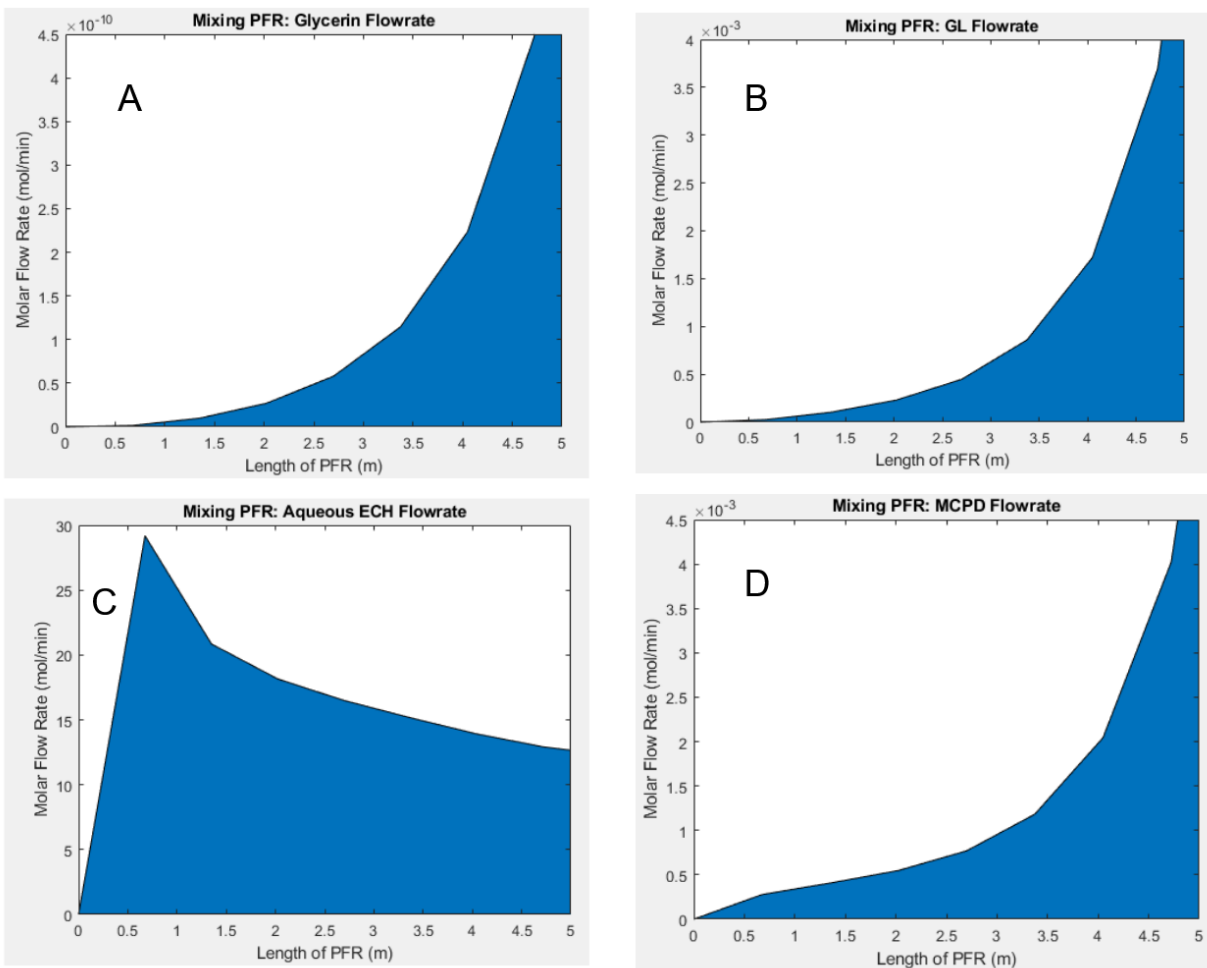


Figure 4.2.3: Mixing PFR MATLAB Coded Simulation Hydrolysis Side Product Mass Flow Rates. (A) describes the molar flow rate of the final hydrolysis product (no further hydrolysis can be done) glycerol as the fluid travels along the length of the mixing PFR. (B) describes the molar flow rate of the secondary hydrolysis product glycidol as the fluid travels along the length of the mixing PFR. (C) describes the molar flow rate of ECH in the aqueous phase, where it can be hydrolyzed as the fluid travels along the length of the mixing PFR.

While the final cumulative simulation of this process used larger inputs of reactants into the mixing PFR, and was accomplished in a much smaller unit, the behavior visible in Figures 4.2.5 and 4.2.6, is consistent with the behavior in figure 4.2.7. In both the Aspen Plus simulation and the coded MATLAB simulation, the amount of α,γ -DCH diminishes sharply over the length of the reaction unit, and ECH forms without much hydrolysis which would turn ECH into MCH (called MCPD in Figure 4.2.6D), which would hydrolyze in two further steps which would yield glycidol (called GL in Figure 4.2.6B), respectively. Notably, the MATLAB and Aspen Plus simulations differ greatly in considerations, because the Aspen Plus simulation does not account for the mass transfer of species between the two liquid phases, or for the fact that reaction only takes place in the aqueous phase, however the input kinetics were the same in both simulations. Researchers Fan et. al [P.1] and Dr. Hook both described the reaction occurring in this mixing PFR as mass transfer limited, which is the cause of the size discrepancy between the two

simulations, if mass transfer from the organic to the aqueous phase in the MATLAB simulation were allowed to increase, then full conversion of the α,γ -DCH could be achieved in a much shorter residence time, and therefore a shorter length of PFR. With this understanding, the mixing PFR was sized according to the smaller size in the Aspen Plus simulation, because researchers Fan et. al reached high α,γ -DCH conversion in a lab-scale PFR only millimeters in length, and the mass transfer rate in the MATLAB simulation were most likely underestimations due to the assumption that mass transfer would occur via Fickian Diffusion. The mixing PFR was priced as a double-pipe heat exchanger unit of stainless steel construction. The relevant coordinate to price such a unit was surface area, but the surface area of the designed mixing PFR was lower than the minimum required for the specific pricing equation, so the minimum **surface area value of 0.1 squared meters** was used (the surface area of the Aspen Plus simulated mixing PFR was 0.057 squared meters). The dimensions of the mixing PFR used for the purpose of pricing was **0.184553 meters in diameter and 0.000615177 meters in length** (see figure 4.2.4B). This unit must be constructed with nickel alloy because of base corrosion considerations. Stainless steel is semi-resistant to base corrosion, but with the scale of caustic soda that would flow through the mixing PFR year over year, it would be advantageous to use nickel alloy which is more resistant to base corrosion so that this unit would not need to be replaced over the lifetime of the plant.

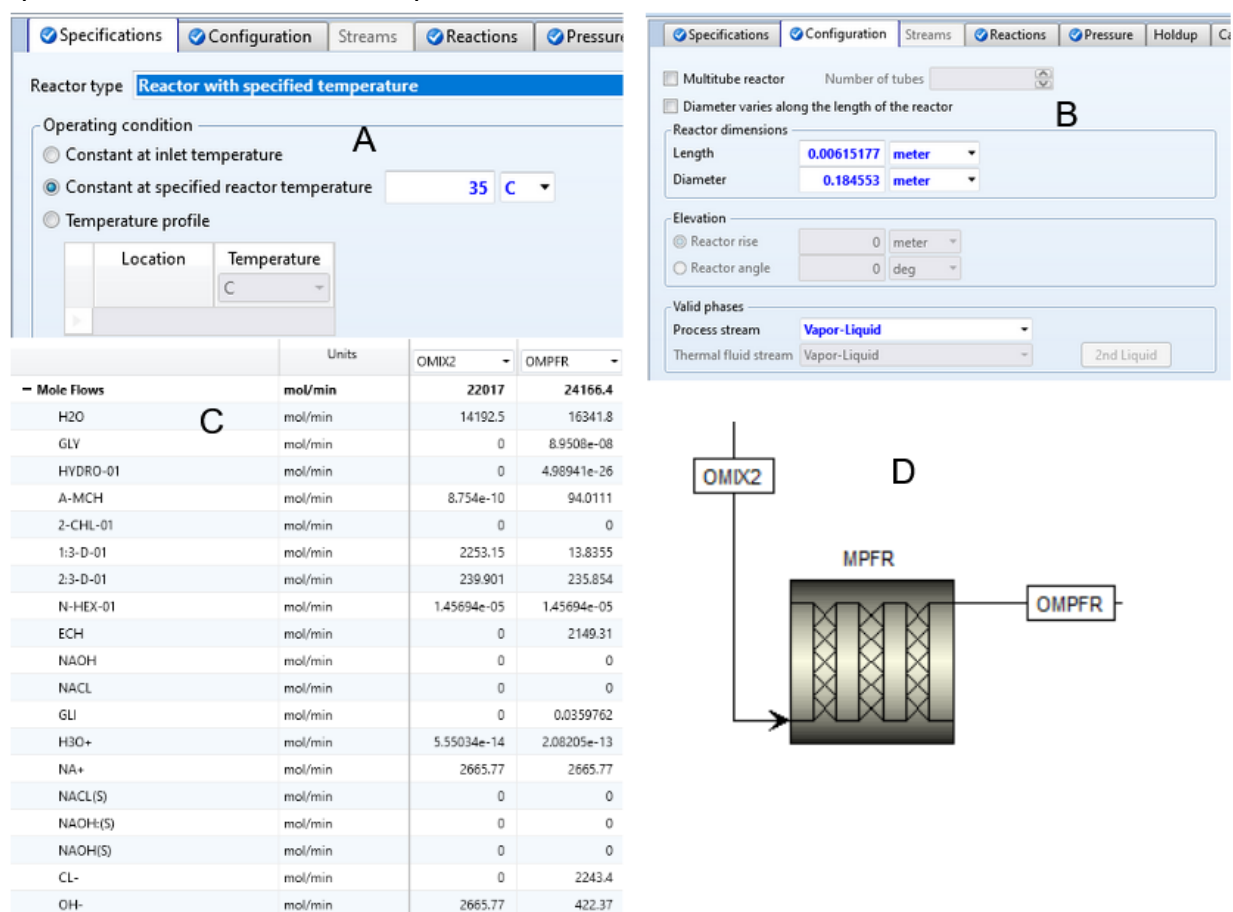


Figure 4.2.4: Dehydrochlorination Mixing PFR Aspen Plus Simulation Parameters and Results. (A) shows the input specifications applied to the mixing PFR Aspen Plus simulation, which was operated at a pressure of 5 bar. (B) shows the final selected size that was determined by

decreasing the dimensions until the whole kinetic behavior was shown in the composition environment (figure 4.2.5). (C) shows the molar flow rates of each component and the cumulative streams that resulted from the mixing PFR Aspen simulation. (D) shows that OMIX2 is the inlet stream of the mixing PFR and OMPFR is the outlet stream of the mixing PFR.

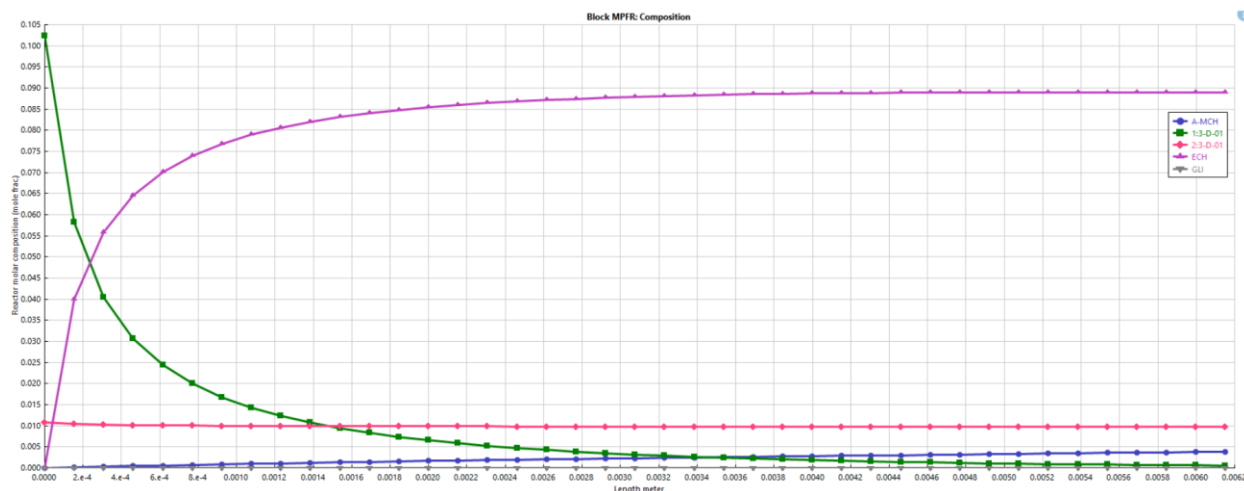


Figure 4.2.5: Dehydrochlorination Mixing PFR Aspen Plus Simulation of Species Mass Flow Rates. This figure describes the change in composition of the fluid stream due to reaction as the fluid travels down the length of the PFR. ECH is produced by consuming α,γ -DCH at the very inlet of the mixing PFR.

Notably, in the piping that follows the mixing PFR, reaction would still be occurring as the fluid is brought to the next unit operation, the reactive distillation column. Therefore, it is pertinent that the piping between the two units be minimized so that the amount of ECH product that is lost to hydrolysis is also minimized, because the transport delay between the two units is essentially extra residence time for reaction in a plug flow reactor.

4.3 Reactive Distillation Column (RDC)

The output stream from the mixing PFR contained ECH formed from α,γ -DCH, as well as the less reactive α,β -DCH. α,β -DCH only accounts for a small amount of potential product (<5%), however due to the large scale of production, it is necessary to ensure conversion of α,β -DCH in order to hit the assigned battery limit. In order to ensure conversion of α,β -DCH as seen in Figure (1.2.2) while avoiding the hydrolysis of the formed ECH (Figure 1.2.3), a reactive distillation column (RDC) was chosen for use in this scenario, as recommended by Dr. Hook. A reactive column allowed for the reaction of remaining α,β -DCH, while minimizing the potential hydrolysis of formed ECH. Fed into the column at the top, RDC contacts remaining caustic soda solution with the slower reacting α,β -DCH flowing down the column, while continually separating ECH formed from the flowing up the column.

To the advantage of this process, ECH and water experience an azeotrope that boils at a significantly lower temperature than the other reactants. This allowed for separation of heavy byproducts from the ECH and produced a distillate of majority ECH and water, suitable for being sent downstream. Additionally, the distillate stream should be exceptionally free of base,

greatly lowering risk of product hydrolysis. Shown below in Figure (4.3.1) is a phase diagram for the epichlorohydrin and water on a mass basis, produced by Aspen Plus

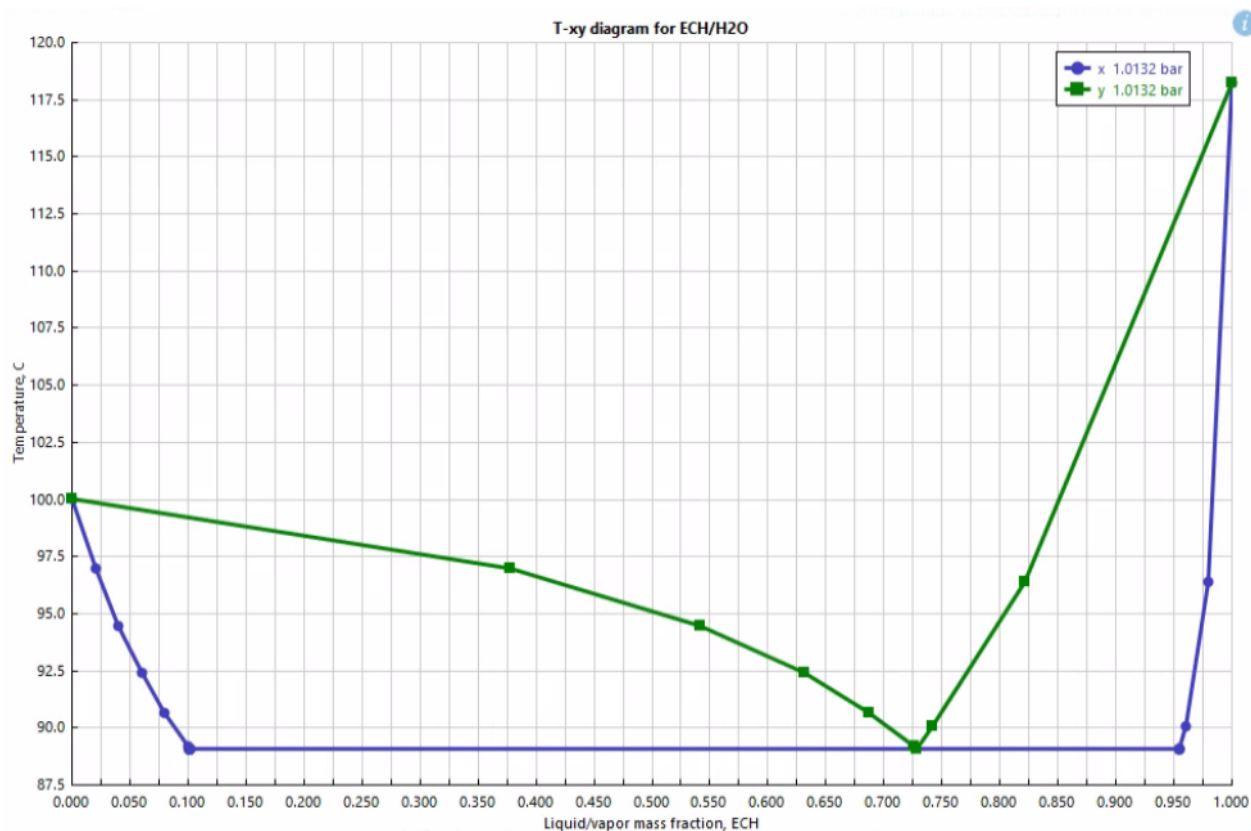


Figure 4.3.1: Water and epichlorohydrin phase diagram, including azeotrope at 74wt% ECH.

Exiting the bottoms of the column is a mixed waste water stream, containing the hydrolysis products and other heavy impurities, saturated with NaCl from the dehydrohalogenation reaction to form ECH. The RDC is also fed with a recycle from the downstream decanter. This recycled stream is chiefly water and ECH and is fed at the same stage as the mixing PFR product stream, allowing for additional separation of the stream without necessitating another piece of equipment.

Researchers at Dow Chemical [P.4] were able to achieve up to a **97% yield** of ECH from fed glycerol, utilizing a counter-current stream of steam to: (1) strip fed and formed ECH from the liquid phase, and (2) maintain a pH as close as possible to neutral to minimize hydrolysis. Differing from the aforementioned patent, the feed to the RDC contained considerably more water. This alleviates the need for counter current stripping steam input into the column. Initial specifications of temperatures, pressures, and internals for the RDC were sourced from Dow Chemical [P.4], with further modeling and studying of the unit within Aspen Plus. Shown below in Table (4.3.1) is a comparison of specifications between Fan et. al [P.4], and the RDC model from Aspen, which achieved an ECH **recovery in the distillate of 97.5%**

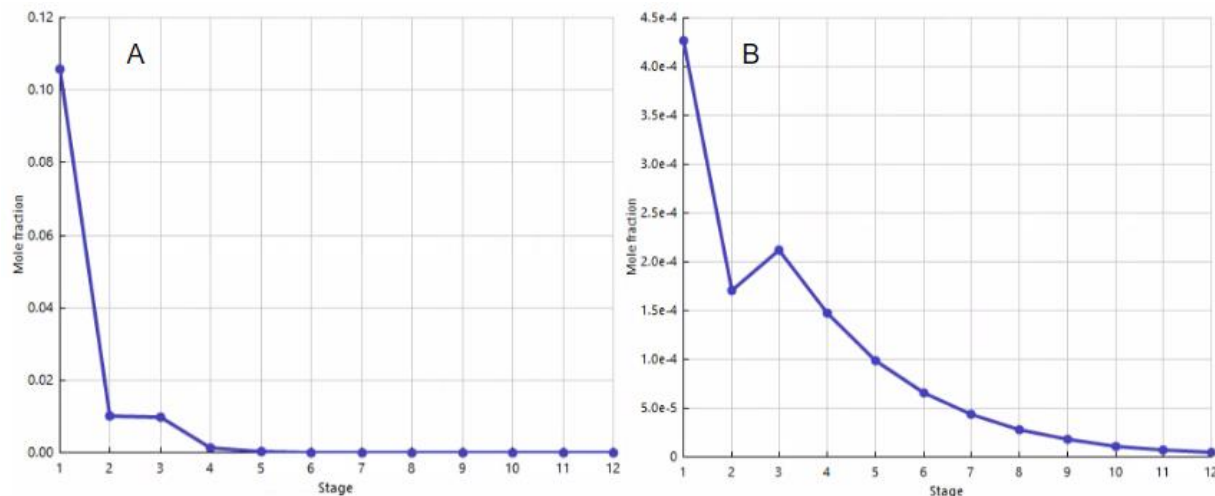


Figure 4.3.2: Concentration profiles along RDC of (A) Epichlorohydrin, (B) α,β -DCH. As shown, below stage 4, ECH concentration becomes negligible. ECH concentration increases nearly 10 times from the feed to the distillate. Very little ECH moves down the column available for hydrolysis.

Table 4.3.1: Reactive Distillation Column Specifications

Parameter	Value	Units
Column Operating Pressure	4.0	Bar
Reboiler Temperature	158.9	°C
Condenser Temperature	129.6	°C
Number of Equilibrium Stages	12	Unitless
Feed Stage	3	Unitless
Reflux Ratio	0.4	Unitless
Boilup Ratio	0.6	Unitless

In Aspen Plus, a RadFrac unit was used to simulate the reactive distillation column using the UNIQUAC fluids package. Compared to Fan et. al. [P.4] with a stated operating temperature of 110°C or less, the RDC operates at up to 160°C. This was necessary due to the high activation energy required for conversion of α,β -DCH to ECH. As a result, the reboiler and condenser must be run at higher pressure to maintain a liquid output at the elevated temperatures. The number of stages was optimized around getting a maximum flow rate of ECH out of the distillate, having

kept the inputs constant. Lowering the number of stages decreased hydrolysis potential, but provided a worse separation of ECH. Increasing the number of stages gave a more effective separation throughout the entire column, but decreased the total flow rate of ECH in the distillate. The maximum ECH distillate flow rate was found at **12 stages** fed on stage 3, compared to the patent given [P.4] specifications of 8 total stages with a feed at stage 2.

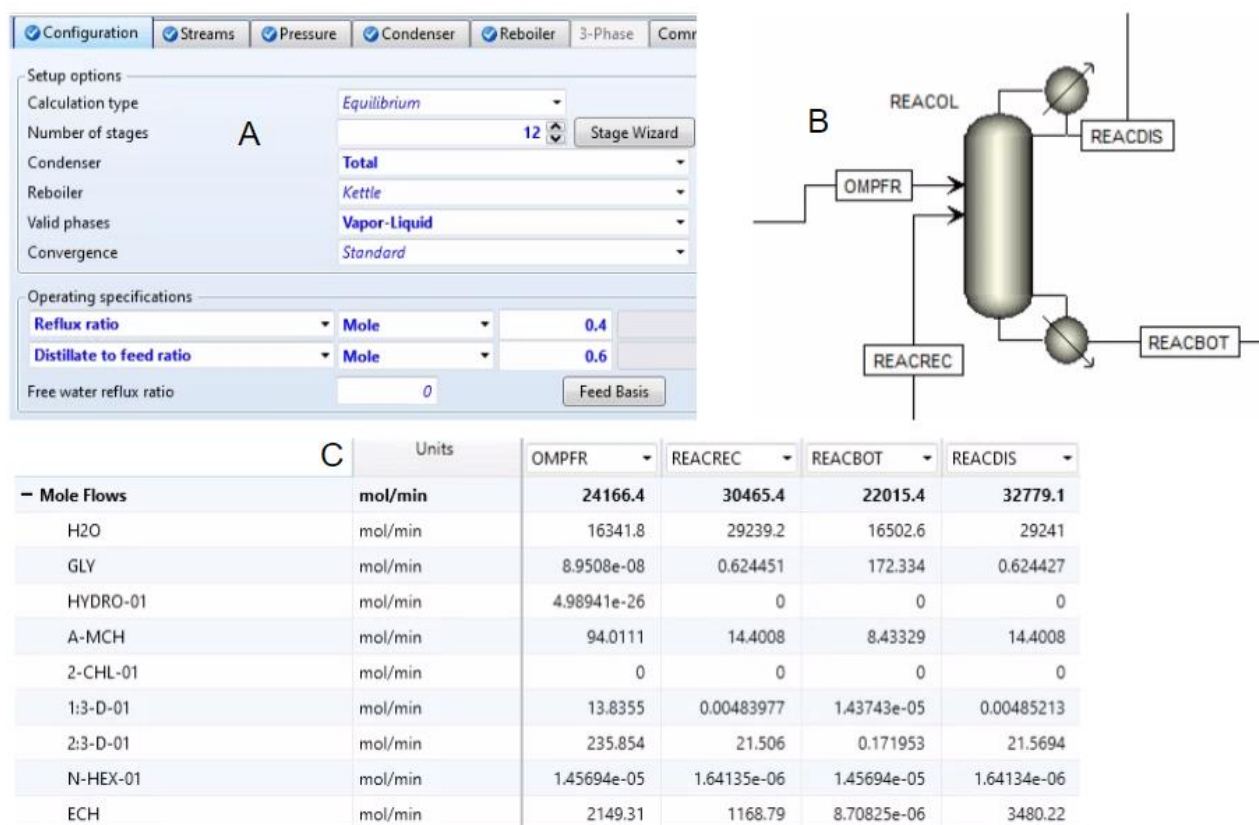


Figure 4.3.3: ASPEN Plus Reactive Distillation Column (A) Configuration, (B) Schematic design, (C) Stream results. Full Aspen stream notation available in Table 6.2.1.

Equipment cost and sizing for the reactive distillation column was done via the Cost Formulas spreadsheet provided by Dr. Weimer. The corrosive sodium hydroxide feed necessitated two material design choices. The column was determined to use packing instead of trays due to the corrosive potential of the sodium hydroxide feed. Within Aspen Plus, column internals can be specified, porcelain was chosen as a material due to its relatively low cost and alkaline chemical resistance. Additionally, nickel alloy is used in the construction of the column, providing enhanced long term resistance to the alkaline conditions compared to a stainless or carbon steel. As previously determined, 12 stages were to be used for the column. Using a standard value of HETP of 0.3048 m, a total column height was calculated to **3.657 m**. Specifying a standard height to diameter ratio of the trays of 1.8, a column diameter of **0.3048 m** was calculated. Material and sizing results are shown below.

Table 4.3.2: Reactive Distillation Column Sizing and Materials

Parameter	Value	Units
Column Height	3.65	m
Column Diameter	0.457	m
HETP	0.3048	m
Number of Equilibrium Stages	12	Unitless
Maximum Pressure Rating	1035	kPa
Packing Material	Porcelain	Unitless
Construction Material	Nickel Alloy	Unitless

4.4 1st Purification Column

Flowing to the next stage of the process is a stream that is sufficiently concentrated in epichlorohydrin, but still containing a substantial amount of water, along with contamination from hydrolysis products. Still needing to increase the purity to the level specified by Dow Chemical of 99.97% (mass basis), another purification column is used. The goal of this column was to remove the water and more volatile impurities from the ECH. Modeling and simulation of this unit was done in Aspen Plus, utilizing a shortcut column for initial specifications, followed by a full simulation using a RadFrac unit with the UNIQUAC fluids package. To reduce the bottoms composition to less than 0.1% water, a 99.7% recovery of water in the distillate is specified. Using the Winn Method, Aspen estimated the minimum number of stages to be 5. The number of stages was adjusted and its effect on the recovery of ECH in the bottoms, as well as impurity concentration was tracked. It was determined that increasing the number of stages to 9 gave the largest increase in ECH recovery, and increasing stages anymore lead to much smaller yield increases. Additionally, the shortcut column used the Gilliland correlation to calculate the required reflux ratio for 9 stages, in this case about 1.55.

Table 4.4.1: 1st Purification Column Specifications

Parameter	Value	Units
Column Operating Pressure	4.5	Bar

Reboiler Temperature	148.3	°C
Condenser Temperature	175.4	°C
Number of Equilibrium Stages	9	Unitless
Feed Stage	1	Unitless
Reflux Ratio	2.0	Unitless
Bottoms to Feed Ratio	0.65	Unitless

Having used the specifications of the shortcut column as a starting point, a RadFrac unit was put in its place for the full simulation. The number of stages and reflux ratio were again inputs, with an additional input chosen as bottoms to feed ratio. The reflux ratio was adjusted to 2.0 up from 1.55. This was found to decrease the total flow rate of distillate from the column, a stream that still contained considerable amounts of ECH. In order to find the optimal bottoms to feed ratio, the parameter was adjusted by 0.05 and the effect on the ECH bottoms concentration was observed. It was determined to get the best separation and retain as much ECH as possible, a bottoms to feed ratio of 0.65 is ideal. The full column was able to reach a **76.8% recovery** of ECH in the bottoms. However ECH in the distillate is not lost to waste, and is instead returned to the reactive distillation column for further separation.

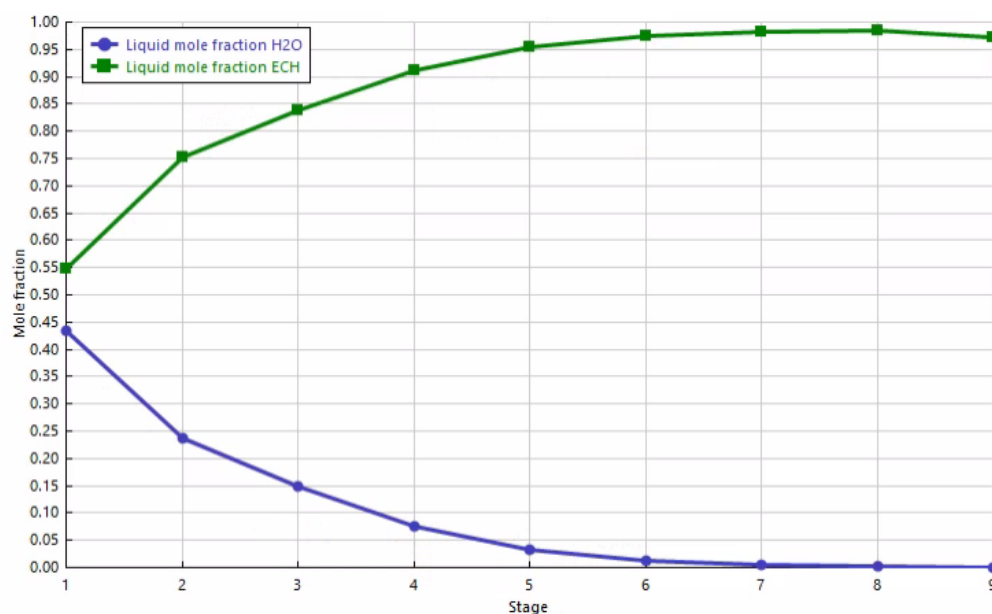


Figure 4.4.1: Epichlorohydrin (green) and water (blue) concentration profiles along the column.

Fed on stage 1, the concentration of water decreases substantially with each stage until stage 6, with the remaining three stages decreasing in water content much less until it is below 0.1%. Epichlorohydrin concentration reaches a maximum at stage 8, the last stage above the bottoms and reboiler of the column. The reason for this is likely due to the concentration of heavy byproducts in the liquid phase in the lower stages of the column. Running at an elevated pressure and below the boiling temperature of these compounds results in a majority of these compounds ending up in the bottoms outlet of this column.

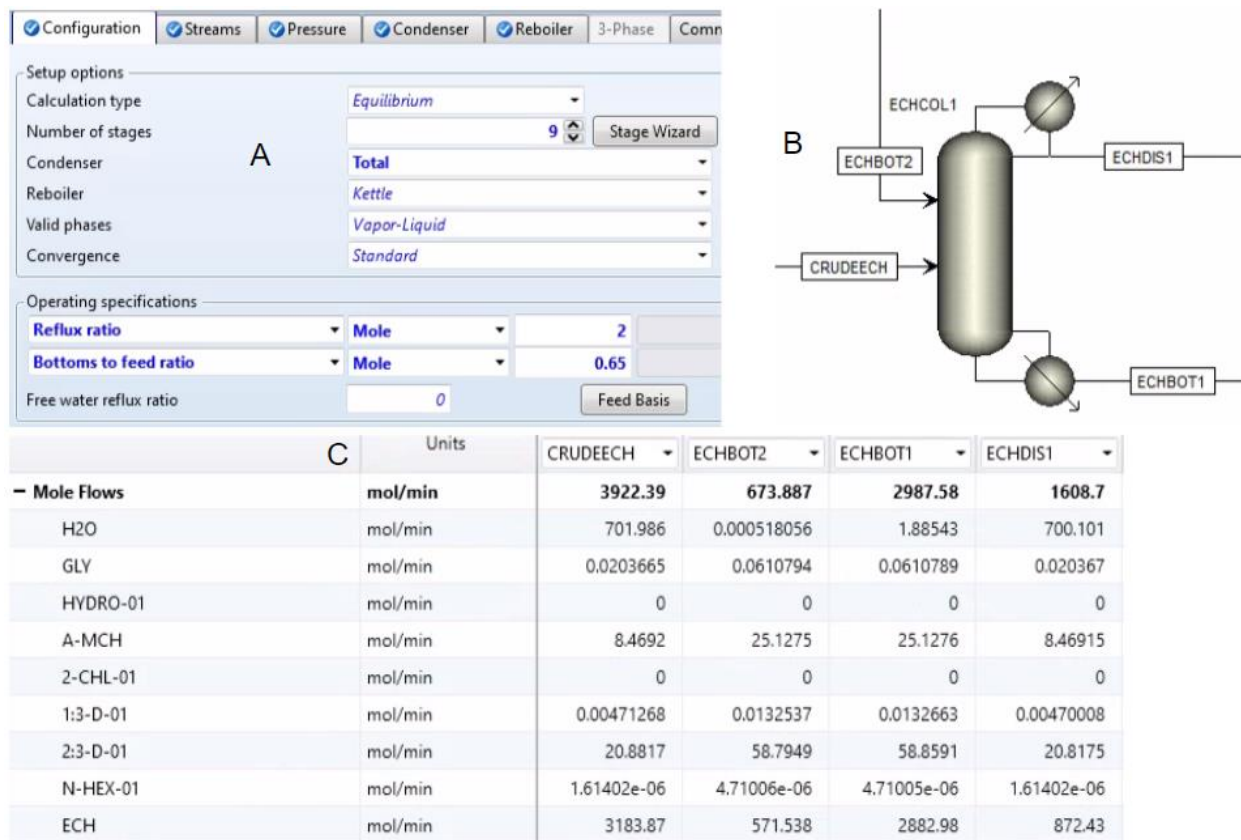


Figure 4.4.2: ASPEN Plus 1st Purification Column (A) Inputs, (B) Schematic design, (C) Stream results. Full Aspen stream notation available in Table (6.2.1). ECHBOT2 is a recycle stream from the next downstream purification column.

Equipment cost and sizing for the 1st ECH purification column was done via the Cost Formulas spreadsheet provided by Dr. Weimer. Trays were determined to be sufficient to handle the compounds within the feed stream: chiefly water and epichlorohydrin, along with several hydrolysis products. Additionally due to the reduced overall cost and simplicity of design, sieve trays are chosen over other designs such as bubble caps. Stainless steel is chosen as the material of construction for the construction of the column as well as the trays, showing excellent chemical resistance to water and chlorinated organics. As previously determined, 9 stages were to be used for the column. A tray height to diameter is specified, attempting to reach a total column height to diameter ratio of 20, as given by Linninger et. al[4.4.1]. With 9 stages, this provides an optimal tray height to diameter ratio of 2. Using the above information, column dimensions were determined, used later in the pricing of the column.

Table 4.4.2: 1st Purification Column Sizing and Materials

Parameter	Value	Units
Column Height	36	m
Column Diameter	2	m
Tray Height/Diameter Ratio	18	Unitless
Number of Equilibrium Stages	9	Unitless
Maximum Pressure Rating	1035	kPa
Tray Material	Stainless Steel	Unitless
Construction Material	Stainless Steel	Unitless

4.5 ECH Design Setbacks

Several setbacks occurred during the design of the second reaction sequence. First of which was the fluids package handling within Aspen. The entire of the first reaction sequence was operating using the NRTL fluid package to best model the azeotropic behavior of α,γ -DCH, α,β -DCH, HCl, and water. However as the second reaction sequence utilizes an ionic base, an electrolyte system is being managed. As a result, the electrolyte wizard within Aspen Plus is run to generate components and dissociation reactions. The fluids package was changed to NRTL for electrolyte handling as well. It is important to note that an additional section within the Aspen Plus flowsheet simulation is required, as using the ELECNRTL fluids package for the equipment in the first reaction sequence leads to non-convergence of the Aspen simulation. The next setback during the ECH design was the azeotrope considerations within Aspen Plus for the reactive distillation column. As stated above, ELECNRTL is the optimal fluids package to use for the NaOH system. However, the epichlorohydrin and water azeotrope parameters within ELECNRTL makes it not suitable for modeling the separation accurately. As a result, the UNIQUAC fluids package is used to achieve the desired azeotropic behavior for the column.

An additional setback occurred during the sizing of the reactive distillation column. Since this column utilizes packing, the HETP method was used to determine sizing specifications. However, with all information provided from the previous semester design slides, this method was producing column dimensions with a diameter much larger than the height. This would likely not be realistic or lead to a favorable separation. As a result, HETP calculations were bypassed and a standard HETP of 1 ft (0.3048 m) was used instead for the sizing.

Another setback that was encountered during the design of the ECH reaction sequence was Aspen's handling of multiple fluid phases. During simulation when Vapor-liquid-liquid models are chosen for the mixing PFR the simulation will not complete without errors in results. As a result, within Aspen the specified valid phases must be set to liquid-only.

Setbacks in the coded MATLAB simulation were also encountered. Due to the limited amount of information available concerning mass transfer and mixing due to two-impingement jets. It was understood that the impinging jets would result in heavily turbulent fluid flow, however mass transfer due to turbulence was discovered to be dependent on many flow parameters which are not categorized for the specific species in the mixing PFR. It was discovered that mass transfer due to micromixing occurs via diffusion, and this was the basis of the Fickian Diffusion assumption used in the MATLAB model. Notably, diffusion that occurs in a turbulent flow regime can be modeled either theoretically via mass transfer equations which depend on three-dimensional species balances or via experimentally derived mass balances that depend on flow characteristics specific to the stream composition and conditions. Application of the former proved impossible given the iterative nature of the MATLAB simulation, and application of the latter was impossible without laboratory experimentation. However, it was important that mass transfer in the dehydrochlorination mixing PFR was modeled in some respects because it was understood that the reaction of α,γ -DCH to ECH was mass transfer limited, and that conversion was to take place in the mixing PFR.

5 Cumulative Process Development and Completion

5.1 Process Improvement

At this point, equipment was accumulated for all of the major unit operations that were known going into this process since their necessity could be deduced from available literature. Along the way in compiling these units, holes in the overall process were identified and the need for further installations was acknowledged. Below is a compiled PFD showing the progress made up to before the additions were implemented (Figure 5.1.1):

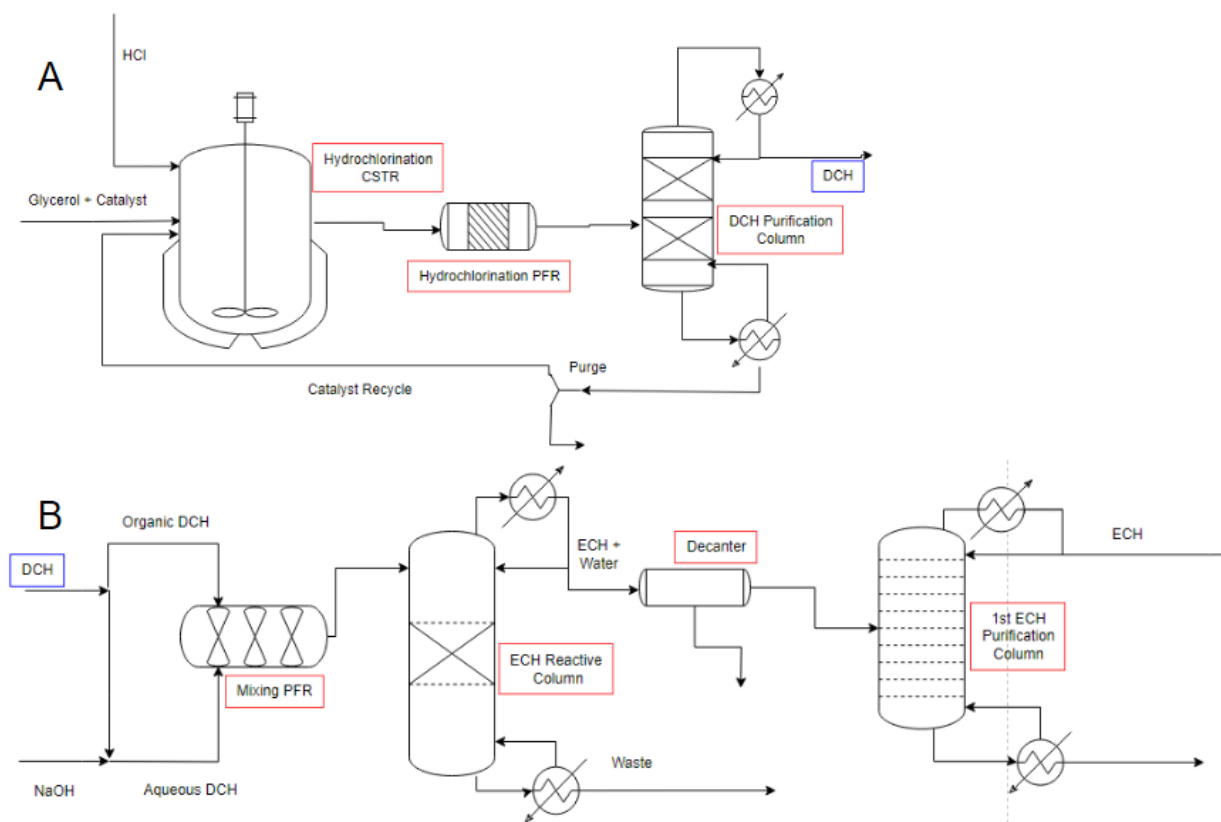


Figure 5.1.1: Progressed overall PFD containing (A) DCH reaction scheme and (B) ECH reaction scheme.

It was recognized that there were significant deficiencies in this design across the PFD, and so several different units were designed and implemented such as a glycerol separation chain, DCH column decanter, heat exchangers, pumps, and further ECH purification columns. These equipment were either deemed directly necessary to the completion of the process or substantially compelling from an economical standpoint.

5.2 Glycerol Flash Drum

Market research of available forms of our reactants made it clear that for biodiesel-production-derived glycerol, purifying a feedstock from crude glycerol would be advantageous. Glycerol is sold in a few distinct purities: USP grade, technical grade, and crude [5.2.1]. USP grade being the highest, it is 97% or greater purity of glycerol, technical grade consists of 95% pure glycerol, and crude glycerol varies in purity depending on the seller (purities were reported by mole). All these grades of glycerol feed have water as the primary impurity, but biodiesel-byproduct glycerol is in most cases sold as crude glycerol with minimal purification from the seller.

Due to the low costs of crude glycerol compared to the higher grades, and the ease of separating glycerol from water, a separation process to purify feedstock of glycerol was implemented. Starting from an assumed (minimal deviation) feed of 80% glycerol and 20% water, as could be sourced from Univar Solutions [5.2.1], it was desired for the purified feed of glycerol to be up to 95% (by mol) glycerol with 5% water impurity, which is more pure than assumed in the material balance spreadsheet calculations. Purification of glycerol up to this standard was in fact so energy-efficient that it could be carried out in an Aspen Plus simulation

with just a flash drum. Knowing the feed stream to the process was more pure than in the material balance, it was deduced that the process simulation was started with an overestimation of glycerol flow. Using an equilibrium separator flash drum in Aspen Plus would in reality translate to a boiler held at constant temperature, which would have a much lower utility cost compared to a whole distillation tower to reach a higher purity of glycerol. It was determined with the feed flow rate and physical properties from the cumulative Aspen Plus simulation that a **31.4 cubic meter** flash drum would be sufficient for the volumetric flow rate of purified glycerol to be fed to this process. While this unit would require further investment into this process on top of the other process equipment, the year-over-year savings from buying crude glycerol compared to a technical or USP grade greatly outweighed the cost associated with this flash drum.

Table 5.2.1: Fed Glycerol Flow Rates Around Flash Drum

Stream Name	Total Molar Flow (kmol/hr)	Mole Fraction of Glycerol	Mole Fraction of Water
Crude Glycerol	192	0.8	0.2
Purified Glycerol	152	0.944	0.056
Waste Water 1	39	0.238	0.762

5.3 Heat Exchangers

Heat exchangers (other than the reboiling and condensing units associated with distillation columns) were required at a couple of points in this process. Specifically, heat exchangers were placed on either side of the ECH reaction scheme decanter, to ensure that phase separation and ECH purification could both occur at the respective optimum temperatures. The first of these heat exchangers heats the process stream up and the second (after the decantation) cools the process stream down.

These two heat exchangers were modeled mathematically using the heat duty for temperature change calculated by the cumulative Aspen Plus simulation rigorously and modeled as one shell pass, two tube pass heat exchangers (see Figure 5.3.1). The size and utilities of the condensers and reboilers associated with the various distillation columns of this process were also calculated, but this was done in a less rigorous mathematical model of the energy balances, which is similar to the preliminary calculation used for the heating heat exchanger. All the aforementioned heat transfer process unit calculations were accomplished using spreadsheets where the heat exchangers were assumed to be shell-and-tube heat exchangers. It is worth noting that these calculations were done in the SI and imperial unit systems because Aspen Plus is able to output values of heat duty in both and most of the parameters taken from the textbook sources were only available in imperial units. The unit exchange done from system to system was consistently performed and compared with much scrutiny. Heuristics used in these calculations were taken from tables in chapter six of *Product and Process Design and Principles: Synthesis, Analysis and Evaluation* [5.3.1]. Other pertinent information was found in chapter twelve of the same textbook.

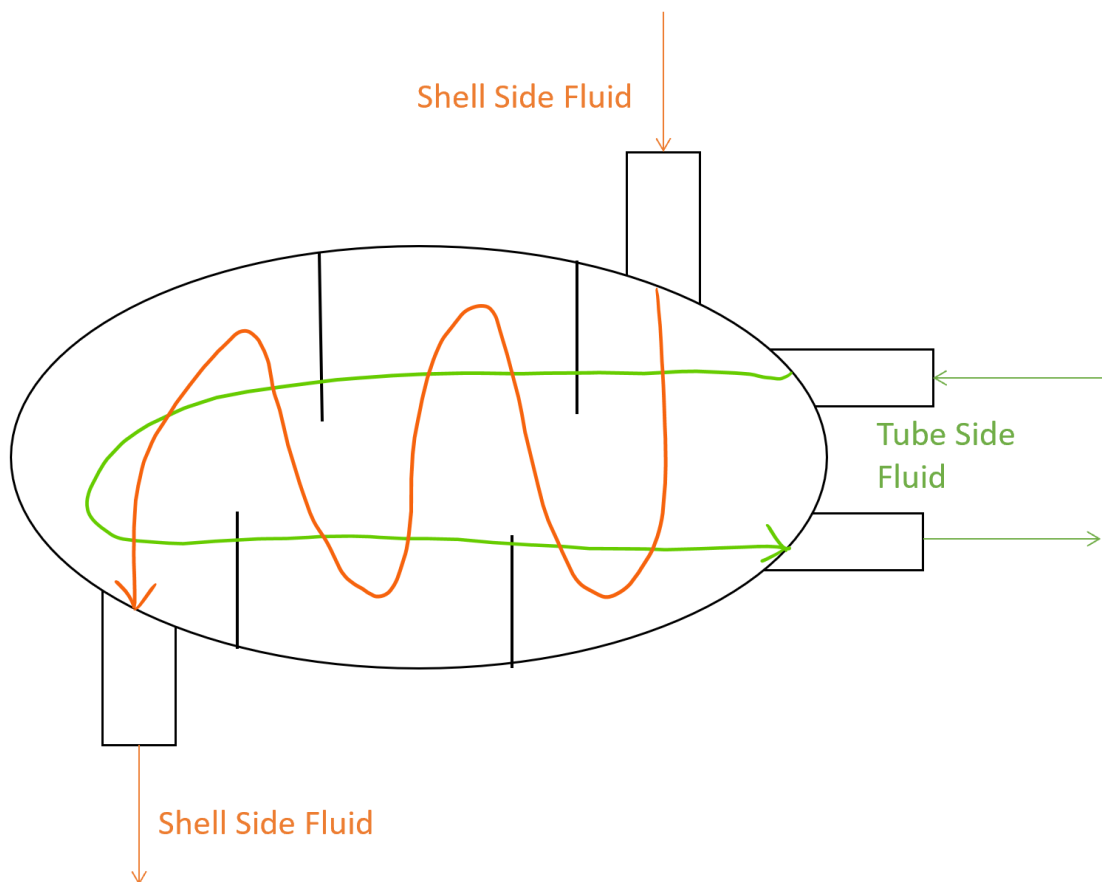


Figure 5.3.1: 1-2 Shell and Tube Heat Exchanger Schematic. Both the cooling and heating heat exchangers were implemented as 1-shell-pass and 2-tube-pass heat exchangers. Additionally, the models of the reboiler and condenser units were assumed to be 1-2 shell and tube heat exchangers. This figure illustrates the need for the correction factor in modeling these units because the fluids flow past each other in countercurrent and concurrent directions, the correction factor adjusts the heat transfer to account for the flow non-idealities that would negatively affect heat transfer.

The first step in the design of the heating and cooling heat exchangers was to select cooling and heating utilities based on the valid temperature ranges for different utilities, Table 12.1. The utilities chosen for the heating and cooling heat exchangers were condensing steam and chilled brine respectively. These were chosen because the outlet process stream temperature was within the valid temperature ranges by a large margin so that minimum approach temperatures could be met at the process stream outlet side of both units. Minimum approach temperatures were selected in both cases based on heuristic 26, which compared the temperature of the process stream to ambient temperature conditions. A twenty degree Fahrenheit minimum approach temperature was selected for the heating heat exchanger and a ten degree Fahrenheit minimum approach temperature was selected for the cooling heat exchanger. The minimum approach temperatures were applied to the outlet of the utility streams with a guess of temperature change in both cases so that the adiabatic energy balance around both heat exchangers could be completed. After evaluation of the energy balance (Equation 5.3.1 for the heating heat exchanger and Equation 5.3.2 for the cooling heat exchanger) to establish the required mass flow rate of utility, the two calculation methods diverged slightly.

$$Q = m_{steam}H_{vap} = m_{proc}C_{p,proc}(T_{proc,out} - T_{proc,in}) \quad (5.3.1)$$

$$Q = m_{brine}C_{p,brine}(T_{brine,in} - T_{brine,out}) = m_{proc}C_{p,proc}(T_{proc,out} - T_{proc,in}) \quad (5.3.2)$$

The cooling heat exchanger was specified using an assumed brine temperature change of nine degrees Fahrenheit. The heat capacity and density of chilled brine in the heat exchanger was assumed to be equal to the heat capacity and density of the same composition brine (20% by weight of NaCl) at twenty degrees Celsius, as this was the information that was readily available [5.3.2]. This heat exchanger was modeled the most rigorously using the F_T correction factor method which involved using the inlet and outlet stream temperatures to calculate the log mean temperature difference in the heat exchanger. The correction factor was then calculated by first using the stream inlet and outlet temperatures to determine factors R and S, which were used in Equation 5.3.7) to calculate F_T for this system, which assumed a one-shell-pass and two-tube-pass shell-and-tube heat exchanger geometry. The correction factor was calculated to be 0.867, which being greater than 0.85, was acceptable for this design.

$$Q = UAF_T\Delta T_{lm} \quad (5.3.3)$$

$$\Delta T_{lm} = \frac{\Delta T_{proc} - \Delta T_{brine}}{\ln \left(\frac{\Delta T_{proc}}{\Delta T_{brine}} \right)} \quad (5.3.4)$$

$$R = \frac{T_{proc,in} - T_{proc,out}}{T_{brine,out} - T_{brine,in}} \quad (5.3.5)$$

$$S = \frac{T_{brine,out} - T_{brine,in}}{T_{proc,in} - T_{brine,in}} \quad (5.3.6)$$

$$F_T = \frac{\sqrt{R^2 + 1} \cdot \ln \left(\frac{1-S}{1-RS} \right)}{(R-1) \cdot \ln \left[\frac{2-S(R+1-\sqrt{R^2+1})}{2-S(R+1+\sqrt{R^2+1})} \right]} \quad (5.3.7)$$

The heat exchanger surface area required was determined by solving Equation 5.3.3 for the surface area term. The heat transfer coefficient was first determined by using table 12.5 from *Product and Process Design and Principles: Synthesis, Analysis and Evaluation* [5.3.1]. Assumptions were made in order to make use of this table, in the case of this cooling heat exchanger the heat transfer coefficient was assumed to be the same as a shell-and-tube heat exchanger system where jacket water is present on the shell side and water present on the tube side. The required heat exchange area, which is equal to the surface area of the heat exchanger, was calculated to be 63.4 square meters, which was needed in order to price the major heat exchange units.

The final modeled aspects of both the heating and cooling heat exchanger was the tube placement, number, and fluid velocities in the shell-and-tube heat exchanger based on heuristics and pertinent tabulated values. Given the required mass flow rates of utilities, and tabulated values of tube inner and outer diameters, which depend on birmingham wire gauge, number of tubes required and other parameters were determined. These parameters were chosen mostly via guess and check, looking for a combination of parameters that allowed a tube fluid velocity of less than ten feet per second, but even more desirable, between three and five feet per second. Tube parameters were determined from tabulated values in Table 12.3 from *Product and Process*

Design and Principles: Synthesis, Analysis and Evaluation [5.3.1]. The total surface area required was divided by the surface area of a singular tube (dependent on tube outer diameter) of given specifications to determine the number of tubes required. Then that number of tubes multiplied by the cross sectional area of a single tube (dependent on the inner tube diameter) yielded total cross sectional area, which when used to divide the volumetric flow rate of process fluid yielded the fluid velocity on the tube side. Heuristic 54 offered a starting point for this guess and check method, starting with a tube outer diameter of three quarter inches and a starting length of 16 feet. Other pertinent shell-and-tube heat exchanger model parameters like shell diameter, baffle cut, and tube layout were determined arbitrarily with heuristics. This process was done for both the heating and cooling heat exchangers but not for the reboiler and condenser units.

Table 5.3.1: Shell and Tube Heat Exchanger Design Specifications

Specification	Cooling Heat Exchanger	Heating Heat Exchanger
Heat Duty	-17,526,064 BTU/hr	3,262,563 BTU/hr
Utility	Chilled Brine (20% wt salt)	Sat. Steam (277 °C, 0.3 MPa)
Utility mass flow rate	183 kg/s	0.442 kg/s
Number of Tubes Required	174	20
Tube O.D., I.D., and BWG	0.75 in, 0.641 in, 12 gauge	1.5 in, 1.4 in, 18 gauge
Tube Length	20 ft	8 ft
Velocity in Tube	1.00 ft/s	7.63 ft/s
Tube Layout and Pitch	Triangular layout, 1 in pitch	Square layout, 2 in pitch
Shell Inner Diameter	48 in	19 in

The reboiler and condenser units were sized and their utilities estimated using a similar method to the heating heat exchanger placed after the decanter. This was necessary for pricing of these units and utilities to be accurate. It was desirable that these units used saturated steam (condensing or vaporizing if heating or cooling was required, respectively) that only experienced phase change so that the energy balance calculations could be carried out in the same way they were for the heating heat exchanger, denoted in Equation 5.3.1. It is common for chemical processing plants to have access to a couple of different temperatures and pressures of saturated steam, which would have distinct heats of vaporization. For the reboiler and condenser units, the units that required the highest heat transfer used higher pressure steam in order to minimize the required heat transfer area and utility flow rate due to the higher heat of vaporization. For both the heating heat exchanger and the reboiler and condenser units, saturated steam conditions were taken from tabulated values in *Introductory Chemical Engineering Thermodynamics* [5.3.3]. The heat transfer coefficients of these units were estimated from the same Table 12.5 used for the cooling and heating heat exchangers. Utility mass flow rate required was determined by dividing the heat duty of a given unit (provided by the cumulative Aspen Plus simulation) by the heat of

vaporization of the saturated steam. Then dividing the heat duty by the mean temperature change and the assumed heat transfer coefficient yielded the required heat transfer area for a singular unit.

Table 5.3.2: All Heat Exchange Unit Basic Specifications

Unit Name	Heat Duty (BTU/hr)	Utility Steam T and P (°C and MPa)	Utility Mass Flow rate (kg/s)	Surface Area Required (ft ²)
DCH Purifying Reboiler	28,688,948	133.52 °C, 0.3 MPa, condensing	3.87	1338
DCH Purifying Condenser	-31,494,070	133.52 °C, 0.3 MPa, vaporizing	4.27	647.0
ECH Reactive Reboiler	128,044,040	400 °C, 0.2 MPa, condensing	11.5	1434
ECH Reactive Condenser	-100,593,699	400 °C, 0.2 MPa, vaporizing	9.00	4762
ECH Purifying Reboiler 1	10,349,265	133.52 °C, 0.3 MPa, condensing	1.40	1078
ECH Purifying Condenser 1	-8,824,345	400 °C, 0.2 MPa, vaporizing	0.789	1495
ECH Purifying Reboiler 2	7,335,798	133.52 °C, 0.3 MPa, condensing	0.994	8580
ECH Purifying Condenser 2	-7,773,439	400 °C, 0.2 MPa, vaporizing	0.695	4546

Table 5.3.3: Heat Exchanger Nomenclature

Variable	Units	Notes
Q	kW or BTU/hr	Heat duty of unit, output of cumulative Aspen Plus simulation.
m _i	kg/hr or lb/hr	Mass flow rate of component <i>i</i> .
H _{vap}	kJ/kg or BTU/lb	Heat of vaporization of steam. Heat is transferred away from the steam stream when condensing and transferred to the steam stream when vaporizing.
T _{i,dir}	°C or °F	Temperature of stream <i>i</i> either entering or leaving the heat exchanger, as denoted by <i>dir</i>

		being <i>in</i> or <i>out</i> .
$C_{p,i}$	J/mol-K or J/kg-K or BTU/mol-°F	Heat capacity of stream <i>i</i> , could be on a basis of moles or mass of stream.
U	J/K-m ² -hr or BTU/°F-ft ² -hr	Overall heat transfer coefficient, which is dependent on stream species exchanging heat as well as heat exchanger material of construction.
A	m ² or ft ²	Surface area of heat transfer
F_T	unitless	Geometric correction factor, most desirable between values of 0.85 and 1.
ΔT_{lm}	°C or °F	Log-mean temperature difference, the driving force of heat transfer between the shell and tube streams.
ΔT_i	°C or °F	Temperature difference of component <i>i</i> (inlet temperature subtracted from outlet temperature)
R	unitless	R-factor, used to calculate F_T using either an equation derived for the heat exchanger geometry or geometry-specific graphs that relate values of R and S to F_T .
S	unitless	S-factor, used to calculate F_T using either an equation derived for the heat exchanger geometry or geometry-specific graphs that relate values of R and S to F_T .

5.4 Decanters

In addition to distillation and flash separation, it was advantageous for this process to separate streams via equilibrium phase separation. After DCH purification and ECH production, the species present in the same streams separate into two immiscible liquid phases. In both cases these phases are aqueous and organic in nature, the first organic phase predominantly made up of DCH, the second organic phase predominantly made up of ECH and both aqueous phases were dominated by water content. However, there was still significant water content in both DCH and ECH organic phases.

Table 5.4.1: Decanter Stream Information

Stream Name	Mole Flow Rate (kmol/hr)	Main Component	Mole Fraction of Main Component
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DCH DC Distillate	406	Water	0.680
Aqueous DCH	207	Water	0.996
Organic DCH	218	DCH	0.620
Reactive DC Distillate	1967	Water	0.892
Aqueous ECH	1731	Water	0.989
Organic ECH	235	ECH	0.812

Both decanters, in order to price them, were modeled and sized as horizontal storage vessels with pricing criteria using parameters from the Vanderbilt Spreadsheet [7.2.1]. It was determined that 1110 cubic feet of capacity at an operating pressure of two bar would be sufficient to achieve the full separation of liquid phases in a real continuous gravitational decanter, so those specifications were used to price the decanters as horizontal storage tanks. It was determined that the DCH decanter be constructed of stainless steel because of negligible corrosivity of components leaving the DCH purification column, however the ECH decanter should be constructed with nickel alloy because the reactive distillation column could allow significant amounts of caustic soda to exit in the distillate stream, which year over year would corrode a stainless steel construction. These units would be operated horizontally in practice, the length being much longer than the diameter of the units so that the force exerted by the weight of the fluid on the bottom of the decanters would be distributed over a large area and not exceed the pressure rating of the vessels.

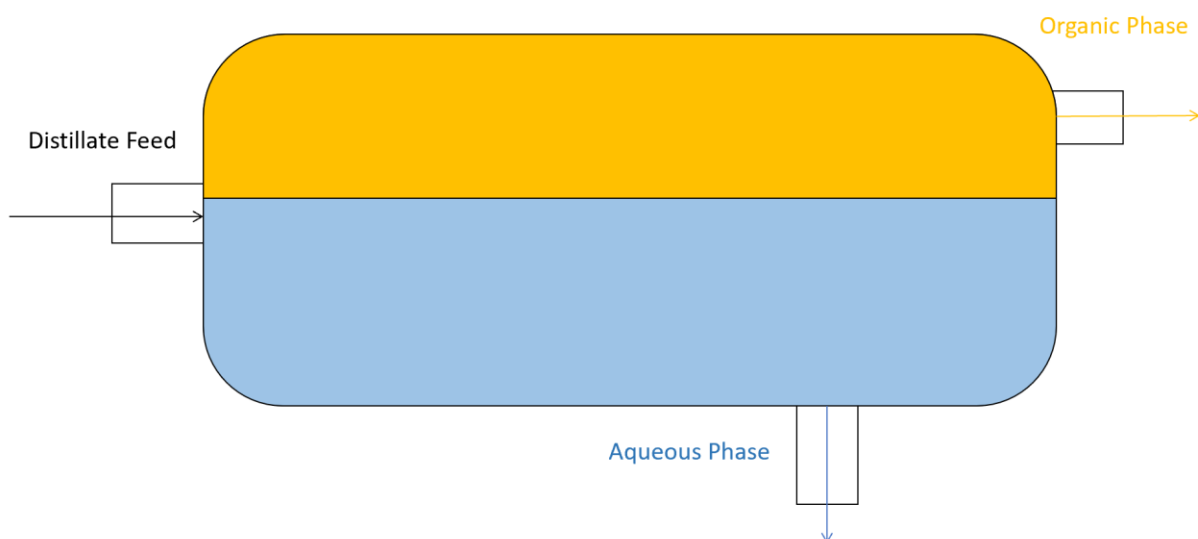


Figure 5.4.1: Decanter Phase Separation diagram. Both the DCH and ECH decanters are fed distillate from respective distillation columns, the fluid separates into two immiscible liquid phases, an organic phase and an aqueous phase. In both decanters the aqueous phase is composed mainly of water while the organic phase in the DCH decanter is mainly composed of DCH and

the ECH decanter organic phase mainly composed of ECH. In both decanters the density of the organic phase is less than that of the aqueous phase, therefore the organic phase will separate out on top of the aqueous phase.

The DCH decanter was required in this process because the DCH purification distillation column before the decanter is only able to separate so much of the water. Water, DCH and HCl experience a ternary azeotrope in the distillation column, so while the distillate product contains significant amounts of DCH, the main component of that distillate stream is water. It was desired in the unit operation after the DCH decanter (the dehydrochlorination mixing PFR) that caustic soda be mixed with a significant amount of water, so separation of the DCH from the water of the distillate could supply the necessary water for the next reaction unit. After the dehydrochlorination mixing PFR was better understood, it was also clear that having a more pure organic phase stream of DCH fed to that unit would aid in the mass transfer of DCH from the organic phase to the aqueous phase, and would therefore also aid the reaction and production of the ECH product.

Similarly, the ECH decantation step was required for this process because in order to purify ECH to the desired 99.97%, water must be removed from the purification process at the beginning. ECH and water also experience a binary azeotrope, but this could be avoided to achieve higher purity of ECH (than azeotropic composition) if water content fed to a distillation column is less than the azeotropic amount. The majority of the water was removed by this decantation, however the main impurity in the stream of ECH at this point of the process was still water, which could be removed by separation train because the water content was less than azeotropic. Later, it was found that increasing the feed of water to the bottom of the reactive distillation column would benefit the production of ECH in that unit, so the aqueous stream removed via decantation was recycled to the reactive distillation column to act as stripping steam. Production of ECH is benefitted by additions of stripping steam from the bottom of the reactive distillation column by the increased flow of water, driving increased solubility of ECH.

5.5 2nd Purification Column

In order to hit the specified purity requirements of 99.97% (mass basis), another purification unit must be used. Although the water content has been reduced to less than 0.1% in the previous purification column, there is still notable contamination from the heavy hydrolysis byproducts. Design of this column was done in a similar method as the previous ECH purification column. Within Aspen Plus, another shortcut column is used for initial estimations of column specifications. To achieve 99.97% purity of the ECH distillate stream, a recovery of 80% is specified. Significant increases beyond 80% ECH recovery in the distillate lead to a deteriorating separation, necessitating another separation unit downstream. Using the Winn Method, Aspen estimated the minimum number of stages to be 8, however this was raised to 10 to increase purity. Additionally, the shortcut column used the Gilliland correlation to calculate the required reflux ratio for 10 stages of 0.8. These two inputs were used for the full simulation of the column using a RadFrac unit. RadFrac also requires an additional parameter: chosen for this case was the boil up ratio. Initial estimates for the boil up ratio started at 2, but this was adjusted throughout to maximize purity and yield of ECH.

Table 5.5.1: 2nd Purification Column Specifications

Parameter	Value	Units
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Column Operating Pressure	4	Bar
Reboiler Temperature	185.4	°C
Condenser Temperature	156.5	°C
Number of Equilibrium Stages	12	Unitless
Feed Stage	8	Unitless
Reflux Ratio	0.8	Unitless
Boilup Ratio	6	Unitless

The number of stages in the column was increased from 9 to 12 to achieve the desired purity of the distillate stream. The reflux ratio was however not adjusted as raising it greatly increased the ECH lost to the bottoms while lowering it yielded an inadequate separation. Running at a boilup ratio of 2, a significant portion of the output exits the bottoms. The bottoms stream is concentrated in ECH enough to represent a significant yield loss, but still not near pure enough for sale. To help rectify this, the boilup ratio was increased incrementally to 6, lower the flow rate of the bottoms was significantly sparingly impacting the distillate purity. Also to note is that the bottoms stream contains a significant amount of α,β -DCH. With the bottoms stream containing ECH that should be separated, and α,β -DCH that should be reacted, this stream can be recycled back to the reactive distillation column. The implementation of this recycle stream not only helped increase overall yield, but also entirely eliminated an output waste stream for this process. The distillate stream produced is **80% recovery** of 99.97 wt% ECH.

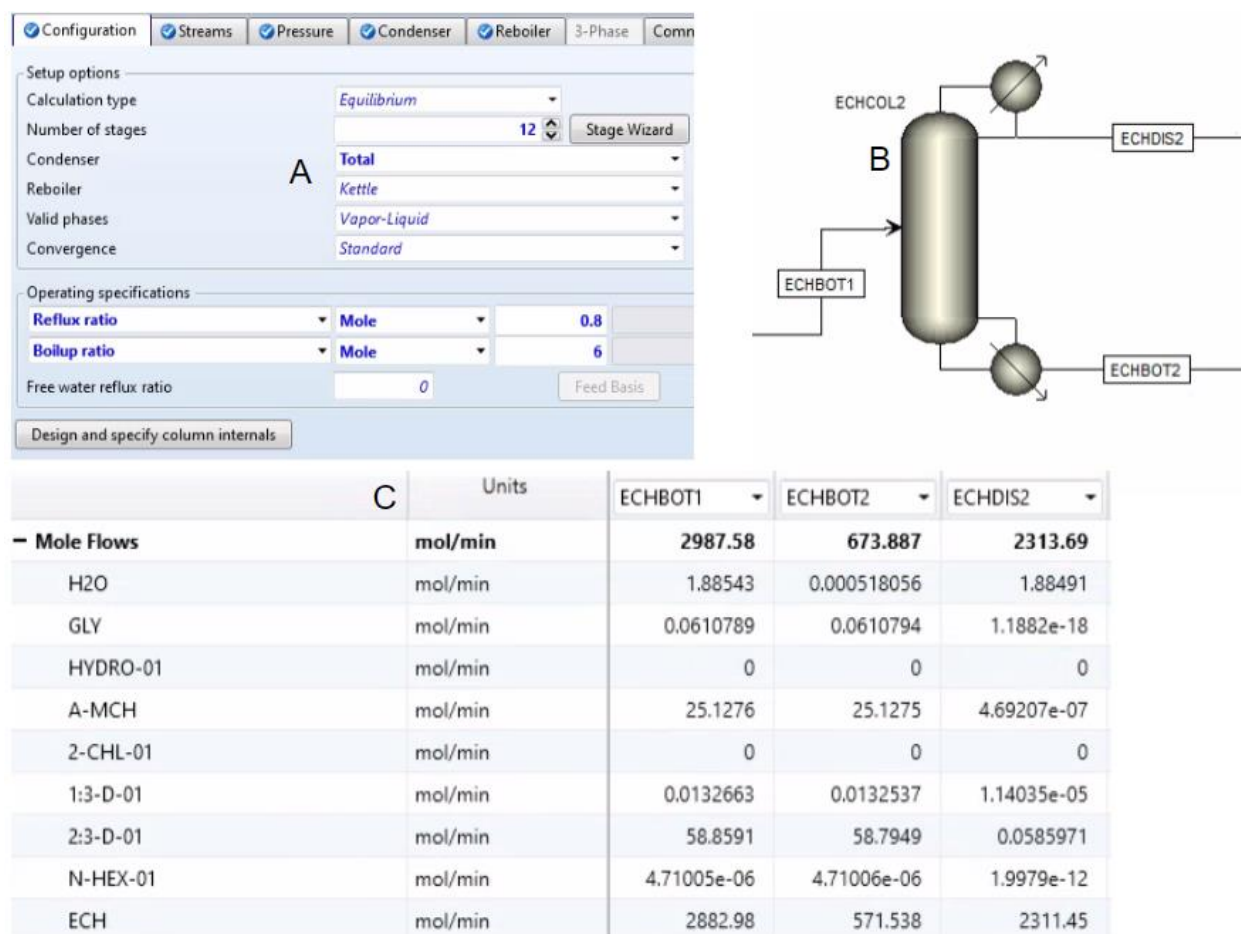


Figure 5.5.1: ASPEN Plus 2nd ECH Column (A) Inputs, (B) Schematic design, (C) Stream results. Recovery of α, β -DCH in the bottoms stream of 99.89%, and recovery of ECH in the distillate reaches up to 80%. The ECH distillate stream is also at sufficient purity.

Equipment cost and sizing for the 2nd ECH purification column was done exactly the same as the previous ECH purification column, via the Cost Formulas spreadsheet provided by Dr. Weimer. Trays were determined to be sufficient to handle the compounds within the feed stream: chiefly epichlorohydrin, along with several hydrolysis products and trace amounts of water. Additionally due to the reduced overall cost and simplicity of design, sieve trays are chosen over other designs such as bubble caps. Stainless steel is chosen as the material of construction for the construction of the column as well as the trays, showing excellent chemical resistance to water and chlorinated organics. As previously determined, **12 stages** were to be used for the column. A tray height to diameter is specified, attempting to reach a total column height to diameter ratio of 21.6, as given by Linninger et. al [4.4.1]. With 12 stages, this provides an optimal tray height to diameter ratio of 1.8. Using the above information, column dimensions were determined, used later in the pricing of the column.

Table 4.4.2: 1st Purification Column Sizing and Materials

Parameter	Value	Units
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Column Height	43.2	m
Column Diameter	2	m
Column Height/Diameter Ratio	21.6	Unitless
Tray Height/Diameter Ratio	1.8	Unitless
Number of Equilibrium Stages	9	Unitless
Maximum Pressure Rating	1035	kPa
Tray Material	Stainless Steel	Unitless
Construction Material	Stainless Steel	Unitless

5.6 Pumps

Pumps were chosen to be designed later in the process, after the final Aspen simulation had been converged, reached battery limit, and fully converged. The chosen pump design were centrifugal pumps, due to previous experience designing as well as availability of pump curves. It was determined that a total of 4 pumps would be needed for our process. One pump is needed each for the: CSTR recycle stream and reactive distillation column distillate output, as well as an additional two pumps for the mixing PFR. Three different pump systems were considered for each of the four pump requirements. All pump specifications and curves are provided by Fristam [5.6.1]. The main criteria for pump selection was the calculated efficiency of each system. Using the pump curves provided by Fristam, and the stream density from Aspen, brake horsepower (BHp), theoretical horsepower, and efficiency can be calculated as shown in Equations 5.6.1-5.6.3.

$$BHp = MHp * SG \quad (5.6.1)$$

$$THp = \frac{Q * \Delta p}{1714} \quad (5.6.2)$$

$$Efficiency = \frac{THp}{BHp} \quad (5.6.3)$$

One safety consideration was made at the same time as pump design: net positive suction head (NPSH). Essentially, there needs to be enough pressure at the inlet of the pump so as the

fluid does not flash to vapor and cavitate within the pump. Fristham pump curves have a secondary axis on which the NPSH required (NPSH_R) at the inlet is plotted versus capacity. The NPSH available (NPSH_A) can be calculated in Equations 5.6.4 and 5.6.5, given the inlet pressure, fluid velocity, inlet diameter, and fluid vapor pressure. These values can be obtained from Fristham pump specifications and Aspen stream properties.

$$NPSH_A = \frac{p_i}{\rho g} + \frac{V_i^2}{2g} - \frac{p_v}{\rho g} \quad (5.6.4)$$

$$V_i = \frac{Q}{\pi(\frac{d_i}{2})^2} \quad (5.6.5)$$

Pump 1 is used in the recycle leaving the bottoms of the DCH purification column entering the CSTR. The pressure of the stream must be raised to above that of the CSTR to ensure that there is no back flow through the recycle stream into the reboiler.. The pump curve for this selection, a Fristam 741, is shown below in Figure 5.6.1. Note: the capacity and head values have rounded up for ease of use within pump curves.

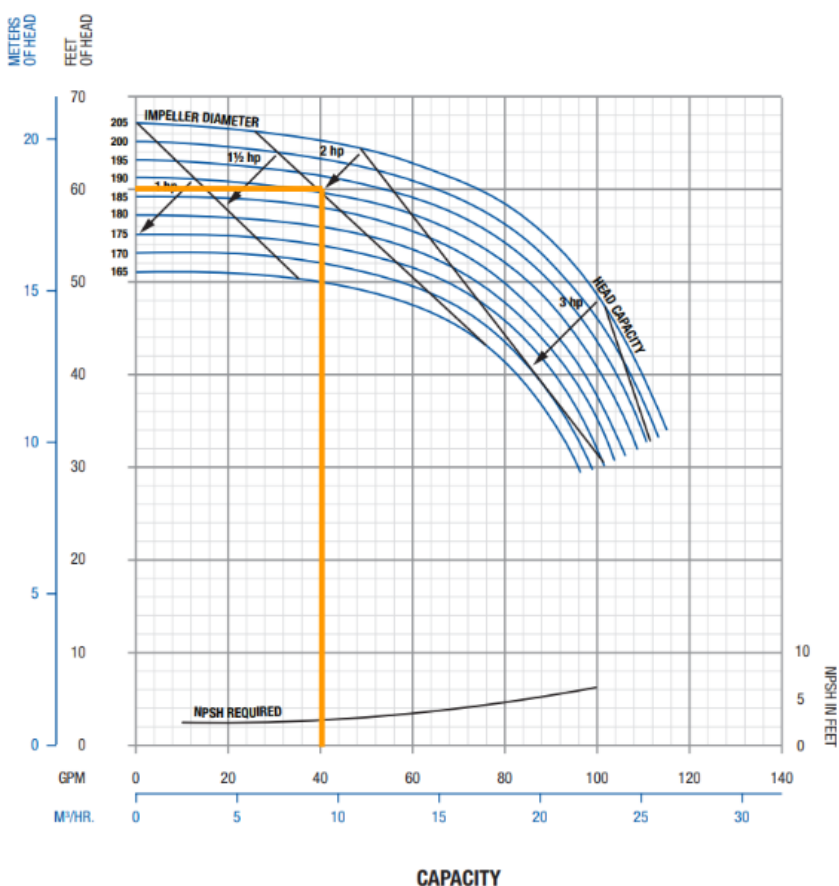


Figure 5.6.1: Pump curve for Fristam 741. Operating at the desired capacity (40 gpm) and head (60 ft), the best suited impeller diameter is 192 mm with a motor horsepower of 2 Hp. Shown in the bottom right is the NPSH_R- for this capacity, 4.5 feet of NPSH is required.

Pumps 2a and 2b are used to pressurize each stream going into the mixing PFR. The DCH purification column that precedes the pump and mixing PFR is run at sub-atmospheric

pressure, so the pressure must be brought back up to more reasonable levels. Additionally, the mixing PFR utilizes opposing impingement jets on the inlet to promote mass transfer, so each of the streams flowing in must be pressurized to 5 Bar to achieve optimal performance. These two pumps were chosen to be grouped together in design as the capacity and head requirements for the streams were nearly identical: approximately **55 gpm** and **125 feet** of head. The same pump is chosen for both streams, a Fristam 3522, with the pump curve for this selection shown below in Figure (5.6.2). Note: capacity and head values are rounded up for ease of use within pump curves.

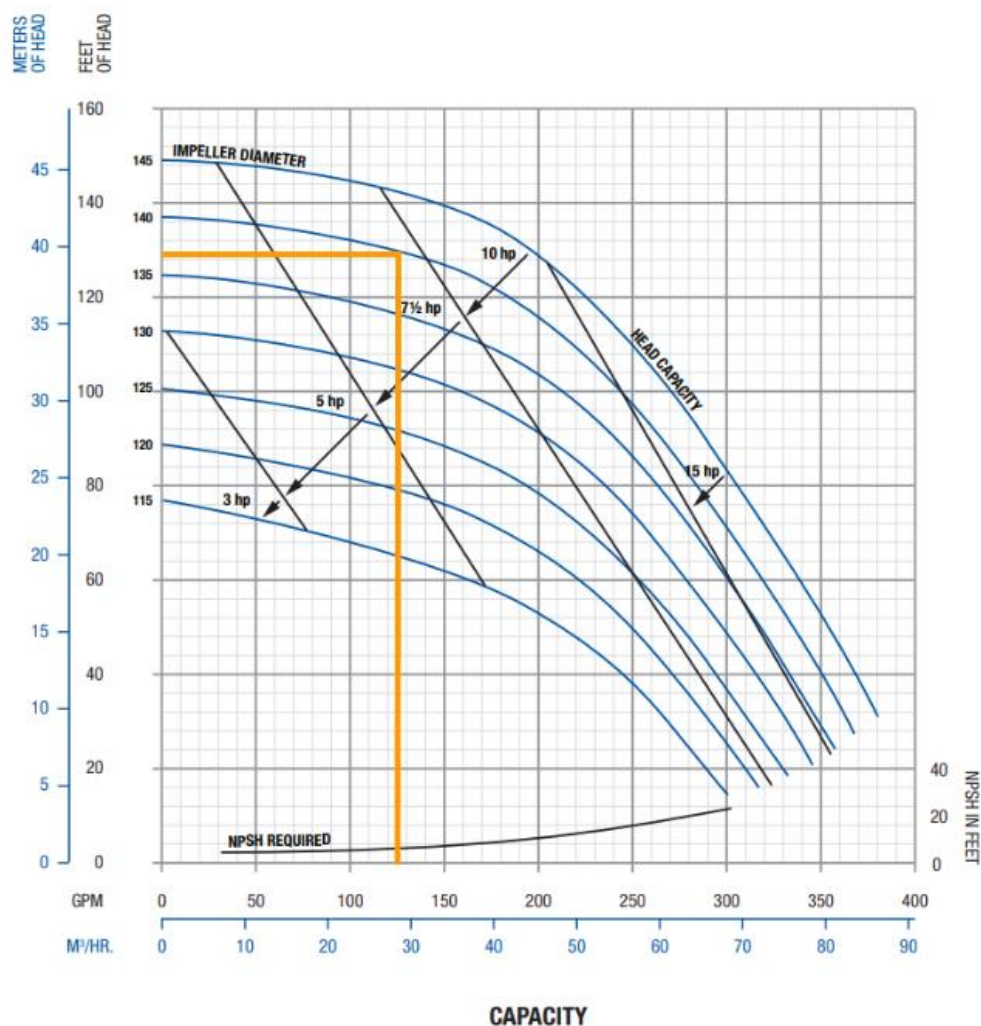


Figure 5.6.2: Pump curve for Fristam 3522. Operating at the desired capacity (65 gpm) and head (130 ft), the best suited impeller diameter was 140 mm with a motor horsepower of 7.5 Hp. Shown in the bottom right is the $NPSH_R$ for this capacity, 24 feet of NPSH is required.

Pump 3 is the final pump used in the process, prior to the ECH purification section. The stream leaving the condenser of the RDC must be pumped from 4 bar to 4.5 bar minimum to reach the operating pressure of the first ECH purification column. Additionally, the pump must also provide enough pressure to the stream through the heat exchangers and decanters. The pump design for this system was slightly different. Due to the low capacity required for this stream, an array of 4 pumps in series was chosen, effectively reducing the head required for each unit by

four. This decision was made after observing the low efficiencies (25-30%) for single pump systems. Ultimately the choice of using four smaller pumps in series instead of a single large unit may be more expensive upfront, but will lead to overall economic savings in the long term with electricity costs. Shown below is the pump curve for the given selection: 4 Fristam 3531s. $NPSH_A$ for this pump is very large due to the high inlet pressure of the pump. Note: capacity and head values are rounded up for ease of use within pump curves.

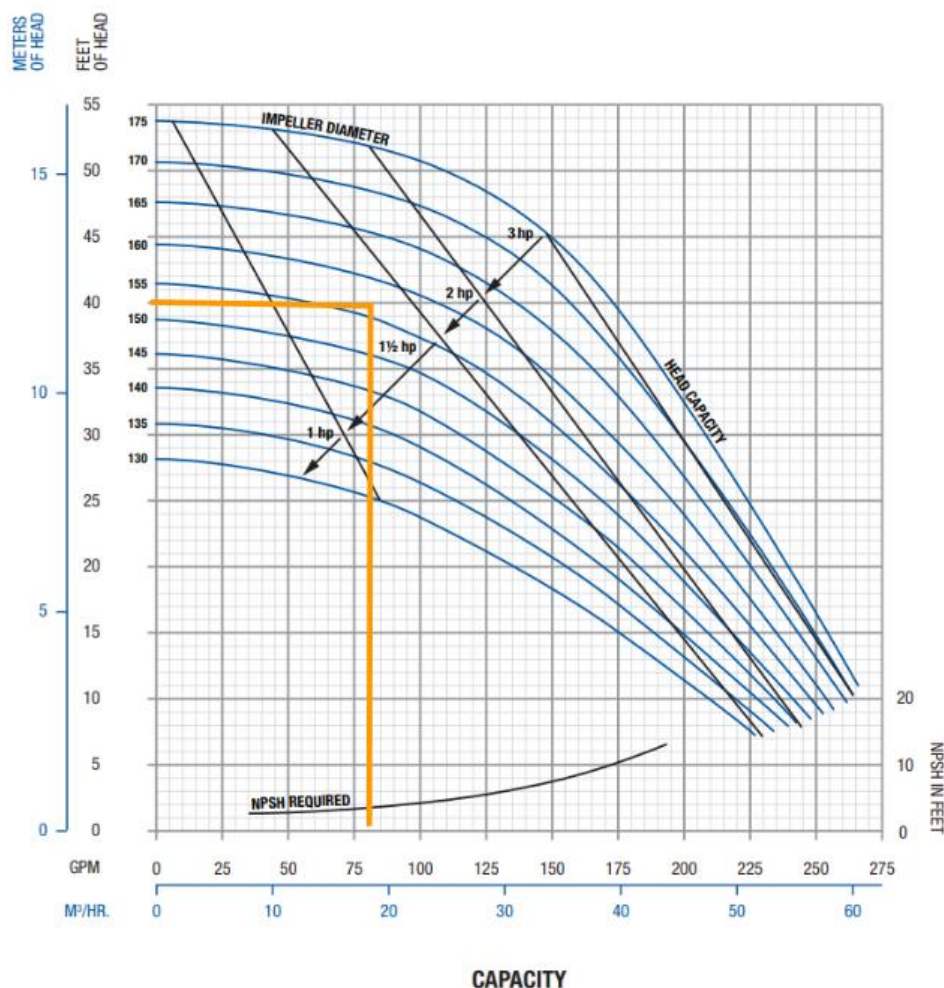


Figure 5.6.3: Pump curve for Fristam 3531. Operating at the required capacity (80 gpm) and 25% of the required head per unit (40 ft), the best suited impeller diameter was 160 mm with a motor horsepower of 1.5. Shown in the bottom right is the $NPSH_R$ - for this capacity, 6 feet of NPSH is required.

Using the above equations and figures, pump specifications were compiled as seen in the table below, summarizing all pertinent information for the four pumps. A full comparison of all 12 considered pump systems with their calculations and specifications compared can be found in Appendix A.

Table 5.6.1: Summary of Pump Specifications

Parameter	Pump-1 Value	Pump-2a Value	Pump-2b Value	Pump-3 Value	Units
Pump Model	3541	3522	3522	3531 (x4 in series)	(provided by Fristam)
Inlet Pressure	0.028 (0.406)	0.015 (0.217)	0.015 (0.217)	4	Bar (psi)
Outlet Pressure	1.50 (21.7)	5.00 (72.5)	5.00 (72.5)	8	Bar (psi)
Head Required	17.1 (55.9)	38.2 (125)	38.2 (124)	43.9 (144)	m (ft)
Capacity Required	0.822 (217)	0.209 (55.4)	0.190 (50.4)	0.270 (71.4)	m ³ /min (gpm)
BHp	1.76	4.656	4.656	1.39	Hp
THp	0.498	2.741	2.53	0.677	Hp
Efficiency	63.67%	58.89%	54.36%	48.64%	Unitless
Impeller Diameter	195	140	140	160	mm
Inlet Diameter	2.5	3	3	2.5	in
NPSH _R	4.5	24	24	6	ft
NPSH _A	4.86	40.6	34.5	127	ft

Table 5.6.2: Pump Design Variables

Variable	Units	Notes
MHp	Hp	Motor Horsepower
BHp	Hp	Brake Horsepower
THp	Hp	Theoretical Horsepower
Q	gpm	Volumetric Flow Rate
d _i	in	Pump Inlet Diameter
Δp	psi	Pressure Change
p _i	psi	Inlet Pressure

p_v	psi	Vapor Pressure
ρ	lb/ft ³	Fluid Density
V_i	ft/s	Average Fluid Velocity
SG	Unitless	Specific Gravity
NPSH _A	ft	Net Positive Suction Head Available
NPSH _R	ft	Net Positive Suction Head Required

6 Finalized Process

6.1 Cumulative Process Flow Diagram

After preliminary development of the DCH and DCH reactions schemes as well as the missing equipment listed in the previous section, a cumulative file displaying all of the relevant units was developed and is shown below in Figure 6.1.1:

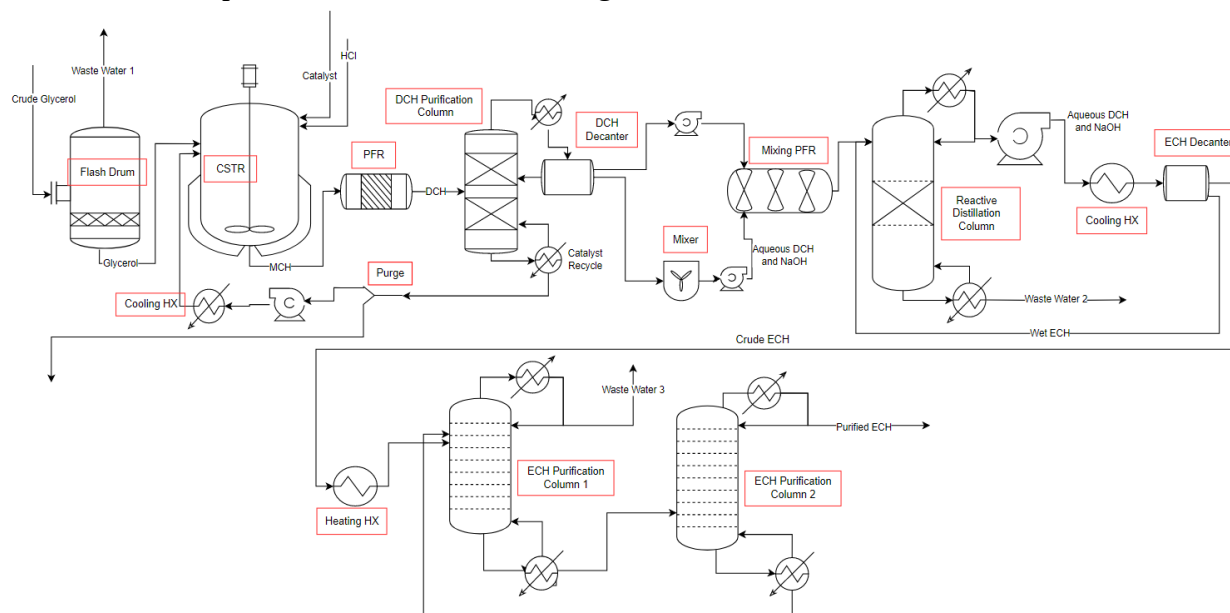


Figure 6.1.1: Overall Process Flow Diagram. Units in Red and Streams Non-colored

6.2 Cumulative Aspen Simulation

Aspen Plus is an industry-trusted software and so it was used in conjunction with other platforms to model this process as accurately as theoretically possible. For some equipment it was used as mere confirmation of expected behavior while other equipment it was the sole determinant in such design. Aspen references have been made throughout this report for individual unit operations in one or both of two scenarios: equipment could have been simulated individually or cumulatively. At the initial stages of the project, there was skepticism about how

accurately this simulation software could predict the process of interest. These fears were validated on several occasions but the overall results of this process were deemed successful.

The first concern was how well the reactors, that is the Hydrochlorination CSTR and PFR as well as the Mixing PFR and Reactive Distillation Column could be simulated with the plethora of reaction rates. There was initial turbulence in entering the kinetics of the Hydrochlorination and Dehydrochlorination/hydrolysis due to Aspen's unique custom equation option but eventually the equations were formatted properly for Aspen to compute. The next concern with the reactors, particularly for the Hydrochlorination CSTR with liquid glycerol and gaseous hydrogen chloride as well as the Mixing PFR with organic and aqueous DCH streams, was modeling the mass transfer that would occur between the respective two phases. It was discovered that mass transfer can only be considered with a user-defined subroutine which we were advised from discussion with Dr. Clough would require a significant amount of time given the lack of experience with such software. The reactors were thus modeled using solely the kinetic equations provided from literature. Any mass transfer design was done externally and results were compared with that of Aspen to scale how accurate the Aspen simulation was. The primary goal of the reactors was to hit conversion and so that is what each reactor that was implemented into Aspen was done so for. Volumes and even dimensions were changed to from what was theoretically derived with software such as MATLAB for the sake of keeping conversion and the outputs of those reactors in line with what was predicted from literature.

The columns were perhaps the most interesting component of the Aspen simulation as distillation columns are much more difficult than reactors to theoretically model from the ground up and should thus be simulated using software rather than mathematical predictions. Column sizing estimations are possible but become much more complicated with more components and with azeotropes between those components. The azeotropes were the most challenging aspect of this project as alluded to by the prompt because Aspen was not able to implement all of them column simulations, that is there was no data on how particular solutions separated. To recap, the azeotropes of interest were:

- DCH with Water
- HCl with Water
- DCH with Water, HCl
- ECH with Water

Aspen had data for every azeotrope except the ternary azeotrope between DCH, water, and HCl. The first three azeotropes listed were relevant in the DCH Purification Column while the last was applicable for the ECH Reactive Distillation Column. For the DCH column, the ternary azeotrope was used for advising the preliminary sizing of the column in conjunction with the boiling points for selecting light and heavy keys. Upon failure to implement the characterization of the ternary azeotrope into Aspen, the binary azeotrope between DCH and water was used which resulted in good recovery of α,γ -DCH but very poor recovery of α,β -DCH which was due to this assumption. Adjusted design of the column from preliminary findings were based on what gave the best performance in Aspen. It was expected that the isomer distinguishment between α,γ -DCH and α,β -DCH would not impact volatility levels such that the recovery of both isomers should be the same. A feed stream of α,β -DCH was thus added to the process downstream from the DCH Purification Column (12DCH in Figure 6.2.1) to compensate for this loss. It would be expected that a higher recovery of α,β -DCH would result in a lower recovery of α,γ -DCH and

GLY	Refined, technical-grade glycerol feedstock
CAT	Hexanoic acid catalyst feedstock
HCL	Gaseous hydrogen chloride feedstock
OCSTR	CSTR product
OPFR	PFR product
ORG	Organic DCH stream from decanter
AQ	Aqueous DCH stream from decanter
BOT	DCH Purification Column bottom stream
REC	DCH Reaction Scheme recycle feed
PURGE	DCH Reaction Scheme recycle purge stream
NAOH	Aqueous sodium hydroxide feed
23DCH	Compensated α,β -DCH feed
OMIX1	Combined sodium hydroxide and organic DCH stream
OMIX2	Combined sodium hydroxide, organic and aqueous DCH stream
OMPFR	Mixing PFR product stream
REACDIS	ECH Reactive Column distillate stream
REACBOT	ECH Reactive Column bottoms stream
COOLED	Cooled ECH Reactive Column bottoms stream
REACREC	ECH Reactive Distillation Column recycle stream
DECAQ	Water impurity that was extracted

	from REACREC stream
DECORG	ECH stream after decanter purification
CRUDEECH	Heated ECH stream after decanter purification
ECHBOT1	ECH stream purified from 1st purification column
ECHDIS1	Impure stream of ECH, sent back to ECH Reactive Distillation Column
ECHBOT2	Impure ECH stream sent back to 1st purification column
ECHDIS2	Finalized pure ECH stream (Overall Product)

Table 6.2.2: Aspen Plus Simulation Unit Notation

Equipment Notation	Equipment Description
FLASH	Flash drum for glycerol purification
CSTR	Hydrochlorination CSTR
PFR	Hydrochlorination PFR
DCHCOL	DCH Purification Column
SPLIT	DCH Purification Column recycle stream splitter
AQMIX	Aqueous DCH and sodium hydroxide feed mixer
ORGMIX	Aqueous DCH, organic DCH, and sodium hydroxide stream mixer
MPFR	Mixing PFR
REACOL	ECH Reactive Distillation Column
HX2	ECH Reactive distillate stream cooler
DECANT	ECH Stream decanter
RECMIX	Aqueous ECH and impure ECH mixer

HX1	Organic ECH stream heater
ECHCOL1	1st ECH Purification Column
ECHCOL2	2nd ECH Purification Column

The PFDs of both the designed process and Aspen simulation (Figures 6.1.1 and 6.2.1) are reasonably similar and it was fortunate that Aspen had all of the requested units including a reactive distillation column. The biggest difference between these two is the mixer (ORGMIX) that is required before the mixing PFR (MPFR) that combines the two streams that would otherwise be fed separately into the mixing PFR. Aspen only accepts one stream to be fed to a PFR and since this reactor was not taking into consideration the mass transfer this was negligible from a performance standpoint but was worth clarifying from a visual standpoint. On the same note, mixers and splitters had to be implemented for on each occasion where streams were combined or separated. It is expected that actual equipment units in this sense will not be required since this is realistically indicative of a Y-split pipe fitting.

Convergence was more of a challenge in the DCH Reaction Scheme as opposed to the ECH Reaction Scheme. Convergence delays were encountered essentially anywhere in the process that involved a recycle stream since multiple units need to be simultaneously run in these scenarios. The ECH scheme was particularly difficult because the feed streams were substantially different than what they should have been as the amounts of these streams were selected based on material balance approximations as well as kinetic behavior. Material streams thus had to be adjusted to account for the changing amount of accumulation in the recycle stream which is why a purge disposal (PURGE) had to be implemented.

Non-column heat exchangers are unnecessary for Aspen simulations as the streams will automatically be heated or cooled to whatever equipment that they are being fed into. Also unnecessary and so not listed in the Aspen PFD are pumps because Aspen models streams as not only thermally autonomous but also mechanically autonomous such that streams do not need any driving force to get from one piece of equipment to another.

Aspen produced an overall yield from Glycerol to ECH of 90.07%. More Results are posted in Appendix A.3 containing the mast flow sheet with important information on the streams.

6.3 Additional Equipment

In addition to major unit operations like reactors and separators, and heat exchangers and pressure changers, other equipment must be accounted for to accurately estimate the investment required for this production facility. The specific additional equipment that must be considered due to their large costs are storage tanks and piping. Clearly, while piping and storage tanks are required for this process, their specifications do not alter the overall behavior of this process in simulations.

The storage tanks that this process requires would be used for the storage of some raw materials as they are received from shipment or pipeline, the final purified ECH product before distribution, and the mixed waste water before being sent to waste water treatment facilities. The raw materials that require respective storage tanks are crude glycerol received from shipment, anhydrous HCl received from pipeline, and hexanoic acid catalyst received from shipment. For these storage tanks, the key parameters considered were materials of construction, volume and

type. The materials these tanks must be constructed out of was determined based on the compatibility of the stored chemical with a given material. The only storage tank for which stainless steel was inappropriate would have been the anhydrous HCl tank. Stainless steel is very susceptible to corrosion when in contact with acidic species, so the strong gaseous acid HCl would corrode a tank of stainless steel construction very quickly. It was determined that instead of investing in an expensive anti-corrosive storage tank, most likely of a glass-lined stainless steel construction, that receiving the anhydrous HCl via a pressurized pipeline would be more cost effective. However stainless steel is an appropriate material for the hexanoic acid storage tank because hexanoic acid is a weak acid that would not effectively corrode the tank. While stainless steel is also susceptible to salt corrosion, the waste water storage tank could still feasibly be made of a stainless steel construction because the salt in that tank would be greatly diluted due to the sheer amount of water in the tank.

Table 6.3.1: Storage Tank Specifications and Pricing

Stored Process Material	Tank Type	Material of Construction	Volume (m ³)	Purchase Cost (USD)
ECH	Large Field Erected	304 Stainless Steel	10,000	\$1,962,909
Glycerol	Large Field Erected	304 Stainless Steel	10,000	\$1,962,909
Hexanoic Acid	Large Field Erected	304 Stainless Steel	5,000	\$1,194,702
Wastewater	Large Field Erected	304 Stainless Steel	10,000	\$1,962,909

Piping considerations also heavily relied on corrosive resistivity, because in the DCH Reaction Scheme there is significant HCl concentrations throughout. This necessitated the use of nickel alloy and glass-lined stainless steel piping in that upstream process, while stainless steel was used for piping for streams in the bulk of the ECH Reaction Scheme. Glass-lined stainless steel piping is specifically required around the hydrochlorination CSTR (for the anhydrous HCl stream) and PFR units because of the significant quantities of HCl presence there, however nickel alloy piping is needed around the dehydrochlorination mixing PFR and reactive distillation column unit due to the presence of caustic soda which would effectively erode stainless steel piping many times over the lifetime of this plant. Stainless steel piping could be used everywhere else in this process where non-significant amounts of acids or bases are present. For the purpose of pricing the required piping, an arbitrary (most likely overestimation) length of 1100 total meters of piping was assumed. Considering the general distribution of equipment in this process it was assumed that 100 meters of glass-lined piping, 200 meters of nickel alloy piping, and 800 meters of stainless steel piping would be required respectively. The diameter of these pipes was set to the maximum of 0.51 meters, and not specifically determined for individual regimes of the process because for the purpose of analyzing economic feasibility, overestimated costs set higher revenue conditions for profitability.

After specifications were determined for the CSTR impeller and pumps, specifications for the motors and utilities required to operate these units were determined. The motor power requirements were determined through the use of pump curves and rigorous calculations discussed in section 5.6. The CSTR impeller motor requirement was determined by the power to mass ratio, given the specifications of the gas-inducing impeller discussed in section 3.2. Calculations to determine the power utility were pertinent because the power requirements for these units would significantly change the overall operational cost of this process.

Table 6.3.2: Motor Specifications and Pricing

Motor Requiring Unit	Motor Power Requirement (kW)	Energy Required for Operation (kW-hr/yr)	Motor Cost (USD)	Energy Cost (USD/yr)
Pump-1	5.49	43957	\$1,189.49	\$3,727.74
Pump-2a	2.90	23200	\$820.23	\$1,967.42
Pump-2b	2.90	23200	\$820.23	\$1,967.42
Pump-3	4.71	37677	\$1,078.65	\$3,195.21
CSTR Impeller	263	2103275	\$34,897.47	\$178,366.60

7 Economic Analysis

7.1 Economic Estimation Approach

The whole purpose of designing this process is to make something that will generate revenue over a consistent period of time. In other words, this process needed to not only be profitable to the point of putting money in the pockets of people that run it but also so that further expansion, say by means of constructing another plant, could be an option. Finding the economic summary for a business is always more reflective of an ideal scenario as forecasting a cash flow can not take into account a seriously impactful event or series of events. A cash flow can not consider whether the economy is about to crash or whether a distillation column is going to crash and burn. Cash flows typically only show decreasing and increasing linear behavior over its timeline such that major bumps in the road are given relatively little consideration. This is why an ideal case, which is what is predicted in these sections, must show a really promising opportunity for such a business (process) to get interest and subsequent investors.

There are two main categories of expenses that chemical manufacturers face in a start-up scenario: capital investment and operational costs. The primary difference between these two is the former is the upfront cost paid for the facility installation while the latter refers to the expenses that are continuously encountered throughout the lifetime of the plant. Expectedly, capital investment is substantially greater than operational costs over the first few years (most important period) and so the challenge with most plants is how fast the capital investment is overcome to the point where operational costs dominate. This is around the point where the cumulative cash flow turns positive and the plant is officially not classified as an overall liability. Operational costs can dominate if a process is designed poorly such that a process holds a low yield or if a unit requires an excessive amount of utility. Efficiently managing capital costs has the most effect on how fast a process becomes profitable while great management of operational costs, that is designing a high-performing process, is indicative of a highly profitable process.

The main consideration for capital costs pertained to equipment prices. The process used for this plant in efforts to diminish equipment costs was first selecting equipment that got the job done while fulfilling the mentioned sustainability criteria. Once an initial unit or collection of units were considered for implementation and design, thought was put into whether there was a better alternative in terms of equipment costs that had marginally less performance. It was gathered through literature and discussions with Dr. Hook that performance is usually indicative of profits and that is why performance is the first consideration and cheaper alternatives the second.

Getting into equipment costs, the most costly equipment were expected to be the units that had the most impact on the process, which in this context was reactors and columns. Reactors aimed to be as small as possible, particularly the Hydrochlorination CSTR which was expected to be expensive due the heating jacket and impeller system required. Column packing was foreseen to be really expensive and so it was envisioned that near complete conversion through preceding reactors should be aimed not only to diminish column size but also to mitigate the amount of packing replacement. Heat exchangers were not foreseen to be too expensive from a material standpoint but had a much larger impact on costs due based on the amount of utility required. Design of the heat exchangers was done with a much heavier concentration on performance and subsequently very little focus on cheaper alternative designs. Storage tanks are also critical in terms of cost but are thought to save money in the long run due to lack of operational costs associated with continuous transport of goods. Pumps were designed similar to heat exchangers, that is with a prioritization of long-term operational costs as opposed to raw equipment costs.

7.2 Capital Costs

There were 3 main input variables that determine the pricing for a given piece of equipment. The most notable was materials of construction and so materials such as stainless steel or glass-lined stainless steel were selected in part because they fulfilled the sustainable criteria but also because pricing on different units could readily be found with these more common materials. If pricing on a material was not available, a material factor was applied which applied a linear correction towards whatever price is estimated. The second most important consideration was the size of the equipment and so throughout the design of the process, equipment was first aimed to be as small as possible and then increased when necessary. The last input was pressure ratings which were not used for all equipment but used for a significant amount of selections. No substantially high pressures are expected in this process but higher than performance ratings were implemented as a safety measure. Two primary sources used for pricing equipment were a cost formula spreadsheet provided by Dr. Weimer and Dr. Clough of University of Colorado Boulder and another cost formula spreadsheet provided by Professor Russell Dunn of Vanderbilt University [7.2.1][7.2.2]. Boulder's spreadsheet was primarily used with most sourced equipment equations from Peters and Timmerhaus[7.2.5]. The Vanderbilt spreadsheet draws equipment estimate equations from Sieder [7.2.6]. Both of these spreadsheets yield purchase equipment cost. With these resources available, the bare module factor method was thus elected to be used such that FBM's would be applied towards these cumulative costs of equipment (for example, all of the pumps added up) and these resulting values used for further calculations.

The flash drum was calculated using the Boulder spreadsheet with material of carbon steel, diameter of 2 meters and a moderately low pressure rating of 1035 kPa (Eq 7.2.1):

$$Flash\ Drum\ PE = 6.17(Height_{Drum})^2 + 6433(Height_{Drum}) + 14686.23 \quad (7.2.1)$$

Heat exchangers were calculated using the Boulder spreadsheet equation for pressure ratings of 1035 kPa with varying material factors (Equation 7.2.2):

$$Heat\ Exchanger = 1.28(10^{(0.0032\log_{10}(Area_{HX})^3 + 0.1377\log_{10}(Area_{HX})^2 + 0.2168\log_{10}(Area_{HX}) + 3.37)}) \quad (7.2.2)$$

Pumps were calculated using the Boulder spreadsheet based on stainless steel material models for moderately low pressure ratings of 1035 kPa (Equation 7.2.3):

$$Pump = -6.4E7(Capacity_{Pump})^2 + 2.04E6(Capacity_{Pump}) + 6514 \quad (7.2.3)$$

The columns were priced by calculating the external material, that is the vessel and then adding that to the pricing for the internal material, whether that be the trayed or packed material. The first DCH purification column was priced using a nickel alloy. The external portion of the DCH purification column was calculated using the Boulder spreadsheet with a low pressure rating of 1035 kPa since this column was operated under vacuum conditions (Equation 7.2.4):

$$Column_{DCH} = 45.63(Height_{Column})^2 + 4.7E4(Height_{Column}) + 1.1E5 \quad (7.2.4)$$

The internal packing of the DCH Purification Column were calculated from the Boulder spreadsheet using a porcelain (ceramic) packing material at a column diameter of 2 meters (Equation 7.2.5):

$$Packing_{DCH} = 1372(Height_{Packing})^{0.9857} \quad (7.2.5)$$

The ECH Reactive Distillation column, also a packed column, was priced using the same method as the DCH purification column. With a moderately low pressure rating of 1035 kPa and a diameter of 2 meters, Equation 7.2.6 was used below to estimate the glass-line stainless steel material using a nickel alloy pricing:

$$Column_{ReacDis} = 45.66(Height_{Column})^2 + 4.7E4(Height_{Column}) + 1.1E5 \quad (7.2.6)$$

The internal packing of the ECH Reactive Distillation column was modeled to be ceramic porcelain material of a structured orientation for a column diameter of 1 meter (Equation 7.2.7):

$$Packing_{ReacDis} = 1372(Height_{Packing})^{0.9857} \quad (7.2.7)$$

The trayed columns, those being the two ECH Purification columns, were modeled as trayed columns and so the internal pricing differed from the packed method while the external portion of the column was modeled similar to the DCH Purification Column and the ECH Reactive Column. For a stainless steel material, the first vertical column was priced using a low pressure rating of 1035 kPa and a diameter of 2 meters (Equation 7.2.8):

$$Column_{ECH1} = 18.51(Height_{Column})^2 + 1.93E4(Height_{Column}) + 4.4E4 \quad (7.2.8)$$

The trays for the first ECH purification column were priced per tray for a 9-sieved trayed column of stainless steel material (Equation 7.2.9):

$$Trays_{ECH1} = -179.4(Diameter_{Column})^3 + 1348.76(Diameter_{Column})^2 - 959Diameter_{Column} + 1636 \quad (7.2.9)$$

The second ECH purification column was calculated the same way as the first, that is with the external portion calculated as a vertical column of a stainless steel material at a diameter of 2 meters (Equation 7.2.10):

$$Column_{ECH2} = 18.51(Height_{Column})^2 + 1.93E4(Height_{Column}) + 4.4E4 \quad (7.2.10)$$

The tray pricing for the second ECH purification column was calculated using the same Boulder spreadsheet for a stainless steel material with a diameter of 2 meters (Equation 7.2.11):

$$Trays_{ECH2} = -152.2(Diameter_{Column})^3 + 1144.4(Diameter_{Column})^2 - 814(Diameter_{Column}) + 1388 \quad (7.2.11)$$

Storage tanks used for holding ECH, Catalyst, Glycerol, and Waste were all modeled as large field-erected storage tanks at various volumes and either stainless steel or glass-lined stainless steel (Equation 7.2.12):

$$Tank = 95.85(Volume_{Tank}) + 2.66E5 \quad (7.2.12)$$

The Mixing PFR was modeled as a double pipe heat exchanger of nickel alloy material for very small dimensions (Equation 7.2.13):

$$PFR_{Mixing} = 1.37(10^{(0.0032\log_{10}(SurfaceArea_{MPFR})^3 + 0.1377\log_{10}(SurfaceArea_{MPFR})^2 + 0.2168\log_{10}(SurfaceArea_{MPFR}) + 3.3695)}) \quad (7.2.13)$$

The Hydrochlorination PFR was calculated using the same double-pipe heat exchanger model of the Boulder spreadsheet but due to size limitation of these equations, the total price of the unit was calculated using 5 pricings of a double pipe heat exchanger corresponding to 5 cumulative units (Equation 7.1.14):

$$PFR = 5(2761(\frac{SurfaceArea_{PFR}}{5})^{0.0699}) \quad (7.2.14)$$

The Hydrochlorination CSTR was priced using the Vanderbilt spreadsheet in which the pricing was determined from the material factor, the amount of fluid inside of the reactor at a given time, and the size of the vessel (Equation 7.1.15). This spreadsheet does not price reactors himself but does price horizontal and vertical vessels which were used for decanters and the CSTR, respectively.

$$CSTR = e^{7.139 + 0.18255\ln(\ln(Weight_{Fluid})) + 0.02297(\ln(\ln(Weight_{Fluid}))^2)} + 5.4(410.3(Diameter_{Vessel})^{0.7396})(Length_{Vessel})^{0.7065} \quad (7.2.15)$$

Decanters for both the DCH Purification Column and the ECH Purification process were priced using the horizontal vessel method listed (Equation 7.2.16). The DCH decanter was estimated using a pressure rating of 2 bar, a length of 10 meters, and a diameter of 2 meters of nickel alloy material. The ECH decanter was modeled to for a pressure rating of 2 bar, length of 10 meters, and diameter of 2 meters of a stainless steel material.

$$Decanter = e^{5.6336 + 0.4599\ln(\ln(Weight_{Fluid})) + 0.00582(\ln(\ln(Weight_{Fluid}))^2)} + 2.1(2274(Length_{Vessel})^{0.20294}) \quad (7.2.16)$$

The agitator (impeller) for the Hydrochlorination CSTR was priced using the Boulder spreadsheet and was modeled based on the power required (Equation 7.2.17):

$$Agitator = 2(5033.5(Power^{0.1732})) \quad (7.2.17)$$

The piping was calculated using the Boulder spreadsheet and was done for glass lined-stainless steel, nickel alloy, and stainless steel materials.

$$Piping = 3215.5(Diameter_{piping})^2 + 857.58(Diameter_{piping}) + 25.93 \quad (7.2.18)$$

Motors for powering the pumps and agitators were calculated from the Boulder spreadsheet in which an enclosed, fan-cooled alternating current motors were selected (Equation 7.2.19):

$$Motor = 468 + 10.92 \ln \ln (Power) + 2.85(\ln \ln (Power))^2 + \frac{11.88(\ln \ln (Power))^3}{1.28 - 0.456 \ln \ln (Power) + 0.0574(\ln \ln (Power))^2 - 0.002(\ln \ln (Power))^3} \quad (7.2.19)$$

Next, the cost index was determined and applied to the two spreadsheets which the latest value was told to be 801.4 [7.3.4]. Using the design specifications listed in equipment sections and plugging these into respective equipment equations, the cumulative price of each equipment was calculated and is shown in the Table below:

Table 7.2.1: Purchase Cost of Equipment (PE)(2023 Values)

Equipment	Total Cost (\$k)	Equations Used
Reactors	498	7.1.13, 7.1.14, 7.1.15
Columns	10,522	7.1.4-7.1.11
Flash Drums	127	7.1.1
Storage Tanks	9,724	7.1.12
Pumps	66	7.1.3
Heat Exchangers	43	7.1.2
Piping	7,394	7.1.18
Decanters	18	7.1.16
Motors	140	7.1.19
Agitators	140	7.1.17

The cumulative equipment cost was totaled to be **\$28,397k** or \$28,397,110.

To implement the bare-module factor method in accounting for things such as installation, the bare module factors (F_{BM}) were collected for each type of equipment (Table 7.2.2):

Table 7.2.2: Bare-module Factors of All Equipment Types [7.2.1][7.2.6]

Equipment	Bare-module Factors
Reactors	4.3
Columns	4.3
Flash Drums	4.3
Storage Tanks	4.16
Pumps	3.4
Heat Exchangers	3.3
Piping	1.5
Decanters	4.16
Motors	3.3
Agitators	4.1

Applying the bare-module factors the PE costs of Table 7.2.1, the updated costs of equipment are as follows (Table 7.2.3):

Table 7.2.3: Adjusted Equipment Costs After F_{BM} Application [7.3.4]

Equipment	Adjusted Equipment Cost (\$k)
Reactors	2,143
Columns	45,248
Flash Drums	142
Storage Tanks	142
Pumps	226
Heat Exchangers	142
Piping	5,989
Decanters	78
Motors	462

Agitators	574
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The adjusted cumulative cost for equipment is **\$95,867k** or \$85,867,000. It was anticipated that there would be a 10% additional cost from this value in miscellaneous equipment, needed either to install or maintain equipment. This cost is **\$9,587k** or \$9,580,000 which results in a DIC equipment cost of **\$105,454k**. Bare Module costs for computers, instrumentation, spares, process machinery, were not considered in these calculations such that the total bare-module investment is the same as the DIC equipment cost.

Listed below are other parameters used to determine capital costs (Table 7.2.4):

Table 7.2.4: Capital Cost Economic Parameters For Capital Cost Estimation [7.3.4]

Parameter	Value	Units
Cost of Site Preparation	15	% of Total Bare-module Cost
Cost of Service Facilities	20	% of Total Bare-module Cost
Cost of Contingencies and Contractor's Fee	18	% of Direct Permanent Investment
Inflation	4.5	%
Inflation Period	15	years
Processing Plant Type	Fluids	

Additionally, lang factors were found based upon the processing plant type, as shown below in Table 7.2.5:

Table 7.2.5: Lang-factors For Capital Cost Estimation [7.3.4]

Consideration	Lang Factor
Installation	47
Electrical	11
Service Facilities	70
Total Direct Plant Cost	360
Engineering and Supervision	33

Construction Expenses	41
Total Direct and Indirect Plant Costs	434
Contractor's Fee and Legal Expenses	26
Contingency	44
Fixed Capital Investment	504

These variables resulted in the following costs (Table 7.2.6):

Table 7.2.6: Cumulative Capital Costs [7.3.4]

Expense	Cost (\$k)
Subtotal DIC Equipment Costs	105,454
Total Direct Permanent Investment (DPI)	105,454
Bare Module Total Depreciable Capital (TDC)	167,989
Fixed Capital Investment	325,100

In calculating the working capital, a raw-inventory start up of 6,100k kg of Catalyst was considered resulting at a total price of \$6,000k. Start up spare parts were estimated to be 2.5% of these total capital investment and so from the fixed capital investment, \$8,128k was the total cost of total working capital.

7.3 Operating Costs

Costs for species such as utilities and ingredients are shown in Tables 7.3.1 and 7.3.2, respectively:

Table 7.3.1: Utility Costs Per Unit [7.3.3]

Utility (Unit)	Cost (\$/Unit)
Cooling Water (gal)	0.000075
HP Steam (kg)	0.0105
Waste Treatment (kg)	0.33
Electricity (kWh)	0.06

Table 7.3.2: Ingredient Costs Per Unit [7.3.2]

Ingredient	Cost (\$/tonne)
Glycerol	600
HCl	191
NaOH	566
Hexanoic Acid	950

Recalling the amount of ingredients and utilities required of this process (Table 7.3.3):

Table 7.3.3: Required Amounts of Utilities and Ingredients

Ingredient/Utility (Units)	Units of Utility/Ingredient/ Tonne of Product
Glycerol (tonne)	1.064
HCl (tonne)	0.80
NaOH (tonne)	0.72
Hexanoic Acid (tonne)	0.0216
HP Steam (kg)	9223
Cooling Water (gal)	1532820
Waste Treatment (kg)	9.59
Electricity (kWh)	22.3

Using these tables in conjunction with the amount of utilities and ingredients required for this process, the cost for each of the species per tonne of product is listed below in Table 7.1.4:

Table 7.3.4: Utility and ingredients Costs Per Tonne of ECH Produced

Utility/ Ingredient	Cost of Utility/Ingredient per Tonne of Product
Glycerol	638
HCl	152
NaOH	407
Hexanoic Acid	20.5

Cooling Water	114.962
HP Steam	96.8
Waste Treatment	3.16
Electricity	1.33

The cumulative costs are thus calculated to be the following:

Table 7.3.5: Cumulative Material Costs

	Cost per Tonne Product (\$)
Total Ingredient Cost	1198
Total Utilities Cost	216
Total Catalysts Cost	20.5
Cumulative Materials Cost (Total Variable Costs)	1435

It was assumed that there would be no credit for bi-products since products are of high purity and waste streams are undesirable for usage. The purge stream out of the DCH recycle stream is not desirable as it is >50% weight the undesirable isomers, β -MCH and α,β -DCH due to low reactivity capabilities.

The DuPont shift schedule, suggested by Dr. Clough was utilized for this plant to reduce operating costs and shifts needed. The DuPont shift schedule is a four week rotation of 12 hour operator shifts. Each operator works an equal number of night shifts and day shifts throughout the 4 week cycle. Also included in every monthly shift cycle is full week off. This helps offset other weeks in which operators may work 6 shifts in a 7 day time frame [7.3.1].

Table 7.3.6: Example DuPont Shift Schedule [7.3.1]

Week 1	Four Night Shifts Three Days Off
Week 2	Three Day Shifts One Day Off Three Night Shifts
Week 3	Three Days Off Four Day Shifts
Week 4	Seven Days Off

Ultimately this reduces the number of shifts needed to operate the plant from 5 to 4, reducing that fixed cost by **20%**. Operator wages varied based on a multitude of factors, so salaries were determined off of an average of Dow Chemical salary. These ranged anywhere from \$50k up to \$100k, so the average value of **\$75k per year** was chosen. An additional economic analysis would be done with increased operator wages of \$100k per year.

Table 7.3.7: Operator Specifications and Costs

Operators Per Shift	5
Shifts Required	4
Total Number of Operators	20
Average Operator Salary	\$75k
Annual Operator Costs	\$1,500k

7.4 Profitability Analysis

Profitability analysis was carried out using the economics spreadsheet provided by Dr. Weimer of University of Colorado Boulder [Weimer.X]. A preliminary study was done using the macro solved unit selling price as a starting point. Using the capital, variable, and fixed costs also calculated within the spreadsheet, return on investment (ROI), internal rate of return (IRR), payback period (PBP), and net present value (NPV) can be determined. Shown below is a summary of these values, as well as yearly and cumulative cash flow charts.

Table 7.4.1: Preliminary profitability analysis metrics. \$ units are in (\$k)

Unit Selling Price	\$3.247/metric ton
IRR	12.0%
ROI	7.0%
PBP	14.2 years
NPV	\$96,567

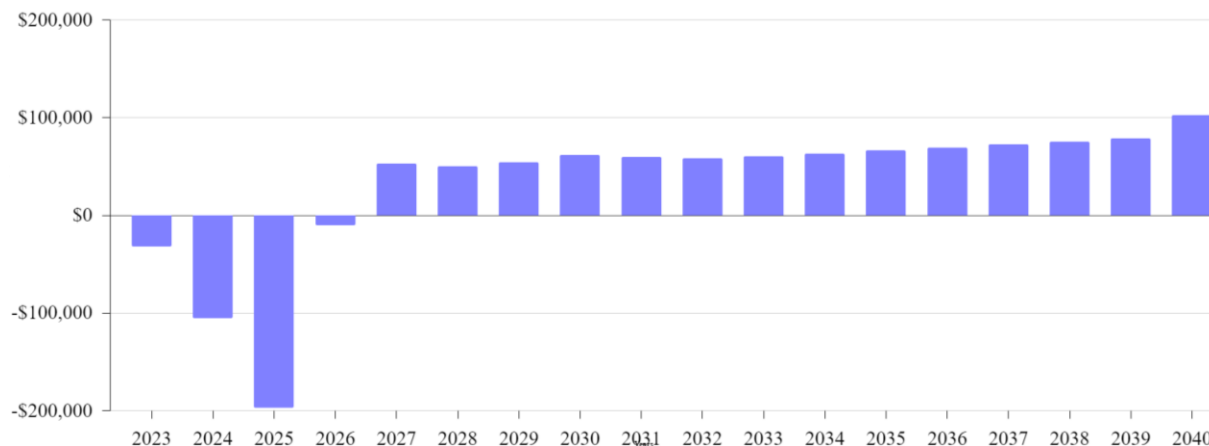


Figure 7.4.1: Yearly cash flow chart for a base case of unit selling price of \$3.247/metric ton (\$). Construction begins in 2023, with plant startup occurring in 2026. Yearly net positive profits begin in 2027. Year three startup loss can be explained by the capacity at which the plant is operating at in this first year, currently 76%.

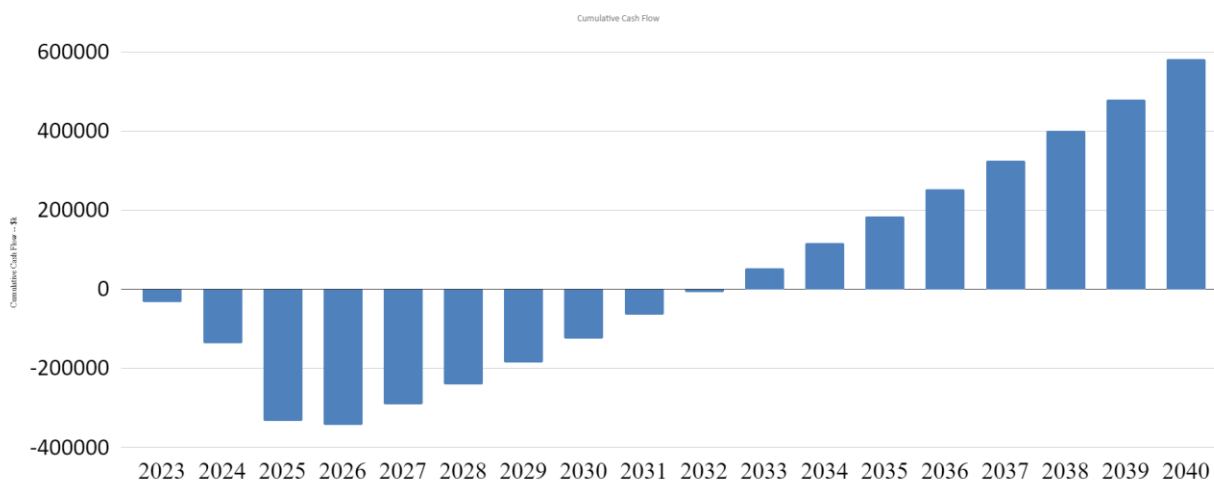


Figure 7.4.2: Cumulative cash flow chart for a base case of unit selling price of \$3.247/metric ton (\$). Construction begins in 2023, with plant startup occurring in 2026. Plant reaches a cumulative net profit in 2033. It is desirable to attempt to move the date at which cumulative profit is reached to a sooner year.

A unit selling price of \$3247 per metric ton determined by the included unit selling price macro. Return on investment is a measure of the efficiency of the net income of the process against the initial investment. The ROI for this process is fairly low at **7.0%**. Ideally, ROI would be in the range of 20%-25%. Also important to note is that extended payback period for this scenario of **14.2 years**. Again ideally, it would be advantageous to reduce this significantly. Further case studies using the economics spreadsheet can be done for several other scenarios.

Market research at the beginning of this project revealed an average market spot price for our product of approximately **\$3300** per metric ton. This figure is not far off from the suggested price set using the marco, and the effect of raising the price was tracked with the profitability metrics and cash flow charts.

Table 7.4.2: Market spot price profitability analysis metrics. \$ units are in (\$k)

Unit Selling Price	\$3.30/metric ton
IRR	20.4%
ROI	15.1%
PBP	6.6 years
NPV	\$17,583

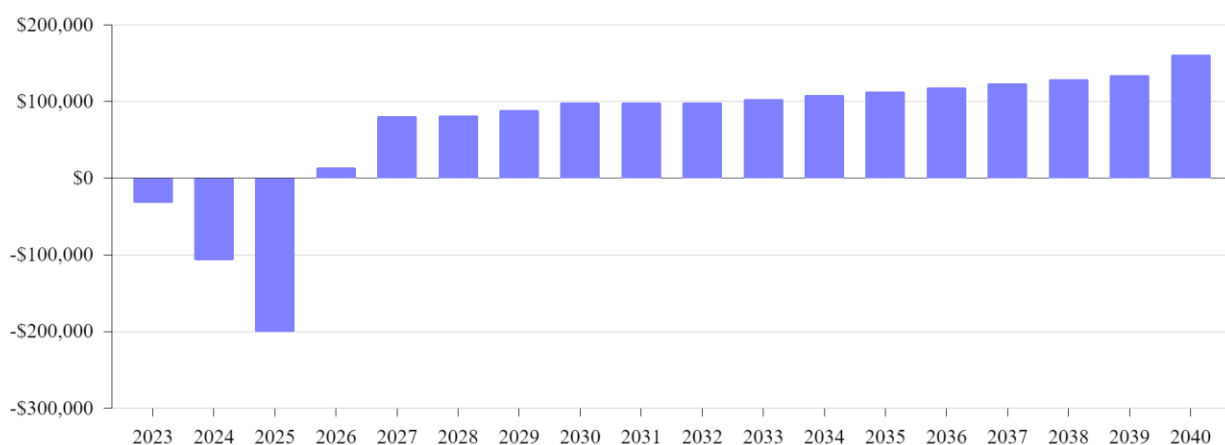


Figure 7.4.3: Yearly cash flow chart for a unit selling price of \$3.3/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. Yearly net positive profits begin a year earlier in 2026. Year three startup instead produces a profit, however only a marginal one due to the 76% operating capacity.

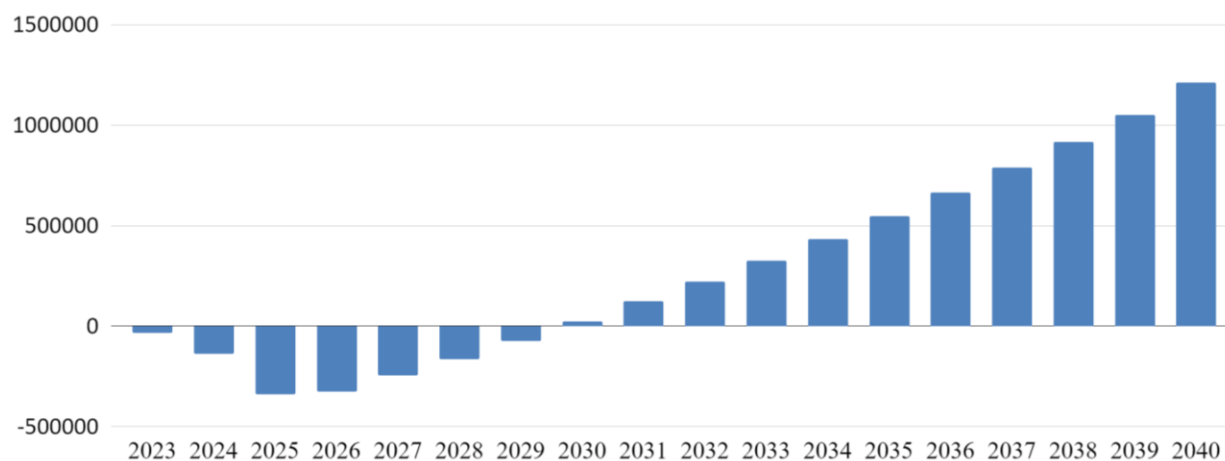


Figure 7.4.4: Cumulative cash flow chart for a unit selling price of \$3.3/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. Plant reaches a cumulative net profit in 2032, a whole year sooner than the preliminary scenario.

This scenario provides a more accurate representation of how this plant will likely fare economically, given current epichlorohydrin (and epoxy resin) market use. The ROI and IRR are much higher for this case making investment in this design more advantageous. The payback period is also reduced to only **6.6** years, much better than the preliminary scenario. However, other potential economic changes are very possible with this process, so other scenarios were observed in yet another case study: the price of the raw starting materials. Both a 25% increase and decrease in the purchase price of the starting reactants.

Table 7.4.3: 25% increase in starting material price analysis metrics. \$ units are in (\$k)

Unit Selling Price	\$3.30/metric ton
IRR	2.3%
ROI	0.4%
PBP	247.3 years
NPV	\$161,680

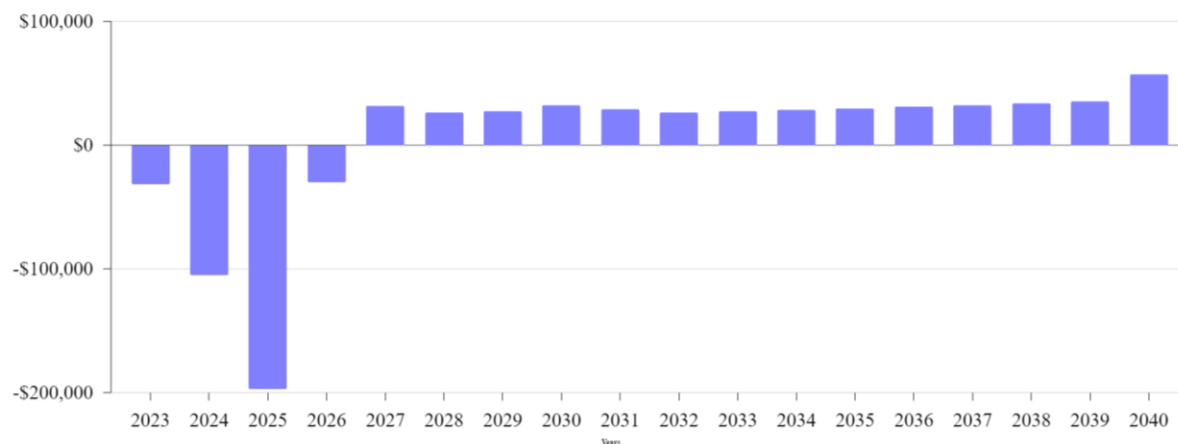


Figure 7.4.5: Yearly cash flow chart for a unit selling price of \$3.30/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. Yearly net positive profits begin again in 2027. It is also important to note that the yearly cash flow averages to only 20% of the two previous scenarios; profits are significantly limited after a starting materials price increase.

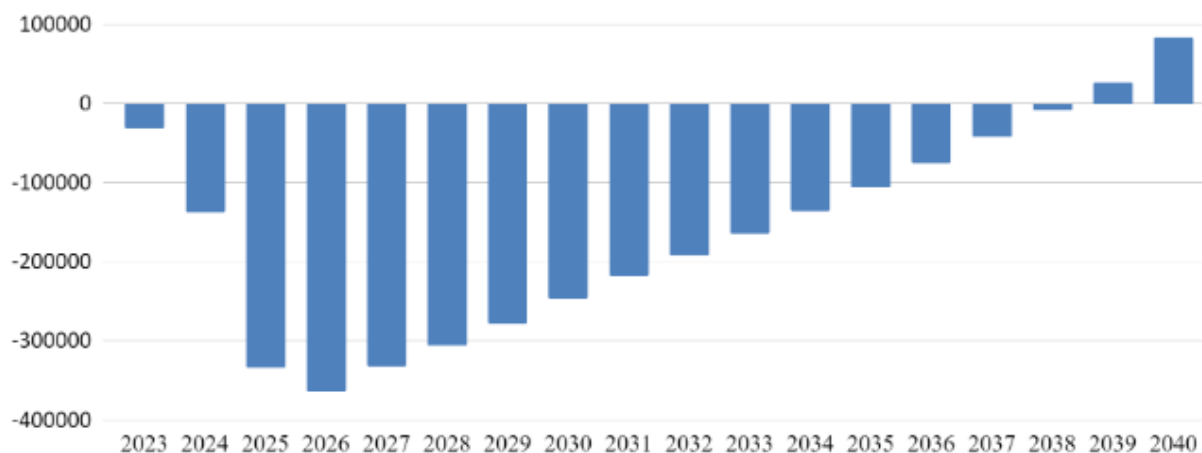


Figure 7.4.6: Cumulative cash flow chart for a unit selling price of \$3.30/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. The plant reaches a cumulative net profit in 2039, significantly later than the previous two scenarios.. The plant operates at a loss for a significant portion of the lifespan.

According to this information, an increase in the starting material cost would be catastrophic for this plant economically. An IRR of only **2.3%** is not sufficient in any way, and a **0.4% ROI** and **247.3 year PBP** means that in this scenario, the process would not be a worthwhile investment. However, due to the use of mainly byproducts as reactants, it is quite feasible to consider a significant drop in starting material purchase price as well, shown below.

Table 7.4.4: 25% decrease in starting material price analysis metrics. \$ units are in (\$k)

Unit Selling Price	\$3.30/metric ton
IRR	25.4%
ROI	20.9%
PBP	4.8 years
NPV	\$39,565

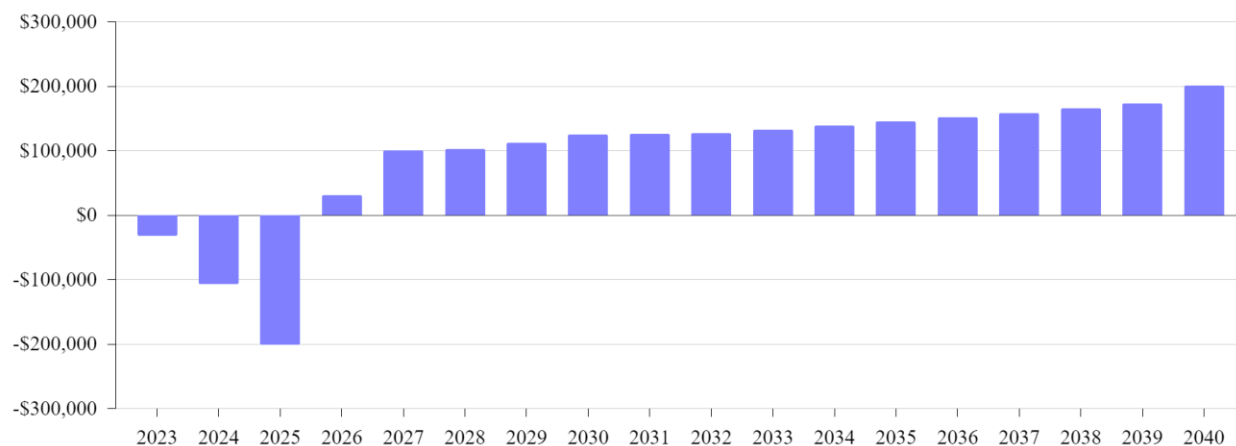


Figure 7.4.7: Yearly cash flow chart for a unit selling price of \$3.30/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. Yearly net positive profits begin a year earlier in 2026. Profit is achieved in the first operating year at only 76% capacity, again showing that the starting materials are a significant portion of costs within this process.

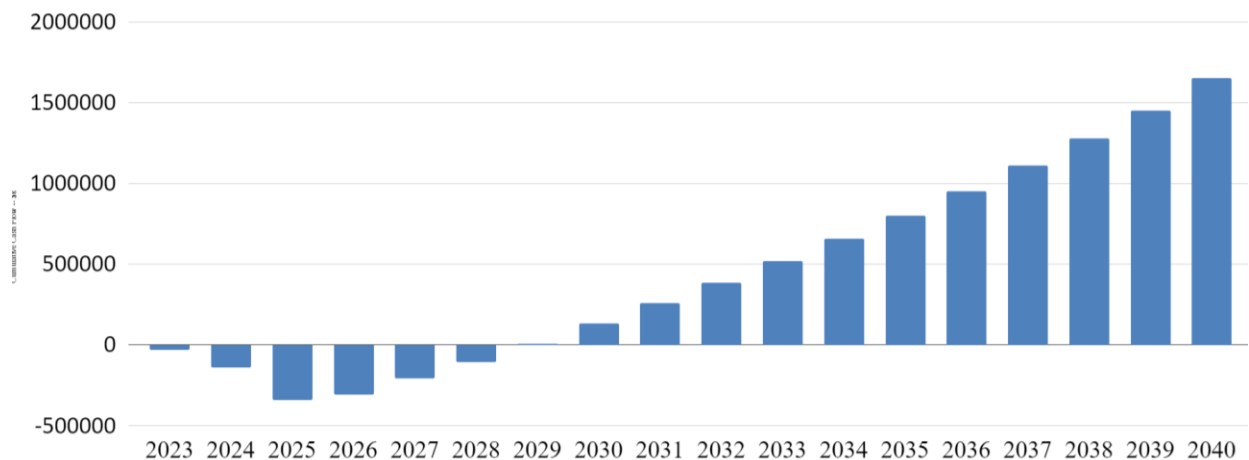


Figure 7.4.8: Cumulative cash flow chart for a unit selling price of \$3.30/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. The plant reaches a

cumulative net profit in 2029, slightly earlier than the market spot scenario. This scenario also reaches a much higher end cumulative cash amount of over \$1.5 million.

This scenario provides a much better outlook on this plant. Both the IRR and ROI are up to considerable and sufficient levels to make this process favorable. PBP has been reduced to only **6.4 years**, a significant improvement from the base case and market spot price scenarios. It is likely that the true economics of this plant will lie somewhere between this scenario and the market spot price scenario.

The last economic scenario that was observed for this process was a 33% increase in operator wages. All previous scenarios have used a figure of \$75k per year per operator, the average salary of a chemical plant operator employed by Dow Chemical. This plant will also run on the Du-Pont shift schedule, with 4 shifts of 5 operators each, as recommended by Dr. Hook. However, due to the health concerns of the product produced and intermediate compounds within, extra worker compensation may be needed.

Table 7.4.5: 33% increase in operator wages analysis metrics. \$ units are in (\$k).

Unit Selling Price	\$3.30/metric ton
IRR	12.8%
ROI	14.9%
PBP	6.7 years
NPV	\$20,172

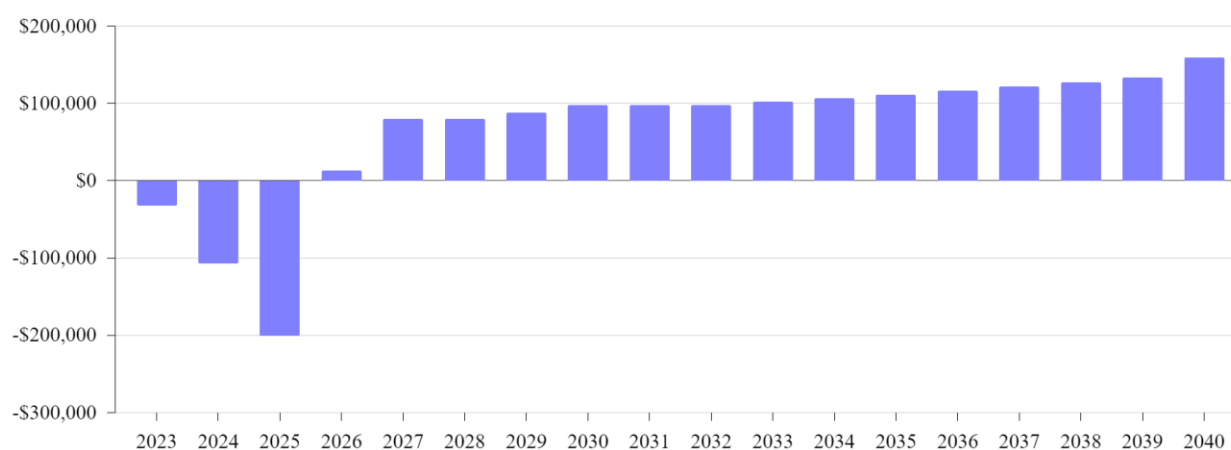


Figure 7.4.9: Yearly cash flow chart for a unit selling price of \$3.30/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. Yearly net positive profits begin a year earlier in 2026. Profit is achieved in the first operating year at only 76% capacity, showing that even a significant increase in worker wages this process is still economically viable.

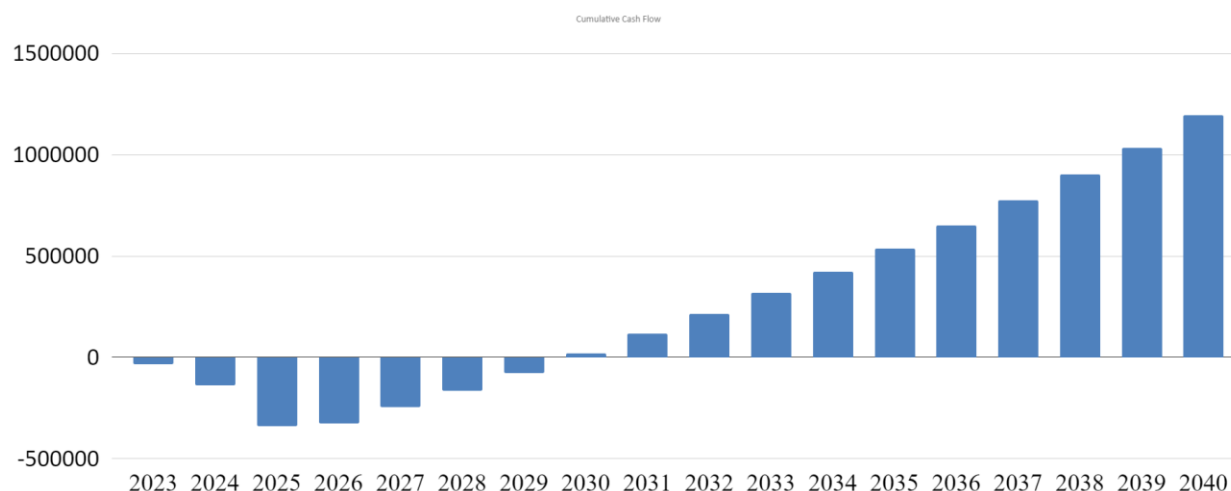


Figure 7.4.10: Cumulative cash flow chart for a unit selling price of \$3.30/metric ton (\$k). Construction begins in 2023, with plant startup occurring in 2026. The plant reaches a cumulative net profit in 2030, notably earlier than the base case and market spot scenarios. This scenario also reaches a much higher end cumulative cash amount.

8 Safety, Environmental, and Health Considerations

Any design of a chemical processing facility must of course be concerned first and foremost with the safety of its employees and the community at large. Many considerations must be made in order to ensure the health and safety of those on and off-site. On-site staff and the process and facilities themselves are protected in part by the parameters of the process being monitored and controlled through instrumentation that alert operators to deviations from nominal process operation in order for the deviation to be corrected as quickly and safely as possible. On-site staff specifically are also physically protected from injury by use of personal protective equipment (PPE), the creation and distribution of appropriate standard operating procedures (SOP) for individual operation units, and the distribution of relevant chemical hazard information in case of spills or leaks.

8.1 Chemical Hazards

Table 8.1.1: Chemical Hazards Summary.

Chemical Name	Flammability	Corrosivity	Special Considerations	Source
Glycerol	Flammable	Not Corrosive	Can develop combustible gas in the event of a fire	[8.1.1]
Hydrochloric Acid	Not flammable	Very corrosive to skin and metals	Toxic if inhaled, can cause burns to skin and eye damage	[8.1.2]

Hexanoic Acid	Not flammable	Corrosive to skin	Can cause burns to skin and eye damage	[8.1.3]
Monochlorohydrin	Not Flammable	Corrosive to skin, some corrosivity towards metals	Carcinogenic, toxic if inhaled or swallowed,	[8.1.4]
Dichlorohydrin	Flammable	Not corrosive	Carcinogenic, acutely toxic to skin and if swallowed,	[8.1.5]
Sodium Hydroxide	Not flammable	Highly corrosive to metals and to skin	Can cause severe burns to eyes and skin	[8.1.6]
Epichlorohydrin	Flammable	Highly corrosive to skin	Carcinogenic, can cause severe burns to skin and eyes	[8.1.7]
Glycidol	Combustible as a liquid	Not corrosive	Carcinogenic, fatal if inhaled	[8.1.8]

8.2 Personal Protective Equipment

Understanding the chemical species present in this process, and the threats that they pose to on-site employees, personal protective equipment (PPE) is required. The Occupational Health and Safety Administration (OSHA) describes the distribution of PPE to employees as a responsibility of the employer, to overall ensure the health and safety of employees as it relates to physical injury and harm due to contact with hazardous chemical species [8.2.1]. Compliance with OSHA regulations also necessitates the employer to make material safety data sheets (MSDS) available to employees and first responders by placing collections of pertinent MSDS around the workplace where staff could be exposed to these chemicals. With these in mind, it is recommended that all personnel in the facilities of this process have access to hard hats, to prevent physical cranial injuries, safety glasses, to prevent eye damage due to liquid splash, and corrosive-resistant coveralls so that in the event that one of the corrosive materials comes into contact with staff, personnel can take off the coveralls after leaving the spill area and be minimally harmed.

8.3 Standard Operating Procedures and Instrumentation

A necessity in minimizing damage to equipment and to on-site personnel is the distribution of knowledge to ensure that any facility staff that comes into contact with a piece of equipment knows how to use it. This is done through the creation and maintenance of standard operating procedures (SOPs). OSHA outlines in the Occupational Health and Safety Standards that employers are responsible for ensuring SOPs are up to date and understood by all employees who might operate a specific operation unit [8.2.1]. All pieces of equipment must have associated SOPs that specifically speak to the operation of that equipment, with no exceptions. SOPs should outline the parameters of a unit that need to be controlled within a certain range to ensure nominal operation as well as equipment-specific procedures that aid in the control of those parameters. Additionally, SOPs should inform an operator to document pertinent parameters for a unit's operation so that deviations from nominal operation can be investigated

and corrected in a timely manner. Finally, SOPs should also contain the information which would allow an operator to correct deviations and document their solution for further reference.

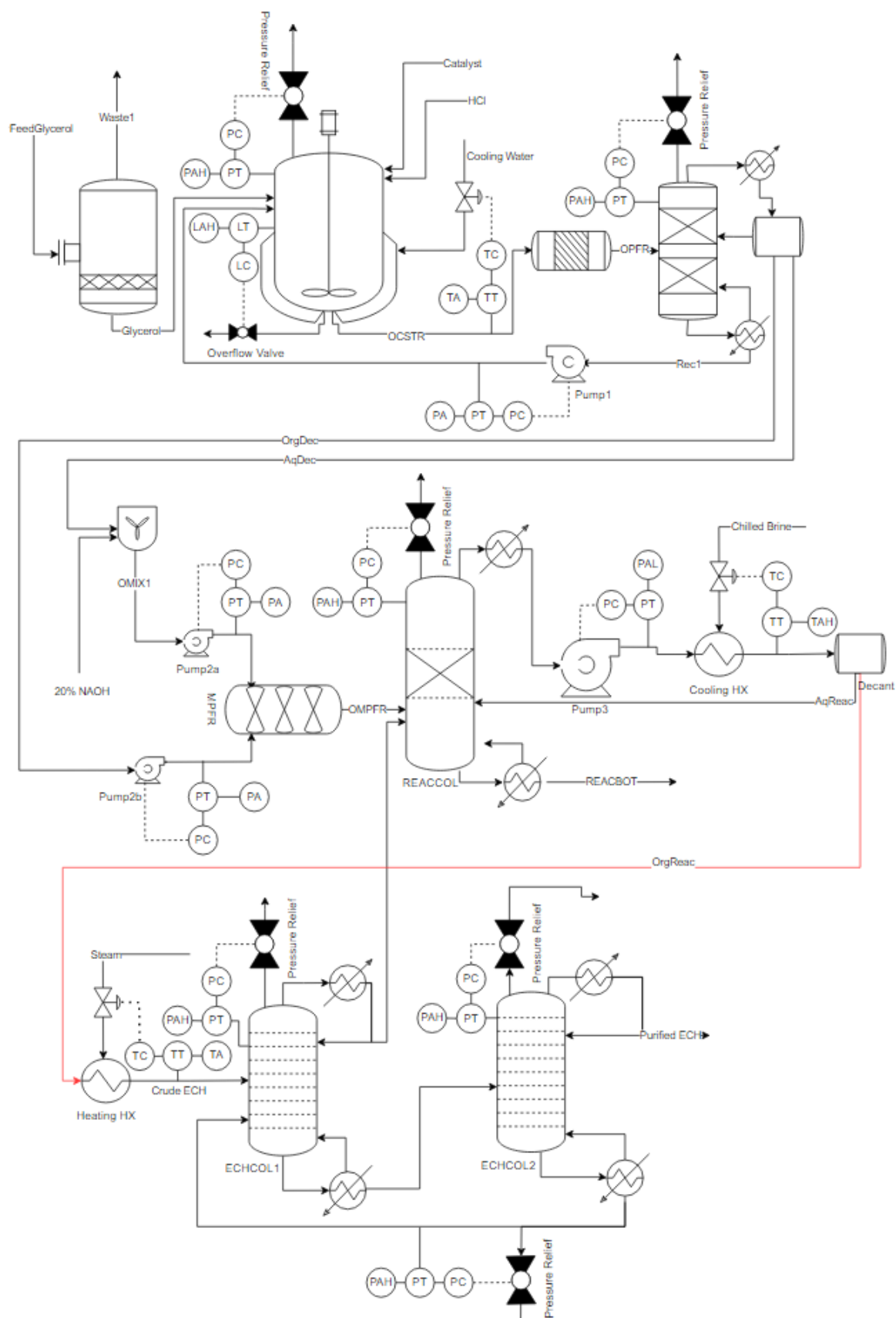


Figure 8.3.1: Overall Process and Instrumentation Diagram (P&ID). The base level of instrumentation which would allow for safe process operation is outlined in this figure. Operation units must be monitored so that parameters like pressure and temperature are held within safe ranges. This is accomplished through use of temperature transmitters, controllers and alarms (TT, TC, TA, respectively), pressure transmitters, controllers, and high pressure alarms (PT, PC, PAH, respectively). Liquid level must also be monitored and controlled via use of level transmitters, controllers, and high level alarms (LT, LC, LAH, respectively) to minimize employee contact with hazardous materials.

8.4 HAZOP Analysis and Worst Case Scenario

Table 8.4.1: HAZOP Study of the Hydrochlorination CSTR

Deviation	Possible Causes	Consequences	Safeguards	Recommendations
High Pressure	- HCl feed rate too high	- Vessel Rupture	- PC and PAH with pressure relief	- Pressure control on HCl inlet
High Flow	- Piping blockage	- Vessel Overflow	- LC and LAH with overflow protection	- Flow control on liquid inlets
High Temperature	- Insufficient cooling water - HCl feed rate too high	- Runaway reaction - NNC	- TC and TA on CSTR outlet controls cooling water flow	- NNR - NNR
High Level	- Glycerol feed rate too high - Piping blockage	- Vessel Rupture - Vessel/Piping Leakage	- LC and LAH with overflow protection - LC, PC, LAH, PAH with overflow protection	- NNR - NNR

Table 8.4.2: HAZOP Study of the DCH Purification Distillation Column

Deviation	Possible Causes	Consequences	Safeguards	Recommendations
High Pressure	- Apparatus failure or leakage - HCl feed rate too high	- Poor separation, excess vapor - Downstream equipment corrosion	- PC and PAH with pressure relief - PC and PAH with pressure relief	- NNR - NNR
High	- Reboiler	- Catalyst	- TC and TA on	- Apply TA to

Temperature	Malfunction	contaminates downstream process	CSTR outlet	bottom stage of column
Low Flow	- OPFR piping blockage - Upstream composition change	- Poor separation, excess vapor - Recycle stream composition change	None	- Apply flow or composition controls to OPFR stream and shut down column - NNR

This hazard and operability (HAZOP) study conducted around two unit operations offers a first glance at some safety concerns that are not immediately addressed by the instrumentation of the process. Deviations that are caused by upstream composition changes are largely not protected against. While it would be wise to apply some composition measurement devices to monitor compositions before the inlet of the reaction units, it would be excessive and costly to apply composition monitoring devices around every or even almost every reaction unit. The most important units to monitor composition and flow for, and to keep these in a given range, would be the separator units, especially the glycerol flash drum which could be subject to a change in fed crude glycerol composition, which could greatly affect the ability of this process to produce ECH at specifications. Furthermore, this process could be prone to piping corrosion if the HCl is allowed to go past the DCH purification distillation column, where piping is no longer glass-lined but constructed of nickel alloy which is resistant to acid corrosion, however overexposure to the strong acid HCl would eventually cause damage to the piping which could result in a spill.

Based on the current level of instrumentation, and assuming the recommendations of the HAZOP study were carried out, the worst case scenario surrounding this process would involve leakage of HCl into the plant facilities. If the hydrochlorination CSTR vessel were to rupture or leak, there would be release of anhydrous HCl, supplied via pressurized pipeline, into the plant. HCl is a strong acid, which when inhaled, causes irreparable damage to lung tissues, not to mention damage to the eyes and skin which can occur even at low gaseous concentrations. To safeguard against this event, an emergency shut off valve should be implemented on the CSTR anhydrous HCl feed line, and high-volume ventilation systems should be operational if a leak were to occur.

8.5 Waste Considerations

The impact of this process on the natural environment in the vicinity of the plant largely is determined by the treatment of the waste streams this process creates. The individual waste streams of this process contain significant amounts of water, not only because of the water supplied to this process system but also the water that is created by the hydrochlorination, ECH production, and hydrolysis reactions. It was assumed that steam and cooling water used as utilities in this process are recyclable internally, so that these do not add to the overall volume of the waste streams. Due to our plant being located in the Gulf Coast region of the United States, it was assumed that the exact location would be within the service range of an industrial waste management firm which could aid this process in disposing of the waste water streams while being compliant with local laws and regulations. One such industrial waste management company is Excel Industrial Group, located in Houston, Texas. Excel Industrial Group offers a

drum-waste pickup service, where a routine pickup schedule is established for the transportation of 55 gallon drums from a process facility to their waste management site [8.5.1]. This ECH production process could contractually do business with Excel Industrial Group or another such waste management company by first centralizing the waste streams of this process into a storage tank, which then is used to fill 55 gallon drums to be picked up by the waste management company.

Table 8.4.1: Waste Water Stream Specifications

Waste Stream	Mass Flow Rate (kg/hr)	Mass Fraction of Water	Primary Impurity	Mass Fraction of Primary Impurity
Waste Water 1	1,393	0.38	Glycerol	0.62
Waste Water 2	28,179	0.63	NaCl	0.33
Waste Water 3	5,793	0.13	ECH	0.84
Mixed Wastewater	35,365	0.54	NaCl	0.26

Acknowledgements

This report would not have been possible without the help of several important people. Dr. Bruce Hook provided so much meaningful guidance for this project and overcoming the setbacks mentioned would not have been possible without his advice. His experience in this industry not only made it possible to avoid the mistakes made in this project but also to progress things that would have otherwise taken a longer amount of time. It can not go unsaid how appreciated it is that he put in the time and effort to offer his services throughout the duration of these projects as it will leave a lasting impact.

Dr. Alan Weimer was the one who made this project possible, not only through his years of experience at Dow Chemical but also through his efforts towards garnering projects of this caliber on a consistent basis. He took a lot of faith in the authors to not only complete this project but to also complete this project at a higher level than previously done. The team in charge of this project was dropped two members in the early duration and Dr. Weimer had to graciously be in more frequent communication with members of this group regarding things such as logistics, deadlines, and expectations. His consistent willingness to keep the hope of this project alive despite major setbacks also made this project possible.

Dr. David Clough, a professor Emeritus at the University of Colorado Boulder who specializes in Aspen Plus, was a huge help to this project. It was identified early on that Aspen simulations would be challenging for reasons pertaining to azeotropes, kinetics, and selected fluid packages. The expertise required to design this project through simulation software was not up to par but Dr. Clough alleviated this learning curve through consistent communication.

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Appendices

A.1: Chemical Species Notations

Species	Chemical Formula	Abbreviation	Notes
Glycerol	C ₃ H ₈ O ₃	GLY	
Water	H ₂ O	H ₂ O	Reactant and Cooling Utility
Hydrogen Chloride	HCl	HCl	
Hexanoic Acid	C ₆ H ₁₂ O ₂	CAT	Catalyst
3-Monochloropropane-1,2-diol	C ₃ H ₇ ClO ₂	α-MCH	1/2 MCH Isomers
2-Monochloropropane-1,3-diol	C ₃ H ₇ ClO ₂	β-MCH	2/2 MCH Isomers
1,3-Dichloropropan-2-ol	C ₃ H ₆ Cl ₂ O	α,γ-DCH	1/2 DCH Isomers
1,2-Dichloropropan-3-ol	C ₃ H ₆ Cl ₂ O	α,β-DCH	2/2 DCH Isomers
Epichlorohydrin	C ₃ H ₅ ClO	ECH	Desired Product
Glycidol	C ₃ H ₆ O ₂	GL	Undesired hydrolysis product
Sodium Hydroxide	NaOH	NaOH	Caustic Soda
Sodium Chloride	NaCl	NaCl	
Methanol	CH ₃ OH	MeOH	

A.2: Species Properties

Species	MW	Density -kg/m ³ (at T _{room})
Glycerol	92.09	1263.8
Water	18.01	997.87
Hydrogen Chloride	36.46	Liquid: 1194.3 Gas: 1.49
Hexanoic Acid	116.16	927.2
3-Monochloropropane-1,2-diol, 2-Monochloropropane-1,3-diol	110.54	1350.0
1,3-Dichloropropan-2-ol,	114.92	1350.0

1,2-Dichloropropan-3-ol		
Epichlorohydrin	92.52	1180.0
Glycidol	74.08	1110.0
Sodium Hydroxide	39.98	2130.0
Sodium Chloride	58.44	2160.0
Methanol	32.04	792.0

A.3 Aspen Full Stream Summary

Stream Name	Units	23DCH	AQ	BOT	CAT	COOLED	CRUDEECH	DECAQ	DECORG	ECHBOT1
Description										
From			DCHCOL	DCHCOL		HX2	HX1	DECANT	DECANT	ECHCOL1
To		ORGMIX	AQMIX	SPLIT	CSTR	DECANT	ECHCOL1	RECMIX	HX1	ECHCOL2
Stream Class		CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN
Maximum Relative Error										
Cost Flow	\$/hr									
MIXED Substream										
Phase		Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase
Temperature	C	12	12.75988209	108.9807249	25	0	125	0	0	175.6858205
Pressure	bar	1	0.015	0.028	1	4	6	4	4	4.5
Molar Vapor Fraction		0	0	0	0	0	0	0	0	0
Molar Liquid Fraction		1	1	1	1	1	1	1	1	1
Molar Solid Fraction		0	0	0	0	0	0	0	0	0
Mass Vapor Fraction		0	0	0	0	0	0	0	0	0
Mass Liquid Fraction		1	1	1	1	1	1	1	1	1
Mass Solid Fraction		0	0	0	0	0	0	0	0	0
Molar Enthalpy	cal/mol	-91630.18928	-68578.26239	-118408.4626	-138909.0118	-65298.55822	-38189.56797	-68360.93892	-42532.02025	-31010.99774
Mass Enthalpy	cal/gm	-710.3917255	-3708.819483	-1029.517004	-1195.84122	-2504.017761	-481.0417221	-3630.229149	-535.7399247	-332.6196701
Molar Entropy	cal/mol-K	-119.4776811	-39.87688899	-125.3811812	-176.005943	-44.81220462	-63.30965835	-40.73991272	-76.62821064	-65.66539351
Mass Entropy	cal/gm-K	-0.9262881228	-2.156604405	-1.090142167	-1.515201633	-1.718423184	-0.7974582773	-2.163446275	-0.9652208278	-0.7043179233
Molar Density	mol/cc	0.010733864910	0.0547668764	0.00923959346	0.00799750196	0.0373324749	0.0098921552	0.0536787304	0.0117092476	0.0077453570
Mass Density	gm/cc	1.384512289	1.012671886	1.062678961	0.9289904701	0.9735381374	0.7853313317	1.01082556	0.9295890317	0.7221198033
Enthalpy Flow	cal/sec	-338013.5871	-3951388.598	-3074464.159	-92220.14948	-35673780.14	-2496574.321	-32877840.53	-2780454.329	-1544131.172
Average MW		128.98544	18.49059053	115.0136055	116.16008	26.07751399	79.38930494	18.83102584	79.38930494	93.23260326
Mole Flows	kmol/hr	13.28	207.4272292	93.47364818	2.39	1966.744933	235.3435253	1731.401408	235.3435253	179.2548652
H2O	kmol/hr	0	206.5387711	0	0	1754.461892	42.11916971	1712.342655	42.11916971	0.1131256662
GLY	kmol/hr	0	0	0	0	0.0374656108	0.00122199061	0.0362436188	0.00122199061	0.0036647339
HYDRO-01	kmol/hr	0	0	0	0	0	0	0	0	0
A-MCH	kmol/hr	0	0	29.25039336	0	0.8640472957	0.5081521338	0.3558953244	0.5081521338	1.507654781
2-CHL-01	kmol/hr	0	0	24.9351768	0	0	0	0	0	0
1-3-D-01	kmol/hr	0	0.880242671	1.825399223	0	0.0002911278	0.0002827607	0.0000083672	0.0002827607	0.0007959790
2-3-D-01	kmol/hr	13.28	0.0082154995	13.56268755	0	1.294161908	1.252904449	0.0412579007	1.252904449	3.531545405
N-HEX-01	kmol/hr	0	0.000000042	23.89999126	2.39	0.0000000984	0.0000000968	0.000000016	0.0000000968	0.0000002826
ECH	kmol/hr	0	0	0	0	208.8132484	191.0323863	17.78092881	191.0323863	172.9788503
NAOH	kmol/hr	0	0	0	0	0	0	0	0	0
NACL	kmol/hr	0	0	0	0	0	0	0	0	0
GLI	kmol/hr	0	0	0	0	1.273827043	0.4294078875	0.8444192666	0.4294078875	1.119228052
H3O+	kmol/hr	0	0	0	0	0	0	0	0	0
NA+	kmol/hr	0	0	0	0	0	0	0	0	0
NACL(S)	kmol/hr	0	0	0	0	0	0	0	0	0
NAOH(S)	kmol/hr	0	0	0	0	0	0	0	0	0
NAOH(S)	kmol/hr	0	0	0	0	0	0	0	0	0
CL-	kmol/hr	0	0	0	0	0	0	0	0	0
OH-	kmol/hr	0	0	0	0	0	0	0	0	0
Mass Flows	kg/hr	1712.926643	3835.45196	10750.7413	277.6225912	51287.818518	18683.758897	32604.064658	18683.758897	16712.397731
H2O	kg/hr	0	3720.853791	0	0	31607.122228	758.788636	30848.332379	758.788636	2.037991
GLY	kg/hr	0	0	0	0	3.450385	0.112539	3.337846	0.112539	0.337503
HYDRO-01	kg/hr	0	0	0	0	0	0	0	0	0
A-MCH	kg/hr	0	0.0000000004	3233.340821	0	95.51185719	56.17117752	39.34069763	56.17117752	166.6562801
2-CHL-01	kg/hr	0	0	2756.336438	0	0	0	0	0	0
1-3-D-01	kg/hr	0	113.5384882	235.4499219	0	0.0375512555	0.0364720207	0.0010792476	0.0364720207	0.1026697128
2-3-D-01	kg/hr	1712.926643	1.059679829	1749.389221	0	166.9280432	161.6064316	5.321668478	161.6064316	455.517938
N-HEX-01	kg/hr	0	0.0000004955	2776.224897	277.6225912	0.0000114394	0.0000112490	0.0000001904	0.0000112490	0.0000328272
ECH	kg/hr	0	0	0	0	19320.40405	17675.23333	1645.176882	17675.23333	16004.83353
NAOH	kg/hr	0	0	0	0	0	0	0	0	0
NACL	kg/hr	0	0	0	0	0	0	0	0	0
GLI	kg/hr	0	0	0	0	94.364394	31.81029584	62.55410639	31.81029584	82.91178733
H3O+	kg/hr	0	0	0	0	0	0	0	0	0
NA+	kg/hr	0	0	0	0	0	0	0	0	0
NACL(S)	kg/hr	0	0	0	0	0	0	0	0	0
NAOH(S)	kg/hr	0	0	0	0	0	0	0	0	0
NAOH(S)	kg/hr	0	0	0	0	0	0	0	0	0
CL-	kg/hr	0	0	0	0	0	0	0	0	0
OH-	kg/hr	0	0	0	0	0	0	0	0	0

Stream Name	ECHBOT2	ECHDIS1	ECHDIS2	FGLY	GLY	HCL	NAOH	OCSTR	OMIX1	OMIX2
Description										
From	ECHCOL2	ECHCOL1	ECHCOL2		FLASH			CSTR	AQMIX	ORGMIX
To	ECHCOL1	RECMIX		FLASH	CSTR	CSTR	AQMIX	PFR	ORGMIX	MPFR
Stream Class	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN
Maximum Relative Error	0.00009594284									
Cost Flow										
MIXED Substream										
Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Vapor Phase	Liquid Phase			Liquid Phase
Temperature	185.4626539	148.3828214	156.5269925	80	250	25	40	80	27.23210878	31.37267191
Pressure	5	4.5	3	5	1	1	1	1	0.015	0.015
Molar Vapor Fraction	0	0	0	0	0	1	0	0.2436481382	0.0217483156	0
Molar Liquid Fraction	1	1	1	1	1	0	1	0.7563518618	0.9782516843	1
Molar Solid Fraction	0	0	0	0	0	0	0	0	0	0
Mass Vapor Fraction	0	0	0	0	0	1	0	0.1216558157	0.0210488968	0
Mass Liquid Fraction	1	1	1	1	1	0	1	0.8783441843	0.9789511032	1
Mass Solid Fraction	0	0	0	0	0	0	0	0	0	0
Molar Enthalpy	-37297.18941	-47128.20889	-29979.46885	-140264.7813	-143330.7734	-22060	-63258.58162	-79201.37665	-64270.11857	-67730.73088
Mass Enthalpy	-389.0150795	-777.865104	-324.2334145	-1815.047894	-1629.07878	-605.036006	-3376.553512	-1225.99189	-3439.077514	-2180.571379
Molar Entropy	-67.35882593	-52.07562583	-67.05265489	-121.1513892	-114.1290193	2.407491301	-31.54366415	-62.7497074	-33.91315531	-44.27430145
Mass Entropy	-0.7025622961	-0.8595236921	-0.725186672	-1.567717653	-1.29717547	0.0660298695	-1.683706262	-0.9713294849	-1.814684218	-1.425398387
Molar Density	0.0077950924	0.0126312163	0.0079862511	0.0155527049	0.0114120473	0.0000403401	0.0751361477	0.0001388263	0.0000276109	0.0428150678
Mass Density	0.7473618794	0.7652825667	0.7384296514	1.201894872	1.004062908	0.0014708291	1.407650172	0.0089684431	0.0005159994	1.329878888
Enthalpy Flow	-418901.2114	-1263583.87	-1156053.802	-7430328.551	-6038857.282	-1722518.333	-15496910.58	-11424638.24	-19447873.14	-24853835.7
Average MW	95.87594767	60.58660897	92.4626134	77.278832	87.98271466	36.46064	18.73465988	64.60187648	18.68818551	31.0610015
Mole Flows	40.43319041	96.5218505	138.8214617	190.7049121	151.6763337	281.1	881.9179418	519.292712	1089.345171	1321.022339
H2O	0.0000310833	42.00607513	0.1130945835	38.14098242	8.419257675	0	562.0258312	175.3795821	768.5646023	851.5471737
GLY	0.0036647645	0.0012220212	0	152.5639297	143.257076	0	0	37.64323635	0	0
HYDRO-01	0	0	0	0	0	281.1	0	114.1396756	0	0
A-MCH	1.507651834	0.5081491866	0.0000000281	0	0	0	0	67.80277561	0	0
2-CHL-01	0	0	0	0	0	0	0	25.23158497	0	0
1-3-D-01	0.0007952229	0.0002820045	0.0000006842	0	0	0	0	62.79465431	0.880242671	135.189022
2-3-D-01	3.52769112	1.249050163	0.0035158289	0	0	0	0	12.40121097	0.0082154995	14.39403194
N-HEX-01	0.0000002826	0.000000968	0	0	0	0	0	23.89999213	0.000000042	0.0000008741
ECH	34.29225735	52.34579331	138.6867199	0	0	0	0	0	0	0
NAOH	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0
GLI	1.101098757	0.411278592	0.0181306604	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0
NA+	0	0	0	0	0	0	159.9460553	0	159.9460553	159.9460553
NACL(S)	0	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0	0
CL-	0	0	0	0	0	0	0	0	0	0
OH-	0	0	0	0	0	0	159.9460553	0	159.9460553	159.9460553
Mass Flows	3876.570448	5847.931614	12835.79515	14737.45286	13344.89559	10249.0859	16522.43268	33547.28364	20357.88464	41032.27686
H2O	0.000560	756.751205	2.03743	687.12048	151.67528	0	10125.05272	3159.512278	13845.90651	15340.86077
GLY	0.337505	0.112542	0	14050.3324	13193.2203	0	0	3466.743311	0	0
HYDRO-01	0	0	0	0	0	10249.0859	0	4161.605621	0	0
A-MCH	166.6559543	56.17085174	0.000003111970	0	0	0	0	7494.92424	0.000000004	0.0000000580
2-CHL-01	0	0	0	0	0	0	0	2789.101421	0	0
1-3-D-01	0.1025721771	0.0363744851	0.0000882533	0	0	0	0	8099.596116	113.5384882	17437.41548
2-3-D-01	455.0207912	161.1092849	0.4534907503	0	0	0	0	1599.575653	1.059679829	1856.620544
N-HEX-01	0.0000328272	0.00001124905	0	0	0	0	0	2776.224998	0.0000004955	0.00010154290
ECH	3172.884253	4843.284057	12831.96103	0	0	0	0	0	0	0
NAOH	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0
GLI	81.56877927	30.46728778	1.343109173	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0
NA+	0	0	0	0	0	0	3677.035053	0	3677.035053	3677.035053
NACL(S)	0	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0	0
CL-	0	0	0	0	0	0	0	0	0	0
OH-	0	0	0	0	0	0	2720.344914	0	2720.344914	2720.344914

Stream Name	OMPFR	OPFR	ORG	PURGE	REACBOT	REACDIS	REACREC	REC	WASTE
Description									
From	MPFR	PFR	DCHCOL	SPLIT	REACOL	REACOL	RECMIX	SPLIT	FLASH
To	REACOL	DCHCOL	ORGMIX				REACOL	CSTR	
Stream Class	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN
Maximum Relative Error								0.00004026281	
Cost Flow									
MIXED Substream									
Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Vapor Phase
Temperature	35	154.1915171	12.75988209	109.8158761	158.8638892	129.6718839	14.79073794	109.8158761	250
Pressure	5	1	0.015	0.028	4	4	4	0.028	1
Molar Vapor Fraction	0	0	0	0	0	0	0	0	1
Molar Liquid Fraction	1	1	1	1	1	1	1	1	0
Molar Solid Fraction	0	0	0	0	0	0	0	0	0
Mass Vapor Fraction	0	0	0	0	0	0	0	0	1
Mass Liquid Fraction	1	1	1	1	1	1	1	1	0
Mass Solid Fraction	0	0	0	0	0	0	0	0	0
Molar Enthalpy	-61637.25343	-79200.56322	-83538.68982	-118408.4626	-62342.51499	-62525.73803	-67239.77801	-118408.5897	-74107.8613
Mass Enthalpy	-2178.114389	-1225.978179	-962.194257	-1029.517004	-2920.563287	-2397.687833	-3196.426254	-1029.517954	-2076.987801
Molar Entropy	-36.8380896	-62.53047195	-89.95628614	-125.2201782	-27.47874925	-36.91559865	-41.04969494	-125.2201972	-25.40313749
Mass Entropy	-1.30177074	-0.9679349617	-1.036111795	-1.088742307	-1.287298503	-1.415610348	-1.951409218	-1.088742307	-0.7119623444
Molar Density	0.0400428447	0.0163956920	0.0154513840	0.0092315621	0.0541147074	0.0332994010	0.0467377931	0.0092315607	0.0000229903
Mass Density	1.133150298	1.059193438	1.34150497	1.06175525	1.155135715	0.8683655964	0.9831726389	1.06175525	0.0008203078
Enthalpy Flow	-24825831.3	-11424638.24	-5067948.133	-307446.4159	-22874943.13	-34158938.46	-34141461.4	-2767023.839	-803423.4658
Average MW	28.29844646	64.60193549	86.82102311	115.0136055	21.34605857	26.07751399	21.03592345	115.0136229	35.68045093
Mole Flows	1449.983373	519.2980455	218.397168	9.347364818	1320.925139	1966.744933	1827.924849	84.12637834	39.02857843
H2O	980.5082081	289.5213425	82.98257144	0	990.15766	1754.461892	1754.349497	0	29.72172474
GLY	0.0000000537	0	0	0	10.34004199	0.0374656108	0.03746706994	0	9.306853684
HYDRO-01	0	0	0	0	0	0	0	0	0
A-MCH	5.640667101	29.25039336	0	2.925039336	0.505997271	0.8640472957	0.8640459199	26.32535148	0
2-CHL-01	0	24.9351768	0	2.49351768	0	0	0	22.44165423	0
1:3-D-01	0.8301287373	137.0144212	134.3087793	0.1825399223	0.0000008624	0.00029112786	0.0002903863	1.642793157	0
2:3-D-01	14.15122369	14.67671949	1.105816445	1.356268755	0.0103171640	1.294161908	1.290357939	12.20658734	0
N-HEX-01	0.0000008741	23.89999213	0.0000008698	2.389999126	0.0000008741	0.00000009848	0.00000009848	21.50999213	0
ECH	128.9588758	0	0	0	0.0000052245	208.8132484	70.12744441	0	0
NAOH	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0
GLI	0.0021585734	0	0	0	0.0190059974	1.273827043	1.255745723	0	0
H3O+	0	0	0	0	0	0	0	0	0
NA+	159.9460553	0	0	0	159.9460553	0	0	0	0
NACL(S)	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0
CL-	134.6038601	0	0	0	159.946059	0	0	0	0
OH-	25.34219524	0	0	0	0	0	0	0	0
Mass Flows	41032.27686	33547.65883	18961.46557	1075.07413	28196.54539	51287.81852	38452.08719	9675.679556	1392.557277
H2O	17664.12991	5215.808051	1494.95426	0	17837.96749	31607.12223	31605.09741	0	535.4451934
GLY	0.0000004945	0	0	0	952.2632714	3.450384936	3.450519316	0	857.1120841
HYDRO-01	0	0	0	0	0	0	0	0	0
A-MCH	623.5197926	3233.340822	0.0000000053	323.3340821	55.93297882	95.51185719	95.51170511	2910.006458	0
2-CHL-01	0	2756.336438	0	275.6336438	0	0	0	2480.702254	0
1:3-D-01	107.0745204	17672.8654	17323.87699	23.54499219	0.00011124423	0.0375512555	0.0374556136	211.8963982	0
2:3-D-01	1825.301814	1893.083121	142.6342207	174.9389221	1.330763947	166.9280432	166.4373866	1574.472039	0
N-HEX-01	0.0001015429	2776.224998	0.0001010473	277.6224897	0.0001015429	0.00001143948	0.00001143953	2498.602407	0
ECH	11931.89419	0	0	0	0.0000483437	19320.40405	6488.527769	0	0
NAOH	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0
GLI	0.1599059116	0	0	0	1.407953649	94.364394	93.02493997	0	0
H3O+	0	0	0	0	0	0	0	0	0
NA+	3677.035053	0	0	0	3677.035053	0	0	0	0
NACL(S)	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0
NAOH(S)	0	0	0	0	0	0	0	0	0
CL-	4772.144302	0	0	0	5670.607617	0	0	0	0
OH-	431.017269	0	0	0	0	0	0	0	0

A.4 Hydrochlorination CSTR MATLAB Code

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%CSTR Input
VCSTR = 18; %m^3, Reactor Volume of CSTR (130 m^3 max volume)
PRatio = 1.5; %bar, Pressure facotr of HCl gas in CSTR (multiplied by atmosperic)

%PFR Input
Length = 14; %meters, PFR Length
PFR_Length = Length;
RatioLD = 8; %Ratio of length to diameter
PFR_Diameter = Length/RatioLD; %m, PFR Diameter

%Export Variables
global PFR_Length
global PFR_Diameter

%%CSTR DESIGN
%Variable Ranges (Initial)
%Temperature Range = 60 - 90 Celsius (Very little performance indications)
TCSTR = 80; %Celsius, Temperature of Isothermal CSTR
global TCSTR
T = TCSTR;
%Reactor Volume = 20-25 m^3 (No performance indications)
%Reactor Length (L) to Diameter Ratio: 2.5 - 5
global VCSTR
LDRatio = 1.5; %Reactor Length to Diameter Ratio
CSTR_Diameter = (VCSTR*4/1.5/pi())^(1/3); %m, Reactor Diameter
global CSTR_Diameter
CSTR_Length = LDRatio * CSTR_Diameter; %m, Reactor Length
global CSTR_Length
VL = VCSTR*1000; %Liters, Reactor volume
global VL

%Component Properties
%Densities
rhoGLY = (-0.0003125*T + 1.26275)*1000; %kg/m^3, Glycerol
rhoH2O = (-0.0004122*T + 0.99987)*1000; %kg/m^3, Water
rhoHCl = 1.194 * 1000; %kg/m^3, Hydrogen Chloride
rhoORG = 1.23 * 1000; %kg/m^3, Hypothetical Impurit
rhoMCH = (-1.02*10^-3*T + 1.35)*1000; %kg/m^3, monochloropropanol
rhoDCH = 1.35 * 1000; %kg/m^3, assumption, dichloropropanol
rhoCAT = 0.927 * 1000; %kg/m^3, %Hexanoic Acid Catalyst

%Molecular Weigts
MWGLY = 92.09382; %g/mol,Glycerol
MWH2O = 18.01528; %g/mol, Water
MWHCl = 36.46; %g/mol, Hydrogen Chloride
MWMCH = 110.54; %g/mol,monochloropropanol
MWDCH = 114.192; %g/mol, dichloropropanol
MWORG = 100; %g/mol, arbitrary
MWCAT = 116; %g/mol, Hexanoic Acid
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%Inlet Feed
%Total Flow Rate
FT = 9297; %mole/min

%Catalyst Feed
PercentWeightCat = 0.07; %Percent weight catalyst

%Inlet Flow Composition
GLY = 0.284; %Mole fraction of Glycerol
H2O = 0.017; %Mole fraction of Water
HCl = 0.557; %Mole fraction of Hydrogen Chloride (Use ratio of HCl to GLY) %0.521 - Original Value
MCH = 0.097; %Mol fraction of (Total) MCH (The isomer mole fractions are based on selectivity - take average value over space time)
aMCH = 0.54*MCH; %Mol fraction of %1-monochloropropanol
bMCH = 0.46*MCH; %Mol fraction of bMCH
DCH = 0.046; %Mol fraction of DCH (The isomer mole fractions are based on the proportions of the yields)
agDCH = 0.07*DCH; %mol fraction of aDCH
abDCH = 0.93*DCH; %mol fraction of bDCH
ORG = 0.0001; %Mole fraction of Impurities (Organics)

%Liquid Feed - Redefine Molar Flow Fractions
xTOTAL = (TotalFraction - HCl);
xGLY = GLY*xTOTAL*1; %Glycerol
xH2O = H2O*xTOTAL; %Water
xaMCH = aMCH*xTOTAL; %1-monochloropropanol
xbMCH = bMCH*xTOTAL; %3-monochloropropanol
xagDCH = agDCH*xTOTAL; %1,3-dichloropropanol
xabDCH = abDCH*xTOTAL; %1,2-dichloropropanol
xORG = ORG*xTOTAL; %Hypothetical Impurity

%Inlet Molar Flow Rates (without Catalyst)
FGLYi = FT*xGLY; %mole/min, Feed of Glycerol
FH2Oi = FT*xH2O; %mole/min, Feed of Water
FORGi = FT*xORG; %mole/min, Feed of Impurities
FaMCHi = FT*xaMCH; %mole/min, Feed of 1-monochloropropanol
FbMCHi = FT*xbMCH; %mole/min, Feed of 3-monochloropropanol
FagDCHi = FT*xagDCH; %mole/min, Feed of 1,3-dichloropropanol
FabDCHi = FT*xabDCH; %mole/min, Feed of 1,2-dichloropropanol

%Inlet Mass Flow Rates - Liquid Feed (without catalyst)
fGLY0 = FGLYi*MWGLY/1000; %kg/min, %Glycerol
fH2O0 = FH2Oi*MWH2O/1000; %kg/min, Water
fORG0 = FORGi*MWORG/1000; %kg/min, Hypothetical Impurity
faMCH0 = FaMCHi*MWMCH/1000; %kg/min, 1-monochloropropanol
fbMCH0 = FbMCHi*MWMCH/1000; %kg/min, 3-monochloropropanol
fagDCH0 = FagDCHi*MWDCH/1000; %kg/min, 1,3-dichloropropanol
fabDCH0 = FabDCHi*MWDCH/1000; %kg/min, 1,2-dichloropropanol
fT0T = fGLY0 + fH2O0 + fORG0 + faMCH0 + fbMCH0 + fagDCH0 + fabDCH0;

%Mass Fractions - liquid Feed (without catalyst)
XGLYi = fGLY0/fT0T; %Mass fraction of Glycerol
XH2Oi = fH2O0/fT0T; %Mass fraction of Water
XORGi = fORG0/fT0T; %Mass fraction of Impurities
XaMCHi = faMCH0/fT0T; %Mass fraction of 1-monochloropropanol
XbMCHi = fbMCH0/fT0T; %Mass fraction of 3-monochloropropanol
XagDCHi = fagDCH0/fT0T; %Mass fraction of 1,3-dichloropropanol
XabDCHi = fabDCH0/fT0T; %Mass fraction of 1,2-dichloropropanol

%Gas Feed
%Molar
FHCl1 = FT*HCl; %mole/min, Feed of HCL Gas Feed
%Mass
fHCl0 = FHCl1*MWHCl/1000; %kg/min, Hydrogen Chloride
%Redefined Mass Flow Rates
fTOTm = fT0T + fHCl0; %kg/min, Flow rate of gas and liquid
XHCl1 = fHCl0/fTOTm; %Mass fraction of HCl

%Catalyst Adjustment
fCAT1 = PercentWeightCat*(fTOTm)/(1 - PercentWeightCat); %kg/min, Hexanoic Acid Catalyst
fTOT = fTOTm + fCAT1; %kg/min, Total mass flow rate (with Catalyst)

%Gas Feed (Adjusted)
CFX = 1 - PercentWeightCat; %Factor
fCAT2 = PercentWeightCat*(fGLY0 + fH2O0 + fORG0 + faMCH0 + fbMCH0 + fagDCH0 + fabDCH0)/(1 - PercentWeightCat); %kg/min, feed of catalyst
fTOTAL1 = fCAT2 + fGLY0 + fHCl0 + fH2O0 + fORG0 + faMCH0 + fbMCH0 + fagDCH0 + fabDCH0; %total flow rate with catalyst, gas and liquid
%Mass
XHCl1 = CFX*XHCl1; %Mass fraction of HCl
fHCl1 = fTOTAL1*XHCl1; %kg/min, Feed of HCL Gas Feed
%Molar
fHCl0 = fHCl1/MWHCl * 1000; %mole/min, Feed of HCL Gas Feed
global fHCl0

%Redefined Mass Fractions (Liquid) (with catalyst)
XGLY = CFX*XGLYi; %Mass fraction of Glycerol
XH2O = CFX*XH2Oi; %Mass fraction of Water
XORG = CFX*XORGi; %Mass fraction of Impurities
XaMCH = CFX*XaMCHi; %Mass fraction of 1-monochloropropanol
XbMCH = CFX*XbMCHi; %Mass fraction of 3-monochloropropanol
XagDCH = CFX*XagDCHi; %Mass fraction of 1,3-dichloropropanol
XabDCH = CFX*XabDCHi; %Mass fraction of 1,2-dichloropropanol
XCAT = fCAT1/fTOT1; %Mass fraction of Hexanoic Acid Catalyst
rho11 = XGLY*rhoGLY + XH2O*rhoH2O + XHCl1*rhoHCl + XORG*rhoORG + XaMCH*rhoMCH + XbMCH*rhoMCH + XagDCH*rhoDCH + XabDCH*rhoDCH + XCAT*rhoCAT; %kg/m^3

%Redefined Mass Flow Rates (Liquid) (with Catalyst)
fGLY1 = fTOT*XGLY; %kg/min, Feed of Glycerol
fH2O1 = fTOT*XH2O; %kg/min, Feed of Water
fORG1 = fTOT*XORG; %kg/min, Feed of Impurities
faMCH1 = fTOT*XaMCH; %kg/min, Feed of 1-monochloropropanol
fbMCH1 = fTOT*XbMCH; %kg/min, Feed of 3-monochloropropanol
fagDCH1 = fTOT*XagDCH; %kg/min, Feed of 1,3-dichloropropanol
fabDCH1 = fTOT*XabDCH; %kg/min, Feed of 1,2-dichloropropanol

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%Redefined Molar Flow Rates (liquid) (with Catalyst)
FGLY0 = fGLY1/MwGLY * 1000; %mole/min, Feed of Glycerol
FH2O0 = fH2O1/MwH2O * 1000; %mole/min, Feed of Water
FORG0 = fORG1/MwORG * 1000; %mole/min, Feed of Impurities
FaMCH0 = faMCH1/MwMCH * 1000; %mole/min, Feed of 1-monochloropropanol
FbMCH0 = fbMCH1/MwMCH * 1000; %mole/min, Feed of 3-monochloropropanol
FagDCH0 = fagDCH1/MwDCH * 1000; %mole/min, Feed of 1,3-dichloropropanol
FabDCH0 = fabDCH1/MwDCH * 1000; %mole/min, Feed of 1,2-dichloropropanol
FCAT0 = fCAT1/MwCAT * 1000; %mole/min, Feed of Hexanoic Acid Catalyst

%ASPEN INPUTS: redefined mole fractions
FTOTAL = FGLY0 + FH2O0 + FHC10 + FORG0 + FaMCH0 + FbMCH0 + FagDCH0 + FabDCH0 + FCAT0; %mole/min, Total Liquid flow rate going into reactor
AX_GLY = FGLY0/FTOTAL; %Glycerol
AX_H2O = FH2O0/FTOTAL; %Water
AX_HCl = FHC10/FTOTAL; %Hydrogen Chloride
AX_ORG = FORG0/FTOTAL; %Hypothetical Impurity
AX_aMCH = FaMCH0/FTOTAL; %1-monochloropropanol
AX_bMCH = FbMCH0/FTOTAL; %3-monochloropropanol
AX_agDCH = FagDCH0/FTOTAL; %1,3-dichloropropanol
AX_abDCH = FabDCH0/FTOTAL; %1,2-dichloropropanol
AX_CAT = FCAT0/FTOTAL; %Hexanoic Acid Catalyst

%Volumetric Flow Rates (Liquid Phase)
VGLY = fGLY1/(rhoGLY); %m^3/min, %Glycerol
VH2O = fH2O1/(rhoH2O); %m^3/min, Water
VHCl = 0; %m^3/min, No Liquid HCl being fed
VORG = fORG1/(rhoORG); %m^3/min, Hypothetical Impurity
VaMCH = faMCH1/(rhoMCH); %m^3/min, 1-monochloropropanol
VbMCH = fbMCH1/(rhoMCH); %m^3/min, 3-monochloropropanol
VagDCH = fagDCH1/(rhoDCH); %m^3/min, 1,3-dichloropropanol
VabDCH = fabDCH1/(rhoDCH); %m^3/min, 1,2-dichloropropanol
VCAT = fCAT1/(rhoCAT); %m^3/min, Hexanoic Acid Catalyst
VTotal = VGLY + VH2O + VHCl + VORG + VaMCH + VbMCH + VagDCH + VabDCH + VCAT; %m^3/min, Total Volumetric flowrate of Liquid into reactor
global VTotal

%Volumetric Flow Rate (Gas Phase)
VHC10 = fHC11/rhoHClgas; %m^3/min, volumetric flow rate of hydrogen chloride
global VHC10

%Time (tau) Domain for Iteration
%Best Time Rane (50-100 min)
tau_total = VCSTR/(VTotal + fHC10/rhoHCl); %min, Total residence time
tau_interval = 1; %min, time interval
global tau_interval
tau_domain = [0 : tau_interval : tau_total]; %min, time domain with iteration
tau = tau_total; %Redefine
global tau
time = round(tau/tau_interval); %Collect final integer time for extracting solutions from vectors

%Mass Transfer
%Initial Values
CHC1i = 0 ; % mole/m^3, Initial Amount of Liquid HCl
Na0 = 0; %mole/m^3-min - Flux of HCl from gas to Liquid

%Inputs
muHCl = 0.005; %m/s, Superficial Gas Velocity
global muHCl
RPS = 1.5; %Rotations per Second, Impeller Frequency
global RPS
ID_Ratio = 0.4; %Impeller Lengh to Reactor Diameter
ID = ID_Ratio*CSTR_Diameter; %meters, Impeller Length (Diameter)
global ID
V_Imp_Ratio = 1.1; %Ratio of HCl flow rate through impeller to feed stock
global V_Imp_Ratio
H_Ratio = 0.1; % Portion of Impeller Height From Bottom
HI = H_Ratio*CSTR_Length; %meters, impeller height off bottom of reactor
global HI
Np = 3.2; %Power number based on impeller
global Np
Cs = 3.6*rholiq; %mole/m^3 - Saturation Cocentration of HCl in solution
global Cs

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%ODE SOLVER - CSTR
IC = [FGLY0; FH2O0; FHC10; FORG0; FaMCH0; FbMCH0; FagDCH0; FabDCH0; FCAT0; TCSTR; CHC1i; VLiquid; Na0]; % Array of Inlet Conditions
[Xsol, Ysol] = ode15s('CSTR1', tau_domain, IC);

% Extracting solutions for each variable
FGLY_sol = Ysol(:,1); %Glycerol
FH2O_sol = Ysol(:,2); %Water
FHC1_sol = Ysol(:,3); %Hydrogen Chloride
FORG_sol = Ysol(:,4); %Hypothetical Impurity
FaMCH_sol = Ysol(:,5); %1-monochloropropanol
FbMCH_sol = Ysol(:,6); %3-monochloropropanol
FagDCH_sol = Ysol(:,7); %1,3-dichloropropanol
FabDCH_sol = Ysol(:,8); %1,2-dichloropropanol
FCAT_sol = Ysol(:,9); %Hexanoic Acid Catalyst
Temp1_sol = Ysol(:,10); %Reactor Temperature
CHC1_sol = Ysol(:,11); %Liquid HCl Concentration
VLiquid_sol = Ysol(:,12); %Liquid Volume
Na_sol = Ysol(:,13); %HCl Flux

%Outlet flow rates (last value of matrices)
FGLY1 = FGLY_sol(time); %mole/min, %Glycerol
global FGLY1
FH2O1 = FH2O_sol(time); %Water
global FH2O1
FHC11 = FHC1_sol(time); %Hydrogen Chloride
global FHC11
FORG1 = FORG_sol(time); %Hypothetical Impurity
global FORG1
FaMCH1 = FaMCH_sol(time); %1-monochloropropanol
global FaMCH1
FbMCH1 = FbMCH_sol(time); %3-monochloropropanol
global FbMCH1
FagDCH1 = FagDCH_sol(time); %1,3-dichloropropanol
global FagDCH1
FabDCH1 = FabDCH_sol(time); %1,2-dichloropropanol
global FabDCH1
FCAT1 = FCAT_sol(time); %Hexanoic Acid Catalyst
global FCAT1
VLiquidout = VLiquid_sol(time); %Liquid Volume
global VLiquidout
NaOut = Na_sol(time); %HCl Flux
global NaOut

%Yield
YagDCH = (FagDCH_sol)./FGLY0 * 100; %Percent Yield (Glycerol to agDCH)
YabDCH = (FabDCH_sol)./FGLY0 * 100; %Percent Yield (Glycerol to abDCH)

%Selectivity
saMCH = FaMCH_sol./(FaMCH_sol + FbMCH_sol); %Selectivity of aMCH (0 to 1)
sbMCH = FbMCH_sol./(FaMCH_sol + FbMCH_sol); %Selectivity of bMCH
sagDCH = YagDCH./(YabDCH + YagDCH); %Proportion of ag to ab DCH

%Conversions
cGLY = (FGLY0 - FGLY_sol)./FGLY0; %Conversion of Glycerol to aMCH and bMCH (from 0 to 1)
cGLY_final = (FGLY0 - FGLY1)/FGLY0; %Final Conversion value of Glycerol
IaMCH = cGLY.*saMCH.*FGLY0 + FaMCH0; %mole/min, (Intermediate) amount of Glycerol that converts into aMCH
IbMCH = cGLY.*sbMCH.*FGLY0 + FbMCH0; %mole/min, (Intermediate) amount of Glycerol that converts into bMCH
caMCH = (IaMCH - FaMCH_sol)./IaMCH; %Conversion of aMCH to agDCH
cbMCH = (IbMCH - FbMCH_sol)./IbMCH; %Conversion of bMCH to abDCH

```

```

%Plotting Results
% fig1= figure(1);
% set(fig1, 'Name', 'GLY Flowrate');
% area(Xsol, FGLY_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: Glycerol Dissapearance');

% fig2= figure(2);
% set(fig2, 'Name', 'H2O Flowrate');
% area(Xsol, FH2O_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: H2O Flowrate');

% fig3= figure(3);
% set(fig3, 'Name', 'HCl Flowrate');
% area(Xsol, FHCl_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: HCl Flowrate');

% fig4= figure(4);
% set(fig4, 'Name', 'ORG Flowrate');
% area(Xsol, FORG_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: ORG Concentration');

% fig5= figure(5);
% set(fig5, 'Name', 'aMCH Flowrate');
% area(Xsol, FaMCH_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: aMCH Flowrate');

% fig6= figure(6);
% set(fig6, 'Name', 'bMCH Flowrate');
% area(Xsol, FbMCH_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: bMCH Flowrate');

% fig7= figure(7);
% set(fig7, 'Name', 'agDCH Flowrate');
% area(Xsol, FagDCH_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: agDCH Flowrate');

% fig8= figure(8);
% set(fig8, 'Name', 'abDCH Flowrate');
% area(Xsol, FabDCH_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: abDCH Flowrate');

% fig9= figure(9);
% set(fig9, 'Name', 'CAT Flowrate');
% area(Xsol, FCAT_sol);
% xlabel('Time (min)');
% ylabel('Molar Flow Rate (mol/min)');
% title('CSTR: Catalyst FlowRate');

% fig10= figure(10);
% set(fig10, 'Name', 'GLY Conversion');
% area(Xsol, cGLV);
% xlabel('Time (min)');
% ylabel('Conversion');
% title('CSTR: Glycerol Conversion');

% fig11= figure(11);
% set(fig11, 'Name', 'aMCH Conversion');
% area(Xsol, caMCH);
% xlabel('Time (min)');
% ylabel('Conversion');
% title('CSTR: aMCH Conversion');

% fig12= figure(12);
% set(fig12, 'Name', 'bMCH Conversion');
% area(Xsol, cbMCH);
% xlabel('Time (min)');
% ylabel('Conversion');
% title('CSTR: bMCH Conversion');

% fig13= figure(13);
% set(fig13, 'Name', 'aMCH Selectivity');
% area(Xsol, saMCH);
% xlabel('Time (min)');
% ylabel('Selectivity');
% title('CSTR: aMCH Selectivity');

% fig14= figure(14);
% set(fig14, 'Name', 'agDCH Yield');
% area(Xsol, YagDCH);
% xlabel('Time (min)');
% ylabel('Yield (%)');
% title('CSTR: agDCH Yield');

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% fig15= figure(15);
% set(fig15, 'Name', 'abDCH Yield');
% area(Xsol, YabDCH);
% xlabel('Time (min)');
% ylabel('Yield (%)');
% title('CSTR: abDCH Yield');

% fig16= figure(16);
% set(fig16, 'Name', 'agDCH Selectivity');
% area(Xsol, sagDCH);
% xlabel('Time (min)');
% ylabel('Selectivity');
% title('CSTR: agDCH Selectivity');

% fig17= figure(17);
% set(fig17, 'Name', 'CSTR Temperature ');
% area(Xsol, Temp1_sol);
% xlabel('Time (min)');
% ylabel('Temperature (C)');
% title('CSTR: Reactor Temperature');

% fig18= figure(18);
% set(fig18, 'Name', 'CSTR Liquid HCl Concntration');
% area(Xsol, CHCl_sol);
% xlabel('Time (min)');
% ylabel('mol/m^3');
% title('CSTR: HCl Concentration');

% fig19= figure(19);
% set(fig19, 'Name', 'CSTR Liquid Volume');
% area(Xsol, Vliquid_sol);
% xlabel('Time (min)');
% ylabel('m^3');
% title('CSTR: Liquid Volume');

% fig61= figure(61);
% set(fig61, 'Name', 'CSTR HCl Flux');
% area(Xsol, Na_sol);
% xlabel('Time (min)');
% ylabel('Na (mole/m^3/min)');
% title('CSTR: HCl Flux (Mass Transfer)');

function [per_ode] = CSTR1(X, Y)
% Output Variables
FGLY = Y(1);
FH2O = Y(2);
FHCl = Y(3);
FORG = Y(4);
FaMCH = Y(5);
FaMCH = Y(6);
FagDCH = Y(7);
FabDCH = Y(8);
FCAT = Y(9);
TR = Y(10);
CHCl1 = Y(11);
V10 = Y(12);
Na0 = Y(13);

T = 80; %Celsius, Reactor Temperature - Isothermal Case

%Imported Vairables (From Overall File)
global VCSTR
global CSTR_Diameter
global tau
global CSTR_Length
global tau_interval
%Space Time and Iterations
tau1 = 1; %Min, Time pass per interval
Iteration = X/tau_interval; %Live count of iteration number
TotalIterations = tau/tau_interval; %Total amount of iterations performed

%Species and Stream Properties
%Molecular Weights
MWGLY = 92.09382; %g/mol, Glycerol
MWH2O = 18.01528; %g/mol, Water
MWHCl = 36.46; %g/mol, Hydrogen Chloride
MWMCH = 110.54; %g/mol, monochloropropanol (isomer independent)
MWDC = 114.192; %g/mol, dichloropropanol (isomer independent)
MWORG = 100; %g/mol, arbitrary, Hypothetical Impurity
MWCAT = 116; %g/mol, Hexanoic Acid, Hexanoic Acid Catalyst
%Densities (Liquids) (Function of Reactor Temperature)
rhoGLY = (-0.0003125*T + 1.26275)*1000; %kg/m^3, Glycerol
rhoH2O = (-0.0004122*T + 0.99987)*1000; %kg/m^3, Water
rhoHCl = 1.194 * 1000; %kg/m^3, LIQUID: Hydrogen Chloride
rhoMCH = 1.23 * 1000; %kg/m^3, Hypothetical Impurity
rhoDC = (-1.02*10^-3*T + 1.35)*1000; %kg/m^3, monochloropropanol (isomer independent)
rhoDC = 1.35 * 1000; %kg/m^3, assumption, dichloropropanol (isomer independent)
rhoCAT = 0.927 * 1000; %kg/m^3, Hexanoic Acid Catalyst

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%Inlet Feed to CSTA
%Mass Flow Rates (Liquid)
fGLY = FGLY*MMGLY/1000; %kg/min, Glycerol
fH2O = FH2O*MMH2O/1000; %kg/min, Water
fHCl = fHCl1*MMHCl*V10/tau1/1000; %kg/min, Hydrogen Chloride
fORG = fORG*MMORG/1000; %kg/min, Hypothetical Impurity
fbMCH = fbMCH*MMbMCH/1000; %kg/min, 1-monochloropropanol
fbMCH = fbMCH*MMbMCH/1000; %kg/min, 2-monochloropropanol
fbgDCH = fbgDCH*MMbgDCH/1000; %kg/min, 1,3-dichloropropanol
fbgDCH = fbgDCH*MMbgDCH/1000; %kg/min, 1,2-dichloropropanol
fCAT = fCAT*MMCAT/1000; %kg/min, Hexanoic Acid Catalyst
fTOTAL = fGLY + fH2O + fHCl + fORG + fbMCH + fbgDCH + fCAT; %kg/min - Total Liquid Feed

%Mass Fractions - Liquid Flow
XGLY = fGLY/fTOTAL; %Glycerol
XH2O = fH2O/fTOTAL; %Water
XHCl = fHCl/fTOTAL; %Hydrogen Chloride
XORG = fORG/fTOTAL; %Hypothetical Impurity
XaMCH = fbMCH/fTOTAL; %1-monochloropropanol
XbMCH = fbMCH/fTOTAL; %2-monochloropropanol
XagDCH = fbgDCH/fTOTAL; %1,3-dichloropropanol
XabDCH = fbgDCH/fTOTAL; %1,2-dichloropropanol
XCAT = fCAT/fTOTAL; % Hexanoic Acid Catalyst
rho_liq = XGLY*rhoGLY + XH2O*rhoH2O + XHCl*rhoHCl + XORG*rhoORG + XaMCH*rhoMCH + XbMCH*rhoMCH + XagDCH*rhoDCH + XabDCH*rhoDCH + XCAT*rhoCAT; %kg/m^3, Density of Liquid Feed

%Mass Transfer
%Imported Variables
global VHC10
global V_Imp_Ratio
global muHCl
global RPS
RPM = RPS*60; %RPM, Impeller Frequency
global ID
IV = RPM*pi()*ID; %m/min, Angular Velocity of Impeller
Fg = VHC10*V_Imp_Ratio/(IV*ID^3); %Aeration Number
global HI
PGPL = 0.1*F1g^(-0.25)*(ID^3/V10)^(-0.25)*((RPM^2*ID^4)/(9.81*HI*V10^(2/3)))^(-0.2); %Ratio of Gass to Ungassed Power required
global Np %
PL = Np*rho_liq*(RPM^3)*ID^5; %Ungassed Power required to stirr impeller
PG = PGPL*PL; %Gas Power Required to stirr impeller

%Mass Transfer Coefficients
alpha = 0.8;
beta = 0.2;
k = 2.6*10^-3;

%Mass Transfer Rates
KLA = k*(PG/V10)^alpha*muHCl^(beta); %min^-1, Mass transfer coefficient
global Cs
Na = KLA*(Cs - CHCl1); %moles/m^3-min, Flux of HCl transferring to liquid phase
dNa = Na - Na0; %moles/m^3-min, Change in Flux, used for Iterative property
CHCl1 = Na + CHCl1; %mole/m^3, Updated concentration of HCl present based on mass transfer
dCHCl1 = Na; %mole/m^3, Change in HCl concentration (For heat of dissolution)

%Head Space
%Redefine Liquid Mass Fractions
fHCl1 = CHCl1*(V10)/tau1; %mole/min, HCl Liquid
fHCl1 = fHCl1*MMHCl/1000; %kg/min, HCl Liquid
fTOTAL1 = (fHCl1) + fTOTAL; %kg/min, Adjusted total liquid flow rate - accounting for HCl addition
%Redefine Mass Fractions
XGLY1 = fGLY/fTOTAL1; %Glycerol
XH2O1 = fH2O/fTOTAL1; %Water
XHCl1 = fHCl1/fTOTAL1; %Hydrogen Chloride
XORG1 = fORG/fTOTAL1; %Hypothetical Impurity
XaMCH1 = fbMCH/fTOTAL1; %1-monochloropropanol
XbMCH1 = fbMCH/fTOTAL1; %2-monochloropropanol
XagDCH1 = fbgDCH/fTOTAL1; %1,3-dichloropropanol
XabDCH1 = fbgDCH/fTOTAL1; %1,2-dichloropropanol
XCAT1 = fCAT/fTOTAL1; %Hexanoic Acid Catalyst
rho_liquid = XHCl1*rhoHCl + XGLY1*rhoGLY + XH2O1*rhoH2O + XORG1*rhoORG + XaMCH1*rhoMCH + XbMCH1*rhoMCH + XagDCH1*rhoDCH + XabDCH1*rhoDCH + XCAT1*rhoCAT; %kg/m^3, Updated density
V1 = fTOTAL1/rho_liquid*tau1; %m^3, Volume of Liquid Inside Reactor - After mass transfer
dV1 = V1 - V10; %m^3, Volume of liquid change (for iteration)

%Concentrations of Components - used for reaction Kinetics
CGLY = FGLY*tau1/V1; %mol/m^3, Glycerol
CH2O = FH2O*tau1/V1; %mol/m^3, Water
CaMCH = fbMCH*tau1/V1; %mol/m^3, 1-monochloropropanol
CCAT = fCAT*tau1/V1; %mol/m^3, Hexanoic Acid Catalyst

%Reaction Rate Constants
kp = 0.00043; %Non-catalyst Reaction Parameter
KSP = 4.2522; %1st Esterification Reaction Constant (Catalyzed Reaction) - Notated as K-Single Prime (K')
KDP = 2.2390; %2nd Esterification Reaction Constant (Catalyzed Reaction) - Notated as K-Double Prime (K'')
k3m = 2.409; %Pre-exponential constant - AlphaMCH Reaction
EA3 = 93.75; % kJ/mol, Activation Energy - AlphaMCH Reaction
k4m = 0.101; %Pre-exponential constant - BetaMCH Reaction
EA4 = 116.79; % kJ/mol, Activation Energy - BetaMCH Reaction
k7m = 0.1785; %Pre-exponential constant - Alpha,Gamma DCH Reaction
EA7 = 54.07; %kJ/mol, Activation Energy - Alpha,Gamma DCH Reaction
k8m = 0.00323; %Pre-exponential constant - Alpha,Beta DCH Reaction
EA8 = 95.1516; %kJ/mol, Activation Energy - Alpha,Beta DCH Reaction
R = 8.314/1000; %kJ/mol-K, Adjusted Gas constant for units of EA
aH2O = 1256.71; %Activity coefficient of water
aHCl3 = 1098.42; %Activity coefficient of HCl (MCH Reactions)
aHCl7 = 3988.72; %Activity coefficient of HCl (DCH Reactions)
TK = T + 273.15; %Kelvin, Temperature in Kelvin
Tm = 373.15; %Kelvin, Reference Temperature

%Arrhenius Equations
k3 = k3m*exp(-EA3/(R)*(1/TK - 1/Tm)); %Kinetic Constant of Alpha MCH Reaction
k4 = k4m*exp(-EA4/(R)*(1/TK - 1/Tm)); %Kinetic Constant of Beta MCH Reaction
k7 = k7m*exp(-EA7/(R)*(1/TK - 1/Tm)); %Kinetic Constant of Alpha,Gamma DCH Reaction
k8 = k8m*exp(-EA8/(R)*(1/TK - 1/Tm)); %Kinetic Constant of Alpha,Beta DCH Reaction

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%Component Material Balances
rGLY = (-r3 - r4); %mol/m^3-min, Total glycerol disappearance rate
rH2O = (r3 + r4 + r7); %mol/m^3-min, Total H2O appearance rate
rHCl = (-r3 - r4 - r7 - r8); %mol/m^3-min, Total HCl disappearance rate
raMCH = (r3 - r7); %mol/m^3-min, Total alpha-MCH appearance/disappearance rate
rbMCH = (r4 - r8); %mol/m^3-min, Total beta-MCH appearance/disappearance rate
ragDCH = r7; %mol/m^3-min, Total alpha-gamma-DCH appearance/disappearance rate
rabDCH = r8; %mol/m^3-min, Total alpha-beta-DCH appearance/disappearance rate
rCAT = 0; %mol/m^3-min, Total Catalyst appearance/disappearance rate
rORG = 0; %mol/m^3-min, Total Impurities appearance/disappearance rate

%Resulting Concentration of HCl
dCHClf = (Na) + (rHCl); %mol/m^3 (Liquid Concentration after Reaction)
% dCHClf = CHCl - CHClf; %Change in Concentration (Liquid HCl)

%Heat of Reactions
%Heat Capacities of Components
Cp_GLY = 313.15; %J/mol-K
Cp_H2O = 75.68; %J/mol-K
Cp_HCl = 29.15; %J/mol-K
Cp_ORG = 50; %J/mol-K
Cp_aMCH = 155.35; %J/mol-K
Cp_bMCH = 155.35; %J/mol-K
Cp_agDCH = 142.19; %J/mol-K
Cp_abDCH = 142.19; %J/mol-K

%Denominator Terms
GLY = Cp_GLY*FGLY; %J/K-s
H2O = Cp_H2O*FH2O; %J/K-s
HCl = Cp_HCl*FHCl; %J/K-s
ORG = Cp_ORG*FORG; %J/K-s
aMCH = Cp_aMCH*FaMCH; %J/K-s
bMCH = Cp_bMCH*FbMCH; %J/K-s
agDCH = Cp_agDCH*FagDCH; %J/K-s
abDCH = Cp_abDCH*FabDCH; %J/K-s

%Cumulative Denominator Term
Denominator = GLY + H2O + HCl + ORG + aMCH + bMCH + agDCH + abDCH; %J/K-s

%Heat of Reaction Per Mole (of each species)
Hrxn_aMCH = -49; %kJ/mol, 1-monochloropropanol
Hrxn_bMCH = -41.5; %kJ/mol, 2-monochloropropanol
Hrxn_agDCH = 91; %kJ/mol, 1,3-dichloropropanol
Hrxn_abDCH = 94.9; %kJ/mol, 1,2-dichloropropanol
Hdis_HCl = -71; %kJ/mol, Heat due to HCl dissolution

%Heat of Reaction over 1 Interval (each reaction)
HaMCH = raMCH*Hrxn_aMCH; %kJ/min,
HbMCH = rbMCH*Hrxn_bMCH; %kJ/min,
HagDCH = -1*ragDCH*Hrxn_agDCH; %kJ/min,
HabDCH = -1*rabDCH*Hrxn_abDCH; %kJ/min,
HDissolution = -1*dCHClf*Hdis_HCl; %kJ/min, Due to HCl dissolution

%Numerator Term
Numerator = HaMCH + HbMCH + HagDCH + HabDCH + HDissolution; %kJ/min

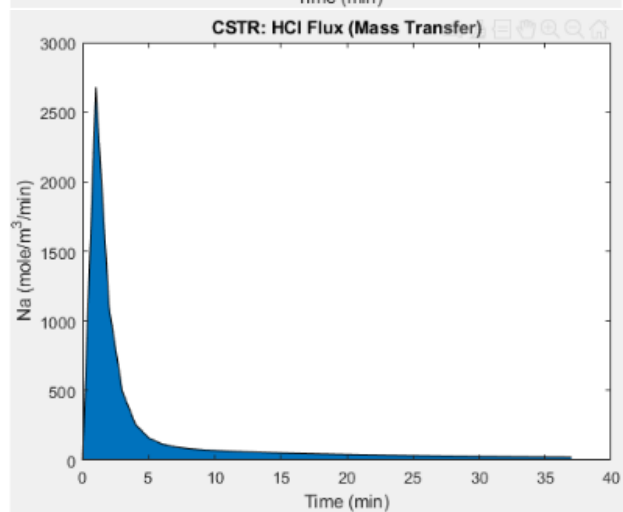
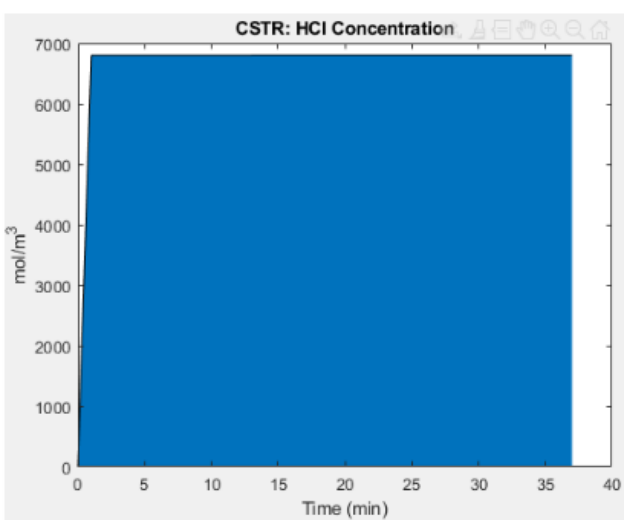
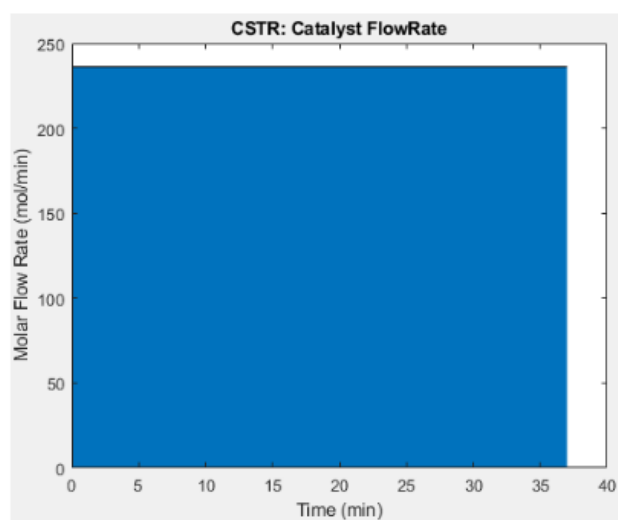
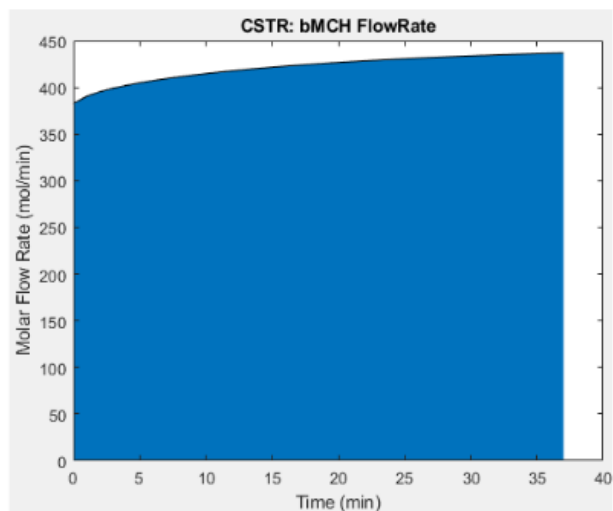
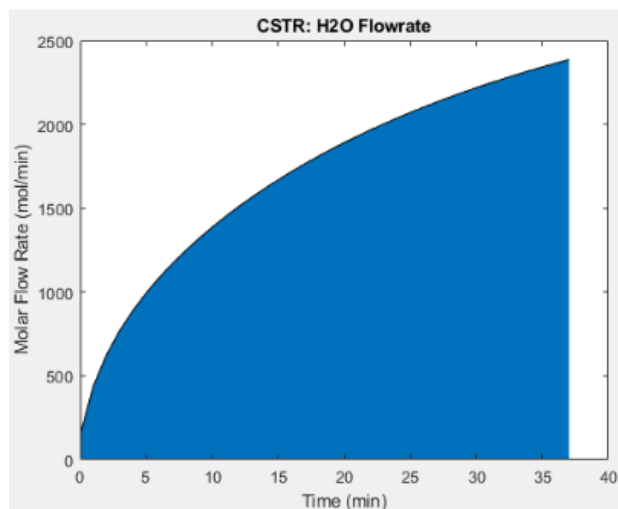
%Temperature Rise from Reaction
dTHeating = (Numerator*1000)/Denominator; %Kelvin (Celsius), change of temperature due to heating

%Cooling
%Coolant Fluid (Cooling Water)
Fc = 1200; %mole/s, Coolant Molar Flow Rate
CpC = 75.6; %J/mole-K, Coolant Heat Capacity
U = 1000; %W/m^2-K, Overall Value for Fluid: find function eventually
SA = (2*pi()*CSTR_Diameter/2)^2 + (2*pi()*CSTR_Length)*(CSTR_Diameter/2)); %m^2, surface area of reactor
TC = 15; %Celsius, Temperature of Coolant
dTCooling = U*SA*(T - TC)/(CpC*Fc); %Kelvin, change of temperature due to cooling
dTReactor = dTHeating - dTCooling; %Celsius, Overall Change in Temperature of Reactor over time

%Sends ODE solutions back to array for iteration
per_ode = [rGLY; rH2O; rHCl; rORG; raMCH; rbMCH; ragDCH; rabDCH; rCAT; dTReactor; dCHClf; dV1; dNa]; %Amount of change in each variable

end

```



A.5: Hydrochlorination PFR MATLAB File

```
%%PFR DESIGN
%%PFR Starter File
%PFR Volume
Diameter = Length/(RatioLD); %meters, Diameter of Reactor (Max ~ 13.5 ft = 4.1 meters)
VPFR = pi()*(Diameter/2)^2*Length; %meters^3, Volume of Reactor
global VPFR

%Volumetric Flow Rate into PFR
VGLY1 = FGLY1*MWGLY/rhoGLY/1000; %m^3/min, Glycerol
VH2O1 = FH2O1*MWH2O/rhoH2O/1000; %m^3/min, Water
VHC11 = FHC11*MWHC1/rhoHC1/1000; %m^3/min, Hydrogen Chloride
VORG1 = FORG1*MWORG/rhoORG/1000; %m^3/min, Hypothetical Impurity
VaMCH1 = FaMCH1*MWmCH/rhoMCH/1000; %m^3/min, 1-monochloropropanol
VbMCH1 = FbMCH1*MWbMCH/rhoMCH/1000; %m^3/min, 3-monochloropropanol
VagDCH1 = FagDCH1*MWDCH/rhoDCH/1000; %m^3/min, 1,3-dichloropropanol
VabDCH1 = FabDCH1*MWDCH/rhoDCH/1000; %m^3/min, 1,2-dichloropropanol
VCAT1 = FCAT1*MWCAT/rhoCAT/1000; %m^3/min, Hexanoic Acid Catalyst
VDot = VGLY1 + VH2O1 + VHC11 + VORG1 + VaMCH1 + VbMCH1 + VagDCH1 + VCAT1; %m^3/minute
global VDot
Volume_domain = [0 : VDot : VPFR]; %Independent Variable (Vdot is converted to seconds)

%%ODE
IC1 = [FGLY1; FH2O1; FHC11; FORG1; FaMCH1; FbMCH1; FagDCH1; FabDCH1; FCAT1; TCSTR];

[Xsolution, Ysolution] = ode15s('PFR1', Volume_domain, IC1);

%Flow Rate solutions over entire PFR Volume
FGLY2_sol = Ysolution(:,1); %mole/min, Flow rate of Glycerol into PFR
FH2O2_sol = Ysolution(:,2); %mole/min, Flow rate of Water into PFR
FHC12_sol = Ysolution(:,3); %mole/min, Flow rate of Hydrogen Chloride into PFR
FORG2_sol = Ysolution(:,4); %mole/min, Flow rate of Hypothetical Impurity into PFR
FaMCH2_sol = Ysolution(:,5); %mole/min, Flow rate of 1-monochloropropanol into PFR
FbMCH2_sol = Ysolution(:,6); %mole/min, Flow rate of 3-monochloropropanol into PFR
FagDCH2_sol = Ysolution(:,7); %mole/min, Flow rate of 1,3-dichloropropanol into PFR
FabDCH2_sol = Ysolution(:,8); %mole/min, Flow rate of 1,2-dichloropropanol into PFR
FCAT2_sol = Ysolution(:,9); %mole/min, Flow rate of Hexanoic Acid Catalyst into PFR
T2_sol = Ysolution(:,10); %Celsius, Temperature of PFR

%Exiting Flow Rates (mole/min)
Vfinal = round(VPFR/VDot);
FGLY2 = FGLY2_sol(Vfinal); %Glycerol
global FGLY2
FH2O2 = FH2O2_sol(Vfinal); %Water
global FH2O2
FHC12 = FHC12_sol(Vfinal); %Hydrogen Chloride
global FHC12
FORG2 = FORG2_sol(Vfinal); %Hypothetical Impurity
global FORG2
FaMCH2 = FaMCH2_sol(Vfinal); %1-monochloropropanol
global FaMCH2
FbMCH2 = FbMCH2_sol(Vfinal); %3-monochloropropanol
global FbMCH2
FagDCH2 = FagDCH2_sol(Vfinal); %1,3-dichloropropanol
global FagDCH2
FabDCH2 = FabDCH2_sol(Vfinal); %1,2-dichloropropanol
global FabDCH2
FCAT2 = FCAT2_sol(Vfinal); %Hexanoic Acid Catalyst
global FCAT2
TPFR2 = T2_sol(Vfinal); %Temperature of CSTR (Variation monitored for cooling utility impact)
global TPFR2

%Total Flow Rate (into Distillation Column)
FTOT2 = FGLY2 + FH2O2 + FHC12 + FORG2 + FaMCH2 + FbMCH2 + FagDCH2 + FabDCH2 + FCAT2; %mol/min

%Exiting Flow Rate Compositions
xGLY2 = FGLY2/FTOT2; %Mole fraction of glycerol
xH2O2 = FH2O2/FTOT2; %Mole fraction of water
xHC12 = FHC12/FTOT2; %Mole fraction of hydrogen chloride
xORG2 = FORG2/FTOT2; %Mole fraction of impurities
xaMCH2 = FaMCH2/FTOT2; %Mole fraction of 1-monochloropropanol
xbMCH2 = FbMCH2/FTOT2; %Mole fraction of 3-monochloropropanol
xagDCH2 = FagDCH2/FTOT2; %Mole fraction of 1,3-dichloropropanol
xabDCH2 = FabDCH2/FTOT2; %Mole fraction of 1,2-dichloropropanol
xCAT2 = FCAT2/FTOT2; %Mole fraction of Hexanoic Acid Catalyst

%Selectivity
saMCH2 = FaMCH2_sol./(FaMCH2_sol + FbMCH2_sol); %Selectivity of aMCH (0 to 1)

%Conversion
cGLY_final2 = (FGLY1 - FGLY2)/FGLY1; %Conversion of Glycerol in PFR
```

```

%Plotting Results
% fig20= figure(20);
% set(fig20, 'Name', 'GLY2 Flowrate');
% area(Xsolution, FGLY2_sol);
% xlabel('Volume (m^3)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: GLY Flowrate');

% fig21 = figure(21);
% set(fig21, 'Name', 'H2O-2 Flowrate');
% area(Xsolution, FH2O2_sol);
% xlabel('Volume (Liters)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: Flowrate');

% fig22= figure(22);
% set(fig22, 'Name', 'HCl-2 Flowrate');
% area(Xsolution, FHCl2_sol);
% xlabel('Volume (m^3)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: HCl(1) Flowrate');

% fig23= figure(23);
% set(fig23, 'Name', 'ORG2 Flowrate');
% area(Xsolution, FORG2_sol);
% xlabel('Volume (Liters)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: FlowRate');

% fig24= figure(24);
% set(fig24, 'Name', 'aMCH2 Flowrate');
% area(Xsolution, FaMCH2_sol);
% xlabel('Volume (m^3)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: aMCH Flowrate');

% fig25= figure(25);
% set(fig25, 'Name', 'bMCH2 Flowrate');
% area(Xsolution, FbMCH2_sol);
% xlabel('Volume (m^3)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: bMCH FlowRate');

% fig26= figure(26);
% set(fig26, 'Name', 'agDCH Flowrate');
% area(Xsolution, FagDCH2_sol);
% xlabel('Volume (m^3)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: agDCH Flowrate');

% fig27= figure(27);
% set(fig27, 'Name', 'abDCH2 Flowrate');
% area(Xsolution, FabDCH2_sol);
% xlabel('Volume (Liters)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: Flowrate');

% fig28= figure(28);
% set(fig28, 'Name', 'CAT2 Flowrate');
% area(Xsolution, FCAT2_sol);
% xlabel('Volume (Liters)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: Catalyst FlowRate');

% fig29= figure(29);
% set(fig29, 'Name', 'GLY Conversion');
% area(Xsolution, XGLY2);
% xlabel('Volume (Liters)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: Glycerol Conversion');

% fig30= figure(30);
% set(fig30, 'Name', 'aMCH Selectivity');
% area(Xsolution, saMCH2);
% xlabel('Volume (L)');
% ylabel('Selectivity');
% title('PFR: aMCH Selectivity');
|
% fig31= figure(31);
% set(fig31, 'Name', 'agDCH Yield');
% area(Xsolution, YagDCH2);
% xlabel('Volume (L)');
% ylabel('Yield (%)');
% title('PFR: agDCH Yield');

% fig32= figure(32);
% set(fig32, 'Name', 'abDCH Yield');
% area(Xsolution, YabDCH2);
% xlabel('Volume (L)');
% ylabel('Yield (%)');
% title('PFR: abDCH Yield');

% fig33= figure(33);
% set(fig33, 'Name', 'TPFR');
% area(Xsolution, T2_sol);
% xlabel('Volume (m^3)');
% ylabel('Reactor Temperature (Celsius)');
% title('PFR: Reactor Temperature');

```

```

function [per_ode] = PERI(X, Y)
% Input Variables
FGLY = Y(1);
FH2O = Y(2);
FHCL = Y(3);
FORG = Y(4);
FaMCH = Y(5);
FbMCH = Y(6);
FagDCH = Y(7);
FadDCH = Y(8);
FCAT = Y(9);
TR = Y(10);
T = 80;

%Nomenclature Adjustment
fGLY = FGLY; %Glycerol
fH2O = FH2O; %Water
fHCL = FHCL; %Hydrogen Chloride
faMCH = FaMCH; %1-monochloropropanol
fCAT = FCAT; %Hexanoic Acid Catalyst

%Imported Variables (From Overall File)
global VDot

%Volume Iteration
V = VDot; %m^3/minute, Amount of volume fluid travels in singular iteration

%Reaction Rate Constants
kp = 0.00043; A = 100; %Non-catalyst Reaction Parameter
KSP = 4.2522; %1st Esterification Reaction Constant (Catalyzed Reaction) - Notated as K-Single Prime (K')
KDP = 2.2390; %2nd Esterification Reaction Constant (Catalyzed Reaction) - Notated as K-Double Prime (K'')
k3m = 2.409; %Pre-exponential constant - AlphaMCH Reaction
EA3 = 93.75; % kJ/mol, Activation Energy - AlphaMCH Reaction
k4m = 0.101; %Pre-exponential constant - BetaMCH Reaction
EA4 = 116.79; % kJ/mol, Activation Energy - BetaMCH Reaction
k7m = 0.1785; %Pre-exponential constant - Alpha,Gamma DCH Reaction
EA7 = 54.07; %kJ/mol, Activation Energy - Alpha,Gamma DCH Reaction
k8m = 0.00323; %Pre-exponential constant - Alpha,Beta DCH Reaction
EA8 = 95.1516; %kJ/mol, Activation Energy - Alpha,Beta DCH Reaction
R = 8.314/1000; %kJ/mol-K, Adjusted Gas constant for units of EA
aH2O = 1256.71; %Activity coefficient of water
aHCL3 = 1098.42; %Activity coefficient of HCL (MCH Reactions)
aHCL7 = 3988.72; %Activity coefficient of HCL (DCH Reactions)
TK = T + 273.15; %Kelvin, Temperature in Kelvin
Tr = 373.15; %Kelvin, Reference Temp

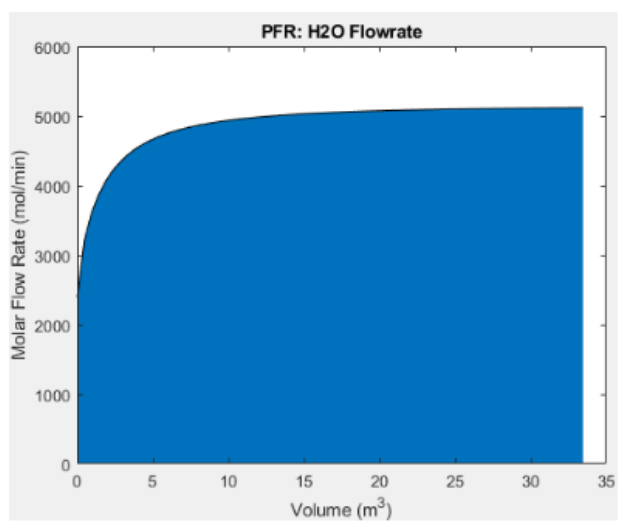
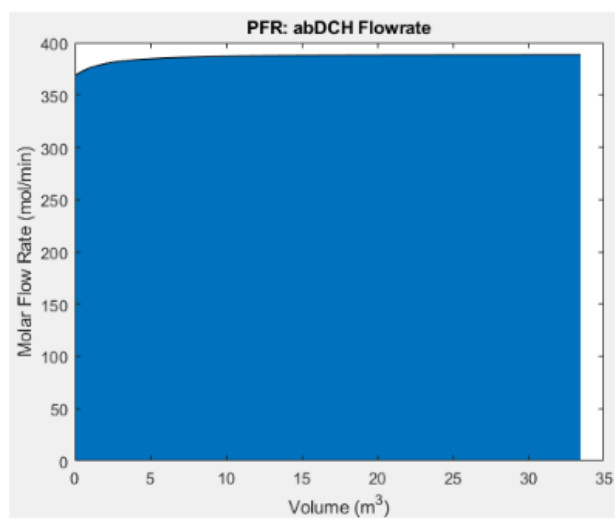
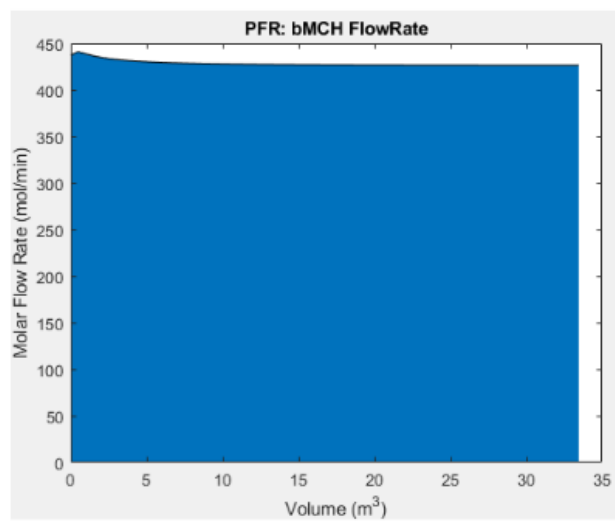
%Arrhenius Equations
k3 = k3m*exp(-EA3/(R*(1/TK - 1/Tr))); %Kinetic Constant of Alpha MCH Reaction
k4 = k4m*exp(-EA4/(R*(1/TK - 1/Tr))); %Kinetic Constant of Beta MCH Reaction
k7 = k7m*exp(-EA7/(R*(1/TK - 1/Tr))); %Kinetic Constant of Alpha,Gamma DCH Reaction
k8 = k8m*exp(-EA8/(R*(1/TK - 1/Tr))); %Kinetic Constant of Alpha,Beta DCH Reaction

%Reaction Rates
r3 = (k3*fGLY./V.*(fHCL./V.^2)).*((fCAT./V.)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))+ kp)/((((fCAT./V.*fH2O./V)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))+(aHCL3.*fHCL./V)+(aH2O.*fH2O./V))^A); %mol/m^3-min, Reaction rate of step 3 (Formation of aMCH)
r4 = (k4*fGLY./V.*(fHCL./V.^2)).*((fCAT./V.)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))+ kp)/((((fCAT./V.*fH2O./V)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))+(aHCL3.*fHCL./V)+(aH2O.*fH2O./V))^A); %mol/m^3-min, Reaction rate of step 4 (Formation of bMCH)
r7 = (k7*fMCH./V.*(fHCL./V.^2)).*((fCAT./V.)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))/((((fCAT./V.*fH2O./V)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))+(aHCL7.*fHCL./V))^A); %mol/m^3-min, Reaction rate of step 7 (Formation of agDCH)
r8 = (k8*fMCH./V.*(fHCL./V.^2)).*((fCAT./V.)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))/((((fCAT./V.*fH2O./V)/(fH2O./V.*(KSP*fGLY./V)+(KDP*fMCH./V)))+(aHCL7.*fHCL./V))^A); %mol/m^3-min, Reaction rate of step 8 (Formation of abDCH)

%Component Material Balances
rGLY = (-r3 - r4); %mol/min, Total glycerol appearance/disappearance rate
rH2O = (r3 + r4 + r7 + r8); %mol/min, Total H2O appearance/disappearance rate
rHCL = (-r3 - r4 - r7 - r8); %mol/min, Total HCL appearance/disappearance rate
raMCH = (r3 - r7); %mol/min, Total alpha-MCH appearance/disappearance rate
rbMCH = (r4 - r8); %mol/min, Total beta-MCH appearance/disappearance rate
ragDCH = r7; %mol/min, Total alpha-gamma-DCH appearance/disappearance rate
radDCH = r8; %mol/min, Total alpha-beta-DCH appearance/disappearance rate
rCAT = 0; %mol/min, Total catalyst appearance/disappearance rate
rORG = 0; %mol/min, Total impurities appearance/disappearance rate

%Heat of Reactions
%Heat Capacities of Components
Cp_GLY = 313.18; %J/mol-K, glycerol
Cp_H2O = 75.68; %J/mol-K, water
Cp_HCL = 29.15; %J/mol-K, Hydrogen Chloride
Cp_ORG = 98; %J/mol-K, Hypothetical Impurity
Cp_aMCH = 159.35; %J/mol-K, 1-monochloropropanol
Cp_bMCH = 155.35; %J/mol-K, 2-monochloropropanol
Cp_agDCH = 142.19; %J/mol-K, 1,3-dichloropropanol
Cp_abDCH = 142.19; %J/mol-K, 1,2-dichloropropanol
%Denominator Terms
GLY = Cp_GLY*fGLY; %J/K-s, glycerol
H2O = Cp_H2O*fH2O; %J/K-s, water
HCL = Cp_HCL*fHCL; %J/K-s, Hydrogen Chloride
ORG = Cp_ORG*fORG; %J/K-s, Hypothetical Impurity
aMCH = Cp_aMCH*fMCH; %J/K-s, 1-monochloropropanol
bMCH = Cp_bMCH*fMCH; %J/K-s, 2-monochloropropanol
agDCH = Cp_agDCH*fagDCH; %J/K-s, 1,3-dichloropropanol
abDCH = Cp_abDCH*fabDCH; %J/K-s, 1,2-dichloropropanol
%Cumulative Denominator Term
Denominator = GLY + H2O + HCL + ORG + aMCH + bMCH + agDCH + abDCH; %J/K-s
%Heat of Reaction Per Mole (of each species)
Hrxn_aMCH = -49; %kJ/mol, 1-monochloropropanol
Hrxn_bMCH = -41.5; %kJ/mol, 2-monochloropropanol
Hrxn_agDCH = 91; %kJ/mol, 1,3-dichloropropanol
Hrxn_abDCH = 94.9; %kJ/mol, 1,2-dichloropropanol
%Heat of Reaction over 1 Interval (each reaction)
HaMCH = raMCH*Hrxn_aMCH; %kJ/min, 1-monochloropropanol
HbMCH = rbMCH*Hrxn_bMCH; %kJ/min, 2-monochloropropanol
HagDCH = -1*ragDCH*Hrxn_agDCH; %kJ/min, 1,3-dichloropropanol
HabDCH = -1*radDCH*Hrxn_abDCH; %kJ/min, 1,2-dichloropropanol
%Numerator Term
Numerator = HaMCH + HbMCH + HagDCH + HabDCH; %kJ/min
%Temperature Rise from Reaction
dHeating = (Numerator*1000)/Denominator; %Kelvin (Celsius), Temperature rise due to heating
dReactor = dHeating; %Celsius, Change in Temperature of Reactor over Iteration (Volume)
%Sends ODE solutions back to array for iteration
per_ode = [rGLY; rH2O; rHCL; rORG; raMCH; rbMCH; ragDCH; radDCH; rCAT; dReactor]; %Change in variables
end

```



A.6 Mixing PFR MATLAB File

```

%% Mixing PFR Reactor Design
%Distillate Fractions = (amount leaving column towards ECH reactor)/(amount
%entering column) %
D_GLY = 0; %Glycerol
D_H2O = 1;
D_HCl = 1;
D_ORG = 0.01;
D_aMCH = 0.000175;
D_bMCH = 0.000175;
D_agDCH = 0.9975;
D_abDCH = 0.9975;
D_CAT = 0.01;

%Reflux Drum Fractions (Amount Leaving (org/Aq) Stream)/(Amount Entering
%Decanter)
%Organic
RD_GLY_org = 0; %Glycerol
RD_H2O_org = 0.103;
RD_HCl_org = 0;
RD_ORG_org = 1;
RD_aMCH_org = 1;
RD_bMCH_org = 1;
RD_agDCH_org = 0.897;
RD_abDCH_org = 0.897;
RD_CAT_org = 1;

%Inlet Flow Rates (to MPFR, from Decanter) - ORGANIC Stream
FGLY3 = 0; %FGLY2*D_GLY*RD_GLY_org; %mol/min, %Glycerol
FH2O3 = 1300; %FH2O2*D_H2O*RD_H2O_org; %mol/min
FHC13 = 0; %FHC12*D_HCl*RD_HCl_org; %mol/min RN THE ECH_ORG FLOW IS WHERE THIS SHOULD BE
FORG3 = 0; %FORG2*D_ORG*RD_ORG_org; %mol/min
FaMCH3 = 0; %FaMCH2*D_aMCH*RD_aMCH_org; %mol/min
FbMCH3 = 0; %FbMCH2*D_bMCH*RD_bMCH_org; %mol/min
FagDCH3 = 1600; %FagDCH2*D_agDCH*RD_agDCH_org; %mol/min
FabDCH3 = 200; %FabDCH2*D_abDCH*RD_abDCH_org; %mol/min
FCAT3 = 0; %FCAT2*D_CAT*RD_CAT_org; %RN THE DCH_AQ FLOW IS WHERE THIS SHOULD BE
F_org_Total = FGLY3 + FH2O3 + FHC13 + FaMCH3 + FbMCH3 + FagDCH3 + FabDCH3 + FCAT3;

%Sodium Hydroxide Addition
FNaOH = 40; %g/mol
rhoNaOH = 2.13 * 1000; %kg/m^3
FNaOH3 = 1.1*(FagDCH3 + FabDCH3); %mol/min
FNaCl3 = 0; %mol/min
%Ratio of NaOH to Aqueous H2O
R_NaOH = 0.2;
%Ratio of Organic to Aqueous (not original) Stream
R_Aq = 1;

%Molar Flow Rates
FH2O3_aq = (FNaOH3^4) + 2760; %mole/min - Flow rate of Water in NaOH, 2760 mol/min is contribution from aqueous phase out of DC
FGL3 = 0; %mole/min - Flow rate of Glycidol
FECH3 = 0; %mole/min - Flow rate of Epichlorohydrin
FNaCl = 0; %mole/min - Flow rate of salt
FaMCH_aq = 0; %mol/min - Flow rate of aMCH in AQUEOUS PHASE
VMPFR = 50; %m^3 Jet ratio of 120 for 1000 m^3 volume
Velo_Ratio = 0.3; %0.3 estimation of kinetic energy lost due to inelastic collision
Jet_Ratio = 6; %2.05 = minimum usable ratio (in reality), 100.85 = minimum ratio that gives positive rECH (rdhDCP>rhECH) with 100 m^3 reactor
T = 40; %Celsius
Diff = 4.8*10^-9; %m^2/s
Diameter = 200*(10^-6)^1.12; %meters, droplet diameter
%Volumetric Flow Rate into PFR
VGLY3 = FGLY3*MMGLY/rhoGLY; %L/min, %Glycerol
VH2O3_aq = FH2O3_aq*MMH2O/rhoH2O; %L/min
VH2O3 = FH2O3*MMH2O/rhoH2O; %L/min
VHC13 = FHC13*MMHCl/rhoHCl; %L/min
VORG3 = FORG3*MMORG/rhoORG; %L/min
VaMCH3 = FaMCH3*MMMCH/rhoMCH; %L/min
VbMCH3 = FbMCH3*MMMCH/rhoMCH; %L/min
VagDCH3 = FagDCH3*MMDCH/rhoDCH; %L/min
VabDCH3 = FabDCH3*MMDCH/rhoDCH; %L/min
VCAT3 = FCAT3*MMCAT/rhoCAT; %L/min
VNaOH3 = FNaOH3*MMNaOH/rhoNaOH; %L/min

% Collision Regime Calculations
%Pm = 3; %Watts/kg
%Mass Flow Rates(kg/min)
FGLY = FGLY3*MMGLY/1000; %kg/min, %Glycerol
FH2O_aq = FH2O3_aq*MMH2O/1000;
FH2O_org = FH2O3*MMH2O/1000;
FHC1 = FHC13*MMHCl/1000;
FaMCH = FaMCH3*MMMCH/1000;
FbMCH = FbMCH3*MMMCH/1000;
FagDCH = FagDCH3*MMDCH/1000;
FabDCH = FabDCH3*MMDCH/1000;
FORG = FORG3*MMORG/1000;
FCAT = FCAT3*MMCAT/1000;
FNaOH = FNaOH3*MMNaOH/1000;
MMGL = 74.08; %g/mol
FGL = FGL3*MMGL/1000;
MMECH = 92.52; %g/mol
FECH = 0; %FECH3*MMECH/1000;
FECH3_org = 0; %mol/min
fTOTAL = FH2O_aq + FH2O_org + FaMCH + FbMCH + FagDCH + FabDCH + FORG + FCAT + FNaOH + FGL + FECH; %kg/min %Cumulative Stream
fTOTAL_aq = FH2O_aq + FNaOH + FHC1; %kg/min %Aqueous Stream
fTOTAL_org = fTOTAL - fTOTAL_aq; %kg/min %Organic Stream

% Mass Fractions
%Cumulative Stream
Xx_totGLY = FGLY/fTOTAL;
X_totH2O_aq = FH2O_aq/fTOTAL;
X_totH2O_org = FH2O_org/fTOTAL;
X_totHCl = FHC1/fTOTAL;
X_totaMCH = FaMCH/fTOTAL;
X_totbMCH = FbMCH/fTOTAL;
X_totagDCH = FagDCH/fTOTAL;
X_totabDCH = FabDCH/fTOTAL;
X_totORg = FORG/fTOTAL;
X_totCAT = FCAT/fTOTAL;
X_totNaOH = FNaOH/fTOTAL;
Xx_totGL = FGL/fTOTAL;
Xx_totECH = FECH/fTOTAL;

```



```

%Flow Rate solutions over entire PFR Volume
FGLV3_sol = YMPFRsol(:,1); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FH2O3_aq_sol = YMPFRsol(:,2); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FH2O3_org_sol = YMPFRsol(:,3); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FECH3_org_sol = YMPFRsol(:,4); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FORG3_sol = YMPFRsol(:,5); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FaMCH3_org_sol = YMPFRsol(:,6); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FbMCH3_sol = YMPFRsol(:,7); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FagDCH3_sol = YMPFRsol(:,8); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FabDCH3_sol = YMPFRsol(:,9); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FDCH3_aq_sol = YMPFRsol(:,10); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FNaOH3_sol = YMPFRsol(:,11); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FGL3_sol = YMPFRsol(:,12); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FECH3_aq_sol = YMPFRsol(:,13); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FNaCl3_sol = YMPFRsol(:,14); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)
FaMCH_aq_sol = YMPFRsol(:,15); %mole/min, Flow rate of Glycerol into Reactive DC (out of MPFR)

% fig40= figure(40);
% set(fig40, 'Name', 'Aqueous ECH Flowrate');
% area(XMPFRsol."mu_film"/TS, FECH3_aq_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: Aqueous ECH Flowrate');
% xlim([0 5]);
%
% fig41= figure(41);
% set(fig41, 'Name', 'GL Flowrate');
% area(XMPFRsol."mu_film"/TS, FGL3_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: GL Flowrate');
% xlim([0 5]);
%
% fig42 = figure(42);
% set(fig42, 'Name', 'Organic agDCH Flowrate');
% area(XMPFRsol."mu_film"/TS, FagDCH3_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: Organic agDCH Flowrate');
% xlim([0 5]);
% %
% fig43 = figure(43);
% set(fig43, 'Name', 'Glycerin Flowrate');
% area(XMPFRsol."mu_film"/TS, FGLV3_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: Glycerin Flowrate');
% xlim([0 5]);
%
% fig44 = figure(44);
% set(fig44, 'Name', 'Organic ECH Flowrate');
% area(XMPFRsol."mu_film"/TS, FECH3_org_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: Organic ECH Flowrate');
% xlim([0 5]);
%
% fig45 = figure(45);
% set(fig45, 'Name', 'Aqueous aMCH = MCPD Flowrate');
% area(XMPFRsol."mu_film, FaMCH_aq_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: MCPD Flowrate');
% xlim([0 5]);
%
% fig48 = figure(48);
% set(fig48, 'Name', 'NaOH Flowrate');
% area(XMPFRsol."mu_film, FNaOH3_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: NaOH Flowrate');
% xlim([0 5]);
%
% fig46 = figure(46);
% set(fig46, 'Name', 'Aqueous agDCH Flowrate');
% area(XMPFRsol."mu_film, FDCH3_aq_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: Aqueous agDCH Flowrate');
% xlim([0 5]);
%
% fig47= figure(47);
% set(fig47, 'Name', 'Organic aMCH Flowrate');
% area(XMPFRsol."mu_film, FaMCH3_org_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('PFR: Organic aMCH Flowrate');
%
% fig44 = figure(44);
% set(fig44, 'Name', 'Total ECH Flowrate');
% area(XMPFRsol."mu_film, FECH3_org_sol + FECH3_aq_sol);
% xlabel('Length of PFR (m)');
% ylabel('Molar Flow Rate (mol/min)');
% title('Mixing PFR: Total ECH Flowrate');
% xlim([0 5]);

```

```

function [MPFR_ode] = MPFR(X,Y)
% DELETE ABOVE DELETE ABOVE DELETE ABOVE DELETE ABOVE DELETE ABOVE
% DELETE ABOVE DELETE ABOVE DELETE ABOVE DELETE ABOVE DELETE ABOVE
%Iterative Scale (Units)
%Time = Seconds
%Length/Volume = Meters
%Mass = kg
%Temp = C
%Pressure = Pa
% to use the GLOBAL mu_film variable, in the line
%Iterative Solutions
%Flows below all in mol/min
FGLY = Y(1); %mol/min
FH2O_aq = Y(2);
FH2O_org = Y(3);
FECH_org = Y(4);
FORG = Y(5);
FaHCH = Y(6);
FbHCH = Y(7);
FagDCH = Y(8);
FabDCH = Y(9);
FDCH_aq = Y(10);
FNaOH = Y(11);
FGL = Y(12);
FECH_aq = Y(13);
FNaCl = Y(14);
FaHCH_aq = Y(15);

FTOTAL_aq = FH2O_aq + FNaOH + FNaCl; %*FHC1

global TS

%Initial Guess = Isothermal Reactor
VS = 1000; %Volume scale factor for concentrations
T = 40 + 273.15; %K
Diff = (3*10^-11)/TS; %m^2/ms
Diameter = 200*(10^-6)*1.12;%meters, droplet diameter

%Properties (Inletting Streams)
%Molecular Weights
MWGLY = 92.09382; %g/mol
MH2O = 18.01528; %g/mol
MHCl = 36.46; %g/mol
MHCH = 110.54; %g/mol
MDCH = 114.192; %g/mol
MWORG = 100; %g/mol, arbitrary
MWCAT = 116; %g/mol, Hexanoic Acid
MNaOH = 39.997; %g/mol
MWGL = 74.06; %g/mol
MHCH = 92.52; %g/mol
%Mass Flow Rates(kg/min)
FGLY = FGLY*MWGLY/1000;
FH2O_aq = FH2O_aq*MH2O/1000;
FH2O_org = FH2O_org*MH2O/1000;
FHC1 = 0; %FHC1*MHCl/1000;
FaHCH = FaHCH*MHCH/1000;
FbHCH = FbHCH*MHCH/1000;
FagDCH = FagDCH*MDCH/1000;
FabDCH = FabDCH*MDCH/1000;
FDCH_aq = FDCH_aq*MDCH/1000;
FORG = FORG*MWORG/1000;
FCAT = 0; %FCAT*MWCAT/1000;
FGL = FGL*MWGL/1000;
FECH_aq = FECH_aq*MHCH/1000;
FECH_org = FECH_org*MHCH/1000;
FTOTAL = FH2O_aq + FH2O_org + FaHCH + FbHCH + FagDCH + FabDCH + FORG + FNaOH + FGL + FECH_aq + FECH_org + FDCH_aq; %* FCAT kg/min %Cumulative Stream
FTOTAL_aq = FH2O_aq + FNaOH + FECH_aq + FDCH_aq; %* FHC1; %kg/min %Aqueous Stream
FTOTAL_org = FTOTAL - FTOTAL_aq; %kg/min %Organic Stream
% Mass Fractions
%Cumulative Stream
XGLY = FGLY/FTOTAL;
XH2O_aq_tot = FH2O_aq/FTOTAL;
XH2O_org_tot = FH2O_org/FTOTAL;
XHCl = 0; %FHC1/FTOTAL;
XaHCH = FaHCH/FTOTAL;
XbHCH = FbHCH/FTOTAL;
XagDCH = FagDCH/FTOTAL;
XabDCH = FabDCH/FTOTAL;
XORG = FORG/FTOTAL;
XCAT = FCAT/FTOTAL;
XNaOH = FNaOH/FTOTAL;
XGL = FGL/FTOTAL;
XECH = (FECH_aq + FECH_org)/FTOTAL;
%Aqueous Stream
XH2O_aq = FH2O_aq/FTOTAL_aq;
XNaOH_aq = FNaOH/FTOTAL_aq;
XGL_aq = FGL/FTOTAL_aq;
XECH_aq = FECH_aq/FTOTAL_aq;
%Organic Stream
XGLY_org = FGLY/FTOTAL_org;
XH2O_org = FH2O_org/FTOTAL_org;
XaHCH_org = FaHCH/FTOTAL_org;
XbHCH_org = FbHCH/FTOTAL_org;
XagDCH_org = FagDCH/FTOTAL_org;
XabDCH_org = FabDCH/FTOTAL_org;
XORG_org = FORG/FTOTAL_org;
XCAT_org = 0; %FCAT/FTOTAL_org;
XECH_org = FECH_org/FTOTAL_org;
XHCl_org = 0; %FHC1/FTOTAL_org;
%Densities (We need densities for all 3 streams)
%Aqueous Stream
rho_aq = 1000; %kg/m^3 = water for ph of about 7
%Organic Stream
rhoGLY = (-0.00031207*T + 1.26275)*1000; %kg/m^3, density of Glycerol
rhoH2O = (-0.00041227*T + 0.99967)*1000; %kg/m^3
rhoHCl = 1.194 * 1000; %kg/m^3, preliminary value
rhoORG = 1.23 * 1000; %kg/m^3
rhoHCH = (-1.02*10^-3*T + 1.35)*1000; %kg/m^3
rhoDCH = 1.35 * 1000; %kg/m^3, assumption
rhoCAT = 0.927 * 1000; %kg/m^3
XrhoGL = 1.11 * 1000; %kg/m^3
XrhoCH = 1.18 * 1000; %kg/m^3
rho_org = XGLY_org*rhoGLY + XH2O_org*rhoH2O + XHCl_org*rhoHCl + XORG_org*rhoORG + XaHCH_org*rhoHCH + XbHCH_org*rhoHCH + XagDCH_org*rhoDCH + XabDCH_org*rhoDCH + XCAT_org*rhoCAT + XECH_org*rhoECH;
%Cumulative Stream
xaqueous = FTOTAL_aq/(FTOTAL_aq + FTOTAL_org);
xorganic = 1 - xaqueous;
rhoLiquid = (xaqueous)*rho_aq + (xorganic)*rho_org;
%Kinematic Viscosity (m^2/s) (Cumulative Stream - Inlet)
%
%vH2O = 0.475*10^-6; %at 60 C, https://www.engineersedge.com/physics/water_density_viscosity_specific_weight_13146.htm
%
%vCAT = 1.14/1000/rhoCAT;
%
%

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%          vDCH = 10/1000/rhoDCH;
%          vCAT = 1.14/1000/rhoCAT;
%          vORG = 3.5/1000/rhoORG;
%          vMCH = 150/1000/rhoMCH;
%          vLiquid = (XH2O_aq + XH2O_org + XHCl + XNaOH)*vH2O + (XagDCH + XabDCH)*vDCH + XCAT*vCAT + XORG*vORG + (XaMCH + XbMCH)*vMCH;

%Volumes of mixing regime
global mu_film
mu_film1 = mu_film/TS;
global Ac_PFR
global Vol_drops %Fixed
global Area %Fixed
%Iterated calculations (%ms)
V_0_tot = Ac_PFR*mu_film1; %m^3/ms volumetric flow of film
molflowDCH_org = FagDCH/60/TS; %mol/s only care about agDCH going into aq phase bc it reacts
molflowDCH_aq = FbCH_aq/60/TS; %mol/s
cDCH_org = molflowDCH_org/Vol_drops; %mol/m^3
molflowaMCH_org = FaMCH/60/TS; %mol/s only care about aMCH going into aq phase bc it reacts
cMCH_org = molflowaMCH_org/Vol_drops; %mol/m^3
molflowECH_org = FECH_org/60/TS; %mol/sec
molflowECH_aq = FECH_aq/60/TS; %mol/sec
cECH_org = molflowECH_org/Vol_drops; %mol/m^3
volfrac_aq = 1 - (Vol_drops/V_0_tot); %dimless
vol_aq = volfrac_aq * V_0_tot/1000; %L/s - Volume of Aqueous Liquid
cDCH_aq = molflowDCH_aq/(vol_aq*60)*1000; %mol/m^3 only considering alpha,gamma-DCH
cMCH_aq = FaMCH/(vol_aq*60)*1000; %mol/m^3
cECH_aq = molflowECH_aq/(vol_aq*60)*1000; %mol/m^3

V_it = (X*mu_film1*Ac_PFR - (X-1)*mu_film1*Ac_PFR)/1000; %L
t_res = X; %s

%Mass transfer of components agDCH, aMCH, and ECH aq->org
%agDCH
dcDCH = cDCH_org - cDCH_aq; %mol/m^3
%DCH = Diff*dcDCH/(Diameter/2); %mol/m^2-s, assuming all molecules are points at the center of the droplet
H_DCH = %DCH*Area*t_res; %mol (that transfer between the two phases)
dc_DCH = H_DCH/vol_aq; %mol/L
dc_DCH1 = dc_DCH/V5; %mol/cm^3
%%aMCH
dcMCH = cMCH_org - cMCH_aq; %mol/L
%MCH = Diff*dcMCH/(Diameter/2); %mol/m^2-s, assuming all molecules are points at the center of the droplet
H_MCH = %MCH*Area*t_res; %mol (that transfer between the two phases)
dc_MCHD = H_MCH/Vol_drops/1000; %mol/L
FaMCH_org_mt = dc_MCHD*1000*FTOTAL_org/rho_org; %mol/min
%ECH (Aqueous to Organic)
dc_back_ECH = cECH_aq - cECH_org; %dc_DCH*1000; %mol/m^3
%DCH = Diff*dc_back_ECH/(Diameter/2); %mol/m^2-s, assuming all molecules start at the outside edge of the bubble and diffuse to the center of the droplet
H_ECH = %ECH*Area*t_res; %mol
dc_ECH = H_ECH/Vol_drops/1000; %mol/L
FECH_org_mt = dc_ECH*1000*FTOTAL_org/rho_org; %dc_ECH*1000*FTOTAL_org/rho_org; %mol/min

%Concentrations in aq phase, bc rxn occurs in aq phase only
OH = FNaOH/60/TS/vol_aq/V5; %mol/cm^3
H = 0; %HCl/60/vol_aq/V5; %mol/cm^3
GL = FGL/60/TS/vol_aq/V5; %mol/cm^3
MCPD = (FaMCH_aq/60/TS/vol_aq/V5) - (H_MCH/vol_aq/V5); %mol/cm^3
ECH = (FECH_aq/60/TS/vol_aq/V5) + (FOCH_aq/60/vol_aq/TS/V5) + dc_DCH1 - (H_ECH/vol_aq/V5); %mol/cm^3
DCH = (FbDCH_aq/60/TS/vol_aq/V5) + dc_DCH1; %mol/cm^3
H2O = FHD2O_aq/60/TS/vol_aq/V5; %mol/cm^3
NDCP = FagDCH/60/vol_aq; %mol/L

% Constant = 0.5
% dmax = Constant*(ST/rhoC)^(0.6)/(Pm^(0.4))

%Reaction Kinetics (FROM PAPER NAMED "hydrolysis kinetics" need to check preExp k units (make sure its in seconds))
%Pre-exponential Constants (lto cm
pekHGLV_ac = (2.769*10^7)/TS/(V5^2); %L^2/mol^2-s
pekHGLV_n = (2.77*10^3)/TS/(V5^2); %L^2/mol^2-s
pekHGLV_al = (3.42*10^5)/TS/(V5^2); %L^2/mol^2-s
% pekCLGLV_ac = 1.61*10^8; %L/mol^2-s
% pekCLGLV_n = 2.68*10^3; %L^2/mol^2-s
pekdhMCPD_al = (1.10*10^19)/TS/(V5); %L/mol^2-s
pekHECH_ac = (2.02*10^8)/TS/(V5^2); %L^2/mol^2-s
pekHECH_n = (2.89*10^10)/TS/(V5^2); %L^2/mol^2-s
pekHECH_al = (5.24*10^19)/TS/(V5^2); %L^2/mol^2-s
% pekCLECH_ac = 2.05*10^9;
% pekCLECH_n = 4.95*10;
% pekCLECH_al = 1.47*10^11;
%pekdhDCP_al = (1.47*10^11)/TS; %L/mol-s

%Activation Energies
R = 8.3145; %J/mol-K
EAHGLV_ac = 6.6*10^4; %J/mol-K
EAHGLV_n = 6.5*10^4; %J/mol-K
EAHGLV_al = 6.3*10^4; %J/mol-K
% EACLGLV_ac = 5.7*10^4; %J/mol-K
% EACLGLV_n = 7.0*10^4; %J/mol-K
EadhMCPD_al = 1.2*10^5; %J/mol-K
EAHECH_ac = 7.5*10^4;
EAHECH_n = 4.9*10^4;
EAHECH_al = 8.8*10^4;
% EACLECH_ac = 6.7*10^4;
% EACLECH_n = 4.8*10^4;
% EACLECH_al = 6.0*10^4;
%EAhdhDCP_al = 6.0*10^4; %J/mol-K

%Kinetic Constants (time basis of seconds from pre-exponential coeff)
khGLV_ac = pekHGLV_ac*exp(-EAHGLV_ac/(R*T));
khGLV_n = pekHGLV_n*exp(-EAHGLV_n/(R*T));
khGLV_al = pekHGLV_al*exp(-EAHGLV_al/(R*T));
kdhMCPD_al = pekdhMCPD_al*exp(-EadhMCPD_al/(R*T));
kHECH_ac = pekHECH_ac*exp(-EAHECH_ac/(R*T));
kHECH_n = pekHECH_n*exp(-EAHECH_n/(R*T));
kHECH_al = pekHECH_al*exp(-EAHECH_al/(R*T));
% kCLECH_ac = pekCLECH_ac*exp(-EACLECH_ac/(R*T));
% kCLECH_n = pekCLECH_n*exp(-EACLECH_n/(R*T));
% kCLECH_al = pekCLECH_al*exp(-EACLECH_al/(R*T));
%kdhDCP_al = pekdhDCP_al*exp(-EadhDCP_al/(R*T)); %J/mol-K

%Hydrolysis Kinetics: dh is hydrochlorination, h is hydrolysis
%rdhDCP = kdhDCP_al*OH*DCP; % formation of ECH (disappearance of DCP = DCH) THIS IS INSTANT
%all in mol/m^3-s
rdhDCP = DCH; %mol/cm^3-ms formation of ECH (disappearance of DCP = DCH) THIS IS INSTANT THIS IS FROM MASS TRANS OF DCH FROM ORG PHASE
rHECH = ECH*H2O*(kHECH_al*OH + kHECH_n + kHECH_ac*H); %mol/cm^3-ms formation of MCPD = aMCH (disappearance of ECH)
rdhMCPD = kdhMCPD_al*OH*MCPD; %mol/cm^3-ms formation of glycidyl (disappearance of MCPD = aMCH)
rHGL = GL*H2O*(khGLV_al*OH + khGLV_n + khGLV_ac*H); %mol/cm^3-ms formation of glycerin (disappearance of glycidyl)

%Material Balances
rGLV = 60*V_it*V5*rHGL*TS; %mol/min
rHD2O_aq = 60*V_it*V5*(rdhMCPD - rHGL)*TS; %mol/min
rHD2O_org = 0; %mol/s
%rHCl = 0; %mol/s
rORG = 0; %mol/s

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%Material Balances-
rGLY = 60*V_it*VS*rhGL*TS; %mol/min
rH2O_aq = 60*V_it*VS*(rdhMCPD - rhGL)*TS; %mol/min
rH2O_org = 0; %mol/s
%rHCl = 0; %mol/s
rORG = 0; %mol/s
rMCPD = 60*V_it*VS*(rhECH - rdhMCPD)*TS; %mol/min
rbHCH = 0; %mol/min
ragDCH_org = 60*V_it*VS*(-dcDCH)*TS; %mol/min
rabbDCH = 0; %mol/min
%rCAT = 0; %mol/min
rDCH_aq = 60*V_it*VS*(-rdhDCP)*TS; %mol/min want FDCH_aq = 0 on it 2, so that DCH can mt from org to aq in it 2
rNaOH = 60*V_it*VS*(-rdhDCP - rdhMCPD)*TS; %mol/min
rGL = 60*V_it*VS*(rdhMCPD - rhGL)*TS; %mol/min
rECH = 60*V_it*VS*(rdhDCP - rhECH)*TS; %mol/min
rNaCl = 60*V_it*VS*(rdhDCP + rdhMCPD)*TS; %mol/min

MPFR_ode = [rGLY; rH2O_aq; rH2O_org; FECH_org_mt; rORG; FaHCH_org_mt; rbHCH; ragDCH_org; rabbDCH; rDCH_aq; rNaOH; -rGL; rECH - FECH_org_mt; rNaCl; rMCPD];
%
% n = 1;
% while n < 16
%     if (MPFR_ode(n)+Y(n))<0
%         MPFR_ode(n) = 0;
%     end
%     n = n+1;
% end
end

```