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Process Simulation for Styrene Prodcution from Toluene and Methanol

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Process simulators have been integral in the design and optimization of various chemical processes. These simulators feature drag and drop modular process equipment that allows users to input conditions and specifications to model that equipment's behavior within the simulation. Streams of chemicals preloaded in the system interact with the process equipment in the program in the attempt to model physical phenomena. Even though CHEMCAD offers an expansive suite of process equipment, there are processes that includes equipment that may not be included. It can be a challenge to determine a way to use CHEMCAD's existing process equipment to match the desired outcome. In this study, a chemical process that employs the reaction between toluene and methanol to yield styrene is simulated using CHEMCAD. The simulation must be able to produce 350,000 tons of styrene per year. In addition, there are other design specifications that must be met within the process. These specifications help to define the way in which the CHEMCAD simulation is built. Once the simulation is completed, sensitivity analysis and controllers are added to the simulation to increase the accuracy of the simulation.

KEYWORDS: toluene, CHEMCAD, Simulation, Styrene, methanol, Process

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NOMENCLATURE

Q	Amount of heat transferred in kJ
M	Mass of heated substance in g
ΔT	Change in temperature in °C
p_i	Partial pressure of a compound, i
y_i	Mole fraction of a compound, i, in a mixture
A, B, C	Antoine's Equation physical constants to determine compound's vapor pressure at a given pressure and temperature
$X_{o,\,m}$	Mole fraction of methanol in the organic stream
$X_{a,\,m}$	Mole fraction of methanol in the aqueous stream
$X_{f,\,m}$	Mole fraction of methanol in the feed stream
$X_{g,\,m}$	Mole fraction of methanol in the gaseous stream
P	Pressure
$P_m^*(T)$	Vapor pressure of methanol at a given temperature, T

CHAPTER 1

I. INTRODUCTION

1.1 Introduction to Process Simulators

Process simulators, appearing near the late 1970's, pioneered a novel way in which designing chemical engineering processes can be completed. At first, many engineers completed most of the plant's specifications by hand, such as material and energy balances. Longer iterative processes, such as calculating the enthalpy of streams containing a mixture of various chemicals were tedious and arduous to complete. To ease in calculations heuristics were created. Heuristics, otherwise known as "Experienced-Based Principles" are rule-of -thumb calculations that are derived by analyzing the design of previous chemical plants. Through this analysis, "shortcuts" can be determined. These shortcuts can give an engineer a range of where the calculation should be numerically. These heuristics can give rough estimates; however, for overall design, these calculations should not be used. (Turton, Bailie, Whiting, Shaeiwitz, & Bhattacharyya, 2012). Once process simulators were created, process simulators can be created using more accurate calculations in comparison to heuristics.

Most process simulators have a similar structure in which a user may begin to simulate the process. Each part of process simulators intrinsically works together to provide the user with the necessary tools to accurate depict a process. According to *Analysis, Synthesis, and Design of Chemical Processes,* the following is a list of basic computational element involved in creating a process simulator.

1. Component Database
2. Thermodynamic Model Solver
3. Flowrate Sheet Builder
4. Unit Operation Block Solver
5. Data Output Generator
6. Flowsheet Generator

In a similar sense, Turton (2013) states that each Element of Process Simulators are interwoven with steps that the user must take in order to complete the simulation successfully, outlined in the list below.

1. Select all the chemical components that are required in the process form the component database.
2. Select the thermodynamic models required for the simulation. These may be different from different pieces of equipment.
3. Select the topology of the flow sheet to be simulated by specifying the input and output streams for each stream for each piece of equipment.
4. Select the properties (temperature, pressure, flow rate, vapor fraction, and composition) of the feed streams to the process.
5. Select the equipment specifications (parameters) for each piece of equipment in the process.
6. Select the way in which the results are to be displayed.
7. Select the convergence method and run the simulation.

For this study, each of the steps outlined below will be used to simulate the process of styrene production from toluene and methanol using the process simulator, CHEMCAD.

1.2 Introduction into CHEMCAD and Styrene

CHEMCAD was first introduced in 1983 as microCHESS. Over a timespan of two to three years, CHEMCAD has evolved to help many chemical engineering simulate " initial design of new process, optimization or de-bottlenecking of existing process, heat exchanger sizing, pressure and flow balancing of complex piping networks" and many other challenges that chemical engineers may face (CHEMSTATIONS, 2016, p. 2). CHEMCAD features drag and drop style equipment, named "UnitOps", that can simulate real-life physical equipment. Each type of UnitOps has its own set of parameters. These parameters give CHEMCAD specifications on how these UnitOps systems should run in the program. After setting each parameter for the UnitOps and selecting and defining other parts of the simulation, CHEMCAD is ready to tackle any problem or challenge that may arise.

One current chemical engineering challenge is to optimize and diversify the ways in which styrene is made. Styrene is widely used in a myriad of products. These products include "refrigerator liners, medical devices, food containers, polystyrene foam, and composite products. In 2013, the global demand for styrene is 27,180,000 metric tons, growing each year (The Styrene You Know: Uses and Benefits, 2013). This study aims to simulate a process using toluene and methanol to produce styrene.

1.3 Inputting Process into CHEMCAD

In order to input this process into CHEMCAD, a brief process description is needed. This process description follows the PFD diagram shown on page 21.

Saturated liquid streams, streams 2 and 3, are carrying methanol and toluene, respectively. These streams are directed to vaporizers to heat each stream so that the compounds are vaporized. The hot reactor effluent is flowing counter-currently in the tube-side of the exchanger. From there,

the newly vaporized streams are mixed into one stream, Stream 5, and it passes through an interchanger heat exchanger, with reactor effluent flowing cross-currently on the tube side. From there, the mixed reactant stream goes into the fired heater raising the temperature of Stream 6 from 304.7 °F to 977 °F. The reactor is operating at 82% conversion of toluene. The toluene will follow two reaction pathways, with one reaction creating Styrene, and the other reaction creating ethylbenzene. The selectivity towards the Styrene reaction is 72%. The reactor pressure is set at 5.52 atm, and the operation is considered adiabatic. The reactor effluent, labeled as Stream 10, leaves the reactor at 825.31 °F, containing ethylbenzene, water, styrene, hydrogen, toluene, and methanol is pumped into the interchanger first, warming up the reactants in Stream 5. The effluent leaves the interchanger at 772 °F and enters the toluene vaporizer as Stream 11. After vaporizing the incoming toluene stream, the effluent travels to the methanol vaporizer to vaporize the incoming methanol as well, labeled as Stream 12. Leaving the vaporizer, the effluent is at 285 °F and is subsequently cooled to 100 °F by cooling water before entering the decanter, labeled as Stream 14. The decanter has three outlet streams, streams 16, 17, and 18. Stream 16 contains toluene, methanol, ethylbenzene and styrene, and this stream goes into T-101. Stream 17 contains small amounts of volatized compounds of styrene, ethylbenzene, water, toluene, methanol, and all the hydrogen produced. This stream goes as an off-gas product. Stream 18 contains all the water produced in the reaction including a set amount of methanol that may have fractionated along with the water. This water is sent to a wastewater facility to be cleaned and sent to the municipal wastewater system. Stream 16 enters T-101, which is a tray column, with 24 theoretical stages and a R/R_{MIN} of 1.6. The distillate stream of T-101, labeled as stream 22, contains the unreacted toluene and methanol, and this stream is recycled back into the reactant stream. This stream has less than five weight percent of ethylbenzene and Styrene. The

bottoms stream of T-101 contains the crude styrene and ethylbenzene. The bottoms stream, labeled as Stream 22, enters tower T-102. T-102 is a tray column with 75 trays. This tower will produce the ethylbenzene product stream in the distillate, and it will also produce the styrene product in the bottom stream. The ethylbenzene product stream can have 0.8 weight percent at most, of toluene, and three weight percent of styrene. The styrene product can only have up to 300 ppm of ethylbenzene in the stream.

1.4 Design Basis:

This process has various design specifications that exist to help define the process more accurately. In addition, these specifications given allow for ease in calculation when designing the process within CHEMCAD.

Overall Process Assumptions:

- The process is in steady state operation.
- The plant must have a capacity of 350,000 tons per year of crude styrene with less than 300 ppm of ethylbenzene present within the final product stream
- The working year equates to 8322 hours of operation.
- The pressure drop across pipes are negligible.
- Methanol and toluene streams are considered free of impurities.

Feed:

- Both feeds, toluene and methanol, are entering the process as a saturated liquid at 5.52 atm.
- The specific quantity of each feed stream is calculated so that the reactants enter the reactor in stochiometric ratios.
- The feed streams are pulling the reactants from a tank that is that is not factored into the CHEMCAD simulation.

Heat Exchangers:

- The toluene and methanol vaporizers, HX-101 and HX-102, are used to vaporize the saturated liquid feeds of the respective feed streams. The feed streams (Streams 1 and 2)

are fed via tube side, while the reactor effluent is used to heat the feed on the shell side (Streams 3 and 8).

- The number of tubes is not calculated during this preliminary determination.
- There is a 0.13 atm pressure drop across the heat exchanger.
- It is assumed that Stream 4 and Stream 19 is fully vaporized before mixing to form Stream 5.
- The Interchanger (HX-104) is used to condense the reactor effluent (stream 9) to a saturated liquid using cooling water, entering HX-104 at 88 °F (Stream 12). The cooled reactant fluid must be cooled to 100 °F. The cooling water must not be heated over 100 °F.

Fired Heater:

- This heater must heat the incoming reactants in Stream 9 to 977 °F before the reactants enter the reactors.
- Any radiant heat loss from the fired heater is neglected.
- There is a 0.70 atm pressure drop.

Reactor:

- The reactor is modeled as a packed bed reactor with a bulk density of 1000 kg/m^3 and a void fraction of 0.4.
- The reactor is adiabatic.
- The reactor involves two chemical reactions, with one yielding styrene and one yielding ethylbenzene. The reactor is split into two reactors for the two separate reactions in CHEMCAD.

- The feed of toluene and methanol entering the reactor must be equimolar.
- There is a pressure drop of 0.70 atm across the reactor.
- The two reactions occurring within the reactor are assumed to be irreversible.
- The overall conversion of toluene is 0.72.
- The selectivity regarding the styrene reaction is 0.68.

Decanter

- The decanter is a phase separator that takes the condensed reactor effluent and separates the effluent into three streams: an aqueous stream, gaseous stream, and an organic stream.
- The gaseous stream will contain all hydrogen created from the reactor as well as amounts of Styrene, toluene, methanol, and ethylbenzene.
- There is a negligible amount of water within the organic stream.
- These amounts will be calculated using Raoult's Law to determine the partial pressure of each substance in the gaseous phase.
- The aqueous stream contains all the water created in both reactions as well as a significant amount of methanol. For ease in calculation, a partition coefficient, 1.32, is used to determine the actual amount of methanol of that leaves via the aqueous stream.
- The organic stream contains all the rest of the feed that is not contained within the aqueous and gaseous streams.

Vaporizers:

- The vaporizers are shell and tube heat exchangers.
- Reactor effluent is pumped to the shell-side of the exchanger, and the incoming feed is pumped to the tube-side of the exchanger.

- There is a pressure drop of 0.13 atm.

Tower:

- The distillate stream from T-101 recycles unused methanol and toluene and is routed back to the beginning of the process.
- Column temperature must not exceed over 300 °F.
- Fractional Recovery of the light keys in both T-101 and T-102 is 0.999 and for the bottoms is 0.001.

CHAPTER II

II. METHODS

2.1 Selecting Chemical Components for Use in CHEMCAD

From chemical reactions being carried out in this simulation, the components listed below should be selected in from CHEMCAD's component database. CHEMCAD's component database hosts up to 2476 chemicals. Each of these chemicals holds physical property constant data for that specific component. For instance, selecting methanol allows CHEMCAD to auto populate the physical parameters for that compound, including Antoine's Equation constants, densities at various temperatures, heat capacity constants, and more. CHEMCAD also supports both common names and IUPAC names, and CAS numbers, and chemical formulas to help users find their desired compound quickly. For clarity, these are the equations that will be used in the simulation.

$$Toluene\ (C_7H_8) + Methanol\ (CH_3OH) \rightleftharpoons Styrene\ (C_8H_8) + Water\ (H_2O) + Hydrogen\ (H_2) \quad (1)$$

$$Toluene\ (C_7H_8) + Methanol\ (CH_3OH) \rightleftharpoons Ethylbenzene\ (C_8H_{10}) + Water\ (H_2O) \quad (2)$$

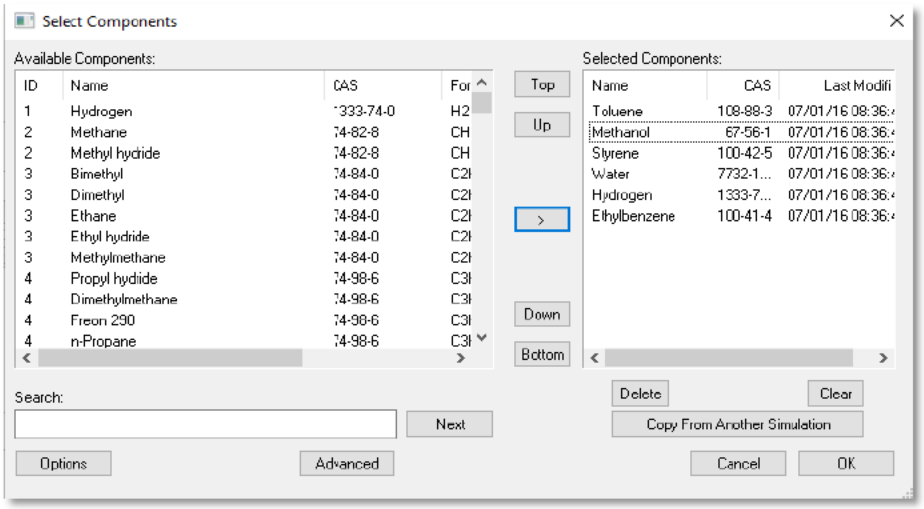

Figure 1 *Chemical Selection Dialog Box*

2.2 Selecting Thermodynamic Models for CHEMCAD

To begin each simulation, CHEMCAD asks the user to input the minimum and maximum of the system's pressure and temperature. Once this data is inputted, CHEMCAD employs the use of a "Thermodynamic Wizard". This "Thermodynamic Wizard" is an expert system that critically analyzes the model's current selected chemicals to determine each respective chemical's phases and compositions. From there, if a high temperature or high pressure is indicated by the user, CHEMCAD will label the process "Highly Non-Ideal" (Edwards, 2008, p. 28). The method in which CHEMCAD uses to determine the method to conduct thermodynamic equilibrium is called the "K-Value Method". For this process, CHEMCAD chose the K-value method to be NRTL (Non-Random-Two-Liquid) since this process involves liquid to liquid interaction. This equation is considered to accurately depict "local composition", "which is a composition that is different from the overall mixture composition". These compositions contain nonrandom molecular orientations that result from differences in molecular size and intermolecular forces" (Smith, Van Ness, Abbott, & Swihart, 2018, p. 471).

Upon selecting the K-value, CHEMCAD will choose a method to calculate the enthalpy of each stream. For this process, since NRTL was chosen for the K-Value, CHEMCAD chose the LATE method to calculate enthalpy. "Enthalpy is calculated using Latent Heat (LATE) in the liquid and VLE [Vapor-Liquid Equilibrium] phases and E-o-S [Equation-of-State] (SRK) in the superheated or gas phase." (Edwards, 2008, p. 8). Figure 2 shows the "Thermodynamic Settings" dialog box in CHEMCAD. Here, users can select the K-Value and H method to for CHEMCAD to use. It is important to note that the CHEMCAD's Thermodynamics Wizard built into CHEMCAD may choose the wrong thermodynamic model. To help ensure that the user knows which thermodynamic model is apt for each situation, Table 1 shows a table crafted by CHEMCAD that outline specific applications in which each method should be chosen.

Table 1 *CHEMCAD Thermodynamic Modelling Application Table*

CHEMICALS		
K-VALUE METHOD	APPLICATION	H-ENTHALPY
Vapor Pressure (VAP)[3]	Ideal solutions	SRK
UNIFAC[2]	P (0-4atm) T (275-475°K) Non-ideal - two liquid phases Heterogeneous azeotrope Group Contribution Predictive	LATE
Wilson[2]	Non-ideal solution with dissolved solids Homogeneous azeotrope	LATE
NRTL[2]	Highly non-ideal - two liquid phases Heterogeneous azeotrope	LATE
UNIQUAC[2]	Highly non-ideal - two liquid phases Heterogeneous azeotrope	LATE
Margules[2]	Highly non-ideal - two liquid phases Homogeneous azeotrope	LATE
T.K.Wilson[2]	Highly non-ideal - two liquid phases Homogeneous azeotrope	LATE
Hiranuma (HRNM)[2]	Highly non-ideal - two liquid phases	LATE
Regular Solution[2]	Moderately non-ideal (Predictive)	SRK
Van Laar[2]	Moderately non-ideal Homogeneous azeotrope	LATE
Modified SRK (MSRK)[1] 4 parameter	Polar compounds in regular solutions	SRK
Predictive SRK (PSRK)[1]	Polar compounds in non-ideal solutions Better than UNIFAC at high pressures	LATE

Note: Edwards, J. E. (2008, November). *Process Modelling.* Corporation web site: https://www.chemstations.com/content/documents/Technical_Articles/thermo.pdf,

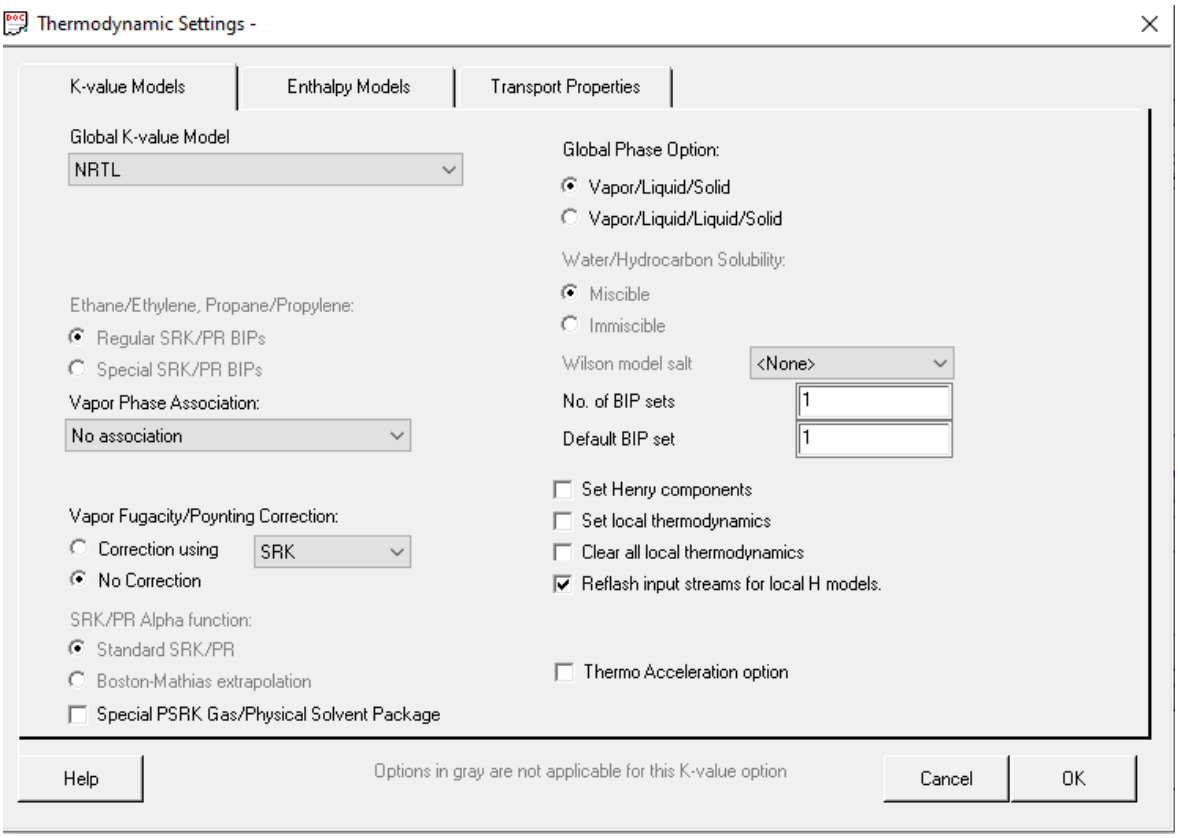

Figure 2 *A screenshot of the Thermodynamic Settings from CHEMCAD*

2.3 Selecting Topology for Simulation

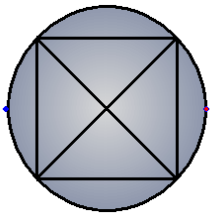

Figure 3 *A screenshot of the Controller UnitOps in CHEMCAD*

In order to simulate this process correctly, a PFD must be drawn of the process. Having a PFD of the process allows users to accurately see the way in which streams are heading. The direction of the streams is most definitely important to CHEMCAD simulations. The figure below shows a depiction of one of the UnitOps in CHEMCAD. The left side has a dark blue dot, while the right side has a dark pink dot. The incoming feeds are always tethered to a dark blue dot and the outgoing feeds are always tethered to a dark pink dot. A pink dot from one UnitOps can connect to the dark blue dot from another UnitOps as well. Once the PFD is finalized, different UnitOps are dragged into the simulation in their respective locations.

The simulation will differ from the PFD in a few aspects that is beyond the user's control. In a normal PFD, a stream that is mixing with another stream is easy to show, such as Stream 7 on the PFD (Recycle stream going into the incoming feed stream). Both streams will have to be mixed using the UnitOps called Mixers. In addition, there are various controllers placed throughout the simulation. These controllers are not included in the PFD since these controllers are meant for solving purposes only. They do not have a physical equivalent. These type of UnitOps are sometimes referred to as Phantom UnitOps.

Adding mixers and controllers also add extra streamlines to the simulation. For instance, from the PFD, there is a controller placed in the middle of stream 15. The controller has no physical

representation, so it is left out of the PFD. However, in the simulation, when stream 15 enters the controller, the outlet stream coming from the controller is listed as a new stream, rather than still being stream 15. These streams are not there physically, so the numbering of streams between the simulation and the PFD will be different.

Lastly, the two reactors and the two decanter tanks shown on both the PFD and CHEMCAD may only be one unit for each. However, for clarity since the reactor and decanter are integrally important to the process, the reactor and decanter were shown as two vessels rather than one.

The next two figures will show a full PFD and the simulation modeled after the PFD.

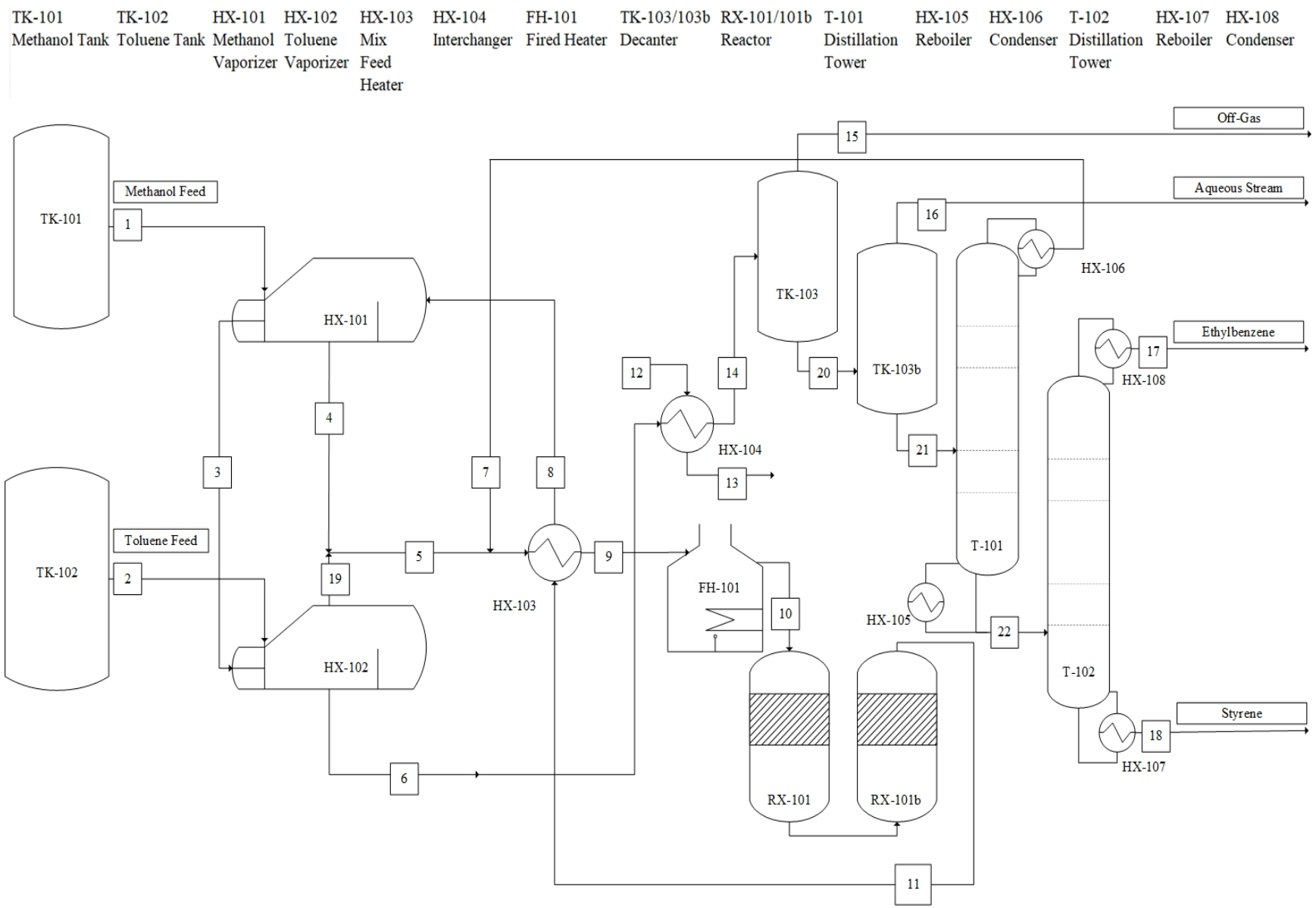

Figure 4 *PFD of Chemical Process*

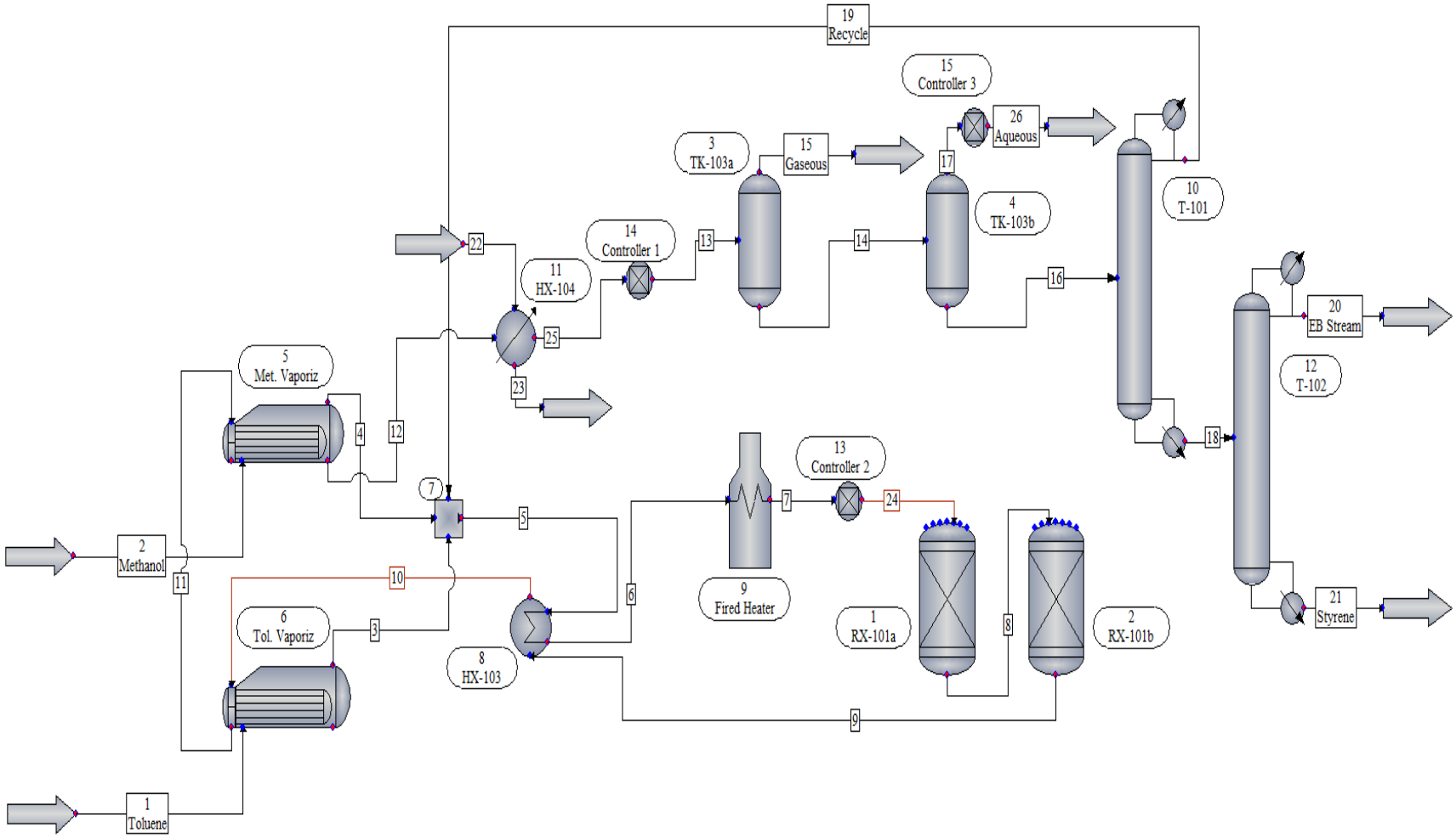

Figure 5 *Screenshot of CHEMCAD simulation*

2.4 Selecting the Properties of Feed Stream

This process has two feed streams entering the simulation. A feed stream is depicted as an arrow with a small pink dot at the top of the arrow. An example of these arrows is shown on the prior Figure with toluene and methanol streams. When feed streams are created, the streams must be specified. The figure below is an example of the "Edit Streams" dialog box in CHEMCAD.

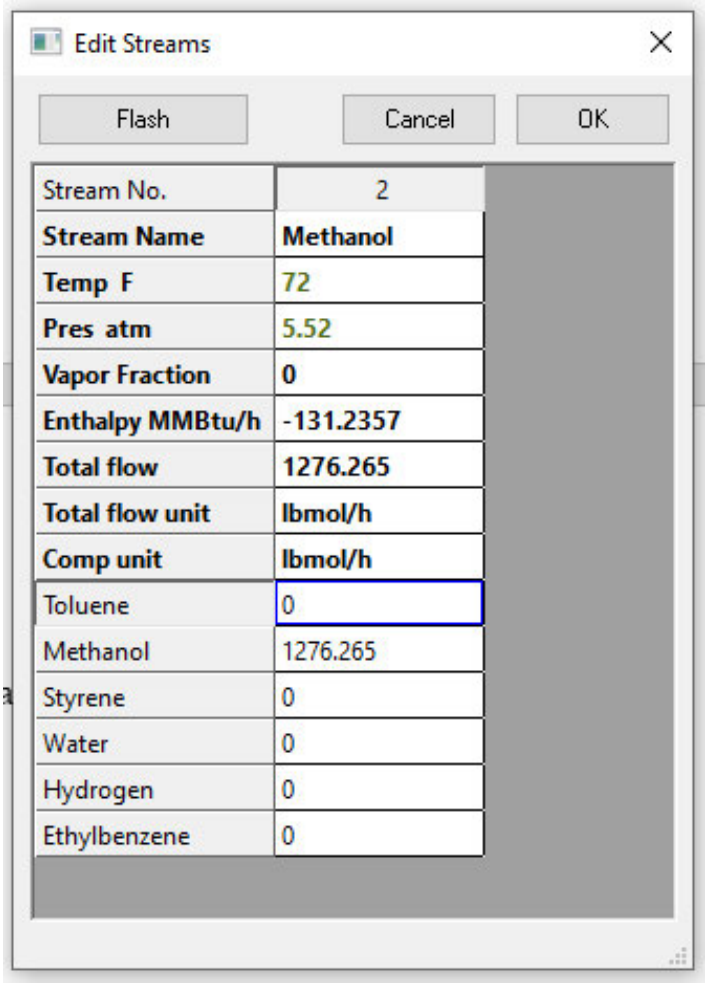

Figure 6 *Edit Streams Dialog Box*

Figure 7 shows the Edit Stream dialog box for the incoming methanol stream. From the design basis, the stream enters at 72 °F, and the pressure of the stream is at 5.52 atm. CHEMCAD must

only have two specifications of temperature, pressure, or vapor fraction. If there is only one specification, CHEMCAD will show the error: “Feed Streams are not well defined. Calculation bypassed.” CHEMCAD will not allow a third specification. Once each feed stream has two specifications, depending on the temperature and pressure, CHEMCAD can determine if the substance will be in the vapor phase or liquid phase. The button located on the upper left-hand corner labeled as “Flash”, tells CHEMCAD to determine the current enthalpy for the stream. The “Comp Unit” can allow users to freely change between units, such as lb/h or lbmol/h. The user will input the numeric value of the quantity of the respective substances. This will determine the ultimate amount of raw materials will be entering the process.

Using the stochiometric ratios given in the chemical equations, percent conversion and percent selectivity, it was determined that there needs to be a flow of 1200 lbmol per hour of toluene entering the process so that 350,000 tons of styrene is produced per year. Note: The working year is equivalent to 8322 hours.

2.5 CHEMCAD Specifications

2.5.1 Heat Exchangers

There are eight heat exchangers in this process, with four of those exchangers being attached to the distillation column UnitOps. The other four shell and tube heat exchangers must be specified using the dialog box depicted in the figure below. CHEMCAD only allows one specification per heat exchanger. CHEMCAD can also determine the changes in temperature of both outlet streams without a specification. These specifications are designed around the outlet streams of the exchanger. For instance, for HX-101, the outlet methanol Stream must be saturated vapor. In the specification dialog box, the vapor fraction of the methanol outlet stream should be set to "1". In addition, each heat exchanger resulted in a pressure drop of 0.13 atm, which was outlined in the design basis.

Table 2 *Heat Exchanger Specification*

Name	Type of Exchanger	Fluid in the Shell Side	Fluid in the Tube Side	Exchanger Specification
HX-101 (methanol Vaporizer)	Shell and Tube Exchanger	Heated Reactor Effluent	Incoming methanol Feed	The methanol outlet must be saturated vapor.
HX-102 (toluene Vaporizer)	Shell and Tube Exchanger	Heated Reactor Effluent	Incoming toluene Feed	The toluene outlet must be saturated vapor.
HX-103 (Interchanger)	Shell and Tube Exchanger	Heated Reactor Effluent	Incoming methanol and toluene Feed	No specification added
HX-104 (Product Condenser)	Shell and Tube Exchanger	Heated Reactor Effluent	Cooling Water	-Reactor Effluent must be at 100 °F. -Cooling water must also be at 100 °F.

HX-104 poses a problem. Here, there is a need for two specifications. However, CHEMCAD can only support two specifications. CHEMCAD controllers can help solve this need.

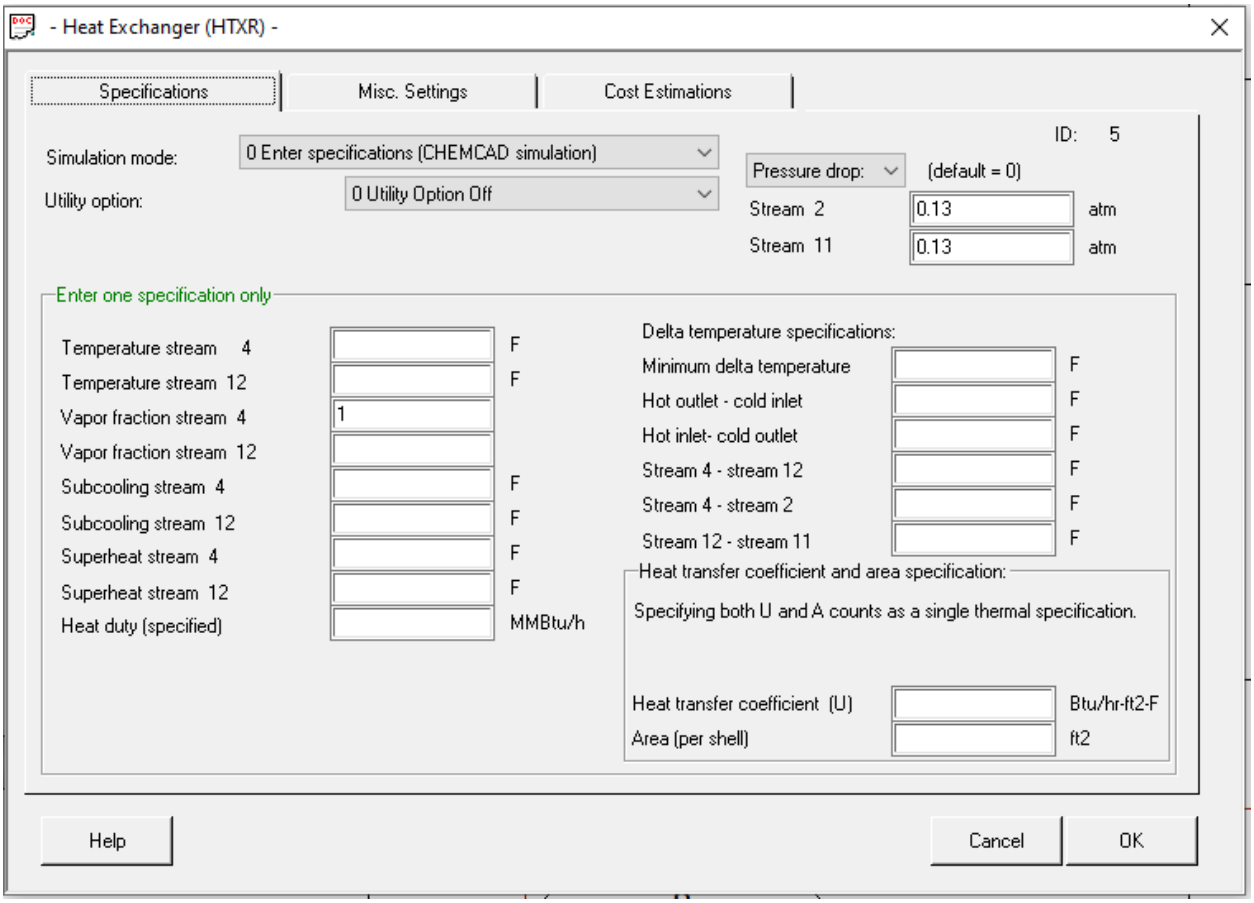

Figure 7 *Heat Exchanger parameter dialog box*

2.5.2 Controllers

Controllers are a type of process equipment located within CHEMCAD. It has one inlet stream and one outlet stream. These are used as the “Excel Solver” of CHEMCAD.

There are three controllers located within the simulation. These controllers ensure that all the design specifications are met accurately. These specifications could be met without the use of a controller, but it would take some time to accurately find the correct settings needed.

The first controller in the simulation ensures that the interchanger HX-104 has enough water flow so that the reactor effluent reaches 100 °F and that the water being used to cool the interchanger is set to 100 °F. In the specification window of each heat exchanger, CHEMCAD offers various ways in which users can determine how the exchanger works. Users can set the outlet temperature of the outlet tube side or outlet shell side streams, or users can set the vapor fractions of the outlet streams of the tube and shell sides. However, it is important to note that CHEMCAD can only handle one specification per heat exchanger. Natively, it is impossible for CHEMCAD to control both temperatures of both tube-side and shell-side streams. In order to control both stream temperatures, a controller is needed. The inlet of the cooling water on the shell side is set as 88 °F, so the only variable pertaining to the cooling water that can be modulated is the mass flow rate. Changing the mass flow of the water can allow for a change in the heat transferred. Using the heat capacity equation,

$$Q = mc\Delta T$$

CHEMCAD will modulate the mass of water needed to reach the desired cooling water outlet temperature.

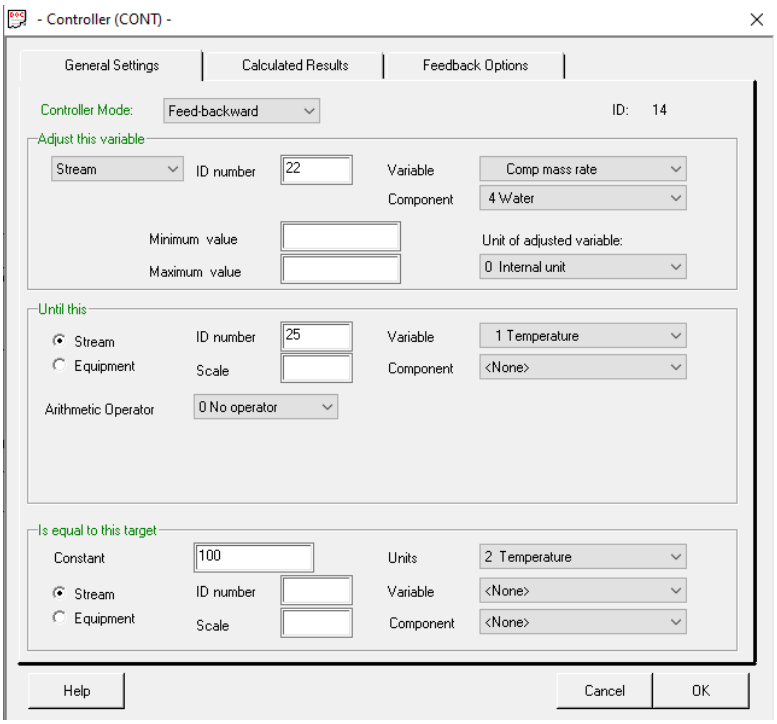

Figure 8 *Controller Parameter CHEMCAD Dialog Box*

Figure 8 is the specification sheet for the controller. The mode of the controller can be set as "Feed-Backward" or "Feed-Forward". This refers to the position of the controller in relation to the variable that it is controlling. For this simulation, the controller is placed downstream after the variable that is being modulated, so the "Feed-Backward" option is chosen.

Right below "Adjust this variable", users can determine the location in which the variable is located within the simulation. Here, stream 22 is selected, which is stream number of the inlet cooling water in the simulation (This stream is labeled as stream 12 on the PFD). Once the stream is selected, the "Variable" section will feature a drop-down menu. This drop-menu includes all the physical properties that can be changed of that chosen stream, including Total Mass Rate, Component Mass Rate, and Temperature. In this case, the mass flow rate of the water is selected to be adjusted. Next, under the "Until This" section, there is a similar setup as the

previous section. This is the section in which the user inputs dependent variable that will change in response to the independent variable. Since the native heat exchanger specification is already setting the temperature of the outlet tube side (reactor effluent) to 100 °F, the temperature of the outlet cooling water is chosen to be the dependent variable.

In the last section, under the “Is equal to this target”, this is the target goal at which the dependent variable will reach. Since the desired goal is for the outlet water stream temperature to only reach 100 °F, the constant “100” is inputted in the box. After the controller specification is finished, the simulation will determine the exact mass flow rate of the cooling water needed to reach the desired goal.

The second controller in the simulation ensures that the feed going into the reactor is equimolar in respect to toluene and methanol. The controller is placed on stream 10 when using the PFD. In the process, not all the toluene and methanol are used in the reaction, so there is a recycle stream. The methanol in the recycle stream is always less abundant than the toluene in the recycle stream because some of the methanol exits the reactor effluent along with the water in the aqueous stream produced by the decanter. In addition, the way in which the distillation towers are configured will also play in a role in the amount of methanol that is present within the recycle stream. This reaction must be equimolar amounts of both toluene and methanol. The amount extra methanol needed to make the reactor feed stream equimolar could be done by hand, but if a change is made in the simulation, the amount may change, and the process would to be done again, slowing down productivity. This controller is set to adjust the total molar flow rate of the methanol feed stream (Stream 1 in the PFD) until the component molar flow rate of methanol is equal to the component molar flow rate of toluene in stream 10. In Figure 8, under the “is equal to this target” instead of typing the current molar flow rate of toluene in stream 10, the stream

number is selected instead. Once the stream number is inputted, the variable is changed to the Total Component Rate" of the toluene. If done in this manner, if the molar flow rate of the toluene changes, the flow of the methanol will change in response. The controller's tolerance can be set by the user; for this application, the tolerance was set at ± 0.001.

The third controller used in this simulation is inputted so that the partition coefficient of the methanol is satisfied. The partition coefficient states that the mole fraction of the methanol in the organic phase divided by the mole fraction of the methanol in the aqueous stream. Since the Decanter is being simulated via two Component Separators, the controller will be placed downstream of the Component Separator that separates the aqueous stream from the organic stream. Since each Component Separator works by the user inputting mole fractions for either the top or bottom streams, these mole fractions are variables that can be manipulated by a controller. From Figure 8, under the "Until This", there is an option for "Arithmetic Operator", once this is selected, the controller can adjust the molar fraction of either the aqueous stream or the organic stream so that when divided, the constant can equal 1.32.

2.5.4 Decanter Conditions

In the process, there is a three-phase separator, or decanter. This separator takes the reactor effluent, and fractionates the product based on their state of matter. The decanter has four streams. For simplicity, these streams have been named: the organic stream, aqueous stream, gaseous stream, and feed stream. The gaseous stream exiting via the top of the decanter, carries all the hydrogen and various amount of volatized styrene, toluene, methanol, and water.
There is no UnitOps available in CHEMCAD that can accurately model the decanter's behavior. The decanter must be modeled using a combination of UnitOps equipment. The first option is to model the Decanter using two component separators, a type of UnitOps in CHEMCAD. Component separators separates compounds in a stream based on user input with no other calculation. One compound separator will separate the gaseous stream, and the other separator will separate the aqueous stream. The second option is to model the decanter using a flash drum (another type of UnitOps in CHEMCAD) and a component separator. A flash drum can determine how much of the stream is volatized at a given V/F or temperature and pressure. Both options are explored to see the differences in calculations.

2.5.4.1 First Decanter Model Operation:

In order to use two component separators, the amount of each substance that is volatized must be determined. These varying amounts are calculated following Raoult's Law. This law describes this relationship between the molar fraction of volatized compounds and the vapor pressure of each respective species :"If a gas at temperature T and pressure P contains a saturated vapor whose mole fraction is y_1 (mol vapor/mol total gas), and if this vapor is the only species that would condenses if the temperature were slightly lowered, then the partial pressure of the vapor

in the gas equals the pure-component vapor pressure $p^*_i(T)$ at the system temperature" (Felder & Rousseau, 2005, p. 249).

$$Raoult's\ Law: p_i = y_i P = p_i^*(T)$$

Raoult's Law will determine the partial pressure of the gaseous stream. In return, since the overall pressure is known, the corresponding molar fractions can be calculated. However, in order to apply Raoult's Law, the pure-component vapor pressure must be calculated. Using the constants in Table 3, Antoine's Equation is applied to each chemical at 100 °F, or 38 °C. This equation is given below.

$$Antoine's\ Equation: p^* = exp\ (A - B * (T + C)^{-1})$$

Table 3 *Antoine Equation Constants* *source

Chemical Name	A	B	C
Methanol	7.88	1473.11	230.0
Water	7.97	1668.21	228.00
Toluene	6.96	1346.77	219.69
Styrene	7.07	1507.43	214.99
Ethylbenzene	6.96	1423.54	213.09

There is also an aqueous phase leaving the decanter. Due to the uncharged nature of the organic compounds (ethylbenzene, toluene, styrene), these compounds easily separate from water; however, methanol is partially attracted to water due to hydrogen bonding between the oxygen attached to methanol's alcohol functional group, and the hydrogens within the water molecules. A partition coefficient was assumed; stating that the molar fraction of methanol in the Organic Stream must be 1.32 bigger in magnitude when compared to the mol fraction of methanol present within the aqueous stream.

To ease in the calculations of modeling the decanter's behavior, Excel Solver was used to accurately determined the total amount of volatized amounts of the compounds leaving in the Gaseous Stream.

To calculate the balance correctly, constraints must be aligned first. For all the compounds entering the decanter from the feed stream, the mol fraction determined from the organic stream for each respective compound was multiplied by the vapor pressure calculated by the Antoine's Equation, resulting in a product. This product is then divided by the total system pressure. Due to Raoult's Law, the product determined should equal the mol fraction of that respective compound within the Gaseous Stream when multiplied by total pressure. If these products were subtracted, the difference should be zero. This constraint is demonstrated by the following equation for methanol.

$$P_m^*(T) * P = X_{o,m} * P_m$$

This difference was the first constraint inputted into Solver. At this point in the calculation, the mol fractions of both the organic and gaseous streams are unknown, so estimates are inputted. The molar fractions in both streams should equal one, which was listed as a constraint within Excel Solver.

In addition, a separate balance was done on each respective compound. To ease in calculation, accumulation within the decanter was neglected. Due to no accumulation and no reactions occurring within the decanter, the amount entering the decanter should leave the decanter. The respective amounts of each compound leaving via the gaseous, aqueous, and organic streams were subtracted from the feed stream. The resulting difference should equal zero, and this calculation was used as a constraint for Excel Solver. The equation below provides a demonstration of this constraint using methanol.

$$X_{f,m} - X_{o,m} - X_{a,m} - X_{g,m} = 0$$

The partition coefficient is also inputted, whereas the mol fraction of methanol in the gaseous stream should be 1.32 times bigger than the mol fraction of methanol in the aqueous stream. The methanol molar fraction in the organic stream was divided by the molar fraction of methanol in the aqueous stream, and the quotient was subtracted from 1.32. This calculation should equal zero and was set as the last Excel solver constraint. After running Excel Solver, the following stream compositions were generated. This partition coefficient equation is shown below.

$$1.32 = X_{o,m} / X_{a,m}$$

Setting all these constraints into Excel Solver, the respective molar fractions of each compound within the gaseous stream was determined. In the simulation, the two component separators will fractionate the incoming feed stream according to the mole fractions determined via Excel Solver. Figure 9 shows the dialog box for setting the component separator's parameters. It is important to note that the user must calculate what percentage of each respective compound is leaving via the gaseous stream or aqueous stream. For instance, the molar fraction of the methanol leaving via the gaseous stream is 0.03, which equates to 26 lbmol per hour. 26 lbmol per hour is 12.9% of the methanol entering into the decanter, so for the component separator parameter, the split fraction of the methanol leaving from the feed stream would be 0.129 instead of 0.03. If all a compound is going out in a stream, a "1" can be used.

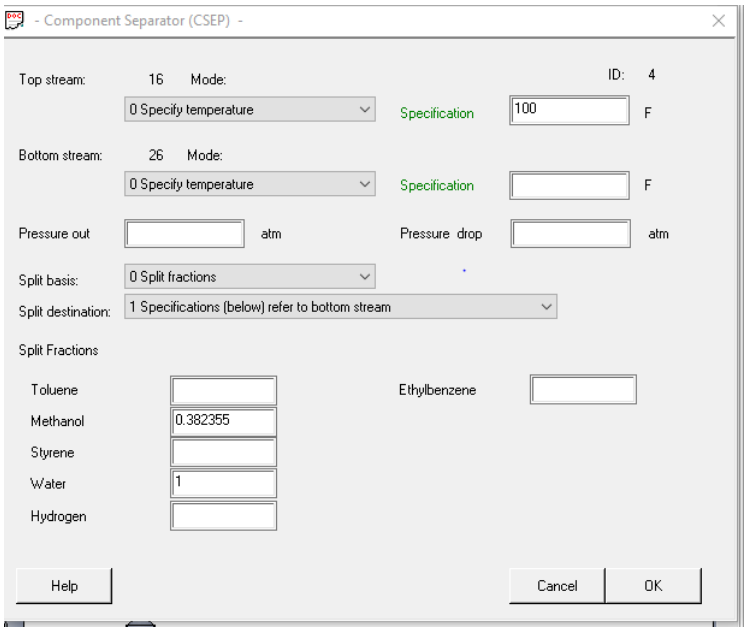

Figure 9 *Component Separator Dialog Box*

2.5.4.2 Second Decanter Operation

The second decanter modeling choice is using a combination of the flash drum UnitOps and the component separator. The flash drum will calculate the volatized substances by using the physical properties preloaded in CHEMCAD for each substance. Figure 10 shows the dialog box to enter the flash drum's parameters. Then, in the same fashion as the first decanter model, the

Then, in the same fashion as the first decanter model, the component separator is set to fractionate the aqueous stream from the incoming feed stream.

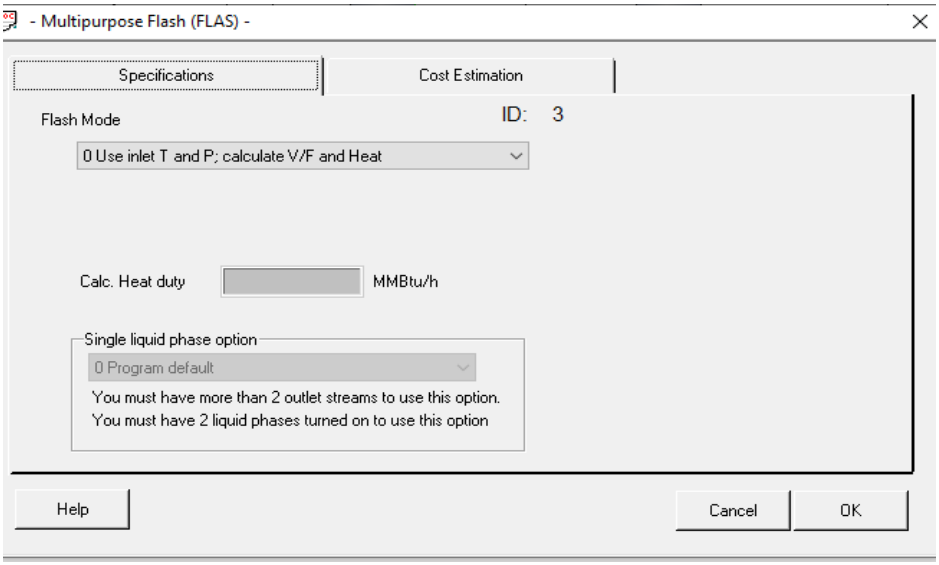

Figure 10 *Parameter Dialog Box for Flash Drums*

2.5.4.3 Main Differences Between the Models

As outlined by Design Basis, all the hydrogen is assumed to exit via the gaseous stream. With a component separator, all the hydrogen exited via the gaseous stream with no trace amount exiting the decanter via the organic stream. However, if the flash drum is used, CHEMCAD uses physical data to determine the volatility of the compounds. CHEMCAD had mostly all the hydrogen leaving the decanter via the gaseous stream, with less than 1 lbmol of hydrogen exiting via the organic stream.

In addition, there were differences in the exact amount of the volatized chemicals in the gaseous stream. Table 4 shows the differences below.

Table 4 *Molar percent of the gaseous stream exiting the Decanter*

Chemical Name	Using Excel Solver	Using Flash Drum UnitOps
Styrene	0.43%	0.38%
Toluene	0.52%	0.52%
Methanol	3.02%	0.35%
Water	2.37%	3.75%
Hydrogen	93.44%	94.67%
Ethylbenzene	0.22%	0.33%

The main difference lies within the methanol mole fraction percentage. The Antoine's Equation constants for methanol that CHEMCAD used were different than the constants used in the Excel Solver spreadsheet, resulting in a 26 lbmol per hour difference. Both models can be used; however, the main difference would be in the amount of incoming methanol feed regulated by controller #2. The first decanter model was ultimately chosen to model the decanter in the simulation.

2.5.5 Reactor

Before inputting the reactor within CHEMCAD, various reactor conditions were given as part of the design basis. The reactor is to operate adiabatically at 977 °F and 4 atm. The conversion of toluene is 82% percent. The selectivity of the toluene being converted to styrene is 72%. Even though both reactions are reversible, in this study, the backwards reaction is negated, and the reactions are irreversible moving in the forward direction only.

CHEMCAD offers a great deal of various reactors. These reactors are all designed to handle specific types of chemical reactions. In this study, there are two reactors that can be used. The first reactor type, the Stochiometric Reactor, is “the simplest reactor type that can be simulated” (Turton, Bailie, Whiting, Shaeiwitz, & Bhattacharyya, 2012, p. 430). This reactor uses the stochiometric ratios, conversion rates, temperature, and pressure to determine the amount of product created. This reactor can only handle one reaction at a time. The second reactor type is the Gibbs Reactor. This reactor calculates the reactor effluent composition using a “free energy minimization technique” (Turton, Bailie, Whiting, Shaeiwitz, & Bhattacharyya, 2012, p. 431). In this case, the reaction conversion, reaction selectivity, and reaction products are all determined via CHEMCAD.

In this study, since there are specific conversion and selectivity rates, the Stochiometric Reactor was chosen. Figure 11 shows the parameter dialog box. Here, the user determines the thermal mode of the reactor, and the key component. CHEMCAD uses this component as the basis for conversion. Since the reactor can only handle one reaction at a time, two Stochiometric Reactors are used in the simulation.

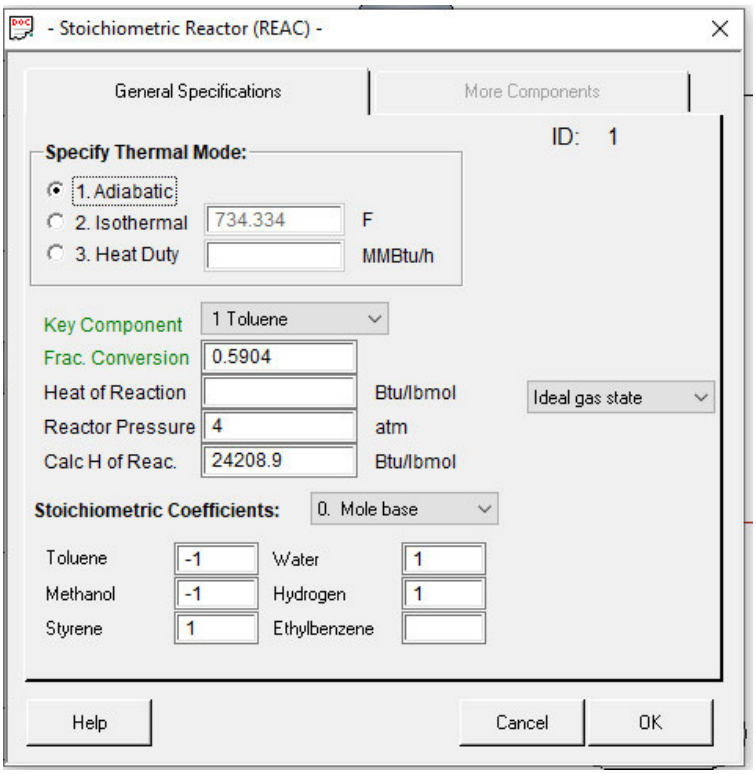

Figure 11 *Stochiometric Reactor Parameter Dialog Box*

2.5.5 Mixers and Dividers:

In the same sense as the controllers, these UnitOps are used to join or separate chemical streams. The only parameter that can be set is the outlet pressure of the mixer. There is one mixer in the process that mixes the recycle stream with the incoming feed stream. This UnitOps is not shown on the PFD.

2.5.6 Distillation Towers (Shortcut Tower):

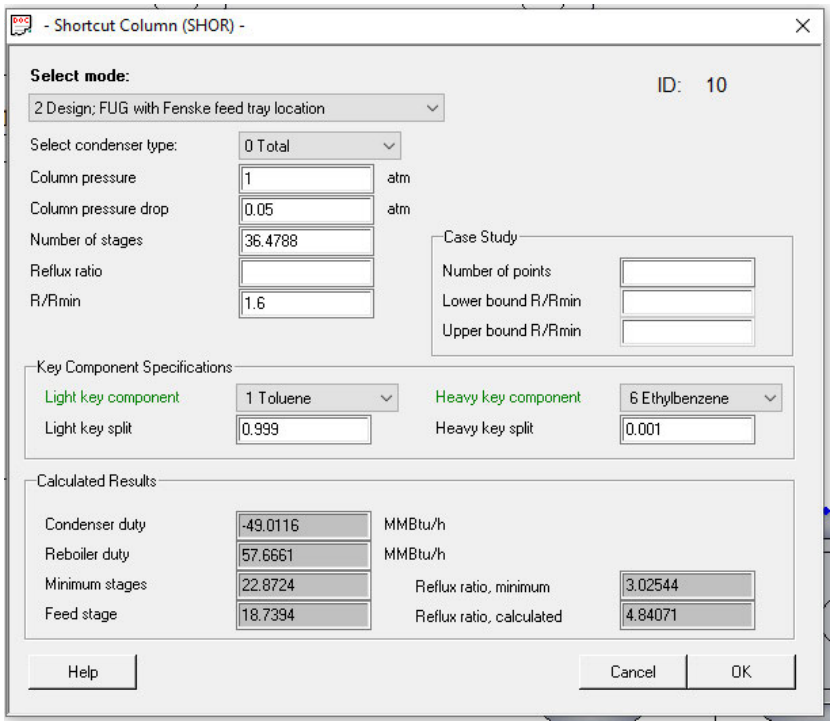

Figure 12 *Shortcut Distillation Tower Dialog Box*

The figure above is a screenshot of the shortcut distillation tower parameter dialog box. In the process, there is two different distillation towers. T-101 takes the organic stream from the decanter and splits the toluene and methanol from the two products, styrene and ethylbenzene. T-102 splits the toluene and ethylbenzene into separate product streams. CHEMCAD offers a "Shortcut Column", that allows for quick distillation without many specifications. Once the Shortcut Column is completed, a rigorous model can be created, which requires more specifications, such as the condenser duty, and reboiler duty.

For the shortcut model, if user select the mode, "Design FUG wit hFenske feed tray location", the user will only have to input the Column pressure, pressure drop, R/Rmin, and the light key component, and the heavy key component. It is important to note that when determining the light

key and heavy key split, this split is only applicable to the distillate stream. These “splits” are referring to amount of each key component that will go into the distaillate stream.

In addition, selecting the condenser type changed the temperature of the distillate stream for T-101. Having the condenser set at “Total”, the temperature of the distillate stream for T-101 is 147 °F; however, if the condenser is set at “Partial”, the temperature increased to 277 °F. This increase in temperature caused a pinch zone error to occur within one of the Heat Exchangers. Pinch zones occur when the LMTD or the “Log Mean Temperature Difference” of the heat exchanger is negative or approaching zero. When this occurs, the two fluids flowing thorugh the exchangers are already close in temperature. If the two streams are close to the same temperature, there is very little heat transfer occuring. Without any heat transfer, CHEMCAD cannot reach the specification of the heat exhcanger set by the user, and an error occurs.

CHAPTER III

III. RESULTS

The data collected by CHEMCAD can be exported in multiple ways. Primarily, CHEMCAD creates a stream report. A stream report essentially characterizes each stream based on the stream numbers on the simulation. This report can be amended within the settings of CHEMCAD. The data that the stream report gives includes the individual mass quantities and mass fractions of each respective compound in the process. The report can also give more specialized information about the streams, such as the stream's enthalpy, specific gravity, and the specific heat coefficient. The next table shows the stream report of the simulation. The stream table has been modified to match the streams on the PFD.

3.1 Meeting Specifications

There are several specifications that were required to be met during this process. After creating the simulation successfully, an overall stream report was generated, and several streams were selected to show verification that these specifications were met.

1. The recycle stream (stream 7) must have a 4 weight % maximum of ethylbenzene present, and the weight % sum of ethylbenzene and Styrene must not exceed 5%
    a. From the stream report, (stream 7), ethylbenzene makes up 0.175 of the weight % of the recycle stream. This is in part due to the specifications of the distillation tower T-101.
2. Reactor influent must be equimolar going into reactor.
    a. Stream 10 shows that the toluene and methanol have the same number of moles. Controller 2 ensures that the incoming methanol feed rate is adjusted so that the when the recycled methanol stream is added to the incoming feed stream, the raw materials can be equimolar.
3. The reactor effluent must be condensed to a saturated liquid at 100 °F using HX-104, and the cooling water outlet must leave HX-104 at 100 °F.
    a. Controller 1 modulates the mass flow rate of the cooling water stream so that the final temperature equilibrium between the reactor effluent and the cooling water is 100 °F.
4. The amount of water and hydrogen in the organic phase are negligible.
    a. Using a component separator as the decanter allows users to push all the water into the aqueous phase, and all the hydrogen into the gaseous phase without any trace of those two chemicals in the organic phase.

    b. If a flash drum and a component separator is used for the decanter instead of two component separators, the amount of Hydrogen present within the organic phase is only 0.654 lbmol/hr, which is a very small amount.

5. The molar fraction of methanol in the organic stream (stream 21) divided by the molar fraction of the methanol in the aqueous stream (stream 16) must equal 1.32.
    a. Controller 3 changes the component separator split fraction parameters so that this specification must be met. The molar fraction of methanol in the organic phase is 0.0736 and the molar fraction of methanol in the aqueous phase is 0.0557, when divided equals 1.32
6. The ethylbenzene product stream (stream 17) must have 0.8 weight % maximum of toluene and 3 weight % of styrene
    a. The ethylbenzene product stream has trace amounts of toluene and styrene present within the system.
7. The styrene product stream can have at most 300 ppm of ethylbenzene present.
    a. 12 pounds in a 38,396 lb per hour stream is 133 ppm, which is below the specification.
8. There must be 350,000 tons of styrene produced yearly.
    a. The simulation created yields 823 lbmol of styrene every hour. With the working year equaling 8322 hours, this is equivalent to 356,148 tons of styrene produced per year, which is slightly over the intended goal.

Table 5. Stream Tables generated by CHEMCAD

Stream No.	1	2	3	4	5	6	7	8	9	10	11
Component Flowrates (lb/h)											
Toluene	-	110,569	19,062	-	129,186	19,062	18,617	19,049	129,186	129,186	19,049
Methanol	41,377	-	6,628	41,377	44,924	6,628	3,547	6,624	44,924	44,924	6,624
Styrene	-	-	86,273	-	-	86,273		86,214	-	-	86,214
Water	-	-	21,548	-	-	21,548	-	21,533	-	-	21,533
Hydrogen	-	-	1,670	-	-	1,670	-	1,669	-	-	1,669
Ethylbenzene	-	-	39,086	-	39	39,086	39	39,059	39	39	39,059
Total Mass Flow (lb/h)	41,377	110,569	174,267	41,377	174,149	174,267	22,203	174,149	174,149	174,149	174,149
Component Weight Percent											
Toluene	0%	100%	11%	0%	74%	11%	84%	11%	74%	74%	11%
Methanol	100%	0%	4%	100%	26%	4%	16%	4%	26%	26%	4%
Styrene	0%	0%	50%	0%	0%	50%	0%	50%	0%	0%	50%
Water	0%	0%	12%	0%	0%	12%	0%	12%	0%	0%	12%
Hydrogen	0%	0%	1%	0%	0%	1%	0%	1%	0%	0%	1%
Ethylbenzene	0%	0%	22%	0%	0%	22%	0%	22%	0%	0%	22%
Component Mole Percent											
Toluene	0%	100%	6%	0%	50%	6%	65%	6%	50%	50%	6%
Methanol	100%	0%	6%	100%	50%	6%	35%	6%	50%	50%	6%
Styrene	0%	0%	23%	0%	0%	23%	0%	23%	0%	0%	23%
Water	0%	0%	33%	0%	0%	33%	0%	33%	0%	0%	33%
Hydrogen	0%	0%	23%	0%	0%	23%	0%	23%	0%	0%	23%
Ethylbenzene	0%	0%	10%	0%	0%	10%	0%	10%	0%	0%	10%
Stream Conditions											
Pressure (atm)	5.52	5.52	3.74	5.39	5.39	3.61	1.00	3.87	5.26	4.61	4.00
Vapor Fraction	0.00	0.00	1.00	1.00	0.90	1.00	0.00	1.00	1.00	1.00	1.00
Enthalpy (MMBTU/h)	-132.79	6.05	-54.66	-110.77	-84.53	-76.68	-9.59	-24.85	-80.28	-20.60	-20.60

Stream No.	12	13	14	15	16	17	18	19	20	21	22
Component Flowrates (lb/h)											
Toluene	-	-	19,062	427	-	19	-	110,569	18,635	18,620	19
Methanol	-	-	6,628	858	2,223	-	-	-	3,547	3,546	-
Styrene	-	-	86,273	397	-	86	85,791	-	85,876	85,807	85,876
Water	4,435,546	4,435,546	21,548	379	21,170	-	-	-	-	-	-
Hydrogen	-	-	1,670	1,670	-	-	-	-	-	-	-
Ethylbenzene	-	-	39,086	205	-	38,831	12	-	38,882	38,850	38,843
Total Mass Flow (lb/h)	4,435,546	4,435,546	174,267	3,934	23,392	38,936	85,802	110,569	146,941	146,824	124,738
Component Weight Percent											
Toluene	0%	0%	11%	11%	0%	0%	0%	100%	13%	13%	0%
Methanol	0%	0%	4%	22%	10%	0%	0%	0%	2%	2%	0%
Styrene	0%	0%	50%	10%	0%	0%	100%	0%	58%	58%	69%
Water	100%	100%	12%	10%	90%	0%	0%	0%	0%	0%	0%
Hydrogen	0%	0%	1%	42%	0%	0%	0%	0%	0%	0%	0%
Ethylbenzene	0%	0%	22%	5%	0%	100%	0%	0%	26%	26%	31%
Component Mole Percent											
Toluene	0%	0%	6%	1%	0%	0%	0%	100%	13%	13%	0%
Methanol	0%	0%	6%	3%	6%	0%	0%	0%	7%	7%	0%
Styrene	0%	0%	23%	0%	0%	0%	100%	0%	55%	55%	69%
Water	100%	100%	33%	2%	94%	0%	0%	0%	0%	0%	0%
Hydrogen	0%	0%	23%	93%	0%	0%	0%	0%	0%	0%	0%
Ethylbenzene	0%	0%	10%	0%	0%	100%	0%	0%	24%	24%	31%
Stream Conditions											
Pressure (atm)	1.00	1.00	3.47	3.47	3.47	1.00	1.05	5.39	3.47	1.05	1.05
Vapor Fraction	0.00	0.00	0.24	0.99	0.00	0.00	0.00	1.00	0.00	0.00	0.00
Enthalpy (MMBTU/h)	-30193.00	-30140.00	-129.00	-4.48	-150.94	1.70	45.15	35.82	-125.40	45.15	46.78

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