

Group-12

Styrene Production from Ethylbenzene

Overview:

This project focuses on operating a mini-plant to produce styrene from ethylbenzene. The key components include an isothermal reactor that converts ethylbenzene to styrene at around 600°C and a distillation column that separates the styrene from other components.

Objectives:

The primary objective of this project is to operate a "Mini-plant" that simulates the industrial production of styrene from ethylbenzene, incorporating essential process elements such as isothermal dehydrogenation, distillation. The key goals include:

- Startup and Operation
- Reaction Control
- Separation and Distillation Efficiency
- Product and By-product Analysis

This project aims to replicate critical aspects of the industrial process, enabling the analysis and optimization of styrene production on a smaller scale, and providing insights for potential scale-up.

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The overall design of the mini-plant will look like this. Although we would not be getting into the working of the individual element of the plant but rather would focus mostly on the processes and optimization techniques.

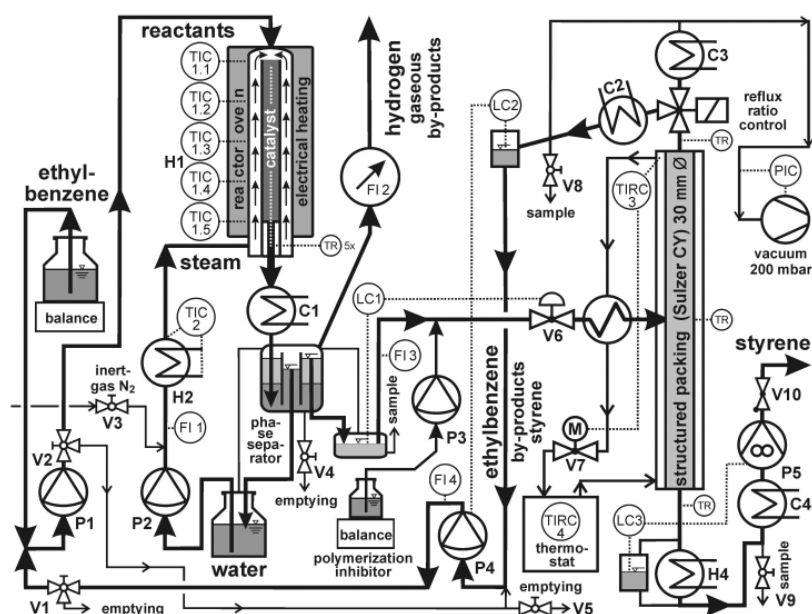


Fig-1 Flow scheme of the experimental plant

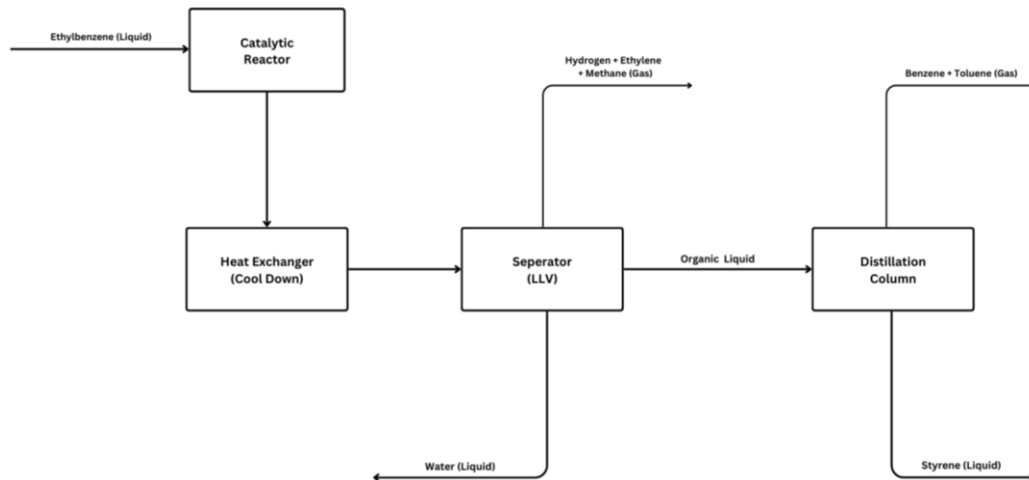


Fig-2 Simplified Flow Scheme

Flowsheet Overview:

The complete process have been simulated in **ASPEN**. And the data analysis for mass balances and energy balances has been obtained from the flowsheets itself. The methods and plots for optimization is also done using **ASPEN**. The various components used in the flowsheet are as follows:

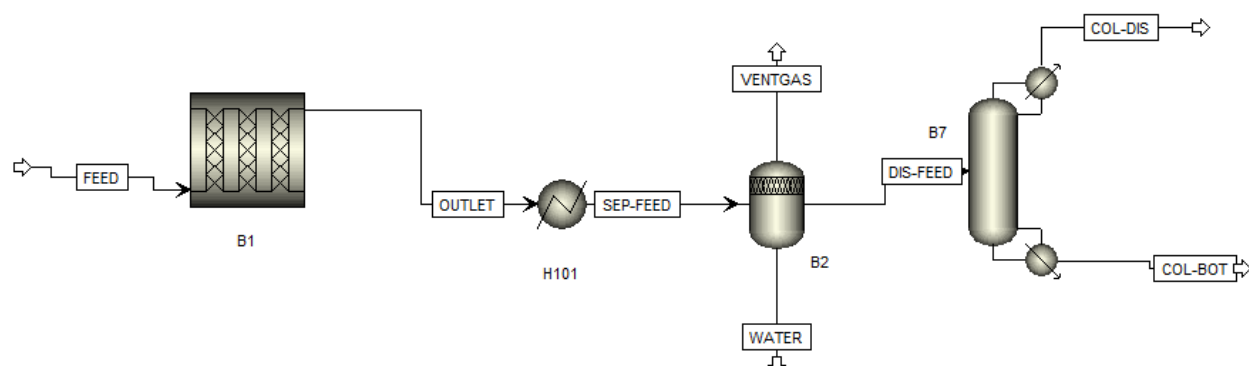


Fig-3 ASPEN Simulation Flow Sheet

- Heat Exchanger – H101
- LLV (Liquid-Liquid-Volume) Seperator – B2
- Distillation Column – B7
- Dehydrogenation Reactor (RPlug Reactor) - B1

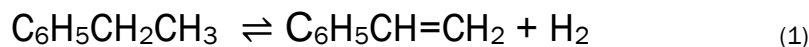
Components:

Name	Formula
Ethylbenzene	$C_6H_5CH_2CH_3$
Styrene	$C_6H_5CH=CH_2$
Hydrogen	H_2
Benzene	C_6H_6
Ethylene	C_2H_4
Toluene	$C_6H_5CH_3$
Methane	CH_4
Water	H_2O

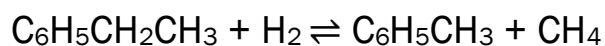
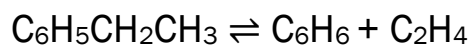
Process Overview:

1. Catalytic Dehydrogenation of Ethylbenzene

Our simulation focuses on production of styrene via catalytic dehydrogenation of ethylbenzene. The major reaction is the reversible, endothermic conversion of ethylbenzene to styrene and hydrogen:



Competing thermal reactions degrade ethylbenzene to benzene and ethylene. It also reacts with hydrogen to form toluene and methane.



The process occurs at above 600° C and a low pressure (0.4-1.4 bar) favor the generation of products. The process utilizes a metal catalyst such as zinc or magnesium oxides on activated carbon to minimize side reactions.

The feed stream is typically preheated to temperatures ranging from 500 °C to 600 °C and fed into a fixed bed reactor at **1 bar**; the larger limit of the range of temperatures will be used. The reaction is endothermic and typically reactor temperatures will range from **600°C to 620°C**. At higher temperatures, the **thermal-decomposition of styrene** begins to occur.

From *Lee et al.[3]* the size of the reactor had an internal diameter of 3.50 meters and a length of 1.43 meters, and the catalyst weight was set to 78330 kg. The iron catalyst particle size was specified to be 0.25-0.42 mm; bed voidage is 0.4.

Kinetic data provided as an example by *Lee et al.[3]* describes rates for 3 relevant reactions in this process.

Frequency Factor $\frac{\text{kmol}}{\text{kg}_{\text{cat}}\text{sec}}$	Activation Energy $\frac{\text{kJ}}{\text{kmol}}$
7.57×10^{-5}	$E_{A_1} = 0.17538$
1.51×10^{-6}	$E_{A_2} = 0.29629$
5.11×10^{-6}	$E_{A_1} = 0.47476$

The rate laws for the corresponding equations have been calculated using the Arrhenius equation and entered into ASPEN directly.

$$k = A \cdot e^{-E_a/RT}$$

2. Liquid – Liquid – Volume (LLV) Separator

After exiting the catalytic reactor as, the outlet stream cools down the 50°C using the heat exchanger. This ensures that majority of liquid organic matter and water are in their liquid phases; this minimizes the amount of organic matter in the vapor stream. Now, the organic matter and water should be easily separable due to their intrinsic immiscible properties.

The initial operating temperature and pressure is set to **50°C** and **1 bar** respectively. The choice for these values are explained in the optimization part of the report.

3. Distillation Column

The last block will focus on the design of distillation column to separate styrene (heavy key) from the rest of the organic liquid recovered from the LLV separator. The light key will be specified as ethyl-benzene. The column have a feed entering at 50°C. The optimum **reflux ratio** and **number of stages** found for maximum yield of styrene are **11** and **52 stages**. The choice for them is explained in the optimization part of the report.

Process Data:

Feed Basis:

- Ethylbenzene: 1000 kmol/h
- Water: 7000 kmol/h

Material and Energy balance for Styrene Production:

The Material and Energy balances for the corresponding unit in the process are as follows:

1. Dehydrogenation Reactor

Inputs: Ethylbenzene(1000kmol/hr) and Water (vapor phase) (7000 kmol/hr)

Outputs: Crude Styrene (mostly Styrene), H₂ (vented), and unconverted Ethylbenzene. The output was going through the stream named outlet in the flow diagram:

Component	Feed (Inlet)				Output (Outlet)			
	Mole Fraction	Molar Flowrate(kMol/hr)	Mass Fraction	Mass Flowrate (Kg/hr)	Mole Fraction	Molar Flowrate(kMol/hr)	Mass Fraction	Mass Flowrate (Kg/hr)
METHANE	0	0	0	0	0.000881642	7.784308864	0.000537648	124.8817989
ETHYL BENZENE	0.125	1000	0.45707757	106167.4	0.018448555	162.8883307	0.074452602	17293.43056
STYRENE	0	0	0	0	0.092398891	815.8200532	0.365812648	84968.89859
HYDROGEN	0	0	0	0	0.091517248	808.0357443	0.007012841	1628.903096
BENZENE	0	0	0	0	0.001529823	13.50730726	0.004542494	1055.104937
ETHYLENE	0	0	0	0	0.001529823	13.50730726	0.001631393	378.9307562
TOLUENE	0	0	0	0	0.000881642	7.784308864	0.003087944	717.2502666
WATER	0.875	7000	0.54292243	126106.96	0.792812376	7000	0.54292243	126106.96
Total	1	8000	1	232274.36	1	8829.32736	1	232274.36

Table-1 Reactor Streams Data

Feed Data:

- Molar Flow rate: 8000 kmol/hr
- Mass flow rate: 232274.6 Kg/h
- Molar Enthalpy: -173410 kJ/kmol

Outlet Data:

- Molar Flow rate: 8829.327 kmol/h
- Mass flow rate: 232274.6 kg/h
- Molar Enthalpy: -144233 kJ/kmol

Mass Balance:

From the above data we can see that the mass flow rate through the feed in the reactor is equal to the mass flow rate of the outlet coming from the reactor.

Energy Balance:

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta H + \Delta E_k + \Delta E_s \quad (W_{\text{net}} = 0; \Delta E_k = 0; \Delta E_s = 0)$$

$$Q_{\text{in}} = \Delta H = H_2 - H_1 = n_2 h_2 - n_1 h_1$$

- n_2 = molar flow rate of output stream = 8829.33 kmol/hr
- n_1 = molar flow rate of input stream = 8000 kmol/hr
- h_2 = molar enthalpy of output stream = -144233 kJ/kmol
- h_1 = molar enthalpy of output stream = -173410 kJ/kmol

Substituting values,

$$Q_{\text{in}} = [(-144233 \times 8829.33) - (-173410 \times 8000)]/3600 = 31610.9 \text{ kW}$$

Which is equal to the **heat duty value of 31611.1659 kW**

2. Heater**Inlet Data:**

- Molar Flow rate: 8829.33 kmol/hr
- Mass flow rate: 232274.6kg/h
- Molar Enthalpy: -144232.6 kJ/kmol

Outlet Data:

- Molar Flow rate: 8829.33kmol/h
- Mass flow rate: 232274.6kg/h
- Molar Enthalpy: -209107 kJ/kmol

Energy Balance:

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta H + \Delta E_k + \Delta E_s \quad (W_{\text{net}} = 0; \Delta E_k = 0; \Delta E_s = 0)$$

$$Q_{\text{in}} = \Delta H = H_2 - H_1 = n_2 h_2 - n_1 h_1$$

- n_2 = molar flow rate of output stream = 8829.33 kmol/hr
- n_1 = molar flow rate of input stream = 8829.33 kmol/hr
- h_2 = molar enthalpy of output stream = -209107 kJ/kmol
- h_1 = molar enthalpy of output stream = -144232.6 kJ/kmol

Substituting values,

$$Q_{\text{in}} = [(-209107 * 8829.33) - (-144232.6 * 8829.33)]/3600 = 159108.9 \text{ kW}$$

Which is equal to the **heat duty value of 159109 kW**

3. Seperator

Inlet Data:

- Molar Flow rate: 8829.33kmol/h
- Mass flow rate: 232274.6kg/h
- Molar Enthalpy: -209107 kJ/kmol

Outlet Data:

Vent Gas:

- Molar Flow rate: 987.4 kmol/h
- Mass flow rate: 8144.2 kg/h
- Molar Enthalpy: -24492.2 kJ/kmol

Water:

- Molar Flow rate: 6873 kmol/h
- Mass flow rate: 123866.5 kg/h
- Molar Enthalpy: -283831.7 kJ/kmol

Dis-Feed:

- Molar Flow rate: 969 kmol/h
- Mass flow rate: 100263.7 kg/h
- Molar Enthalpy: 85148.9 kJ/kmol

COMPONENTS	SEP-FEED		VENT GAS		WATER		DISTILLATION FEED	
	Mole Fraction	Mass Fraction	Mole Fraction	Mass Fraction	Mole Fraction	Mass Fraction	Mole Fraction	Mass Fraction
Methane	0.000881642	0.000537648	0.007755583	0.015085475	1.59084E-05	1.41611E-05	1.73126E-05	2.68402E-06
Ethyl Benzene	0.018448555	0.074452602	0.007460291	0.096031216	9.83787E-06	5.79539E-05	0.160440337	0.164607551
Styrene	0.092398891	0.365812648	0.026497819	0.334611786	6.46593E-05	0.000373669	0.814524717	0.819813161

Hydrogen	0.0915172 48	0.0070128 41	0.8178546 78	0.19989701 2	5.68656E- 05	6.36069E- 06	6.1885E- 05	1.20558E- 06
Benzene	0.0015298 23	0.0045424 94	0.0033439 66	0.03167044 7	4.39831E- 06	1.90635E- 05	0.0105014 71	0.0079272 4
Ethylene	0.0015298 23	0.0016313 93	0.0127390 65	0.04333054	0.000117 088	0.0001822 61	0.0001274 23	3.4545E- 05
Toluene	0.0008816 42	0.0030879 44	0.0008637 14	0.00964908 2	9.94617E- 07	5.08507E- 06	0.0071467 13	0.0063635 88
Water	0.7928123 76	0.5429224 3	0.1234848 85	0.26972444 2	0.999730 248	0.9993414 46	0.0071801 41	0.0012500 26
Total	1	1	1	1	1	1	1	1

Table-2 Seperator Streams Data

Mass Balance:

From the above data we can see that the mass flow rate through the inlet in the separator is equal to the summation of mass flow rates of the outlet streams coming from the separator.

Energy Balance:

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta H + \Delta E_k + \Delta E_s \quad (W_{\text{net}} = 0; \Delta E_k = 0; \Delta E_s = 0)$$

$$Q_{\text{in}} = \Delta H = H_2 - H_1 = n_2 h_2 + n_3 h_3 + n_4 h_4 - n_1 h_1$$

- n_2 = molar flow rate of vent gas stream = 987.4 kmol/h
- n_3 = molar flow rate of water stream = 6873 kmol/h
- n_4 = molar flow rate of dis-feed stream = 969 kmol/h

- n_1 = molar flow rate of input stream = 8829.33 kmol/hr
- h_2 = molar enthalpy of vent gas stream = -24492.2 kJ/kmol
- h_3 = molar enthalpy of water stream = -283831.7 kJ/kmol
- h_4 = molar enthalpy of dis-feed stream = 85148.9 kJ/kmol
- h_1 = molar enthalpy of output stream = -209107 kJ/kmol

Substituting values,

$$Q_{in} = [(-24492.2 * 987.4) + (-283831.7 * 6873) + (85148.9 * 969) - (-209107 * 8829.33)] / 3600 = -12826.4$$

Which is equal to the **heat duty value of -12826.8 kW**

4. Distillation Column: -

Inlet Data:

- Molar Flow rate: 969 kmol/h
- Mass flow rate: 100263.7 kg/h
- Molar Enthalpy: 85148.9 kJ/kmol

Outlet Data:

Col-Dis:

- Molar Flow rate: 242.2 kmol/h
- Mass flow rate: 24456.7 kg/h
- Molar Enthalpy: 100292.8 kJ/kmol

Col-Bot:

- Molar Flow rate: 726.7 kmol/h
- Mass flow rate: 75806.9 kg/h
- Molar Enthalpy: 118020.1 kJ/kmol

Mass Balance:

From the above data we can see that the mass flow rate through the inlet in the distillation column is equal to the summation of mass flow rates of the outlet streams coming from the column.

	Distillation Feed		Output (Vapor Phase)		Output (Liquid Phase)	
Mass Flowrate (Kg/hr)	100263.6782		24456.73569		75806.94255	
Molar Flowrate(k Mol/hr)	968.9216021		242.2304005		726.6912016	
Component	Mole Fraction	Mass Fraction	Mole Fraction	Mass Fraction	Mole Fraction	Mass Fraction
METHANE	1.73126e(-5)	2.68402e(-6)	6.92504e(-5)	1.10035e(-5)	2.33615E(-60)	3.5927e(-61)
ETHYL BENZENE	0.160440337	0.164607551	0.394068049	0.414374063	0.082564433	0.084028209
STYRENE	0.814524717	0.819813161	0.505792558	0.521756905	0.917435436	0.915971676
HYDROGEN	6.1885e(-5)	1.20558e(-6)	0.00024754	4.94242e(-6)	1.8789e(-81)	3.63086e(-83)
BENZENE	0.010501471	0.00792724	0.042005885	0.032498789	7.63122e(-14)	5.71428e(-14)
ETHYLENE	0.000127423	3.4545e(-5)	0.000509693	0.000141822	1.0003e(-50)	2.69006e(-51)

TOLUENE	0.007146713	0.00636358 8	0.028586462	0.026088027	1.30313e(-7)	1.15101e(-7)
WATER	0.007180141	0.00125002 6	0.028720563	0.005124649	1.41955e(-43)	2.4515e(-44)
Total	1	1	1	1	1	1

Table-3 Distillation Column Streams Data

Energy Balance:

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta H + \Delta E_k + \Delta E_s \quad (W_{\text{net}} = 0; \Delta E_k = 0; \Delta E_s = 0)$$

$$Q_{\text{in}} = \Delta H = H_2 - H_1 = n_2 h_2 + n_3 h_3 - n_1 h_1$$

- n_2 = molar flow rate of vent gas stream = 242.2 kmol/h
- n_3 = molar flow rate of water stream = 726.7 kmol/h
- n_1 = molar flow rate of input stream = 969 kmol/h
- h_2 = molar enthalpy of vent gas stream = 100292.8 kJ/kmol
- h_3 = molar enthalpy of water stream = 118020.1 kJ/kmol
- h_1 = molar enthalpy of output stream = 85148.9 kJ/kmol

Substituting values,

$$Q_{\text{in}} = [(100292.8 * 242.2) + (118020.1 * 726.7) - (85148.9 * 969)] / 3600 = 7652.7 \text{ kW}$$

Which is equal to the net heat duty value of $-12448.8 \text{ kW} + 20103.2 \text{ kW} = 7653 \text{ kW}$

Process Optimization:

1. Catalyst Selection for Dehydrogenation of Ethylbenzene:

Iron-Based Catalysts

- **Description:** Iron catalysts are often supported on silica or alumina and are the most commonly used in the industry for dehydrogenation reactions.
- **Advantages:**
 - High activity at operational temperatures (600–620 °C).
 - Good selectivity towards styrene with minimal by-products.
- **Cost:**
 - Iron is relatively inexpensive, priced around **\$1–\$3 per kg**.
 - The total catalyst system costs approximately **\$10,000 to \$20,000 per ton**, making it economically feasible for large-scale production.
- **Current Use:** This is the standard catalyst used in commercial styrene production.

Noble Metal Catalysts (e.g. Platinum, Palladium)

- **Description:** Noble metals are highly effective catalysts for dehydrogenation but are rarely used for this specific reaction due to cost.
- **Advantages:**
 - Extremely high activity and selectivity.
 - Potential for lower operational temperatures.
- **Disadvantages:**
 - Very high costs, making them impractical for large-scale applications.
- **Cost:**
 - Prices range from **\$20,000 to \$60,000 per kg** depending on the metal, significantly higher than iron.
- **Current Use:** Primarily in specialized applications or small-scale operations where the cost can be justified.

Nickel-Based Catalysts

- **Description:** Nickel is used in various catalytic processes but less frequently for the dehydrogenation of ethylbenzene.

- **Advantages:**
 - Moderate cost and reasonable activity.
- **Disadvantages:**
 - Lower selectivity towards styrene and prone to deactivation by coking.
- **Cost:**
 - Typically, around **\$5–\$10 per kg**, which is more affordable than noble metals but still higher than iron catalysts.
- **Current Use:** Not commonly used in commercial dehydrogenation processes.

Conclusion:

Best Catalyst: Iron-Based Catalysts

- Iron-based catalysts are the best choice due to their balance of cost-effectiveness, activity, and selectivity. They are the industry standard in commercial styrene production, providing sufficient performance without the prohibitive costs associated with noble metals.

2. Property Method for Simulation:

In this process, pressures range from 0.4 to 1.4 bar with temperatures above 600 °C. And since the process contains non-polar compounds, the simulator suggests Peng-Robinson method to be used. But it won't be suitable during separation as the feed contains hydrogen and water, alongside hydrocarbons.

Due to water's polarity and its impact on phase behavior, the Peng-Robinson method may not adequately handle interactions in liquid-liquid-vapor (LLV) separation scenarios. Instead, the **NRTL (Non-Random Two-Liquid) model is preferred**, as it better accounts for non-ideal interactions between polar and nonpolar components.

3. Optimum Operating Conditions for LLV Seperator:

We will be analyzing the distillation feed (primarily organic liquid) and the liquid feed (primarily water) outlet from the separator.

First let us look at fig-4. It plots the molar flow rate and the mole fraction of styrene in distillation feed. It can be seen that the mole fractions of styrene also increase as the seperator temperature increases, however after a certain temperature, the mole fraction of styrene in this stream reaches its maximum before decreasing rapidly to 0 at 90°C. This is possibly due to the **sudden vaporization of the organic liquid stream**. The absence of the organic liquid stream leaves water as the only liquid stream, causing the pure water composition and the switch in streams.

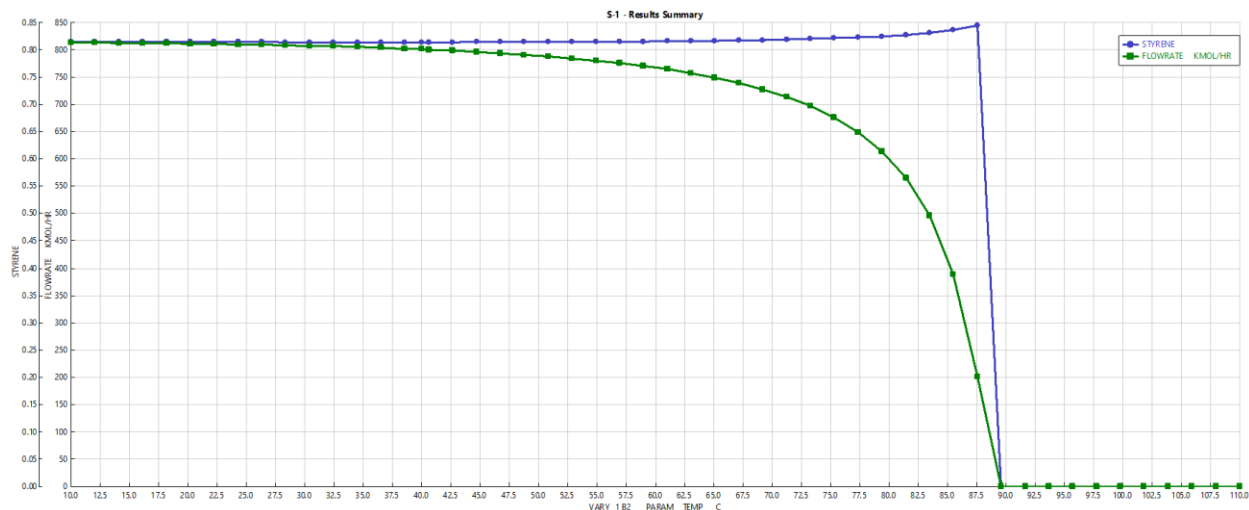


Fig-4 Mole fraction and Flowrate of Styrene in Distillation Feed

Although the mole fraction increases but the flowrate of styrene decreases as temperature increases. Therefore we choose temperature equal to **50°C as the optimum** (Point where flowrate starts to drop).

We can see from the fig-5 which is the plot for mole fraction versus temperature for the water dominant stream, that the mole fractions of both water and styrene increases but shows significantly less change as compared to the organic stream.

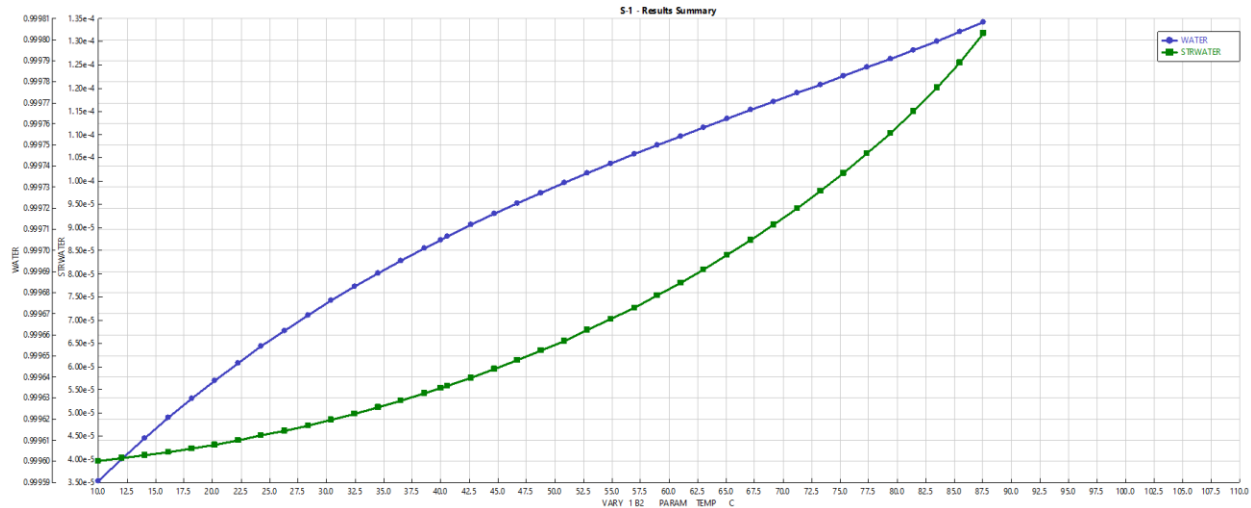


Fig-5 Mole fraction versus Temperature in Water Dominant Stream

4. Optimum Operating Conditions for Distillation Column:

To choose the number of stages we did a simulation to choose the most optimum amount of yield.

In our simulation, we determined that the optimal number of stages for maximizing styrene yield and minimizing ethylbenzene presence in the liquid stream is around **50-52 stages** (fig-6). The temperature profile (fig-7) shows that this range corresponds to the **boiling point of styrene (~140°C)**, allowing effective separation from **ethylbenzene (boiling point ~ 135°C)**.

Beyond 52 stages, there is minimal improvement in styrene purity, indicating that additional stages would increase operational costs without significant benefits. Thus, 50-52 stages provide the most efficient operating conditions for this separation process.

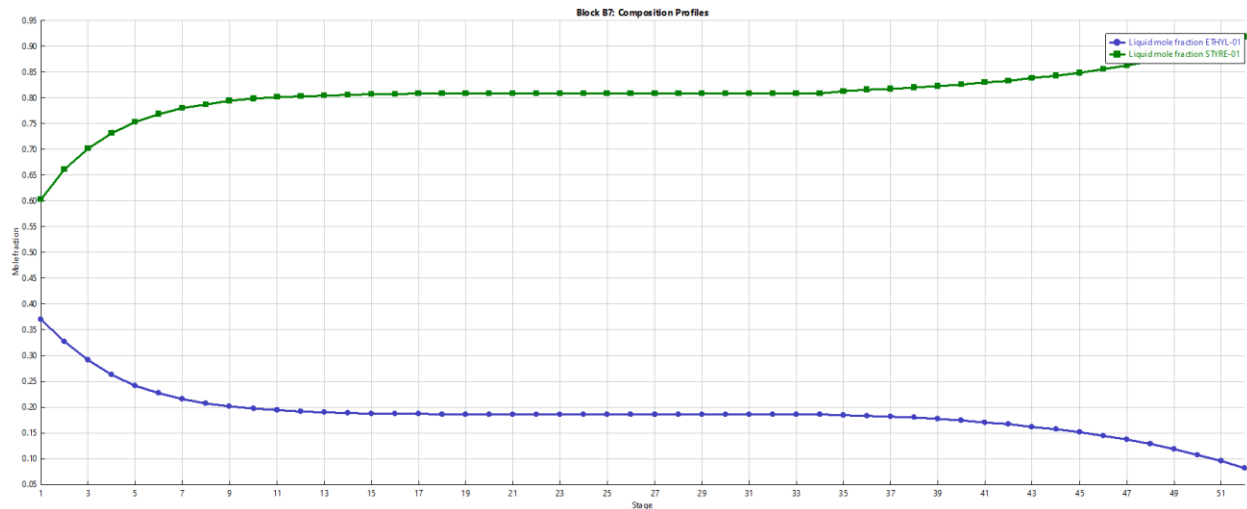


Fig-6 Mole fraction versus Number of Stages in Distillation Column

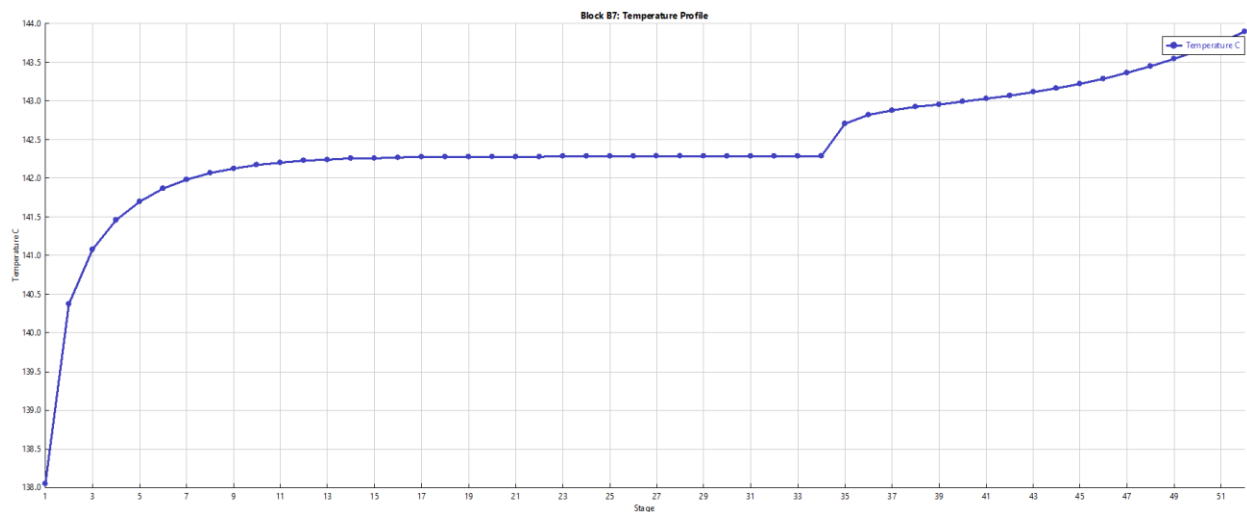


Fig-7 Temperature Profile in Distillation Column

Environmental Impact Analysis:

Vent Gas Analysis:

- The vent gas stream primarily consists of **Methane**, **Hydrogen**, and **Ethylbenzene**, each posing specific environmental and health risks:
- **Methane:** A potent greenhouse gas, methane has a global warming potential over 25 times greater than CO_2 . It contributes to climate change, worsens air quality by forming ground-level ozone, and poses explosion risks in confined spaces.

- **Hydrogen:** While hydrogen itself is clean, its production from natural gas (through steam methane reforming) can release CO₂, contributing to greenhouse gas emissions.
- **Ethylbenzene:** A volatile organic compound (VOC), ethylbenzene contributes to air pollution, and chronic exposure can cause respiratory issues and is a potential carcinogen.

Water Analysis:

- The **upper distillation column** contains a mixture of **Benzene, Toluene, and water**, posing serious risks to aquatic ecosystems and human health:
- **Benzene:** A known carcinogen, it is toxic to both humans and aquatic life. Discharging benzene into water bodies can lead to contamination and bioaccumulation in the food chain.
- **Toluene:** Neurotoxic, it can cause headaches, dizziness, and long-term neurological damage. It also harms aquatic organisms and disrupts ecosystems when discharged into water.

Conclusion:

- Both the vent gas emissions and wastewater discharges associated with this process present significant **environmental and health risks**, including climate change, air pollution, water contamination, and toxicity to both humans and wildlife. Mitigation strategies such as **emission control systems, effective wastewater treatment, and cleaner production methods** are necessary to reduce these impacts.

Deliverables:

- **Operational Data:** Collection and analysis of data regarding the conversion rates, reactor temperature control, and efficiency of the isothermal dehydrogenation process.
- **Process Optimization:** Identification of process variables that maximize styrene yield while minimizing unwanted by-products, with recommendations for scale-up.

- **Environmental Impact Analysis:** A report on energy usage, waste generation, and possible environmental effects of the mini-plant.
- **Final Report:** A comprehensive project report including the methodology, data, analysis, and conclusions, with suggestions for improving the process or equipment.

Timeline:

MONTH	TASK
August	Proposal Writing
September	Detailed Process Flow Sheet Development and Mass balances
October	Energy balances, Process Optimization, Catalyst Selection, and Environmental Impact Analysis
November	Final Report Compilation and Submission

Results:

The complete results along with the flowsheet has been uploaded to the following Google Drive link: [CHE251-Project-Group-12 - Google Drive](#)

References:

[1] Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Vol. 22, chapter “Styrene”, page 956 – 994, Wiley-Interscience, New York 1992

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Team Members

Bipin Kumar	230300	Harshit Jaiswal	230460
Karan Keer	230531	Prabhakar Raj	230761
Pragati Patel	230765	Rutul Bhanushali	230884
Priyanka	230798	Adarsh Raj	230057

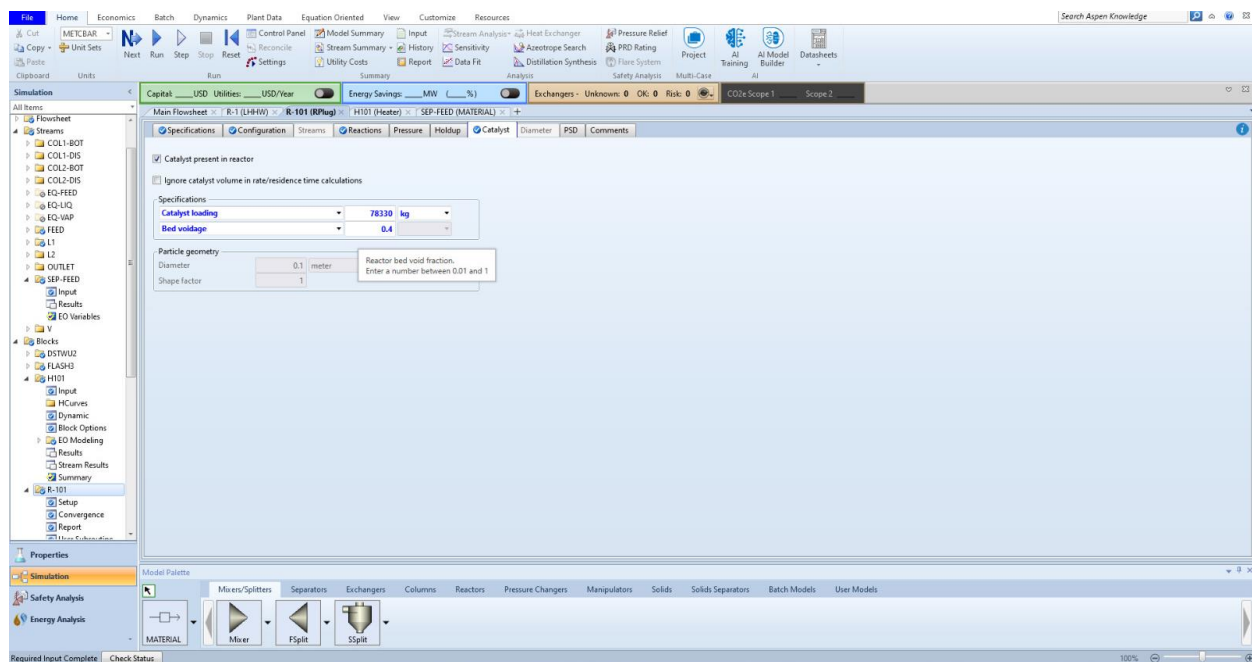
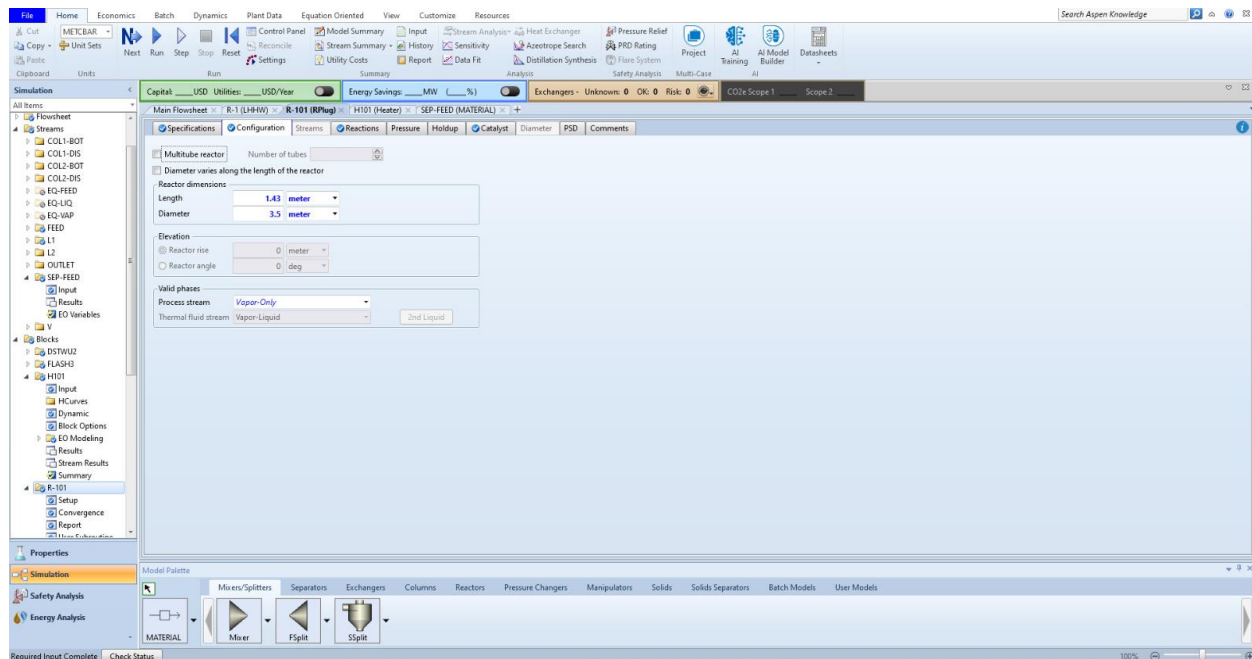
Appendices

Reactor Specifications:

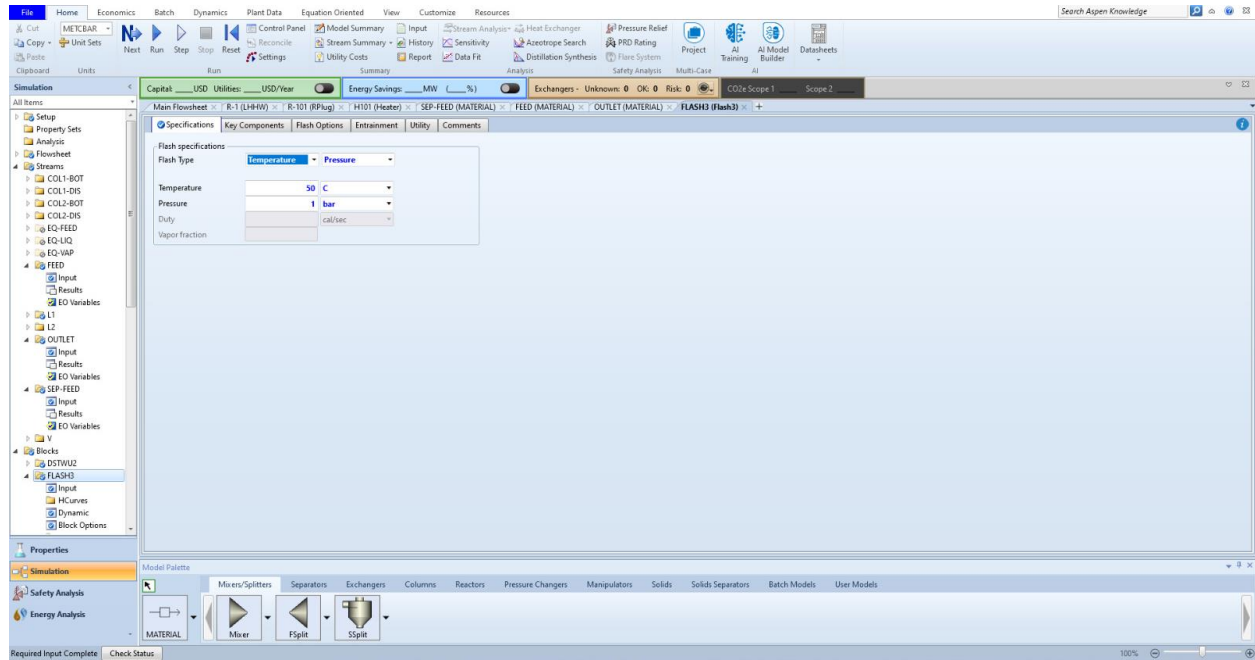
The screenshot displays the Aspen Plus software interface for configuring a reactor. The main window shows the 'Reactor type' as 'Reactor with specified temperature'. The 'Operating condition' is set to 'Constant at specified reactor temperature' with a value of 620 C. The 'Temperature profile' is also visible.

The bottom section of the interface shows the 'Reaction' tab, which contains a table of reactions:

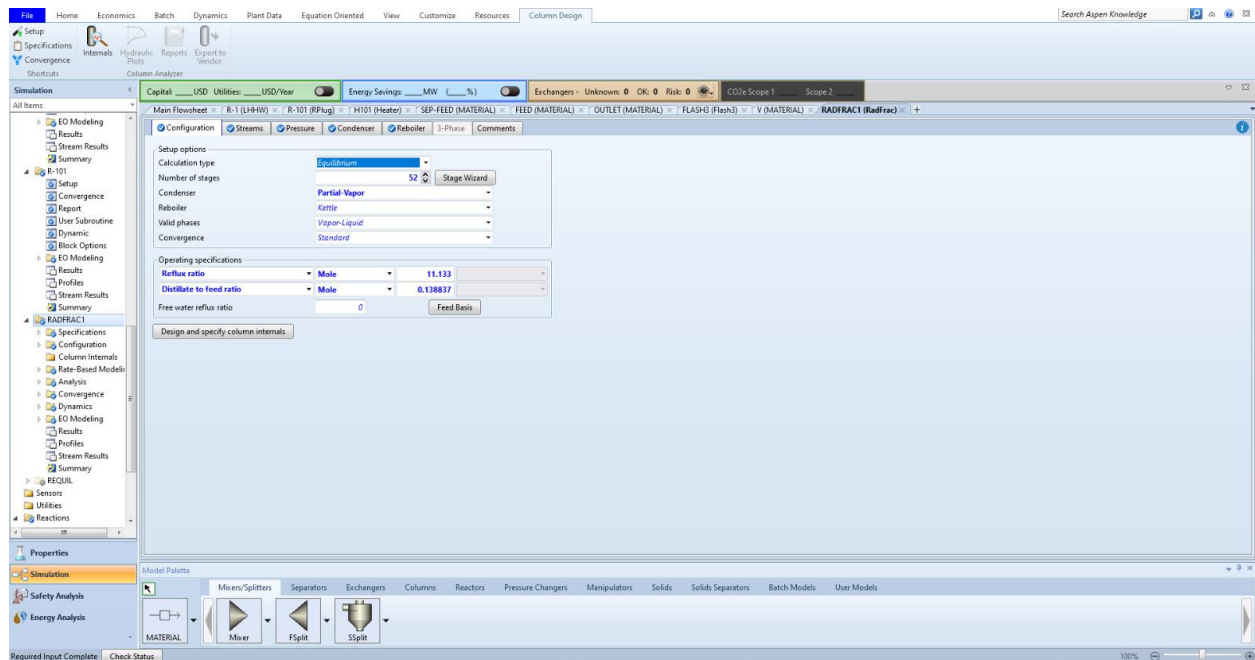
Run No.	Reaction type	Stoichiometry	Delete
1	Kinetic	ETHYL-01 → STYRENE(MIXED) + HYDROGEN(MIXED)	X
2	Kinetic	ETHYL-01 → BENZENE(MIXED) + ETHYLENE(MIXED)	X
3	Kinetic	ETHYL-01 + HYDROGEN → TOLUENE(MIXED) + METHANE(MIXED)	X

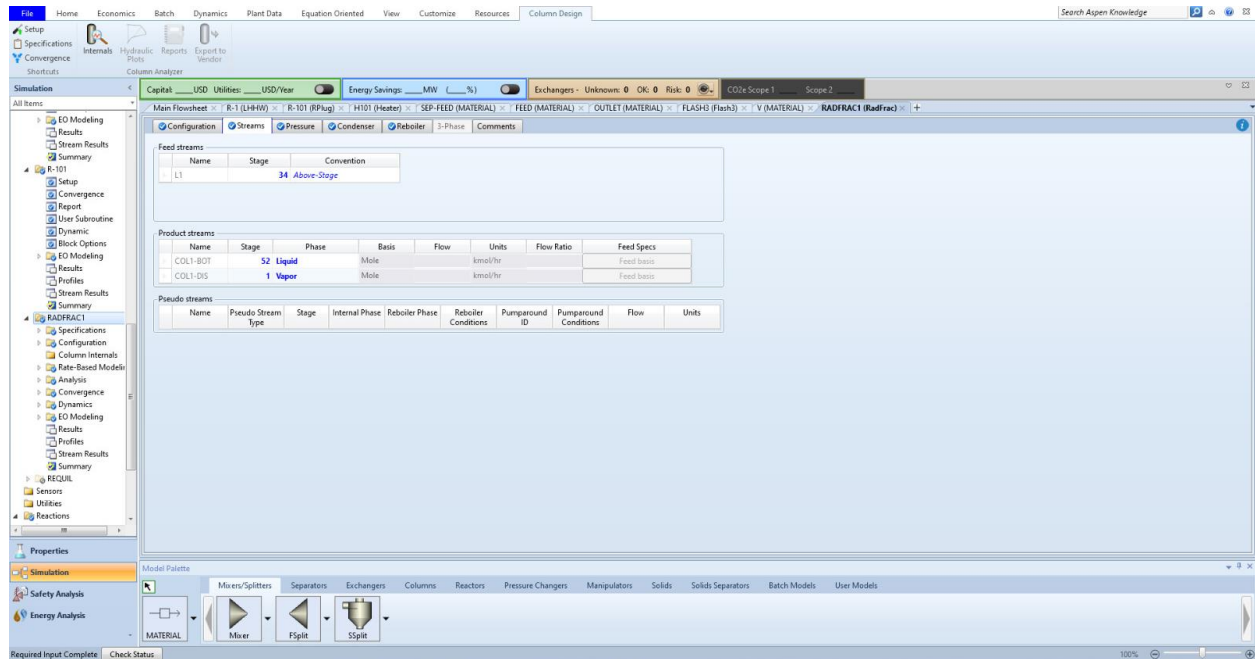


Separator Specifications:



Distillation Column Specifications:





Heater Specifications:

