Nazarbayev University School of Engineering and Digital Sciences
Chemical and Materials Engineering Department
ENG 400 Capstone project
Report 4

Design of Plant for industrial production of Styrene

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Spring 2025
Astana, Kazakhstan
Date: 20.04.2025

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Chapter 1 - Process Introduction

Styrene monomer is a highly versatile intermediate material which is widely used in the production of plastics such as crystalline polystyrene, expandable polystyrene, styrene-acrylonitrile resins, acrylonitrile-butadiene-styrene copolymers, styrene-butadiene latex and unsaturated polyester resins [1].

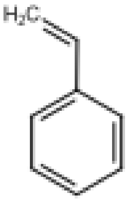
Currently, Kazakhstan is highly reliant on imported styrene to meet its industrial needs. According to Volza's Kazakhstan import data, the country imported 4,064 shipments of styrene and styrene isoprene between August 2023 and July 2024, supplied by more than 200 foreign exporters and distributed among approximately 170 local buyers. In July 2024 alone, 335 shipments were recorded, reflecting strong and consistent demand. Moreover, over 450 Kazakhstani companies were involved in sourcing styrene products from more than 500 global suppliers during the same period [2]. Given these conditions, the development of a local styrene production facility represents a strategic opportunity for import substitution. By producing styrene domestically, Kazakhstan can reduce its dependence on foreign suppliers, minimize logistical and transportation costs, and enhance the competitiveness of its petrochemical sector. Furthermore, this initiative aligns with broader efforts to strengthen national industrial capabilities and support economic growth through value-added chemical production.

The primary goal of this capstone project is to design a highly efficient and economically viable industrial plant for the production of styrene in Kazakhstan, with a planned capacity of 320 kilotons per year. This capacity is estimated to cover approximately 25% of the total demand across the Commonwealth of Independent States (CIS), positioning the project as a major regional supplier.

1.1 Styrene properties

Styrene [CAS: 100-42-5] is a colorless to yellowish liquid that evaporates easily and has a sweet odor at room temperature [3]. Important physical and chemical properties of styrene are presented in Table 1.

Table 1. Physical and chemical properties of styrene.

Molecular Formula [3]	C_8H_8 $C_6H_5CH=CH_2$
Molecular Structure [3]	
Molecular Weight [4]	104.153 g/mol

Color / Form [5]	Colourless to yellowish, oily viscous
Boiling point at 101.3kPa=1 atm [4]	145.15 °C
Freezing point [4]	− 30.6 °C
Flash Point (Tag Open Cup and Tag Closed Cup respectively) [6]	34.4 °C 31.1 °C
Explosive limits air, % [4]	1.1–6.1 vol %
Autoignition Temperature [6]	490 °C

1.2 Review on the Production Routes

The first commercialization of styrene production started in 1925[7]. Since then, styrene production has been rapidly increasing which resulted in the development and optimization of the technologies. Selecting the right manufacturing process is crucial because it directly impacts cost, environmental sustainability, and product quality.

1.2.1 Catalytic Dehydrogenation of Ethylbenzene

The main method accounting for 85% of styrene industrial production is the direct dehydrogenation of ethylbenzene to styrene [4]. The reaction is endothermic (ΔH = 124 kJ/mol), and activation energy of the process is high (152 kJ/mol), therefore the reaction proceeds with high temperatures around 600-650°C [8] .

$$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2 \quad (1)$$

$$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4 \quad (2)$$

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_3 + CH_4 \quad (3)$$

$$C_6H_5CH{=}CH_2 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \quad (4)$$

Ethylbenzene dehydrogenation proceeds as it is illustrated in equation (1), the reaction is reversible, and it produces twice the volume of starting material meaning the low pressure will favor the forward reaction [4]. The equations 2-4 demonstrate that there are several other side reactions that may simultaneously occur, producing side products such as benzene, toluene and other light hydrocarbons [9]. Therefore, in order to obtain the targeted compound, a catalyst with high styrene selectivity is needed. The side reactions also could lead to the formation of coke that will result in catalyst poisoning [4]. This issue is solved by implementing the usage of steam in industrial sites [10]. The steam has multiple important functions in this process which are: a) lowering the partial pressure of ethylbenzene; b) the heat from the steam helps to maintain the reaction temperature; c) the formation of the coke will decrease as the steam reacts with formed carbon layers to produce CO and CO_2 [5].

The direct dehydrogenation of EB can be carried out with two different approaches, either adiabatically or isothermally. Isothermal dehydrogenation in theory has the advantage of preventing extremely high temperatures at the reactor inlet, while ensuring that the temperature remains sufficiently elevated at the reactor outlet [6]. Moreover, it was claimed that this process has high conversion and selectivity [4]. However, in practice the advantages are neglected because of costly tubular reactors that are required to transfer heat from an external source to supply the reaction heat [5]. Also, the temperature of the reaction surpasses the thermal stability limits of molten salts that are typically used as heat-transfer fluids in tubular reactors [6]. These limitations make this route non-suitable for large scale productions.

This makes the adiabatic process the only other option for direct dehydrogenation of EB. It is widely adopted for industrial applications. Overall, the conversion rate of the ethylbenzene for this process is not high, around 50-70 wt%, but it has high yields of styrene, approximately 88-95 mol% [4]. Higher selectivity typically suggests operating at lower conversion levels, which consequently leads to increased costs associated with recycling unreacted materials [11]. However, Luyben states that in this process the raw material cost is dominant and usage of the catalysts with higher selectivity is economically justified [12].

1.2.2 Styrene – Propylene Oxide Process

The only other commercially available option for the styrene production is co-production of styrene monomer (SM) with propylene oxide (PO).

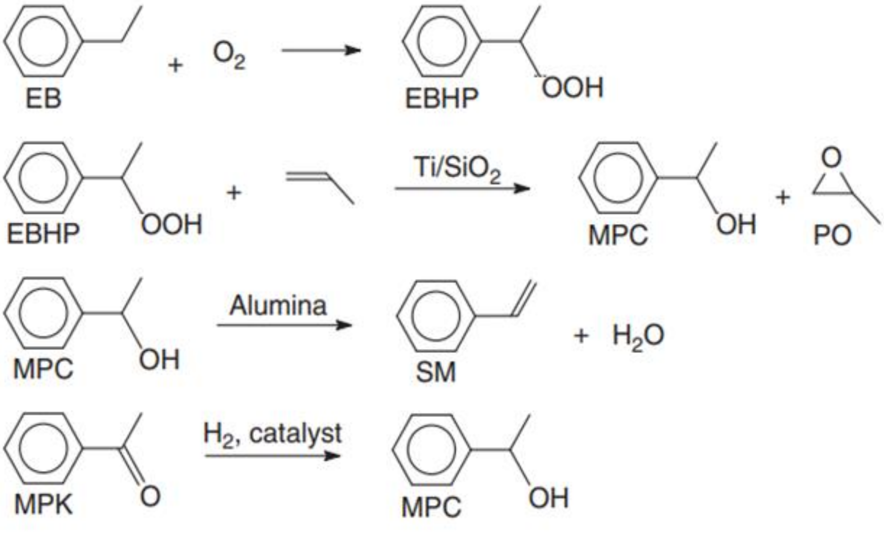


Figure 1. Schematics of the SMPO process [13]

Overall, this method consists of 4 main steps as it is illustrated in Figure 1:

1. Ethylbenzene (EB) oxidation with air to produce ethylbenzene hydroperoxide (EBHP) [13].The conditions for this step are 130 °C and 0.2 MPa, conversion is about 13% to minimize byproduct formation and the selectivity of EBHP is around 90% [1].
2. The propylene proceeds epoxidation reaction with EBHP to produce PO and methyl phenyl carbinol (MPC) [13]. For this step the liquid-phase molybdenum heterogeneous titanium catalysts are needed, operating conditions are 110 °C and 4 MPa, the conversion of EBHP is almost 100% with selectivity of PO around 70-85% [1].
3. Styrene is produced by dehydration of MPC [14]. This reaction proceeds at 250 °C and low pressure with a metal oxide catalyst, commonly Al_2O_3 [1].
4. In order to increase the yield, methyl phenyl ketone (MPK), which is the side product of the first reactions, undergoes hydrogenation to produce MPC [13]. Operating conditions are 90-150 °C and 8 MPa, the catalyst is a mixture of ZnO and CuO, 90% conversion of MPK with selectivity of MPC 92% is achieved [1].

As a product styrene and propylene oxide are obtained in a ratio of 5 to 2 respectively; to obtain separated products further purification is required [1]. Overall, the process requires a high amount of initial investments and the production costs are higher than the conventional dehydrogenation of EB, but the co-product PO can make the overall production more profitable [1].

1.2.3 Other processes

In the last decade new approaches for styrene production have been appearing. One of these new approaches is the synthesis of styrene from toluene with MeOH [15].

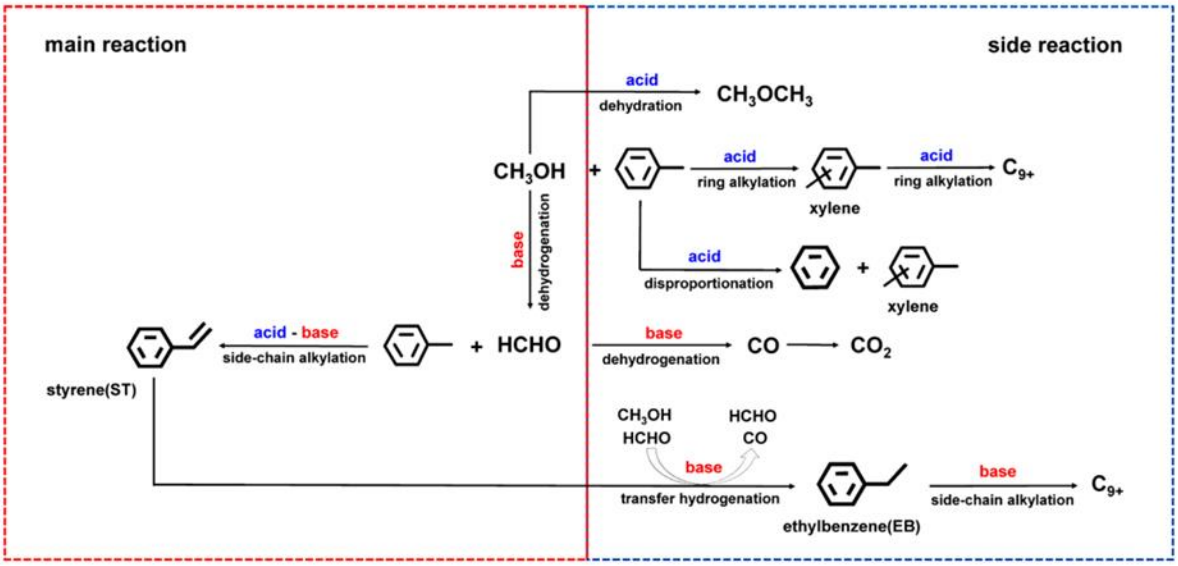


Figure 2. Schematics of styrene production from toluene and methanol [15]

Despite the ongoing research on these topics, the commercialization of this process remains impossible due to the lack of efficient catalysts with high yield of styrene [15]. In a similar way, there are proposals to synthesize styrene from butadiene or gasoline mixtures, but they are also being rejected for reasons of high cost of production [1].

1.3 Process selection

Adiabatic dehydrogenation of EB and SMPO methods are the only economically suitable options, so they have been considered as a choice for industrial design for production of styrene. The advantages and disadvantages of both methods are summarized and described in Table 2.

Table 2. Comparison of Direct Dehydrogenation of Ethylbenzene and SMPO method.

Criteria	Direct Dehydrogenation of Ethylbenzene	SMPO (Styrene Monomer Propylene Oxide) Method
Process Overview	A straightforward process involving the high-temperature dehydrogenation of ethylbenzene to produce styrene	Co-production of styrene and propylene oxide through ethylbenzene oxidation
Energy Consumption	High energy consumption due to the need for high temperatures (around 600°C), but manageable in large-scale operations with energy recovery systems [1]	Lower energy consumption as the reaction is exothermic, but additional complexity from handling multiple products can offset savings [13]
Yield and Efficiency	High-purity styrene, with moderate conversion rates (50-70 wt%); recycling unconverted ethylbenzene improves efficiency [1]	The focus on two products dilutes the efficiency of styrene production
Environmental Impact	Higher emissions due to energy intensity	Lower energy requirements reduce emissions, but the existence of complex reagents in process introduces handling concerns and environmental risks

Economic Feasibility	Mature technology with lower capital costs	Higher initial investment due to process complexity[1]
Industrial Adoption	Most widely adopted method globally due to simplicity, cost-efficiency, and ease of integration into existing plants	Less common, but attractive for integrated plants that need both styrene and propylene oxide, despite the higher complexity [16]
Data Availability	The dataset is highly comprehensive, offering a substantial volume of data	Limited amount of literature

Based on the comparison between methods the adiabatic dehydrogenation of EB is chosen. The main factors for the choice of this method are the data availability and economic feasibility.

1.4 Market Analysis

Currently, styrene is one of the most important components for production of different polymers that are utilized in packaging, plastics, paints and latex [17]. In 2023, the market volume of the compound was estimated to be about 34.44 million tons and valued at $45 billion [16]. It is forecasted that the supply will increase by compound annual growth rate (CAGR) of 5.32% by 2029[16]. In September 2024, the top-rated major suppliers of styrene were Chevron Phillips Chemical (USA), Americas Styrenics LLC (USA), INEOS (United Kingdom), New Process Fibre Company, Inc. (USA), WESTLAKE (USA), Kanto Chemical Co, Inc. (Japan), Denka Company Limited (Japan), HELM AG (Germany), Repsol (Spain), Sabic (Saudi Arabia), Shell (United Kingdom) and many more[16]. Despite the fact that most manufacturing companies are located in North America and Europe, North-East Asian countries have the highest share in demand, taking approximately 61% out of the global market [18]. The market demand of styrene by region in 2024 is shown in Figure A1 in Appendix A.

Moreover, the analysis was conducted for the raw materials as well. Ethylbenzene is the primary raw material in the production of styrene monomers and its market is relatively similar to styrene; the volume is approximately 33.9 million tons, and the value is $23 053 millions [19]. According to the forecast, the CAGR is expected to be 3.03% by 2029, with Asia Pacific being the largest world market [20]. However, despite the geographical location, the Czech Republic has the largest share in the export of ethylbenzene, with a total of $132.03

million [21]. Broader research is described in Chapter 7, with costs of the materials and their suppliers.

1.5 Production Rate

The desired product of the plant is Styrene with a purity of 99.7% for the purpose of polystyrene production. Typically, the purity of the product is between 99.6% and 99.9% [6]. However, considering the impact of increasing the purity of the product on capital cost, it was decided to keep it on the lower bound of the interval.

The production rate is chosen based upon the research on demand. It is estimated through the extrapolation of global styrene production, due to lack of relevant information in CIS countries. Table 3 displays the information on production rate of styrene per gross domestic product (GDP) and population and data for 2019 was used as the basis of estimation, due to insufficient information for years after 2020.

Table 3. Production calculations by country, 2019.

Country	Production, kt	GDP, trillion USD	Production per trillion GDP (kt/trillion USD)	Population, million	Production per million of population (kt/million pop.)
China	10000 [22]	14.28 [23]	700.28	1422.6 [24]	7.029
USA	4680 [25]	21.52[26]	217.47	328.33 [27]	14.25
Russia	727 [28]	1.574 [29]	461.88	146.77 [30]	4.953
South Korea	2724.8 [31]	1.651 [32]	1650.4	51.77 [33]	52.63
Average			757.51		19.71

Table 4 shows the extrapolated information calculated according to the references for each member of CIS region. By taking the total production rates based on GDP and population, the average value was found, which is the total demand for styrene in CIS countries. Using that information, styrene production rate was established to be around 320 thousand tons per annum. The calculations are shown in Appendix A.

Table 4. Extrapolated data for styrene production in CIS for 2023.

Country	GDP, billion USD	Production (GDP), kt	Population, million	Production (population), kt
Kazakhstan	261.42[34]	197.95	20.33[35]	400.7
Azerbaijan	72.36 [36]	54.81	10.32[37]	203.4
Armenia	24.21 [38]	18.34	2.943 [39]	58.01
Belarus	71.86 [40]	54.43	9.498 [41]	187.2
Kyrgyzstan	14 [42]	10.60	6.9 [42]	136.0
Moldova	16.54 [43]	12.53	3.067 [44]	60.45
Tajikistan	12.1 [45]	9.166	10.1[45]	199.1
Turkmenistan	59.89 [46]	45.37	6.516[47]	128.4
Uzbekistan	90.89 [48]	68.85	35.65 [49]	702.7
Total		472.0		2076

Chapter 2 – Process Summary

2.1 Literature review on commercial PFDs

In the first chapter the reasoning behind the choice of the adiabatic dehydrogenation of ethylbenzene was explained. Commercially used manufacturing pathways of this method were reviewed and the obtained information was used to develop the proposed design.

Common commercial process for production of styrene is implemented as shown in Figure 3, however, there are variations in the separation section.

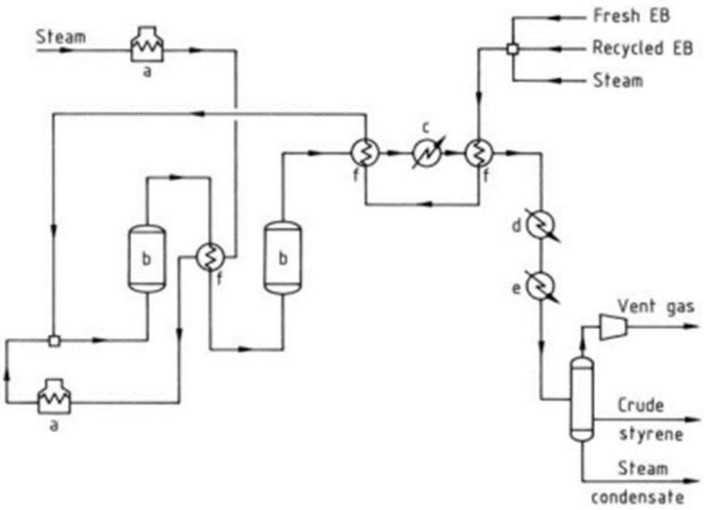


Figure 3. Commercially utilized styrene production: a) Heater; b) Steam superheater; c) Reactor; d) Heat exchanger; e) Condenser [1]

There are two main routes for the separation process: 1) the standard distillation train (Figure 4.a); 2) the Monsanto approach (Figure 4.b). In the standard distillation train, benzene and toluene are first separated from crude styrene, followed by the separation of ethylbenzene from styrene, and finally, purification of styrene from heavy components [6]. In contrast, the Monsanto process combines the separation of styrene from ethylbenzene, benzene, and toluene in a single column [1]. The overhead product of this column is rich in ethylbenzene, while the bottom stream - crude styrene - is directed to a second column for final purification. Although the standard train avoids repeated distillation of the benzene-toluene fraction, the Monsanto configuration offers a more compact and integrated design, reducing capital costs and simplifying control. Despite slightly higher energy usage, the Monsanto process was chosen as the more efficient and streamlined option for modern plant designs.

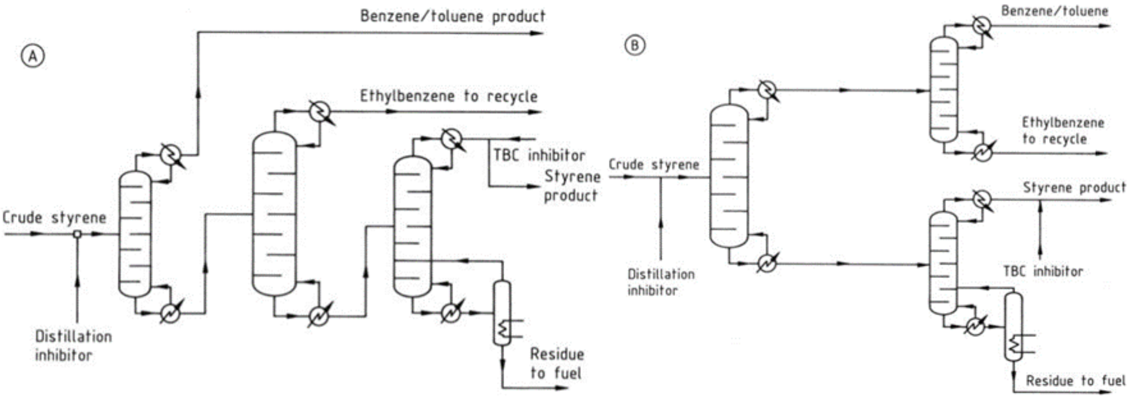


Figure 4. (a-b): a) standard distillation train; b) the Monsanto approach [6]

2.2 Proposed design of PFD

The provided Process Flow Diagram (PFD) shows the selected setup for the production of styrene through adiabatic dehydrogenation of ethylbenzene (Figure 5). Each part of the flow diagram is labeled with stream numbers and pressure/temperature indicators, providing a clear view of the operation conditions at various stages. List of equipment is presented in Table 5.

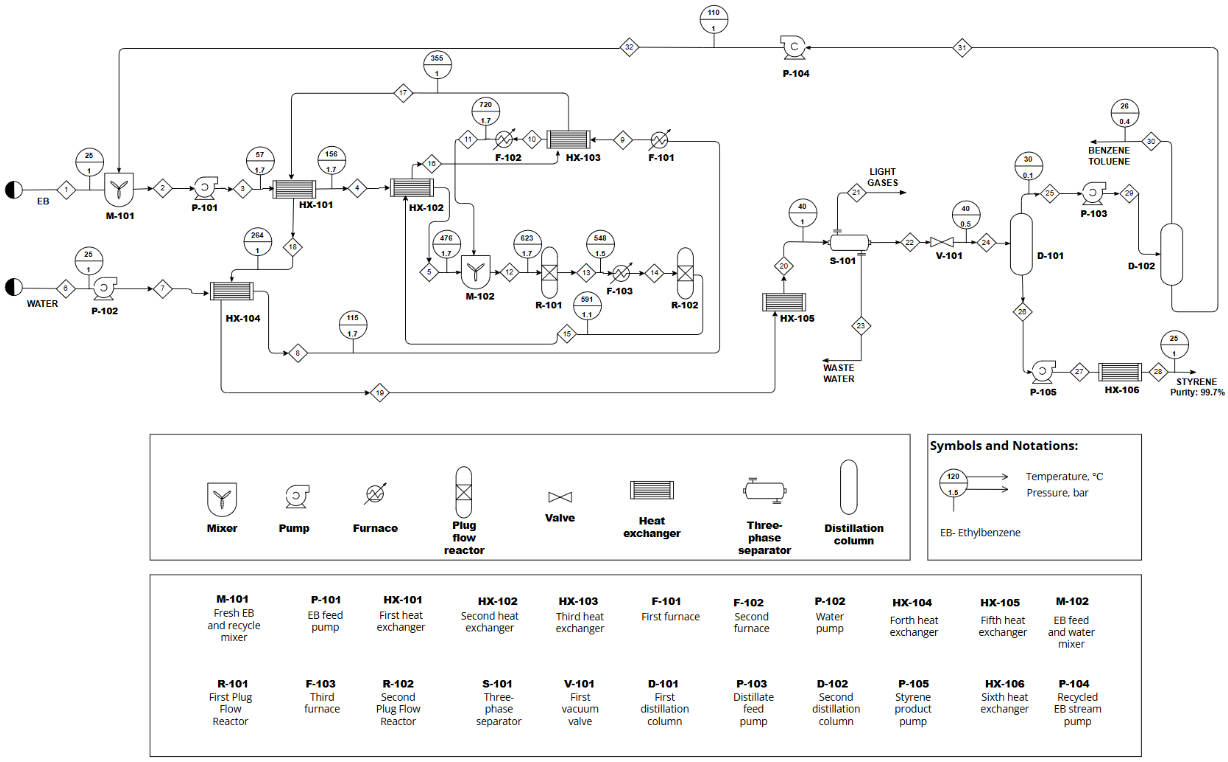


Figure 5. Process Flow Diagram of Styrene production

There are two main inlet streams (ethylbenzene and steam) which are fed into the tubular reactors. The feed conditions are 25°C and 1 bar. Fresh feed of EB is mixed with the recycled stream from the distillation column in the M-101 mixer. Then it is pumped through the P-101 pump to increase the pressure of the stream and afterwards it is vaporized and heated by the series of heat exchangers HX-101 and HX-102. Similarly, a water inlet stream is pumped with a P-102 pump and preheated by HX-104 heat exchanger, followed by vaporization in furnace F-101. Afterwards, the steam underwent further heating with heat exchanger HX-103 and furnace F-102 to reach superheated steam conditions. Subsequently, they are then mixed in a mixer (M-102) to form a combined stream (Stream 12) that is fed into the system of Plug Flow Reactors (PFRs). Proposed design incorporates two PFRs in series with intermediate heating between reactors.

After the reactors, the stream is cooled by a series of heat exchangers HX-101, HX-102, HX-103, HX-104, HX-105. Then it is consequently sent to a three-phase separator (S-101). The operating conditions for the separator were chosen based on research papers on styrene production, which indicate that a temperature range of 30–40°C is optimal for achieving vapor-liquid-liquid equilibrium (VLLE) and effective phase separation [12]. The separator splits the stream into light gasses such as hydrogen, methane and ethylene; liquid organics, and wastewater stream (Streams 21, 22 and 23 respectively).

The liquid hydrocarbon stream goes through two distillation columns. Styrene is highly susceptible to polymerization, especially at elevated temperatures. In atmospheric distillation, the boiling point of styrene (~145°C) could be exceeded, leading to the formation of polymers, which degrades the product quality and clogs equipment. Vacuum distillation reduces the boiling point by lowering the pressure, allowing styrene to be distilled at lower temperatures, minimizing polymerization risk [1]. The first column is D-101, separates the styrene product with the desired purity of 99.7% from the impurities (Stream 28). In the second distillation column D-102, ethylbenzene is separated from byproducts of side reactions, such as benzene and toluene. These side products can be used as a potential source of fuel for the system, or sold to generate extra profit (Stream 30). Recovered ethylbenzene then recycled back into the system (Stream 32).

Table 5. List of equipment used in the styrene production.

Ethylbenzene (EB) Dehydrogenation		
Code	**Equipment type**	**Function and comments**
M-101	Mixer	To mix fresh EB with the recycle stream before pressurization and heating.
P-101	Pump	To pressurize the EB feed for further heating and processing.
HX-101	Heat exchanger	First preheating stage using reactor effluent heat.
HX-102	Heat exchanger	Second preheating stage to raise EB temperature.
HX-103	Heat exchanger	Cool reactor outlet, heat the steam to elevated temperature (~350°C).
HX-104	Heat exchanger	Cool reactor outlet, heat the water to evaporation temperature (~115°C).

F-101	Furnace	Steam generation
F-102	Furnace	Heats up steam to superheated state (~720°C).
M-102	Mixer	To mix EB with steam, creating optimal feed for the reactor.
R-101	Plug flow reactor	First reactor where EB is dehydrogenated to styrene.
F-103	Furnace	Provides intermediate heating to maintain reaction temperature.
R-102	Plug flow reactor	Second reactor to further increase conversion.
Separation and Product Recovery		
Code	**Equipment type**	**Function and comments**
HX-105	Heat exchanger	Cools down the organic stream before entering separation units.
S-101	Three-phase separator	Separates reactor effluent into gas, aqueous, and organic phases.
V-101	Vacuum valve	Reduces pressure to reach distillation conditions.
D-101	Distillation column	Separates styrene from side-products.
P-103	Pump	Increases pressure to reach distillation conditions.
D-102	Distillation column	Separates ethylbenzene from benzene/toluene.
P-105	Pump	Increase pressure to reach storing conditions.

HX-106	Heat exchanger	Cools styrene to reach storing conditions.
P-104	Pump	Recycles unreacted EB back into the feed loop.

2.3 Material Balance

The material balance was done to satisfy the proposed production rate of 320 thousand tons per annum. Assuming that the average plant works for 8000 hours per year, the production rate was adjusted to be around 40000 kg per hour.

Stream 1 represents the feed of the EB, which was mixed with stream 32, recycled ethylbenzene stream, to produce combined stream 2. Then through streams 3-5 the EB conditions were adjusted to required (Table 6).

Table 6. Streams 1-5 Operating conditions and component mass flow rate.

Operating condition	**1**	**2**	**3**	**4**	**5**
Temperature/ °C	25	57	57	156	476
Pressure/ bar	1	1	1.7	1.7	1.68
Components Mass Flow Rate					
Mass (kg/h)	**1**	**2**	**3**	**4**	**5**
Ethylbenzene	45 580	67 256	67 256	67 256	67 256
Styrene	0.00	1 590	1 590	1 590	1 590
Hydrogen	0.00	0.00	0.00	0.00	0.00
Benzene	0.00	0.00	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00	0.00	0.00

Methane	0.00	0.00	0.00	0.00	0.00
Toluene	0.00	20	20	20	20
Water	0.00	0.00	0.00	0.00	0.00
Total	45 580	68 866	68 866	68 866	68 866

Stream 6 represents the initial water supply, the required amount of water was adjusted to have steam to ethylbenzene ratio as 11:1. This stream underwent a series of operations to reach superheated steam conditions, the transformation is shown by streams 7-11. The values of conditions and mass flows are shown in Table 7.

Table 7. Streams 6-11 Operating conditions and component mass flow rate.

Operating condition	**6**	**7**	**8**	**9**	**10**	**11**
Temperature/ °C	25	25	115	115	476	720
Pressure/ bar	1	1.7	1.7	1.7	1.65	1.65
Components Mass Flow Rate						
Mass (kg/h)	**6**	**7**	**8**	**9**	**10**	**11**
Ethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00
Styrene	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	0.00	0.00	0.00	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00

Methane	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	0.00	0.00	0.00	0.00	0.00	0.00
Water	125 730	125 730	125 730	125 730	125 730	125 730
Total	125 730	125 730	125 730	125 730	125 730	125 730

Stream 12 represents a mixed stream of EB and superheated steam which was fed to a series of reactors. Stream 13 is the outlet of the first reactor which was fed to in between heater, stream 14. Stream 15 represents the outlet stream of reactors (Table 8). Total conversion of 2 PFRs is 66% and selectivity values for styrene, benzene and toluene are 96%, 1% and 3% respectively. These values were obtained from the kinetic analysis. They are consistent with literature data, which reports ethylbenzene conversion in the range of 64–70% and styrene selectivity in the range of 94–96% [11].

Table 8. Streams 12-15 Operating conditions and component mass flow rate.

Operating condition	**12**	**13**	**14**	**15**
Temperature/ °C	623	548	620	591
Pressure/ bar	1.7	1.5	1.5	1.1
Components Mass Flow Rate				
Mass (kg/h)	**12**	**13**	**14**	**15**
Ethylbenzene	67 256	36 603	36 603	22 760
Styrene	1 590	30 847	30 847	42 557
Hydrogen	0.00	554	554	748
Benzene	0.00	261	261	454

Ethylene	0.00	94	94	163
Methane	0.00	72	72	320
Toluene	20	436	436	1 863
Water	125 730	125 730	125 730	125 730
Total	194 596	194 596	194 596	194 596

The reactor outlet was cooled by a series of heat exchangers, represented by streams 16-20. The conditions of the streams are represented in Table 9.

Table 9. Streams 16-20 Operating conditions and component mass flow rate.

Operating condition	**16**	**17**	**18**	**19**	**20**
Temperature/ °C	486	355	264	133	40
Pressure/ bar	1.08	1.05	1.05	1.05	1.05
Components Mass Flow Rate					
Mass (kg/h)	**16**	**17**	**18**	**19**	**20**
Ethylbenzene	22 760	22 760	22 760	22 760	22 760
Styrene	42 557	42 557	42 557	42 557	42 557
Hydrogen	748	748	748	748	748
Benzene	454	454	454	454	454
Ethylene	163	163	163	163	163

Methane	320	320	320	320	320
Toluene	1 863	1 863	1 863	1 863	1 863
Water	125 730	125 730	125 730	125 730	125 730
Total	194 596	194 596	194 596	194 596	194 596

Stream 20 enters a three phase separator which divides the stream into three phases. Stream 21-23 represent these phases: the gases, organic, and wastewater streams. The stream 22 contains the crude styrene that undergoes the separation with two distillation columns. D-101 separates the 99.74% styrene from the remaining hydrocarbons (Stream 26), distillate undergoes further separation (Stream 25).

Table 10. Streams 21-26 Operating conditions and component mass flow rate.

Operating condition	**21**	**22**	**23**	**24**	**25**	**26**
Temperature/ °C	40	40	40	40	30	120
Pressure/ bar	1.05	1.05	1.05	0.5	0.1	0.4
Components Mass Flow Rate						
Mass (kg/h)	**21**	**22**	**23**	**24**	**25**	**26**
Ethylbenzene	58	22 185	518	22 185	22 080	105
Styrene	74	41 817	666	41 817	1 593	40 224
Hydrogen	748	0.00	0.00	0.00	0.00	0.00
Benzene	8	375	72	375	375	0.00
Ethylene	163	0.00	0.00	0.00	0.00	0.00

Methane	320	0.00	0.00	0.00	0.00	0.00
Toluene	932	932	0.00	932	932	0.00
Water	607	26	125 096	26	26	0.00
Total	2 910	65 334	126 353	65 334	25 005	40 329

The obtained styrene product is brought to storing conditions of 25°C and 1 bar with the pump and heat exchanger (Streams 27-28). The pressure of distillate product from D-101 is increased through the pump and fed to the second distillation column D-102 (Stream 29). D-102 divided it into stream 30, Benzene-Toluene mixture, and stream 31, EB recycle stream. The pressure of the recycle stream was increased through pump P-104 to adjust it for further fed EB mixing conditions resulting in stream 32.

Table 11. Streams 27-32 Operating conditions and component mass flow rate.

Operating condition	**27**	**28**	**29**	**30**	**31**	**32**
Temperature/ °C	120	25	31	22	112	112
Pressure/ bar	1.05	1	0.5	0.4	0.5	1
Components Mass Flow Rate						
Mass (kg/h)	**27**	**28**	**29**	**30**	**31**	**32**
Ethylbenzene	105	105	22 080	404	21 676	21 676
Styrene	40 224	40 224	1593	2.3	1 590	1 590
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	0.00	0.00	375	375	0.00	0.00

Ethylene	0.00	0.00	0.00	0.00	0.00	0.00
Methane	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	0.00	0.00	932	912	20	20
Water	0.00	0.00	26	26	0.00	0.00
Total	40 329	40 329	25 005	1 718	23 286	23 286

Chapter 3 – Major Equipment Design:

3.1. Reactors

The production of styrene takes place in a Plug Flow Reactor Model. The main components of the reaction are ethylbenzene and excess steam, which is added approximately at an 11:1 ratio. Two adiabatic reactors are placed in series in order to increase the conversion, while keeping a reasonable volume and catalyst weight, which directly affects the cost of the reactor. Furthermore, a heater was added between 2 reactors, because the reaction is endothermic, but the temperature should be kept at 620°C.

3.1.1. Choice of Reactor type

The design of chemical processes requires selecting a suitable reactor, because it directly controls conversion efficiency, operational costs and determines feasibility. Four main reactor configurations such as adiabatic fixed-bed, isothermal fixed-bed, fluidized-bed and membrane reactors were evaluated. Various factors must be taken into consideration when assessing the reactor types because each possesses different operational requirements.

The following Table 12 illustrates reactor types for ethylbenzene dehydrogenation and shows their benefits versus limitations, as well as their suitability in industrial settings.

Table 12. Reactor types with descriptions.

Reactor	**Advantages**	**Disadvantages**
Adiabatic Fixed-Bed Reactor	• Simple design, lower capital cost • No external heating required	• Requires multiple beds with interstage heating • Temperature gradients can lead to

	• Proven industrial success and scalability • Well-established in large-scale styrene production • Widely used in industry (Lummus/UOP, BASF processes) [50]	uneven catalyst deactivation [51]
Isothermal Fixed-Bed Reactor	• Better temperature control • More uniform reaction rate and selectivity	• Requires continuous external heating, increasing energy consumption • More complex design and higher capital cost • Rarely used for styrene production due to high energy demand [52]
Fluidized-Bed Reactor	• Excellent heat and mass transfer • Uniform temperature across catalyst bed • Continuous operation with easy catalyst replacement	• High catalyst attrition, leading to frequent catalyst loss • Complex gas-solid separation required • Lower selectivity compared to packed-bed reactors • Rarely used for styrene due to selectivity issues [53]
Membrane Reactor	• Selective removal of H_2 shifts equilibrium for higher conversion	• Expensive membranes, thus increased capital cost

	• Can operate at lower temperatures, improving energy efficiency • Potential for improved yield and selectivity	• Membrane durability issues at high temperatures • Still in research stage, not commercialized yet • Not implemented in industrial styrene plants yet [54]

The industrial production of styrene uses the adiabatic fixed-bed reactor because it offers simplicity while providing high efficiency along with adjustable processing capacity. An adiabatic procedure controls these reactors, because it maintains complete thermal isolation throughout the reaction process. The reactive process inside the reactor determines all temperature variations throughout its operation. Achieving high conversion rates depends on maintaining optimal temperatures because the dehydrogenation reaction of ethylbenzene to styrene operates with high endothermicity.

3.1.2 Choice of Catalyst

The industry-standard catalyst for this process is based on iron oxide (Fe_2O_3), promoted primarily with potassium oxide (K_2O), often referred to as an Fe-K catalyst system [12]. Iron oxide provides the active phase for dehydrogenation, while potassium acts as an electronic promoter, enhancing styrene selectivity and suppressing undesirable side reactions such as coke formation and hydrogenolysis [1].The addition of potassium also neutralizes the acidic sites on the catalyst surface, which limits the formation of byproducts such as benzene and toluene.

In some cases, secondary promoters such as chromium oxide (Cr_2O_3), molybdenum oxide (MoO_3), or cerium oxide (CeO_2) are introduced to stabilize the iron oxide phase and improve the mechanical strength and longevity of the catalyst under cyclic regeneration conditions [55–57]. For example, Shell 105 catalyst includes chromium as a structural promoter to enhance potassium retention and minimize volatilization losses, which are particularly significant at high operating temperatures.

Despite the exploration of alternative catalytic systems, the Fe-K system remains the most economically and operationally favorable for EB dehydrogenation due to its low cost, resistance to sintering, compatibility with steam as a heat carrier and diluent, and ease of regeneration via controlled oxidation with air. Therefore, considering the advantages mentioned above, the Fe-K catalyst system is selected for this process as the optimal choice to ensure high styrene yield, long catalyst life, and minimal environmental impact.

The choice of a specific catalyst is described in Chapter 7, its diameter is 0.0045m with cylindrical shape. For cylindrical particles, studies have reported mean void fractions ranging from 0.42 to 0.54, thus the bed voidage was selected to be the average value of 0.5 [58].

3.1.3. Reactor design equations

The kinetics of this process was described in detail in the Appendix B.1. The process of styrene production goes along with three side reactions and all are shown in Table 13.

Table 13. Reactions involved in dehydrogenation of ethylbenzene to styrene.

Reaction		Type
R1	$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2$	main
R2	$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	side
R3	$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	side
R4	$C_6H_5CH{=}CH_2 + 2H_2 \rightarrow C_6H_5CH_3 + CH_4$	side

At first, the inlet stream of ethylbenzene is mixed with steam in order to increase the temperature of the EB entering the reactor, because reaction takes place under high temperature of 620°C. EB is continuously consumed during the reaction, however, resulting styrene is also consumed during the side reactions - but at a much lower rate compared to the main one. The reactors work adiabatically, because the reaction is endothermic and operating isothermally would be economically nonviable, as it would require extra-heating to keep the reactor temperature constant.

Volume is one of the most important parameters in PFR design. Since the process involves catalyst, the volume for both reactors was calculated by following equation:

$$V_{reactor} = \frac{V_{cat}}{1-\epsilon} \tag{5}$$

Where, ($V_{reactor}$) - volume of the reactor in m³, (V_{cat}) - volume of the catalyst in m³, (ϵ) - bed voidage.

Volume of the catalyst was calculated as presented below:

$$V_{cat} = \frac{W}{\rho_b} \tag{6}$$

Where, (W) - weight of the catalyst in kg cat, (ρ_b) - bulk density in kg/m³.

The bulk density is the apparent density of the material under the packing conditions [59]. It is calculated by:

$$\rho_b = \rho_{cat}(1 - \epsilon) \tag{7}$$

Where, (ρ_{cat}) is the density of the catalyst in kg/m³

Weight of the catalyst is calculated according to equation 4.

$$W = F_{EB}\tau \cdot 1.1 \tag{8}$$

where, (F_{EB}) - EB inlet molar flow rate, (τ) -space time in gcat*hr/mol, 1.1 - extra catalyst load. The initial calculation of catalyst weight is based on the required amount needed to achieve the desired conversion under ideal conditions. However, in industrial practice, it is common to oversize the catalyst load to account for uncertainties. To ensure a more precise and reliable design, the calculated catalyst weight is multiplied by a safety factor of 1.1, with 10% extra catalyst load. It is important to note that all calculations were made according to flow rates that were lower, but catalyst oversize covers such fluctuations.

From the calculated volume we were able to find the reactor dimensions, according to the formula of cylinder volume. At first, it was assumed that the length of the reactor is approximately 2.5 times the diameter, and obtained values were 8.8 m and 3.53 m. However, the superficial gas velocity and pressure drop were too large with such size, so in order to decrease them the tubes were divided into 19 and 12 tubes for first and second reactors respectively, with dimensions of 1.5 m diameter and 2.5 m length.

Each reactor consists of multiple tubes, and the cross-sectional area of a single tube is calculated using:

$$A = \frac{\pi {d_{tube}}^2}{4} \tag{9}$$

And volume of tube is calculated using:

$$V_{tube} = A \times L \tag{10}$$

Where, (L) - tube length (m)

The total number of tubes required to accommodate the catalyst volume is then determined as:

$$N = \frac{V_{reactor}}{V_{tube}} \tag{11}$$

This ensures that the reactor is properly distributed across multiple tubes, preventing excessive pressure drop, while maintaining sufficient contact time with the catalyst.

In order to calculate the pressure drop in each tube, superficial gas velocity should be determined first, according to equation 12:

$$u_0 = \frac{Q}{An} \tag{12}$$

Where, (Q) - inlet volumetric flow rate (m^3/s)

To evaluate the pressure drop across the reactor, the Ergun equation is used:

$$\frac{dP}{dz} = \frac{150(1-\epsilon)^2 \mu u_0}{d_p^2 \epsilon_b^3} + \frac{1.75(1-\epsilon_b)\rho u_0^2}{d_p \epsilon_b^3} \tag{13}$$

Where, $(\frac{dP}{dz})$ - pressure drop per unit length (Pa/m), (μ) - gas viscosity (Pa·s), (ρ) - gas density (kg/m^3), and (d_p) - catalyst particle diameter.

Since our catalyst is not spherical, diameter of catalyst for was calculated using the given formula:

$$d_p = \sqrt[3]{\frac{6 d_{actual}^2 l_{actual}}{4}} \tag{14}$$

All calculation results made are available in Reactor specification sheet and Appendix B.2.

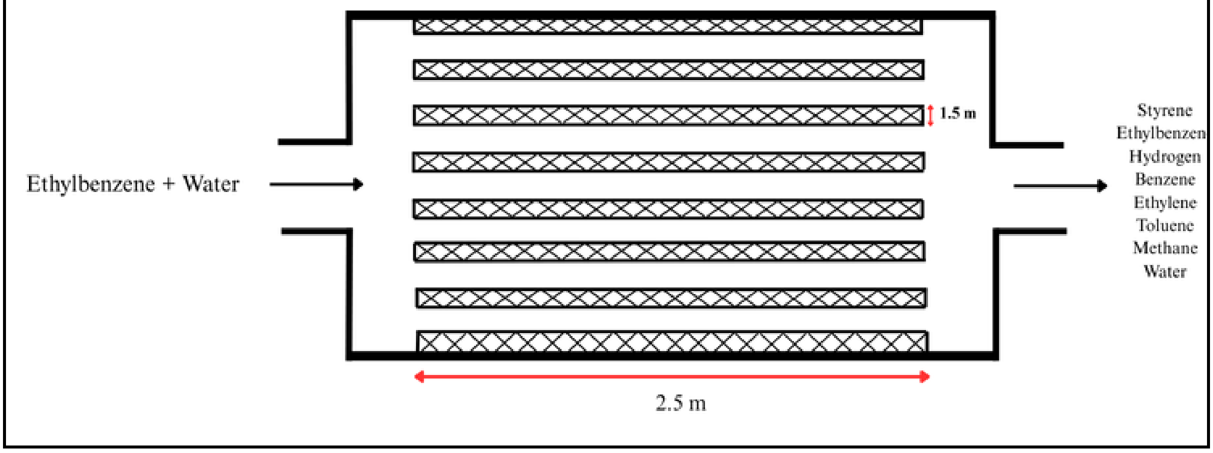
3.1.4. Material choice

The selection of SS316 material for the adiabatic fixed-bed reactor relied on a comparison between SS321, SS309 and SS347 to find the material best suited for resisting corrosion, as well as maintaining high-temperature compatibility and superior mechanical properties while ensuring cost-saving operation. The molybdenum content in SS316 material provides superior resistance to corrosion that enables it to withstand aggressive chemical environments by protecting against oxidation and pitting and crevice corrosion [60]. Styrene production requires specific attention to reactor design since the elevated temperatures combined with exposure to hydrocarbons and steam and oxidative conditions represent critical operational requirements. The addition of titanium in SS321 helps stabilize the material while improving its resistance to intergranular corrosion, yet the absence of molybdenum reduces its capability to combat pitting and crevice corrosion when exposed to chloride media [61]. SS316 works better for applications that need extreme high temperatures, since it demonstrates stable performance at operating temperatures spanning from 500 to 650°C, however SS309 and SS347 work better for higher temperatures [62]. The oxidation resistance excellence of SS309 makes it a superior material for applications needing exposure to temperatures between 980°C and above, but it performs poorly in chemical processes such as styrene dehydrogenation [63]. SS347 with niobium addition shows high-temperature performance, but would offer unnecessary strength to this particular system as the operational temperature remains below 800°C [64]. SS316 demonstrates excellent tensile strength and endurance capabilities, which allow the material to prevent structural damage throughout reactor pressure changes. [65]. The high-temperature resistance of SS309 and SS347 remains insufficient due to their higher costs and lower use in industry for this project. The processability of SS316 exceeds that of SS321 because it does not require intense titanium-controlled welding requirements [65]. SS316 presents an optimal combination of durability, corrosion resistance and cost-effectiveness combined with thermal stability [64]. The temperature properties of SS309 and SS347 do not outweigh their elevated cost compared to typical operations between 500 to 650°C. Analysis of these parameters led to choosing SS316 as the best material for achieving long-lasting reactor performance through resistance to chemical degradation and thermal conditions.

3.1.5. Reactor unit specification sheet

Table 14. R-101, R-102 specification sheet

<table>
<tr><th colspan="3">Operating conditions</th></tr>
<tr><td colspan="2">Temperature, °C</td><td>620</td></tr>
<tr><td colspan="2">Pressure, bar</td><td>1.09</td></tr>
<tr><td colspan="2">Catalyst diameter, m</td><td>0.0045</td></tr>
<tr><td colspan="2">Catalyst density, kg/m³</td><td>2500</td></tr>
<tr><td colspan="2">Bed Voidage</td><td>0.5</td></tr>
<tr><th colspan="3">Type and sizing</th></tr>
<tr><td></td><td>Reactor 1</td><td>Reactor 2</td></tr>
<tr><td>Type of reactor</td><td>Adiabatic fixed bed reactor</td><td>Adiabatic fixed bed reactor</td></tr>
<tr><td>Catalyst weight, kg</td><td>53896</td><td>31628</td></tr>
<tr><td>Material</td><td>SS316</td><td>SS316</td></tr>
<tr><td>Number of tubes</td><td>19</td><td>12</td></tr>
<tr><td>Length of reactor, m</td><td>2.5</td><td>2.5</td></tr>
<tr><td>Inner diameter of the tube, m</td><td>1.5</td><td>1.5</td></tr>
<tr><td>Outer diameter of the tube, m</td><td>1.504</td><td>1.504</td></tr>
<tr><td>Volume of the reactor, m</td><td>84</td><td>53</td></tr>
</table>

Pressure drop, bar	0.195	0.391
Schematic diagram of reactors		
		

Figures B.2.1 and B.2.2 in Appendix B show the change of temperature with change of length of the reactor.

3.2. Heat exchangers

3.2.1. Basic heat exchanger design calculations

Heat exchangers are critical components in thermal systems, designed to transfer heat efficiently between two or more fluids at different temperatures. The design and performance evaluation of heat exchangers rely on fundamental heat transfer equations and empirical correlations. This section outlines the essential calculations used in heat exchanger design.

The design of a heat exchanger begins with an assumption for the overall heat transfer coefficient (U). Next, the log mean temperature difference is calculated to account for varying temperature differences along the heat exchanger.

$$\Delta T_{lm} = \frac{(T_1 - t_2) - (T_2 - t_1)}{ln\,(\frac{T_1 - t_2}{T_2 - t_1})} \tag{15}$$

where ΔT_{lm} - log mean temperature difference (K) ; T_1 - hot fluid temperature, inlet (K); t_1 - cold fluid temperature, inlet (K); T_2- hot fluid temperature, outlet (K); t_2- cold fluid temperature, outlet (K).

A correction factor is applied to obtain effective mean temperature:

$$\varDelta T_m = F_t * \varDelta T_{lm} \tag{16}$$

The correction factor F_t is determined from empirical charts or equations as a function of the flow arrangement, expressed in terms of the temperature effectiveness parameters:

$$R = \frac{(T_1 - T_2)}{(t_2 - t_1)} \tag{17}$$

$$S = \frac{(t_2 - t_1)}{(T_1 - t_1)} \tag{18}$$

$$F_t = \frac{\sqrt{(R^2+1)}ln(\frac{(1-S}{(1-RS})}{(R-1)ln\left[\frac{2-S(R+1-\sqrt{R^2+1})}{2-S(R+1+\sqrt{R^2+1})}\right]} \tag{19}$$

The initial assumption of overall heat transfer coefficient helps estimate the required heat exchanger area using combination of the following equations:

$$Q = mc\varDelta T \tag{20}$$

where m - mass flow rate (kg/s); c - specific heat capacity (J/kg·K); $\varDelta T$- temperature change (K)

$$Q = \varDelta T_m \, A_{total} \, U \tag{21}$$

where heat transfer coefficient - U, total heat transfer area - A_{total}, and temperature difference- $\varDelta T_m$.

The tube and shell geometry are then defined, determining the number of tubes Nt, tube diameter d_o, tube pitch p_t, and bundle diameter D_b. For shell-and-tube heat exchangers, the tube area is calculated as:

$$A_{tube} = \pi d_o L \tag{22}$$

where d_o - outer tube diameter (m), L - tube length (m).

The total number of tubes (N_t) required is:

$$N_t = \frac{A_{total}}{A_{tube}} \tag{23}$$

The bundle diameter (D_b) can be estimated using an empirical relationship:

$$D_b = d_o(\frac{N_t}{K_1})^{\frac{1}{n_1}} \tag{24}$$

where (K_1) and (n_1) are constants dependent on the arrangement of tubes, obtained from the design chart for different pitches and tube passes (see Appendix B.2, Figure B.2.5).

Heat transfer coefficients for both the shell and tube sides are evaluated using empirical correlations. The convective heat transfer coefficients for internal and external flows (h_i and h_s) are determined using equations related to Nusselt Number:

$$\frac{h_i d_i}{k_f} = j_h Re Pr^{0.33} (\frac{\mu}{\mu_w})^{0.14} = \mathrm{Nu} \tag{25}$$

where h_i - heat transfer coefficient ($W/(m^2K)$; j_h - heat transfer factor (see Appendix B.2 Figures B.2.3-B.2.6); Re - Reynolds number; Pr - Prandtl number; k_f - thermal conductivity of fluid ($W/(m^2K)$; μ - viscosity ($Nsec/m^2$), μ_w - viscosity on the wall ($Nsec/m^2$). Viscosity correction factor term ($\frac{\mu}{\mu_w}$) can be neglected in vapor phase heat transfer cases.

Pressure drops on both sides are also estimated to ensure the design meets operational constraints.

$$\Delta P_t = N_p \left[8 j_f (\frac{L}{d_i})(\frac{\mu}{\mu_w})^{-m} + 2.5\right] \frac{\rho {u_t}^2}{2} \tag{26}$$

where, j_f - friction factor (see Appendix B.2 Figures B.2.4 - B.2.7), N_p - number of tube passes, u_t - velocity at tube outlet (m/s).

For the shell-side, an equivalent diameter d_e is used for calculations:

$$d_e = \frac{1.27}{d_o}({p_t}^2 - 0.785{d_o}^2) \tag{27}$$

where p_t - tube pitch (m) which typically equals $1.25d_o$.

$$p_t = 1.25d_o \tag{28}$$

The shell-side pressure drop is:

$$\Delta P_s = 8 j_f (\frac{D_s}{d_e})(\frac{L}{l_B}) \frac{\rho {u_s}^2}{2} (\frac{\mu}{\mu_w})^{-0.14} \tag{29}$$

where D_s is the shell diameter and l_B is the baffle spacing.

Finally, the overall heat transfer coefficient U_{total} is recalculated based on internal and external heat transfer coefficients, fouling factors, and tube wall resistance. If the new U_{total} significantly deviates from the initial assumption, the process iterates until a feasible and optimized design is achieved.

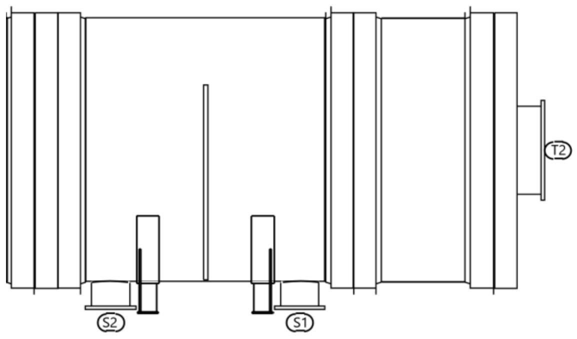
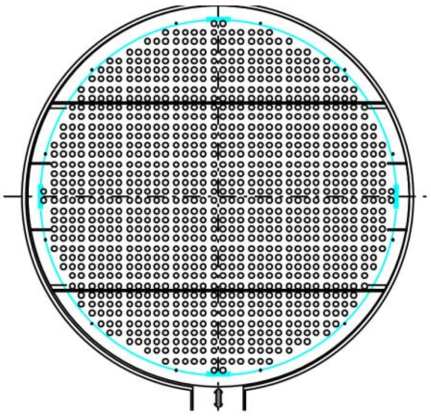
$$\frac{1}{U_{total}} = (\frac{1}{h_i} + R_i)\frac{d_o}{d_i} + \frac{d_o ln(\frac{d_o}{d_i})}{2k_f} + \frac{1}{h_s} + R_s \tag{30}$$

where h_s - shell-side heat transfer coefficient, R_i and R_s - fouling resistances and k_f - tube thermal conductivity.

3.2.2. Heat Exchanger HX-102

In order to optimize the energy consumption in the system, it was decided to combine reactor outlet stream (Stream 15) with the vaporised EB stream (Stream 4). It results in simultaneous cooling of reactor outlet stream and heating of EB stream. The design layout of the heat exchanger device is shown in the table below.

Table 15. Design layout of the heat exchanger HX-102.

Setting Plan	**Tube Layout**
	
TEMA Type	AEW
In series	1

In parallel	5
Design Parameters	
Length of the tube, m	2.44
Outside diameter, mm	38
Thickness, mm	2.1
Baffle spacing, m	0.79
Bundle diameter, m	1.87
Shell diameter, m	1.97
Baffle cut, %	25
Number of tubes	1177
Tube pattern	90° square pattern
Configuration	1-Shell, 1-Pass
Type of material	Stainless steel, SS316

The TEMA type of AEW heat exchanger was chosen, because it is well-suited for high-temperature applications. Its floating head (W-type) accommodates thermal expansion, preventing mechanical stress, while the removable bundle (A-type) ensures easy maintenance and cleaning [64]. The one-pass shell design (E-type) minimizes pressure drop, making it efficient for high-flow applications. The material of the heat exchanger was chosen to be stainless steel SS316, due to its ability to withstand the high temperatures and corrosive substances as it was discussed previously. Design parameters were calculated using equations shown in section 3.2.1. Detailed calculations are provided in ESI. Calculated and Aspen values were in reasonable consistency, the deviations are explained due to the different methods of Aspen calculations. The results of the design are shown in the table below. The values of fooling coefficients were taken from literature review [11].

Table 16. Parameters of exchanger HX-102.

	Reactor outlet	EB inlet
Location	Shell side	Tube side
Inlet temperature, °C	591	156
Outlet Temperature, °C	486	476
Inlet pressure, bar	1.09	1.7
Outlet pressure, bar	1.07	1.68
Mass flow rate, kg/hr	194812	68975
Fouling coefficients, m^2K/W	0.00035	
Heat duty, MW	13.3	
Heat transfer Area, m^2	1481.7	
Effective LMTD, °C	196.61	

In order to assess the performance of the heat exchanger the TQ curve was constructed. The T-Q curve suggests a well-balanced heat exchanger design, maintaining a consistent temperature gradient to facilitate efficient energy transfer.

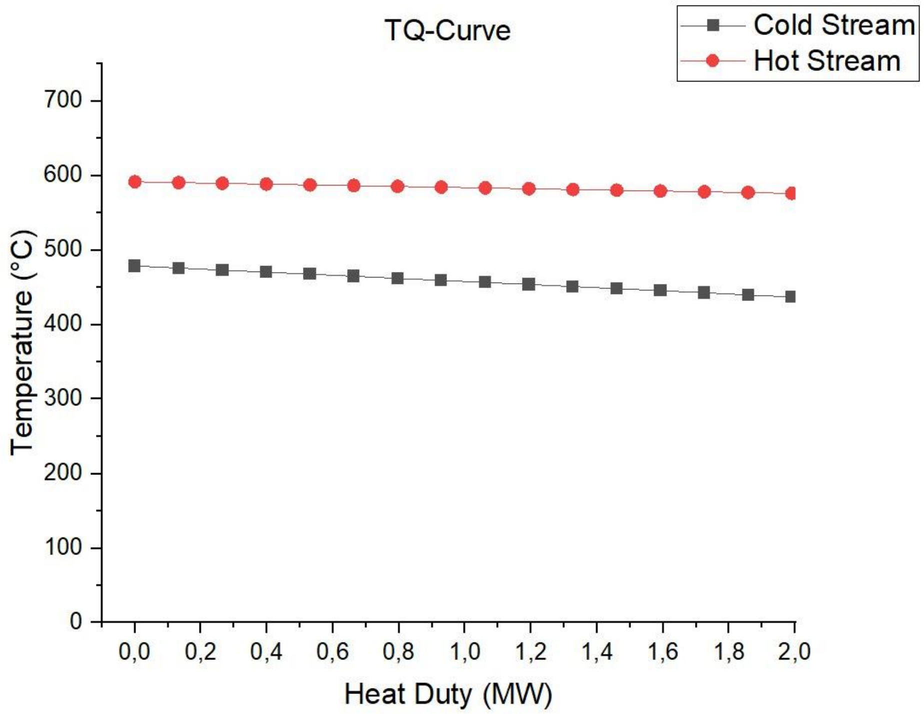


Figure 6. T-Q curve of the process.

3.2.3. Heat Exchanger HX-103

Second heat exchanger, which is considered a major unit, functions as a cooler for the reactor outlet stream in the dehydrogenation of ethylbenzene to styrene. This reaction occurs at high temperatures, with the reactor effluent typically exiting at around 550-590°C. To ensure downstream processing and separation efficiency, as well as to prevent thermal degradation of the product, the stream must be gradually cooled to 40°C.

In order to reach such a big cooling degree, it was decided to enhance this process piece by piece using heat exchangers in series. Second heat exchanger in this series is HX-103. HX-103 cools initial reactor outlet stream from 486°C to 355°C using 115°C steam. Steam stream at 115°C and 1 bar pressure was chosen as a coolant. Physical properties, inlet and outlet temperatures, pressures and flow rates of each stream in heat exchanger are presented in the table below.

Table 17. Parameters of exchanger HX-103.

	Steam	Reactor Outlet
Location	Shell side	Tube side
Inlet temperature, °C	115.21	487.35

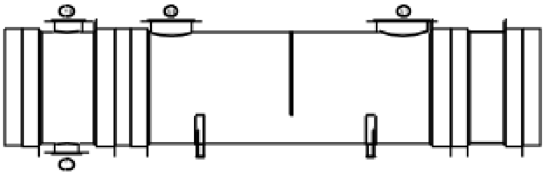
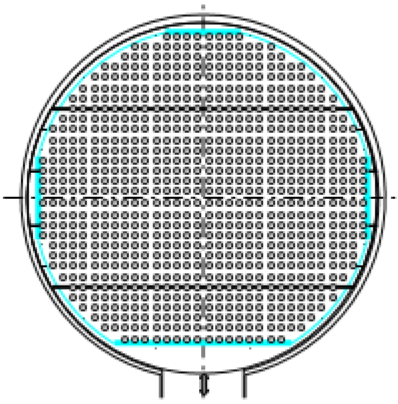
Outlet Temperature, °C	345.56	355.55
Mean Temperatures, °C	230.38	421.5
Effective LMTD, °C	160.17	
Inlet pressure, bar	1.0763	1.7
Outlet pressure, bar	1.045	1.648
Mass flow rate, kg/hr	125 837	194 814
Fouling coefficient, m^2K/W	0.0002	0.00035
Heat duty, MW	15.3386	
Heat transfer Area, m^2	2131.06	

Physical properties for each stream are presented for mean temperatures of each stream, since these temperatures can be considered as operating conditions. On both shell side and tube side pressure drop occurs - 0.0313 bar and 0.052 bar, respectively, this amount of pressure drop occurs due to sensitivity of vapor phase fluids to temperature changes. However, in the following design of heat exchanger these values of pressure drops were taken into account.

In order to achieve a desirable change in temperature of the reactor outlet stream and make suitable design according to TEMA standards, it was decided to separate the reactor outlet stream into 5 parallel flows, each of one entering separate heat exchangers. Each heat exchanger has the same geometry and working conditions.

All calculated and estimated values were then entered into heat exchanger design parameters in Aspen Plus (V14) simulation software. A-type front head (channel with removable cover) was chosen, since it can handle moderate to high-pressure applications on the tube side. Another advantage of this type of front head is bolted and removable cover, operators can inspect or clean the tube-side interior without disassembling the entire exchanger. The one-pass shell design (E-type) was chosen in order to minimize pressure drop and make it suitable for high-flow streams. The outside packed head with pull-through floating tubesheet (W-type) rear head was chosen due to its ability to accommodate differential thermal expansion between the shell and the tube bundle. Since the rear tube sheet is not fixed and is free to float, it can move in response to temperature changes, which helps reduce thermal stresses and prevents mechanical damage to the tubes and shell [64].Similar to HX-102, corrosion-resistant stainless steel (SS316) was chosen as the material for the pipes [64]. Resultant design specifications are presented below:

Table 18. Design layout of the heat exchanger HX-103.

Setting Plan	**Tube Layout**
	
In series	1
In parallel	5
Design Parameters	
Heads and Shell Types	(A) - (E) - (W)
Length of the tube, m	6.1
Outside diameter of the tube, mm	50
Thickness, mm	2.8
Baffle spacing, m	1.7
Bundle diameter, m	2
Shell diameter, m	2.04
Baffle cut, %	25

Number of tubes	492
Tube pattern	90° square pattern
Configuration	1-Shell, 2-Tube passes

The values from the simulation in Aspen Plus were close to the hand-written data. Most of the values varied within 2-4% inaccuracy, indicating acceptable preciseness of manual calculations.

Some differences in values can be explained by the fact that Aspen Plus itself corrects some values of the heat exchanger geometry during the simulation (parameters such as the number of pipes, clearance, nozzles and shell clearance). The simulation calculates the values of the Heat Transfer Area and Shell Side Velocity according to the corrected data, which creates this discrepancy. A lot of assumptions were made during manual calculations and approximations, especially when the values were taken from handbook graphs.

The corresponding TQ curve shown below:

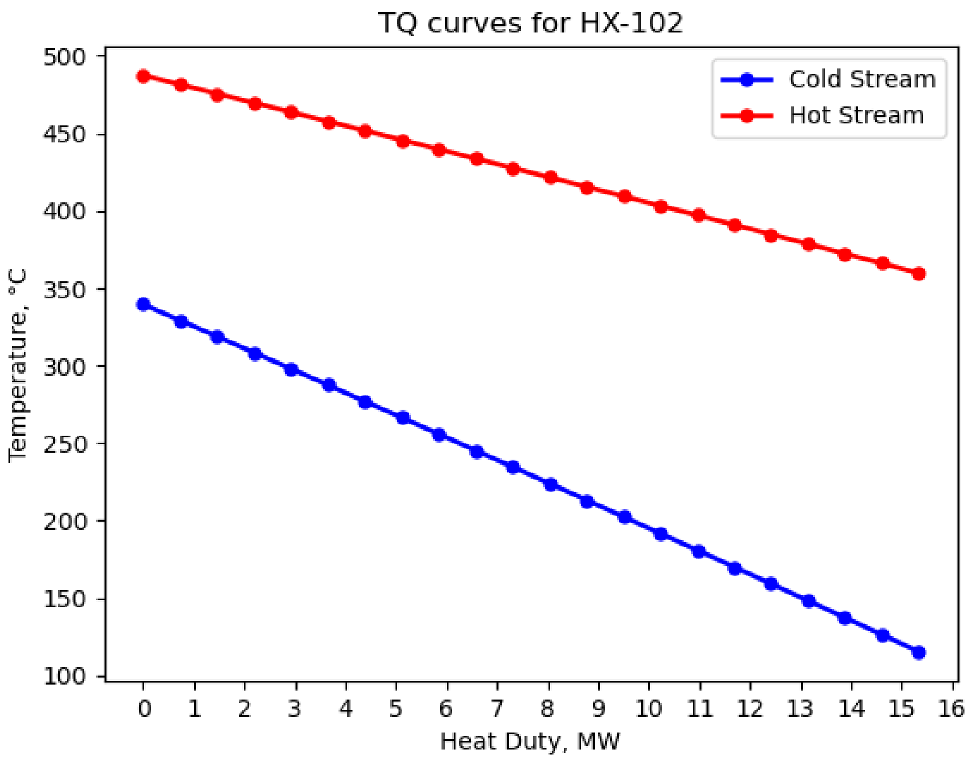


Figure 7. TQ curve for 2nd major Heat Exchanger

3.3. Distillation Columns

3.3.1. D-101 Distillation column

Upon completion of the reactor outlet separation in the three-phase separator, the organic stream is introduced into the D-101 distillation column. Within this column, styrene is separated as the bottom product with a molar purity of 99.7%, while a mixture of benzene, toluene, ethylbenzene, and water is separated in the top product. The feed conditions entering the D-101 column are 0.5 bar and 40°C. This section presents detailed information on the design parameters for the D-101 distillation column.

3.3.1.1. D-101 distillation column working principle

The feed compositions are derived from the organics outlet of the three-phase separator. For the calculations, based on the difference in boiling points of the components, ethylbenzene was selected as the light key (LK), being the less volatile component, and styrene was chosen as the heavy key (HK) in the column.

The primary challenge in the ethylbenzene-styrene separation is the similar volatilities of the components and the requirement for high purity in the styrene product. Given these considerations, the column is designed as a vacuum column with a large number of stages. Since packed columns are particularly effective for vacuum distillation, the internal design selected for this column is packed.

3.3.1.2. Component relative volatility.

The saturation pressure of the components were calculated using the Antoine equation to approximate the relative volatility. The coefficients for the Antoine equation can be obtained in Appendix B.2, Table B.2.1. The saturation pressures at the condenser and reboiler conditions are determined using the following equation:

$$log_{10}(P_{sat}) = A - \frac{B}{T + C} \tag{31}$$

where $P_{\,sat}$ is saturation pressure (bar); T is temperature (Celsius); A, B, C are Antoine coefficients

Relative volatilities of the component were calculated using this equation:

$$\alpha_{ij} = \frac{P_{sat}, i}{P_{sat}, j} \tag{32}$$

Where α_{ij} is the relative volatility of component i with respect to component j; P_{sat}, i is saturation pressure of the component *i*; P_{sat}, j is saturation pressure of the component j.

For ethylbenzene-styrene separation the reference component is styrene. Results of relative volatilities calculations are presented in Table 19.

Table 19. Saturation pressure and relative volatilities of components.

Component	Condenser		Reboiler		Geometric mean
	P_{sat}, bar	Relative volatility	P_{sat}, bar	Relative volatility	Relative volatility
Benzene [13]	0.166	14.173	2.997	6.065	9.272
Toluene [13]	0.0514	4.383	1.313	2.656	3.412
Ethylbenzene [13]	0.0178	1.520	0.642	1.299	1.405
Styrene [13]	0.0117	1	0.494	1	1
Water [13]	0.0448	3.817	1.987	4.022	3.918

3.3.1.3. D-101 column design

For the initial design of the D-101 column, the Fenske-Underwood-Gilliland (FUG) equations were applied. These equations are sourced from Chemical Engineering Design by Towler and Sinnott [64]. Using the FUG method, the minimum number of theoretical stages, reflux ratios, and actual theoretical stages were calculated. The Fenske equation, presented below, is used to determine the minimum number of stages required for the separation:

$$N_{min} = \frac{log[(\frac{X_{LK}}{X_{HK}})_D (\frac{X_{HK}}{X_{LK}})_B]}{log(\alpha_{LK})} \tag{33}$$

where X_{LK} is a molar fraction of the light-key component; X_{HK} is a molar fraction of the heavy-key component; α_{LK} is a relative volatility of the light-key component; B, D subscripts refer to bottom and distillate products

The Underwood correlations, presented below, is used to determine the minimum number of reflux ratio required for the separation:

$$\Sigma \frac{\alpha_i x_{i,d}}{\alpha_i - \Theta} = R_{min} + 1 \tag{34}$$

$$\Sigma \frac{\alpha_i x_{i,f}}{\alpha_i - \Theta} = 1 - q \tag{35}$$

where α_i is the relative volatility of the component i with respect to the heavy-key component; $x_{i,d}$ is the molar fraction of the component in the distillate; $x_{i,f}$ is the molar fraction of the component in the feed; Θ is equation root; R_{min} is minimum reflux ratio; q is the quality of the feed stream.

The θ value should fall between the relative volatility of the heavy-key and light-key components, which in our case ranges from 1 to 1.407. The quality of the feed is defined as the molar fraction of liquid in the stream.

At 40°C and 0.5 bar, the feed is entirely in the liquid phase, so the quality is considered to be 1. Based on the calculations, the minimum number of stages required is 31, with a θ value of 1.2338, resulting in a minimum reflux ratio of 6.52.

In order to approximate design for the column, it is necessary to determine the reflux ratio and the corresponding number of stages. The relationship between the reflux ratio and the number of stages can be determined using Gilliland's correlation:

$$\Psi = \frac{R - R_{min}}{R + 1} \tag{36}$$

$$\frac{N - N_{min}}{N + 1} = 1 + exp(\frac{1 + 54.4\Psi}{11 + 117.2\Psi} + \frac{\Psi - 1}{\Psi^{0.5}}) \tag{37}$$

where R is the reflux ratio; Ψ is correlation coefficient; N is the number of theoretical stages at a given reflux ratio.

The R value was taken as 1.2 times the minimum reflux ratio, which resulted in approximately 64 theoretical stages. A comparison with the DSTWU unit under the same feed conditions showed that the minimum reflux ratio value of 6.59 matches the value calculated using the Underwood equation. However, the minimum number of stages in the DSTWU unit, which is 43, is higher than the 31 stages calculated using the Fenske equation. This discrepancy is likely due to the limiting assumptions of constant relative volatility and constant molar overflow in the FUG method, as well as the fact that Aspen Plus uses the Winn equation instead of the Fenske equation to estimate the minimum number of theoretical stages [66].

Once the overall design of the distillation column is completed, the design of the internal components must be addressed. For the ethylbenzene-styrene separation, which is necessary to prevent styrene polymerization, the mixture needs to be distilled in a multi-stage column with 70 to 100 low-pressure drop stages under vacuum [12,67,68].

An analysis by Luyben, which considered columns with 72, 82, and 102 stages, was conducted to determine the optimal distillation column design for styrene separation. The results revealed that the column with 82 stages is the most effective in terms of energy cost and capital investment over a 3-year period. For this reason, the distillation column will be designed with 82 stages [11, 12].

Given the requirement for low pressure drop per tray, plate columns with low weir heights lead to lower stage efficiency and a higher number of trays [64]. Therefore, packings are preferred for the internal design of the vacuum distillation column. The use of a vacuum distillation column for styrene separation, characterized by a large diameter, a substantial number of stages, and high reboiler and condenser duties, necessitates the use of performance internals, such as structured packing (Mellapack Plus) [69].

The estimation of the inside diameter of the packed column requires the calculation of the specific pressure drop at flooding, which can be determined using the empirical correlation provided below:

$$\Delta P_{flood} = 0.115 F_p^{0.7} \tag{38}$$

where ΔP_{flood} is a pressure drop at flooding; F_p is a packing factor

Further kinetic energy ratio F_{LV} is calculated:

$$F_{LV} = \left(\frac{LM_V}{VM_L}\right)\left(\frac{\rho_V}{\rho_L}\right)^{0.5} \tag{39}$$

where L is the molar flow rate of reflux that goes back down the distillation column; V is the molar flow rate of reflux that goes back down the distillation column and that is collected in the distillate; M is the molar mass; ρ_v is the density of vapor; ρ_L is the density of liquid

Taking values of ΔP_{flood} and F_{LV}, modified empirical capacity factor F_c can be determined from the correlation for specific pressure drop for towers with structured packing.

Next determine estimated flooding velocity using formula below:

$$u_{vf} = \frac{F_c}{F_p^{0.5}\left(\frac{\rho_V}{\rho_L - \rho_V}\right)^{0.5} \upsilon_L^{0.05}} \tag{40}$$

Selecting flooding between 50 - 70 %, calculate inside diameter of the packed tower:

$$D_t = \left(\frac{4VM_v}{fu_f \pi \rho_v}\right)^{0.5} \tag{41}$$

Table 20 below demonstrates results of those calculations:

Table 20. Results of packed tower inside diameter calculations

F_p , packing factor	12, ft^2/ft^3
ΔP_{flood} , pressure drop at flooding	0.655 $inches\ H_2O\ /\ ft\ packed\ height$
F_{LV} , kinetic energy ratio	0.0196
F_c , modified empirical capacity factor	1.6
u_{vf} , estimated flooding velocity	22.26 $ft\ /\ s$
D_t , inside diameter of the packed tower	7.9 m

Column packing height is determined by Height equivalent to a theoretical plate (HETP):

$$H = HETP * number\ of\ stages \tag{42}$$

Experimental values of HETP are a function of a superficial-vapor-velocity F-factor, F_v

$$F_v = u_v(\rho_v)^{0.5} \tag{43}$$

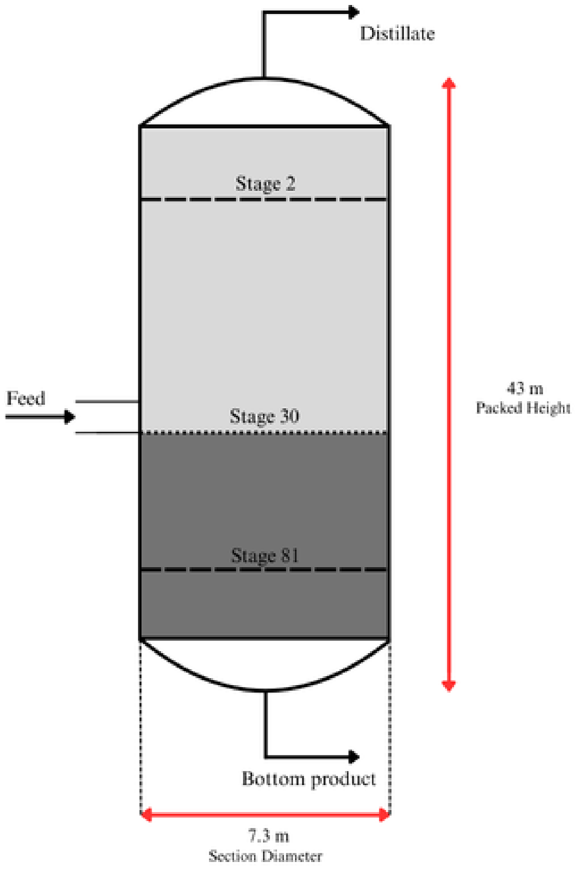
By utilizing separation efficiency graphs for MellapakPlus 252Y [69], the HETP (Height Equivalent to a Theoretical Plate) was determined to be 0.4, and the height of packing was calculated to be 32.8 meters.

3.3.1.4. D-101 Distillation column unit specification.

Table 21 below shows the unit specification sheet of the distillation column.

Table 21. D-101 unit specification sheet.

Unit	D-101	Schematic diagram
Feed flow rate, kmol/hr	627.89	
Inlet temperature, °C	39.98	

<table>
<tr><td>Inlet pressure, bar</td><td>0.5</td><td rowspan="14">
</td></tr>
<tr><td>Distillate flow rate, kmol/hr</td><td>240</td></tr>
<tr><td>Bottoms flow rate, kmol/hr</td><td>387.89</td></tr>
<tr><td>Reflux ratio</td><td>11</td></tr>
<tr><td>Number of Stages</td><td>82</td></tr>
<tr><td>Internal type</td><td>Packing</td></tr>
<tr><td>Packing type</td><td>Sulzer MellapakPlus structured</td></tr>
<tr><td>Packing material</td><td>Metal</td></tr>
<tr><td>Packing size</td><td>252Y</td></tr>
<tr><td>Packing surface area, m^2/m^3</td><td>250</td></tr>
<tr><td>Void fraction</td><td>0.98</td></tr>
<tr><td>Diameter, m</td><td>7.5</td></tr>
<tr><td>Height, m</td><td>43</td></tr>
<tr><td>Column construction material</td><td>SS316</td></tr>
</table>

Condenser conditions		Reboiler conditions	
Type	Total	Type	Kettle

Pressure, bar	0.1	Pressure, bar	0.5
Temperature, °C	31	Temperature, °C	120
Heat duty, kW	-37 427	Heat duty, kW	39 093

3.3.1.5. D-101 Aspen simulation

The D-101 distillation column is simulated using the RadFrac unit with a rate-based calculation type in Aspen Plus. The simulation results, including composition, molar flow rate, temperature, and pressure profiles, are presented in Appendix B.3, Figure B.3.1 - B.3.5.

As shown in Figure B.3.1 & B.3.2 of Appendix B.3, the molar liquid and vapor fractions of benzene and toluene rapidly drop to zero within the first few stages. This occurs because these components are the most volatile in the mixture, allowing them to vaporize easily and be carried upward by the rising vapor phase.

A noticeable initial increase in the molar vapor fraction of ethylbenzene is observed in the first few stages. This is due to the rapid vaporization of ethylbenzene caused by the heat input at the bottom of the column. After reaching a peak, the vapor fraction gradually decreases as ethylbenzene condenses back down the column.

For styrene, an increasing trend in both vapor and liquid fractions is expected because styrene is the least volatile and is being concentrated in the bottom product.

Figure B.3.3 of Appendix B.3 illustrates the vapor flow rate behavior along the column. A steep increase in vapor flow is observed up to stage 3, driven by the intense vaporization of volatile components. Beyond this point and up to the feed stage, the vapor flow remains relatively constant as equilibrium is maintained between the rising vapor and the falling liquid. Immediately after the feed stage, a slight increase in vapor flow is observed due to the presence of more volatile components in the feed, temporarily enhancing vaporization.

Regarding the liquid molar flow rate, a significant increase occurs at the feed stage. This is attributed to the introduction of the feed liquid, which increases the downflow of liquid in the stripping section of the column.

From Figure B.3.4 of Appendix B, a rapid increase in temperature is observed over the first stages that is attributed to the intense vaporization of these volatile components, which absorb latent heat as they transition from the liquid to the vapor phase.

3.3.2. D-102 Distillation Column

The D-102 distillation column is designed to separate benzene and toluene from ethylbenzene in the second distillation step. The feed to D-102 is obtained as a distillate from the first distillation column and consists primarily of benzene, toluene, ethylbenzene and trace amounts of water. The primary objective of D-102 is to recover ethylbenzene for recycling back to the reaction feed. The overhead distillate, which consists mostly of benzene and toluene with minimal water, is removed for further disposal. To prevent backflow and ensure proper feed transport, a pump is used to increase the pressure of the distillate stream before entering D-102. The feed enters the D-102 column at 0.5 bar and 30°C. This section provides a detailed overview of the design parameters for the D-102 distillation column.

3.3.2.1. D-102 distillation column working principle

The D-102 distillation column operates based on relative volatility, enabling the separation of components by their boiling points. Benzene and toluene, having higher volatilities compared to ethylbenzene, are removed as overhead distillate, while the less volatile ethylbenzene remains in the bottom product for recycling. The separation of benzene and toluene is relatively easier compared to the separation of ethylbenzene from styrene. As a result, it requires a much smaller distillation column with fewer stages to achieve the desired separation.

3.3.2.2. Component relative volatility.

The saturation pressures of the components in the D-102 distillation column were calculated using the same method as for the first distillation column, applying the Antoine equation to approximate the relative volatility. The Antoine equation coefficients used for these calculations can be found in Appendix B.2 in Table B.2.1. For the ethylbenzene-benzene-toluene separation, ethylbenzene was chosen as the reference component. The calculated relative volatilities are summarized in Table 22.

Table 22. Saturation pressure and relative volatilities of components.

Component	Condenser		Reboiler		Geometric mean
	P_{sat}, bar	Relative volatility	P_{sat}, bar	Relative volatility	Relative volatility
Water	0.0263	2.459	1.533	3.041	2.735
Benzene	0.110	10.325	2.462	4.886	7.103
Toluene	0.0324	3.038	1.053	2.090	2.520
Ethylbenzene	0.0107	1	0.504	1	1
Styrene	0.0069	0.641	0.384	0.763	0.699

3.3.2.3. D-102 column design

To determine the minimum number of theoretical stages (N_{min}) and the minimum reflux ratio (R_{min}), the same equations used in the previous distillation column design (Section 2.4.3) were applied (The Fenske-Underwood-Gilliland (FUG) equations, sourced from *Chemical Engineering Design* by Towler and Sinnott). Using the FUG method, the minimum number of theoretical stages, reflux ratios, and actual theoretical stages were calculated, where, X_{LK} was chosen as molar fraction of the toluene and X_{HK} as a molar fraction of the ethylbenzene.

The value of θ should lie between the range from 1 to 2.52. The feed quality is determined by the molar fraction of liquid in the stream. At a temperature of 30°C and a pressure of 0.5 bar, the feed is entirely in the liquid phase, meaning the quality is 1. According to the calculations, the minimum number of stages needed is around 12, with a θ value of 2.34, leading to a minimum reflux ratio of 8.0631.

The R value was taken as 1.2 times R_{min}, resulting in around 24 theoretical stages. A comparison with the DSTWU unit under the same feed conditions showed that the minimum reflux ratio value of 8.0631 and feed point doesn't match the value calculated using the Underwood equation. This discrepancy is likely due to the limiting assumptions of constant relative volatility and due to the fact that equations involving theta (θ) can have multiple roots, which can lead to different values in the FUG method, as well as the fact that Aspen Plus uses the Winn equation instead of the Fenske equation to estimate the minimum number of theoretical stages. The actual number of stages (35) was calculated based on the efficiency value of 0.75 [64] and adjusted to obtain higher purity of ethylbenzene in the recycle stream.

The following equation, derived from the Souders and Brown equation (Lowenstein, 1961), can be used to estimate the maximum permissible superficial vapor velocity, as well as the column's area and diameter [64]:

$$u_v = (-0.171 * l_t^2 + 0.27 * l_t - 0.047) * (\frac{\rho_l - \rho_v}{\rho_v})^{1/2} \tag{44}$$

where u_v is maximum allowable vapor velocity, $l_t$plate spacing

The column diameter can be calculated [64]:

$$D_c = \sqrt{\frac{4 * V_w}{\pi * \rho_v * V_w}} \tag{45}$$

where V_w is the maximum vapor rate

Shell thickness was calculated using the following equation [64]:

$$t = \frac{P_i * D_i}{2 * S * E - 1.2 * P_i} \tag{46}$$

where S is the maximum allowable stress and Pi the internal pressure.

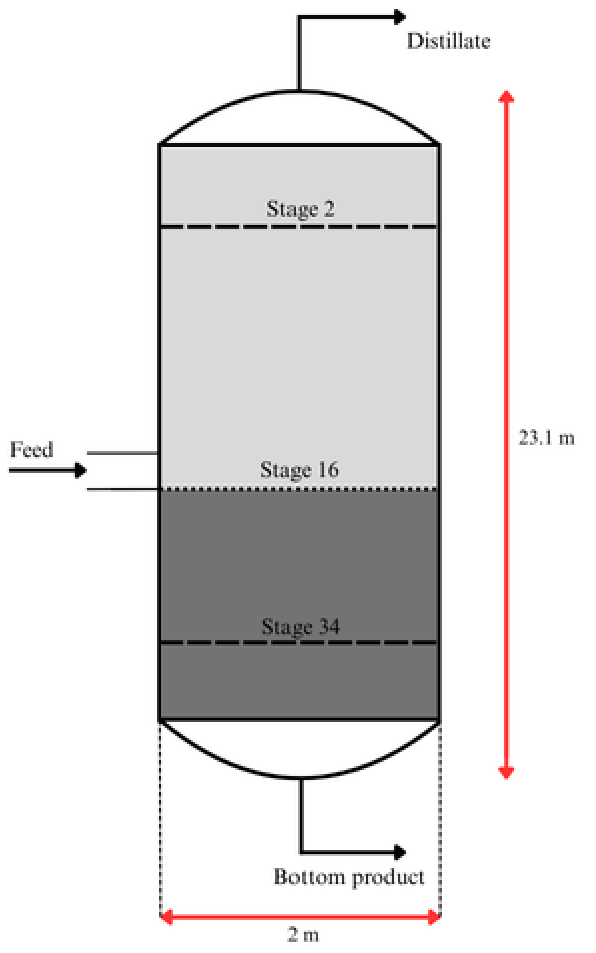
Table 23. Comparison between calculated values for number of stages and from Aspen Simulation

	Calculated	Aspen value
R_{min}	8.063	2.865
R	9.676	3.068
N_{min}	11.454	12.183
N	32	35
Feed point (above stage)	6	16.814
Column diameter	1.75	2

3.3.2.4. D-102 Distillation column unit specification.

Table 24. D-102 unit specification sheet.

Unit	D-102	Schematic diagram
Feed flow rate, kmol/hr	240	
Inlet temperature, °C	31.03	
Inlet pressure, bar	0.5	
Distillate flow rate, kmol/hr	20	

Bottoms flow rate, kmol/hr	220		
Reflux ratio	7		
Number of Stages	35		
Internal type	Tray		
Tray type	Sieve		
Diameter, m	2		
Height, m	23.1		
Column construction material	SS316		
Shell thickness (mm)	4.1		
Condenser conditions		Reboiler conditions	
Type	Total	Type	Kettle
Pressure, bar	0.4	Pressure, bar	0.5
Temperature, °C	22	Temperature, °C	112
Heat duty, kW	-1960.2	Heat duty, kW	2978.8

3.3.2.5. D-102 Aspen simulation

The D-102 distillation column was simulated using the RadFrac unit with a rate-based calculation type in Aspen Plus. The simulation results, including composition, molar flow rate, temperature, and pressure profiles, are presented in Appendix B.3. As shown in Figures B.3.6

and B.3.7 of Appendix B.3, the molar liquid and vapor fractions of benzene rapidly drops within the first few stages, however the molar fraction of toluene is increasing in these stages. The possible reason for this composition profile could be that benzene has a significantly lower boiling point than toluene, which causes benzene to volatilize more easily. As a result, the fraction of toluene increases at the top. Ethylbenzene's composition slightly decreases at the feed point due to feed stage disruption and relative volatility effects. When the feed enters, more volatile components like benzene and toluene tend to vaporize, while ethylbenzene, with its higher boiling point, may momentarily decrease in concentration.

Figure B.3.9 of Appendix B.3 illustrates the molar flow rate behavior along the column. The sharp increase in molar flow rate as the number of stages increases is due to the significantly smaller distillate flow rate compared to the bottom flow rate. Since most of the feed components, including ethylbenzene, are directed toward the bottom, the accumulation of liquid in the lower stages leads to a noticeable rise in molar flow. This imbalance between distillate and bottom flow causes a steeper increase in molar flow rate across the column stages.

As seen in Figure B.3.8 of Appendix B.3**,** the temperature rises sharply across the initial stages, primarily due to the vigorous vaporization of volatile components. This phase change requires latent heat, which is absorbed as the liquid converts into vapor, leading to the observed temperature increase.

Chapter 4 – Minor Equipment Design:

In addition to the major equipments discussed in detail, there are other several industrial units involved in the production of styrene. This chapter provides an overview of the key parameters for minor equipment such as furnaces, heat exchangers, pumps, and storage tanks.

4.1. Heating and Cooling units.

This process requires several heating and cooling units to ensure that the streams meet the necessary inlet temperature conditions. In designing this equipment, it is essential to determine the heat duty value, which can be calculated using the following formula:

$$Q = mc_p \mathit{\Delta} T \tag{47}$$

where Q is heat duty of equipment; m is mass flow rate of the stream; c_p is heat capacity of the component; ΔT is temperature change.

For units that involve a phase change, the heat duty value is calculated using the following formula:

$$Q = mc_p \mathit{\Delta} T + m\lambda \tag{48}$$

where λ is latent heat of vaporization / latent heat of condensation

The furnace is required to convert water into steam, superheat the steam up to required temperature, and also the furnace is used as a heater between two reactors. All heat duty values, along with the inlet and outlet conditions, are provided in Table 25.

Table 25. The design values of the heating and cooling units.

Unit	**F-101**	**F-102**	**F-103**
Inlet temperature, °C	25	346	548.3
Outlet temperature, °C	115	720	620
Heat duty, MW	77.5	28.2	9.3

To reduce the overall energy consumption of the process, a network of heat exchangers was strategically implemented. The design specifications, including inlet and outlet streams as well as corresponding heat duties, are summarized in Table 26 (heat exchangers without additional utility requirements) and Table 27 (heat exchangers requiring additional utility).

The integration of the heat exchanger network resulted in an energy savings of 53 MW, indicating a significant recovery of thermal energy within the process. However, despite this optimization, certain units - HX-105 and HX-106 - still required external cold utility (cooling water), amounting to 94.3 MW of unrecovered thermal energy.

Table 26. The design values of the heat exchangers without extra utility.

Unit	Utility type	Stream in	Tin	Stream out	Tout	Heat duty, MW	Unit type
HX-101	Hot utility	17	356	18	265	10.3	Minor
	Cold utility	3	57	4	157		
HX-102	Hot utility	15	591	16	487	13.2	Major
	Cold utility	4	157	5	474		

HX-103	Hot utility	16	486	17	355	15.76	Major
	Cold utility	9	115	10	345		
HX-104	Hot utility	18	264	19	133	13.75	Minor
	Cold utility	7	25	8	115		

Table 27. The design values of the heat exchangers with extra utility.

Unit	Utility type	Stream in	Tin	Stream out	Tout	Heat duty, MW	Unit type
HX-105	Hot utility	19	133	20	40	92.2	Minor
HX-106	Hot utility	15	591	16	487	2.1	Minor

4.2. Pressure changing units.

This production process also involves pressure-changing units. As most of the process fluids are in the liquid phase, pumps were used in Aspen Plus with an efficiency of 80%. Pumps 1 and 2 are used to increase the pressure of the inlet ethylbenzene and water streams, respectively. Pump 3 boosts the pressure of the distillate product from the first distillation column to the feed of the second distillation column. Pump 4 increases the pressure of the recycled ethylbenzene stream, while Pump 5 raises the pressure of the styrene product stream.

$$\boldsymbol{W = V\Delta T} \tag{49}$$

Table 28. The design values of pressure changing units.

	P-101	**P-102**	**P-103**	**P-104**	**P-105**	**V-101**
Inlet pressure, bar	1	1	0.1	0.5	0.5	1

Outlet pressure, bar	1.7	1.7	0.5	1.7	1	0.5
Heat duty, kW	2	3	0.4	1.2	0.8	0
Efficiency	0.8	0.8	0.8	0.8	0.8	

4.3. Three-phase Separator

Three phase separator is needed in order to achieve some amount of purification of the product stream before entering the distillation columns. The reactor effluent contains light gases (H_2, CH_4, C_2H_4) that do not condense under typical column operating conditions. If these gases enter the distillation columns, they can disrupt vapor-liquid equilibrium, increasing column pressure and reducing separation efficiency. TPS works based on the difference of compounds in density and phase behavior.

Table 29. Design Specifications of TPS

Compound	**Split fraction**
EB	0.00253
Styrene	0.00174
Hydrogen	1
Benzene	0.0175
Ethylene	1
Toluene	0.5
Methane	1
Water	0.00483

Table 30. Inlet and Outlet Flow Rates of TPS

	Inlet	**Outlet**	**Gas Outlet**	**Water Outlet**
Compound	**Flow Rates (kmol/h)**			
EB	215	209.7	0.5	4.89
Styrene	409	402	0.72	6.41
Hydrogen	374	0	374	0
Benzene	5.82	4.80	0.10	0.92
Ethylene	5.82	0	5.82	0
Toluene	20.25	10.12	10.12	0
Methane	20.03	0	20.03	0
Water	6985	1.46	33.74	6949.8
Overall	8034.73	627.76	760.79	6962.02

Table 31.Working conditions of TPS

Pressure (bar)	1.05
Temperature (°C)	40
Heat Duty (MW)	-7.93

4.4. Storage units

4.4.1 Styrene Storage Tank

The processing facility requires storage for purified styrene before it is transported or used in polymerization. Manufacturers determine storage tank dimensions by evaluating process requirements along with the needed storage volume using material weight and density information. A temperature of less than 40°C is maintained in storage tanks to avoid unwanted chemical reactions. The stabilizer 4-tert-butylcatechol (TBC) is added to storage solutions to prevent polymerization through a typical dose of 45–55 ppm for long-term preservation and 10–15 ppm for short-term or low-risk applications. TBC requires the precise delivery of oxygen to function as a radical scavenging agent preventing the unwanted polymerization of polystyrene. Air should be periodically added to the storage vessels; however, the level of oxygen should be less than 8 vol % to eliminate the possibility of fire [6]

Our production operates for 8,000 hours per year, which averages to approximately 21.92 hours per day. Given that our product has a mass flow rate of 40,388 kg/hr and the density of the product, as retrieved from Aspen, is 906 kg/m^3, the corresponding volumetric flow rate is:

$$q_{prod} = \frac{m}{\rho_f} = \frac{40388.13}{906.26} = 44.566 \text{ m}^3\text{/hr} \tag{50}$$

$$44.566\ m^3/hr * 21.92\ hr/day = 976.8 \text{ m}^3\text{/day} \tag{51}$$

Since our product is mainly sold to Tajikistan, Uzbekistan and Kyrgyzstan, it is essential to store styrene at our plant for an estimated duration of roughly 12 days to meet the demand and ensure a smooth supply chain.

$$976.8 \text{ m}^3\text{/day} * 12 \text{ days} = 11722 \text{ m}^3 \tag{52}$$

The styrene product storage tank is designed with a capacity of 3000 m^3, ensuring sufficient storage for stable plant operation and transportation logistics. The selected volume is based on industry practices for styrene storage, as referenced in [70]. We would need approximately 4 storage tanks of this volume.

In addition to styrene storage, the processing facility also requires dedicated storage tanks for raw materials and byproducts such as ethylbenzene and the combined stream of toluene and benzene. Proper storage ensures continuous operation during logistical delays, supports safety and handling protocols, and aligns with industry practices.

4.4.2 Ethylbenzene Storage (1 stream)

Ethylbenzene, as the main feedstock in styrene production, must be stored on-site to account for transportation time and potential supply interruptions. In our case, ethylbenzene is imported from China, which introduces a longer supply chain duration. Based on typical plant operations, we assume a storage period of 15 days to ensure uninterrupted production.

Given the ethylbenzene mass flow rate of 45,651.98 kg/hr and its density of 867 kg/m³ (as retrieved from Aspen), the volumetric flow rate is calculated as:

$$q_{EB} = \frac{45651.98\ kg/hr}{867\ kg/m^3} = 52.66\ m^3/hr \tag{53}$$

The daily volume output, based on 21.92 hours of operation per day, is:

$$52.66\ m^3/hr \times 21.92\ hr/day = 1154.5\ m^3/day \tag{54}$$

To cover 15 days of operation:

$$1154.5\ m^3/day \times 15\ day = 17317.5\ \ m^3 \tag{55}$$

Therefore, the facility requires approximately 17,318 m³ of ethylbenzene storage, so a tank of 18,000 m³ will be designed.

4.4.3 Toluene and Benzene Storage (23 stream)

Bottom product of the three-phase separator generated during ethylbenzene and styrene processing contains EB, styrene, benzene, toluene and water. These aromatic compounds are flammable and volatile, necessitating safe and controlled storage under nitrogen blanketing or floating roof tanks.

The combined mass flow rate for given stream is $1724.3\ kg/hr$. And densities of all compounds are following:

EB density = 867 kg/m³

Styrene density = 906.26 kg/m³

Benzene density = 876 kg/m³

Toluene density = 867 kg/m³

Water density = 998 kg/m³

Average density of toluene and benzene mixture:

$$\rho_{avg} = \frac{\dot{m}_1 + \dot{m}_2 + \dot{m}_3 + \dot{m}_4 + \dot{m}_5}{\frac{\dot{m}_1}{\rho_1} + \frac{\dot{m}_2}{\rho_2} + \frac{\dot{m}_3}{\rho_3} + \frac{\dot{m}_4}{\rho_4} + \frac{\dot{m}_5}{\rho_5}} \tag{56}$$

$$= \frac{1724.3}{\frac{423.58}{867} + \frac{2.198}{906.26} + \frac{371.27}{876} + \frac{900.996}{867} + \frac{26.26}{998}} = 870.713\ kg/m^3$$

Where, $\dot{\mathrm{m}}_1, \dot{\mathrm{m}}_2, \dot{\mathrm{m}}_3, \dot{\mathrm{m}}_4$= mass flow rates (kg/hr), $\rho_1, \rho_2, \rho_3, \rho_4$ = densities (kg/m^3)

Using an average density of 870 kg/m^3 for the mixture:

$$q_{T+B} = \frac{1724.3\ kg/hr}{870.7\ kg/m^3} = 1.98\ m^3/hr \tag{57}$$

Operating at 21.92 hours/day:

$$1.98\ m^3/hr \times 21.92\ hr/days = 43.4\ m^3/day \tag{58}$$

To provide storage for 10 days of operation a single 450 m^3 tank is needed.

4.4.4 Wastewater stream storage tank

The wastewater stream, consisting of water with ethylbenzene, styrene, benzene, is generated at a rate of 126462 kg/hr. Assuming all given compound density as previously average density of stream was calculated.

$$\rho_{avg} = \frac{126462}{\frac{522.83}{867} + \frac{665.45}{906.26} + \frac{70.88}{876} + \frac{125203}{998}} = 996.77\ kg/m^3 \tag{59}$$

Using an average density of 870 kg/m^3 for the mixture volumetric flow rate was calculated:

$$q_{ww} = \frac{126462\ kg/hr}{996.77\ kg/m^3} = 126.87\ m^3/hr \tag{60}$$

Given an operational time of 21.92 hours per day, the facility produces approximately 2780.99 m^3/day of wastewater. To account for potential delays in treatment or disposal, a storage capacity of 3 days is a can be managed using one storage tank of 8500 m^3

4.4.5 Water Storage Tank Design

To ensure a continuous and uninterrupted operation of the styrene production plant, adequate storage capacity for technical water is essential. One of the primary feedstocks, delivered to the site in bulk quantities, has a volumetric flow rate of $126.089\ m^3/hr$. Based on an operational schedule of 8,000 hours per year, this translates to an average of 21.92 hours per day.

The daily volume consumed by the process is:

$$126.089\ m^3/hr \times 21.92\ hr/days = 2763.87\ m^3/day \tag{61}$$

Assuming a storage period of 4 days, the total required storage capacity becomes:

$$2772.05\ m^3/day \times 3\ days = 8291.61\ m^3 \tag{62}$$

To satisfy this requirement, the plant would need approximately **a storage tank** of 8500 m^3 each. This volume provides a safety buffer for raw material supply, accommodating delivery intervals and minimizing production downtime.

Chapter 5 – Plant Location and Layout

5.1 Plant Location and Site Selection

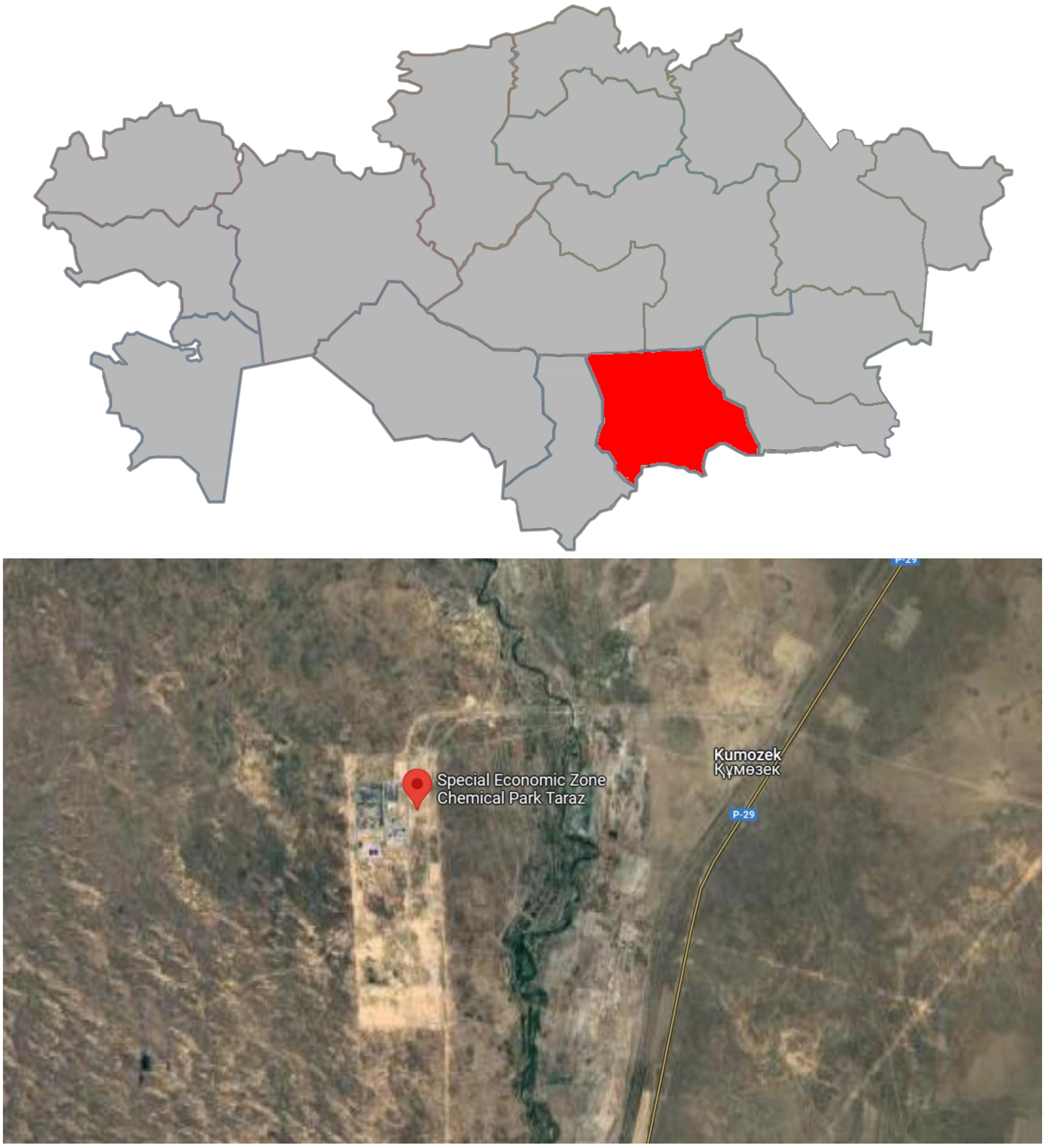


Figure 8. a) Zhambyl region on map and b) plant location on map

The Special Economic Zone (SEZ) "Jibek Joly", formerly known as "Taraz Chemical Park", located at Zhambyl Region, was strategically chosen as the location for the styrene manufacturing plant due to its unique combination of logistical advantages, infrastructure readiness, and financial incentives. Primarily , the selection of the plant location for styrene production was based on several critical factors that affect both the operational efficiency and overall operational costs of the project. There were factors that were taken into consideration such as proximity to raw materials and transportation, availability and cost of utilities, tax incentives, environmental considerations and market proximity. A detailed analysis of each factor is as follows:

5.1.1 Proximity to Raw Materials and Transportation

One of the most critical aspects in site selection was the proximity to suppliers of raw materials. The primary raw material for styrene production is ethylbenzene (EB), which will be imported from suppliers in China due to favorable pricing and well-established supply chains (this supplier selection is discussed further in Chapter 7). The plant's location in the Zhambyl Region ensures efficient transport of raw materials and products, supported by access to Kazakhstan's national railway system and an extensive highway network. The region is well connected to Almaty, Karaganda, and South Kazakhstan through the "Almaty–Tashkent–Termez" and "Merke–Shu–Burybaytal" highways (two of the most frequently used transportation corridors in the area) [71]. Additionally, access to reliable international trade networks through the Khorgos dry port and Kazakhstan's rail system enhances the efficiency of material procurement and distribution [72].

5.1.2 Infrastructure and Utilities

The location of the plant within the Special Economic Zone is a strategic decision due to the significant infrastructure advantages it offers. The SEZ provides ready-to-use utilities such as water, electricity, gas, and waste management systems, which significantly reduce the capital investment required for plant construction. The plant site is equipped with access to high-capacity electrical grids, water supply networks, and waste treatment facilities, all of which are essential for the smooth functioning of a chemical production facility. The region provides stable and cost-effective supply of essential utilities, with the following current tariffs: technical water supply at 114 tenge per cubic meter, drinking water at 171 tenge per cubic meter, and water disposal services at 212.8 tenge per cubic meter. Electricity transmission and distribution services are priced at 27 tenge per kilowatt-hour, while gas supply is available at 26.3 tenge per cubic meter [73]. Moreover, the region's proximity to the national power grid ensures uninterrupted energy supply for the plant's operations.

5.1.3 Tax Incentives and Financial Support

The plant will benefit from a comprehensive package of financial incentives available in SEZ, which are designed to attract industrial investment. These incentives include full exemptions from corporate income tax (CIT), land tax, and property tax. In addition, companies operating within the SEZ are exempt from value added tax (VAT) when selling goods that are fully consumed in the production process within the SEZ. Imported raw materials and production equipment also benefit from exemptions on customs duties. Investors are further supported by the provision of a free plot of land and the application of a special customs and tax regime. Collectively, these financial advantages significantly reduce both capital and operational expenditures, thereby enhancing the overall economic feasibility and long-term profitability of the project [74].

5.1.4 Environmental Considerations

The climatic conditions in Taraz are highly favorable for the establishment and operation of a styrene production plant. The region maintains an average relative humidity of approximately 52% [75], which is moderate and does not pose significant risks for corrosion of processing equipment. Additionally, the area receives relatively low annual precipitation, averaging around 350 millimeters [76]. This minimizes the risk of flooding and weather-related disruptions, contributing to infrastructure stability and construction efficiency. Overall, the stable, dry climate of Taraz supports safe, reliable, and cost-effective plant operations, making it an advantageous location from an environmental and operational standpoint.

5.1.5 Market proximity

The plant location in the southern part of Kazakhstan, near Shymkent and Taraz, is strategically advantageous for serving both domestic consumers and nearby export markets. For example, Tajikistan has emerged as the fastest-growing market for styrene polymer exports from Kazakhstan between 2022 and 2023, with export values reaching $55.6 thousand. Similarly, Kyrgyzstan and Uzbekistan represent important regional markets, with exports valued at $49.4 thousand and $8.48 thousand, respectively, over the same period. This proximity enhances the competitiveness of Kazakhstan’s styrene products in Central Asia and supports broader market expansion goals by reducing delivery times and transportation costs to neighboring countries [77].

5.2 Plant Layout Design

The styrene production plant layout was developed to ensure safe operation, efficient process flow, and easy maintenance. The site is divided into three main areas: the production and utility zone, the storage and control area, and the administrative and support zone. Each section was planned according to the process steps and safety requirements. The overall layout is shown in Figure 9.

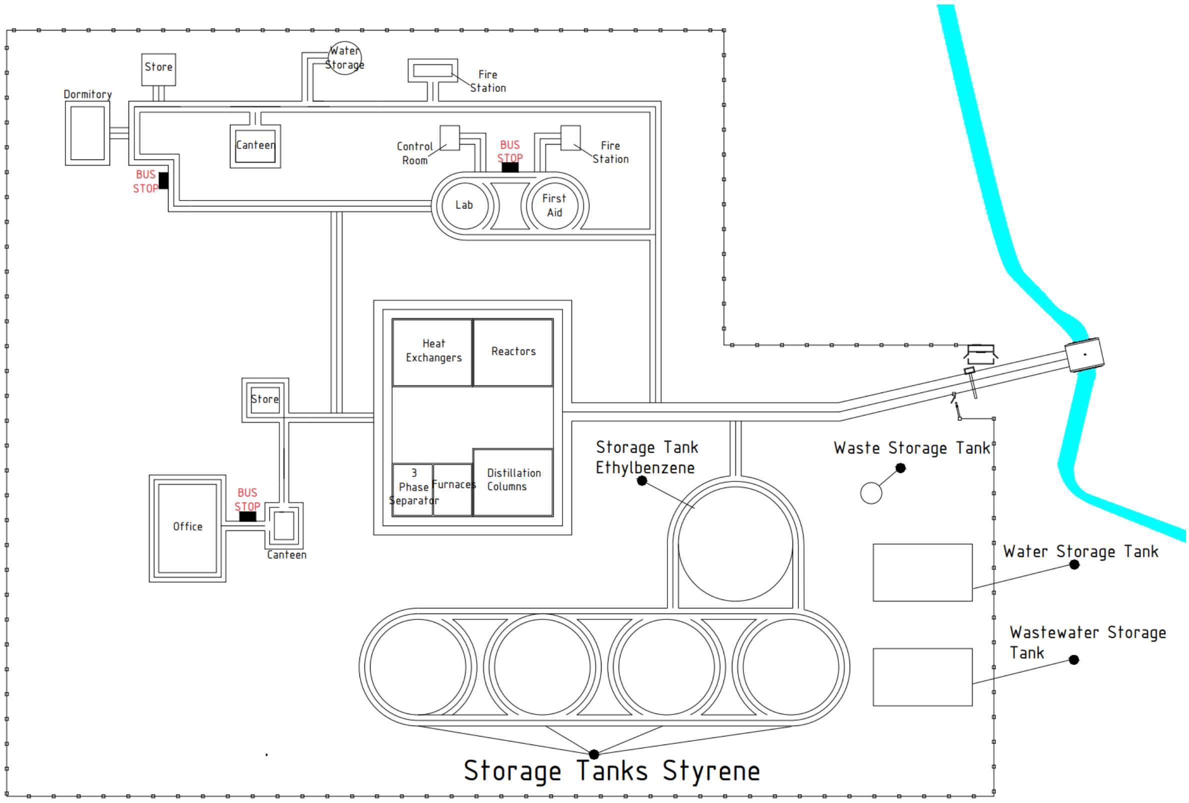


Figure 9. Styrene Plant Layout

5.2.1. Production and Utility Zone

The main production units are situated at the center of the plant, acting as the operational center for the whole facility. This area includes two fixed-bed reactors for ethylbenzene dehydrogenation, supported by two distillation columns and two heat exchangers as major units, forming the primary flow path of the styrene production process. Surrounding the central reaction area are minor units such as furnaces, a three-phase separator, and other heat integration systems essential for process control.

Utility systems such as steam generation, cooling water, and power distribution are located nearby to support the process without delays or pressure drops. On both sides of the plant, fire stations are installed to provide full coverage of the facility, complying with industrial safety protocols and enabling rapid emergency response. The equipment layout also allows enough space for maintenance access, safe distances between hazardous units, and vehicle movement when needed.

5.2.2 Storage, Monitoring, and Waste Management

The storage area is located near but separate from the process units with careful attention to safety and environmental considerations. It includes tanks for raw materials like ethylbenzene, final product storage for styrene, and waste tanks for two different streams that come from the process including a wastewater storage tank. There is also a water storage tank that holds water taken from the Koragaty River. This water is primarily used for steam generation, which is essential for heating and energy input in the dehydrogenation process.

Each tank is placed with fire safety and spill prevention in mind - for example, styrene tanks are kept under inert gas to avoid polymerization, and ethylbenzene is stored away from hot areas due to its flammability. Waste tanks are isolated to prevent contamination of other streams.

Close to the production area the control room and laboratory are located. The control room oversees the whole plant through automated systems, alarms, and sensors, while the lab handles quality checks and testing of materials throughout the process. A first aid station is placed nearby to respond quickly in case of incidents in this zone.

5.2.3. Administrative and Support Zone

All non-process and personnel-related facilities are grouped together and placed at a safe distance from the main process area. This zone includes an administrative building with offices, where engineers and managers work, as well as a dormitory, designed to accommodate operational and technical staff, and equipped with basic facilities including a gym to support worker wellbeing.

Next to the dorm and office buildings, there are canteens and stores so that workers have access to meals and basic supplies without needing to leave the plant site. In addition, bus stops are placed near these facilities with plant shuttles (buses) operate within the site to support organized transportation, helping staff move safely and efficiently between different areas of the facility.

The plant has its own road system that makes it easy to move materials, workers, and emergency vehicles around the site. Heavy trucks use separate routes from people walking to keep things safe. There’s also extra space planned in case the plant needs to expand in the future.

Chapter 6 – Environment and Waste Streams

There are 3 main waste streams in the entire process system - outlet vapor and liquid waste streams of Three-Phase Separator and top product of the 2nd Distillation Column. Composition (Mass flow rates) of these streams is presented in the table below:

Table 32. Main waste streams flow rates and vapor/liquid fractions.

Compound	Mass flow Rates (kg/hr)		
	3-phase separator vapor stream	2nd distillation column top product	3-phase separator liquid waste stream
Ethylbenzene	58	404	518
Styrene	74	2.25	666
Hydrogen	748	0.00	0.00
Benzene	8	375	72
Ethylene	163	0.00	0.00
Methane	320	0.00	0.00
Toluene	932	912	0.00
Water	607	26	125096
Total	2910	1718	126353

6.1. Vapor stream of Three-phase separator

Half of this waste stream consists of high-energy-value aromatic hydrocarbons toluene, ethylbenzene, and benzene, styrene with minor amounts of water. While these compounds are commercially valuable as solvents and chemical feedstocks, their recovery may be economically or technically infeasible due to stream purity and integration into existing processes.

For reuse of the materials from this waste stream a significant amount of additional investments are required. Stream comes out at forty degrees in the form of gas and consists of materials with various boiling points which require another separation process, decanting and distillation. Liquid organics (EB, styrene, benzene and toluene) need another distillation column in order to separate them and make it possible to reuse them in the primary production process. Additionally, all light organic materials (hydrogen, methane and ethylene) have almost the same autoignition point (around 480 °C) [78] and very low boiling points which make it technologically difficult and economically unviable to separate them.

Stream contains a significant amount of water and this compound is the most easily separated of all the mixtures and can potentially be used in cooling processes (heat exchangers) and as an additive to the main water flow in the manufacturing process. But it must be taken into account that this water, even after the separation process by distillation (which involves additional costs), will be to some extent contaminated with other substances of the waste stream. This will create the need for additional wastewater treatment (biological, adsorption, or stripping). The 20 percent water content in the stream makes its separation and purification unprofitable in the context of the overall production process.

Incinerating this stream is more effective than using it directly as a fuel because it contains significant amounts of light gases like hydrogen, methane, and ethylene, which are highly flammable and pose safety and handling challenges in conventional fuel systems. Incineration in a controlled environment ensures complete combustion, better emissions control, and safer energy recovery without the need for extensive gas conditioning or specialized burners. Properly designed thermal oxidizers can ensure complete combustion while minimizing harmful emissions, making incineration a safe and efficient solution. Due to the production of huge amounts of gas and the explosions that will occur as a result of burning flammable gases (hydrogen, methane and ethylene), it is necessary to carry out this process in a ventilated environment. Cost of the proper thermal oxidizer with appropriate capacity will cost 100,000$ with installation. Operational costs including electricity, repairment needs and consumables will be around 207,000$ annually [79, 80].

6.2 Top product of the 2nd Distillation Column

The second waste stream can be used as fuel for the main production processes, since this stream does not contain flammable light organic gases and hydrogen. Recovery of the materials from this stream is also not profitable from an economic point of view, taking into account all the same economic investments in distillation columns. All organics in this stream have significant fuel potential given the Gross Heat Value of the total stream around 41795 kj/kg (calculated in AspenPlus). The amount of water in the stream is insignificant and this stream can be directly burned to supply energy to the main production process. And given the large amount of combustion energy, the waste stream can be divided into several parts to supply energy to individual units in the system.

In order to use this stream as a fuel, it is necessary to construct a suitable fuel storage system, which must be monitored and the appropriate safety precautions taken into account. Combustion will be carried out using an electric fuel burner nozzle. Complete combustion of all organic matter in the stream will be envisaged, but some amount of incomplete combustion products such as carbon monoxide, ethane, unburned toluene and benzene will still be present. For such cases the system should have adequate emission controls (scrubbers and afterburners).

Cost of such a waste treatment method will include expenses on an industrial liquid waste burner (electric flame burner), waste storage tank, flame and gas sensors and heat transfer piping system. Products of incomplete combustion may require a thermal oxidizer system for complete incineration, this stream may be transferred to thermal oxidizer that were installed for the 1st waste stream (Vapor stream of Three-Phase Separator). Considering the small volume of waste, it can be concluded that adding these products of incomplete combustion to the thermal oxidizer will not affect its productivity. Table of cost expenses for fuel usage of this stream presented below:

Table 33. Cost of Top product of the 2nd Distillation Column waste stream treatment system.

Expenses		Cost per piece, USD	Pieces needed	Total cost, USD
Equipment	Waste Storage Tank [81]	50 000	1	50 000
	Liquid Fuel Burner [82]	5 000	3-5	15 000-25 000
	Flame & Gas regulatory system [83]	200	8-10	1 600-2 000
	Combustion chamber [84]	11 000	2-3	22 000-33 000
Installation costs, USD		100 000-150 000		
Total equipment cost, USD		186 600-260 000		
Operational costs, USD		70 000-80 000 (annually) [85]		

6.3 Three-phase Separator (Wastewater)

This stream will consist mainly of water, which can be purified for further reuse in the production process. The stream is water containing some amount of light organic substances (0.5% styrene, 0.4% ethylbenzene, 0.05% benzene) and it can be considered as a wastewater stream that will be subjected to proper purification. The most effective and cost-effective method of purification is the reverse osmosis (RO) membrane system. RO can effectively separate and concentrate the small fraction of organic contaminants - such as ethylbenzene, styrene, and benzene - allowing for the recovery of clean water suitable for reuse or discharge. This reduces freshwater consumption, minimizes environmental impact, and lowers overall treatment costs [86].

The costs of this type of water purification technology include the reverse osmosis unit itself, which can be ordered as a complete set from various suppliers, the installation price and operating costs including electricity, replacement of RO membranes, labor and repairs. Cost of installation, equipment and operational expenses for such water treatment system presented below:

Table 34. Cost of RO water treatment system

Equipment cost, USD [87]	90 000
Installation cost, USD [88]	80 000
Operational cost (Annual), USD [89]	793 000

However, pretreatment (filtration or adsorption) may be required to protect the membranes from fouling due to the presence of aromatic compounds. The waste coming out of the treatment consisting of ethylbenzene, benzene and styrene will be subjected to further combustion through a thermal oxidizer used in the incineration of the 1st waste stream (Vapor stream of Three-Phase Separator).

6.4 Greenhouse gases emissions

During the combustion of waste from waste streams 1 (Vapor stream of Three-phase separator), 2 (Top product of the 2nd Distillation Column) and 3 (Three-phase Separator (Wastewater)), significant amounts of CO2 will be released. The amounts of CO2 produced per year by the combustion of these streams were calculated taking into account the complete conversion of aromatics (Ethylbenzene, Styrene, Toluene, Benzene) and light organics (ethylene, methane) into CO2 and water using Python.

Table 35. CO2 emissions produced by combustion of waste streams

Waste Stream	Amount of organics	CO2 emissions, tons/year

	combusted, kg/hr	
Vapor stream of Three-phase separator	1 538	43 117
Top product of the 2nd Distillation Column	1 698	49 754
Three-phase Separator (Wastewater)	1 352	36 993
Overall	4 588	129 864

Using the AspenPlus simulation program, namely the Energy Analysis function (Total Greenhouse gases), the total rate of greenhouse gases production by the designed facility was calculated as 33400 kg/hr which results in 267,200 tons of GHGs per year.

According to the UNFCC [90], the chemical industrial sector in Kazakhstan is responsible for 20,000 kilotons of CO2 pollution per year. In recent years, this figure has grown by 19% (from 2019 to 2024), which also applies to oil production, oil refining, mining and other industries. In accordance with subparagraph (7) of Article 16 of the Environmental Code of the Republic of Kazakhstan [91], chemical industrial facilities have the right to emit from 10,000 tons to 700,000 tons of GHG emissions per year depending on the volume of production of the enterprise. The legislation includes restrictions on GHG emissions for all large and significant chemical enterprises in Kazakhstan. In accordance with the laws on environmental protection of the Republic of Kazakhstan, the designed plant will be included in the list of industrial facilities that will allocate annual quotas for the amount of greenhouse gas emissions. For approximate calculations of the quota size, a KazAzot Mineral Fertilizer Plant was selected as a reference since they have a close rate of annual production - 300,000 tons of nitrate produced every year [92]. The company has a quota of 378,000 tons of greenhouse gases emissions per year. In the designed plant the production rate is 320,000 tons of Styrene per year. By analogy with the KazAzot plant, the facility can count on a state quota of 403200 tons of greenhouse gases per year. It is worth considering that each extra ton of GHG emissions will cost the enterprise 16 MCI ($107). According to the calculations of all greenhouse gas emissions during the styrene production process in the designed plant of approximately 397,064 tons per year, it can be concluded that the requirements of the legislation on greenhouse gas emissions for chemical enterprises of the Republic of Kazakhstan are met. There is also a gap of 6,136 tons of GHG emissions per year, which provides room for maneuver in case of unexpected increases in the amount of reproducible CO2 and other greenhouse gases.

6.5 Emission control systems

In chemical plants that handle aromatic-rich liquid waste streams - such as those containing ethylbenzene, benzene, toluene, and styrene - emission control systems play a critical role in ensuring environmental safety, regulatory compliance, and process reliability. These compounds are not only flammable but also toxic and, in the case of benzene, carcinogenic. Therefore, managing their release during combustion or incineration is essential to protect human health and reduce environmental harm.

One of the central objectives of emission control is to limit the release of hazardous air pollutants (HAPs) and greenhouse gases. This includes volatile organic compounds (VOCs), carbon monoxide (CO), particulate matter (PM), and especially carbon dioxide (CO_2), which is a major greenhouse gas. To monitor and optimize combustion efficiency, integrated sensor systems are used to track CO_2 and CO concentrations in flue gases. These sensors provide real-time feedback, ensuring complete combustion and helping to minimize emissions. Typical costs for high-accuracy CO_2 sensors cost 345$ for each piece [93], while CO sensors used to detect incomplete combustion typically cost $20 for each piece [94]. 7-10 CO2 sensors would be enough for sufficient level of monitoring on the plant side (sensors should be installed for each combustion, incineration, waste stream storage units and for processing units [95]. Typically, one CO sensor can effectively monitor an area of approximately **7,500 square feet (696 m).** However, CO sensors also should be placed near incineration, combustion and heating units in order to monitor the level of incomplete combustion products, therefore 5-7 units of CO sensors are needed [96]. Based on these preliminary calculations, costs of CO2, CO and oxygen control systems are calculated as 2 515$ - 4 590$.

For effective monitoring, CO_2 sensors should be placed within the breathing zone, excluding human breathing factors approximately 4 to 6 feet above the floor.

In addition to gas monitoring, the designed plant may employ more advanced emission control units such as thermal oxidizers, wet scrubbers, baghouse filters, or selective catalytic reduction (SCR) systems. These systems are tailored to the specific waste stream and emission profile of the plant. For instance, a wet scrubber may be used to neutralize acid gases and capture soluble VOCs, while baghouses are employed to remove fine particulate emissions. To invest and install such technologies, it is necessary to conduct test runs of the entire production to measure the level of pollutants emitted.

Chapter 7 –Total Investment and Profitability

This section presents an economic evaluation of the plant’s profitability, covering key calculations such as total fixed capital investment, fixed and variable costs, net present value (NPV), internal rate of return (IRR), and the payback period. The calculations were carried out both manually and with the aid of the Aspen Process Economic Analyzer (APEA).

7.1. Price of Raw Materials and Final Product

Table 36 represents the export prices of ethylbenzene in different countries. It is important to note that the price of ethylbenzene is not stable and fluctuates all the time. For example, in China, April 2019 the price was $1180, whereas in 2018 it retailed for $1280 [97].

Table 36. Export price of ethylbenzene for 2023 [98]

Country	Price, USD/kg
Czech Republic	1.066
Germany	1.063
France	1.087
Netherlands	1.018
China [99]	1.1
Canada	1.013
Japan	2.45

From the global market, China was selected as the main source of raw material, as it has the most options available for purchasing. Furthermore, it is more convenient and affordable to transport the materials from China due to the geographical location, compared to the other European countries presented in Table 35. According to the supplier (Career Henan Chemical Co), 1 metric ton of ethylbenzene (purity 99.5%) costs $1000 [100].

The catalyst is purchased and transported from China as well, due to high market supply and ease of shipping. The price is 186 USD/ton, so the initial catalyst supply would cost around 16,000 USD [101].

As of September 2024, styrene prices in China were falling due to oversupply, with prices averaging around $1,200 per ton [102]. Table 37 below summarizes the average styrene prices across key regions.

Table 37. Average Styrene Prices by Region (Q2 2024) [103]

Region	Price, USD/ton	Change (%)	Key Factors
North America	1 150	-11% (U.S.), -14.3%	Supply surpluses, reduced demand from packaging and automotive sectors
Asia-Pacific	1 450	+5.4%	Rising raw material prices, supply chain disruptions
Europe	1 320	Steady	Stable demand, high environmental regulations
China	1 200	-4%	Market oversupply, declining demand in key industrial sectors
Average	1 280		

The price of styrene is also expected to rise during the period. Based on the average price from Table 38, the prognosed prices until 2028 were calculated using the expected compound annual growth rate of 6.6% [104]. The forecast is shown in Table 37 and the calculations are made using Equation C1 in Appendix C. Using the gathered information, the preliminary product price for styrene will be 1380 USD per ton.

Table 38. Price of styrene from 2024 to 2028.

Year	2025	2026	2027	2028
Styrene price, USD/ton	1 380	1 475	1 573	1 675

7.2. Cost of Equipment and Storage Tanks

The cost for the equipment was approximated using APEA, except for the reactor costs. The reactor cost could not be estimated using the APEA function due to missing equipment specification data. Therefore, the cost was calculated manually using following correlation [105]:

$$C_e = 110000 * (\frac{V_r}{20})^{0.52} \tag{63}$$

$$C_{installation\ factor} = C_e * 2.3 + 63000 \tag{64}$$

$$C_{total\ cost} = C_{reactor} + C_{catalyst} \tag{65}$$

The summarized costs are presented in Table 39.

Table 39. Cost of Equipment.

Equipment type	Notation	Equipment Cost, USD	Installed Cost, USD	Location factor, USD
Heat exchangers	HX-101	27 800	1 020 200	1 560 906
	HX-102	3 737 900	5 755 100	8 805 303
	HX-103	1 043 800	3 354 800	5 132 844
	HX-104	44 600	376 300	575 739
	HX-105	599 100	1 744 200	2 668 626
	HX-106	28 100	136 300	208 539
Heaters	F-101	5 280 400	5 660 900	8 661 177
	F-102	4 230 400	4 436 100	6 787 233
	F-103	1 784 000	1 892 100	2 894 913
Pumps	P-101	9 800	75 500	115 515
	P-102	12 000	90 000	137 700
	P-103	7 000	59 900	91 647
	P-104	7 100	60 700	92 871
	P-105	8 100	62 200	95 166

Reactors	R-101	252 611	620 048	948 673
	R-102	198 295	500 359	765 549
Three-phase separator	S-101	39 500	209 900	321 147
Distillation columns	D-101	10 179 800	15 487 100	23 695 263
	D-102	480 100	1 152 100	1 762 713
Total	65 321 525			

The cost of the storage units was estimated via the weight of the tank and unit price for material per kg. The unit price for SS316 was taken as 2.68 USD/kg and for fiberglass as 50 USD/m^3 [106]. The total cost required for storage tanks was found to be 3 300 000 USD. The results for cost estimations are presented in Table 40.

Table 40. Cost of Storage Tanks.

ID	Volume, m^3	Weight, kg	Cost, USD
TK-101, EB	18 000	400 900	1 074 400
TK-102, raw water	9 000	-	450 000
TK-103-106, styrene	3 000	118 200	316 700
TK-107, toluene/benzene	450	21 120	56 700
TK-108	8 500	-	425 000

7.3 Total Fixed Capital Investment Estimation

To estimate the total capital investment, it is necessary to assess several components, including Inside Battery Limits (ISBL), Outside Battery Limits (OSBL), engineering expenses, and contingency charges. The ISBL encompasses all expenditures associated with acquiring and installing the process equipment required for the new facility. This includes both direct and indirect field costs, such as major equipment, civil construction, labor, supervision, construction services, and on-site expenses.

The ISBL value can be estimated using the economies of scale, which establishes a correlation between plant costs and capacity of production based on existing process licensors [64]:

$$\frac{C_2}{S_2} = a \cdot {S_2}^{n-1} \tag{64}$$

where C is ISBL value, S_2 is annual production rate, *a* and *n* are process cost correlations.

Given that the plant's annual production capacity is 320,000 tonnes, it falls within the typical capacity range for styrene production licensed by ABB Lummus/UOP, which spans from 300,000 to 700,000 tonnes per year. For cost estimation purposes, the parameters *a* and *n* are taken as 0.0355 and 0.6, respectively. The calculated value is based on data from January 2006 and has been updated to 2024 values using the Chemical Engineering Plant Cost Index (CE Index). Taking into account the CE Index, which was 478.6 in 2006 and 798 in 2024, the ISBL value has been estimated at USD 118.9 million [107].

The OSBL cost accounts for the expenses associated with site infrastructure to support the construction of a plant. These offsite costs are typically estimated at 40% of the ISBL value. In this case, the OSBL cost was estimated to be USD 47.6 million.

Engineering Costs (EC) represent the expenses associated with detailed design work and other engineering services necessary for project execution. A common rule of thumb for large-scale projects estimates EC as 10% of the combined ISBL and OSBL costs. Based on this approach, the Engineering Costs were determined to be approximately USD 11.9 million.

Contingency Charges are additional funds included in the project budget to account for potential uncertainties or deviations from the initial cost estimate, such as fluctuations in prices, changes in project scope, or currency variations. It is recommended that contingencies be estimated as 10% of the combined ISBL and OSBL costs. Based on this guideline, the Contingency Charges were calculated to be approximately USD 11.9 million. The table below summarizes the results of the Total Fixed Capital Investment estimation.

Table 41. Total Fixed Capital Investment estimation.

Component of Capital Cost	Capital Cost Value, USD
ISBL	118 950 000
OSBL	47 578 000

Engineering Costs	11 895 000
Contingency Charges	11 895 000
Total Cost	190 313 000

7.4. Fixed and Variable Operating Costs

7.4.1 Operating Labor Cost Estimation

An important consideration for estimation of fixed cost of production is the cost of operating labor, which is estimated using a correlation equation developed by Alkhayat and Gerrard [108]:

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \tag{65}$$

where NOL is number of operators per shift, P is number of processing steps with the handling of particulate solids, NNP is number of nonparticulate processing steps

As the styrene production process does not involve solid handling, the value of P is assumed to be 0. The number of equipment units required for process steps involving non-particulate matter is summarized in the table below:

Table 42. Equipment in the styrene production plant.

Equipment Type	Number of equipment	NNP
Reactor	2	2
Distillation Column	2	2
Three-phase separator	1	1
Heaters	3	3
Heat Exchangers	6	6
Pumps & Valves	6	-

Mixers	2	2
Total	22	16

Based on the formula above, it is estimated that approximately three operators are required to operate the process unit per shift. For a plant operating continuously throughout the year (365 days), a total of 1 153 shifts are needed annually. Each operator works 46 weeks per year, with a standard schedule of five 8-hour shifts per week, resulting in 230 shifts annually per operator. The average monthly salary for an operator is 400 000 KZT, equivalent to approximately USD 9 412 per year. The total operating labor cost is calculated using the following equation:

$$Operating\ labor\ = N_{OL} * N_{np} \tag{66}$$

The calculated number of operating labor is 15.82, which is rounded to the nearest whole number, resulting in 16 operators. The total operating labor cost is determined using the following formula:

$$C_{OL} = Operating\ Labor \cdot Average\ Salary \tag{67}$$

In addition to the operators, the plant staffing requirements also include supervisory and general labor personnel. An additional 5 supervisors and 200 general workers were accounted for the assessment. The calculations indicate that the annual operating labor cost is approximately 2 080 000 USD.

7.4.2. Estimation of the Fixed Costs of Production

The total fixed cost of production includes operating labor expenses along with other components such as supervision, direct salary overhead, maintenance, insurance, plant overhead, and environmental charges. These costs are calculated based on the operating labor cost and the Inside Battery Limits value.

Supervision costs are estimated at 25% of the operating labor cost, while direct salary overhead is calculated as 50% of the combined cost of operating labor and supervision. Maintenance expenses amount to USD 5 950 000, representing 5% of the ISBL. Insurance is estimated at 1% of the ISBL, and general plant overhead for research and development, information technology and human resources is calculated as 65% of the sum of labor, supervision, and maintenance costs. Table 43 presents a summary of fixed production costs, with detailed calculations available in the Excel file in ESI.

Table 43.Production fixed costs estimates.

Fixed cost component	Value, USD/year
Cost of operating labor	2 080 000
Supervision	520 000
Direct salary overhead	1 300 000
Maintenance	5 947 900
Insurance	1 189 500
General plant overhead	2 535 000
Total	13 570 000

7.5. Variable Cost of Production

7.5.1. Cost of Raw Materials

The production of styrene via ethylbenzene dehydrogenation requires ethylbenzene and water as steam. The costs of raw materials are taken into account for the calculation of the production plant's profit. As outlined in Chapter 7.1, the annual cost of ethylbenzene, based on a consumption rate of 365 200 tonnes per year at a unit price of USD 1 000 per tonne, amounts to USD 365.2 million. Water consumption is estimated at 1 012 800 cubic meters per year, with a unit cost of USD 0.2235 per cubic meter, resulting in an annual cost of approximately USD 226 400. The cost of the catalyst has been incorporated into the reactor cost estimation. Therefore, the total annual cost of raw materials is calculated to be approximately USD 365.46 million.

7.5.2. Cost of Utilities

Utility costs were assessed using the ASPEN Economic Analyzer. The primary utilities identified for the plant include electricity, cooling water, and medium-pressure (MP) steam. Considering the applicable tariffs for electricity and technical water within the Special Economic Zone, along with the utility requirements for both major and minor equipment across the facility, the total annual utility cost was estimated to be approximately USD 56.94 million.

7.5.3. Cost of Waste Treatment

As mentioned in Chapter 6, the waste treatment system involves four major cost components. First, for the incineration of the vapor stream from the Three-Phase Separator, a thermal oxidizer with appropriate capacity is required, with an estimated equipment and installation cost of $100 000. The operational costs, including electricity, maintenance, and consumables, are approximately $207 000 annually. Second, for the treatment of the waste stream from the top product of the Second Distillation Column, the system requires a waste storage tank, liquid fuel burner, flame and gas regulatory system, and combustion chamber. The total equipment cost is estimated at $230 000, with operational costs of about $75,000 per year. Third, for the treatment of wastewater from the Three-Phase Separator, a reverse osmosis (RO) water treatment system is needed, with an equipment and installation cost of $170 000 and annual operational costs estimated at $793 000. Finally, for emission control, CO_2 and CO sensors are required, each costing approximately $345. The total cost of equipment and installation for all components is included in the total capital investment, while operational costs are accounted for under environmental charges related to waste treatment that are calculated as 1% of the combined ISBL and OSBL values.

7.6. Economic Analysis

The economic performance for the plant was calculated using Excel that is available in the Excel file titled “Group 3, Economic Analysis” located in the ESI. As the construction of the chemical plant is planned to take two years, the economic evaluation covers a 9-year period, spanning from 2027 to 2035.

7.6.1. Profit Estimation.

The total revenue of the plant is derived from the sale of three main product streams: high-purity styrene (99.7%), the light gas stream from the three-phase separator, and the overhead product from the second distillation column. The primary source of income is the sale of styrene. With a production rate of 40 000 kg/h (equivalent to 320 000 tonnes per year) and a market price of USD 1 380 per tonne, the annual revenue from styrene sales is estimated at USD 441.6 million. Additional revenue might be generated from by-product streams, including a benzene–toluene mixture (produced at 1 720 tonnes/year) and the light gas stream (produced at 2 900 tonnes/year). The sale of these by-products is projected to contribute an additional USD 34.2 million to the annual revenue. As a result, the total projected annual revenue of the plant amounts to approximately USD 475.84 million

The initial capital investment for the project is estimated at approximately USD 190.3 million. The annual fixed production cost amounts to USD 13.57 million, while the variable production cost is estimated at USD 424.06 million. To determine the unlevered income, the total revenue was adjusted by subtracting both fixed and variable production costs, as well as accounting for equipment depreciation.

7.6.2. Financial performance indicators.

For the purpose of the economic analysis, a weighted average cost of capital of 12% was assumed, and an inflation rate of 9.8% was projected over a 9-year period from 2027 to 2035. Depreciation was considered over a 15-year period. The gross profit in the first year of operation is estimated at USD 121.2 million, with the unlevered income calculated at USD 37.38 million.

Key financial performance indicators - including Net Present Value (NPV), Internal Rate of Return (IRR), Free Cash Flow, and Payback Period were evaluated. A summary of economic indicators is provided in Table 44. Appendix C provides the graphs illustrating the cumulative cash flow for each year and the NPVs at various discount rates.

Table 44. Financial performance indicators for 2027, 2031, 2034 years.

Economic indicator	Values
NPV, USD	90 795 000
IRR, %	22.81
Payback Period	3.93 years

The financial assessment of the project indicates strong profitability and overall viability. The Net Present Value of 90.8 million USD highlights that the project is expected to generate substantial value over the 9-year accounting period from 2027 to 2035. An Internal Rate of Return of 22.81% further reinforces this conclusion, as it exceeds the assumed cost of capital of 12%, indicating an attractive return on investment. Furthermore, the payback period of 3.93 years reflects a reasonable timeframe for recovering the initial investment, enhancing the project's appeal from a risk management perspective.

Chapter 8 – Conclusions and future work

8.1 Conclusion

This capstone project presents a comprehensive and fully integrated design for a 320 kt/y styrene production plant achieving 99.7% purity. At this production rate, the plant is estimated to satisfy approximately 25% of the regional demand within the Commonwealth of Independent States (CIS). The design is based on a rigorous comparative analysis of industrial production routes. Adiabatic dehydrogenation of ethylbenzene was selected due to the abundance of kinetic and operational data, and favorable economic feasibility.

The core reaction section comprises of two plug-flow reactors in series, with interstage heating to maintain the highly endothermic conversion at around 620 °C. This is complemented by an optimized steam-to-EB ratio of 11:1 and high-selective catalyst beds, achieving approximately 66% single-pass conversion and 96% styrene selectivity.

The separation train adopts a Monsanto-style distillation system augmented by a three-phase separator, enabling the recovery of 99.7%-pure styrene along with valuable benzene–toluene and light-gas by-product streams. Detailed specifications for both major and minor equipment were designed in this project.

The plant location within the Jibek Joly Special Economic Zone in the Zhambyl Region was strategically selected for its access to utilities, multimodal transportation infrastructure - including national railways, highways, and its favorable tax incentives, such as full exemptions from corporate income, land, and property taxes.

Environmental compliance is addressed via advanced emission control systems, with total greenhouse gas (GHG) emissions maintained below Kazakhstan’s annual chemical-sector quota, offering operational flexibility. From an economic perspective, capital investments, as well as fixed and variable costs, were thoroughly analyzed using both Aspen APEA functions and manual calculations. The project demonstrates a Net Present Value (NPV) of USD 91 million, an Internal Rate of Return (IRR) of 22.8%, and a payback period of 3.93 years over 2027–2035. These metrics underscore the project's profitability and strategic relevance to Kazakhstan’s petrochemical sector and regional market positioning.

8.2 Limitations and Future Work

While the current design achieves strong technical and economic performance, several areas remain open for further optimization. First, energy consumption across the plant can be further reduced by implementing advanced heat integration techniques and optimizing utility usage. Reducing the energy intensity of separation and heating units would enhance overall sustainability and reduce operating costs.

Second, the current design does not include a separation unit for the benzene–toluene stream. In future work, a targeted separation strategy for these by-products should be developed and implemented to further increase profitability, as both benzene and toluene have significant market value as standalone petrochemical feedstocks.

Lastly, future research could explore the potential integration of hydrogen sources to further enhance the environmental performance of the plant.

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Chapter 1

Appendix A

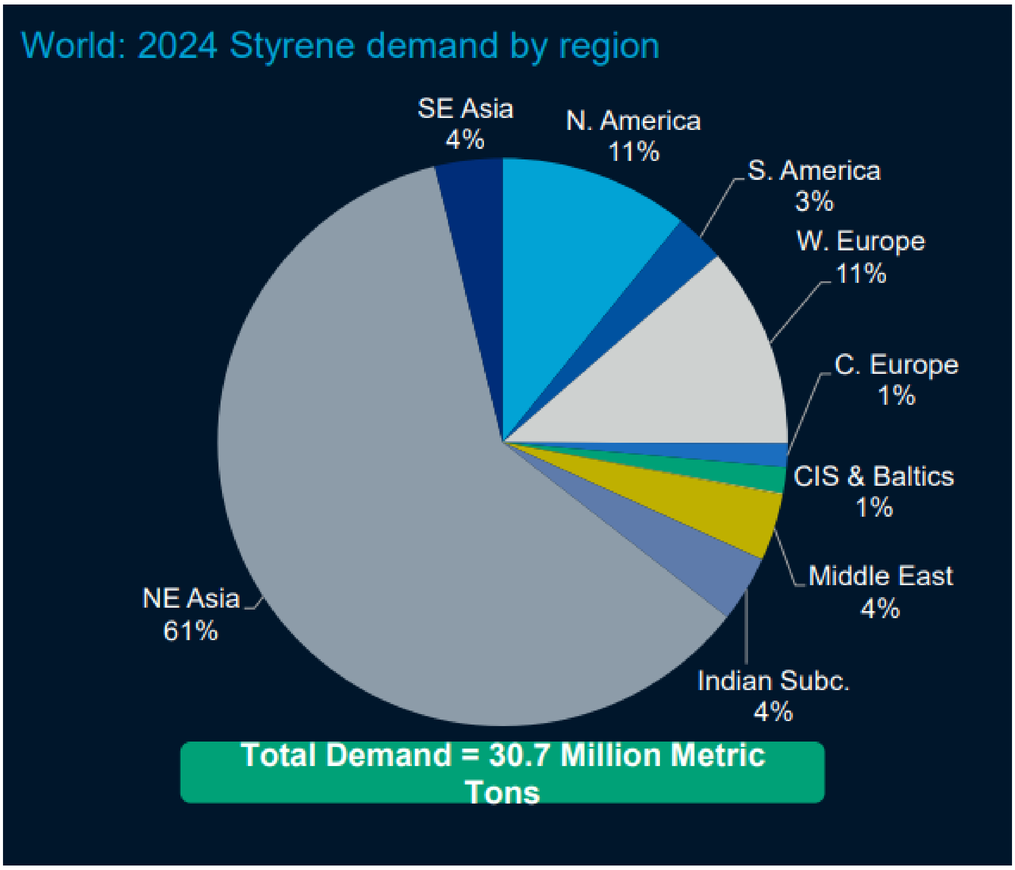

Figure A1. Styrene demand by region [1]

$$rate = \frac{\sum production}{n} \cdot 0.25 = \frac{472.0 \ + 2076}{2} \cdot 0.25 = 318.5\ kt/year \tag{1}$$

Chapter 3

Appendix B.1

B.1.1. Reactions

The kinetics of the styrene production process via dehydrogenation of ethylbenzene have been extensively studied by Lee [50]. In this study, Lee employed the fundamental Hougen-Watson kinetic model and presented the results of parameter estimation, including rate coefficients and adsorption equilibrium constants, using a nonlinear regression approach. The ethylbenzene dehydrogenation to styrene is accompanied by three side reactions that are listed in Table B.1.1.

Table B.1.1. Reactions involved in dehydrogenation of ethylbenzene to styrene.

Reaction		Type	Activation energy (kJ/mol)
R1	$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2$	main	175.38

R2	$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	side	296.29
R3	$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	side	474.76
R4	$C_6H_5CH{=}CH_2 + 2H_2 \rightarrow C_6H_5CH_3 + CH_4$	side	213.78

B.1.2 Kinetics of production process

For styrene production, the rate equations for the reactions R1, R2, R3, and R4 are expressed as follows.

$$r_{c1} = \frac{k_1 K_{EB}(P_{EB} - P_{ST}P_{H_2}/K_{eq})}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{B.1.1}$$

$$r_{c2} = \frac{k_2 K_{EB}P_{EB}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{B.1.2}$$

$$r_{c3} = \frac{k_3 K_{EB}P_{EB}K_{H_2}P_{H_2}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{B.1.3}$$

$$r_{c4} = \frac{k_4 K_{ST}P_{ST}K_{H_2}P_{H_2}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{B.1.4}$$

Where, r_{ci} is the rate of catalytic reaction *i* in kmol/(kg cat·hr); K_{eq} is the equilibrium constant in bar; P_j is the partial pressure of component *j*

As indicated, the steam to ethylbenzene ratio in the system impacts the kinetic rates for the production, and consequently, the rate equations are the functions of partial pressures. The expression of the partial pressure of ethylbenzene, styrene, and hydrogen in terms of feed mole fractions and conversions are expressed below:

$$P_{EB} = \frac{y_{EB}^0(1 - X_{ST} - X_{BZ} - X_{TO})}{1 + y_{EB}^0(X_{TO} + X_{BZ} + X_{H_2})} P_T \tag{B.1.5}$$

$$P_{ST} = \frac{y_{ST}^0 + y_{EB}^0 X_{ST}}{1 + y_{EB}^0(X_{TO} + X_{BZ} + X_{H_2})} P_T \tag{B.1.6}$$

$$P_{H_2} = \frac{y_{H_2}^0 + y_{EB}^0 X_{H_2}}{1 + y_{EB}^0(X_{TO} + X_{BZ} + X_{H_2})} P_T \tag{B.1.7}$$

The steady state continuity equations for ethylbenzene is:

$$\frac{dX_{EB}}{d(W/F_{EB}^{\circ})} = r_{EB} \tag{B.1.8}$$

The rate of ethylbenzene consumption can be expressed as the sum of the rates of reactions 1, 2, and 3.

$$r_{EB} = r_{c1} + r_{c2} + r_{c3} \tag{B.1.9}$$

Combining equations 9 & 10, steady state continuity equations for ethylbenzene becomes:

$$\frac{dX_{EB}}{d(W/F_{EB}^{\circ})} = r_{c1} + r_{c2} + r_{c3} \tag{B.1.10}$$

where F_{EB}° is the feed molar flow rate of ethylbenzene in kmol/hr; W/F_{EB}° is the space time in kgcat·hr/kmol

Likewise, the steady-state continuity equations for styrene, hydrogen, benzene, and toluene can be formulated as follows:

$$\frac{dX_{ST}}{d(W/F_{EB}^{\circ})} = r_{c1} - r_{c4} \tag{B.1.11}$$

$$\frac{dX_{H_2}}{d(W/F_{EB}^{\circ})} = r_{c1} - r_{c3} - 2r_{c4} \tag{B.1.12}$$

$$\frac{dX_{BZ}}{d(W/F_{EB}^{\circ})} = r_{c2} \tag{B.1.13}$$

$$\frac{dX_{TO}}{d(W/F_{EB}^{\circ})} = r_{c3} + r_{c4} \tag{B.1.14}$$

To validate the kinetic model in both Aspen Plus and Python, thermal reactions occurring in the void regions of the catalyst bed were excluded from the analysis. Table B.1.2 summarizes the kinetics parameters including pre-exponential factors and equilibrium constants for reactions R1, R2, R3, and R4.

Table B.1.2. Reactions involved in dehydrogenation of ethylbenzene to styrene.

Parameter	**Unit**	**Value**
K_{EB}	$\frac{1}{bar}$	8.466
K_{ST}	$\frac{1}{bar}$	34.00
K_{H2}	$\frac{1}{bar}$	3.091
k_1	kmol/(kgcat·hr)	0.2725
k_2	kmol/(kgcat·hr)	0.00544
k_3	kmol/(kgcat·hr)	0.0184
k_4	kmol/(kgcat·hr)	0.0302
K_{eq}	bar	0.336

For validation of reaction kinetics for conversion ratios, data at T = 620 °C & P_T = 1.04 bar; H2O/EB = 11 (mol/mol); P_{N2} = 0.432 bar was taken. Validation of kinetics was done by Python and Aspen Plus V14 that are available in the supplementary materials. A single isothermal PFR, with a length of bed of 1.33 m and inner radius of 3.5 m instead of three adiabatic reactors was employed for Aspen validation with Python calculations. For the Aspen Plus simulations, a catalyst loading of 32500 kg and a bed voidage of 0.4312 were taken for the reactor. The reactor operates at constant temperature of inlet feed. Table 7 below presents the inlet data used to validate the experimental results from the literature. For validation of the Python calculations, the total pressure and mole fraction of ethylbenzene were set to match the conditions used in the Aspen simulations.

Table B.1.3. Input information for Aspen Plus validation.

Aspen Plus validation	
Temperature, °C	620
Pressure, bar	1.04
Ethylbenzene inlet flow rate, kmol/hr	541.667
Water inlet flow rate, kmol/hr	5958.33
N_2 inlet flow rate, kmol/hr	4618.42
$y_{EB,0}$	0.04872
Catalyst loading & bed voidage	32500 kg & 0.4312

The ODE was solved in Python, and a sensitivity analysis was conducted in Aspen Plus to validate the kinetics. The catalyst weight in the reactor was varied to examine the relationship between conversions and space time. Figures B.1.1 and B.1.2 present the kinetics validation plots, showing experimental data points (red & pink dots), the mathematical solution from Python (yellow & purple lines), and the modeling results from Aspen Plus (orange & blue lines).

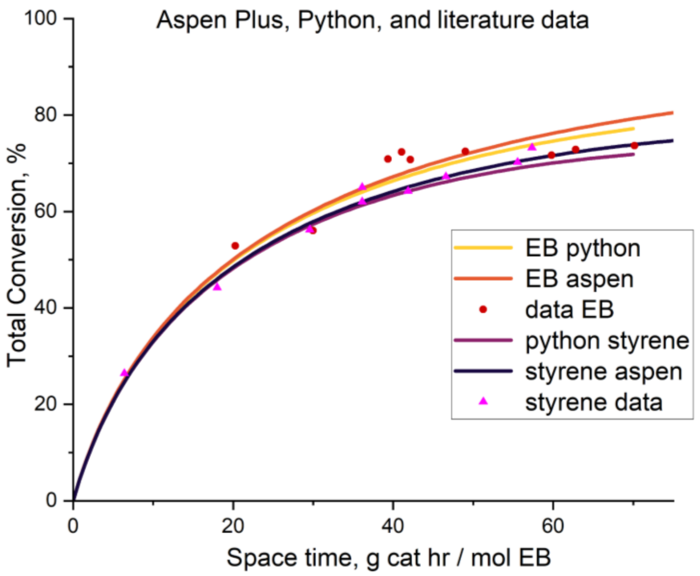

Figure B.1.1. Conversions for EB & styrene versus space time

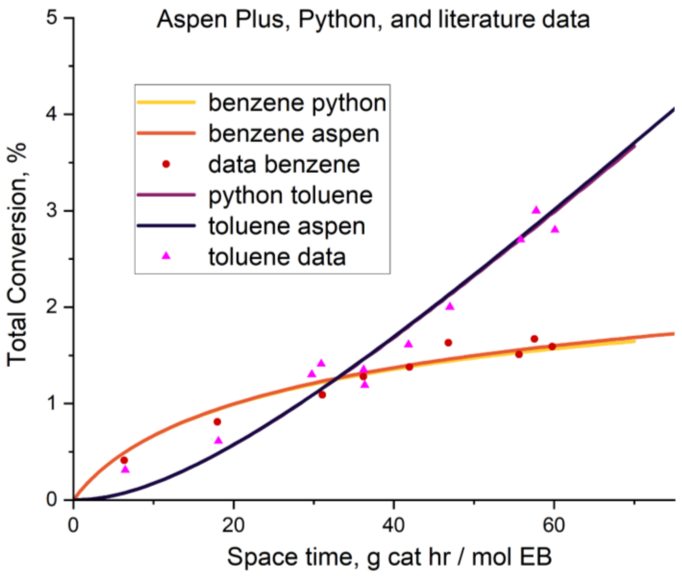

Figure B.1.2. Conversions for benzene & toluene versus space time

Overall, the conversion trends for all components in both the Python and Aspen validations show strong agreement with the data points from the literature.

Appendix B.2

The calculations are shown for Reactor 1 only, and all results are available in the Reactor Excel Spreadsheet.

$$\rho_b = \rho_{cat}(1-\epsilon) = 2500(1-0.5) = 1250\ kg/m^3 \tag{B.2.1}$$

$$W = F_{EB}\tau \cdot 1.1 = \frac{612450 \cdot 80}{1000} \cdot 1.1 = 53895.6\ kg\ cat \tag{B.2.2}$$

$$V_{cat} = \frac{W}{\rho_b} = \frac{53895}{1250} = 43.11648\ m^3 \tag{B.2.3}$$

$$V_{reactor} = \frac{V_{cat}}{1-\epsilon} = \frac{43.11648}{0.5} = 86.23296\ m^3 \tag{B.2.4}$$

$$A = \frac{\pi {d_{tube}}^2}{4} = \frac{\pi 1.5^2}{4} = 1.76625\ m^2 \tag{B.2.5}$$

$$V_{tube} = A \times L = 1.76625 \times 2.5 = 4.415625\ m^3 \tag{B.2.6}$$

$$N = \frac{V_{reactor}}{V_{tube}} = \frac{86.23296}{4.415625} = 19.52904968 \tag{B.2.7}$$

Which is rounded down to 19 tubes, so that the volume does not exceed the specified one.

$$u_0 = \frac{Q}{An} = \frac{101.0868982}{19 \times 1.76625} = 3.01 m/s \tag{B.2.8}$$

$$u = \frac{u_0}{\epsilon} = \frac{3.01}{0.5} = 6.02 m/s \tag{B.2.9}$$

$$\begin{aligned} dP &= \left(\frac{150(1-\epsilon)^2 \mu u_0}{d_p^2 \epsilon_b^3} + \frac{1.75(1-\epsilon_b)\rho u_0^2}{d_p \epsilon_b^3}\right) * l = \\ &= \frac{150(1-0.5)^2 \times\ 3.18E-05 \times 3.01}{0.0045^2 \times 0.5^3} + \\ &+ \frac{1.75(1-0.5) \times 0.502344 \times 3.01^2}{0.0045\ \times 0.5^3} = 1.95E-01 \end{aligned} \tag{B.2.10}$$

$$d_p = \sqrt[3]{\frac{6 d_{actual}^2 l_{actual}}{4}} = \sqrt[3]{\frac{6 \times 3.2^2 \times 5}{4}} = 0.004250634277 m \tag{B.2.11}$$

Which is rounded up to 0.0045m.

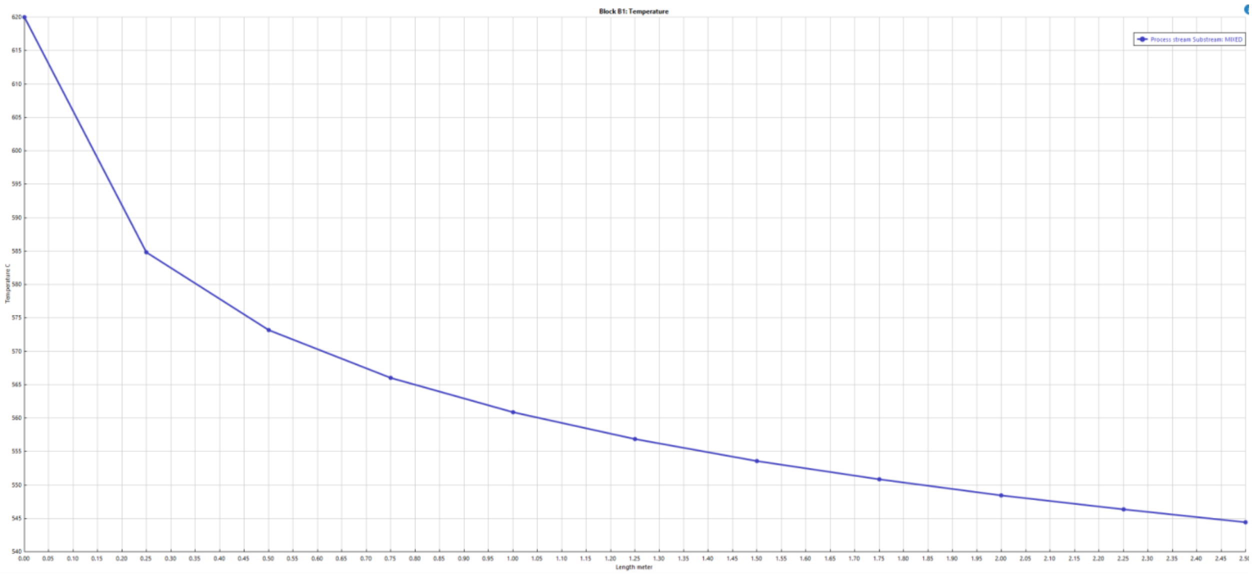

Figure B.2.1. First reactor temperature vs length

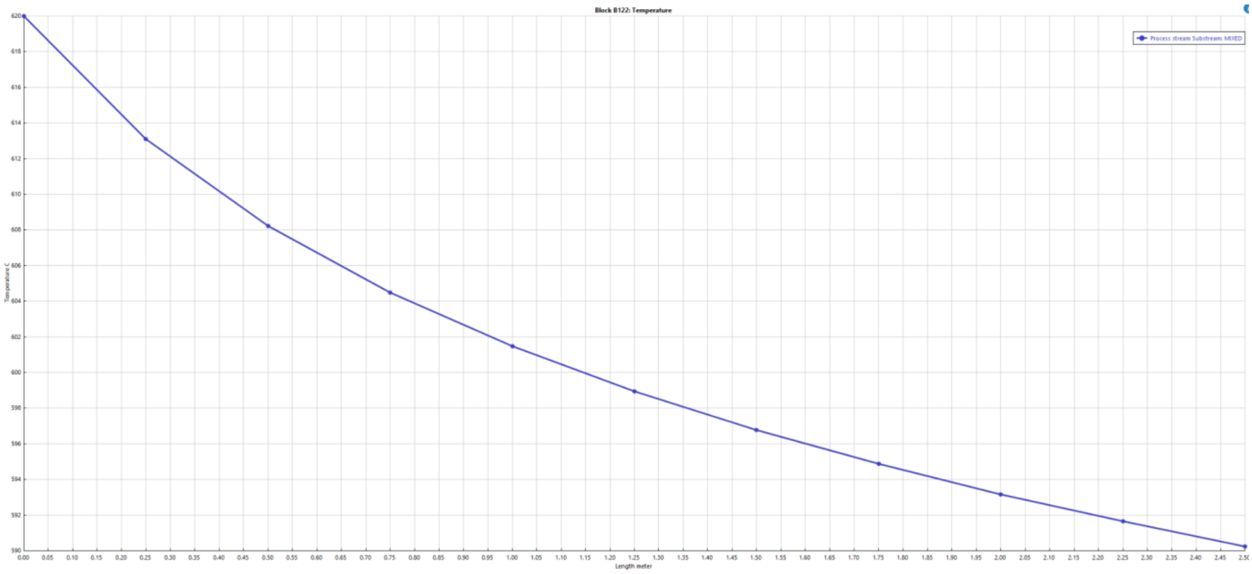

Figure B.2.2. Second reactor temperature vs length

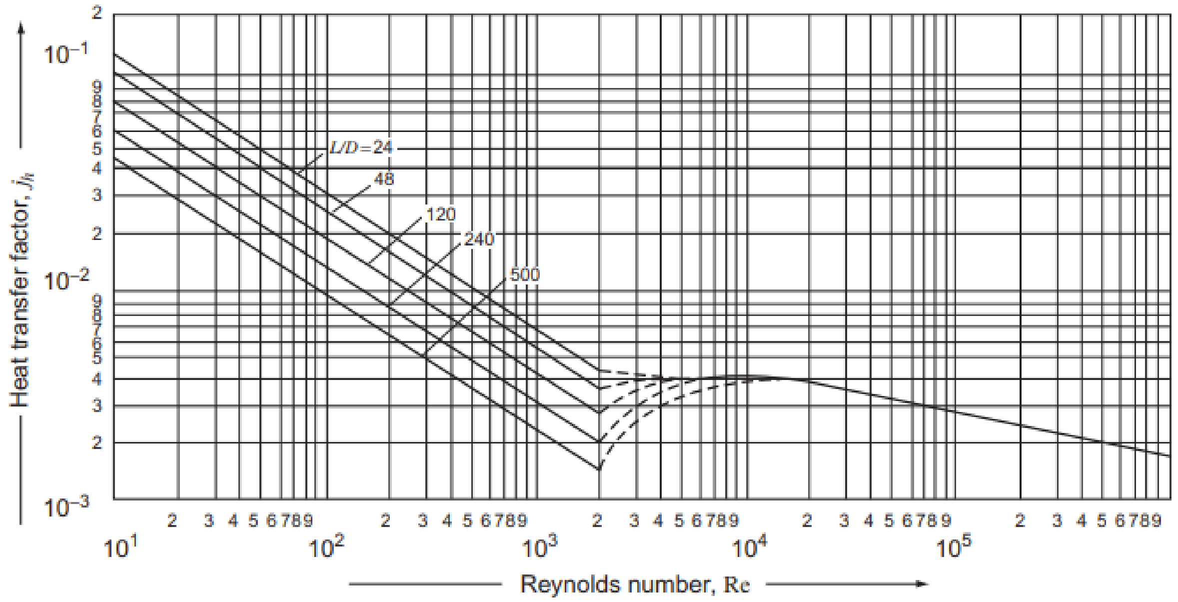

Figure B.2.3. Heat transfer factor correlation for tube side.

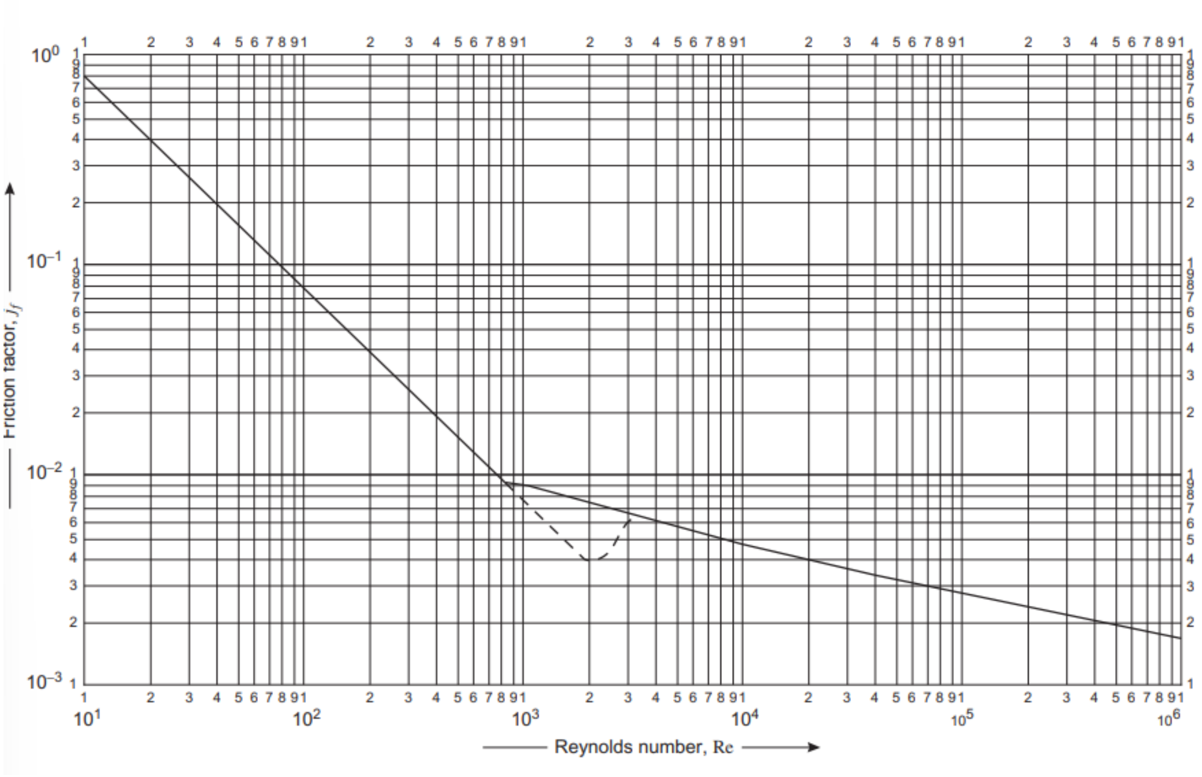

Figure B.2.4. Friction factor correlation for tube side.

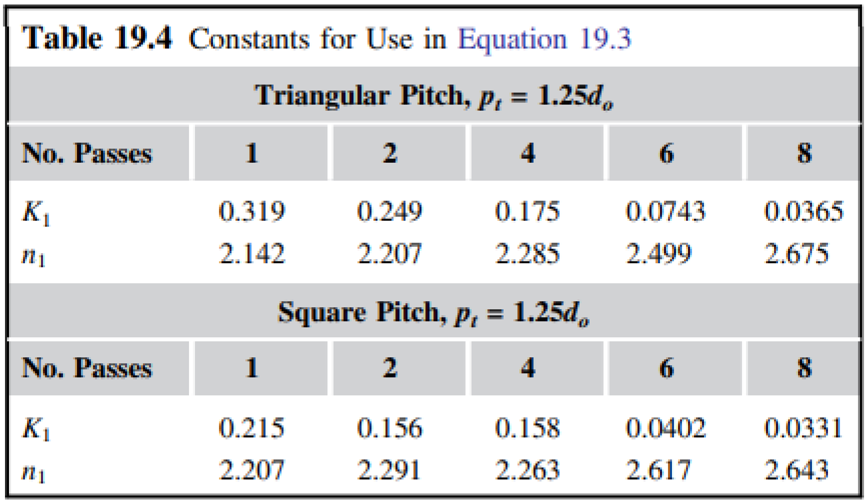

Table 19.4 Constants for Use in Equation 19.3

Triangular Pitch, $p_t = 1.25d_o$					
No. Passes	**1**	**2**	**4**	**6**	**8**
K_1	0.319	0.249	0.175	0.0743	0.0365
n_1	2.142	2.207	2.285	2.499	2.675
Square Pitch, $p_t = 1.25d_o$					
No. Passes	**1**	**2**	**4**	**6**	**8**
K_1	0.215	0.156	0.158	0.0402	0.0331
n_1	2.207	2.291	2.263	2.617	2.643

Figure B.2.5. Standard parameters for bundle diameter calculations.

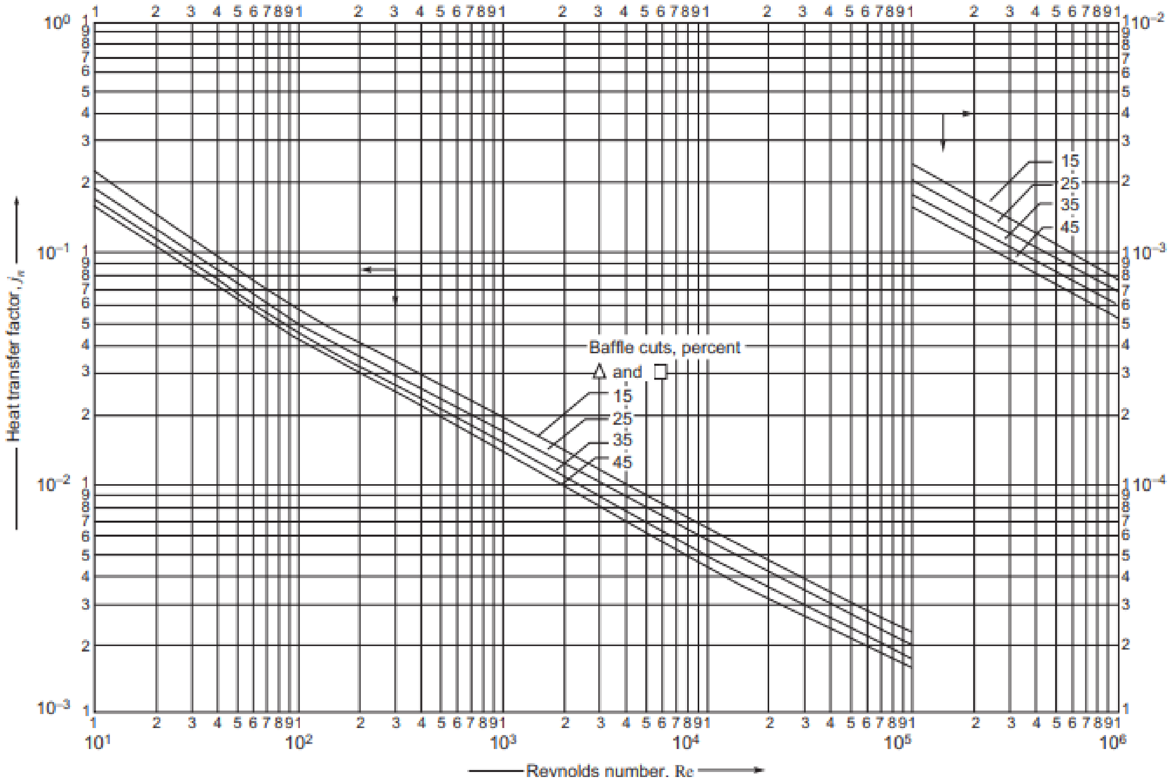

Figure B.2.6. Heat transfer factor correlation for shell side.

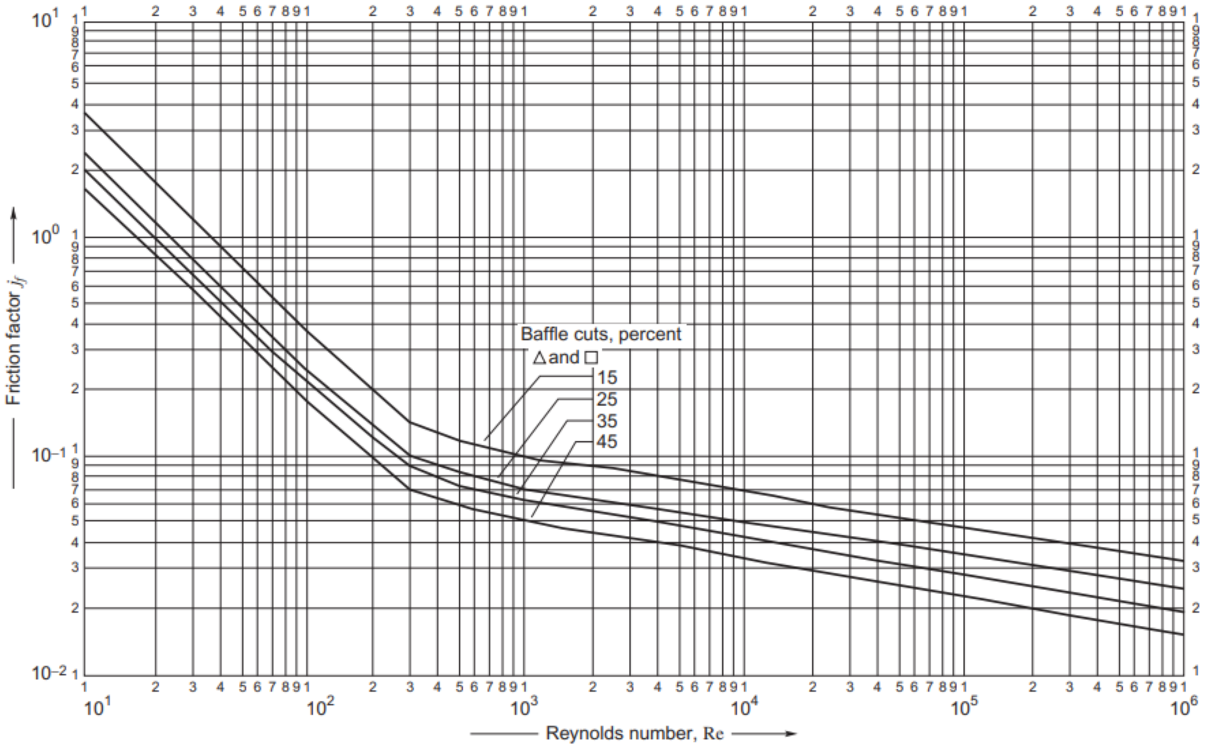

Figure B.2.7. Friction factor correlation for shell side.

Table B.2.1. Antoine equation coefficients

	A	B	C
H2	2.94928	67.5078	275.7
CH4	3.7687	395.744	266.681
C2H4	3.95405	663.72	256.681
water	5.109459	1678.948	228.97
benzene	4.02232	1206.53	220.291
toluene	4.0854	1348.77	219.976
ethylbenzene	4.0928	1431.71	214.099
styrene	4.082	1445.58	209.43

Appendix B.3

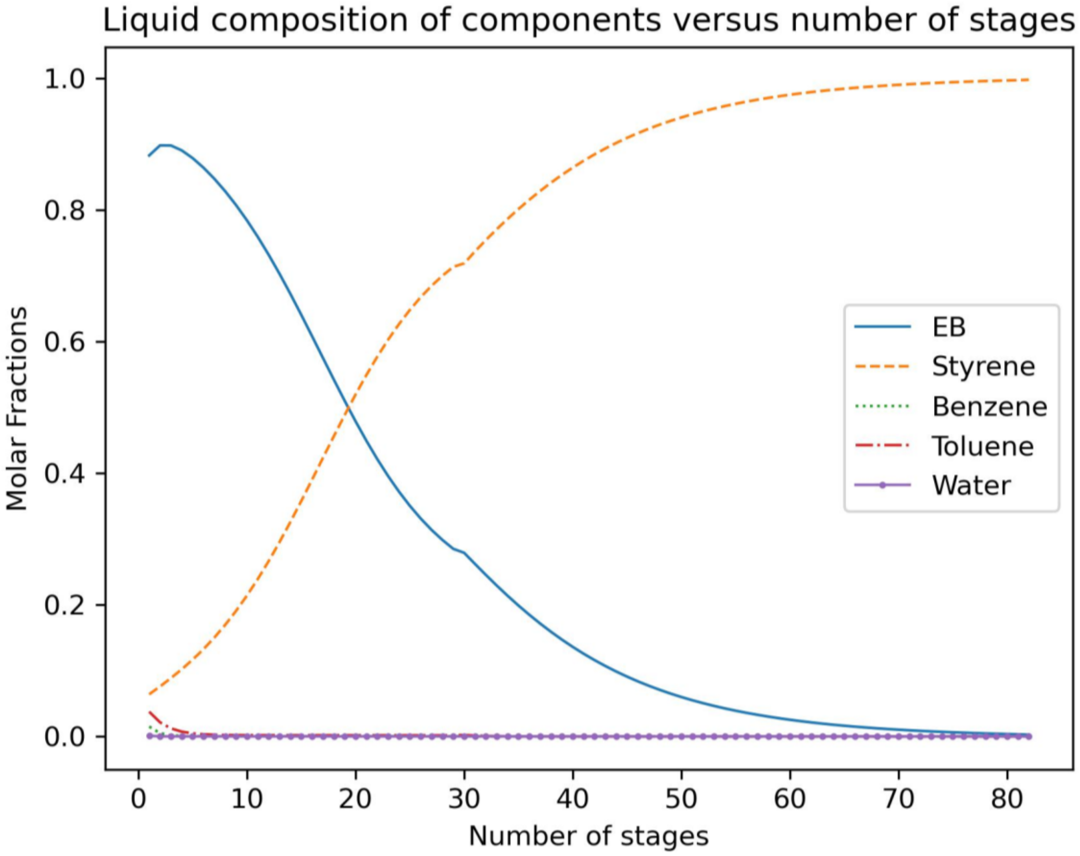

Figure B.3.1. Liquid composition of components versus number of stages

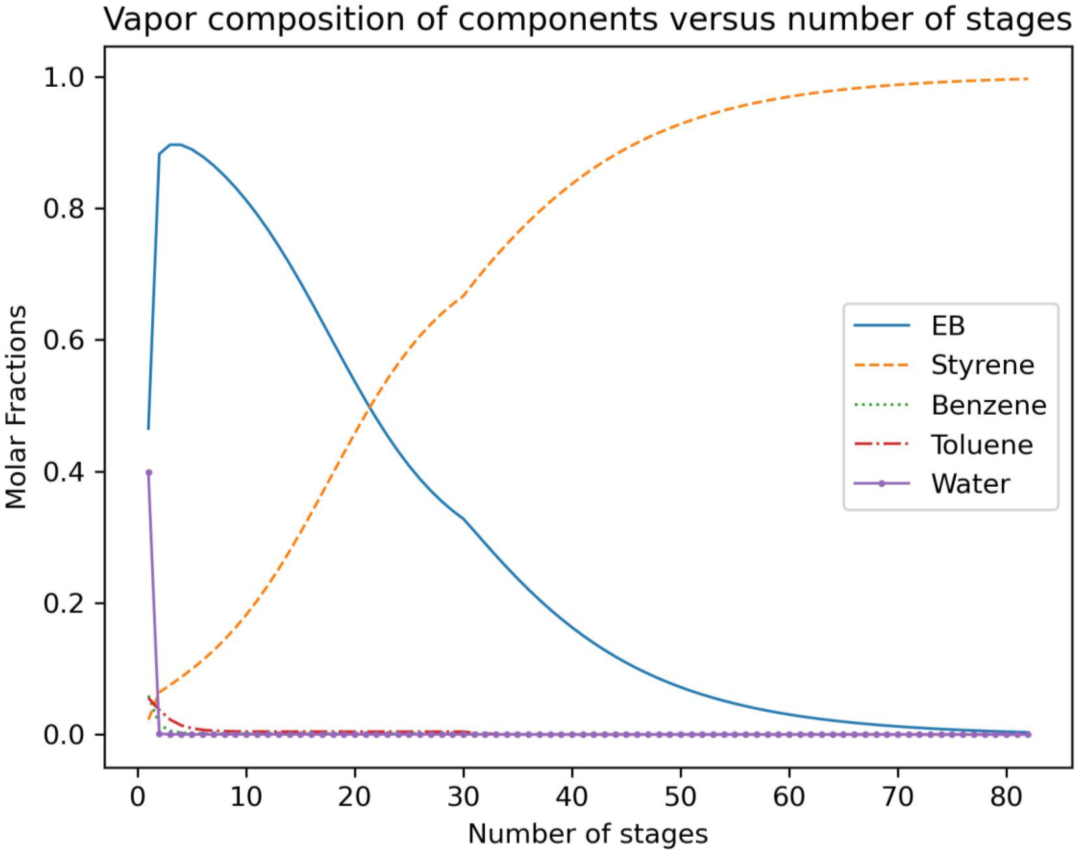

Figure B.3.2.Vapor composition of components versus number of stages

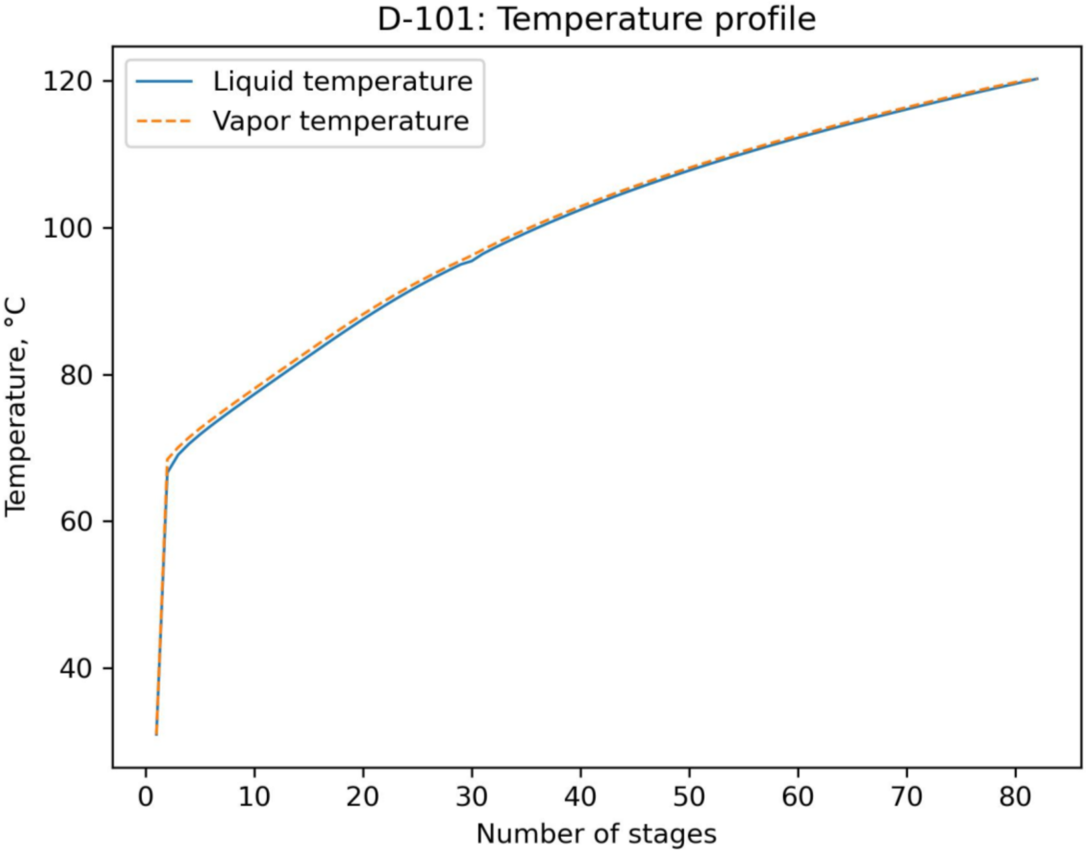

Figure B.3.3. Temperature profile versus number of stages

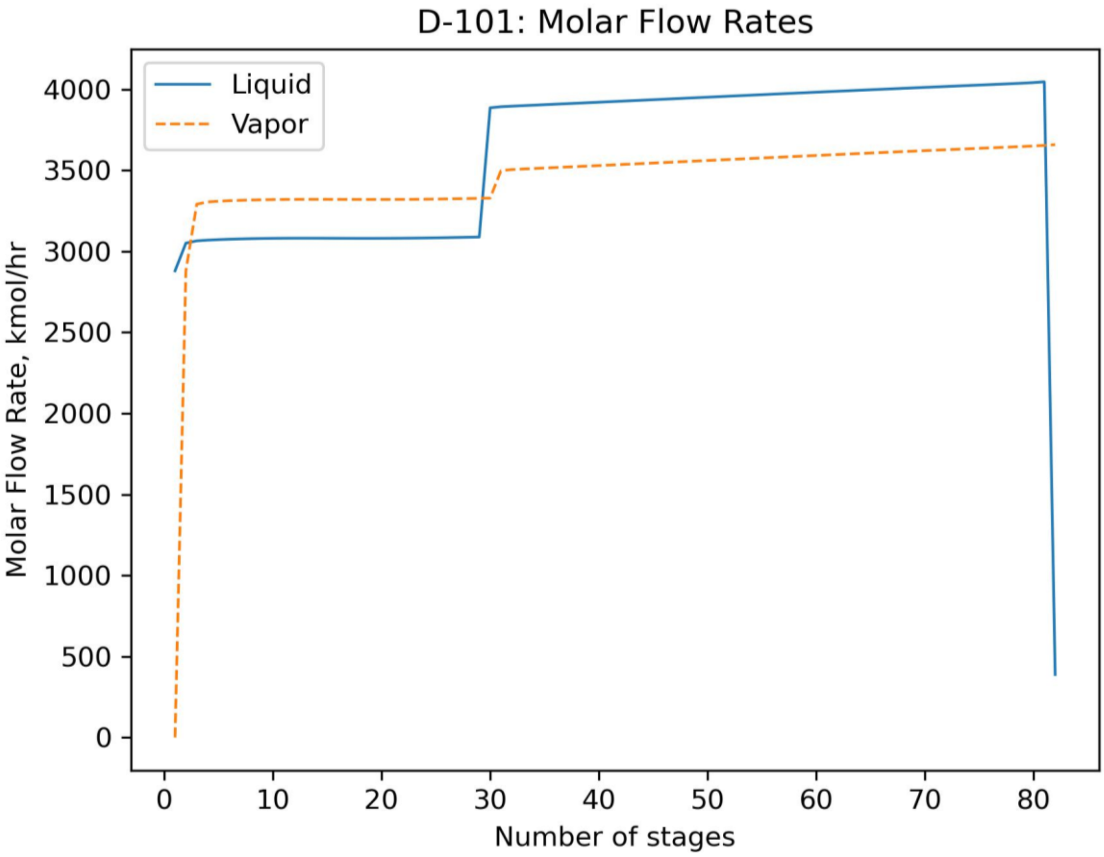

Figure B.3.4. Molar flow rate versus number of stages

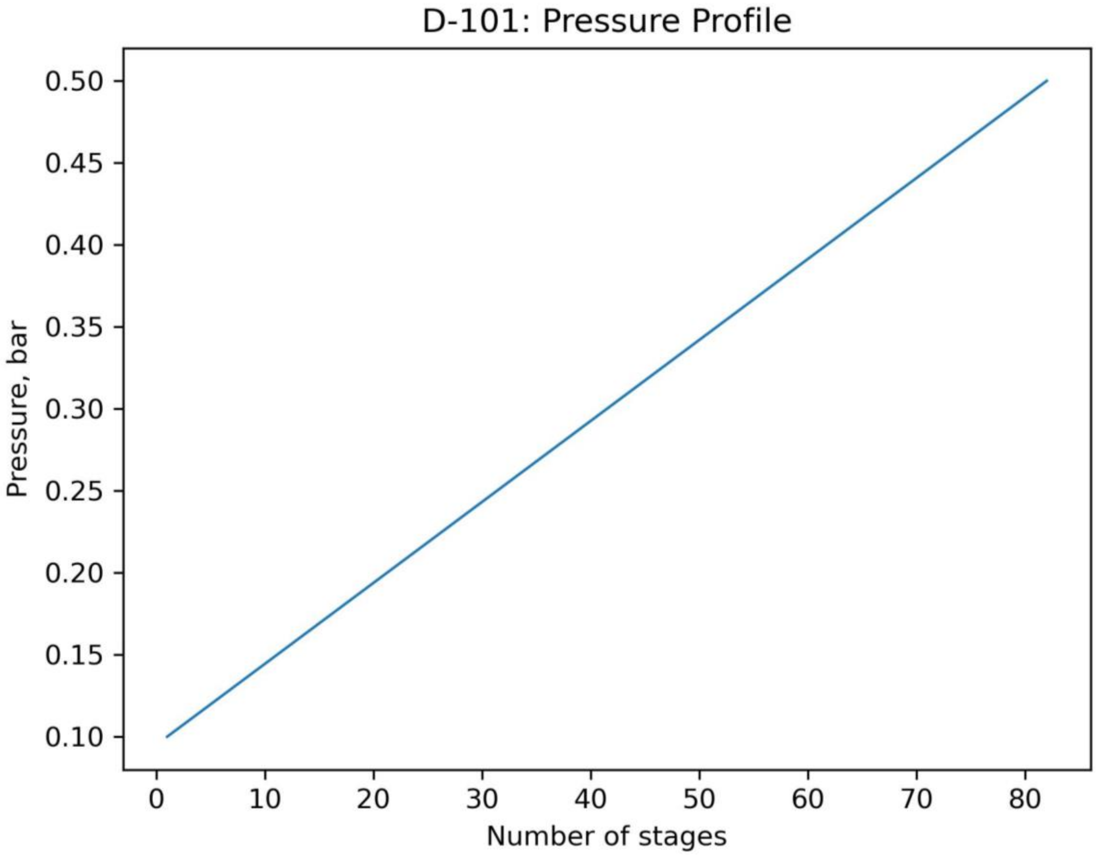

Figure B.3.5. Pressure versus number of stages

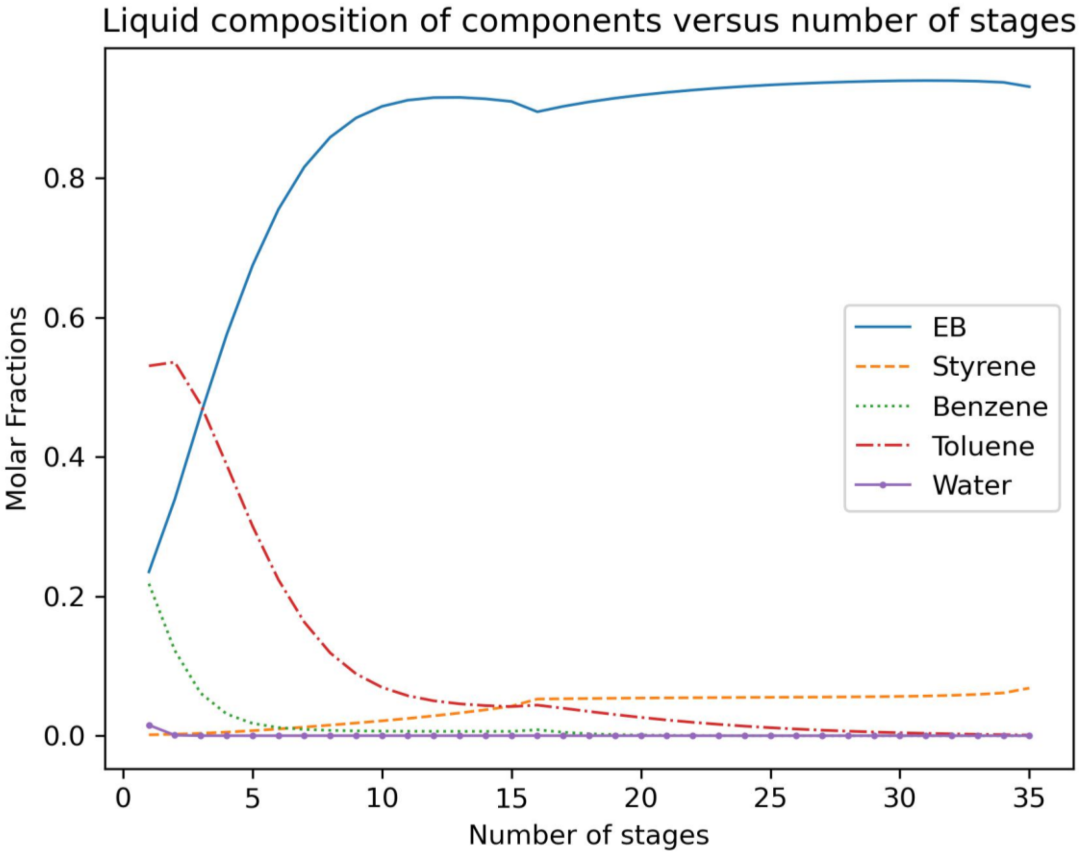

Figure B.3.6. Liquid composition of components versus number of stages

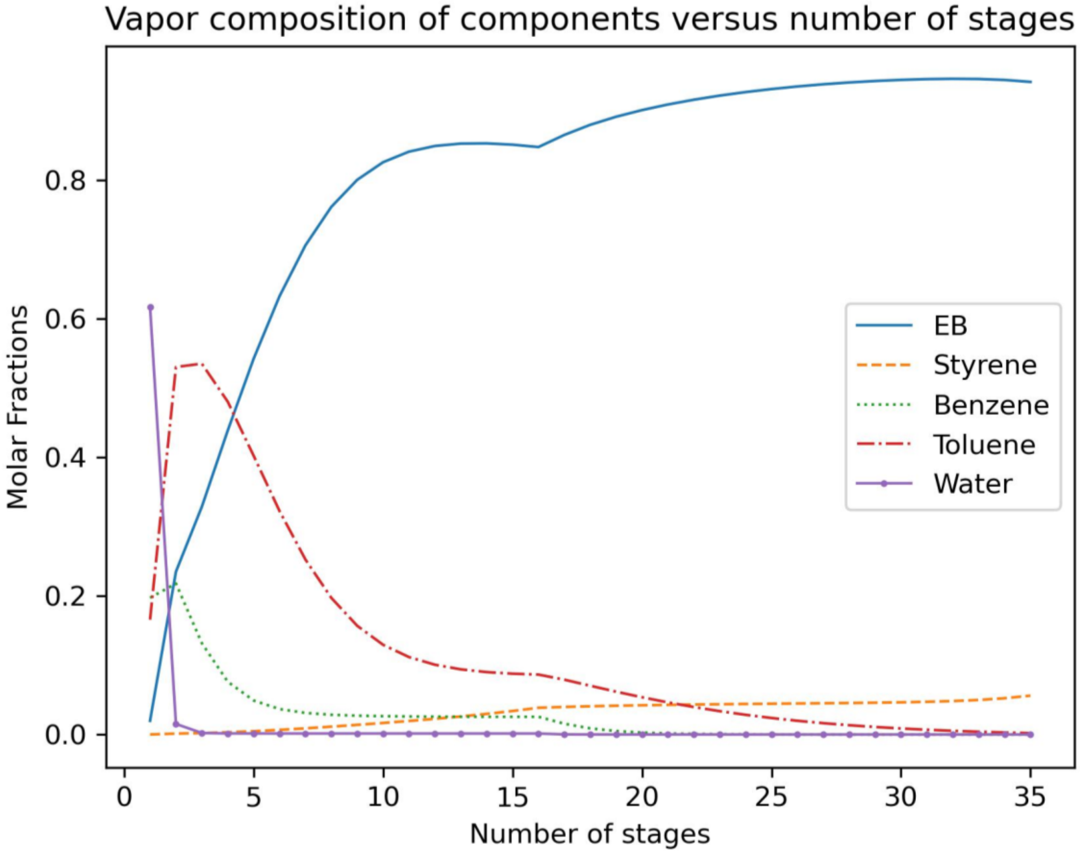

Figure B.3.7. Vapor composition of components versus number of stages

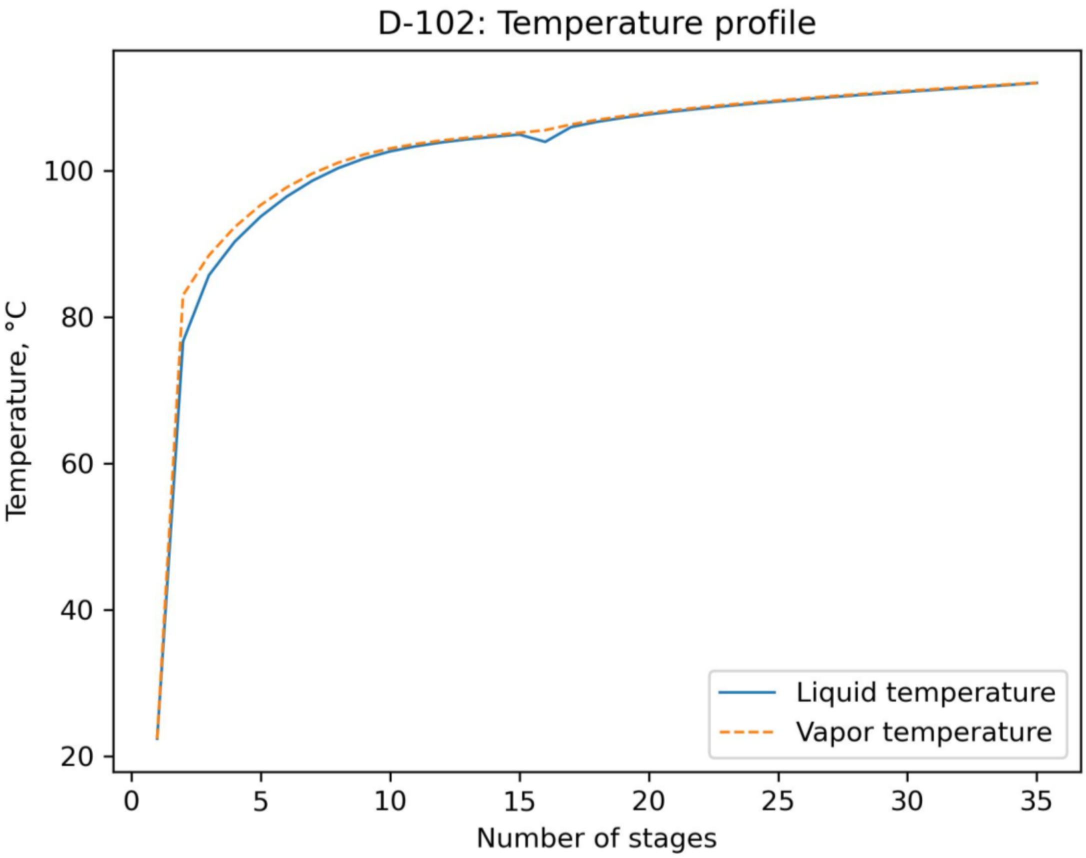

Figure B.3.8. Temperature profile versus number of stages

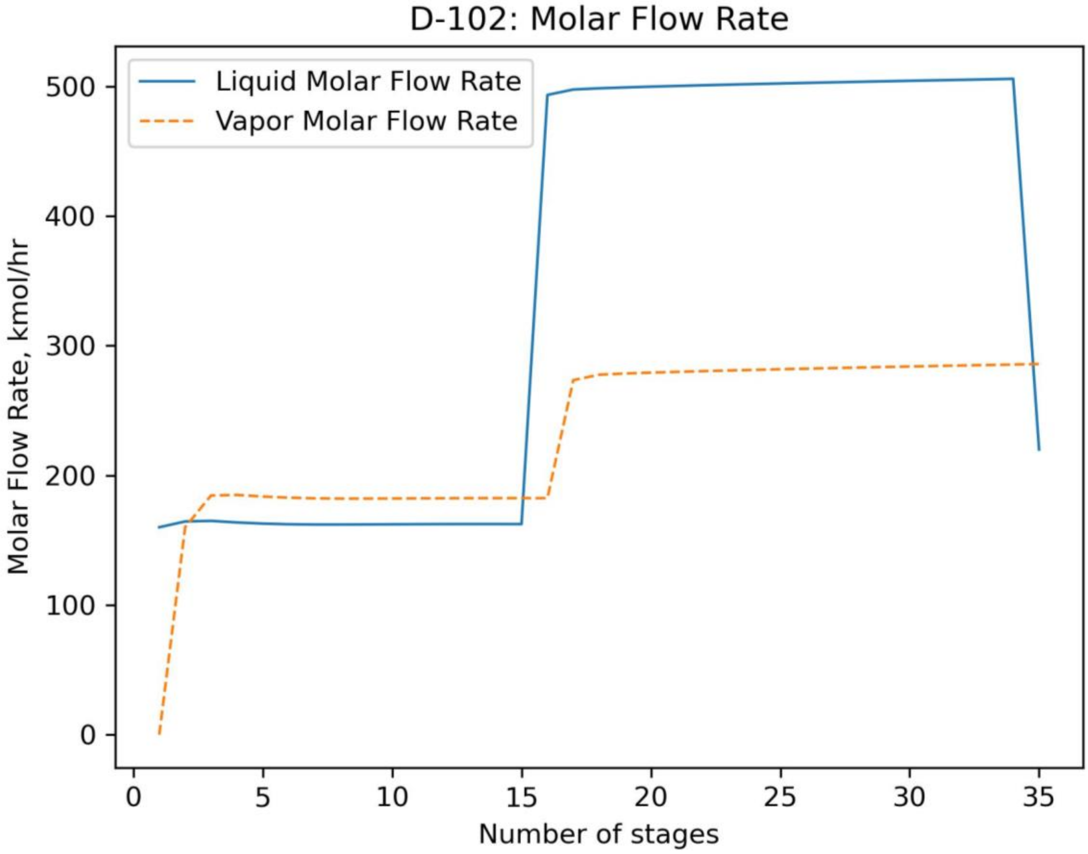

Figure B.3.9. Molar flow rate versus number of stages

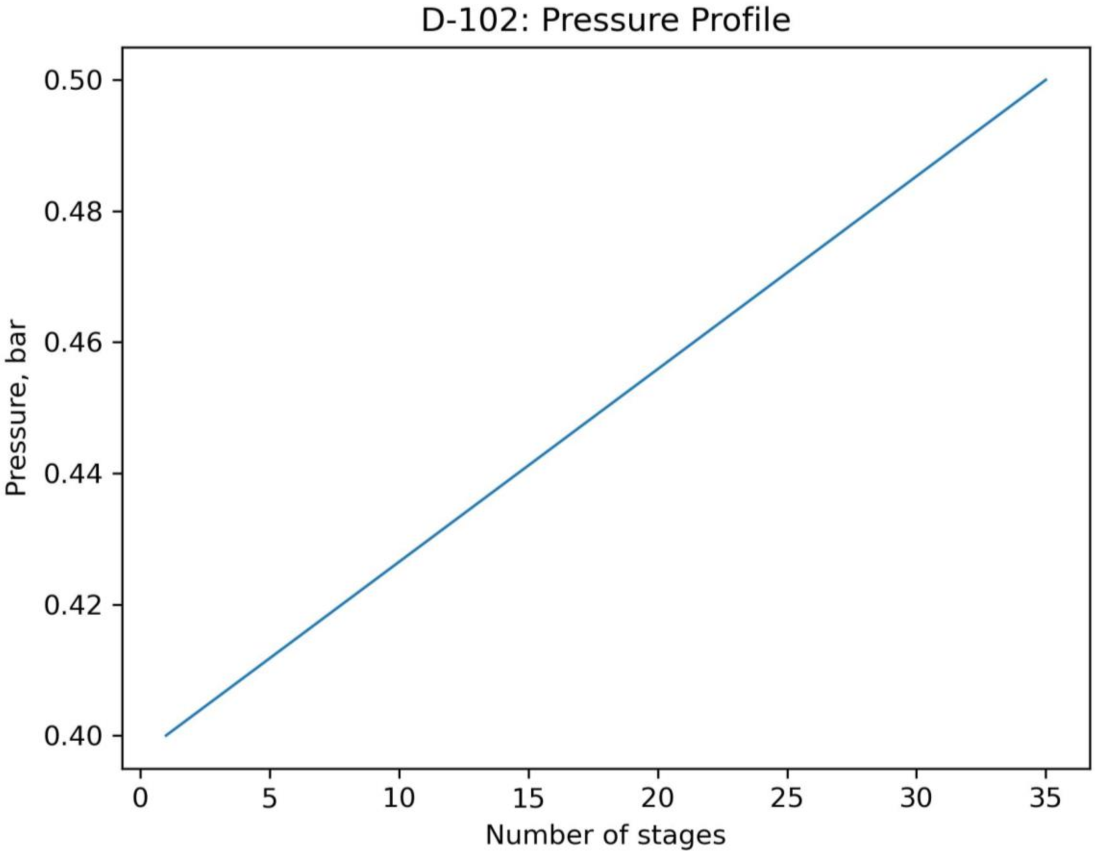

Figure B.3.10. Pressure vs number of stages

Appendix C

$$price\ (2017) = present\ value \cdot (1 + CAGR)^{n\ of\ years} \tag{C.1}$$

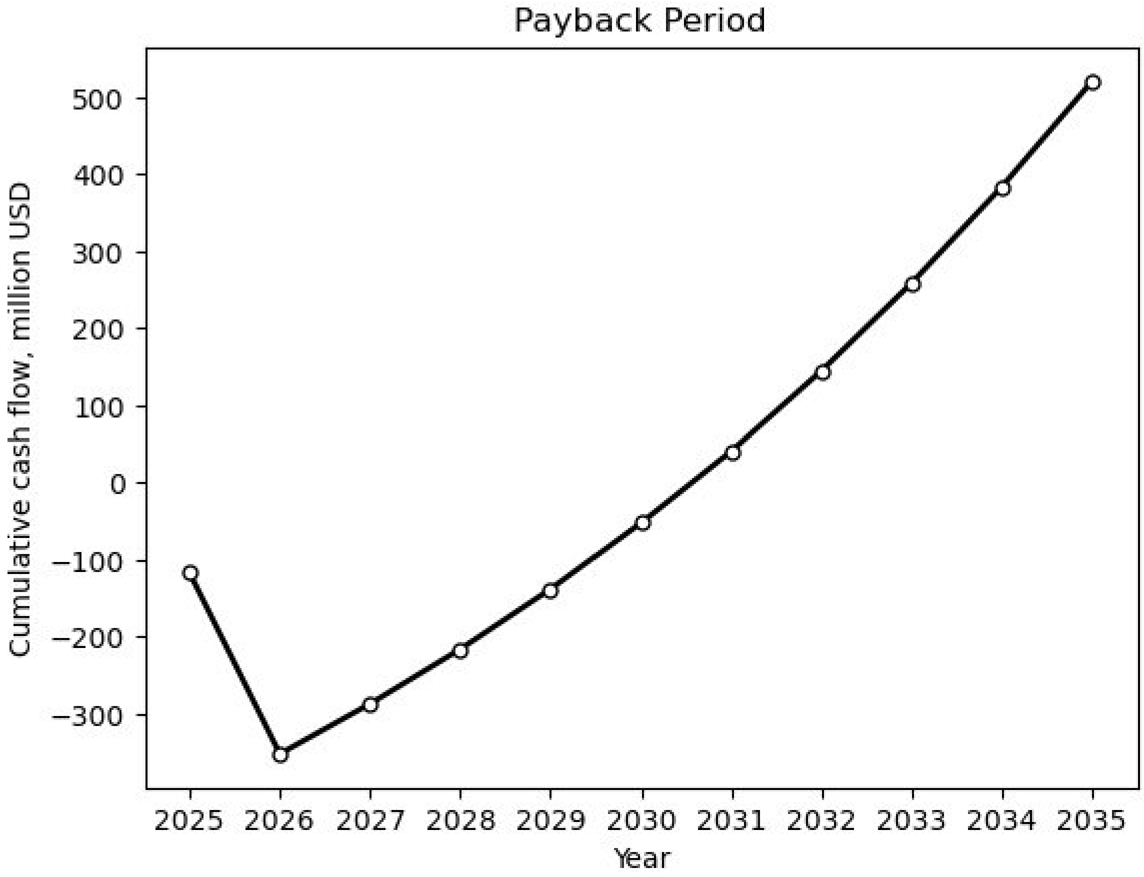

Figure C.1. Cumulative cash flow between 2025-2035.

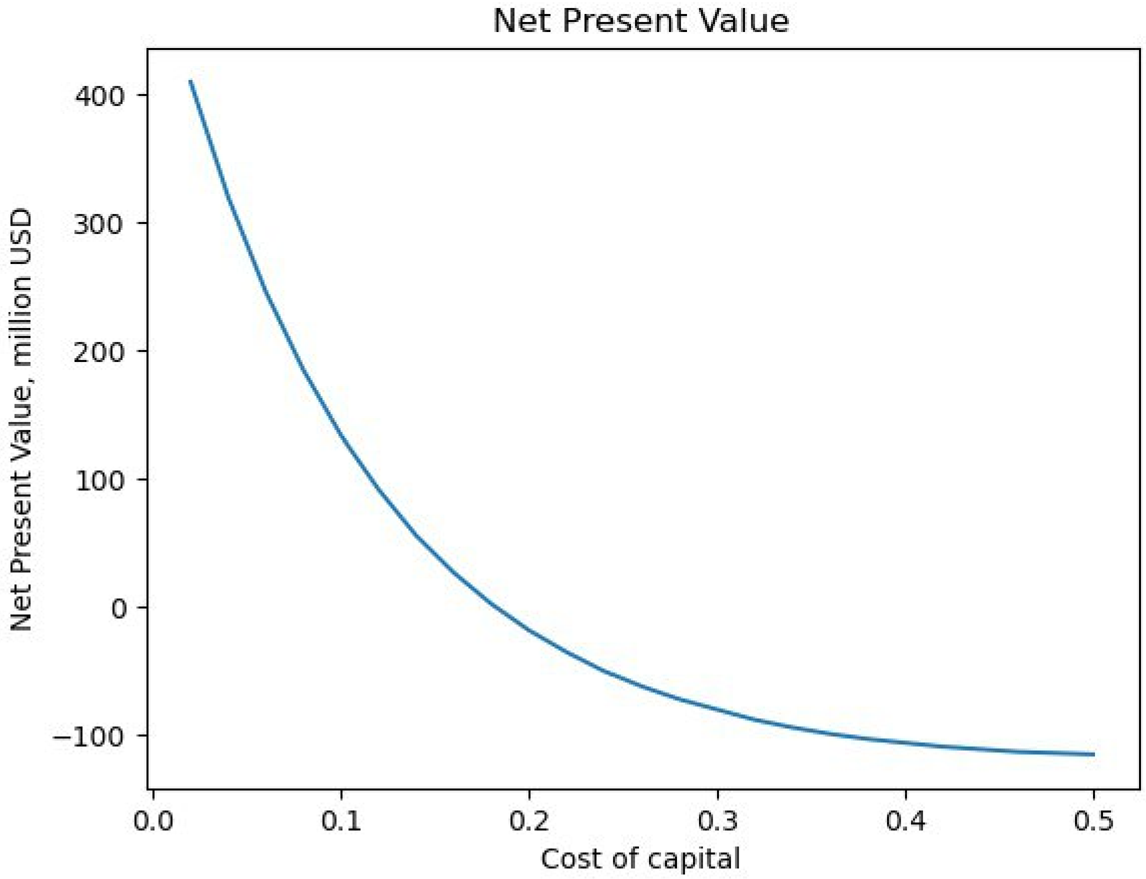

Figure C.2. Net Present Value at different cost of capital

Appendix Reference

[1] B. Lee, “Styrene Market Outlook Preparing For Tomorrow’s Styrenics Industry: Tackling The Impact Of Overcapacity,” 2024. Available: https://www.scic.sg/images/1._Preparing_for_Tomorrows_Styrenics_Industry_-_Tackling_the_Impact_of_Overcapacity_Brian_LeeChemical_Market_Analytics_by_OPIS_1.pdf