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DESIGN OF THE STYRENE PROCESS BY DEHYDROGENATION OF ETHYLBENZENE

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ABSTRACT

The styrene monomer dates back more than 80 years and the uses of the styrene is in wide range like Acrylonitrile butadiene styrene (ABS), polystyrene (PS), expanded polystyrene and more as shown in this report. Since the demand on styrene monomer rises, this project seeks to increase the production in Saudi Arabia by producing 100,000 tons annually.

Data about the different processes that produce styrene were collected and explained in detail with final comparison. The adiabatic dehydrogenation of EB process was selected, since it was the most effective and economic one. This process was modified in order to produce Toluene and Benzene as by-product by adding a third distillation.

Material and energy balance were calculated using MS-Excel software. The energy balance was calculated for each stream and the required heat of each equipment.

For producing Styrene monomer with this process, two plug flow reactors were designed to give overall conversion 64% of Ethylbenzene. Rate equations and kinetics of the reactions and heat of reactions were derived and used in the design. The change of the flow rates, temperature, conversion and reaction rates inside both reactors were calculated. The catalyst used is potassium-promoted iron with total amount of 12 tons, where the dimeters of first and second reactors are 1.19 and 1.3 m, respectively. The height of the first and second reactors are 2.97 and 3.43 m, respectively. Also, control of the reactors was proposed and cost for both vessels was determined.

Design of the separation columns was conducted using two different methods. The vapor-liquid equilibrium was determined to get the number of stages in all columns. The number of stages for the distillation columns by using short-cut method are 60, 23 and 19 stages in the first, second and the third distillation, respectively. McCabe-Thiele method was selected to design both columns T-101 and T-102, where the number of stages in the first and the second distillations are 75 and 26, respectively. The size of the third column was determined to calculate its cost.

The cost of each equipment was determined, and the equipment that where not designed are just sized to estimate the cost of the project, and to calculate the fixed capital cost. The cost of operating labor was calculated, and the pay-back period was determined to be at the end of the 9th year.

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LIST OF ABBREVIATIONS

EB	:	Ethylbenzene.
BZ	:	Benzene.
C1	:	Methane.
C2	:	Ethylene.
CO	:	Carbon Monoxide.
CO_2	:	Carbon dioxide.
H_2	:	Hydrogen.
ST	:	Styrene.
TO	:	Toluene.
W	:	Water.
W_C	:	Weight of catalyst.
ΔH_{fi}°	:	Stander heat of formation.
d_p	:	Catalyst equivalent pellet dimeter, m.
K_{eq}	:	Equilibrium constant, bar.
ρ_m	:	stainless steel density, in kg/m^3
ρ_B	:	Catalyst bulk density, in kgcat/m^3
F_{EB}°	:	initial flowrate of Ethylbenzene.
w/F_{EB}°	:	Space time.
ε_B	:	Void fraction of the bed, m3/m^3
ρ_s	:	Catalyst pellet density, kgcat/m^3
ΔG_{fi}°	:	Stander Gibbs energy.
ΔH_{298i}°	:	Stander heat of reaction.
ΔH_{ri}	:	Heat of reaction.
$\Delta H_{a,j}$	:	Heat of adsorption.

VLE	:	Vapor-Liquid Equilibrium.
U_d	:	Overall heat transfer coefficient.
K_i	:	Equilibrium constant.
α	:	Relative volatility.
N_m	:	Minimum number of stages.
E_0	:	Overall column efficiency.
E_{mV}	:	Murphree plate efficiency.
E'	:	Modules of elasticity.
C_{OL}	:	Cost of operating labor.
N_{OL}	:	Number of operators per shift.
N_{np}	:	Non-particular processing step.
FCI	:	Fixed capital investment.
PBP	:	Pay-back period.

CHAPTER 1:
INTRODUCTION AND HISTORY

Styrene has many common names, such as phenylethylene, styrol, vinylbenzene or cinnamene. Its chemical formula C8H8, but it's structure formula, C6H5−CH=CH2. It arises naturally in small quantities in several plants and foods such coal tar, coffee beans, cinnamon and in peanuts. In the 19th century, styrene was produced by distillate the natural balsam storax only.

1.1 HISTORY OF STYRENE PRODUCTION

In 1930s the commercial processes of styrene manufacturing by dehydrogenation of ethylbenzene was achieved. During the second World War the production of synthetic styrene – butadiene rubber was elevated in a large scale to provide a high capacity for manufacturing of monomer in high purity at 1946, that could be used to polymerize a stable, colorless, clear and cheap plastic. The uses of styrene based plastics expanded rapidly in peace time, and polystyrene now one of the least expensive thermoplastic on a cost per volume basis. Styrene is a liquid phase and its easy and safe to be handled. Because the styrene belongs to the active vinyl group, it is easy to be polymerized and copolymerized. When the proper styrene process technology became accessible through licensors, it was quickly flipped into a bulk-commodity chemical, growing to a world-wide capacity estimated at 17 MMT/y in 1993, 18 MMT/y in 1995, and 35 MMT/y in 2015.[1, 2]

1.2 STATEMENT OF THE PROBLEM

Since the demand on styrene product in the world is increasing globally and Kingdom of Saudi Arabia lays out targets for diversification and improving competitiveness in global market, our project enhances this goal by designing a plant that produce 300,000 t/y by the dehydrogenation of ethylbenzene which is the most commercial process used in the world for styrene production. We also can get benefit from sales of the by-products, benzene and toluene.

Material and energy balances will be conducted with manual calculations using the standard procedure by the help of MS-Excel. In addition, simulation of the process using Aspen-Hysys program will be performed for comparison and producing process flow diagrams.

All the equipment in the process flow diagram for styrene production will be sized and some of them will be designed in detail. This design includes chemical and mechanical design and costing, suggestion of appropriate control scheme. Finally, an economic study will be developed in order to demonstrate the feasibility of the project.

CHAPTER 2:
THEORETICAL BACKGROUND

2.1 IMPORTANCE AND USES OF STYRENE

About 65% of world production of styrene is polymerized to make various types of derivatives, each having a wide range of applications across various sectors of the market, it's mostly used to produce 46% Polystyrene, 16% EPS, 14% ABS and the remainder of styrene produced is demonstrated in Figure 2-1.[3]

Specific uses of styrene:

- Acrylonitrile butadiene styrene (ABS): Appliances, automotive parts, pipe, business machines, telephone components.
- Styrene/butadiene co-polymer (SBR): Automobile tires, latex adhesives, wire insulation, footwear.
- Polystyrene (PS): Packaging, domestic appliances, consumer electronics, construction insulation, medical tissue culture trays.
- Styrene-acrylonitrile (SAN): Cosmetics, household containers and mixing bowls, thermally insulated jugs.

Expanded polystyrene (EPS): Household trays and plates, molded sheets for building insulation, packing peanuts.
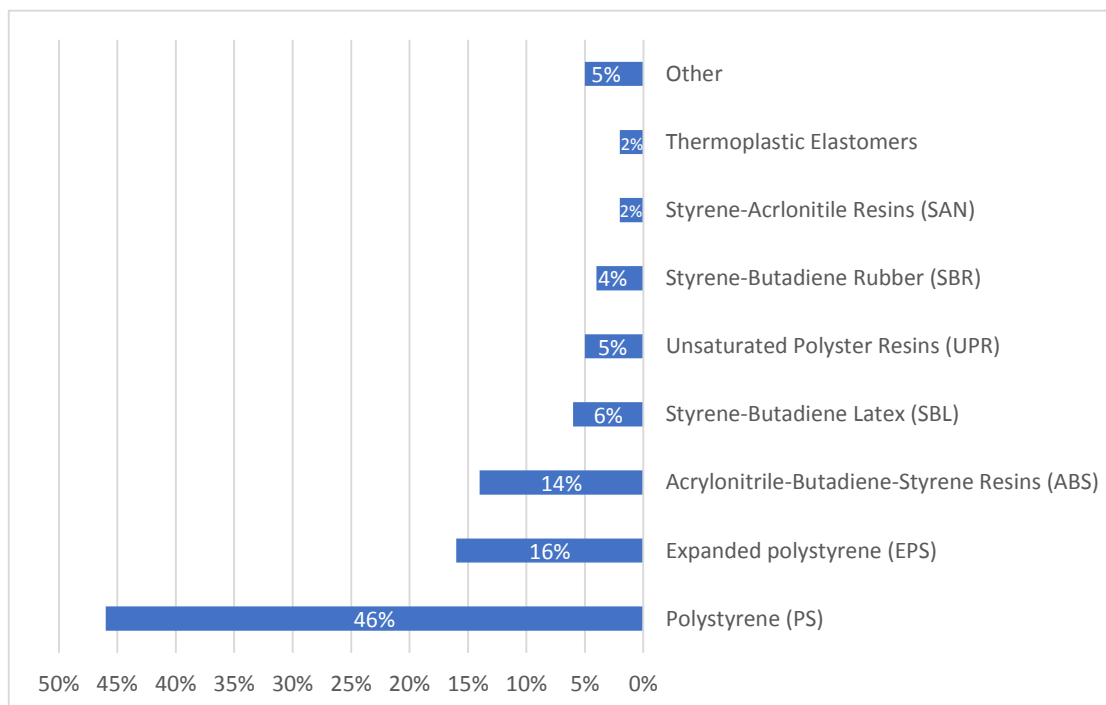
Figure 2-1: Types of styrene polymers.

2.2 PHYSICAL AND CHEMICAL PROPERTIES

It is very mandatory to identify the properties of the materials that we will deal with since the procedure of the production process is strongly dependent on the physical and chemical properties of materials.

2.2.1 Properties of Styrene

At room temperature and pressure, styrene is a clear, colorless liquid. It's an important monomer of synthetic rubber, adhesives and plastics, such as styrene sheet. The physical for styrene are illustrated in the Table 2-1.

Table 2-1: Physical properties for styrene.[4]

Chemical Formula	C_8H_8
Molar mass	104.15 g/mol
Liquid density	0.906 g\L @20 ℃
Vapor pressure	12.4 mm Hg
Form at room temperature	liquid
Color	colorless
Liquid heat capacity	151.29 (J/mol*K)
Melting point	-30 ℃
Boiling point	145 ℃
Vapor specific gravity (vs Air)	3.6 @ 25 ℃
Flash point	31.14 ℃
Solubility in water	0.3 g\L (20℃)
Conductivity	0.035 (W/m*K)
Viscosity @25 ℃	0.695 cP

Stability

Styrene is stable but may polymerize upon exposure to light. Substances to be avoided include strong acids, aluminum chloride, strong oxidizing agents, copper, copper alloys, metallic salts,

polymerization catalysts and accelerators. Flammable, vapor may travel considerable distance to ignition source.

Reactivity

The most important reaction of styrene is its polymerization to polystyrene, but it also copolymerizes with other monomers. The copolymerization with butadiene to give Buna S synthetic rubber (emulsion styrene – butadiene rubber, E-SBR) was the reaction that led initially to the development of the styrene industry. The halohydrins are important intermediates in preparative chemistry. They react with alkali to form styrene oxide, while further hydrolysis leads to phenyl glycol. Iodohydrin is formed from styrene in the presence of iodine, mercury(II) oxide, and water.

1-Phenylethanol is an important intermediate product in the perfume industry (→Flavors and Fragrances). It is formed by the hydration of styrene via quantitative addition of mercury(II) acetate: Numerous reactions of styrene with sulfur and nitrogen compounds have been reported. Thus, styrene reacts with sulfur dioxide, sulfur monochloride, sodium or ammonium dithionite, mercaptans, aniline, amines, diazomethane, and sodium hydrazide to give cleavage of the C=C double bond. Heating styrene with sulfur at high temperature gives hydrogen sulfide, styrene sulfide, and diphenylthiophenes.

Styrene forms solid complexes with copper and silver salts at low temperature. These compounds are suitable for the purification of styrene, or for separating styrene from mixtures with other hydrocarbons. The color of the copper complexes makes this metal and its alloys unsuitable for use in contact with styrene. Styrene also undergoes many cyclization reactions Lithium alkyls, such as C2H5Li, initiate a polymerization of styrene. In the presence of ethers, styrene is polymerized almost completely by sodium. Controlled polymerization (telomerization; →Organometallic Compounds and Homogeneous Catalysis) with olefins has generated a great deal of industrial interest, leading to new polymers that show promise as plasticizers, lubricants, and textile auxiliaries.

Aromatic hydrocarbons such as benzene can be added to styrene in the presence of aluminum chloride, just as they can to other olefins. The high reactivity of the double bond, which is due to the resonance-stabilized aromatic ring, usually means that reactions must be carried out in several steps, with the double bond protected until the final step.

2.2.2 Properties of Ethylbenzene

Ethylbenzene is found in nature as a vapor in the air since it can easily move from water and soil. A median concentration of 0.62 parts per billion (ppb) was found in urban air in 1999. A study conducted in 2012 found that in country air the median concentration was found to be 0.01 ppb and indoors the median concentration was 1.0 ppb. It can also be released into the air through the burning of coal, gas, and oil.

As of 2012, according to the EU Dangerous Substances Directive, ethylbenzene is not classified as hazardous to the environment.

Table 2-2: Physical properties for Ethylbenzene.[5]

Chemical formula	C_8H_{10}
Molar mass	106.17 g/mol
Liquid density	0.8665 g/L @20 ℃
Vapor pressure at 25 ℃	9.998 mmHg
Form at room temperature	liquid
Color	colorless
Liquid heat capacity	183.25 J/(mol*K)
Melting point	−95 ℃
Boiling point	136 ℃
Vapor specific gravity (vs Air)	3.66 @ 25 ℃
Flash point	18 ℃
Solubility in water	0.15 g/L (20 ℃)
Conductivity	0.129 (W/m. K)
Viscosity	0.669 cP

Stability

Ethylbenzene is stable under recommended storage conditions.

Reactivity

It can be vigorous reactions, sometimes amounting to explosions, can result from the contact between aromatic hydrocarbons, such as polyethylbenzene, and strong oxidizing agents. They can react exothermically with bases and with diazo compounds. Substitution at the benzene nucleus occurs by nitration, halogenation (acid catalyst), sulfonation, and the Friedel-Crafts reaction.

2.3 HAZARDS

2.3.1   Hazard of Styrene

ORAL (LD50): Acute: 2650 mg/kg [Rat].

Styrene is considered as flammable material with Auto-Ignition Temperature: 490 ℃, and flash point in closed cup of 31.1 ℃ and 36.7 ℃ in open cup. The lower flammable limit is 1.1 mol% and the upper limit is 6.1 mol%. It's highly flammable in presence of open flames and sparks and slightly explosive in presence of heat. We can use dry chemical powder in small fire or use alcohol foam, water spry or fog.

If there is a release of the styrene, we follow to different approach:
- Small spill: Absorb with an inert material and put the spilled material in an appropriate waste disposal.
- Large spill: Keep away from heat and from sources of ignition, absorb with dry earth, sand or other non-combustible material. Do not touch spilled material and prevent entry into sewers, basements or confined areas.

In handling of styrene, it should be kept away from heat and sources of ignition and ground all equipment containing material and avoid contact with eyes. Wear suitable protective clothing.

Store in a separate safety storage cabinet or room. Keep away from heat. Keep away from sources of ignition. Keep container tightly closed. Keep in a cool, well-ventilated place.[4]

2.3.2   Hazards of Ethylbenzene

ORAL (LD50): Acute: 3500 mg/kg [Rat].

The ethylbenzene considered as flammable material with Auto-Ignition Temperature: 432 ℃, and flash point in closed cup of 15 ℃ and 26.67 ℃ in open cup. The lower flammable limit is between 0.8 – 1.6 mol% and the upper limit between 6.7 – 7 mol%. It's highly flammable in presence of open flames and sparks and slightly explosive in presence of heat. We can use dry chemical powder in small fire or use alcohol foam, water spry or fog.

If there is a release of the ethylbenzene, we follow to different approach
- Small spill: Absorb with an inert material and put the spilled material in an appropriate waste disposal.

- Large spill: Keep away from heat and from sources of ignition, absorb with dry earth, sand or other non-combustible material. Do not touch spilled material and prevent entry into sewers, basements or confined areas.

In handling of ethylbenzene, it should be kept away from heat and sources of ignition and ground all equipment containing material and avoid contact with eyes. Wear suitable protective clothing.

Store in a segregated and approved area and container in a cool and well-ventilated area and keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition. Sensitive to light and in light resistant.[5]

2.4 PRODUCTION CAPACITIES

Asia controls the majority of the market, holding about half of the world's styrene capacity and production. Europe, North America, the Middle East, and Latin America account for the other half of the world's styrene capacity. Saudi Arabia is responsible for about 1,160,000 metric tons per year, which is 3.24% of global production. The world styrene production by country, 2012 is shown in Figure 2-2.[6]

Some of the leading companies active in the worldwide styrene market: Styrolution, Total Petrochemicals, CNPC, Shell, LyondellBasell Chemical Co, Chemicals and Fibre Corp (FCFC), Formosa, Americas Styrenics and Saudi Petrochemical Co (Sadaf).

October 2018 price for Styrene is 1715 $/ton[7], January 2014 price for Ethylbenzene is 1500 $/ton[8].
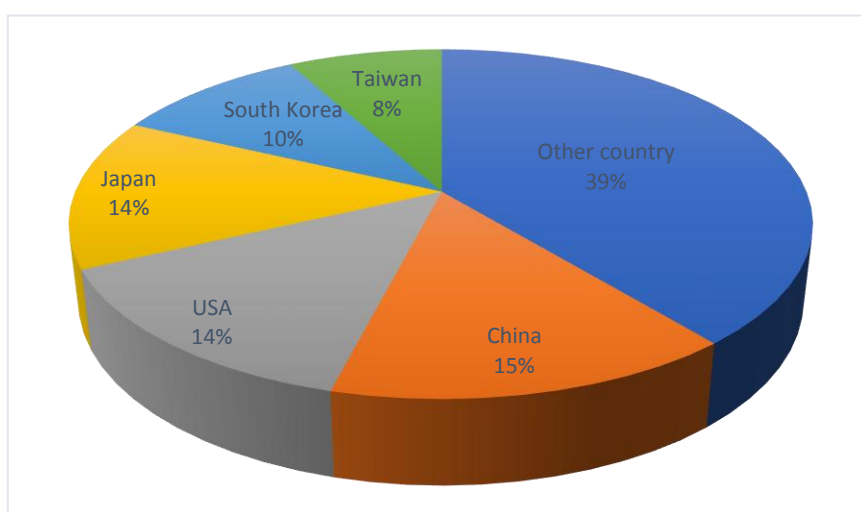
Figure 2-2: World styrene production by country, 2012.

CHAPTER 3:

PRODUCTION TECHNOLOGIES OF STYRENE

Back more than 80 years, production of styrene is world-wide. However, many variations are established on the ancient processes are continually been developed. Investors are building or buying out older processes. Ethylbenzene still is the main feed stock to produce commercial styrene. This ethylbenzene is converted to crude styrene which seeks finishing to separate out the pure product.[1]

3.1 CATALYTIC DEHYDROGENATION OF ETHYLBENZENE

Direct dehydrogenation of ethylbenzene to styrene take place of 85% of commercial production, and can be achieved either adiabatically or isothermally, both methods are used in plants but over 75% of all operating styrene plants perform the dehydrogenation reaction adiabatically.[1]

3.1.1   Adiabatic Dehydrogenation

Styrene reaction:

$$C_6H_5CH_2CH_3 \leftrightarrow C_6H_6CHCH_2 + H_2 \qquad (3.1)$$
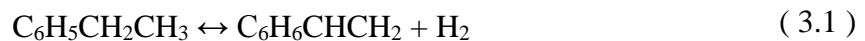
$$\Delta H (600 \ C) = 124.9 \ kJ/mol[1]$$

The reaction is endothermic, reversible and non-equimolar, so low pressures and high temperatures are favorable to high conversion in the adiabatic vapor-phase reactors. Furthermore, ethylbenzene feed is mixed with steam before feeding to the reactors to lower the partial pressure and increase the conversion.

Furthermore, there are some undesirable by-product that are produced by other side reactions occurring in the reactor increasingly with temperature and partial pressures, which are benzene, toluene, ethylene and carbon dioxide.

The major variables must be considered in the design optimization are the steam-to-EB ratio, reactor inlet temperature, reactor size and EB recycle flowrate. High reactor temperature energizes the side reaction, but it will not require more EB recycle to achieve the desired styrene production rate as if the reactors run at low temperature. The side reactions could be suppressed by increasing steam-to-EB ratio but that will increase the furnace fuel cost and steam supply cost.

Reaction Kinetics

The production of styrene is done by the dehydrogenation of ethylbenzene in a high-temperature, gas-phase adiabatic reactor. The reaction is reversible and endothermic, and as it

is a reversible gas-phase reaction producing 2 mol from 1 mol of starting material, low pressure favors the forward reaction to shift equilibrium of the reversible reaction towards the products.

There are several other side reactions that consume EB and produce undesirable by-products.

Benzene/ethylene reaction:

$$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_2 \qquad (3.2)$$
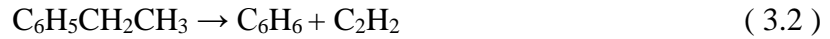
Toluene/methane reaction:

$$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad (3.3)$$
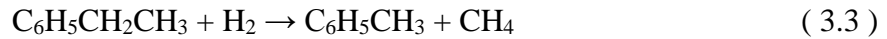
Carbon monoxide reactions:

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2 \qquad (3.4)$$

$$H_2O + CH_4 \rightarrow CO + 3H_2 \qquad (3.5)$$

Carbon dioxide reaction:

$$H_2O + CO \rightarrow CO_2 + H_2 \qquad (3.6)$$

Design Process Flowsheet

Figure 3-1 shows the flowsheet of the process with the conditions derived from the paper by "Vasudevan et al".[9]

The fresh feed is EB, it is combined with a recycle stream of mostly EB, then steam is added to the combined feed. The combined feed is heated in a feed-effluent heat exchanger (E2), which uses the hot reactor effluent to heat the feed stream to 487 °C. Additional low-pressure process steam is heated in a furnace (E1) to 777 °C and mixed with the stream from (E2) to achieve a reactor inlet temperature of 650 °C.
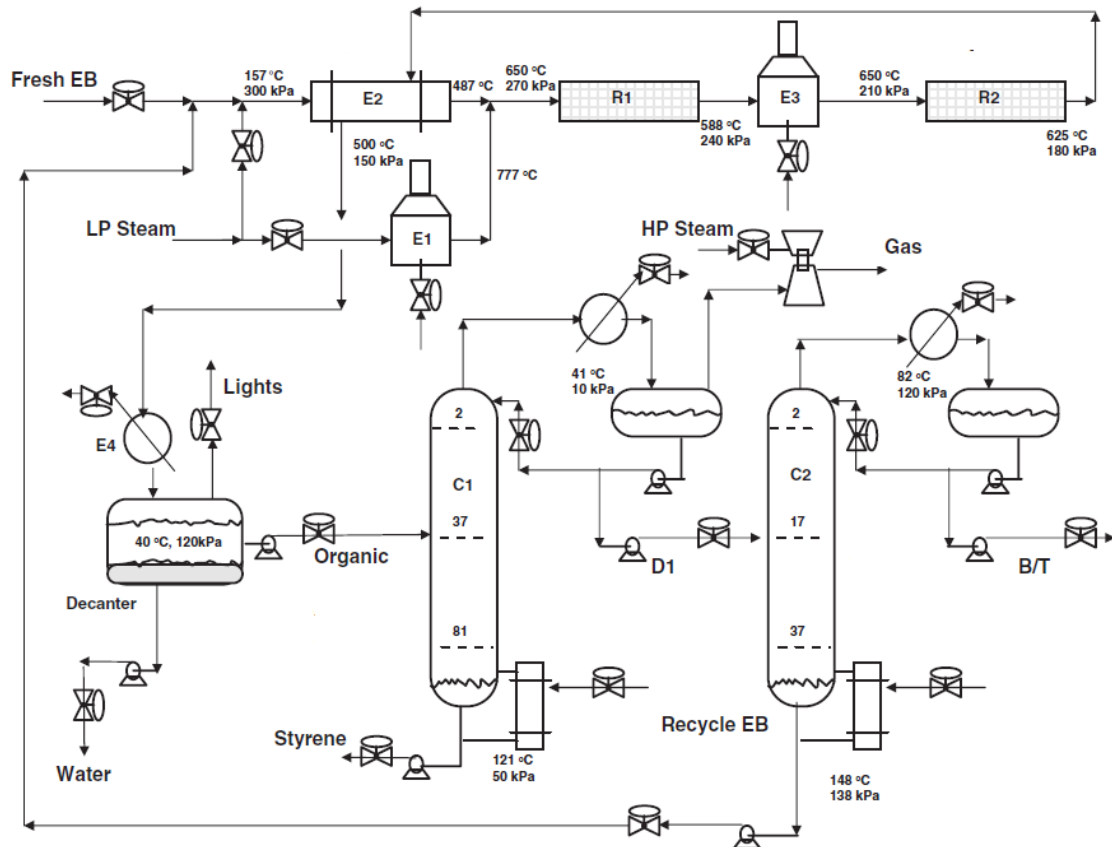
Figure 3-1: "Vasudevan et al." design for styrene production.

Reactors

There are two gas-phase adiabatic reactors in series. The exit temperature of the first reactor is 588 ℃ because of the endothermic reaction. A furnace (E3) heats this stream back up to 650 ℃ before it enters the second reactor.

Many catalysts maybe use for this reaction. One catalyst, Shell 105, dominated the market for many years, and was the first to include potassium as a promoter for the water-gas reaction. This catalyst is typically 84.3 wt% iron as Fe_2O_3, 2.4 wt% chromium as Cr_2O_3, and 13.3 wt% potassium as K_2CO_3. It has good physical properties and good activity, and it gives fair yields.

Product Separation

After being cooled in (E2) and partially condensed in heat exchanger (E4) using cooling water, the process stream enters a decanter operating at 40 ℃ and 120 kPa, were water is withdrawn from the bottom of the decanter. The gas phase ("Lights") leaving the top of the decanter contains most of the hydrogen formed in the basic reaction, but it also contains significant amounts of other component; styrene and EB also losses.

Product Purification

The organic phase is fed to the distillation column (C1) having EB, styrene, benzene, toluene, water, and a small amount of some of the light components.

The two design specifications for the column are a bottoms purity of 99.75 mol% styrene and a distillate impurity of 1 mol% styrene.

The bottoms stream from column (C1) is fed to distillation column (C2), which recovers EB for recycle. The two design specifications are a bottoms impurity of about 1 mol% toluene and a distillate impurity of about 1 mol% EB. The distillate is mostly benzene and toluene with some water. The bottoms are recycled back to the reaction section. The column operates at 120 kPa.[10]

3.1.2   Isothermal Dehydrogenation

The majority of industrial production of styrene follows from the dehydrogenation of ethylbenzene. This dehydrogenation process involves the catalytic reaction of ethylbenzene. In the isothermal process, as shown in Figure 3.2, fresh ethylbenzene is mixed with a recycle stream and vaporized. Steam is then added before feeding the effluent into a train of 2 to 4 reactors. This process involves a highly endothermic reaction carried out in the vapor phase over a solid catalyst. Steam is used to provide heat of this reaction, to prevent excessive coking or carbon formation, to shift equilibrium of the reversible reaction towards the products, and to clean the catalyst of any carbon that does form. The reactors are run isothermally at 600 ℃ in multiple reactors with steam added before each stage with typical yields of 88-94%.

Crude styrene from the reactors is then fed into a distillation train. Because of the possibility of polymerization of the styrene during distillation, small residence time, avoidance of high temperature, and addition of inhibitor are necessary.

Some companies use the oxidation of ethylbenzene as an alternative to dehydrogenation. This reaction path produces water as a by-product as opposed to hydrogen and is therefore an exothermic reaction. 5% of styrene is produced by oxidation.[1]
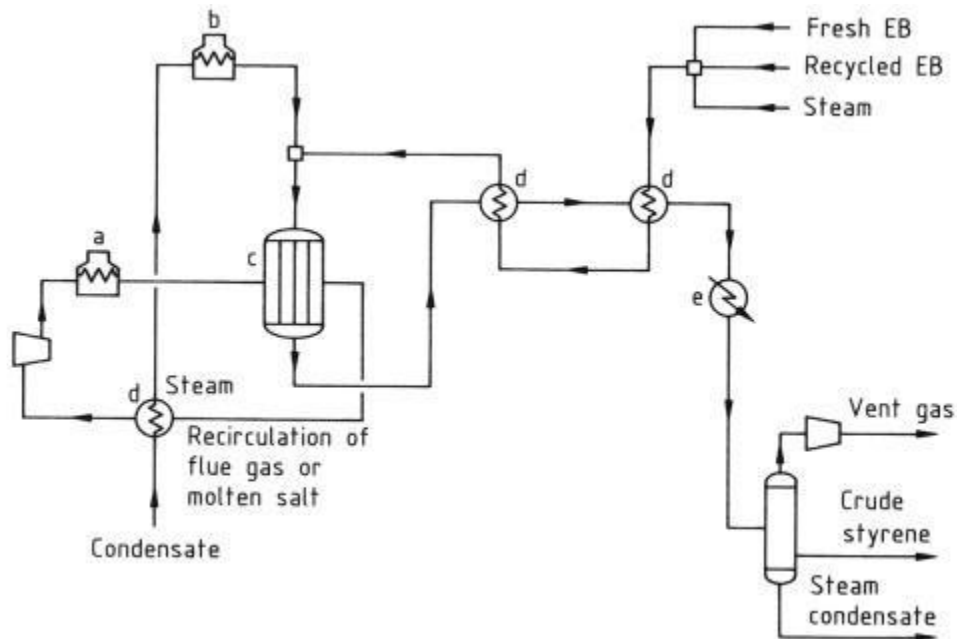
Figure 3-2: Isothermal dehydrogenation of ethylbenzene (EB).[1]

a) Heater; b) Steam super heater; c) Reactors; d) Heat exchanger; e) Condenser

Reaction Kinetics

Dehydrogenation of ethylbenzene to styrene:

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH=CH_2 + H_2 \tag{3.7}$$
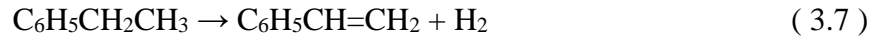
Enthalpy (600 C) = 124.9 kJ/mol

Side reactions:

$$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4 \tag{3.8}$$

$$C_6H_5CH_2CH_3 \rightarrow 8\ C + 5\ H_2 \tag{3.9}$$

$$C_6H_5CH=CH_2 + 2\ H_2 \rightarrow C_6H_5CH_3 + CH_4 \tag{3.10}$$
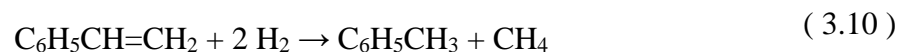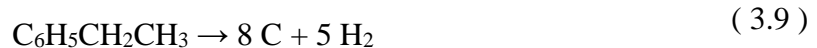
3.2 STYRENE / PROPYLENE OXIDATION PROCESS

This process is for co-production of propylene oxide and styrene monomer and it's concerned in to improve the recovery of 1-phenyl ethanol and the styrene from heavy residual stream by the acid treatment and cracking. Also uses different distillation steps to separate unreacted reagents and caustic treatment to reduce the acidic characteristics of the streams.

The patents issued to ARCO and Shell but the first development of the process was by ARCO and this process that will be explain in detail is ARCO's and about 15% of the world uses this process to produce styrene.
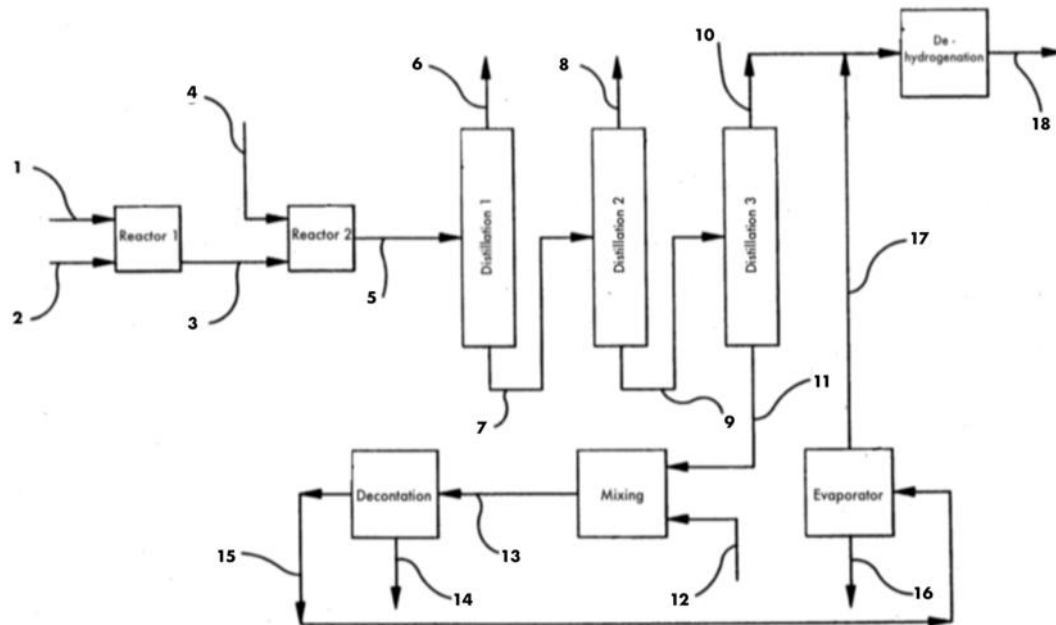
Figure 3-3: Styrene / propylene oxidation process.[11]

Reaction Kinetics

$$C_6H_5C_2H_5 + O_2 \rightarrow C_6H_5CH(OOH)CH_3 \qquad (3.11)$$

$$C_6H_5C_2H_5 + 1/2\ O_2 \rightarrow C_6H_5CH(CH_3)OH \qquad (3.12)$$

$$C_6H_5C_2H_5 + xO_2 \rightarrow C_6H_5CO(CH_3) + acids \qquad (3.13)$$

$$C_6H_5CH(OOH)CH_3 + C_3H_6 \rightarrow C_3H_6O + C_6H_5CH(CH_3)OH \qquad (3.14)$$

$$C_6H_5CO(CH_3) + H_2 \rightarrow C_6H_5CH(CH_3)OH \qquad (3.15)$$

$$C_6H_5CH(CH_3)OH \rightarrow C_6H_5CH=CH_2 + H_2O \qquad (3.16)$$
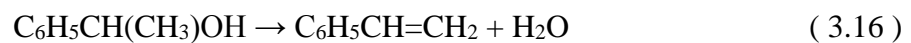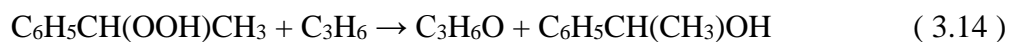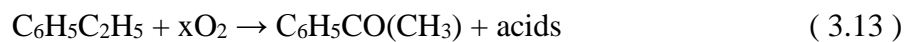
Design Process Flowsheet Details

As shown is Figure 3.3, reactor 1 is fed with ethylbenzene via line 1 and oxidized occurs to form ethylbenzene hydro peroxide by reaction with molecular oxygen fed via line 2 with Oxidation conditions in reactor 1 are 135°-145 ℃ and 50-55 psig.

The reaction mixture from reactor 1 contain of unreacted ethylbenzene, ethylbenzene hydro peroxide, 1-phenyl ethanol, acetophenone and heavies carried via line 4 to be fed into

epoxidation Reactor 2 where the ethylbenzene hydro peroxide is catalytically reacted at range 95 ℃ to 115 ℃ and 600 psia with propylene via line 4 to form propylene oxide (line 5).

The epoxidation reaction mixture (reactor 2) is treated with aqueous caustic to neutralize acidic materials and to remove the epoxidation catalyst (not shown) and the treated epoxidation reaction mixture comprised of unreacted propylene, propylene oxide, ethylbenzene, 1-phenyl ethanol, acetophenone and heavy materials flowing via line 7 to distillation 1. In distillation 1, the overhead is the unreacted propylene and product propylene oxide is separated via line 6.

The bottoms fraction contained of ethyl benzene, 1-phenyl ethanol, acetophenone and heavies is removed from distillation 1 via line 7 into distillation 2. the overhead ethyl benzene stream is separated from distillation 2 via line 8 and can be recycled to reactor 1.

The bottoms stream from distillation 2 contained of 1-phenyl ethanol, acetophenone and heavies flowing via line 9 to distillation 3. The overhead fraction from distillation 3 contained of 1-phenyl ethanol and acetophenone is separated via line 10 the combined streams from distillation 2 and evaporator unit are reacted in dehydration and cracking zone 16 at 200°-230 ℃ and 100 -300 mmHg and passed to dehydration unit where 1-phenyl ethanol is converted to styrene monomer which is recovered via line 18.

The bottoms stream from distillation 3 flowing via line 11 to mixing unit where it is mixed with aqueous sulfuric acid which is fed via line 12.

The admixture from mixing unit exiting via line 13 to decantation 24 where the immiscible phases are separated. The aqueous sodium-containing phase is separated by means of line 14 and may be further treated or discarded. The organic phase reduced in sodium is removed via line 15 and passes to wiped film evaporator unit where up to 40% by weight of the stream is separated as a distillate fraction via line 17 a vapor stream is separated at 175 ℃ and 50 mmHg.

This fraction contains various 1-phenyl ethanol condensation products, some 1-phenyl ethanol, esters and the like. In this embodiment, the distillate fraction passes to dehydration unit wherein components of the distillate are cracked and/or dehydrated to provide supplemental styrene monomer values. The heavy bottoms from wiped film evaporator unit is recovered via line 16 and represents an upgraded stream suitable as heavy fuel.[12]

3.3 TOLUENE ALKYLATION WITH METHANOL

As shown in Figure 3-4, the fresh methanol and toluene are entered to fired heater then the out of heater are get in alkylation reactor at 425 ℃ and 1 atm pressure, The overall reaction is

endothermic and the catalyst used is zeolite catalyst, then the product from reactor is send it to feed/effluent interchanger with toluene recycle from toluene recovery column, then get to cooler, after cooling and gas off is fed to phase separator to separate water from product then fed to toluene recovery column the result from bottom is fed to EB/SM splitter and the top is toluene recycle to feed/effluent interchanger, then we splitter the EB from top and SM from bottom then the product from bottom is fed to SM column to get our product (SM) from top and C6+ aromatic from bottom.

$$2C_6H_5CH_3 + O_2 \rightarrow C_6H_5CH=CHC_6H_5 + 2H_2O \qquad (3.17)$$
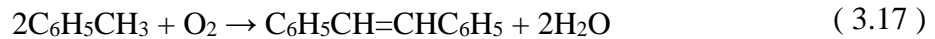
$$\Delta H = -77.26 \text{ kJ/g.mol}$$

Stilbene ($C_6H_5CH=CHC_6H_5$) is then reacted with ethylene over a molybdenum catalyst to give styrene:

$$C_6H_5CH=CHC_6H_5 + C_2H_4 \rightarrow 2C_6H_5CH=CH_2 \qquad (3.18)$$

$$\Delta H = -15.99 \text{ kJ/g.mol}$$
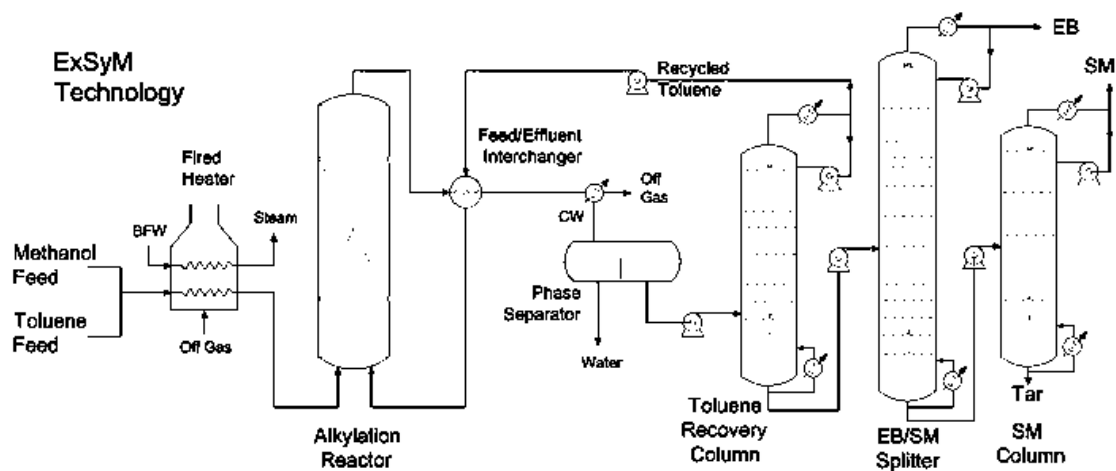
Figure 3-4: Toluene alkylation with Methanol process.

3.4 PROCESS SELECTION

Table 3-1 shows a comparison between the two process of styrene production by dehydrogenation of ethylbenzene and propylene oxide depending on simplicity, economics and using.

Table 3-1 : Comparison between two different process of styrene processes used world-wide.

Criteria	Dehydrogenation of ethylbenzene	Propylene oxide
Using	Uses by around 85% of styrene production	Around 15 % of styrene production
Economic	Need high amount of utilities	Requires high capital cost
Simplicity	One stage to produce styrene	PO>EBHP>MPA>Styrene

According to this comparison, the best process is dehydrogenation of ethylbenzene.

Direct dehydrogenation of ethylbenzene to styrene accounts for 75% of commercial production, and it was chosen for this project mainly for the following reasons:[1]

1. It accounts for 75% of commercial production of styrene and it has proved its effectiveness.[1]
2. Its relatively better for environmental and economic considerations.[1]
3. Availability of the process information and description is more than the other processes.[1]
4. Possibility to sell benzene and toluene as by-products.

3.4.1   Process Description

Figure 3-5 shows the process flow sheet of the styrene production process for this project, the fresh feed to the plant is composed of 99.7% Ethylbenzene and 0.3% Benzene at 30 ℃. It is combined with the recycled stream containing mainly Ethylbenzene with styrene and Toluene then enters to a second mixer with steam. The ethylbenzene to water ratio in the reactor influent is adjusted to 1:15.

The combined stream is then fed to two reactors where the total conversion in both of them to ethylbenzene is 64%. The reactor will be run at high temperature of 650 ℃ since the reaction is endothermic and the pressure of the reaction is slightly above atmospheric. The selectivity to styrene, Benzene and Toluene are 76.6%, 10.6% and 12.8% respectively.

The reactor's outlet is cooled, then fed to a three-phase decanter that will separate most of the water to the heavy liquid stream and all the non-condensable gases from the top of the three-phase decanter will be removed and maybe used as secondary fuel. The oil stream is fed to distillation column 1, the first distillation will separate styrene as the main product with the required concentration of 99.75% and the recovery is 97%. The top product of the first

distillation column is sent to a second distillation which separates ethylbenzene to be recycled to the reactor and toluene benzene streams that will be further separated in another distillation to be sold as by-product.
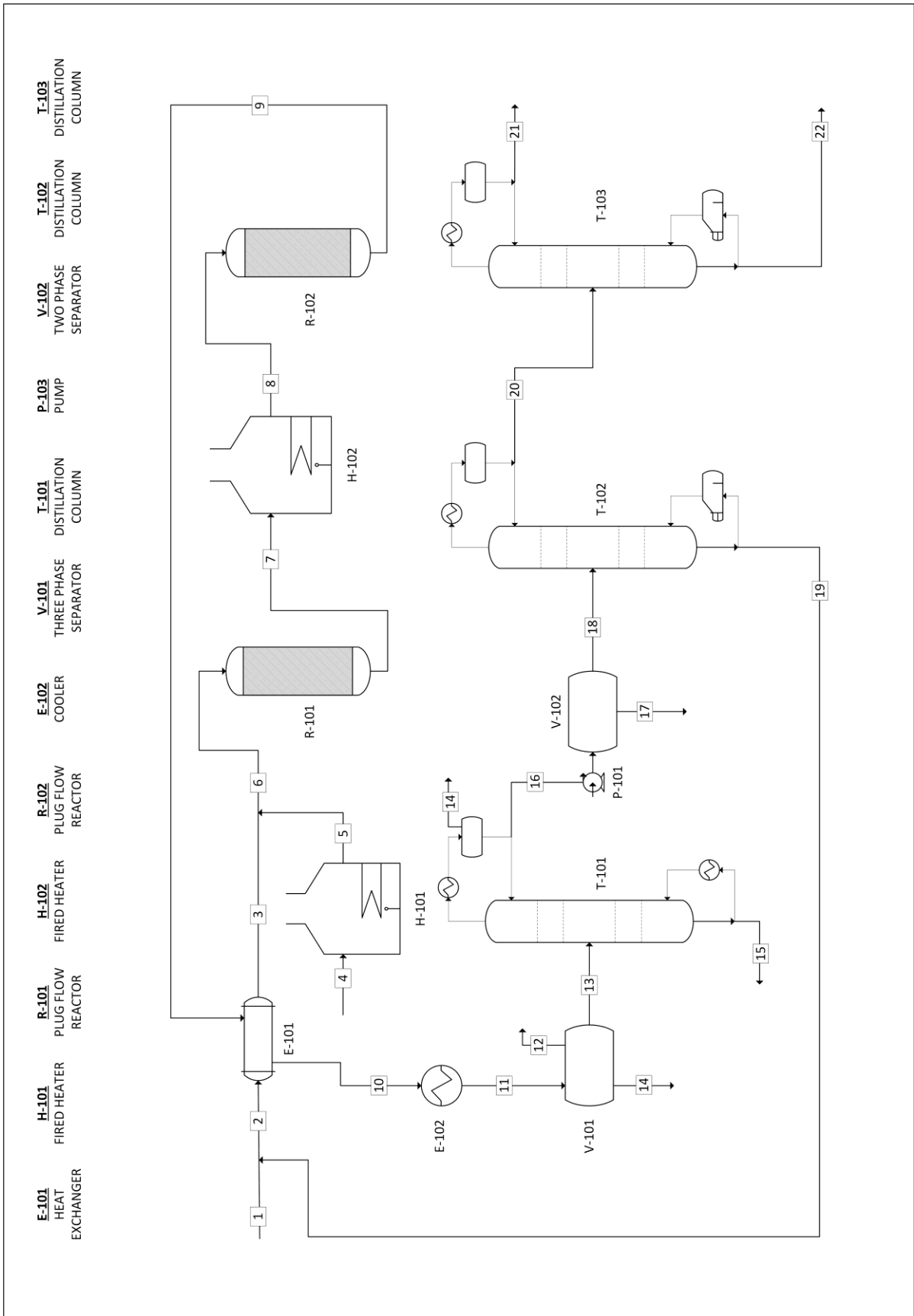
Figure 3-5: Process Flow Diagram of Styrene Production.

CHAPTER 4:

MATERIAL AND ENERGY BALANCE

4.1 MATERIAL BALANCE

Material balance was conducted using spread sheet. A basis of 150 kmol/h of fresh feed was used. The results of the material balance are shown in Tables 4.1-4.8 where the mole flow rate kmol/h and mass flow rate in kg/h.

Scale-up was done after finishing the calculation, in order to have a final annual production rate of 100,000 ton of ST.

- Production:
  - 100,000 tons per year of styrene as final product.
- Reactor:
  - The reaction temperature is 650 ℃.
  - The reaction pressure is 2.7 bar.
  - All C_1 generated from reaction (3.3) will react completely with H_2O to form CO and H_2.
  - All CO generated in reaction (3.4) will react to form CO_2.
  - The selectivity of EB to ST, BZ and TO is 76.6%, 10.6% and 12.8% respectively.
- Three phase separator:
  - 99.7% of the water will be removed from the heavy liquid stream.
- Distillation column 1:
  - The purity of ST is 99.75%.
  - The ST recovery is 97%.
  - All non-condensable gases are in the gas stream from condenser.
- Distillation column 2:
  - EB recovery 98%.
  - TO recovery 95%.

4.1.1   Components Flow Rates

Table 4-1 to Table 4-8 show the final results for the material balance calculations. Input and output streams to the process are written in bold.

Table 4-1: Flow of Stream (1-3).

Component	1 (Fresh Feed)		2 (From Mix 1)		3 (HE Outlet)	
	Mole	Mass	Mole	Mass	Mole	Mass
EB	180.77	19192.47	274.55	29148.49	274.55	29148.49
ST	-	-	4.06	422.51	4.06	422.51
BZ	0.54	42.49	0.54	42.49	0.54	42.49
TO	-	-	1.11	102.44	1.11	102.44
H_2	-	-	-	-	-	-
C2	-	-	-	-	-	-
CO_2	-	-	-	-	-	-
W	-	-	-	-	-	-
C1	-	-	-	-	-	-
CO	-	-	-	-	-	-
Total	**181.32**	**19234.96**	280.26	29715.93	280.26	29715.93

Table 4-2: Flow of Stream (4-6).

Component	4 (Fresh Water)		5 (H-101 Outlet)		6 (Feed to R-101)	
	mole	mass	Mole	mass	mole	mass
EB	-	-	-	-	274.55	29148.49
ST	-	-	-	-	4.06	422.51
BZ	-	-	-	-	0.54	42.49
TO	-	-	-	-	1.11	102.44
H_2	-	-	-	-	-	-
C2	-	-	-	-	-	-
CO_2	-	-	-	-	-	-
W	4118.26	74191.60	4118.26	74191.60	4118.26	74191.60
C1	-	-	-	-	-	-
CO	-	-	-	-	-	-
Total	**4118.26**	**74191.60**	4118.26	74191.60	4398.52	103907.53

Table 4-3: Flow of Stream (7-9).

Component	7 (R-101 Outlet)		8 (H-102 Outlet)		9 (R-102 Outlet)	
	mole	mass	mole	mass	mole	mass
EB	244.24	25930.03	244.24	25930.03	98.84	10493.46
ST	27.28	2841.04	27.28	2841.04	138.65	14440.93
BZ	3.76	293.50	3.76	293.50	19.17	1497.40
TO	4.99	459.97	4.99	459.97	23.60	2174.80
H_2	34.86	70.27	34.86	70.27	202.07	407.31
C2	3.21	90.15	3.21	90.15	18.63	522.52
CO_2	3.88	170.77	3.88	170.77	22.49	989.84
W	4110.50	74051.79	4110.50	74051.79	4073.28	73381.23
C1	-	-	-	-	-	-
CO	-	-	-	-	-	-
Total	4432.72	103907.52	4432.72	103907.52	4596.73	103907.48

Table 4-4: Flow of Stream (10-12).

Component	10 (Outlet from HE)		11 (Feed to V-101)		12 (V-101 Water)	
	Mole	Mass	Mole	Mass	Mole	Mass
EB	98.84	10493.46	98.84	10493.46	0.10	10.95
ST	138.65	14440.93	138.65	14440.93	0.21	21.91
BZ	19.17	1497.40	19.17	1497.40	1.68	131.01
TO	23.60	2174.80	23.60	2174.80	0.41	37.42
H_2	202.07	407.31	202.07	407.31	0.06	0.12
C2	18.63	522.52	18.63	522.52	0.39	10.89
CO_2	22.49	989.84	22.49	989.84	2.81	123.50
W	4073.28	73381.23	4073.28	73381.23	4061.06	73161.08
C1	-	-	-	-	-	-
CO	-	-	-	-	-	-
Total	4596.73	103907.48	4596.73	103907.48	**4066.71**	**73496.89**

Table 4-5: Flow of Stream (13-15).

Component	13 (V-101 Gases)		14 (V-101 Oil)		15 (Non-cond. Gases)	
	Mole	Mass	Mole	Mass	Mole	Mass
EB	2.72	289.30	96.01	10193.21	-	-
ST	3.21	334.45	135.23	14084.56	-	-
BZ	1.15	90.21	16.34	1276.18	-	-
TO	0.96	88.71	22.23	2048.67	-	-
H_2	202.01	407.18	0.00	0.01	3.8E-03	7.7E-03
C2	18.24	511.57	0.00	0.06	2.1E-03	6.0E-02
CO_2	19.67	865.63	0.02	0.70	1.6E-02	7.0E-01
W	0.63	11.41	11.59	208.74	-	-
C1	-	-	-	-	-	-
CO	-	-	-	-	-	-
Total	**248.60**	**2598.47**	281.42	27812.12	**0.02**	**0.77**

Table 4-6: Flow of Stream (16-18).

Component	16 (Styrene Product)		17 (Feed To V-102)		18 (V-102Water)	
	Mole	Mass	Mole	Mass	Mole	Mass
EB	0.33	34.90	95.68	10158.30	0.00	0.03
ST	131.17	13662.02	4.06	422.54	0.00	0.06
BZ	-	-	16.34	1276.18	0.00	0.37
TO	-	-	22.23	2048.67	0.00	0.11
H_2	-	-	0	0	1.7E-04	3.4E-04
C2	-	-	0	0	1.1E-03	3.1E-02
CO_2	-	-	0	0	8.0E-03	3.5E-01
W	-	-	11.59	208.74	11.55	208.11
C1	-	-	-	-	-	-
CO	-	-	-	-	-	-
Total	**131.50**	**13696.93**	149.90	14114.42	**11.57**	**209.06**

Table 4-7: Flow of Stream (19-21).

Component	19 (Feed to T-102)		20 (Feed To T-103)		21 (Recycled EB)	
	Mole	Mass	Mole	Mass	Mole	Mass
EB	95.69	10159.21	1.91	203.18	93.78	9956.02
ST	4.06	422.51	0.00	0.00	4.06	422.51
BZ	16.33	1275.92	16.33	1275.92	-	-
TO	22.23	2048.75	21.12	1946.31	1.11	102.44
H_2	-	-	-	-	-	-
C2	-	-	-	-	-	-
CO_2	-	-	-	-	-	-
W	0.03	0.63	0.03	0.63	-	-
C1	-	-	-	-	-	-
CO	-	-	-	-	-	-
Total	138.35	13907.02	39.41	3426.05	98.94	10480.97

Table 4-8: Flow of Stream (22-23).

Component	22 (Benzene Product)		23 (Toluene Product)	
	Mole	Mass	Mole	Mass
EB	0.00	0.00	1.91	203.18
ST	0.00	0.00	-	-
BZ	16.01	1250.40	0.33	25.52
TO	0.42	38.93	20.70	1907.39
H_2	-	-	-	-
C2	-	-	-	-
CO_2	-	-	-	-
W	0.03	0.63	-	-
C1	-	-	-	-
CO	-	-	-	-
Total	**16.46**	**1289.96**	**22.94**	**2136.09**

4.1.2 Decanter Material Balance

After all the products flow out of the second reactor, the water and gases should be removed so, that only the organics enter the first distillation column. For this purpose, the decanter was used before the distillation column.

The water will be removed carrying some of the other component as a liquid from the bottom of the decanter. The liquid organic phase, in equilibrium with the vapor, will be withdrawn from the side of the decanter, while the vapor phase exits the decanter at the top.

To do this process properly, several steps should be considered as follow:

First, water removal calculated by knowing the solubility of each component to know the amount of each component leaving with the water, which is assumed to be 99.7% of the inlet water to decanter. All calculations are shown in

Table 4-9: Flash calculations.

Flash calculation 1		
Comp.	solubility	Amount, kmole/h
EB	0.0000254	0.103150856
ST	0.0000518	0.210362769
BZ	0.000413	1.67721667
TO	0.0001	0.406105731
H_2	0.0000144	0.058479225
C2	0.0000956	0.388237079
CO_2	0.000691	2.806190604

In flash process, after water removal, the gas-vapor will be separated so that the rest of components can exit as or by following calculations:

K_i is the equilibrium ratio, it should be calculated by following equation:

for gas:

$$K_i = \frac{H}{P}$$

(4.1)

Where H is Henry's constant and P is partial pressure.

For Vapors:

The saturated pressure obtained by Antoine equation:[12]

$$P^{sat} = \exp\left(A - \frac{B}{C + T}\right) \tag{4.2}$$

Where P in bar and T in Celsius. A, B and C are Antoine's constant[12] for organic component.

$$K_i = \frac{P^{sat}}{P} \tag{4.3}$$

Then use this equation to get the K_i for vapors.

The composition of the liquid phase is then calculated by the following equation by assuming a suitable value of $\frac{L}{V}$.

$$x_i = \frac{z\left(\frac{L}{V} + 1\right)}{\left(\frac{L}{K_i V} + 1\right)} \tag{4.4}$$

Where L is the liquid flow rate in kmol/h and V is the flow rate of the vapor in kmol/h.

Trial and error procedure will be followed until the summation of all compositions in the liquid phase $(\sum xi)$ is equal to 1. By applying the function "goal seek" in MS-Excel software the value of $(\frac{L}{V})$ was determined to be 1.132. All results are shown in Table 4-10 and Table 4-11.

Table 4-10: Decanter material balance (1).

Parameters	EB	S	B	T
Phase	Liquid	Liquid	Liquid	Liquid
A	7.16	6.95	6.88	6.95
B	1,559.6	1,443.9	1,196.8	1,342.3
C	228.58	210.04	219.16	219.19
H (bar)	-	-	-	-
P_{sat} (kPa)	3.86	3.23	9.60	5.88
K	32.1E-3	26.9E-3	80.0E-3	49.0E-3
z	0.186	0.261	0.033	0.044
y_i	11.0E-3	12.9E-3	4.6E-3	3.9E-3
x_i	0.341	0.481	0.058	0.079

Table 4-11: Decanter material balance (2).

Parameters	H2	C2	CO_2	W
Phase	Gas	Gas	Gas	Liquid
A	-	-	-	16.39
B	-	-	-	3,885.7
C	-	-	-	230.17
H (bar)	71,600	11,550	1,670	-
P_{sat} (kPa)	-	-	-	7.42
K	59,667	9,625	1,392	61.9E-3
z	0.381	0.034	0.037	0.023
y_i	0.813	0.073	0.079	2.5E-3
x_i	13.6E-6	7.6E-6	56.9E-6	0.041

4.2 ENERGY BALANCE

The energy balance is done in a spreadsheet using Microsoft Excel. A references state is taken at 25 °C as a liquid phase for EB, ST, BZ, TO and W, and as a gas phase for H_2, C_2 and CO_2.

The calculation is done by the following equation:

$$H_i = (n_i x_i) \left[\int_{T_{ref}}^{T_b} c_{p_i} dT + H_{vap} + \int_{T_b}^{T_i} c_{p_i} dT \right] \qquad (4.5)$$

Where H_i is the enthalpy of stream i, n_i is the molar flowrate of components, c_{p_i} is the specific heat, T_i is the temperature for stream i, and T_{ref} is the temperature at reference state which is 25 °C.

Two reactors shown in Figure 5-1 were used to reduce the volume of each reactors and reduce the cost of catalyst to give the designed overall conversion of EB. The main reason for using 2 reactors is to reheat the stream between them since it is endothermic process. Thus, the rate could be increased to reach the desired conversion using reasonable amount of catalyst.

In case of phase change the heat of vaporization is added to the above equation. For assumptions, the specific heat c_{p_i} for liquid is taken as constant. The specific heat for vapor, c_{p_v} is equals to $(A + BT + CT^2 + DT^3)$. Where A, B and C is constants gathered from Coulson's Handbook. All constant is listed in Table 4-12. Boiling point temperature, specific heat for liquids and heat of vaporization at normal boiling point are listed in Table 4-13.[13]

Table 4-12: Vapor specific heat constant.

Component	Constant for c_{p_v}			
	A	**B**	**C**	**D**
1. EB	-43.10	7.07E-01	-4.81E-04	1.30E-07
2. S	-28.25	6.16E-01	-4.02E-04	9.94E-08
3. B	-33.92	4.74E-01	-3.02E-04	7.13E-08
4. T	-24.36	5.12E-01	-2.77E-04	4.91E-08
5. H₂	27.14	9.27E-03	-1.38E-05	7.65E-09
6. C₂H₄	3.81	1.57E-01	-8.35E-05	1.76E-08
7. CO₂	19.80	7.34E-02	-5.60E-05	1.72E-08
8. W	32.24	1.92E-03	1.06E-05	-3.60E-09
9. CH₄	19.25	0.05	1.2E-05	-1.13E-08
10. CO	30.87	-0.01	2.79E-05	-1.28E-08

Table 4-13: Components properties.

Component	T_b, °C	c_{p_i}, J/mol.C	H_{vap}, J/mol
1. EB	136	182.61	35588
2. S	145	183.31	36844
3. B	80	173.41	30781
4. T	111	115.18	33201
5. H₂	-253	-	-
6. C₂H₄	-104	-	-
7. CO₂	-79	-	-
8. W	100	75.30	40683
9. CH₄	-161.5	-	-
10. CO	-191.5	-	-

The stream number 9 will be taken for a sample of calculations. Its flow rate 4,596,726 mol/h and it contains 2.15 mol% EB, 3.02 mol% ST, 0.42 mol% BZ, 0.51 mol% TO, 4.4 mol% H_2, 0.41 mol% C_2, 0.49 mol% CO_2 and 88.61 mol% W at 625 °C. Energy balance equation (4.5) is used for the calculations.

The first two terms which is for liquid and vaporization heat is equal to zero for components with gas reference state. Ethylbenzene and hydrogen detailed calculation steps is as follow:

EB: $H_{liquid} = 182.6 * (409 - 298) = 20268$ J/mol

$H_{vaporization} = 35588$ J/mol

$H_{vapor} = \int_{409}^{898} (-43.1) + 7.07 \times 10^{-1}T + (-4.81 \times 10^{-4}) T^2 + 1.3 \times 10^{-7} T^3$

$= 119943$ J/mol

$H_{EB} = (n_i x_i) [H_{liquid} + H_{vaporization} + H_{vapor}]$

$= (4,596,726 * 0.0215) [20,268 + 35588 + 119943]$

$= 1.737 \times 10^{10}$ J/mol $= 17.37$ GJ/h

H₂: $H_{liquid} = 0$

$H_{vaporization} = 0$

$H_{vapor} = \int_{298}^{898} (27.14) + 9.27 \times 10^{-3}T + (-1.38 \times 10^{-5}) T^2 + 7.65 \times 10^{-9} T^3$

$= 17,629$ J/mol

$H_{H_2} = (n_i x_i) [H_{liquid} + H_{vaporization} + H_{vapor}]$

$= (4,596,726 * 0.044) [0 + 0 + 17,629]$

$= 3.56 \times 10^9$ J/mol $= 3.56$ GJ/h

The same procedure to calculate the enthalpies for ST, BZ, TO, C2, CO2 and W in this stream is done and founded to be 23.28, 2.42, 3.47, 0.78, 0.63 and 267.63 GJ/h, respectively. The enthalpy for stream 9 is:

$$H_9 = \sum H_i = 319 \ GJ/h$$

The same steps are followed for all process stream to calculate the enthalpies. All energy balance results are listed in Table 4-14.

Table 4-14: Energy balance of the process results.

Steam number/ Equipment	Temperature, °C	flow rate, kmol/h	Energy/ Duty, GJ/h
1	25	181.32	0.00
2	71	280.26	2.36
3	600	280.26	47.12
4	144	4118.26	197.01
H-101	-	-	81.90
5	675	4118.26	278.91
6	650	4398.52	326.03
R-101	-	-	-15.47
7	588	4433.49	310.56
H-102	-	-	15.63
8	650	4433.49	326.19
R-102	-	-	-5.32
9	625	4596.73	320.87
10	438	4596.73	276.12
E-101	-	-	-268.93
11	40	4596.73	7.18
12	40	248.60	1.87
13	40	281.42	0.73
14	41	0.02	0.00
15	121	131.50	2.30
16	41	149.90	390E-03
17	41	11.57	10E-03
18	41	138.35	380E-03
19	156	98.94	2.36
20	82	39.41	320E-03
21	80	16.46	160E-03
22	126	22.94	980E-03

4.2.1 Heat of Reactions

The heat of reaction will be temperature dependent inside the reactor which will change with respect to space time, so, this change could be taken into account by using following equation:

$$H_i = \int_{T_{ref}}^{T_i} n_i C_{pi} \, dT \qquad (4.6)$$

Where ΔH_{298i}° is the standard heat of reaction at 298.15 K in kJ/kmol and the constants a_i, b_i, c_i and d_i in unit of kJ/kmol.K, kJ/kmol.K^2, kJ/kmol.K^3 and kJ/kmol.K^4 , respectively, and boiling points of each components are shown in Table 4-13.

ΔH_{298i}° is calculated by:

$$\Delta H_{298i}^{\circ} = \sum_{product} \Delta H_{fi}^{\circ} - \sum_{reactant} \Delta H_{fi}^{\circ} \qquad (4.7)$$

Where ΔH_{fi}° is the heat of formation of component i in (J/mol). Values of the heat of formation for each component and specific heat of components are shown in Table 4-15.

Table 4-15: Vales of heat of formation at 25 ℃ and specific heat.[13]

Components	heat of formation (J/mol)	C_p, (J/mol. ℃)
1. EB	29,920	182.61
2. S	147,360	183.31
3. B	82,930	173.41
4. T	50,170	115.18
5. H$_2$	0	0
6. C$_2$H$_4$	-52,510	0
7. CO$_2$	-393,509	0
8. W	-241,818	75.30
9. CH$_4$	-74,520	0
10. CO	-110,525	0

$$\Delta H_{298i}^{\circ} = (147360 + 0) - (29920) = 117440 \frac{J}{mol}$$

To calculate the heat of reaction for each reaction, the recreant should be cooled to 25 ℃ then add the standard heat of reaction, then heat up to the reaction temperature again, this is the followed approach to calculate the heat of reaction.

From equation (4.6):

$$\Delta H_{ri} = \Delta H^{\circ}_{298i} + (n_{ri})\left[H_{product(i)} - H_{reactent(i)}\right]$$

$$H_i = \left[H_{liquid} + H_{vaporization} + H_{vapor}\right]$$

where n_{ri} is mole reactant of component i. All heat of reactions was calculated by previous approach and results are illustrated in Table 4-14.

CHAPTER 5:

EQUIPMENT DESIGN

5.1 REACTORS DESIGN

The most common industrial process to produce styrene monomer is by dehydrogenation of Ethylbenzene in adiabatic process is carried out in plug flow reactor. Usually to reactors are used with an inter-heater. It is my task to design this reactor.

The search to design the PFR includes seeking for the specific heat of component, heat of reactions, kinetic equations for the reactions and the rate of reactions for the styrene production. This information was available in some references such as Vasudevan, S., Rangaiah, G.P., Murthy Konda[11], and Lee's however, it was explained in detail in the dissertation of Won Jae Lee[13] that was approved by Rayford G. Anthony and Gilbert F. Froment in 2005. This dissertation was the main reference used in this report to design both PFRs for production of styrene.

Two reactors shown in Figure 5-1 were used to reduce the volume of each reactors and reduce the cost of catalyst to give the designed overall conversion of EB. The main reason for using 2 reactors is to reheat the stream between them since it is endothermic process. Thus, the rate could be increased to reach the desired conversion using reasonable amount of catalyst.

Polymath was used to calculate the conversion profile, temperature profile, weight of the catalyst, flow rates and the changes that occurs inside both reactors to observe the effect of the catalyst on the reaction, temperature, conversion and flow rates with respect to the space time.

The catalyst used in the design is potassium-promoted iron which is extensively used in styrene production. It was used inside an axial flow reactor at an inlet temperature of 650°C for both reactors.

The steam added to the system at ratio $H_2O/EB = 15$ to provide heat in the reactor and maintain the reaction temperature. To remove the carbonaceous from the surface of the catalyst and keep its activity.

The most temperature inlet to the reactor in many processes is in range of 600 to 650°C, thus the inlet temperature in this report was said to be 650°C to increase the rate of reactions and conversion of EB. Also considering the sintering catalyst that would occur inside the reactors when the heat is above that.
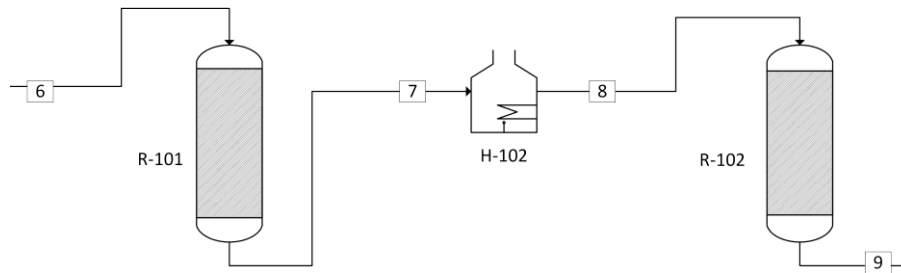
Figure 5-1: The two reactors.

5.1.1 Rate Equations

According to Lee's, there are two types of reactions occur in the reactor, thermal reactions and catalytic reactions. The thermal reactions occur in the void section of the catalyst bed and the catalytic reactions considered to take place on the active site on the surface of the catalyst.

Thermal Reactions

EB $\leftrightarrow$ ST +H$_2$ $\qquad$ $r_{t1} = k_{t1}(P_{EB} - \frac{P_{ST}P_{H_2}}{K_{eq}})$ $\qquad$ (5.1)

EB $\rightarrow$ BZ + C$_2$H$_4$ $\qquad$ $r_{t2} = k_{t2}P_{EB}$ $\qquad$ (5.2)

EB + H$_2$ $\rightarrow$ TO + CH$_4$ $\qquad$ $r_{t3} = k_{t3}P_{EB}$ $\qquad$ (5.3)
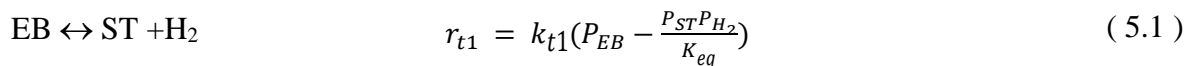
Where the k_{ti} is the constant rate of reaction i in (kmol/m^3.h.bar), r_{ti} is the rate of thermal reaction i in (kmol/m^3.h), P_j is the partial pressure of component j, in bar, and K_{eq} is the equilibrium constant of the first in bar.

The parameters of these reactions are shown in where A_{ti} is the pre-exponential factor in (kmol/m^3.h.barand E_{ti} is the activation energy in (kJ/mol) of thermal reaction i.

Table 5-1 where A_{ti} is the pre-exponential factor in (kmol/m^3.h.barand E_{ti} is the activation energy in (kJ/mol) of thermal reaction i.

Table 5-1: Constants of pre-exponential and activation energy.

i	A_{ti}	E_{ti}
1	2.2215E16	272.23
2	2.4217E20	352.79
3	3.8224E17	313.06

Equilibrium constant was calculated by the thermodynamics standard Gibbs-energy change considering the effect of temperature change in the reactor by using these equations:

$$K_0 = \exp(-\frac{\Delta g_0^{\circ}}{RT_0}) \tag{5.4}$$

$$K_1 = exp\frac{\Delta h_0^{\circ}}{RT_0}\left(1 - \frac{T_0}{T}\right) \tag{5.5}$$

$$K_2 = \exp[-\frac{1}{T}\int_{T_0}^{T}\frac{\Delta C_p^{\circ}}{R}dT + \int_{T_0}^{T}\frac{\Delta C_p^{\circ}}{RT}dT] \tag{5.6}$$

$$K_{eq} = K_0 * K_1 * K_2 \tag{5.7}$$

Where K_0 is equilibrium constant at reference temperature T_0, Δg_0° is standard Gibbs energy change of reaction at T_0, K_1 is multiplier to give the effect of temperature if Δh_0° is independent of T, Δh_0° is standard enthalpy change at T_0, K_2 is multiplier to give the small effect of temperature if Δh_0° is a function of T and ΔC_p° is standard heat capacity change of reaction as function temperature.

Catalytic Reactions

EB $\leftrightarrow$ ST $+H_2$ (5.8)

EB $\rightarrow$ BZ + C_2H_4 (5.9)

EB + H_2 $\rightarrow$ TO + CH_4 (5.10)

ST + $2H_2$ $\rightarrow$ TO + CH_4 (5.11)

r_{ci} is the rate of catalytic reaction i in (kmol/kgcat.h).

$$r_{c1} = \frac{k_1 K_{EB}(P_{EB} - \frac{P_{ST}P_{H2}}{K_{eq}})}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{5.12}$$

$$r_{c2} = \frac{k_2 K_{EB}P_{EB}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{5.13}$$

$$r_{c3} = \frac{k_3 K_{EB}P_{EB}K_{H_2}P_{H_2}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{5.14}$$

$$r_{c4} = \frac{k_4 K_{ST}P_{ST}K_{H_2}P_{H_2}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2} \tag{5.15}$$

Table 5-2: Constants of pre-exponential and activation energy for catalytic reactions.

i	A_{ci}	E_{ci}
c_1	4.594E9	175.38
c_2	1.060E15	296.29
c_3	1.246E26	474.76
c_4	8.024E10	213.78

Where the A_{ci} is the preexponential factor for catalytic reaction in (kmol/kgcat.h), E_{ci} is the activation energy for catalytic reactions in (kJ/mol), k_{ci} is the constant rate of catalytic reaction and r_{ci} is the catalytic rate of reaction i.

k_{ci} was calculated by Arrhenius equation:

$$k_{ci} = A_{ci} * \exp(-\frac{E_{ci}}{RT}) \qquad (5.16)$$

K_j is the adsorption constant calculated for ST, EB and H_2 using this equation:

$$K_j = A_j * \exp(-\frac{\Delta H_{a,j}}{RT}) \qquad (5.17)$$

Table 5-3: Values of kinetic parameters for adsorption constants.

Component	A_j	$\Delta H_{a,j}$
EB	1.014E-5	-102.22
ST	2.678E-5	-104.56
H_2	4.519E-7	-117.95

$\Delta H_{a,j}$ in kJ/mol and A_j in (kmol/kgcat.h).

5.1.2 Material and Energy Balance Equations

5.1.2.1 Material balance

These reactors are designed to produce styrene at a rate of 100,000 ton per year with feed coming from furnace at temperature of 650 °C and pressure of 2.7 bar with flow rates compositions shown in Table 5-4. Two reactors were used to reduce the volume of each and reduce the cost of catalyst to give the designed overall conversion of EB.

Table 5-4: Flow rates and mole fraction feed to reactor 1.

Component	Mole flow (kmol/h)	Mole fraction %
EB	274.5506	6.2419
ST	4.0557	0.0922
BZ	0.5440	0.01234
TO	1.1117	0.0253
H_2O	4118.2595	93.6283
Total	4398.5215	1

The selectivity of the EB to give ST, TO and BZ are 76.6%, 10.6% and 12.8%, respectively.[11]

The assumption of material balance is that the steam will not react with the other components. It's just used to provide heat and maintain the temperature in the reactor and to protect the catalyst as mentioned in the introduction so, the flow of the steam will be constant.[13]

The continuity equation for the EB, ST, BZ, H_2 and TO in respect to space time are written as follows:

$$\frac{dX_{EB}}{d(\frac{W}{F_{EB}^\circ})} = r_{c1} + r_{c2} + r_{c3}(r_{t1} + r_{t2} + r_{t3})\frac{\varepsilon_B}{\rho_B} \tag{5.18}$$

$$\frac{dX_{ST}}{d(\frac{W}{F_{EB}^\circ})} = r_{c1} - r_{c4} + r_{t1}\frac{\varepsilon_B}{\rho_B} \tag{5.19}$$

$$\frac{dX_{BZ}}{d(\frac{W}{F_{EB}^\circ})} = r_{c2} + r_{t2}\frac{\varepsilon_B}{\rho_B} \tag{5.20}$$

$$\frac{dX_{BZ}}{d(\frac{W}{F_{EB}^\circ})} = r_{c3} + r_{c4} + r_{t3}\frac{\varepsilon_B}{\rho_B} \tag{5.21}$$

The r_{ci} were derived before in the rate equations section. These differential equations are solved by the polymath to give the conversions of each component and the profile change of conversions in the reactor will be attached.

ε_B is the void fraction of bed i and ρ_B is the catalyst bulk density in kgcat/m^3. The void fraction of the bed can be calculated by: $\varepsilon_B = 1 - \frac{\rho_B}{\rho_s}$

The measured bulk density is 1422 kgcat/m^3 and the catalyst particle density is 2500 kgcat/m^3[13]. thus,

$$\varepsilon_B = 1 - \frac{1422}{2500} = 0.4312$$

The molar flow rates of components can be calculated using the following equations:

$$F_{EB} = F_{EB}^\circ (1 - X_{ST} - X_{BZ} - X_{TO})$$

$$F_{ST} = F_{ST}^\circ + F_{EB}^\circ X_{ST}$$

$$F_{BZ} = F_{BZ}^\circ + F_{EB}^\circ X_{BZ}$$

$$F_{TO} = F_{TO}^\circ + F_{EB}^\circ X_{TO}$$

$$F_{CH_4} = F_{CH_4}^\circ + F_{EB}^\circ X_{TO}$$

$$F_{C_2H_4} = F_{C_2H_4}^\circ + F_{EB}^\circ X_{BZ}$$

$$F_{H_2O} = F_{H_2O}^\circ$$

(5.22)

The mass flow rate of components that change along the reaction occurs written by

$$\dot{m}_{EB} = Mw_{EB} F_{EB}(1 - X_{EB})$$

$$\dot{m}_{ST} = Mw_{ST}(F_{ST}^\circ + F_{EB}^\circ X_{ST})$$

$$\dot{m}_{BZ} = Mw_{BZ}(F_{BZ}^\circ + F_{EB}^\circ X_{BZ})$$

$$\dot{m}_{TO} = Mw_{TO}(F_{TO}^\circ + F_{EB}^\circ X_{TO})$$

$$\dot{m}_{H_2} = Mw_{H_2}(F_{H_2}^\circ + F_{EB}^\circ X_{H_2})$$

$$\dot{m}_{H2O} = Mw_{H2O} F_{H2O}^\circ$$

(5.23)

5.1.2.2 Energy Balance

For solving the Plug Flow Reactor, energy equation is required to predict the temperature change and the outlet temperature, the equation is as follow:

$$\sum_{j=1}^{6} \dot{m}_j C_{pj} \frac{dT}{d(\frac{W}{F_{EB}^\circ})} = F_{EB}^\circ \sum_{i=1}^{4} (\Delta H_{ri}) r_i$$

(5.24)

Where $\dot{m}_j$ is the mass flow of component j in (kg/h), C_{pj} is the specific heat of component j in (kJ/kg.K), ΔH_{ri} is the heat of reaction and r_i is the rate of reaction for reaction i in (kmol/kgcat.hr), F_{EB}° is the moles inlet to reactor i of EB, T is the temperature inside the reactor i and W_c is the weight of catalyst needed in reactor i.

For calculation the specific heat of component the constant listed in Table 5-5 using following equation:

$$C_{pj} = a_j + b_j T + c_j T^2 + d_j T^3 \qquad (5.25)$$

Table 5-5: constants of specific heat of components in kJ/kg.K.[13]

Component	a_j	b_j*10^3	c_j*10^6	d_j*10^{10}
EB	-0.43426	6.0671	-3.8625	9.1282
ST	-0.26436	5.564	-3.0018	5.3317
BZ	-0.40599	6.6616	-4.5318	12.255
TO	-0.27127	5.9142	-3.8631	9.54
H_2	13.57	4.637	-6.905	38.23
H_2O	1.79111	0.1069	0.58611	-1.998

The heat of reaction will be temperature dependent inside the reactor which will change with respect to space time, so, this change could be taken into account by using following equation:

$$\Delta H_{ri} = \Delta H^{\circ}_{298} + \int_{T_0}^{T} \Delta C_{pi} \qquad (5.26)$$

which could also be written in this form:

$$\Delta H_{ri} = \Delta H^{\circ}_{298} + \Delta a_j (T - 298.15) + \frac{\Delta b_j}{2}(T^2 - 298.15^2)$$
$$+ \frac{\Delta c_j}{3}(T^3 - 298.15^3) + \frac{\Delta d_j}{4}(T^4 - 298.15^4) \qquad (5.27)$$

Where ΔH°_{298} is the standard heat of reaction at 298.15 Kelvin in kJ/kmol and the constants $\Delta a_j, \Delta b_j, \Delta c_j$ and Δd_j in unit of kJ/kmol.k, kJ/kmol.k^2, kJ/kmol.k^3 and kJ/kmol.k^4, respectively and will be shown in

Table 5-6: constants of specific heat of reactions and standard heat of reactions.[13]

Reaction i	Δa_j	Δb_j*10^2	Δc_j*10^5	Δd_j*10^8	ΔH°_{298}
1	41.99	-8.2026	6.499	-2.311	117690
2	12.986	-7.67	9.592	-4.125	105510
3	10.86	-15.1844	23.04	-9.9955	-54680
4	-31.13	-6.9818	16.54	-7.285	-172370

The equilibrium was calculated previously using the Gibbs energy change and the heat of formations, all these parameters and constants are listed in Table 5-7.

Table 5-7: Standard Gibbs energy, standard heat of formations.[13]

Components	$\Delta H_{fi}^{\circ}*10^{-5}$	$\Delta G_{fi}^{\circ}*10^{-5}$
EB	0.2981	1.307
ST	1.475	2.139
H2	-	-

Where ΔH_{fi}° is the standard heat of formation of component j at 298.15 K in kJ/kmol, ΔG_{fi}° is standard Gibbs of formation.

the rate reaction is used to find the temperature profile, the conversion and the weight of the catalyst in both reactors. This data is important to calculate the volumes of both reactors and their dimensions.

A computer program was written on Polymath to calculate both thermal and catalytic reaction rates, equilibrium constant for the first reaction, conversions for both reactors, profiles for temperature and flow rates in both reactors.

The program was run as follows: the feed from the material balance was used as inlet to the first one, then the outlet of the first reactor was used as feed to the second one. The total conversion of both reactors was kept at 64%.

The program was run for several times for both reactors while changing the conversion of the first reactor only. This was done to calculate the optimum conversion for the first reactor, that would give the minimum reactor volumes and hence the minimum amount of catalyst and the minimum cost. Fig (5-2) shows the result for this optimization. It is clear that the minimum weight of catalyst appears at a conversion of about 36.25% in the first reactor. The flow rates out of both reactors under these conditions are shown Table 5-8.
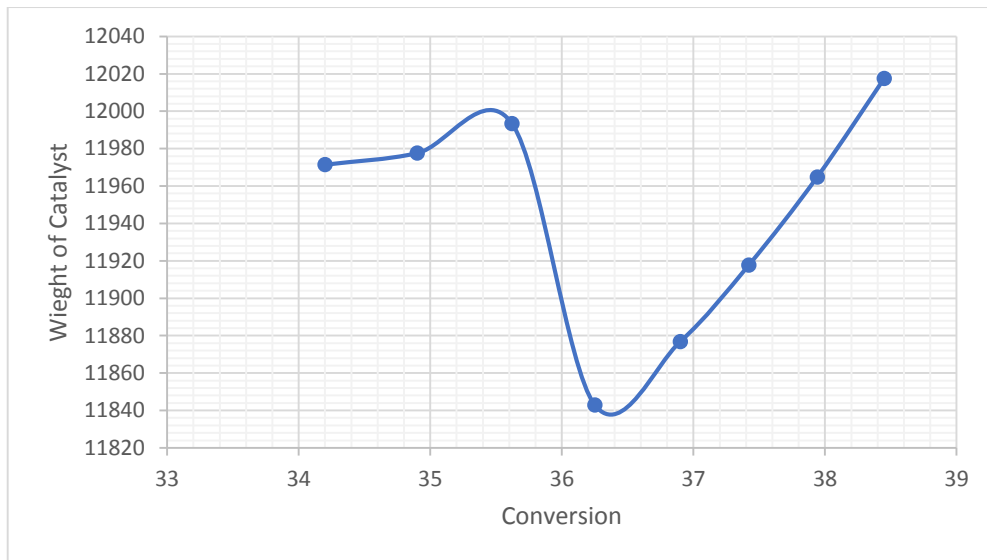
Figure 5-2: Reactors optimization.

Table 5-8: Flow rates.

Components	Reactor 1	Reactor 2
	Flow rates, Kmol/h	Flow rates, Kmol/h
EB	175.015	98.97
ST	99.03	164.42
BZ	2.82	5.04
TO	3.41	11.84
H_2	92.67	149.67
H_2O	4118.26	4118.26
C1	2.29	10.72
C2	2.27	4.5
Total	4495.8	4563.42

The polymath was used to calculate both thermal and catalytic reaction rates, equilibrium constant for the first reaction, conversions for both reactors, change and final temperature of both reactors and flow rates.

The thermal rates were calculated by equations (5.1-5.3) are shown in Table 5-9.

Catalytic rates are shown in Table 5-10 using equations (5.12-5.15).

Table 5-9: Results for thermal reactions.

i	k_{ti}	r_{ti}
1	0.91703	0.07063
2	0.14168	0.01374
3	0.05504	0.00534

Table 5-10: Kinetic and rates for catalytic reactions.

$\square$	$\square\square\square$	$\square\square\square$
1	0.12790	0.00364
2	0.00156	$5.595*10^{-5}$
3	0.00333	$4.192*10^{-5}$
4	0.01091	0.00034

The equilibrium constant used from the equations (5.36) to (5.38) and parameters shown in Table 5-7 and Table 5-6. The results in Table 5-11.

All conversions are with respect to space time W_c/F_{EB}°., also the energy balance derived with respect to W_c/F_{EB}°.

The conversion in the first and the second reactors are 36% and overall conversion is 64 % respectively, and the exit temperature resulted from the polymath in the first reactor is 867.93 K (594.78°C) and the second reactor found to be 895.89 K (622.74°C).

Table 5-11: Equilibrium constant.

K_0	$2.65*10^{-15}$
K_1	$3.44*10^{13}$
K_2	2.262
K_{eq}	0.20604

5.1.3   Figures and Discussion

In this section the profile temperature, flow rates, rate of reactions and conversion of EB will be presented against the space time $(\frac{W}{F_{EB}^{\circ}})$.

Figure 5-3 illustrate the temperature fall in both reactors. This is expected since the reactions are endothermic. It's also noticed that the inlet temperature for both reactors is 923K (650°C).
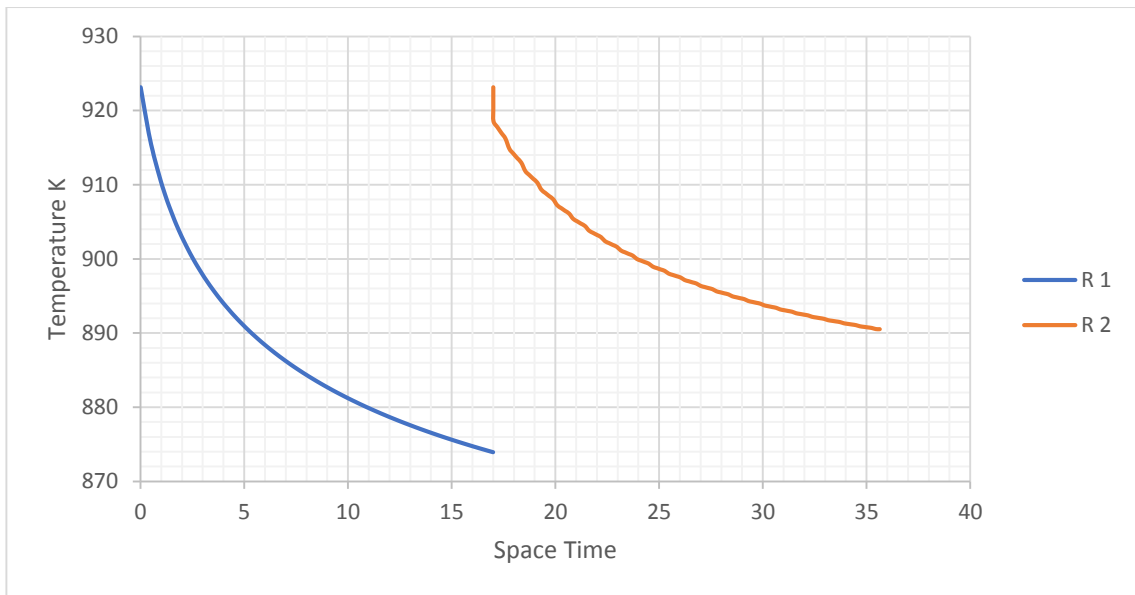
Figure 5-3: The temperature profile inside both reactors.

Figure 5-4 shows the change of the flow rates of all components in both reactors. The flow rates of EB falls from 274 to 175 in the first reactor and from 175 to 99 in second reactor.

On the other hand, the flow rates of ST, BZ, TO, C1, C2 and H_2 increasing along both reactors.
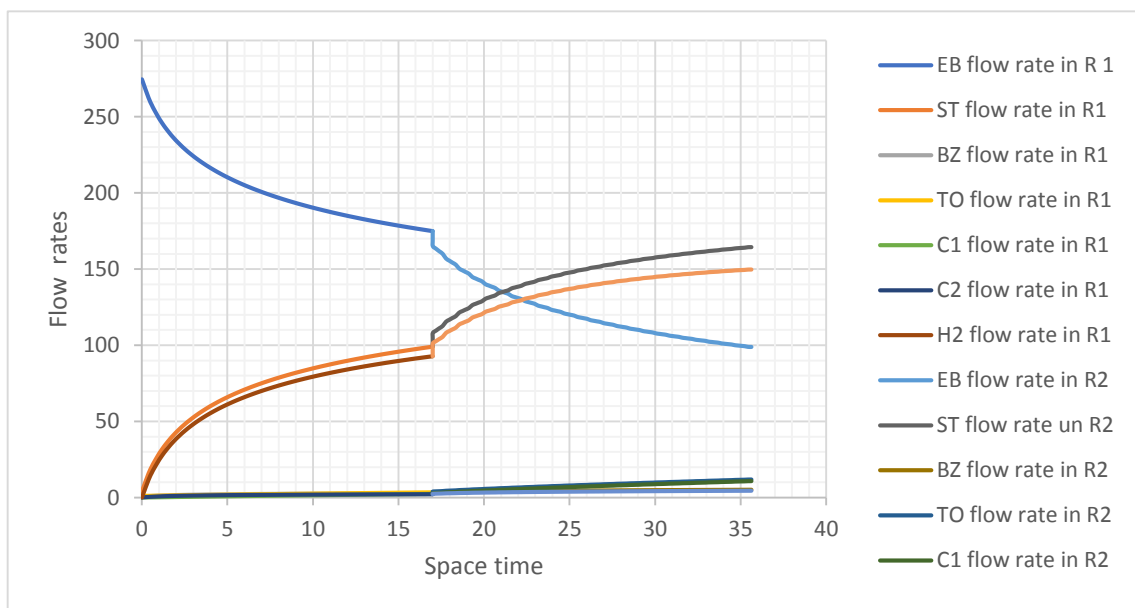
Figure 5-4: Flowrates profile inside R1 and R2.

Figure 5-5 show the change of the rate of reactions along the space time in both reactors. The rate of reaction 1 form equation 18 falls from 0.129703 to 0. 0.005954 in reactor 1.

After being heated to 923K (650°C), it increases at the entrance of reactor 2 to 0.038549, afterwards it falls again to 0.003486.
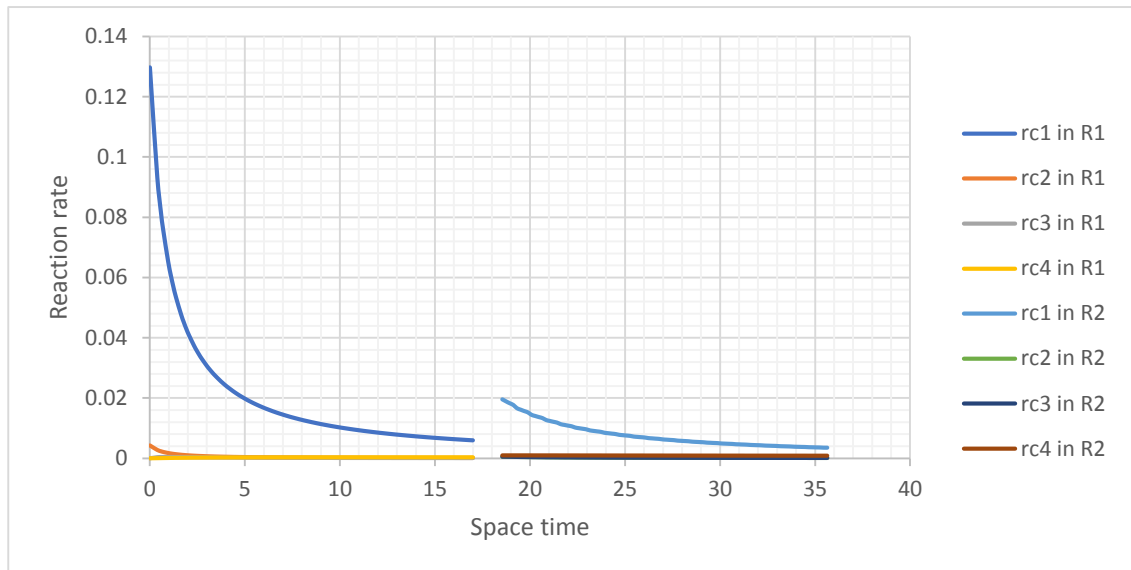
Figure 5-5: Reaction rates as a function of space time.

Figure 5-6 shows that the rate reaction 2 obtained in equation 19 is very similar to reaction 1, however, it's much less in value since this is a side reaction. It is also shown that reaction 3 and 4 start from 0, since both reactions need H_2 as a reactant. Thus, both reactions start taking place after H_2 is produce from the main reaction (5.39).

The rate of reaction 3 increases as the amount of H_2 increases, then, due to the fall of the temperature it decreases again. However, the rate of reaction 4 increases until it reached a constant value after approximately have of the reactor.
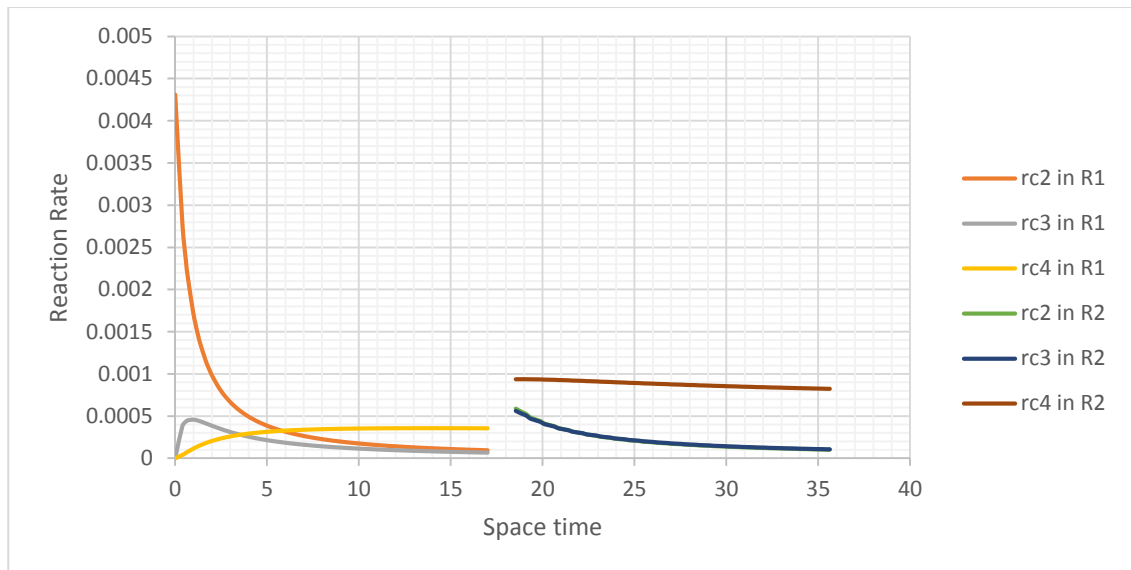
Figure 5-6: Reaction rates without rate of EB.

Figure 5-7 shows the conversion of EB in both reactors. The conversion increases to 36.25% in first reactor, then to 64% as overall conversion.
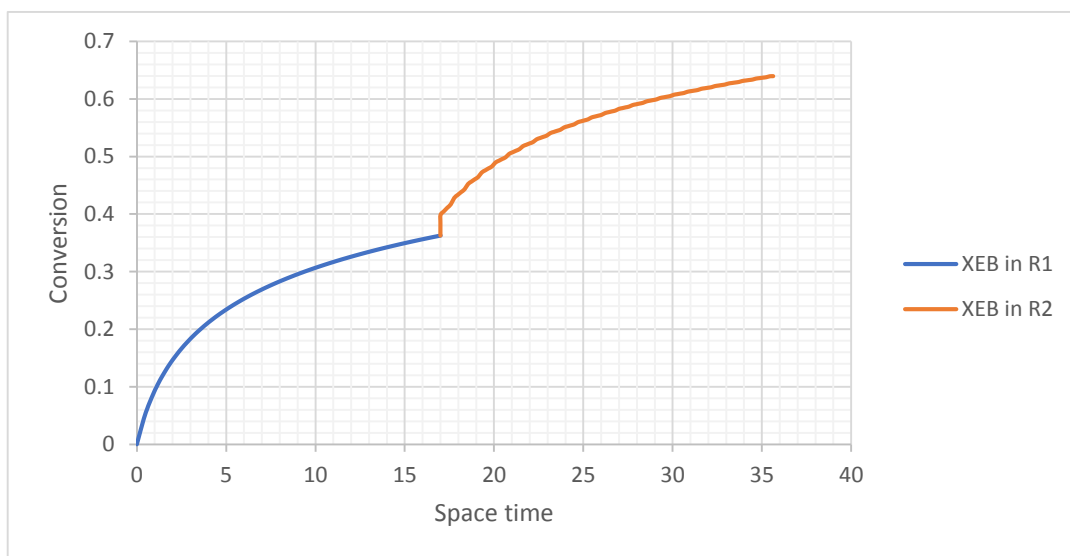
Figure 5-7: Conversions profile in R1 and R2.

5.1.4 Dimensions of Reactor and Vessel Design

Dimensions of reactor

Since all the required parameters and information to solve the system were ether determined, the volume and dimensions can be designed to meet the desired specification of the process production and the amount of catalyst that should be present in both reactors.

The properties of the catalyst are shown in Table 5-12.

Table 5-12: Catalyst properties.[13]

Physical property	Notation	Value
Catalyst bulk density, kgcat/m³	ρ_B	1422
Catalyst pellet density, kgcat/m³	ρ_S	2500
Void fraction of the bed, m³/m³	ε_B	0.4312
Catalyst equivalent pellet dimeter, m	d_p	0.0055

After using polymath software to find the exact amount of catalyst should be present in both reactors, the space time is found to be equal 17 in the first reactor and 41 in the second reactor in kgcat.h/kmol, where the space time is W/F_{EB}° the weight of the catalyst is

$$W_i = F_{EB}^\circ x$$

Where F_{EB}° is the molar flow rate of EB inlet to each reactor

$$W_{c1} = 274.551 * 27 = 7412.89 \text{ kgcat}$$

$$W_{c2} = 161.89 * 40 = 6475.6 \text{ kgcat}$$

The volume of bed can be found by following equation:

$$V_i = \frac{W_{Ci}}{\rho_B} \quad\quad\quad (5.28)$$

Where V in m³ so, the volume of reactor 1 and 2 are:

$$V_1 = \frac{4667}{1422} = 3.282 \ m^3$$

$$V_2 = \frac{7176}{1422} = 5.05 \ m^3$$

As mentioned before the similar volume of reactor was important in this report. For these reactors, it was assumed that the length is 2.5 times the dimeter of the bed where the dimeters where calculated used this equation:

$$V = \frac{\pi}{4} D^2 H \qu\quad\quad\quad (5.29)$$

The dimeter of the first and the second reactors are 1.19 and 1.37 m, respectively, while the length of the first and the second reactors are 2.97 and 3.43 m, respectively.

Vessel design

In designing the vessel, the equation was used from Towler Gavin, Ray Sinnott.[14]

Since the high temperature and the hydrogen content in the reactor, the stainless steel 304L is selected for the vessel. At 650°C (1202°F) the maximum allowable stress is 2900 psi as shown in Figure 5-8.
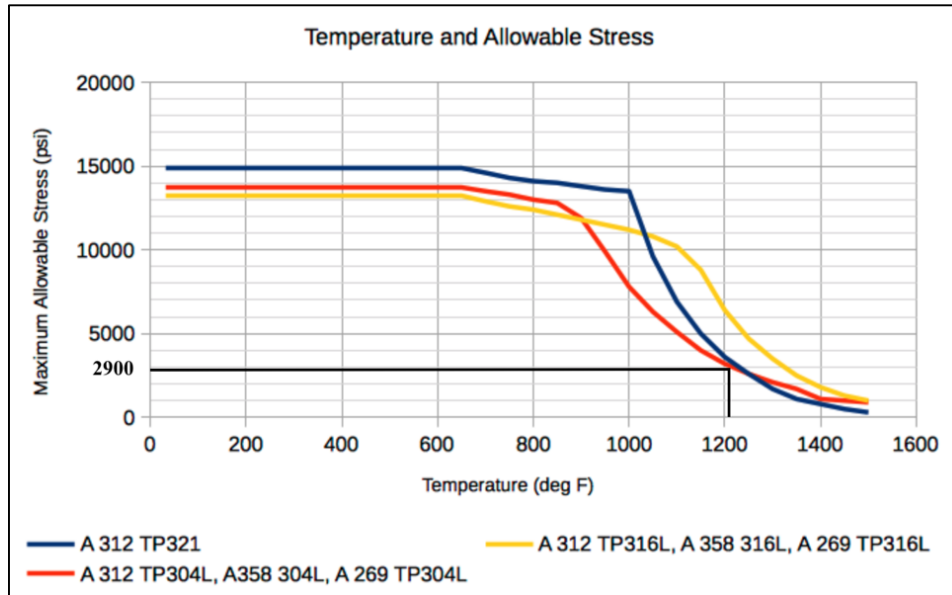
Figure 5-8: The relation between the stress and the temperature.[15]

Since the dimeter of both reactors are more than 1 m, the reactors shells are assumed to be double-welded butt joint. For this type of welding, the efficiency will be 0.85.

Since, corrosion is expected to be moderate, a corrosion allowance of 2 mm is used.

The design pressure of the vessel is

$$P_{i1} = (P - 1) * 1.1 = (2.7 - 1) * 1.1 = 1.87 \; bar$$

$$P_{i2} = (P - 1) * 1.1 = (2.1 - 1) * 1.1 = 1.21 \; bar$$

Where a safety factor of 10% was used.

The equation for calculating the thickness t of a cylindrical vessel according to Towler[14] is:

$$t = \frac{P_i D_i}{2SE - 1.2P_i} + C \qquad\qquad (\,5.30\,)$$

 Where S is the maximum allowable stress, and E is the welding efficiency, D_i is the internal dimeter of the vessel, and C is the corrosion allowance.

The thicknesses for the first and second reactors are 10 and 8 mm respectively.

Ellipsoidal heads were chosen for both reactors with thickness of 10 and 8 mm in the first and the second reactors respectively. The thicknesses of the heads were calculated from the following equation:

$$t = \frac{P_i D_i}{2SE - 0.2Pi} + C \qquad (5.31)$$

5.1.5 Costing of the Catalyst and Vessel

Catalyst price

It's known that the reactor is the most expensive equipment in the industry when the catalyst used. The price of the catalysts is in range of 40 to 300 $/kg. Both reactors need 13 tons of potassium-promoted iron. From U.S. Department of Energy (DOE)[16] and sigma-Aldrich[17] the price of the potassium hexacyanoferrate and iron with nickel is between 120 to 150 $/kgcat, where these catalysts is much higher than the potassium-promoted iron. Since the price of the catalyst used in this report is not available the range of previous catalysts, the assumed price is 80$/kgcat.

The final design of the PFRs gave amount of 4667 and 7176 kgcat. The cost of one kilogram of potassium-promoted iron is equal to 80$/kgcat. Cost of each reactor can be calculated as follows.

$$\$Price_i = amount * cost$$

$$P_1 = 4667 kgcat * 80 \frac{\$}{kgcat} = \$373,360$$

$$P_2 = 7176 \, kgcat * 80 \frac{\$}{kgcat} = \$574,080$$

For converting to Saudi Riyal

$$\$1 = 3.75 \, SR$$

$$P_{1(SAR)} = \$373,360 * \frac{3.75 \, SR}{\$1} = 1,400,100 \, SR$$

$$P_{2(SAR)} = \$574,080 * \frac{3.75 \, SR}{\$1} = 2,152,800 \, SR$$

Vessel Price

The stainless steel 304L is used for the reactor to prevent the hydrogen embrittlement and for its ability to bear high temperature up to 1500°F (815.55°C).

For calculating the price of the vessel, the mass can be calculated from this equation

$$m_i = \rho_m V_i$$

Where ρ_m is the density of the 304L and V is the volume of the vessel which is equal following equation. Volume of the shell and the heads

$$V_i = (\pi D_m H t_i + 2 * 0.8 D_m^2 t_i)$$

Where D_m is mean dimeter that can be calculated by:

$$D_{m1} = D_i + t_i = 1.19 + 0.010 = 1.2 \, m$$

$$D_{m2} = D_\lfloor + t_\lfloor = 1.37 + 0.008 = 1.378 \, m$$

The density of the 304L is 8000 kg/m³[18]

$$m_1 = \rho_m * (\pi D_m H t_i + 2 * 0.8 D_m^2 t_i)$$

$$= 8000 * (\pi * 1.2 * 2.97 * 0.010 + 2 * 0.8 * 1.2^2 * 0.010)$$

$$m_2 = 8000 * (0.135) = 1080 \, kg$$

For vessel 2

$$m_\lambda = \rho_m * (\pi D_m H t_i + 2 * 0.8 D_m^2 t_i)$$

$$= 8000 * (\pi * 1.378 * 3.43 * 0.008 + 2 * 0.8 * 1.378^2 * 0.008)$$

$$m_\lambda = 8000 * (0.143) = 1144 \, kg$$

The price of each in 2014 are $33,200 and $34,600[19]. By using chemical engineering planet cost index

$$\frac{C_{2018}}{C_{2014}} = (\frac{I_{2018}}{I_{2014}})$$

$I_{2018} = 603.1$[20]

$I_{2014} = 576.1$[14]

Where C is the cost of equipment at specified year, where its cost was calculated in 2014 will be using the 2018 index to get their present values

$$C_{2018} = C_{2014}(\frac{I_{2018}}{I_{2014}}) = \$33,200 * \left(\frac{603.1}{576.1}\right) = \$34,756$$

$$C_{2018} = C_{2014}(\frac{I_{2018}}{I_{2014}}) = \$34,600 * \left(\frac{603.1}{576.1}\right) = \$36,222$$

These values equal in SR

$$P_{1(SAR)} = \$34,756 * \frac{3.75\ SR}{\$1} = 130,335\ SR$$

$$P_{2(SAR)} = \$36,222 * \frac{3.75\ SR}{\$1} = 135,833\ SR$$

5.1.6 Plug Flow Reactor Control

For both reactors the control is the same as shown in Figure 5-9, where pressure and temperature indicator where used. The pressure indicator is to measure the pressure difference along the reactors, to see and observe the catalyst activity.

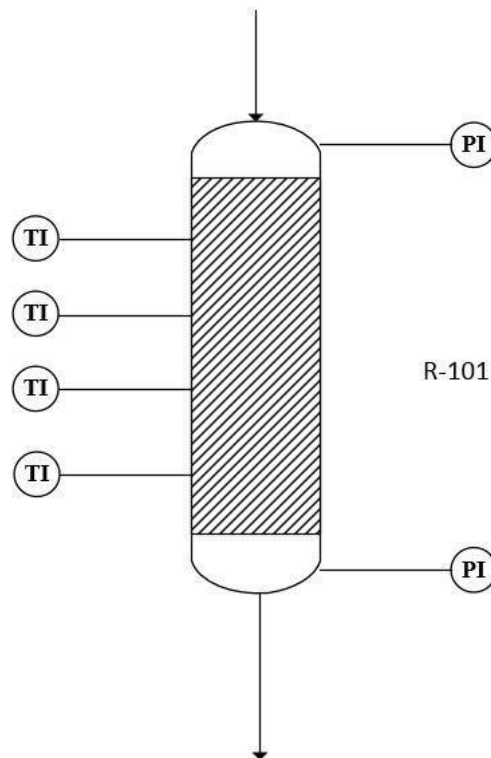The temperature indicator is to compare the calculated temperature profile with the measured.

Figure 5-9: PFR with control system.

Where TI is temperature indicator and PI is the pressure indicator.

5.2 DISTILLATION COLUMN (T-101) DESIGN

This distillation column is placed and designed to distill the desired product of this project, styrene, from the other components with a purity of 99.75%.

After the water and the light gases is withdrawn in the decanter (V-101), the organic liquid (stream 13) is fed to the distillation column (T-101) at a flow rate of 281.4 kmol/h and a composition of 48.1 mol% styrene, 34.1 mol% ethylbenzene, 7.9 mol% toluene, 5.8 mol% benzene, 4.1 mol% water and very small amount of some of the light components.

The separation of the liquid mixture by a distillation column depends on the differences in volatility between the components; the separation becomes easier if the differences in the volatilities between the components are massive. In our case, the difference in the volatilities between the components is insignificant, which make the separation harder, requiring more columns stages and high reflux ratio.

The first step in designing the distillation column is choosing the column operating pressure. Pressure has a major effectiveness on components phase equilibrium in terms of relative volatilities and column temperatures which affect energy requirements, utility costs, and the process configurations. Another different factors should be concerned in some chemical separations, when an olefin compound is present such as in our case, styrene can go under spontaneously thermal polymerization at relatively high temperature without the addition of free-radical initiators. To suppress the styrene polymerization, a low temperature operating is desired, and this can be achieved by running the column under vacuum pressure and dispense of the kettle reboiler. The operating pressure will be at 0.3 bar with assumed pressure drop of 0.4 bar over the column. Thus, the pressure at the top and bottom of the column (T-101) is 0.1 and 0.5 bar.

Thus, the second step after selecting the operating pressure is calculating the dew point and bubble point for the liquid mixture in order to estimate the stage, condenser, and reboiler temperatures. The dew and bubble points can be calculated from the vapor-liquid equilibrium.

After that, shortcut and McCabe-Thiele methods are used to estimate the number of stages required. Once the real number of stages required is known, the overall column size can be estimated, and the material of construction is chosen to evaluate the capital cost for this tower.

5.2.1 Vapor-Liquid Equilibrium

Ethylbenzene and styrene have a similar molecular size and structure. Thus, they are assumed to form an ideal solution which obeys Raoult's law and can be used with Antoine's equation to find the vapor-liquid phase equilibrium.

Using Antoine's equation, the boiling point temperature for ethylbenzene and styrene at 0.3 bars is found to be 95.58 and 104.64 °C. Taking 1 °C step size and calculate the vapor pressure for each component with Antoine's equation and calculate the liquid and vapor fraction for ethylbenzene using Raoult's law. The result is obtained, and it's shown in Table 5-13 and the VLE is plotted in Figure 5-10.

Table 5-13: VLE-Mole-Fraction data for EB-ST system.

T, °C	P_{EB}, bar	P_S, bar	x_{EB}	y_{EB}
95.58	0.30	0.22	1.000	1.000
97	0.31	0.23	0.823	0.864
98	0.33	0.24	0.704	0.765
99	0.34	0.25	0.589	0.661
100	0.35	0.26	0.477	0.554
101	0.36	0.26	0.368	0.442
102	0.37	0.27	0.263	0.326
103	0.38	0.28	0.161	0.207
104.64	0.41	0.30	0.000	0.000
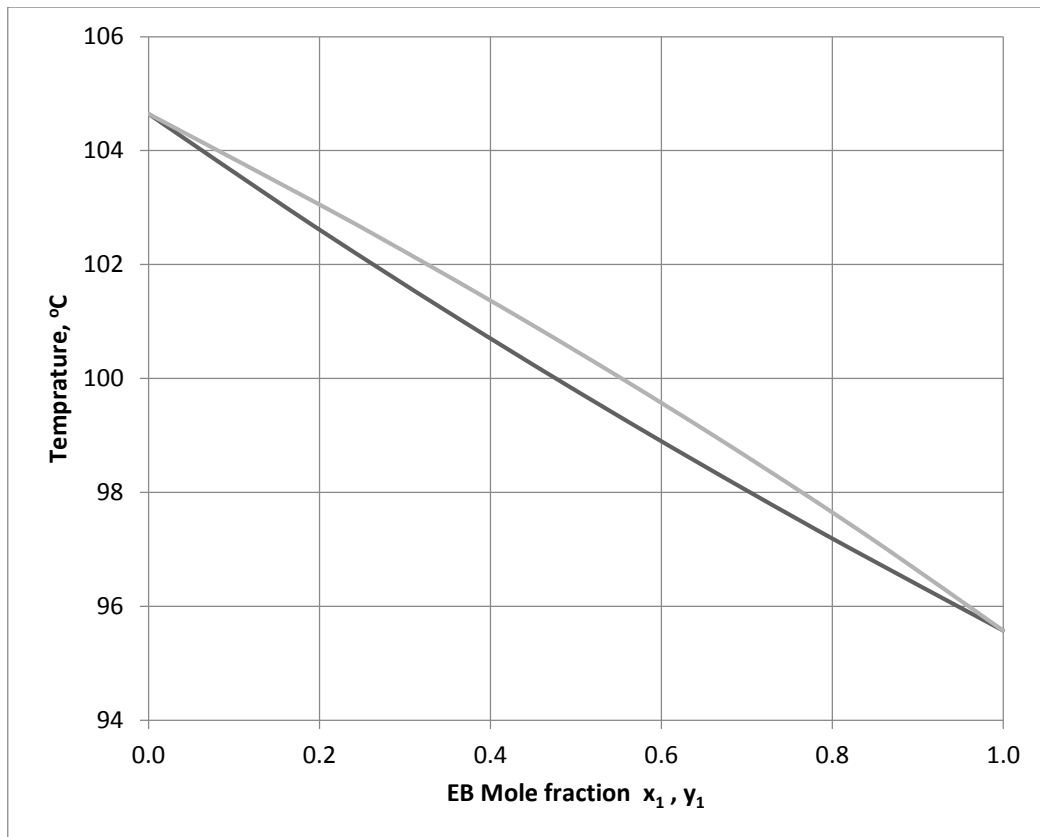
Figure 5-10: Txy diagram from EB/styrene at 0.3 bar.

5.2.1.1 Dew point and bubble point

The calculation is try-and-error process, as follows.[21]

For bubble point, first a temperature is assumed and the values of the vapor-liquid equilibrium constant K_i is calculated to get the relative volatility α_i. Where:

$$K_i = \frac{P_i}{P} \qquad (5.32)$$

$$\alpha_i = \frac{K_i}{K_C} \qquad (5.33)$$

Where "C" refers to the base component, which is either the heavy or the light key, here the base component chosen is the HK, styrene.

After that, K_C is calculated again using this equation:

$$K_C = \frac{1}{\sum \alpha_i x_i} \qquad (5.34)$$

The K_C calculated in equation (5.34) should be equal to one which calculated in equation (5.32), if not, another temperature is assumed until both values is equal. This can be achieved easily using Microsoft excel spreadsheets by goal-seek function.

After final temperature is known, the vapor composition is calculated from:

$$y_i = \frac{\alpha_i x_i}{\sum \alpha_i x_i} \tag{5.35}$$

The same procedure is followed to calculate the dew point except that K_C is calculated by the following equation:

$$K_C = \sum \frac{y_i}{\alpha_i} \tag{5.36}$$

And the liquid composition after the final temperature in know is calculated from:

$$x_i = \frac{\dfrac{y_i}{\alpha_i}}{\sum \dfrac{y_i}{\alpha_i}} \tag{5.37}$$

The calculated bubble point and dew point for the top and bottom of the column are 120.36 and 60.75 $^{\circ}$C respectively. Calculations are shown in Table 5-14 and Table 5-15.

Table 5-14: Bubble point calculation (bottom temperature).

Component	P_i (bar)	K_i	α_i	$\alpha_i x_i$	y_i
1. EB (LK)	0.663	1.325	1.326	0.003	0.003
2. S (HK)	0.500	**0.999**	1.000	0.998	0.997
3. B	3.024	6.049	6.054	0.000	0.000
4. T	1.325	2.651	2.653	0.000	0.000
5. H$_2$	733.231	1466.463	1467.660	0.000	0.000
6. C$_2$H$_4$	206.031	412.063	412.399	0.000	0.000
7. CO$_2$	3229.017	6458.034	6463.303	0.000	0.000
8. W	2.008	4.015	4.019	0.000	0.000
Total				1.001	1

$$K_C = \frac{1}{\sum \alpha_i x_i} = \frac{1}{1.001} = 0.999$$

Table 5-15: Dew point calculation (top temperature).

Component	P_i (bar)	K_i	α_i	y_i / a_i	x_i
1. EB (LK)	0.078	0.784	1.454	0.439	0.814
2. S (HK)	0.054	**0.539**	1.000	0.027	0.050
3. B	0.536	5.359	9.943	0.011	0.020
4. T	0.191	1.908	3.541	0.042	0.078
5. H$_2$	681.269	6812.688	12640.474	0.000	0.000
6. C$_2$H$_4$	104.645	1046.449	1941.614	0.000	0.000
7. CO$_2$	789.031	7890.306	14639.920	0.000	0.000
8. W	0.206	2.062	3.827	0.020	0.037
Total				0.539	1

$$K_C = \sum \frac{y_i}{\alpha_i} = 0.539$$

Summary data for the column streams condition is illustrated in Figure 5-11 and Table 5-16.
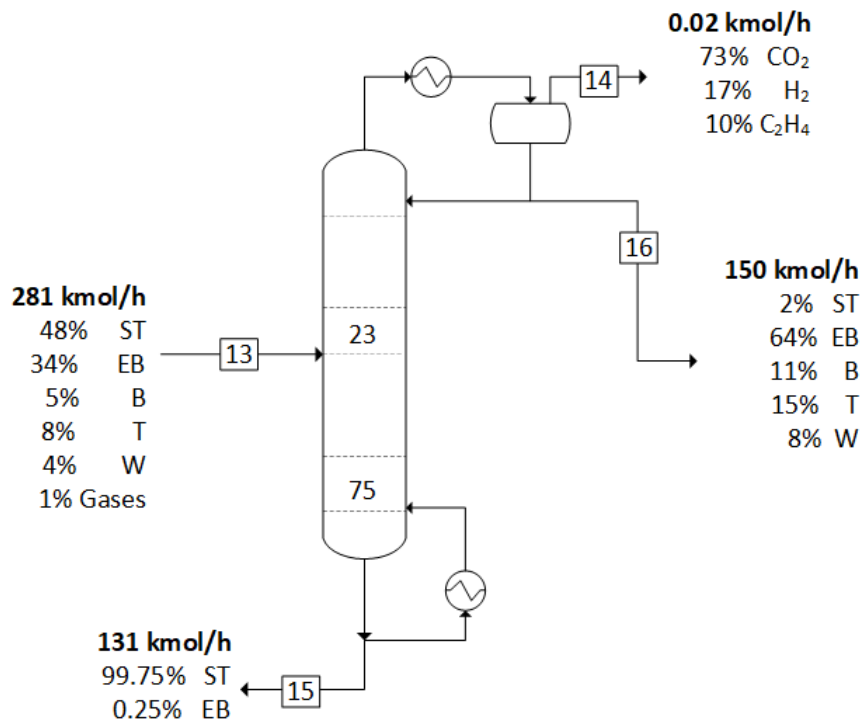
Figure 5-11: Summary diagram for the distillation column (T-101) and streams conditions.

Table 5-16: Summary data for streams conditions.

Condition	Feed	Top product	Bottom product
Stream number	13	19	15
Pressure, bar	0.3	0.1	0.5
T, °C	56.20	60.75	120.36
Molar flow rate, kmol/h	281.42	149.91	131.50
Ethylbenzene mol%	0.341	0.638	0.002
Styrene mol%	0.481	0.027	0.998
Benzene mol%	0.058	0.109	0
Toluene mol%	0.079	0.148	0
Water mol%	0.041	0.077	0

5.2.2   Number of Stage Requirement

After vapor-liquid phase equilibrium and bubble and dew point were calculated, two methods are followed to estimate the number of stages required. First, is the shortcut method for multicomponent system distillation with the correlation published by Gilliland and by Erbar and Maddox, which relate the number of ideal stages required at a given reflux ratio to the number of minimum reflux ratio. Second, is McCabe-Thiele method for binary systems.

5.2.2.1 Shortcut method

Short-cut methods are still useful in the preliminary design work giving an approximate solution, and as an aid in defining problems for computer simulation. For calculating the minimum number stages required in shortcut method, Fenske's equation is used:[21]

$$N_{min} = \frac{\log[\frac{x_{LK}}{x_{HK}}]_d[\frac{x_{HK}}{x_{LK}}]_b}{\log(\alpha_{LK})} \tag{5.38}$$

While $\alpha_{LK} = \sqrt{\alpha_{L,d}\alpha_{L,b}}$. The minimum reflux ratio R_{min} is calculate by the equation derived by Underwood's:

$$\sum \frac{\alpha_{i,avg}x_{i,d}}{\alpha_{i,avg} - \theta} = R_{min} + 1 \tag{5.39}$$

The value of θ lies between α_{LK} and 1 and is found by try-and-error process using the equation:

$$\sum \frac{\alpha_{i,avg}x_{i,f}}{\alpha_{i,avg} - \theta} = 1 - q \tag{5.40}$$

By using these equations above, the minimum number stages are found to be 27.85. Since the feed inlet is part liquid and part vapor, the quantity q will be 0.5, θ is found to be equal to 1.2 and R_{min} is found to be equal to 4.18. The calculations are shown in Table 5.19. Note that all components other than styrene (HK) and ethylbenzene (LK) are lighter than the light key and will be distilled from the top product.

Table 5-17: Minimum reflux ratio calculation.

Component	$\alpha_{i,avg}$	$\dfrac{\alpha_{i,avg}x_{i,f}}{\alpha_{i,avg}-\theta}$	$\dfrac{\alpha_{i,avg}x_{i,d}}{\alpha_{i,avg}-\theta}$
1. EB (LK)	1.39	2.582	4.830
2. S (HK)	1.00	-2.340	-0.132
3. B	7.76	0.069	0.129
4. T	3.06	0.130	0.244
5. H$_2$	4307.19	1.362E-05	0.000
6. C$_2$H$_4$	894.83	7.631E-06	0.000
7. CO$_2$	9727.40	5.686E-05	0.000
8. W	3.92	0.059	0.112
Total		0.5	5.183

After the minimum number of stages and minimum reflux ratio are found, the Erbar-Maddox correlation shown in Figure 5-12 is used to find the actual number of stages at the used reflux ratio. The optimum reflux ratio to use for lowest total cost per year is between the minimum and the total reflux ratio. For many cases, this has shown to be at an operating reflux ratio between $1.2R_{min}$ to $1.5R_{min}$.[21] In our case we took $R = 1.5R_{min} = 6.27$. From the Figure 5-12, N, the theoretical number of trays was found to be 45 trays. Since the overall efficiency of the distillation column for this system is 75%, the actual number of trays is 60.
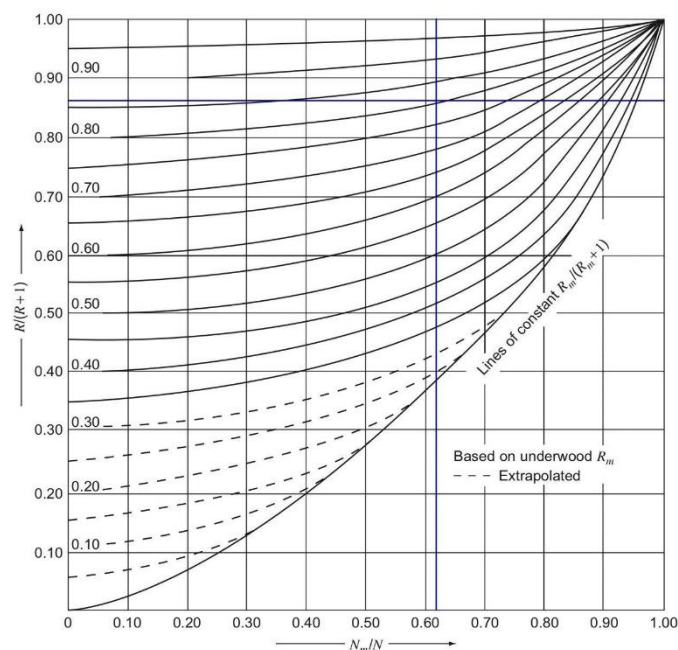

Figure 5-12: Erbar-Maddox correlation.[21]

5.2.2.2 McCabe-Thiele Method

McCabe-Thiele method is a mathematical-graphical method for determining the number of theoretical stages. The method uses material balance around particular parts of the tower and the xy equilibrium curve for the system. It's subject to the following assumptions:

- The mixture is binary i.e. there are only two components.[21] Accordingly, it was assumed that all streams consist of ethylbenzene and styrene only. Thus, the ethylbenzene and styrene compositions will be 0.415 and 0.585 at the inlet, 0.959 and 0.014 at top and 0.002 and 0.998 at the bottom.
- The overflow over the tower between the trays is in equilibrium.[21]
- Trays calculated using the McCabe-Thiele method are called "theoretical trays" assuming its 100% tray efficiency. In practice fluids doesn't reach equilibrium on each tray, and thus, the actual number of stages required is determined using the representative trays efficiencies provided by Towler[14], which's 75% Murphree plate efficiency for ethylbenzene-styrene system.

In general, the distillation column is separated into three sections: stripping section, enriching section and feed section. The stripping section is located bellow the feed section where the more volatile components are stripped from the liquid. Enriching section is located above the feed section where the concentration of the more volatile components is increased.

The procedure for McCabe-Thiele method accomplished by the following steps:

1. The vapor-liquid equilibrium curve from data calculated at the column operating pressure is plotted in xy diagram with 45-degree line tuning from the origin to the top right corner shown in Figure 5-13.
2. Material balance over the column is made to determine the top and bottom compositions, x_d and x_b. This step was done in material balance chapter 4.1.
3. The q line is plotted with slope = $q/(q\text{-}1)$ = -0.5, intersecting the diagonal at x_f.
4. To get the optimum reflux ratio, which was assumed previously at $1.5R_m$. the minimum reflux ratio R_m is calculated by drawing the enriching and stripping operating line intersects with the intersect of q line and VLE, starting from x_d for enriching line and

from x_b for the stripping line. Steps 3 and 4 are plotted in Figure 5-14, and R_m is found

to be 7.28 which has been calculated by: $\frac{R_m}{R_m+1} = \frac{x_d-y'}{x_d-x'}$.[21]

5. After getting R_m, the optimum R is calculated as $R = 1.5R_m$, which found to be 10.92.

6. The enriching line is plotted using this equation:[21]

$$y_{n+1} = \frac{R}{R+1}x_n + \frac{1}{R+1}x_d \qquad (5.41)$$

7. The stripping line is drawn from enriching line and q-line intersect to 45° diagonal line

    at $x = x_d$.

8. The theoretical stages are determined by starting at the top at x_d, the trays are stepped

    off until reaching the bottom at x_b.

9. The feed tray selection is important and impact the number of stages. To keep the

    number of stages as minimum as possible, the shift from the enriching line to the

    stripping line should be made at the first opportunity after passing the q-line

    intersection. The tray shifted will be the feed tray.

10. Finally, apply the overall column efficiency E_0 using this equation in both enriching

    and stripping line:[14]

$$E_0 = \frac{\log[1 + E_{mV}\left(\frac{mV}{L} - 1\right)]}{\log(\frac{mV}{L})} \qquad (5.42)$$

Where m is the slope of the equilibrium line, V and L is the molar flow rate of vapor and liquid,

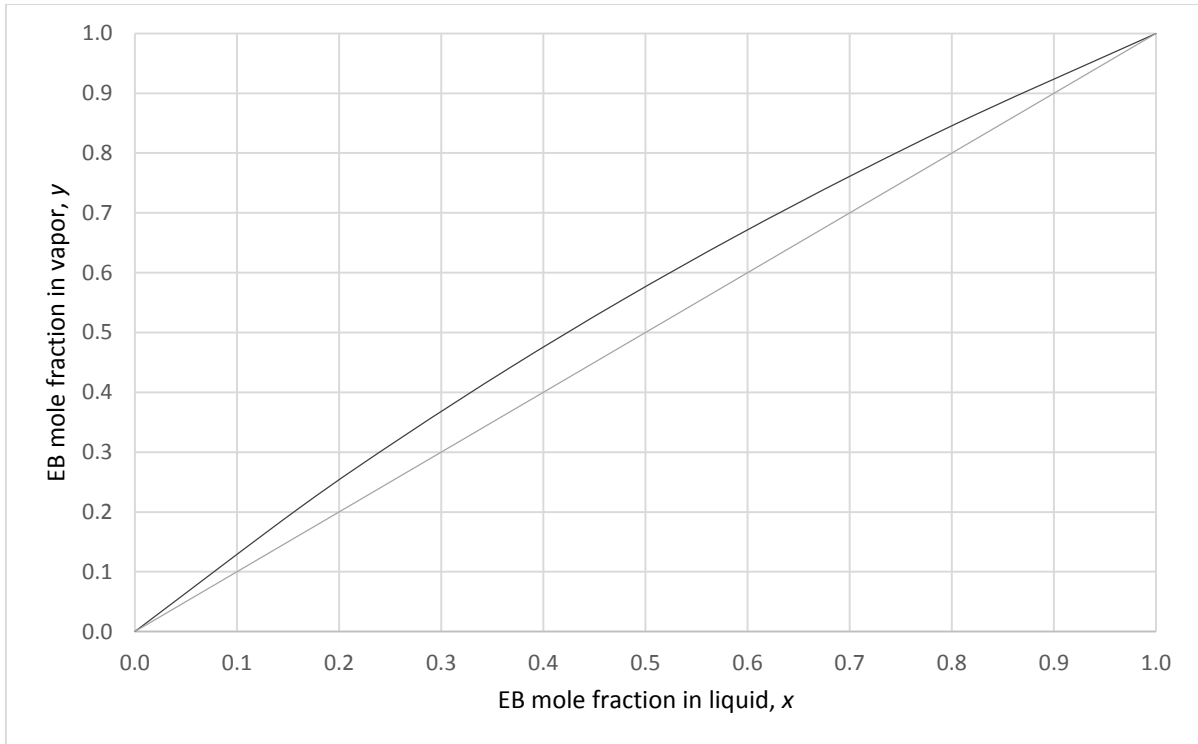E_{mV} is Murphree plate efficiency which is 75%.

Figure 5-13: Step 1, Vapor-Liquid Equilibrium line plot with 45° line.
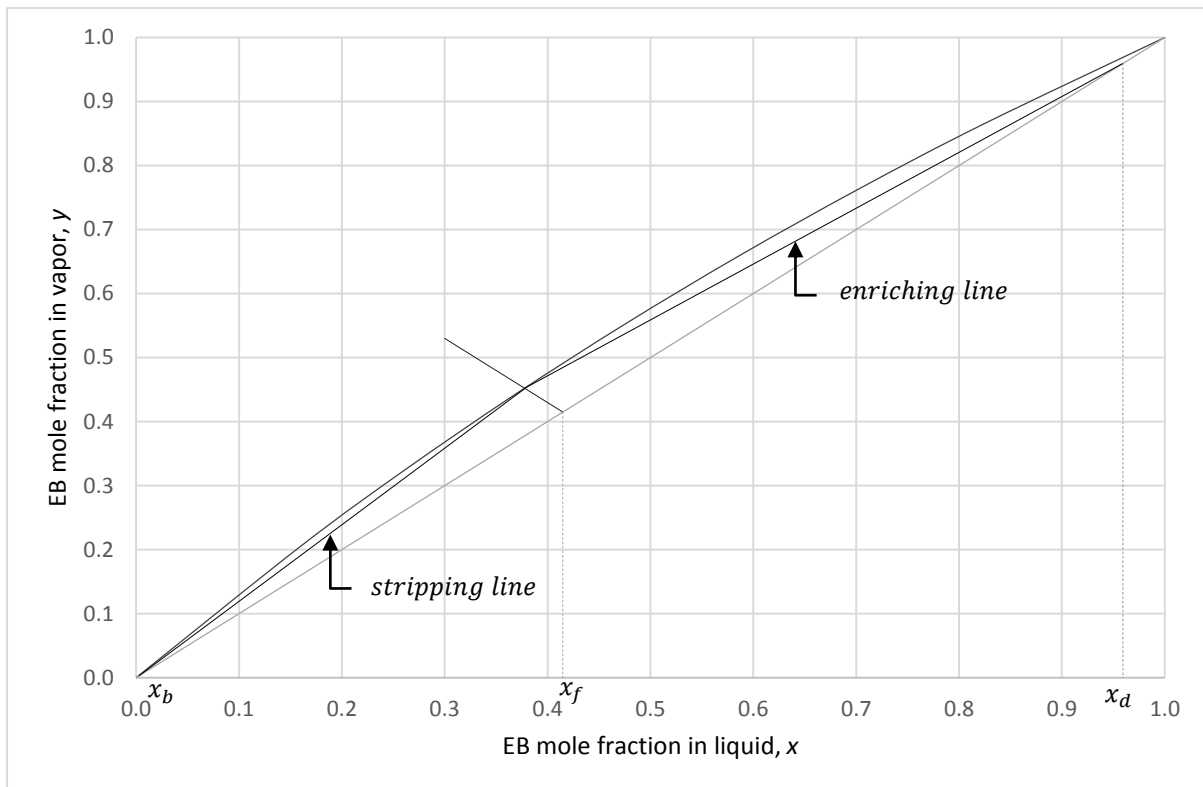
Figure 5-14: Step 3 and 4: Minimum reflux ratio plot.

The number of trays is obtained for this system is 52 before applying the overall efficiency factor and 75 after applying the overall efficiency factor. The feed tray enters at 23rd tray. Note that the feed vapor fraction is 0.5. Hence, in adding the feed to the entering tray the vapor portion of the feed is separated and added from the bottom of entering plate, and the liquid is added from above of entering plate. McCabe-Thiele plot for this system is shown in Figure 5-15 and calculations in Table 5-18.
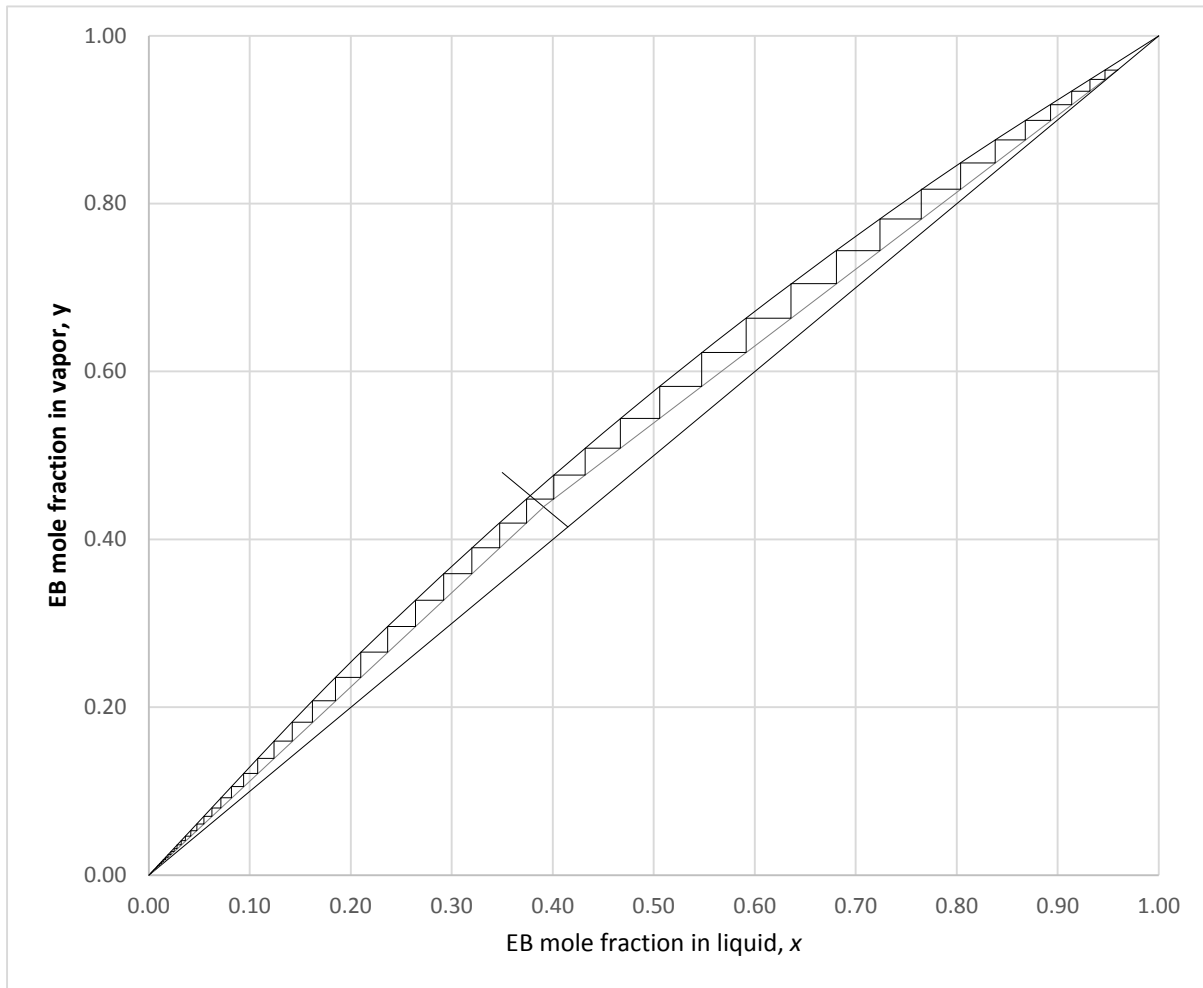
Figure 5-15: McCabe-Thiele Plot.

Table 5-18: Number of Stages Calculations.

Item	Value
Efficiency, E_{mV}	0.75
Enriching line slope, m	0.88
Overall enriching section efficiency, E_0	0.75
Stripping line slope, m	1.19
Overall stripping section efficiency, E_0	0.78
Number of stages in enriching section	23
Number of stages in stripping section	52
The number of stages for the tower	**75**

The minimum number of stages N_m is also has been calculated at total reflux ratio and found to be 35 stages as shown in Figure 5-16.

Figure 5-16: Total reflux and minimum number of stages by McCabe-Thiele method.

5.2.3   Column Design and Sizing

This section covers the basic elements in designing the distillation column for this system, which includes selection and sizing of column internals.

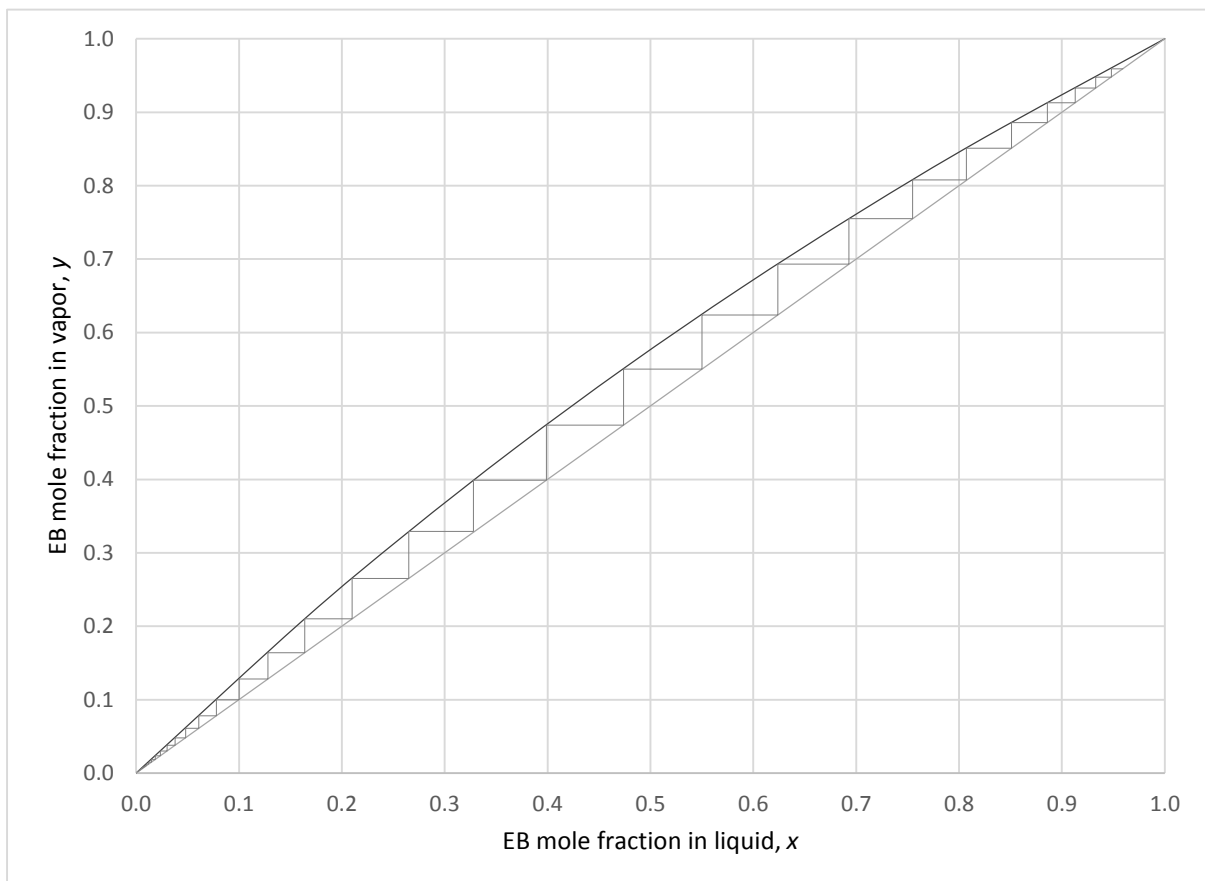Note that the amount of the flow rate feeding to the tower is very large and a huge tower is needed to achieve the separation process, which is high in cost, complicate to design, manufacture and maintain. So, two towers of the same design details will be industrialized to be running in parallel to achieve the separation process required.

5.2.3.1 Material Balance

First of all, material balance is carried out around the top and bottom section of the tower as shown in Figure 5-17 to find the values of V_T, L_T ($= L$), V_B and L_B by knowing the values of V_f, L_f, D, F and the reflux ratio $R = L/D = 10.92$. The calculation result of the material balance is shown in Table 5-19.
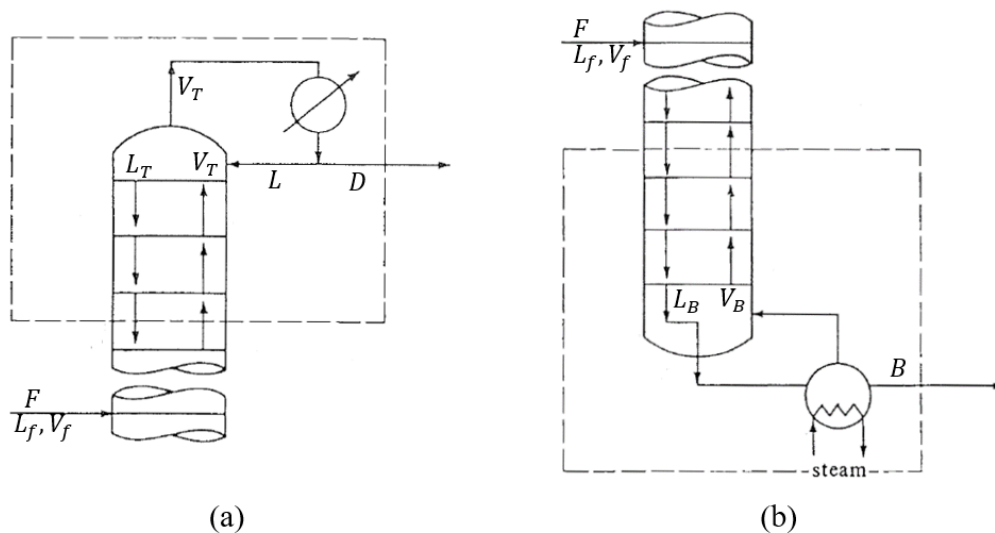
Figure 5-17: Schematic of the tower (a) at the top (b) at the bottom.

Table 5-19: Material balance result for the tower.

Feed Section		
F	0.04	kmol/s
L_F	0.02	kmol/s
	2.05	kg/s
ρ_L	857.50	kg/m^3
V_F	0.02	kmol/s
	2.05	kg/s
ρ_V	0.20	kg/m^3
Top Section		
D	0.02	kmol/s
L_T	0.23	kmol/s
	24.11	kg/s
ρ_L	833.29	kg/m^3
V_T	0.25	kmol/s
	26.32	kg/s
ρ_V	0.30	kg/m^3
Bottom Section		
B	0.02	kmol/s
L_B	-	kmol/s
	26.16	kg/s
ρ_L	813.94	kg/m^3
V_B	-	kmol/s
	24.27	kg/s
ρ_V	1.62	kg/m^3

Note that the average molecular weight for the feed, top and bottom sections is 104.99, 106.09 and 104.16 kg/kmol, respectively.

5.2.3.2 Plate-design

After the vapor and liquid flow rates for the tower are calculated and the system physical properties is collected and estimated, the plate design is completed by the following steps:[14]

1. A trial plate spacing is selected, which is 0.45 m.

2. The column diameter was estimated based on the flooding consideration, which was found to be 5.88 and 3.86 m for the top and bottom sections, respectively.

3. The choice of a liquid flow arrangement is made based on the liquid flow rate and column diameter using the figure provided by Towler, which is found to be cross flow.

4. The weir height is chosen to be 13 and 21 mm for the top and bottom section, respectively. The higher weir height, the higher is the efficiency, but the larger pressure drop which is extreme significant in towers operating under vacuum pressure.

5. The hole size and distance between them is chosen to be 5 and 15 mm at equilateral triangular pattern.

6. The total pressure drop over the plates is calculated and founded to be 77.7 and 96 mm at the top and bottom trays, respectively.

7. For weeping check, the minimum design vapor velocity is calculated and found to be 20.3 m/s. The operating vapor velocity is calculated and found to be 28.5 m/s, which is higher than the minimum. Thus, no weeping will occur.

8. For flooding check, the level of the liquid and froth in the down-comer must be well below the top of the outlet weir on the plate above. This height is designed to be 222.6 and 229.6 mm for top and bottom trays respectively, which is less than half of tray spacing plus the weir height. To prevent the flooding, the entrains amount of liquid droplet carried out by the uprising vapor should not be excessive, it was calculated and found to be 0.095 and 0.06 (kg entrained/kg liquid) for top and bottom trays, respectively. Thus, no flooding will occur.

9. The residence time in down-comer is calculated and found to be 25 and 10 seconds for top and bottom trays, respectively, which is more than enough to prevent the liquid from being heavily aerated.

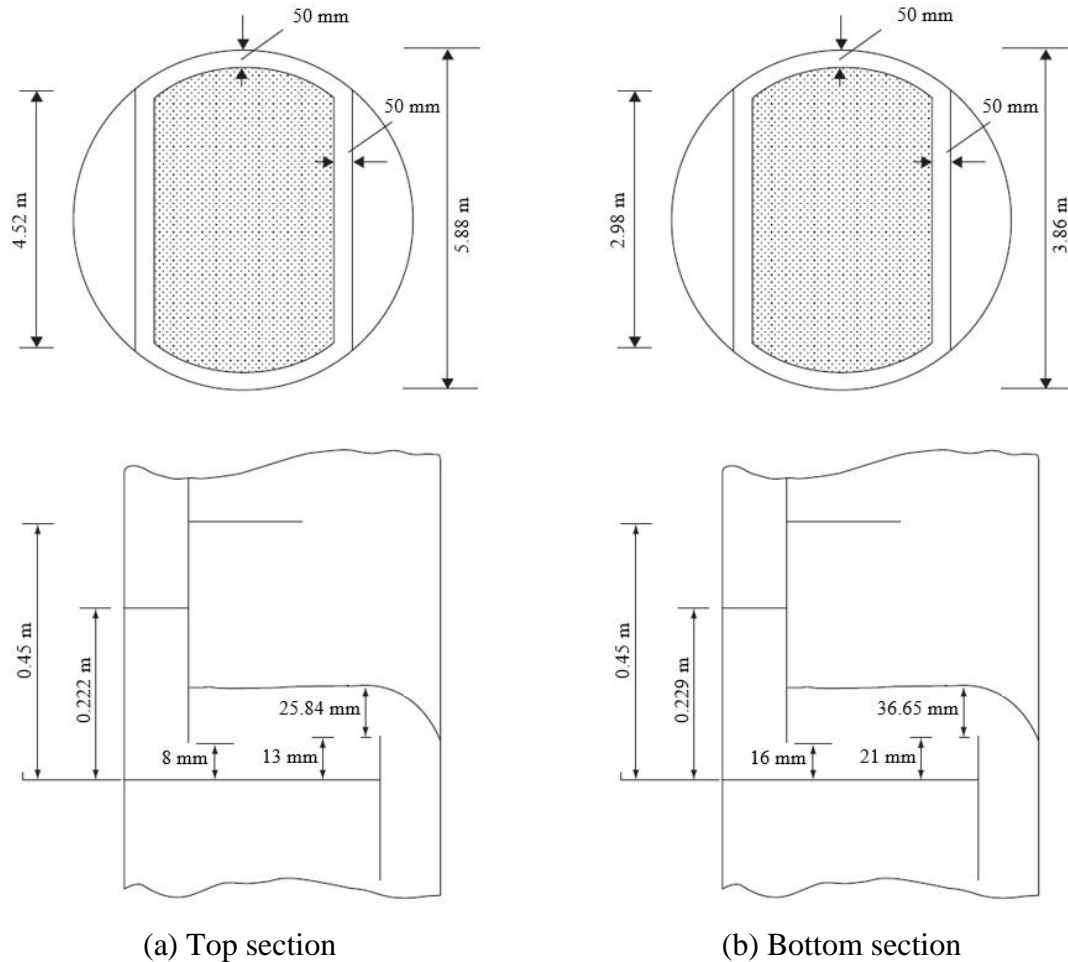The final plate specification is shown in Figure 5-18.

(a) Top section   (b) Bottom section

Figure 5-18: Plate specification for tower (T-101).

5.2.3.3 Vessels Design

Before designing the vessel, a material of construction should be selected based on many considerations such as the mechanical properties of the material, effect of temperature, corrosion resistance, availability and cost.

The selected material for this tower is mild carbon steel. It has good mechanical properties, suitable for use in process containing hydrocarbons at moderate temperatures, available in wide range of sizes, can be easily worked and welded and it is relatively cheap.

Now, because the tower vessel is objected to external pressure since its operating under vacuum pressure, the calculation for the thickness of the wall is done using the method provided by ASME BPV Code[14] as follow:

1. A trial thickness is assumed at the minimum thickness allowed based on the column internal diameter, D_i, which is 19 mm.
2. From the graph provided by the reference, a constant K is evaluated.

3. The thickness is calculated by the equation:

$$t = D_i \sqrt[3]{\frac{P_E}{KE'}} \qquad (5.43)$$

Where P_E, the maximum external pressure with 10% factor of safety which equals 1 bar. E', modulus of elasticity which equals $1.7*10^6$ bar.

Thickness calculated and found to be 10 and 7 mm for the top and bottom sections, respectively.

The calculated thickness will be less than the minimum thickness allowed. Thus, the appropriate thickness design well be as the minimum thickness allowed, 19 mm.

For the vessel heads, an ellipsoidal type is chosen because of the high column diameter. It was calculated by the following equation:[14]

$$t = \frac{P_i D_i}{2SE - 0.2P_i} + C \qquad (5.44)$$

It found to be 6 and 4 mm for the top and bottom sections, respectively. Which is below the minimum thickness allowed. Thus, the appropriate thickness design for the heads well be as the minimum thickness allowed, 19 mm.

5.2.3.4 Pipe Design

There are five pipes to design in distillation column. For the feed vapor liquid mixture, outlet vapor from the top, the refluxed liquid, the outlet liquid from the bottom and the vapor boil-up.

The velocity of the liquid, vapor and mixture is assumed to be 3, 30 and 10 m/s, respectively. Depending on the velocity, mass flow and the density; diameter of the pipes is calculated as shown in Table 5-20.

Table 5-20: Pipes diameter.

Pipe	Diameter, cm
Feed mixture	51.5
Top vapor	181
Refluxed liquid	11
Bottom liquid	12
Boil-up vapor	80

5.2.4 Distillation Column Control

The main objective of this distillation column control is to maintain the bottom product composition at 99.8% mol styrene. Control scheme of the distillation column is shown in Figure 5-19.
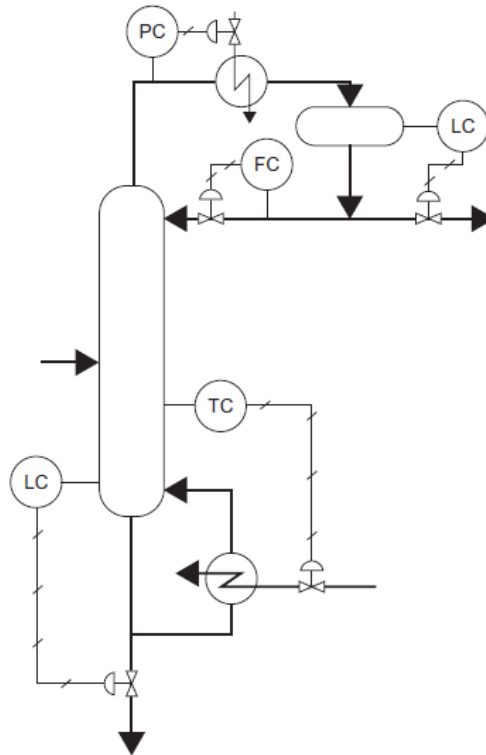

Figure 5-19: Distillation column (T-101) control scheme.

Where, TC : Temperature Controller.

PC : Pressure Controller.

LC : Level Controller.

FC : Flow Controller.

5.2.5 Capital Cost Estimation

After all tower specification is designed, the tower capital cost is estimated by Matches website for the tower vessel using the column weight and by an equation provided by Towler for the trays.

The tower weight is calculated as follow:

$$Mass\ (kg) = Volume\ (m^3) * Density\ (kg/m^3)$$

$$Mass = [\ perimeter * thickness * height] * Density$$

$$Mass = [[\ \pi D * t * H\ ]_{top} + [[\ \pi D * t * H\ ]_{bottom}] * \rho_m$$

Towler's equation for trays:

$$C_e = a + bD^n$$

Where a,b and n are constant.

The calculated tower vessel mass is 88,220 kg. Matches website estimate the capital cost as $518,600 in 2014. The total tower plates cost is estimated to be $515,640 in 2010.

The capital cost index for 2010, 2014 and 2018 is 532.9, 576.1 and 603.1, respectively. Thus, the capital cost for this distillation column is $1,126,480 in 2018 which equals 4,224,300 SR each. The cost for the two-distillation column working in parallel is 8,448,600 SR.

5.3 DISTILLATION COLUMN (T-102) DESIGN

The target of the distillation column is to distil ethylbenzene, from other components with purity 98% to be recycled to the reactor.

After the water is extracted in the decanter (V-102), the organic liquid (stream 21) is fed to the distillation column (T-102) at a flow rate of 138.35 kmol/h and

a composition of 2.9 mol% styrene, 69.2 mol% ethylbenzene, 16.1 mol% toluene, 11.8mol% benzene, and very small amount of water.

In this separation process we depend on the differences in volatility components; when the differences in the volatility is bigger the separation process will be easier. In our case, the difference in the volatilities between the components is wide, which make the separation easier.

Before starting the distillation column design, you must select the operating pressure, because the pressure has a major effectiveness on components phase equilibrium in terms of relative volatilities and column temperatures.

After selecting the operating pressure, the bubble point and dew point must be calculated for the liquid mixture in feed to estimate the reboiler, and condenser temperatures. knowing that the bubble and dew points can be calculated from the vapor-liquid equilibrium.

5.3.1 Vapor-liquid equilibrium

The heavy and light keys in this column are EB and toluene, respectively. EB & TO have a similar structure. Thus, they can be assumed as an ideal solution by following Raoult's law and can be used with Antoine's equation to find the vapor -liquid phase equilibrium.

In the Antoine equation we find that the boiling temperature of the Toluene and Ethylbenzene at 1.5 bar are 125 and 151℃ respectively, knowing that the pressure enter the distillation column is 1.5 bar. Now we can calculate the vapor pressure of both the Toluene and EB and also to calculate liquid and vapor fraction for toluene using Raoult's law. The result is obtained, and the VLE is plotted in Figure 5-20.
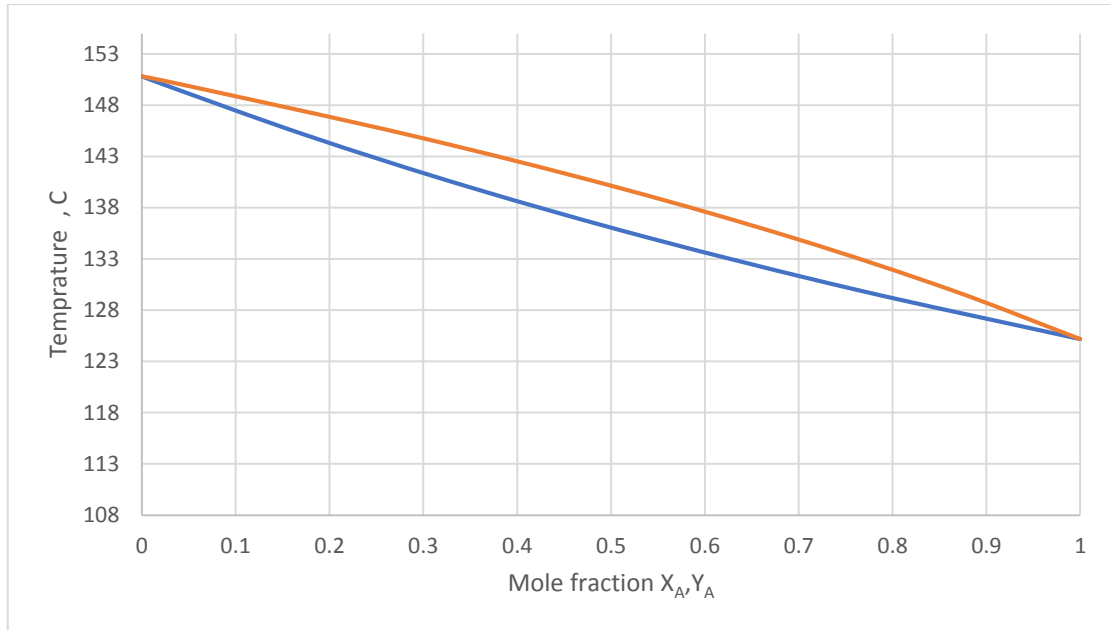
Figure 5-20: Txy diagram from toluene/EB at 1.5 bar.

5.3.1.1 Dew point and bubble point calculation

The calculated results for bubble point in the bottom and dew point in the top is 157.13 and 110.88 °C respectively, calculations are shown in Table 5-21 and Table 5-22.

Table 5-21: Bubble point calculation (bottom temperature).

Component	P_i (bar)	K_i	α_i	$\alpha_i \, x_i$
1. EB (HK)	1.749	**0.999**	1.000	0.948
2. S	1.370	0.783	0.783	0.032
3. B	6.680	3.817	3.819	0.000
4. T (LK)	3.216	1.838	1.839	0.021
5. W	5.724	3.271	3.273	0.000
Total	-	-	-	1.001

$$K_C = \frac{1}{\sum \alpha_i x_i} = \frac{0.999}{1.001} = 0.998$$

Table 5-22: Dew point calculation (top temperature).

Component	P_i (bar)	K_i	α_i	y_i/a_i
1. EB (HK)	0.500	0.396	1.000	0.049
2. S	0.369	0.295	0.745	0.000
3. B	2.390	1.908	4.818	0.086
4. T (LK)	1.016	0.813	2.053	0.261
5. W	1.468	1.174	2.965	0.000
Total	-	-	-	0.396

$$K_C = \sum \frac{y_i}{\alpha_i} = 0.396$$

Summary data for the column streams condition is illustrated in Table 5-23.

Table 5-23: Summary data for streams conditions.

Condition	Feed	Top product	Bottom product
Stream number	21	23	22
Pressure, bar	1.5	1.25	1.75
T, °C	56.20	110.88	157.13
Molar flow rate, kmol/h	138.35	39.41	98.94
Ethylbenzene mol%	0.692	0.049	0.948
Styrene mol%	0.029	0.000	0.041
Benzene mol%	0.118	0.415	0.000
Toluene mol%	0.161	0.536	0.011
Water mol%	0.000	0.001	0.000

5.3.2   Number of Stage Requirement

After vapor-liquid phase equilibrium, bubble and dew point were calculated, there are two methods are followed to estimate the number of stages required: shortcut method for multicomponent system and McCabe-Thiele method for binary systems.

5.3.2.1 Shortcut method

Short-cut methods can be used to know the minimum number of trays, but the method can't be applied because they are inaccurate. The same method and equations applied in chapter 5.2.2.1 has been used.

Note that all other components are lighter than the light key "TO" and it will be distilled from the top section.

After we found N_m=10.29 and R_{min}=3.99 number we would assume $R = 1.5R_{min} = 5.98$. Through Erbar-Maddox correlation shown in Figure 5-12. it found that N=17. Since the overall efficiency of the distillation column for this system is 75%[14], N=23.

5.3.2.2 McCabe-Thiele Method

McCabe-Thiele method is determining the number of theoretical stages by using material balance around particular parts of the tower and the xy equilibrium curve for the system. It's subject to the following assumptions:

- The mixture is binary i.e. there are only two components.
- Number of trays calculated by using the McCabe-Thiele method are called "theoretical trays", you have to divide it on efficiency provided by Towler[14], which's 75% for ethylbenzene-toluene system.

In McCabe-Thiele method the distillation column is split into 3 sections stripping section, enriching section and feed section. The stripping section is located under the feed section where the more volatile components are stripped from the liquid. Enriching section is located above the feed section where the concentration of the more volatile components rises.

The procedure for McCabe-Thiele method accomplished by the following steps:
1. The vapor-liquid equilibrium curve from data calculated at the column operating pressure is plotted in xy diagram with 45-degree line tuning from the origin point to the top right corner as shown in Figure 5-21.
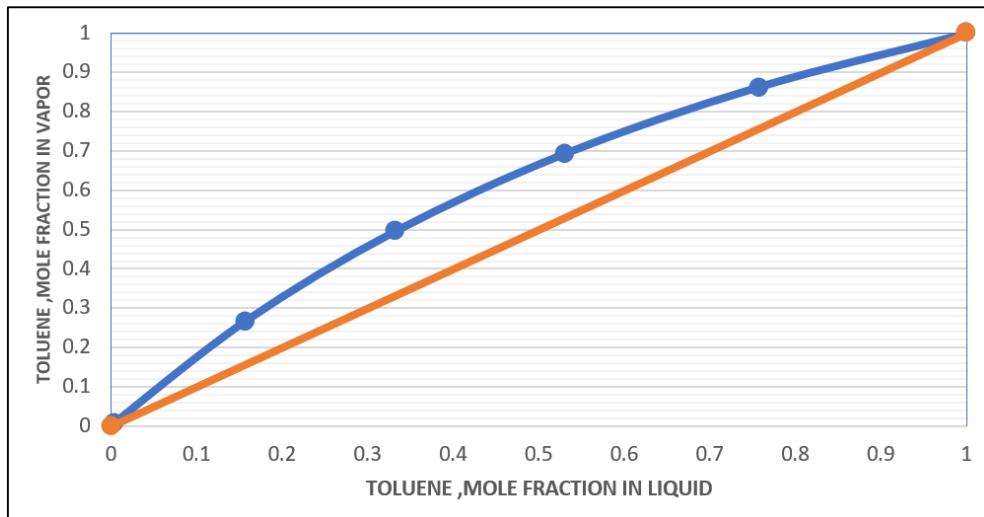
Figure 5-21: VLE line plot with 45° line.

2. Find x_d and x_w by material balance, this step was achieved in chapter 4.1.

3. The q line is plotted with slop $= q/(q\text{-}1) = \text{-}0.5$, intersecting the diagonal at x_f.

4. We have to calculate R that was assumed previously equals to $1.5R_m$. R_m is calculated by drawing the enriching and stripping operating line intersects with the intersect of q line and VLE, starting from x_d for enriching line and from x_w for the stripping line.

   R_m is found to be 4.899 which has been calculated by: $\frac{R_m}{R_m+1} = \frac{x_d-y'}{x_d-x'}$.

5. R is calculated as $R = 1.5R_m$, which found to be 10.92.

6. The enriching line is plotted using equation (5.41).

7. The stripping line is drawn from enriching line and q-line intersect to 45° diagonal line at x_d.

8. The theoretical stages are determined by starting at the top at x_d, the trays are stepped off until reaching the bottom at x_w.

9. Calculate overall column efficiency E_0 by using this equation in both enriching and stripping line. The efficiency for stripping line and enriching line are 60% and 67% respectively.

The number of trays is obtained for this system after applying the efficiency factor is 26. The feed tray enters at 13th tray. McCabe-Thiele plot for this system is shown in Figure 5-21 and calculations under it.

Table 5-24: Number of Stages Calculations.

Item	Value
Efficiency, E_{mV}	0.75
enriching line slope, m	1.20
Overall enriching section efficiency, E_0	0.67
stripping line slope, m	0.63
Overall stripping section efficiency, E_0	0.60
number of stages in enriching section	8
number of stages in stripping section	8
The number of stages for the tower	**26**

5.3.3 Column Design and Sizing

In order to operate for the distillation column to function properly we must calculate a lot of details and then check because perhaps a minor calculation error may cause flooding within the distillation column or possibly exit the compounds from the distillation before they are well separated.

5.3.3.1 Material Balance

The material balance to top and bottom sections of the tower was done to find the values of $V_T, L_T (= L), V_B$ and L_B by knowing the values of V_f, L_f, D, F and the reflux ratio $R = L/D = 7.35$. The calculation results of the material balance are shown in Table 5-25.

Table 5-25: Material balance result for the tower.

Feed Section		
F	0.04	kmol/s
L_F	0.02	kmol/s
	1.96	kg/s
ρ_L	760.14	kg/m^3
V_F	0.02	kmol/s
	1.96	kg/s
ρ_V	4.56	kg/m^3
Top Section		
D	0.01	kmol/s
L_T	0.08	kmol/s
	8.21	kg/s
ρ_L	781.55	kg/m^3
V_T	0.09	kmol/s
	9.33	kg/s
ρ_V	3.58	kg/m^3
Bottom Section		
B	0.03	kmol/s
L_B	010	kmol/s
	10.17	kg/s
ρ_L	738.72	kg/m^3
V_B	0.07	kmol/s
	7.37	kg/s
ρ_V	5.54	kg/m^3

5.3.3.2 Plate-design

After the vapor and liquid flow rates for the tower are calculated and the system physical properties is collected, the plate design is completed by the following steps:

1. A trial plate spacing is selected, which is 0.6 m.
2. The column diameter was estimated and found to be 1.69 m.
3. The weir height is chosen to be 72 mm.
4. The hole size and distance between them is chosen to be 5 and 15 mm Respectively.
5. Total pressure drops over the plates is found to be 162.5 mm.

The speed of the design was calculated to be greater than the minimum speed and this means that there will be no weeping , and we calculated the residence time and we found it 6.9 s and this is enough time to not get "aerated " , and we calculated down-comer back-up we regained it less than half (l_t +h_w) and this means that there will be no flooding.
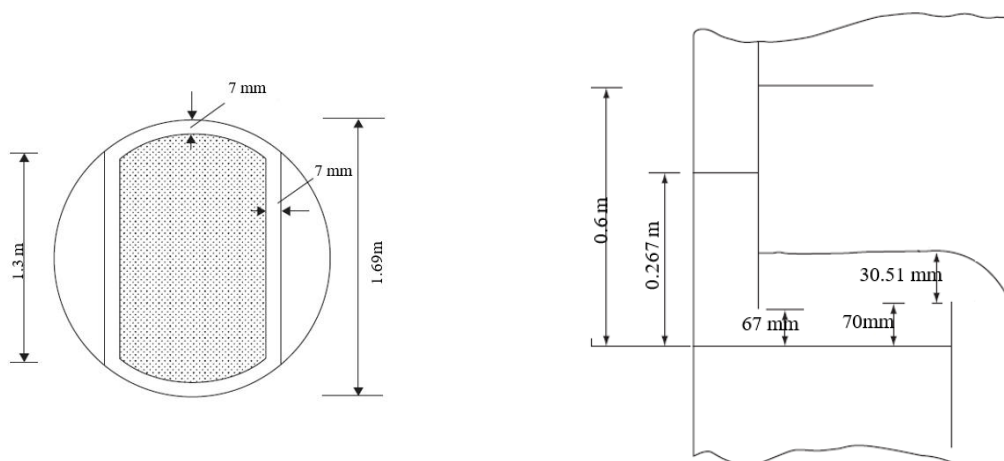
The final plate specification is shown in

Figure 5-22: Plate specification for tower (T-102).

5.3.3.3 Vessels Design

Before designing the vessel, a material of construction has to be chosen based on many considerations such as the mechanical properties of the material, impact of temperature, corrosion resistance, availability and cost.

The material selected for this tower is mild steel. It has good mechanical properties, suitable for use in process containing hydrocarbons at moderate temperatures, available in wide range of sizes, can be easily worked and welded and it is relatively cheap.

Now, because the tower vessel is designed to operating at atmospheric pressure, the thickness of the wall will be the minimum as mentioned in Towler[14] that is 7 mm.

5.3.3.4 Pipes calculated diameters

There are five pipes to design in distillation column. For the outlet vapor from the top, for the refluxed liquid, for the outlet liquid from the bottom and the vapor boil-up.

The velocity of the liquid and vapor is assumed to be 3 and 30 m/s respectively. Depending on the velocity, mass flow and the density; diameter of the pipes is calculated as shown in Table 5-26.

Table 5-26: Calculated pipes diameter.

Pipe	Diameter, m
Feed	0.036
Bottom liquid	0.076
Boil-up vapor	0.260
Refluxed liquid	0.067
Top vapor	0.364

5.3.4 Distillation Column Cost

To calculate the cost of the vessel should be calculated the mass first by using this equation:

$$m = \rho_m * (\pi D_m H t_s + 2 * 0.8 D_m^2 t_h) \tag{5.45}$$

$$m = 5805 \, kg$$

The price is 275,625 SAR[19] in 2014. Using index 2018 to get the price of the vessel in 2018. The cost in 2018 = 288,544 SAR.

The cost of trays calculated by using following equation:

$$\text{Cost of trays} = a + bD^n \tag{5.46}$$

Where a, b and n are constants and D is the diameter of the tower.

After used this equation, found cost of tray = 4744 SAR in 2010. To calculate the cost in 2018 index for 2010 and 2018 is used, which is equal 532.9 and 603.1 respectively.

The cost in 2018 = 5370 SAR for each tray. For all trays price is 139,609 SAR. The cost of the distillation is sum of trays and the vessel cost, the price of the distillation is 428,153 SAR.

5.3.5 Distillation Column Control

The main objective of this distillation column control is to maintain the bottom product composition at 98% mol EB. Control scheme is shown in
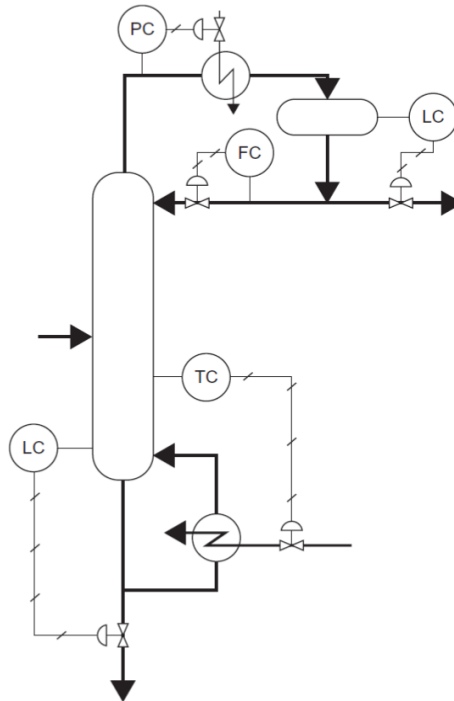

Figure 5-23: Distillation column (T-102) control scheme.

controls boil-up by composition and gives the fastest control response to variations in composition.

Where, LC : Level Controller.

PC : Pressure Controller.

TC : Temperature Controller.

FC : Flow Controller.

CHAPTER 6:

EQUIPMENT SIZING

In this chapter, the E-101, E102, V-101, V-102, T-103, H-101 and H-102 will be sized to estimate the cost of each and hence, calculate the FCI cost.

6.1 HEAT EXCHANGER AND COOLER SIZING

The heat exchanger (E-101) and cooler (E-102) used heat equation to determine the area of each and get the cost. the overall heat transfer coefficients were taken from Kern[22], the vales for both in W/m^2.°C and the heat transfer in J/h, are shown in Table 6-1.

Table 6-1: Values of overall heat transfer

Equipment	U_d (W/m^2.°C)	Q (kJ/h)
E-101	851.47	74,750
E-102	425.87	12,500

The equation used for this equipment is:

$$\dot{Q} = U_d A \Delta T_m \qquad (6.1)$$

where $\dot{Q}$ is the heat transfer, A is the area, U_d is the overall heat transfer officiant and the ΔT_m is the log-mean temperature difference. ΔT_m can be calculated by:

$$\Delta T_m = \frac{\Delta T_{out} - \Delta T_{in}}{\ln(\frac{\Delta T_{out}}{\Delta T_{in}})} \qquad (6.2)$$

For E-101:

$$\Delta T_m = \frac{393 - 10}{\ln(\frac{393}{10})} = 104.3°C$$

For E-102:

$$\Delta T_m = \frac{366.7 - 25}{\ln(\frac{366.7}{25})} = 127.23°C$$

The areas for both are:

$$A = \frac{\dot{Q}}{U_d \Delta T_m} = \frac{74750000}{851.47 * 104.3} = 841 \ m^2 = 9055 \ ft^2$$

$$A = \frac{\dot{Q}}{U_d \Delta T_m} = \frac{12500000}{425.87 * 127.23} = 230.7 m^2 = 2483 \ ft^2$$

The temperature difference between the inlet and outlet for both heat exchangers is too high; 104.3℃ for E-101 and 127.23℃ for E-102. Thus, it was decided to use four similar heat exchangers in series for both of them, to avoid using single huge units with extremely high temperature differences. The prices of heat exchangers and coolers are shown in Table 6-2.

Table 6-2: Prices of heat exchangers

Equipment	A (ft^2)	C_{2014} (SAR)	C_{2018} (SAR)
E-101	9055	1,141,500	1,195,000
E-102	2483	2,854,500	2,988,280

6.2 FIRED HEATER (H-101 AND H-102)

To estimate the furnace price, the duty should be calculated. From Table 4-14 the duty for (H-101) and (H-102) are 81.90 and 15.63 GJ/h, respectively. Using this duty, the prices for both furnaces were estimated by Matches website [19]. Table 6-3 shows the price in Saudi Riyals and duty for the furnaces.

Table 6-3: Furnaces price

Equipment	Q (GJ/h)	C_{2014} (SAR)	C_{2018} (SAR)
H-101	81.90	6,653,250	6,956,000
H-102	15.63	3,173,250	3,321,970

6.3 DECANTERS SIZING (V-101) & (V-102)

To calculate the decanter size, we first calculate the diameter by the following equation:

$$D_v = \sqrt{\frac{4V_v}{\pi\, U_s}}$$

(6.3)

Where V_v is gas or vapor volumetric flow rate, m^3/s U_s is Settling Velocity And which can be calculated by:

$$U_s = 0.07 \sqrt{\frac{\rho l - \rho v}{\rho v}}$$

(6.4)

Where ρl and ρv are density of liquid and vapor respectively.

The calculated U_t is 2.95 m/s and D_v=0.80 m, where D_v= is the smallest diameter can be used, but we hypothesized that the diameter is 2 m to reduce the length of decanter. assume resident time =10 min now we can calculate V_o and V_L through

$V_o = Q_o * 10$ min

$Q_L = Q_L * 10$ min

Where V_o and V_L are oil and liquid volume in m^3, respectively. Q_o and Q_L are oil and liquid volumetric flow rate, m^3/s, respectively.

The height is estimated by following equation:

$$H = \frac{4V}{(Dv)^2\ \pi}$$
(6.5)

H_o found to be 1.7 m and H_L is 3.91 m, H_V and H_{VESSEL} also calculated by using following equation:

$$H_v = Dv + 0.4$$

$$H_{Vessel} = H_o + H_L + H_v + 0.6$$

H_v =2.4 m and H_{Vessel} =8.6 m

knowing that H_L, H_o, H_v and H_{Vessel} are height of liquid, oil, vapor and vessel respectively.

For the second decanter (V-102), the same procedure is followed to size the equipment. H_{vessel} and D_v are 4.14 and 1.07 m, respectively.

Because there is no pressure force applied on both decanter vessels, the vessels thickness will be the minimum thickness required for this diameter which is 7 mm. A schematic diagram for the decanter is shown in Figure 6-1.
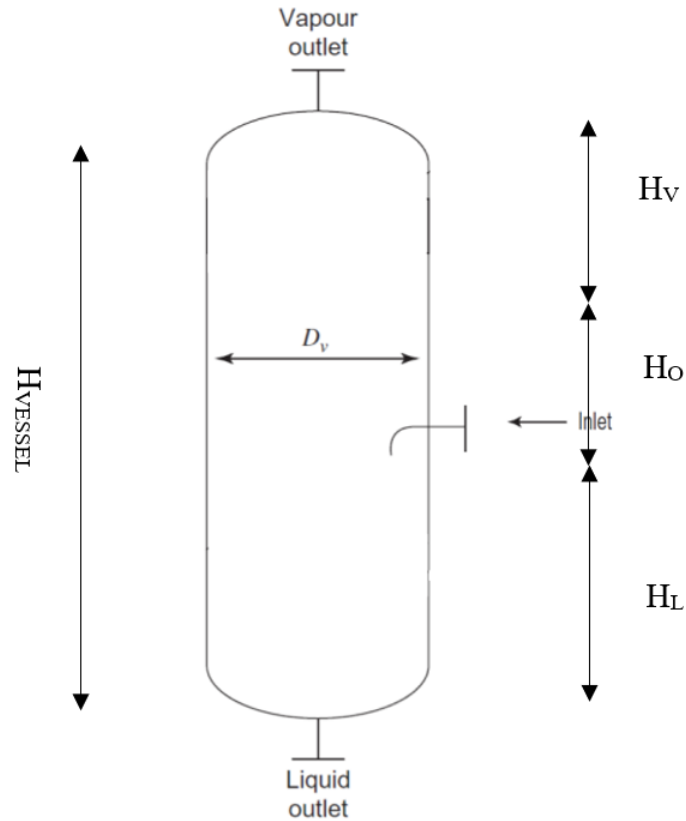
Figure 6-1: Schematic diagram of the decanter

6.4 DISTILLATION COLUMN (T-103) SIZING

For sizing this distillation column, the exact same procedure in designing (T-101) is followed except for estimating the number of stage requirement, only shortcut method was used. And the column operating pressure is at 1 bar.

6.4.1 Vapor-liquid equilibrium

The obtained results for VLE are shown in Table 6-4 and was plotted as presented in Figure 6-2.

Table 6-4: VLE-Mole-Fraction data for BZ-TO system.

T, °C	P_B, bar	P_S, bar	x_B	y_B
80.1	1.01	0.39	1.000	1.000
84.0	1.13	0.44	0.820	0.921
87.8	1.27	0.50	0.661	0.832
91.6	1.42	0.57	0.520	0.730

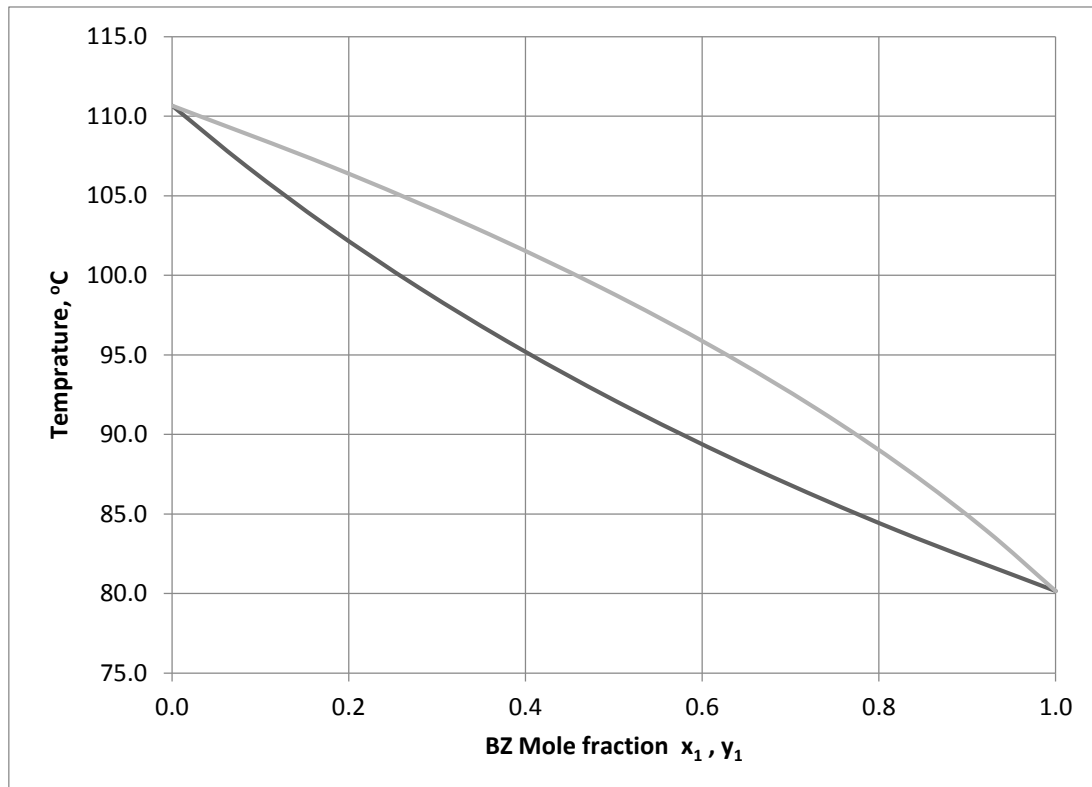|				
95.4	1.58	0.64	0.393	0.615
99.2	1.76	0.72	0.279	0.486
103.0	1.95	0.81	0.177	0.341
106.8	2.15	0.91	0.084	0.179
110.7	2.37	1.01	0.000	0.000

Figure 6-2: Txy diagram from EB/styrene at 0.3 bar.

6.4.2 Dew point and bubble point calculation

The calculated bubble point and dew point for the top and bottom of the column are 119 and 72 °C respectively. Calculations of bubble and dew point are shown in Table 6-5 and Table 6-6, respectively.

Table 6-5: Bubble point calculation (bottom temperature).

Component	P_i (bar)	K_i	α_i	$\alpha_i x_i$	y_i
1. EB (LK)	0.663	1.325	1.326	0.003	0.003
2. S (HK)	0.500	**0.999**	1.000	0.998	0.997
3. B	3.024	6.049	6.054	0.000	0.000

4. T	1.325	2.651	2.653	0.000	0.000
5. H₂	733.231	1466.463	1467.660	0.000	0.000
6. C₂H₄	206.031	412.063	412.399	0.000	0.000
7. CO₂	3229.017	6458.034	6463.303	0.000	0.000
8. W	2.008	4.015	4.019	0.000	0.000
Total				1.001	1

$$K_C = \frac{1}{\sum \alpha_i x_i} = \frac{1}{1.001} = 0.999$$

Table 6-6: Dew point calculation (top temperature).

Component	P_i (bar)	K_i	α_i	y_i / a_i	x_i
1. EB (LK)	0.078	0.784	1.454	0.439	0.814
2. S (HK)	0.054	**0.539**	1.000	0.027	0.050
3. B	0.536	5.359	9.943	0.011	0.020
4. T	0.191	1.908	3.541	0.042	0.078
5. H₂	681.269	6812.688	12640.474	0.000	0.000
6. C₂H₄	104.645	1046.449	1941.614	0.000	0.000
7. CO₂	789.031	7890.306	14639.920	0.000	0.000
8. W	0.206	2.062	3.827	0.020	0.037
Total				0.539	1

$$K_C = \sum \frac{y_i}{\alpha_i} = 0.539$$

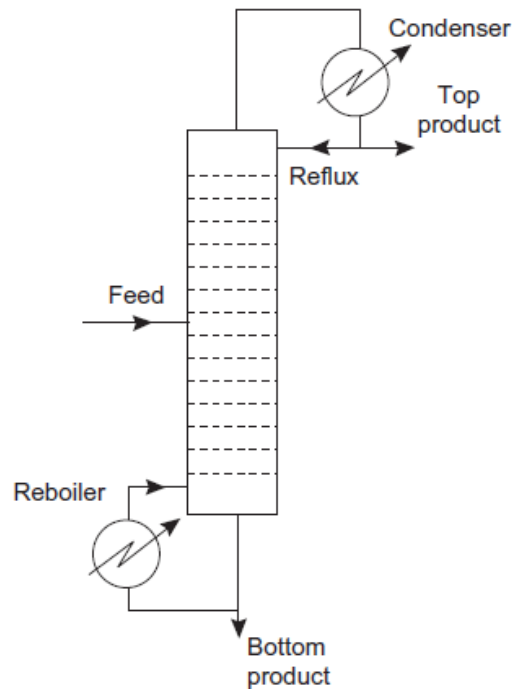Summary data for the column streams condition is illustrated in Figure 6-3 and Table 6-7.

Figure 6-3: Schematic Diagram of the Distillation Column.

Table 6-7: Summary data for streams conditions.

Condition	Feed	Top product	Bottom product
Stream number	15	29	26
Pressure, bar	1	0.75	1.25
T, °C	80	72	119
Molar flow rate, kmol/h	39.404	16.46	22.94
Ethylbenzene mol%	0.049	0	0.08
Benzene mol%	0.415	0.97	0.01
Toluene mol%	0.536	0.03	0.90

6.4.3 Number of Stage Requirement

The calculations of minimum reflux ratio using shortcut method are shown in Table 6-8.

Table 6-8: Minimum reflux ratio calculation.

Component	$\alpha_{i,avg}$	$\dfrac{\alpha_{i,avg}x_{i,f}}{\alpha_{i,avg}-\theta}$	$\dfrac{\alpha_{i,avg}x_{i,d}}{\alpha_{i,avg}-\theta}$
1. EB	0.462635225	-0.018331353	0
2. B (LK)	2.478389513	1.300288584	3.049819577

3. T (HK)	1	-0.778766556	-0.0372774
4. W	1.322632546	-0.003190675	-0.007636439
Total		0.5	3.004905738

After the minimum number of stages and minimum reflux ratio are found, the Erbar-Maddox correlation is used to find the actual number of stages at the used reflux ratio. For $R = 1.5R_{min} = 30.1$, the theoretical number of trays was found to be 14 trays. Since the overall efficiency of the distillation column for this system is 75% [14], the actual number of trays is 19.

6.4.4 Column Sizing

For the same procedure shown in chapter 5.2, material balance result is listed in Table 6-9.

Table 6-9: Material balance result for the tower.

Feed Section		
F	0.011	kmol/s
L_F	0.005	kmol/s
	0.48	kg/s
ρ_L	803.00	kg/m³
V_F	0.01	kmol/s
	0.48	kg/s
ρ_V	2.87	kg/m³
Top Section		
D	0.0046	kmol/s
L_T	0.01	kmol/s
	1.08	kg/s
ρ_L	832.60	kg/m³
V_T	0.02	kmol/s
	1.44	kg/s
ρ_V	2.10	kg/m³
Bottom Section		

B	0.01	kmol/s
L_B	-	kmol/s
	1.55	kg/s
ρ_L	772.60	kg/m³
V_B	-	kmol/s
	0.96	kg/s
ρ_V	3.70	kg/m³

Note that the average molecular weight for the feed, top and bottom sections is 86.9, 78.3 and 93.1 kg/kmol, respectively.

After the vapor and liquid flow rates for the tower are calculated and the system physical properties is collected and estimated, the diameter is estimated by the same procedure and found to be 0.87 m and high of 11.1 m.

6.4.5 Capital Cost Estimating

After finishing all the needed tower specification, the tower capital cost is estimated by Matches website for the tower vessel using the column weight and by an equation provided by Towler for the trays. It's found to be worth of 380,870 SR.

CHAPTER 7:

PROJECT COSTING

7.1 LABOR COST

This calculation based on 305 days of operating with 2 months of maintenance, 3 (shifts/day), 5 (shift/week) and 48 weeks for each operator in a year in total of 240 (shift/yr/operator). Total shifts in a year is 915 (shift/yr), and total operating weeks are 44 weeks.

For finding $C_{OL,}$ (cost of operating labor), the number of operators per shift is calculated as follow:

$$48\frac{week}{y} * 5\frac{shift}{operator.week} = 240\frac{shift}{operator.y}$$

$$305\ day * 3\frac{shift}{day} = 915\frac{shift}{y}$$

Number of operators for single shift is

$$\frac{915\frac{shit}{y}}{240\frac{shift}{operator.y}} = 3.8\ operators$$

For calculating the number of operators per shift, the following equation is used:

$$N_{OL} = [6.29 + (31.7)P^2 + 0.23N_{np}]^{0.5} \qquad (7.1)$$

Where N_{OL} is the number of operator per shift, P is the particulate processing step and N_{Np} is non-particulate processing step.

The number of particulate processing step is zero in this plant because there are no solids materials. The N_{Np} is shown in Table 7-1.

Table 7-1: Non-particulate processing step in the plant.

Equipment	No. equipment (N_p)
Fired heater	2
Heat exchanger	2
Reactors	2
Towers	3
Vessels	-
Total	9

Thus,

$$N_{OL} = [6.29 + (31.7)(0)^2 + 0.23(9)]^{0.5} = 2.89$$

Total operators in the plant

$$(3.8125) * (2.98) = 11$$

The average salary of the operator in Saudi Arabia is 11250 SR/month, equal to 135,000 SR/yr. thus, the C_{OL} is:

$$C_{OL} = 135000 * 11 = 1485000 \ SR/yr$$

The cost of raw material and products, with their amount and annual price (March 2019) are shown in Table 7-2. This is needed to get the gross profit of the project.

Table 7-2: Costs and amount of the materials.

Material	SR/tone	Tone/yr	SR/yr
EB	3553	140378	498,763,034
ST	4502	100000	450,200,000
BZ	2699	9150	24,695,850
TO	2972	13981	41,551,532

The gross profit is

$$Cost \ of \ income - Cost \ of \ raw \ material = 516447382 - 498763000$$

$$= 17684382 \ SR/yr$$

Where the income is the sum of ST, BZ and TO per year, and the cost of raw material is the cost of selling of EB per year.

The life of the project is assumed to be as 20 years, and the depreciation factor is taken as equipment prices/20 = 1.52 million per year. The net profit of the project is

$$Net \ profit = Gross \ rate - C_{OL} - deproteination$$

$$= 17684382 - 1485000 - 1520000$$

$$Net \ Profit = 14679382 \ SR/yr$$

7.2 COSTING OF THE EQUIPMENT

After pricing all the equipment separately, the total cost of the project including the labor and the raw materials used in the project is calculated using Towler. Table 7-3 shows the price of each equipment in Saudi Riyal, all in 2018.

The equipment E-101, E102, V-101, V-102, H-101, H-102 and T-103 are not fully designed just sizing to estimate the costs.

Table 7-3: Equipment prices in December 2018.

Equipment name	Equipment	Cost (SAR)
Furnace 1	H-101	6,956,000
Furnace 2	H-102	3,321,970
Heat Exchanger	E-101	1,195,000
Cooler	E-102	2,988,282
Plug Flow Reactor 1	R-101	1,530,435
Plug Flow Reactor 2	R-102	2,288,633
Decanter 1	V-101	189,615
Decanter 2	V-102	85,975
Distillation 1	T-101	8,474,766
Distillation 2	T-102	428,153
Distillation 3	T-103	380,370
Total		27,839,699

7.3 FIXED CAPITAL INVESTMENT

The Fixed Capital Investment (FCI) is equipment dependents, which includes installation of piping, installation of equipment erection, installation of instrumentation and control, installation of electrical work, installation of civil engineering work, installation of buildings and installation of painting or insulation[14]. Thu, since the material of constriction in the project are not all carbon or stainless steel, where the equation was modified for carbon steel, the price for stainless steel could be estimated by the Materials Cost Factors, f_m, Relative to Plain Carbon Steel 1.5.[14]

The calculation for all equipment is shown below

$$C = \sum_{i=1}^{i=M} C_i \left[(1 + f_p) + \frac{f_{er} + f_{el} + f_i + f_s + f_c + f_l}{f_m} \right] \qquad (7.2)$$

where C is total cost of equipment including all factors, f_p is installation of piping, f_{er} is installation factor for equipment erection, f_{el} is installation for electrical work, f_i is installation factor for instrumentation and process control, f_s is installation for structures and buildings, f_c is installation factor for civil engineering work, f_l is installation factor for lagging, insulation and paint and f_m is the material cost factor. Calculating for H-101 price:

$$C = 6956000 \left[(1 + 0.8) + \frac{0.3 + 0.2 + 0.3 + 0.2 + 0.3 + 0.1}{1} \right] = 24346000 SR$$

Table 7-4: Total equipment cost.

Equipment name	Equipment	Material factor f_m	Total cost (SAR)
Furnace 1	H-101	1	24,346,000
Furnace 2	H-102	1.5	9,744,445
Heat Exchanger	E-101	1.5	3,505,333
Cooler	E-102	1.5	8,765,627
Plug Flow Reactor 1	R-101	1.5	4,489,276
Plug Flow Reactor 2	R-102	1.5	6,713,323
Decanter 1	V-101	1.5	556,204
Decanter 2	V-102	1.5	252,193
Distillation 1	T-101	1.5	24,859,314
Distillation 2	T-102	1.5	1,255,915
Distillation 3	T-103	1.5	1,117,219
Total			85,604,450

The same with the remaining equipment. The total will be the FCI which equal to 146.33 million in SAR

Including factors for offsets which is 30% and design and engineering also 30%. Fixed capital investment equal to 144,672,197 SAR

The pay-back period is 9.8 years found by

$$PBP = \frac{FCI}{Net\ Profit} = \frac{144672197}{14679382} = 9.8\ years$$

The value of calculated pay-back period is relatively too high. However, it was calculated based on some assumptions in the equipment cost and labor cost. Also, it was difficult to collect reliable prices for the chemicals. This may be the reason for this high value.

APPENDIX

The program is to solve reactor 1. Just change the inlet flowrates and the initial conditions and will solve reactor 2.

FOR REACTOR 1

The differential equations:

d(XEB)/d(WFEB)=rc1+rc2+rc3+(rt1+rt2+rt3)*voidB/densB   #EB conversion check

d(XBZ)/d(WFEB)=rc2+rt2*(voidB/densB) #Bz conversion check

d(XTO)/d(WFEB)=rc3+rc4+rt3*(voidB/densB) #Tol conversion check

d(XH2)/d(WFEB)=rc1-rc3-2*rc4+(rt1-rt3)*(voidB/densB) #Hydrogen conversion checked

d(XST)/d(WFEB)=rc1-rc4+rt1*(voidB/densB) #ST conversion check

d(T)/d(WFEB)=(FEB0*((-dHr1*rc1)+(-dHr2*rc2)+(-dHr3*rc3)+(-dHr4*rc4)))/((MEB*CpEB)+(MST*CpST)+(MBZ*CpBZ)+(MTO*CpTO)+(MH2*CpH2)+(MH2O*CpH2O)) #energy balance to get T out let check

T(0)=923.15

Stander heat of reactions:

dHr2981=117690 # in kJ.kmol all check up to the dHr1

dHr2982=105510

dHr2983=-54680

dHr2984=-172370

specific heat of reactions:

 a1=41.99 # in kJ/kmol.K

a2=12.986

a3=10.86

a4=31.13

b1=-8.2026*10^-2 #in kJ/Kmol.k^2

b2=-7.67*10^-2

b3=-15.1844*10^-2

b4=-6.9818*10^-2

c1=6.499*10^-5 #in kJ/Kmol.K^3

c2=9.592*10^-5

c3=23.04*10^-5

c4=16.54*10^-5

d1=-2.311*10^-8 #in kJ/kmol.k^4

d2=-4.125*10^-8

d3=-9.9955*10^-8

d4=-7.685*10^-8

Reference temperature:

Tref=298.15 #in K

Heat of reactions equations:

dHr1=(dHr2981)+(a1*(T-Tref))+((b1/2)*(T^2-Tref^2))+((c1/3)*(T^3-Tref^3))+((d1/4)*(T^4-Tref^4)) #check

dHr2=(dHr2982)+(a2*(T-Tref))+((b2/2)*(T^2-Tref^2))+((c2/3)*(T^3-Tref^3))+((d2/4)*(T^4-Tref^4))

dHr3=(dHr2983)+(a3*(T-Tref))+((b3/2)*(T^2-Tref^2))+((c3/3)*(T^3-Tref^3))+((d3/4)*(T^4-Tref^4))

dHr4=(dHr2984)+(a4*(T-Tref))+((b4/2)*(T^2-Tref^2))+((c4/3)*(T^3-Tref^3))+((d4/4)*(T^4-Tref^4))

Specific heat constants:

 aEB=-43.1 #in kJ/kmol.K NNNNNEW

aST=-28.25

aH2=27.14

bEB=707.2*10^-3 #In kJ/kmol.k^2

bST=615.9*10^-3

bH2=9.274*10^-3

cEB=-48.11*10^-5 #In kJ/kmol.K^3

cST=-40.23*10^-5

cH2=-1.381*10^-5

dEB=130.1*10^-9 #In kJ/kmol.K^4

dST=99.35*10^-9

dH2=7.645*10^-9

Heat of formations

H0EB=0.2981*10^5 #In kJ/kmol

H0ST=1.475*10^5

H0H2=0

Standers Gibbs of formation

G0EB=1.307*10^5

G0ST=2.139*10^5

G0H2=0

CPEB=((aEB)*(T-Tref))+((bEB/2)*(T^2-Tref^2))+((cEB/3)*(T^3-Tref^3))+((dEB/4)*(T^4-Tref^4)) #In KJ/Kmol

CPST=((aST)*(T-Tref))+((bST/2)*(T^2-Tref^2))+((cST/3)*(T^3-Tref^3))+((dST/4)*(T^4-Tref^4))

CPH2=((aH2)*(T-Tref))+((bH2/2)*(T^2-Tref^2))+((cH2/3)*(T^3-Tref^3))+((dH2/4)*(T^4-Tref^4))

dCP=(CPST+CPH2)-CPEB #In kj/kmol

dG0=(G0ST+G0H2)-G0EB

dH0=(H0ST+H0H2)-H0EB

dCPT=(((((aST)*ln(T/Tref))+((bST)*(T-Tref))+((cST/2)*(T^2-Tref^2))+((dST/3)*(T^3-Tref^3)))+(((aH2)*ln(T/Tref))+((bH2)*(T-Tref))+((cH2/2)*(T^2-Tref^2))+((dH2/3)*(T^3-Tref^3))))-(((aEB)*ln(T/Tref))+((bEB)*(T-Tref))+((cEB/2)*(T^2-Tref^2))+((dEB/3)*(T^3-Tref^3)))

K0=exp(-dG0/R1/Tref)

K1=exp((dH0/R1/Tref)*(1-(Tref/T)))

K2=exp(((-1/T)*(dCP/R1))+((1/R1)*dCPT))

Keq=K0*K1*K2

R1=8.314 #In kJ/kmol.K NNNNNEW

Rate of catalytic reactions:

rc1=(k1*KEB*(PEB-(PST*PH2/Keq)))/((1+KEB*PEB+KH2*PH2+KST*PST)^2) #checked

rc2=(k2*KEB*PEB)/(1+KEB*PEB+KH2*PH2+KST*PST)^2

rc3=(k3*KEB*PEB*KH2*PH2)/(1+KEB*PEB+KH2*PH2+KST*PST)^2

rc4=(k4*KST*PST*KH2*PH2)/(1+KEB*PEB+KH2*PH2+KST*PST)^2

Rate of thermal reactions:

 rt1=kt1*(PEB-(PST*PH2/Keq)) #check

rt2=kt2*PEB

rt3=kt3*PEB

Void fraction equation:

voidB=1-(densB/densS) #Void fraction of the bed check

partial pressures:

 PEB= (FEB/FTOTAL1)*PT

PST=(FST/FTOTAL1)*PT

PH2=(FH2/FTOTAL1)*PT

Kinetics:

kt1=At1*exp(-Et1/R/T) #for thermal reactions Check

kt2=At2*exp(-Et2/R/T)

kt3=At3*exp(-Et3/R/T)

k1=A1*exp(-E1/R/T) #for catalytic Reaction Check

k2=A2*exp(-E2/R/T)

k3=A3*exp(-E3/R/T)

k4=A4*exp(-E4/R/T)

Adsorption constant equations:

KEB =AEB*exp((-dHEB/R/T)) #Adsorption constant

KST=AST*exp((-dHST/R/T))

KH2=AH2*exp((-dHH2/R/T))

Pre-experimental values and activation energies for thermal and catalytic reactions:

At1=2.2215*10^16 # In (kmol/mf^3.hr.bar) Check

At2=2.4217*10^20

At3=3.8224*10^17

Et1=272.23 #In (kJ/mol)

Et2=352.79

Et3=313.06

A1=4.594*10^9 #In (kmol/KgCat.hr)

A2=1.060*10^15

A3=1.246*10^26

A4=8.024*10^10

AEB=1.014*10^-5 #In (1/bar)

AST=2.678*10^-5

AH2=4.519*10^-7

E1=175.38 # In (kJ/mol) Check

E2=296.29

E3=474.76

E4=213.78

dHEB=-102.22 # In (kJ/mol) Check

dHST=-104.56

dHH2=-117.95

Densities of the buck:

densB=1422 # In (kgCat/mf^3)

densS=2500 #In (kgCat/mp^3) # In bar

Gas constant:

R=0.008314 #In m^3 bar/kmol.K

Inlet of reactor:

FEB0=274.550635 #In kmol/hr Check

FST0=4.05669955

FBZ0=0.54395546

FTO0=1.11174721

FH2O0=4118.25952

FCH40=0

FC2H40=0

FN20=0

FH20=0

FCO2=16.5661657 #No eq. for CO2

FTOTAL=FEB0+FST0+FBZ0+FTO0+FH2O0+FCH40+FC2H40+FN20+FH20 #Total molar flow reate

Total pressure:

PT=2.7 #In bar

Mole fractions:

y0EB=(FEB0/FTOTAL)#Check

y0ST=(FST0/FTOTAL)

y0H2=(FH20/FTOTAL)

Molecular weight of components:

MwEB=106.16 #Checked

MwST=104.14

MwBZ=78.11

MwTO=92.11

MwH2O=18.02

MwH2=2.01588

MwC2H4=28.054

MwCH4=16.043

Heat capacities of components:

CpEB=(-0.43426)+(6.067*10^-3*T)+(-3.8625*10^-6*T^2)+(9.1282*10^-10*T^3) # in kJ/kg

CpST=(-0.26436)+(5.564*10^-3*T)+(-3.0018*10^-6*T^2)+(5.3317*10^-10*T^3) #

CpBZ=(-0.40599)+(6.6616*10^-3*T)+(-4.5318*10^-6*T^2)+(12.255*10^-10*T^3) #

CpTO=(-0.27127)+(5.9142*10^-3*T)+(-3.8631*10^-6*T^2)+(9.54*10^-10*T^3)#

CpH2=(13.57)+(4.637*10^-3*T)+(-6.905*10^-6*T^2)+(38.23*10^-10*T^3) #

CpH2O=(1.79111)+(0.1069*10^-3*T)+(0.58611*10^-6*T^2)+(-1.998*10^-10*T^3) #

Mass flow rate in the reactor:

MEB=MwEB*FEB0*(1-XEB) #mass flow rate of EB Checked.

MST=MwST*(FST0+FEB0*XST) #mass flow of ST

MBZ=MwBZ*(FBZ0+FEB0*XBZ) #mass flow of BZ

MTO=MwTO*(FTO0+FEB0*XTO) #mass flow of TO

MH2=MwH2*(FH20+FEB0*XH2) #mass flow of H2

MH2O=MwH2O*FH2O0 #mass flow of H2O

MC2H4=MwC2H4*FC2H4

MCH4=MwCH4*FCH4

MTOTAL=MEB+MST+MBZ+MTO+MH2+MH2O+MCH4+MC2H4

Tr=(To+T)/2 #average temperature

To=923.15

Flow rates in the reactor:

FEB=FEB0*(1-XST-XBZ-XTO) #molar flow of EB check

FST=FST0+FEB0*XST #molar flow of ST

FBZ=FBZ0+FEB0*XBZ #molar flow of Bz

FTO=FTO0+FEB0*XTO #molar flow of TO

FH2=FH20+FEB0*XH2 #molar flow of H2

FCH4=FCH40+FEB0*XTO #molar flow of methn

FC2H4=FC2H40+FEB0*XBZ #molar flow of ethylene

FN2=FN20 #molar flow of nitrogen

FH2O=FH2O0 #molar flow of water

FTOTAL1=FEB+FST+FBZ+FTO+FH2+FCH4+FC2H4+FN2+FH2O

Initial conditions:

WFEB(0)=0

XEB(0)=0

XBZ(0)=0

XTO(0)=0

XH2(0)=0

XST(0)=0

WFEB(f)=17

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