Jordan University of Science and Technology

Faculty of Engineering

Chemical Engineering Department

Chemical Industries–CHE422

Production of Polystyrene

Student names:

Yara Zayed	**126999**
Noor Awwad	**126934**
Hedayah Almomani	**127284**

Supervised by:

Eng. Salah Al-Din Abu Yahya

2021

1. Introduction

Polystyrene is one of the most in-demand polymers in the world, only behind polyethylene and polypropylene. Its first commercial production was in 1925, by Naugatuck Chemical Company in Connecticut, U.S.A. However, its production was only lasted for 5 years as it was discontinued due to many economic and technical difficulties. In the early 1930's, Dow Chemical Company became interested in the re commercialization of polystyrene production and by 1937, the company stabilized polystyrene production under the trademark name – Styron.

The target markets for the final product – extruded, general purpose polystyrene – are the plastic, packaging, and construction industries. This report covered physical and chemical properties, main uses, world demand and price trend, synthesis of production, and the fully description of the chosen method of polystyrene. The demand of polystyrene increases year by year especially in food packaging field, and laboratory wear, since these industries require clarity, and when it combined with other compounds, polystyrene is used to make appliances, electronics, automobile, and other domestic equipments. Polystyrene has a density range of 0.96 to 1.04 (g/cm^(3)), it characterizes by its impact strength, toughness, modulus, and elongation, in addition to its thermal properties. Polystyrene can be made in several ways to suit the end user which are illustrated in the report. But it is shown that the thermal bulk method is the best choice to polymerize the styrene monomer. All raw materials needed for the chosen process are listed and talked about. Analysis of equipment like equipment listing and specification, process flow diagrams were employed in this project to provide for better description of the process flow. It is concluded that Asia is the leading region accounting of polystyrene industry. For its price trend, from 2015-2019 the polystyrene prices were in large swings due to the continuing of benzene prices vitality during this period.[1]

Contents

List of tables

List of figures

2. Physical and Chemical Properties of Polystyrene

Polystyrene is a thermoplastic that has many uses and is available in a wide variety of formulations. What makes it a good choice for many applications is its ease of processing, also having a wide range of properties. The chemical and physical properties of it will be shown below.

Table 1:Chemical &physical properties of polystyrene [2,3,4]

Property	Value
Molecular Weight/ Molar Mass (g/mol)	104.1
Molar volume(ml/mol)	98.6 to 99.6
Van-der-Waals Volume	66.28
Density (kg/m³)	10-50
Specific Gravity(g/cm³)	1.03 to 1.06
Water Absorption (%)	0.03 to 0.10
Solubility Parameter δ (MPa)$^{1/2}$	18.5-19.4
Solubility in water	Insoluble
Melting Point	Approximately 240 °C
Boiling point	430 °C
Thermal conductivity (W/m·K)	0.033

Polystyrene is a hard, brilliantly transparent, stiff resin, which is non-biodegradable with a couple of exceptions. It is soluble in most aromatic hydrocarbon and chlorinated solvents but not dissolved in alcohols or water. At room temperature, the thermoplastic polymer is solid but when heated above 100 ° C it flows. It becomes solid again when it cools. These properties of it are due to the presence of weak van der Waals forces between the chains of polymer. On heating, the forces weaken further, and the chains slide past one another. This is the reason polystyrene is highly elastic and softens when heated beyond its glass transition temperature. Polystyrene is chemically stable; it does not interact with most materials due to the transformation of its double bonds (between carbon and carbon) into single bonds. In addition, it is highly flammable and burns with a yellow-orange flame, and it emits carbon particles or soot after combustion. [2,3,4]

3. Major Uses of Polystyrene

A wide variety of consumer products can be made by a versatile plastic called polystyrene. At its hard, solid state, polystyrene is often used in packaging field as food packaging either for food products, cold drinks, or carry out meals, since it protects the product against damage and spoilage. As well as in medical field as laboratory ware and disposal applications of test tubes, Perit dishes or housing for test kits. Other applications of polystyrene are available when it is combined with several colorants, additives, or other plastics, it is used in making appliances, electronics as cassette tape housing, and clear jewel boxes to protect CDC's, toys, gardening pots, equipments. Polystyrene resins are the most popular materials for building and construction applications. Containers for soap, hair cream, lipstick, or talcum powder are other applications for polystyrene in cosmetics field.

Polystyrene is nontoxic, odorless, versatile, and cost-effective solution for rigid packaging and food service disposal, and this why it is dominant in food packaging. While for beverage packaging, the choice of polystyrene over other plastics or traditional materials because of its recyclability and excellent mass to strength ratio. On the other hand, it is flammable and like other organic compounds; it emits CO_2 and water when it is burned.

There is another type of polystyrene which is named as expanded or extruded polystyrene, it is polystyrene made of foam material that is widely known by its valued capabilities in insulation systems. Foam polystyrene is widely used in food service, home appliances insulation. To clarify, refrigerators, microwaves, vacuum cleaners, and blenders, all are some examples of home appliances that are made of foam polystyrene; because it is cost effective, long lasting, and the most important reason is that it does not react with other materials. Excellent thermal insulation in numerous applications as in building of walls, refrigerators, and freezers, is achieved by using this type of polystyrene due to another characteristic it has, which is its lightweight, and its resistance to water damage. Foam polystyrene is also used in child protective seats. [5,6]

One of polystyrene widely use rather than in packaging and insulation is when the polyesters are melted and squeezed through fin holes resulting to form a fiber that is commonly used in clothing either in making suits, shirts, skirts, and parachutes for sky divers, as manufactured or naturally fiber, fundamentally cotton. In addition, polystyrene is included where strength and resistance are the priority, such as car tire cords, and conveyor belts.

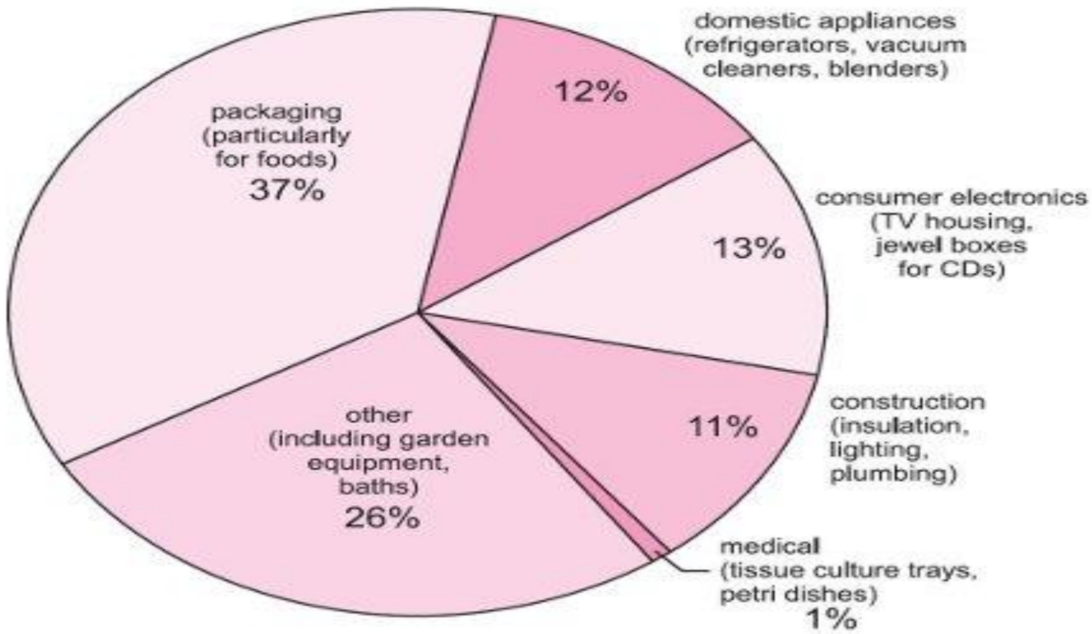

Figure 1/ the percentages of polystyrene applications [21]

The above diagram breaks down the polystyrene usage by general use, it is clearly showing the percentages for each use, and it is observed that using the polystyrene for packaging applications especially for foods, and beverages has the highest percentage which is about 37%, because of its capabilities to protect the food safe from the surrounded environmental conditions that affects the quality of the product. Then in the next rank with percent of 26% for other uses including garden equipments, baths due to its lightweight and resistance to water damage. And of course, due its cost effective, and insulation capabilities, it is used in percent of almost 11% in construction either for insulation, lightening, or plumbing, and about 12% in domestic appliances, as well as about 13% in consumer electronics. But the lowest percent of use with 1% is in medical field either for tissue culture trays, or petri dishes, and this is maybe because the other alternatives that can be used instead of polystyrene at this field.[5]

4. Global polystyrene production capacity

Polystyrene is one of the most in-demand polymers in the world, only behind polyethylene and polypropylene. Global polystyrene capacity in 2016 was 14.7 million tons which also the same as world demand of polystyrene in 2016.

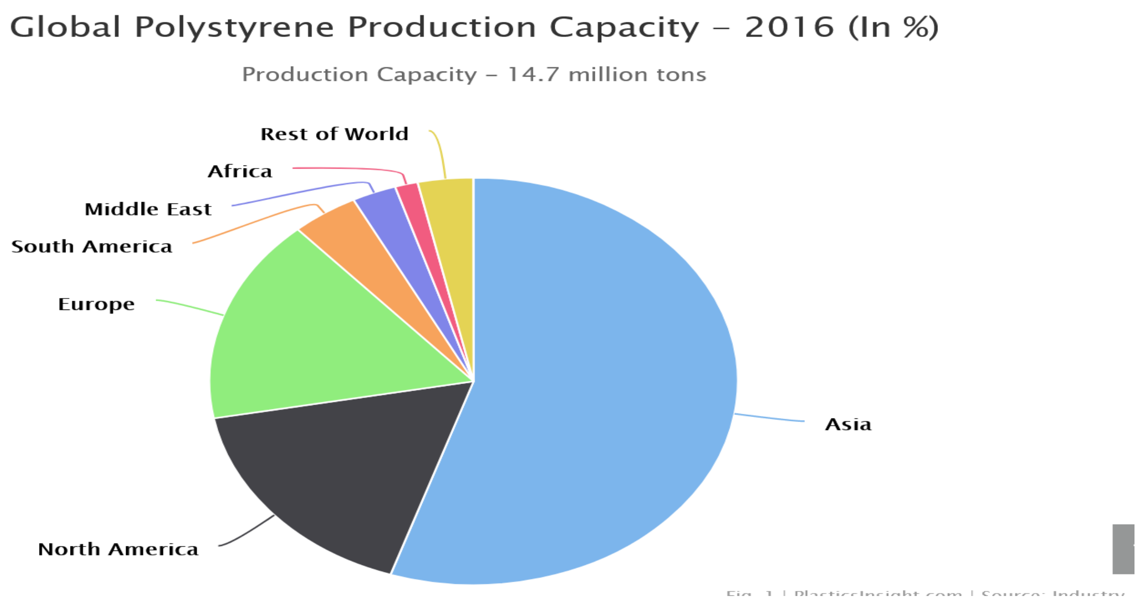

Figure 2Annual Global Production of Polystyrene 2014 [22]

Figure (2) illustrate that Asia is the leading region accounting of polystyrene industry since its occupied 55.1% of the production capacity (more than half of the global production capacity) which equal almost 8 million tons. The second largest region is North America with 2.5 million tons followed by Europe accounting for 2.4 million tons. The fourth country is south America that PS production capacity is 0.602 million tons. Middle east, Africa, rest of the world production is 2.7%, 1.4% , 3.4 % respectively of total global capacity production. [7]

Worldwide demand of polystyrene will increase over the next year since the demand for polystyrene product also increases such as in China and India the demand for packaging product has increased recently.

Since the demand of PS product will increase, also the global polystyrene market is expected to grow at a CAGR of 9.8 % and reach $62.25 billion by 2023. [8]

5. Raw material of Polystyrene industry

The major inputs employed in the production of polystyrene via Bulk Polymerization process are Styrene monomer, toluene, ethylbenzene, zinc stearate and water. Each raw material was discussed according to its price and its availability in Jordan as well as their function in polystyrene manufacture.

1- Styrene monomer

The global price of Styrene amounted to approximately 1,139 U.S. dollars per metric ton in 2018 [9]. Styrene monomer is not available in Jordan since Jordan export it mainly from Saudi Arabia [10]. Styrene monomer is the main object of polymerization for this design; forming strings of chains during polymerization known as polymers.

2- Toluene

According to Pen pet Petrochemical Trading Gmbh Office [11], The price of Toluene is 714 USD per ton. Toluene is partially available in Jordan as it is produced during petroleum refining operations in Jordan petroleum refinery indirectly as a by-product of coke-oven operations [12], but its amount is not enough so Jordan exports it mainly from Europe and Spain [13]. Toluene was the major solvent in this process; controlling the viscosity of the polymer melt and ensuring adequate heat transfer within the process line.

3- Ethylbenzene

US Ethylbenzene was assessed at 30.38-36.97 cents/lb($670-815/ton) in 2016 [14]. Ethylbenzene isn't available in Jordan .Ethylbenzene is used as both an initiator and a chain transfer agent and aids molecular weight distribution of the polymer.

4- Zinc stearate

According to chemical book price of is around 40$ per 1 kg [15]. Zinc stearate is not available in Jordan. Zinc stearate It is the major lubricant used in this design work to increase shear stress, reduce viscosity, and promote ease of flow.

5- Water

The costs of freshwater purchase by the industry which is JOD1/m^3 [16]. Water is available enough in Jordan. The main function of water in polystyrene manufacture that it is used as a stripping agent to increase the purity of the polymer melt.

6. Price trend of Polystyrene

Study period of polypropylene price was taken between 2012 to 2019 as a global price.

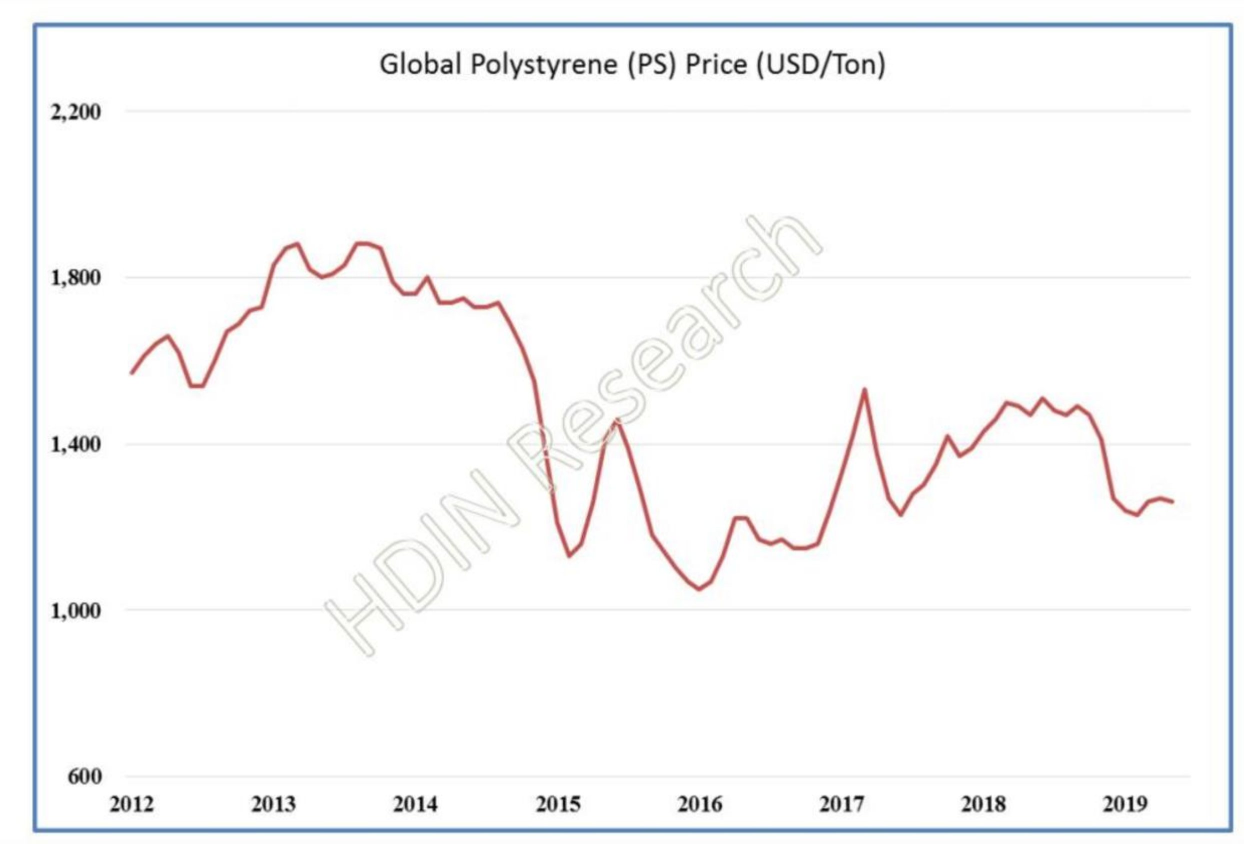

Figure 3:Global price of Polystyrene from 2012 to 2019 [23]

From figure (3) global polystyrene prices were on a small fabrication between the period 2012 to 2014. The last months in 2014 and early 2015 the price of energy as well as the price of benzene was decrease as a consequence the polystyrene price also decrease However, while feed stock costs declined around 43% from July 2014 to February 2015, polystyrene prices only declined around 23% this decrease was clearly illustrated in figure (3) The price retain to increase in 2015 as a result of benzene price also increase. From 2015 until 2019 benzene prices continue to remain volatile, resulting in large swings in polystyrene prices as well.[17]

7. Production Methods

7.1. Solution Polymerization

Solution polymerization is very important method for manufacturing polymers, and it occurs in existence of inert solvent and suitable catalyst. Monomer and initiator must be soluble in the liquid, and the solvent must have the desired chain transfer characteristics, boiling point (above the temperature necessary to carry out the polymerization and low enough to allow for ready removal if the polymer is recovered by solvent evaporation). Solution polymerization is started with a high monomer concentration (70% or more) using a minimal amount of catalyst, initiator, and a solvent with a low chain transfer constant. As the reaction proceeds, more solvent is added to regulate the viscosity and additional catalyst/initiator is added to adjust the reaction rate. The addition of initiator is important for achieving a high degree of polymerization because towards the end of the polymerization, the degree of dilution of the monomer is extremely high, and therefore, the efficiency of the initiator is very low.

The homogeneous polymerization process has many advantages, as pure polymers can be obtained after evaporation of the solvent. Furthermore, the molecular weight can be easily controlled by adding chain transfer agents (halogenated hydrocarbons or thiols) or by adjusting the initiator and monomer concentration. Another advantage is that the polymerization heat can be easily dissipated by mixing and evaporative cooling with or without compression of the vapor and reflux-cooling. While its disadvantages are the increase of viscosity with increasing the molecular weight of the growing polymer chains and solid content. Also, difficulty in removing solvent from final form, that's causing degradation of bulk properties. Another disadvantage is reducing monomer concentration which results in decreasing the rate of the reaction and the degree of polymerization.[18,19,20].

7.2. Suspension polymerization

It is considered as one of the most widely used techniques of polymerization, it is a heterogeneous process with water as the continuous phase, and it is economic and environmentally friendly to use water solvent in place of the solvents used in solution polymerization due to its efficiency as a heat transfer medium. In general, it is defined as a polymerization process of monomers in the form of monomer particles dispersed. Dispersing medium which is usually water, monomers, stabilizing agents, and a monomer soluble initiator, all are the components of suspension polymerization system.

The process consists of initiation, propagation, and termination. It is carried out in the small droplets of liquid monomer, the droplets that are not miscible are transformed into sticky, viscous material of a high enough molecular weight to form solid, rigid particles. Insolubility is the monomer state that must be dispersed in water, if its solubility is not sufficient, they are replaced by prepolymers, or partially polymerized monomers that are compared with the monomer have a much lower solubility, or completely insoluble in the water. During polymerization, it is preferred to stir and sufficiently stabilize the suspension or the agglomeration of particles to compose one big mass. The size of the polymer particles obtained are within the range of 0.1 to 5 mm in diameter.

The typical initiators, stabilizers, and dispersing agents used for this process are peroxides as soluble initiators such as benzoyl, t-butyl, diacetyl, and lauryl peroxide. While surfactants such as sodium, or ammonium salts are adding as stabilizers to the monomer droplets and polymer particles to lower the surface tension, and to reduce the viscosity, as well as polyelectrolytes and inorganic salts as dispersing agents used to stabilize the particles by furnishing a surface charge. The coalescence or agglomeration of sticky particles are avoided by using the stabilizers and the dispersing agents that are building protective coating on the surface of the polymer particles. Usually, large amounts of stabilizing agents are not, small amounts are sufficient to stabilize the monomer.[19]

Several advantages that make this method of polymerization one of the most widely used compared with other methods, are the following:

1- Easy to control temperature and viscosity.

2- Due to the little catalyst required, the purification and processing of the polymer is considered the easiest in comparison to emulsion polymerization.
3- It is economic and environmentally friendly method due to the use of water as solvent instead of others used in solution method.

7.3. Thermal Bulk Polymerization

It is sometime refereed as mass polymerization. This method of polymerization take place when solvent is added to monomer in liquid state, the purity for monomer should equal 85% to make the best result, after adding the main input for this process such as Styrene and lubricants the mixture is heated to polymerization temperature . When the reaction starts, the heating process is stopped since the reaction is highly exothermic. Heating from the reactor is removed either by cooling jacket through the reaction solvent or by modern technology employ self-cooling reactor. A series of continuous stir tank reactor (CSTR) are used, and conversion increase serially. The polystyrene produced in bulk polymerization is in molten form and is purified using separation equipment like condensers and devolatizers.

Batch bulk polymerization process was used in this design as opposed to continuous bulk polymerization since batch process gives a higher conversion of Styrene and higher purity of polystyrene than the contentious bulk polymerization.

<u>Advantages of bulk polymerization</u>

1) The system is simple to set up and requires thermal insulation.
2) The polymer obtained has a high level of purity.
3) it is the most used commercial polymerization process.

<u>Disadvantages of bulk polymerization</u>

1) It is a highly exothermic process.
2) High viscosity increases lead to flow difficulties.

8. Process Description for Bulk thermal polymerization

8.1. Process Flow Diagram

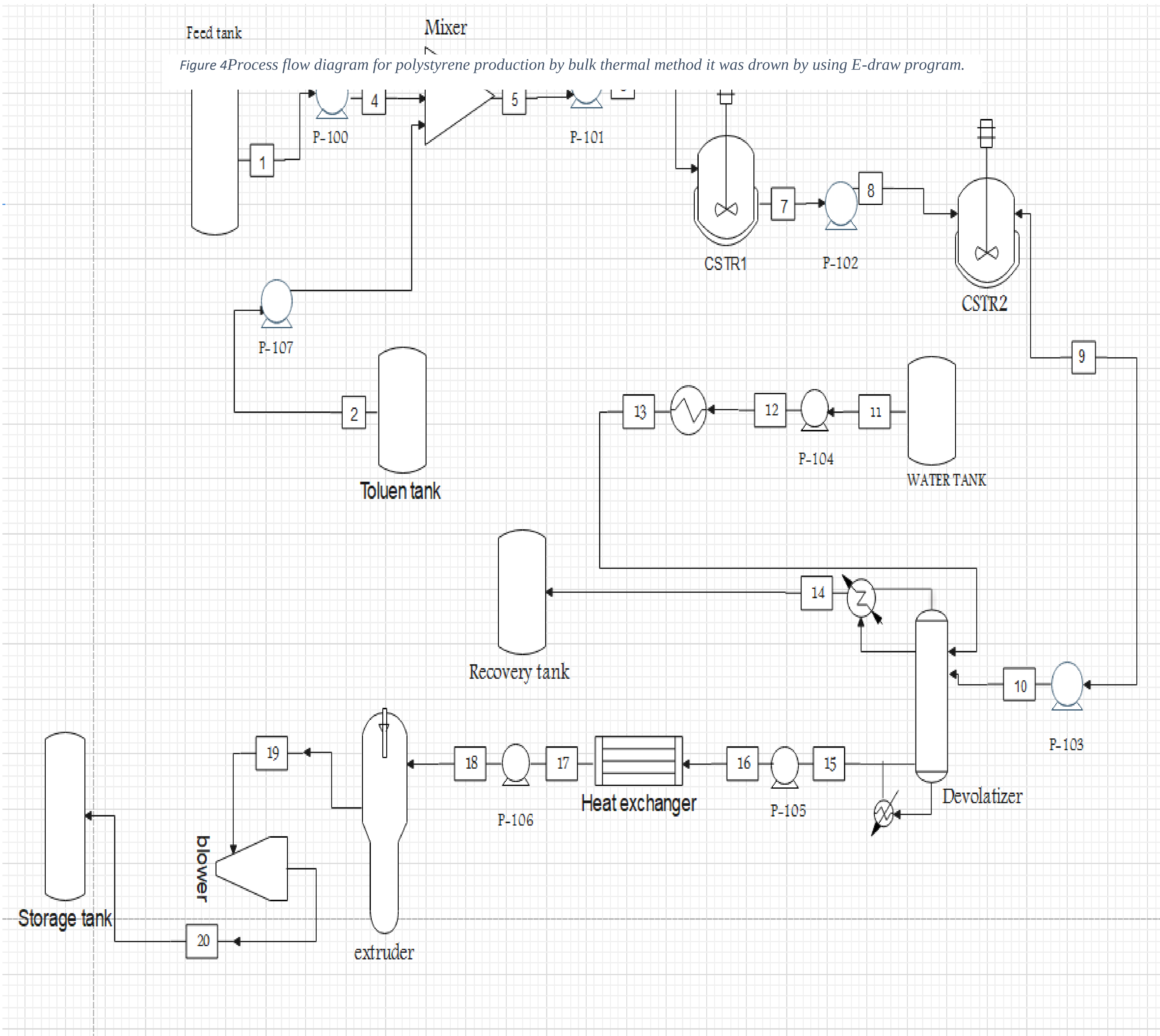

Figure 4Process flow diagram for polystyrene production by bulk thermal method it was drown by using E-draw program.

8.2. Process Description

This process was chosen from among the previous processes mentioned before, and it is one of the techniques used to polymerize the most versatile polymers, since it is considered the most economical polymerization process of styrene that initiated by heat at about 130 to 140 ^{o}C, as well as It is very environmentally friendly method since no purification is needed because the polymer obtained has a high level of purity. However, certain purity is required above the achieved one, separation equipment like condensers and devolatizers can be used. It is referred as bulk or mass polymerization, the reaction mixture consists of only monomers, it is mainly used for step-growth polymers, and it can be proceeded whether homogeneous or nonhomogeneous based on the solubility of the polymer chains formed from the monomers.

The overall reaction:

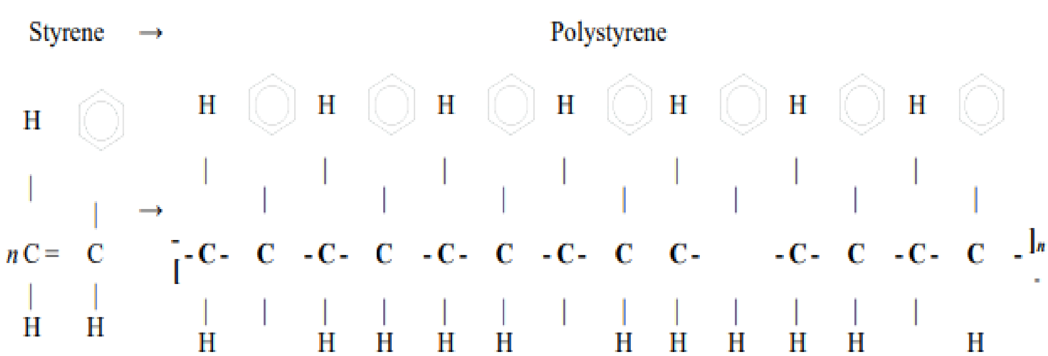

Figure 5:Thermal polymerization reaction [1]

And now the process will be discussed in depth, giving a description of the process units and streams. Styrene monomer, toluene, ethylbenzene, zinc stearate, and water are the major inputs to produce polystyrene using this method. At temperature 25^{o}C and pressure 1 atm, stream of styrene monomer, ethylbenzene, and zinc stearate are pumped from feed tank into the feed mixer containing 100% mass toluene. Agitating for the mixture inside the mixer is taken place for one hour. Then the output from the feed mixer is then pumped to the batch stir tank reactor system which is known as prepolymerizer. Thermal polymerization for about 3-4 hours, and 50% conversion of the monomer is occurred at temperature 90^{o}C and pressure 1atm. Another prepolymizer is placed in series with the first one to achieve higher level of success with conversion of 99% with respect to the mixer and 98% with respect to the first prepolymizer (reactor) for 2 hours polymerization at temperature 120^{o}C and pressure 1atm. While to reach the successive pumping of the mixture to the process units, tower arrangement of the reactors is helpful to reduce the power. Then, the polymer melt is formed containing small quantities of styrene monomer, ethylbenzene, zinc stearate, and toluene, is pumped to the separation unit called vacuum devolatizer to purify the polymer by removing ethylbenzene, monomer, toluene, and zinc stearate after adding pure water, at temperature 210^{o}C and pressure 1atm. The exit stream is then condensed at the condenser at temperature 25^{o}C, then sent to a recovery system. To take off high boiling substances from the melt polymer produced and to obtain high pure product, gas stripping unit is used with steam as stripping agent. After that, cooling and extruding is applied to the melt polymer produced at temperature 150^{o}C and sent to the atmosphere storage tank to be stored at temperature 25^{o}C and pressure 1atm. [1,19]

8.3. Equipment Listing and Detailing

Table 2: Main units included in the process, their uses and operating conditions [1]

Equipment	Equipment functions	Operating temperature (C)	Operating pressure (atm)
Feed Tank	It is the storage site of the reactants from which they are introduced to the mixer.	25	1
Mixer (Agitator)	Used for agitating the reactants to ensure proper mass transfer through mixing.	25	1
Stir Tank Reactor (Prepolymerizer)	The feed is pumped to it and is thermally polymerized for 4 hours and 50% monomer conversion takes place.	90	1
Stir Tank Reactor (Polymerizer)	For polymerization to a successive higher level (99% monomer conversion takes place)	120	1
Devolatizer	It was used to separate volatile materials from the polymer and increase polystyrene purity	210	1
Shell and Tube Heat Exchanger (1 : 2)	It reduced the heat content of the polystyrene from the devolatizers by transferring it to the colder fluid in its shell	50	1
Extruder	It was used to extrude the cooled polymer and separate them into pellets.	25	--
Storage	The pelletized polymer was stored here in preparation for sales.	25	--
Condenser	It condensed the separated components of the polymer melt before they were transferred to the recovery unit.	--	1
Recovery Unit	It collects and stores the condensates from the condenser	25	1

8.4. Equipment parameter design

Table 3:Parameter design for each unit [1]

Equipment	Parameter	Size
Feed Tank	Volume(gal)	10,579,773.69
Mixer (Agitator)	Power(hp)	133,029.00
Stir Tank Reactor (Prepolymerizer)	Volume(gal)	22,634,261.00
Stir Tank Reactor (Polymerizer)	Volume(gal)	22,634,261.00
Devolatizer	Mass (Ib)	60,484,689.68
Shell and Tube Heat Exchanger (1 : 2)	Area(m^2)	6,135.03
Extruder	Capacity(ton/yr)	8,000,000.00
Storage	Volume(gal)	10,579,773.69
Condenser	Area(m^2)	87,962.4
Recovery Unit	Volume(gal)	10,579,773.69

References

1. https://www.coursehero.com/file/52964637/POLYSTYRENE-PROJECTpdf/
2. https://sciencestruck.com/polystyrene-properties
3. https://byjus.com/chemistry/polystyrene/
4. https://en.wikipedia.org/wiki/Polystyrene
5. https://www.essentialchemicalindustry.org/polymers/polyesters.html?fbclid=IwAR0QjrU3MC_QhtBA-ZKrKMro4U0C-JHhKNkV7IbWpzC_t7TRpzRbatNzlgg
6. https://www.chemicalsafetyfacts.org/polystyrene/?fbclid=IwAR30vx5kjcAliL8rW7BE0BSsimKN_3Ucmuh_BMOQ6ypwjKof-39HfDuZ2G8#answering-questions
7. https://www.plasticsinsight.com/resin-intelligence/resin-prices/polystyrene/
8. https://www.globenewswire.com/news-release/2020/02/24/1989032/0/en/Global-Polystyrene-Market-Review-2015-2019-and-Forecast-2020-2030.html
9. https://www.statista.com/statistics/1171073/price-styrene-forecast-globally/
10. https://wits.worldbank.org/trade/comtrade/en/country/ALL/year/2018/tradeflow/Exports/partner/JOR/product/390319
11. https://www.penpet.com/news/news-toluene-january-2021.html
12. https://www.ncbi.nlm.nih.gov/books/NBK524840/
13. https://wits.worldbank.org/trade/comtrade/en/country/ALL/year/2018/tradeflow/Exports/partner/JOR/product/290230
14. https://www.icis.com/explore/resources/news/2016/08/05/10023267/us-ethylbenzene-price-range-widens-on-benzene/
15. https://www.chemicalbook.com/SupplierPriceList_EN.aspx?cbn=CB9677027&c=1kg#price
16. https://www.sciencedirect.com/science/article/pii/S2212371719301222
17. http://read.nxtbook.com/wiley/plasticsengineering/september2015/resinmarketfocus.html
18. https://vulms.vu.edu.pk/Courses/BIO102/Downloads/Handouts%20Lecture%2045.pdf
19. https://polymerdatabase.com/polymer%20chemistry/Solution%20Polymerization.html
20. researchgate.net/publication/330304320_Solution_Bulk_polymerization
21. https://optimisticfatalism.wordpress.com/2016/03/02/polystyrene-blog-update-32816/
22. https://www.plasticsinsight.com/resin-intelligence/resin-prices/polystyrene/
23. https://issuu.com/hdinresearch.com/docs/polystyrene__ps__market_global_review_and_outlook-