PRELIMINARY TECHNO-ECONOMIC FEASIBILITY STUDY FOR ESTABLISHING A 250MM LB/YR POLYSTYRENE PLANT

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Abstract: Polystyrene is a versatile plastic that is used in the manufacture of many consumer products such as appliances, electronics, car parts, foam , insulating and packaging materials .In a previous paper ,the viability of a local plant for producing styrene has been demonstrated suggesting that a techno-economic feasibility study for establishing a polystryrene plant is the next step. Here the results of this study are presented.

After surveying the literature for relevant technologies, a recent US patent was selected as a manufacturing process. The technology is based on anionic polymerization chemistry and has the advantage of recycling part of the product as a heat sink for heat generated during reaction to soften products for further processing, suggesting a three step manufacturing process: feed preparation, adiabatic reaction and product finishing sections.

In feed preparation section commercial grade styrene is inhibited and continuously treated to remove impurities that can interfere with polymerization downstream. The inhibitor is removed in one of two beds of activated alumina, the other being regenerated. Temperature is carefully controlled to prevent thermal initiation.

The adiabatic reaction section is run batch wise. It consists of low temperature initiation reactor and two anionic polymerization reactors one operating while the other is being regenerated. Sufficient amount of solid product enters the reactor to control the temperature to the desired level. The finishing section is run continuously to accomplish termination, product finishing and purification. Material and energy balances in the original patent were reproduced and a preliminary economic feasibility was undertaken. The project is promising, with an internal rate of return in the range of 30 percent for a ten year operation and a payback period of 2.3 years.

Keywords: Ordovician Succession, Mamuniyat Formation, Murzuq Basin, SW Libya.

INTRODUCTION

Polystyrene is an outcome of polymerizing styrene; styrene is derived from Ethyl Benzene. Polystyrene is an important type of polymer that is a final product of diverse chemical processes; Polystyrene is a versatile plastic used to make a wide variety of consumer products. As a hard, solid plastic, it is often used in products that require clarity, such as food packaging and laboratory ware. When combined with various colorants, additives or other plastics, polystyrene is used to make appliances electronics, automobile parts, toys, gardening pots and equipment and more.

Polystyrene follows certain polymer synthesis. For instance, Chain growth Polymerization is performed by employing free-radical polymerization and copolymerization, ionic polymerization, coordination polymerization and cationic polymerization. In the manufacturing personnel, it has been Chosen Growth Polymerization and has applied one of its techniques; Anion Polymerization.

Ionic polymerization follow the steps; initiation, propagation and termination. The initiator in an anionic polymerization may be any strong nucleophile, including Grignard reagents and other organometallic compounds like n-butyl (n-C4H9) lithium. During the initiation process, the addition of the butyl anion to styrene produces a carbanion at the head end in association with the

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positively charged lithium counterion. The chain propagates by insertion of additional styrene monomers between the carbanion and counterion. In this paper;

- The material balance and energy balance have been calculated.
- Based on material and energy balance calculations the essential units of plant have been designed.
- An estimated feasibility study was carried out for the cost of the plant and the time period during which the plant retrieves the capital.

Polystyrene plant will be a successful project in Libya because it will complete the petrochemical plants sequence in Raslanuf (ethylene plant). Moreover, if such enormous project is implemented, it may promote economy and instigate the industrial revolt in Libya.

DESCRIPTION AND APPLICATION OF EQUIPMENT AND PROCESS

The process is based on the use of recycled polymer that acts as a heat sink to control the adiabatic temperature rise to the desired final temperature. The output of this plant is 30,041lb of polystyrene per hour. The process flow sheet is shown in (Fig. 1).

The plant is segregated into three sections:

Section 100 - Feed Preparation involving removal of all polar impurities.

Section 200 - Adiabatic Polymerization to the desired finishing temperature.

Section 300 - Finishing to producing polymer for both sale and for recycle.

Section 100

Feed Preparation Styrene monomer is delivered by rail and stored in T-151. When received, it is inhibited with tertiarybutylcatechol (TBC) and is stored off-site at ambient temperature. Inhibit or level is monitored periodically and (in rare cases) may need to be added shot wise. The monomer (stream 1) is passed through E-101 Where it is heated to 50° C. and sprayed into Flash Tank, V-101, that is under reduced pressure of about 20 mm Hg. Traces of Water, oxygen, and other volatile impurities are vaporized (stream 3) and condensed in E-103. Condensate is drained to decanter V-102 Where Water (stream 5) is removed and the organic layer (stream 6) stored in T-101 to be used for fuel. TBC inhibitor is added to V-102 to prevent the possibility of polymerization of this organic layer. The styrene monomer (stream 2) is then cooled to 10° C. in E-104 then passed upward through a bed of activated alumina in C-101. The activated alumina removes the TBC inhibitor and traces of polar compounds. The clean stream is stored in Surge Tank T-102. Up to this point, the process is continuous. The next step (polymerization) is however, carried out in a batch manner. T-102 is continuously receiving cooled monomer (stream 4) but the monomer is removed batch Wise for the batch adiabatic polymerization to follow. Batch polymerization is necessary to obtain the desired narrow molecular Weight distribution. As these monomer batches are being forwarded to R-201 (stream 8), NBL initiator (stream 7) is added (as a 15% solution in ethyl benzene) and is mixed in static mixer M-101.

Section 200

Adiabatic Polymerization Low temperature initiation takes place in the Well-agitated R-101 over a period of 15 minutes. The adiabatic polymerization is carried out alternately in R-202A and R-202B. Solid polymer pellets at about 70° C. are loaded by gravity (stream 9A) into R-202A, B from Weight Tank V-201. After the Warm solid polymer addition is complete, the monomer stream from R-201, containing the NBL initiator, is added rapidly. The elevated temperature of the pellets is sufficient to increase the polymerization rate. The rapid release of the heat of polymerization causes the temperature to rise and the reaction to accelerate as it rises. The reaction is complete in less than 10 minutes. Longer reaction time is allowed primarily to assure temperature uniformity of the polymer melt, as the newly formed polymer heats the cool granules. The cool polymer pellets serve as a “heat sink” and limit the maximum temperature rise as polymerization proceeds adiabatically to completion with a target of 10 ppm of residue monomer (or 99.99999% conversion). After the polymerization cycle is complete, the molten polymer (stream 10)is removed by a gear pump and transferred to the finishing section. The R-202 reactor is then heated briefly to about 260-300° C. to thermally terminate any living ends. This heating is a precaution to prevent gel build-up on the reactor Walls and may not be required after every batch. Termination is determined with an

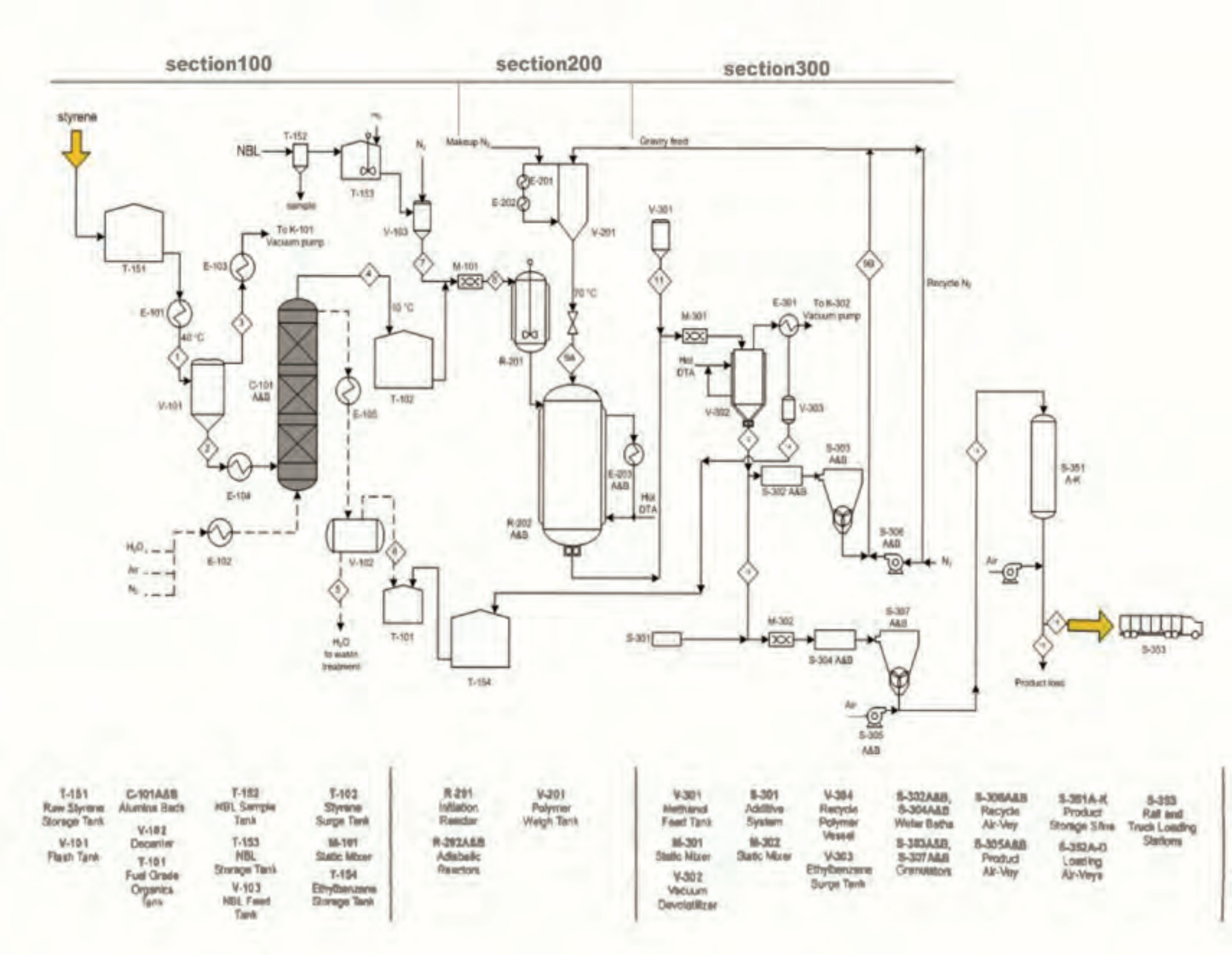


Fig.1. The process flow sheet.

instrument designed to measure the disappearance of the bright color associated with the living styryl anion.

Section 300

Finishing After polymerization in R202A, B, the next step is termination, Which is carried out on stream 10 by precise addition of a stoichiometric amount of methanol from (stream 11) V-301. The methanol is mixed (in Static Mixer M-301) into the living polymer stream where it reacts with the living styryl ends. Adiabatic polymerization has increased the polymer temperature to the 230—260° C. range required for both polymer flow and volatile removal. The small amount of residual ethyl benzene (about 0.2 Wt %)is removed in the Vacuum Devolatilizer (V-302). This very pure ethyl benzene is condensed in E-301, collected in V-303, and (stream 14) stored in T-152. When a railcar full has accumulated in, it is returned to a styrene plant for cracking to styrene. Upon entering high vacuum of V-302, the ethyl benzene vaporizes, causing foaming in the polystyrene. The ethyl benzene vapor quickly disengages from the polymer and the polymer is removed from the bottom of V-302 with gear pumps (M-302A—D). The polymer stream exiting V-302 (stream 12) is split into approximately 2 equal streams, a product stream (13) and a recycle stream (9B). The product stream has the desired additives (lubricants, flow aids, dyes, etc) introduced immediately before static mixer M-303. The polymer is then pumped through S-304A, B. Product is inserted into an extrusion unit and then pellets are the outcome. V-304. In V-201 the polymer temperature is adjusted desired value (70 c) then the polymer is transferred to R-202 by gravity flow where it serves a heat sink to limit the maximum adiabatic temperature. (Eugene, 2005)

PRESENTATION OF DATA AND RESULTS

Material balance is the principal fundament of the process design; it concludes the quantities of raw material in order to seek the necessarily required capacity.

The Material in equals Material out

The inserted quantity of raw material for the plant is 250 million lb per year, which equals 30040Ib per hour. Purification section 100 it is a continuous process, At T-151, the feed stock is inserted and add it along with TBC 12mg per kg of Styrene (Eugene, 2005). Flash Drum will release the traces of impurities in styrene it has used Antoine equation at 20mmHg pruseere and 50 C , while The Adsorber will adsorb the amount of inhibitor TBC from styrene(st4 = st2-adsorbed TBC)

Ethyl Benzene and NBL were mixed in the storage tank

To determine number of moles of NBL (initiator), n = Mass of styrene per batch/Mn. Adiabatic Polymerization section 200 It is a batch process. in Initiation Reactor R-201A, B. Each mole of initiator will react with 1 mole of monomer according to the rapid reaction and the purification of monomer, in Propagation Reactor R-202A, B The monomer Styrene will fully react, approximately 99.999% of reaction has been achieved. The length of chains is nearly equivalent according to the rapid reaction. In order to absorb exothermal heat, we should make sure that the reactor contains 50% wt of Styrene and 50% f Polystyrene. The following equation consists of number average degree of polymerization (Fried, 2014)

$$Xn=[M]0/[I]0 \quad (1)$$

The following equation consists of number-average molecular weight (Fried, 2014)

$$Mn = Xn * [Mw] \quad (2)$$

$$Mn = 1919.4787*104.2 = 200,000$$

Termination section 300: This reaction is principally terminated by Methanol, number of moles of Methanol are equivalent to number of moles of NBL which they possess similar number of chains.

We remove Ethyl Benzene by applying devolatilizer and store it in tanks in order to recycle it afterwards. Energy contradicts with material with regard to form changing status, Energy streams are not equal with respect to inlet and outlet.

Energy has multiple forms: Heat, mechanical energy and electrical, total energy is conserved regardless of its form. In process design, energy balances are made to determine the energy requirements for process heating, cooling and power. In plant operation, an energy balance on the plant will expose the pattern of energy usage, and suggest areas for conservation. Energy exists in many forms, which makes it more complex than material balance. The process is applied by following steady-state system, the processed reaction is the adiabatic reaction. Kinetic and potential energy were neglected in this process subsequently, the reaction is exothermic.

At flash drum the styrene feed stock has been inserted into a heater and was heated to 50 c , The exerted feed from flash drum was cooled to 10 c and went through absorber No temperature change is detected, nor enthalpy is changed. The inserted feed stock from ST8 has a precise temperature of 10 c, this reaction must be executed at low temperature. Initiation reaction is performed by unleashing an approximate temperature of 10C.

Enthalpy and temperature were not changed according to the low percentage of Ethyl Benzene and NBL with comparison to Styrene. At propagation Reactor R-202A, B. The process is described as adiabatic polymerization reaction, the reaction is said to be exothermic. The added feed stock from ST8 was inserted at 10C

General Energy Balance Equation:

$$Q = W + \Delta H + KE + PE$$

According to our assumptions, the equation will be $\Delta H = 0$

The reaction is performed at 240C between Styrene and initial styrene. As the reaction is initiated, it occurs rapidly. Temperature rises to a higher point 360C according to the exothermic attitude, and this behavior is undesirable. In order to dominate and control this upsetting outcome is to recycle the polystyrene product as granules until the temperature becomes constant at 240C, which is the melting point of polystyrene. We also provide warmth to the recycled polystyrene at 70Co to reach the required circumstances.

As the batch is conceived, we apply thermal termination (260 to 300C) to styryl ions. The enthalpy of polymerization reaction equals 288btu/lb. We used the jacket in order to obtain a temperature of 240C of the feed stock (Figs. 2 & 3). In order to measure heat, we must apply the following equation (enthalpy times mass).

$\Delta HR = -288$ btu/lb (Eugene, 2005)

We assumed that the heat capacity of the liquid is approximately equivalent to the heat capacity of the reaction temperature.

$$\Delta H1 = CP\,(Tr - T1) \tag{3}$$

Where :.
CP is specific heat of styrene at 240 c
T1 is initial temperature
Tr is the the reaction temperature

$$\Delta H2 = CP\,(Tr - Tm) \tag{4}$$

Where :.
CP is the specific heat of reacted polystyrene at 360 c
Tm is the maximum temperature

$$\Delta Hrpc = CP\,(Tr - Trp) \tag{5}$$

Where :.
CP is the specific heat at 240 c
Trp is the input temperature of recycled polystyrene
The fallowing equation excludes recycled polystyrene

$$\Delta HR = H1 + H2 \tag{6}$$

$$-\Delta HR + CP\,(Tr - T1) + CP\,(Tr - Tm) = 0 \tag{7}$$

The following equation includes recycled polystyrene :.

$$\Delta HR = \Delta H1 + \Delta HRPS + \Delta HPC \tag{8}$$

$$-\Delta HR + \Delta H1 + \Delta HRPS + \Delta HPC = 0 \tag{9}$$

Where

$$\Delta HRPS + \Delta HPC = \Delta H2 \tag{10}$$

To find out the enthalpy of phase change

$$\Delta HPC = \Delta H2 - \Delta HRPS \tag{11}$$

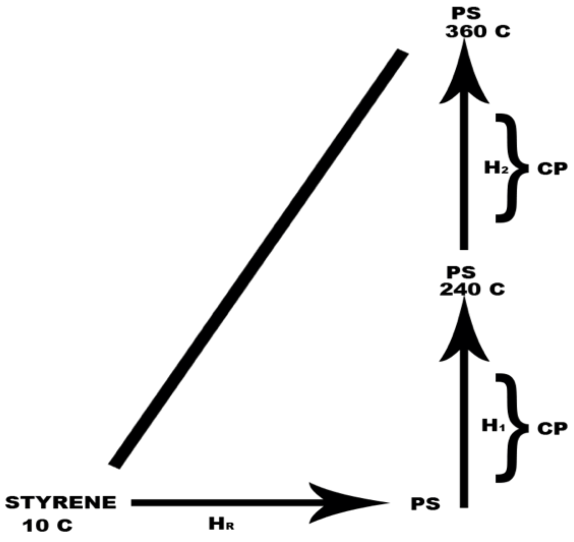


Fig. 2. Change of enthalpy without recycled polystyrene.

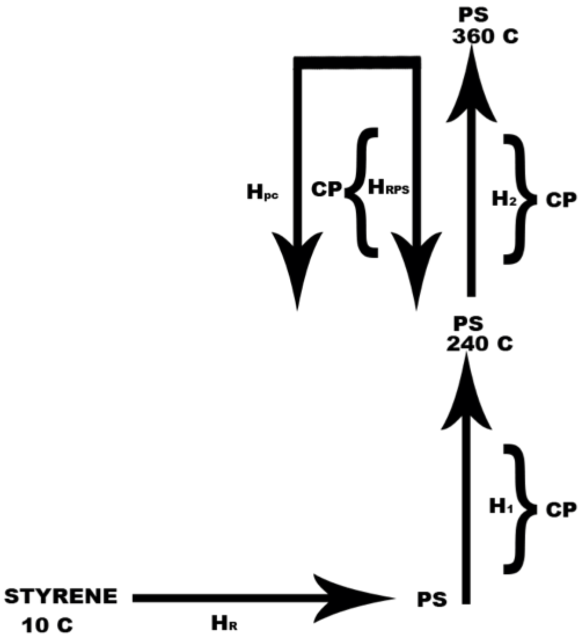


Fig. 3. Change of enthalpy with recycled polystyrene.

Devolatilizer: It has a specified function, which is segregating Ethyl Benzene from Polystyrene by high vacuum pressure at 10mmHg. The inserted temperature from the devolatilizer is equivalent to the exited temperature from mixer, which is 240C.

In order to determine the outlet temperature of Ethyl Benzene, it has used Antoine equation:

$$\ln P = \mathrm{A} - \frac{B}{C + T} \tag{12}$$

The purpose of design is to determine the volume of the utilities in order to evaluate certain requirements such as, economic details. The main function of the factory is to produce polystyrene;

we previously mentioned that the factory consists of three sections. For instance, the purification section promotes the capital cost of factory. However, purification section cannot be underestimated according to its importance and role in the quality of the product and it controls its properties.

In order to distinguish between candidate reactors that may affect the design, We have selected and used packet bed reactor (batch reactor) the reaction is extremely rapid. The essential utilities include flash drum, adsorber, reactors and separators. Styrene intrudes the adsorber to remove the inhibitor (TBC) it penetrates beds that contain aluminia, alumina adsorbs TBC and we employ regeneration to this adsorber each three months because aluminia is saturated with TBC (Rivero *et al*, 2003).

To find out the volume of the adsorber we have to find the amount of alumina that adsorbed the TBC in three month per bulk density of alumina.

Mass of alumina equal amount of TBC in three months divided on q

Whereas q is Langmuir – freundich equation (13)

q = 0.00173*C^0.5/(1+0.00836*C^0.5)

Whereas, C is the quantity of TBC to styrene, Amount of TBC is equal the total mass *C

The calculated volume of the adsorbed was 1435 cubic feet. The Initiation Reactor R-201 is intrusively invaded by Styrene, NBL and EB. The reaction occurs at low temperature. The process is batch. Therefore, we assumed that the volume of the reactor equals the feedstock that entered the reactor.

Additionally, resident time of reaction is few, the total duration of process is 15 min (Eugene, 2005)

Density = M/V
Thus, Volume = Density/Mass
The total volume of feedstock = Volume of Styrene + Volume of EB + Volume of NBL
Volume of Styrene = Mass of Styrene / Density of Styrene
Mass of Styrene = 60081.712lb
Density of Styrene at reaction temperature = 44.29lb/ft3
Volume of Styrene = 1356.5 cubic feet
The volume of NBL = Mass of NBL/Density of NBL
Mass of NBL = 19.24324093lb
Density of NBL = 42.45lb/ft3 at 10C
Volume of NBL = 0.453315452 cubic feet
The volume of EB = Mass of NBL/Density of EB
Mass of EB = 180.7348004lb
Density of EB = 54.68lb/ft3
Volume of EB =3.305 cubic feet
Reactor volume = 1360 cubic feet
In order to determine the diameter of reactor, we use the following equation:
V = πr2h
We assume that the height of the reactor = 19.5 feet
D = (V / h*π)^0.5 * 2
D =9.88 feet

Propagation Reactor R-202 It is the reactor that incubates the propagation process, recycled PS is dumped from above into the reactor and it receives the feedstock, which comes from R-201. This reaction occurs rapidly and at high temperature, resident time of reaction is few. The total duration of this process is 10min (Eugene, 2005). Therefore, it has calculated the product volume to select the method that is suitable for designing the reactor. Rate equation of the reaction (Eugene, 2005)

Rp = Kp [M-][M] (14)

From the rate constant (kp=2L/mol-sec) , it is possible to calculate the approximate overall polymerization rate (Rp) for styrene and the associated heat evolution rate. The kinetics are reported to be simple second order (Eugene, R. M., 2005).

For the case of pure undiluted styrene, [M] is 8.689 mol/L and for MW=200,000, [M]=0.0004525. Then assuming that styrene acting as it's own solvent will have the same kp at 25° C. as benzene (kp=2L/mol-sec), Rp=0.0786 mol (of styrene)/L-sec .

The estimated Volume of the reactor is 1853.7 cubic feet

Diameter of reactor = (V / h*π)^0.5 * 2
We assumed that height of reactor= 32.8084 feet
D= 8.897933662 feet

In Devolatilizer; V-302 Ethyl Benzene is soluble in Polystyrene as liquid phase. As we apply devolatilization to EB, the outcome phase is gaseous which refers to its increment in volume.

In order to determine the volume of Devolatilizer; Volume of EB Gaseous + Volume of

PS , the Volume of Gaseous EB it has used the real gas equation; PV=ZnRT

The calculated devolatilizer volume was 1426 cubic feet

The equipment size, flow rate, raw material, and ploystyrene production are a very important factor in factor in following steps.

Fixed capital cost.

- ISBL Plant Costs
- Offsite Cost.
- Engineering Cost.
- Contingency Charges.

Working Capital.

Cash cost of production.

Total cost of production.

The Cash flow in each year of the project.

The simple payback period.

The net present value with a 15% cost of capital 25 year of production.

Discounted cash flow rate of return (DCFROR) or IRR.

Taking into consideration that the factory may shutdown for 19 days for periodic maintenance or unexpected emergency cases. According to this the factor works for 346 days in a year.

The Total Fixed Capital Cost has calculated 120MM $.

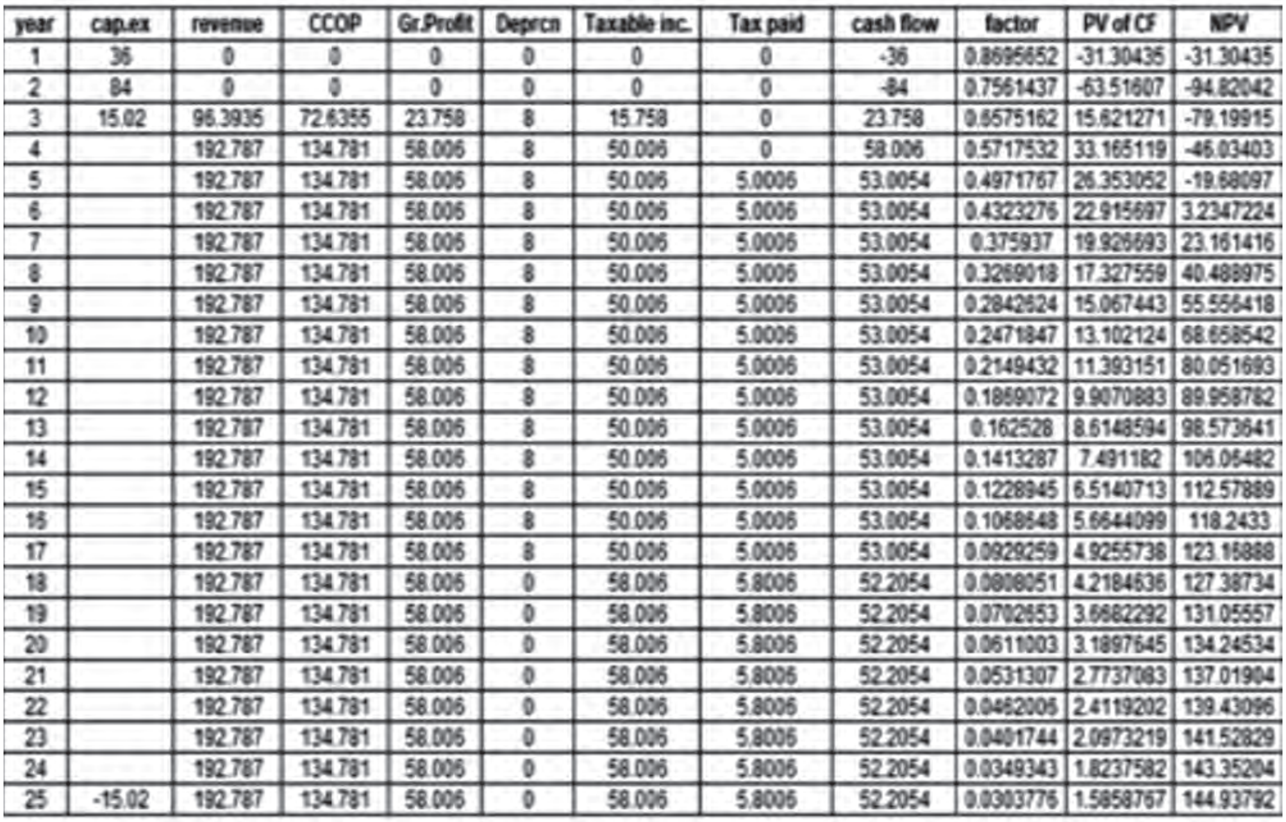
The Total Working Capital has calculated 15.02 MM $ per year.

Cash flow summary of calculation (Table1): In year 1 and 2 of the project, there are capital expenses but no revenues or operating costs. The capital expenses are not operating losses, so they have no effect on taxes or depreciation. They are negative cash flows. All of the working capital must be invested. The plant incurs 100% of the fixed cost of production but only 50% of the variable cost. Because the plant makes a profit, depreciation can be charged. Using the straight-line method of depreciation with a 15-year recovery period, the annual depreciation charge is one-fifteenth of the total fixed capital investment = 120/15 = $8MM.

The effect of charging depreciation is that the table income is negative, so no taxes are owed in year 4 (taxes are paid based on the previous year's income). Simple Pay-Back Time a simple method for estimating the payback time is to divide the total investment by the average annual cash flow:

$$\text{Simple Pay} - \text{Back Time} = \frac{120}{51.67} = 2.32\text{year}$$

Table 1. Summary of calculation.



year	cap.ex	revenue	CCOP	Gr.Profit	Deprcn	Taxable inc.	Tax paid	cash flow	factor	PV of CF	NPV
1	36	0	0	0	0	0	0	-36	0.8695652	-31.30435	-31.30435
2	84	0	0	0	0	0	0	-84	0.7561437	-63.51607	-94.82042
3	15.02	96.3935	72.6355	23.758	8	15.758	0	23.758	0.6575162	15.621271	-79.19915
4		192.787	134.781	58.006	8	50.006	0	58.006	0.5717532	33.165119	-46.03403
5		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.4971767	26.353052	-19.68097
6		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.4323276	22.915697	3.2347224
7		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.375937	19.926693	23.161416
8		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.3269018	17.327559	40.488975
9		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.2842624	15.067443	55.556418
10		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.2471847	13.102124	68.658542
11		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.2149432	11.393151	80.051693
12		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.1869072	9.9070883	89.958782
13		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.162528	8.6148594	98.573641
14		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.1413287	7.491182	106.06482
15		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.1228945	6.5140713	112.57889
16		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.1068648	5.6644099	118.2433
17		192.787	134.781	58.006	8	50.006	5.0006	53.0054	0.0929259	4.9255738	123.16888
18		192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0808051	4.2184636	127.38734
19		192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0702653	3.6682292	131.05557
20		192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0611003	3.1897645	134.24534
21		192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0531307	2.7737083	137.01904
22		192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0462006	2.4119202	139.43096
23		192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0401744	2.0973219	141.52829
24		192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0349343	1.8237582	143.35204
25	-15.02	192.787	134.781	58.006	0	58.006	5.8006	52.2054	0.0303776	1.5858767	144.93792

CONCLUSION

It has selected a Polystyrene manufacturing patent and its methodology. Within reason, it has the privilege to control the properties with no complex interferences regardless of the showcased difficulties of temperature control. It has implemented the energy and material balance onto most plant equipment and has designed the prior units. The calculations of work match the guidelines of the patent, it has bonded the provided hints of patent and has obtained the results by linking our knowledge to those hints.

The industrial advantage of designing this plant is that inlet feedstock is wholly exploited to come up with a product without wasted inlet. The economic distinction of this project is that the plant is quite profitable and its capital is predictably regained after two years and three months of operating.

RECOMMENDATIONS

- Strongly recommend that the patent and its references should be studied with full concentration.
- We suggest that you take your research to an advance level by looking up to similar examples.
- The economic study lacks details about sub-utilities, because we focused on the main utilities and neglected their sub-branches.

NOMENCLATURE

PS	Polystyrene
NBL	Normal Butyl Lithium
EB	Ethyl Benzene
TBC	4-tert-Butylcatechol
Xn	number average degree of polymerization
[M]0	initial concentration of monomer
[I]0	initial concentration of initiator
Mn	number-average molecular weight
ΔHR	Enthalpy of polymerization reaction
ΔH1	Enthalpy of reaction before exothermal
ΔH2	Enthalpy of reaction after exothermal
ΔHRPS	Enthalpy of recycled polystyrene
ΔHPC	Enthalpy of phase change of recycled polystyrene
CP	specific heat
Kp	Rate constant
Rp	Rate of Reaction

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