STYRENE PRODUCTION PLANT

Introduction

Styrene is a colourless, toxic oily organic liquid that evaporates easily and has a sweet smell. The Chemical formula for Styrene is C6H5CH=CH2. Styrene has IUPAC names vinyl benzene and phenyl ethene. Styrene was first commercially produced in the 1930s and was used in the production of synthetic rubber during world war 2. After the war, much of the use of styrene shifted to the manufacture of commercial polystyrene products.

This flowsheet simulation was done for a 700 ktons/year styrene production plant making styrene by the catalytic adiabatic dehydrogenation of ethylbenzene. The plant was considered to be operational for 330 days per year. In order to estimate the actual plant conditions, to gain more insights and to verify our results from analytical mass balance, we simulated our flowsheet in DWSIM, which is a multiplatform and an open source chemical process simulator.

In this process, our main reaction is as follows:

$C_0H_{10} \rightarrow C_8H_8 + H_2$

It is an endothermic process generally conducted at 540-660°C and at 40 kPa. Iron oxide supported on metal oxides as promoters(84.3% iron as iron oxide, 2.4% chromium as chromium (III) oxide & 13.3% potassium as Potassium carbonate) is used as a catalyst for the process. 270 kCal/Kg styrene is being used and there are two or three reactors being used in series. Further, we have an LLV separator which separates the product stream and conversion is generally 35% in the first reactor and after the second reactor 60-65%. Also, selectivity for the same is 90% by weight. After coming from LLV separator, we have three streams- one of gas, containing hydrogen, methane, carbon monoxide and carbon dioxide, second is an organic phase, containing styrene, ethylbenzene, toluene and benzene and the last one is an aqueous phase. The organic phase is separated using distillation columns through the process named Lummus UOP separation. Steam is being used to heat up the feed and thus carry forward the process.

Process Flowsheet in DWSIM

Complete Flowsheet

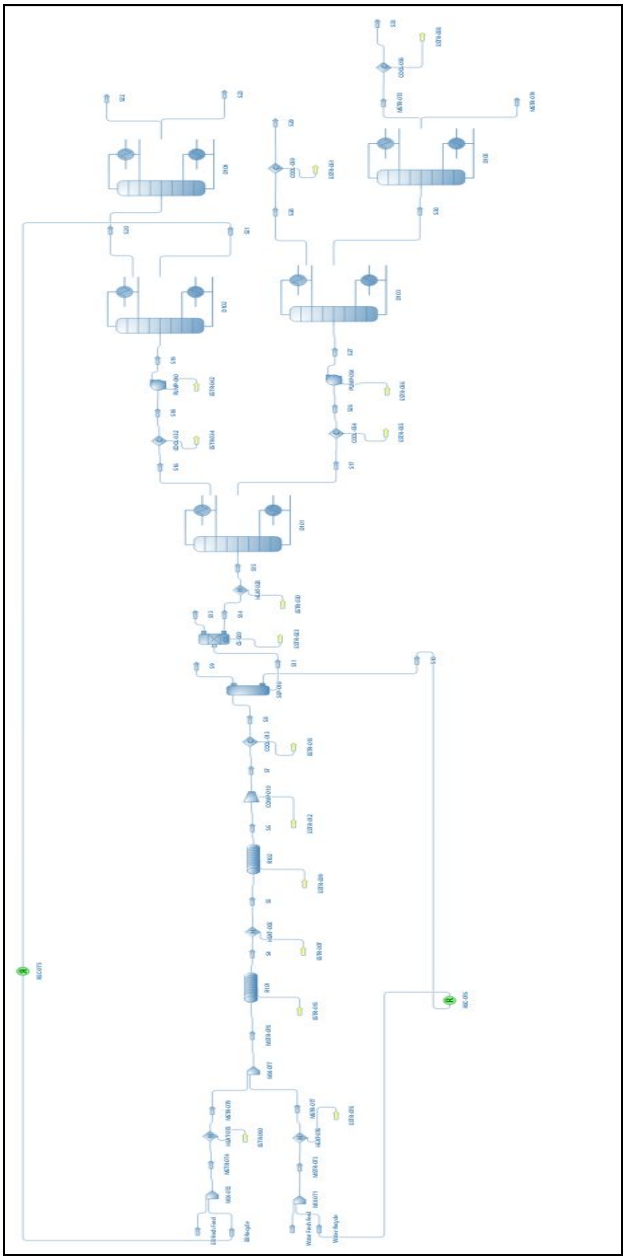

Fig 1 - Complete Flowsheet

Part 1 - Reaction step

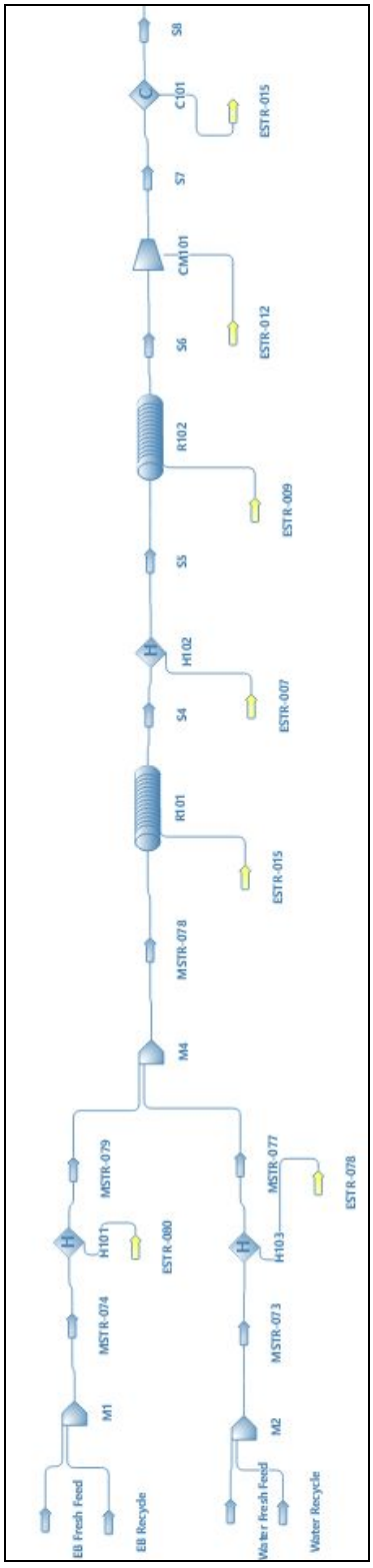

Fig.2 - Reaction step

Part 2 - LLV separator

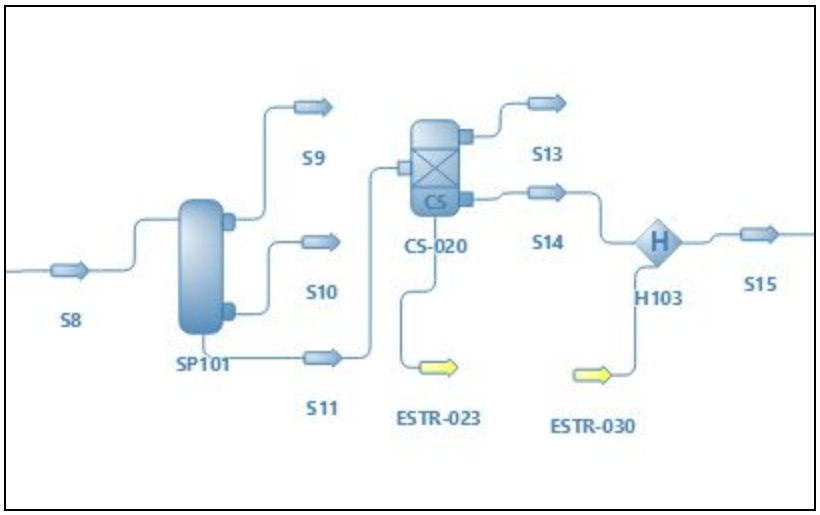

Fig. 3 - LLV Separator

Part 3 - Purification

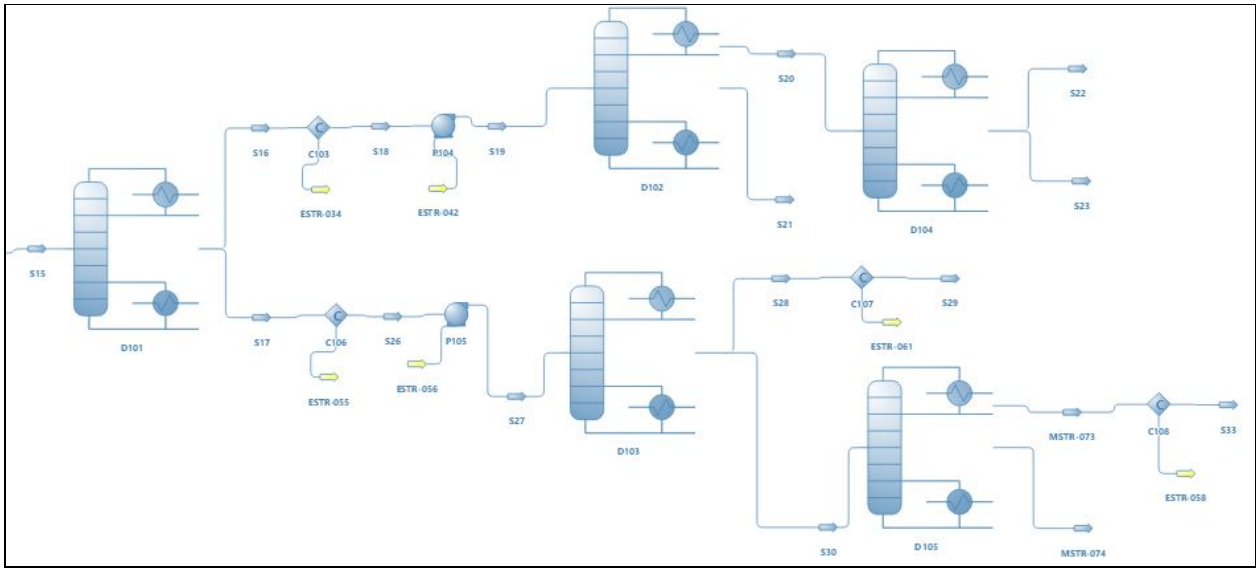

Fig 5.3 - Distillation columns

Equipment

1. Reactors - R101, R102

We have modelled a plug flow reactor considering catalytic heterogeneous reactions as follows:

1. $(C_6H_5)CH_2CH_3 \Leftrightarrow H_2 + (C_6H_5)CHCH_2$ (Main reaction)
2. $(C_6H_5)CH_2H_3 \Leftrightarrow C_2H_4 + C_6H_6$
3. $H_2 + (C_6H_5)CH_2CH_3 \Leftrightarrow (C_6H_5)CH_3 + CH_4$
4. $2H_2O + C_2H_4 \Leftrightarrow 4H_2 + 2CO$
5. $H_20 + CH_4 \Leftrightarrow 3H_2 + CO$

The reaction kinetics which has been used to model the plug flow reactors are as follows:

Table 5.1- Reaction Kinetics

$C_6H_5CH_2CH_3 \rightarrow C_6H_5CHCH_2 + H_2$	$r_1 = k_1 P_{EB}$
$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	$r_2 = k_2 P_{EB}$
$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	$r_3 = k_3 P_{EB} P_{H2}$
$2H_20 + C_2H_4 \rightarrow 2CO + 4H_2$	$r_4 = k_4 P_{H2O} P_{ETH}^{0.5}$
$H_20 + CH_4 \rightarrow CO + 3H_2$	$r_5 = k_5 P_{H2O} P_{CH4}$

The reactor is an adiabatic packed bed radial flow reactor and as the reaction is endothermic, there is an expected temperature drop. The temperature varies along the reactor length. Therefore all the kinetic parameters had to be put as a function of temperature. Thus, the data which we got from the literature survey and which we are using is:

Table 5.2 - Kinetics data for reactions

Reaction no.	Activation Energy (Ea)	Rate constants (ko)
1	207989	4329375423
2	91515	6302.4
3	103996	4059
4	65723	145.3
5	73268	6.03E+12

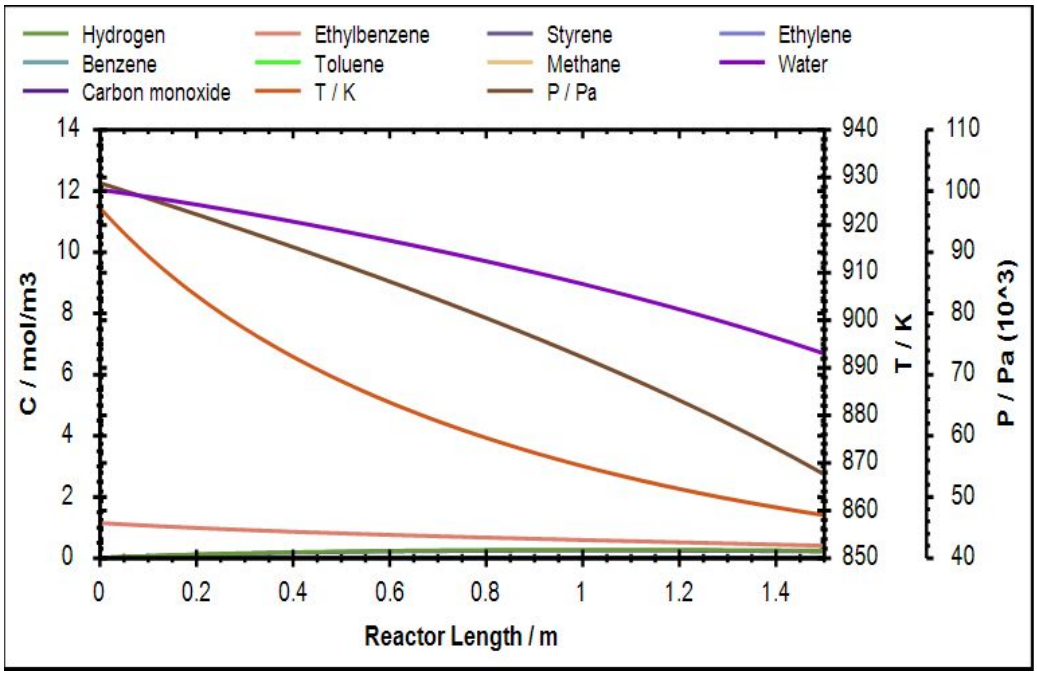

Fig. 4. DWSIM Simulation Results for R101

We found that the typical catalyst amount needed for a 300 kiloton per year plant in Ullmann's Encyclopedia of Industrial Chemistry and considering that our plant is almost double the capacity, 700 kilotons per year, we estimated the amount for our reactors. Also, the catalyst parameters were found from literature as of a typical industrial catalyst, such as the density, void fraction, particle size. The reactor volume was adjusted to match industrial conversions.

2. Liquid-Liquid-Vapour Separator - SP101

After the reactors, we have used a three-phase separator which is dividing the product stream into three components:

1. Off Gas, which contains Hydrogen, Carbon dioxide, Carbon monoxide, Methane
2. The aqueous phase, containing water
3. The organic phase, which contains Styrene, Benzene, Toluene, Ethylbenzene, Naphthalene, Biphenyl

3. Distillation Columns - D101, D102, D103, D104 and D105

There are four distillation columns being used.

1. Distillation column 1: D101

   Shortcut Column
   Minimum reflux ratio: 8.49
   Minimum number of stages at infinite reflux: 22

   Chemsep Column
   No of stages: 75 (literature)
   Feed stage: 38
   Reflux Ratio: 12
   Major components in distillate: Benzene, Toluene, Ethylbenzene, Styrene (1 mol %)
   Major components in bottom: Styrene, Naphthalene, Biphenyl
   Mass flow of distillate: 45374.76 kg/hr
   Mass flow rate of bottom: 90012.24 kg/hr
   Total condenser and partial reboiler are used.

Table 1.- Mass Flows in D101

Mass flow (kg/s)	Feed	Top	Bottom
Water	0.00	0.00	0.00
Carbon dioxide	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00
Benzene	1.32	1.32	0.00
Toluene	0.24	0.24	0.00
Ethylbenzene	11.02	10.98	0.04
Styrene	24.65	0.12	24.53
Methane	0.00	0.00	0.00
Carbon monoxide	0.00	0.00	0.00
Naphthalene	0.19	0.00	0.19
Biphenyl	0.19	0.00	0.19

2. Distillation 2: D102
   Simple distillation column with sieve trays.
   Shortcut Column
   Minimum reflux ratio: 5
   Minimum number of stages at infinite reflux: 20

   Chemsep Column
   No of stages: 30
   Feed stage: 16
   Reflux Ratio: 7.5
   Components in distillate: Benzene, Toluene
   Components in bottom: Ethylbenzene, Styrene
   Mass flow of distillate: 1.47 kg/s
   Mass flow rate of bottom: 11.12 kg/s
   Total condenser and partial reboiler are used.

Table 2.- Mass Flows in D102

Mass flows (kg/s)	Feed	Top	Bottom
Water	0	0	0
Carbon dioxide	0	0	0
Hydrogen	0	0	0
Ethylene	0	0	0
Benzene	1.32711	1.3271	2.57E-06
Toluene	0.327721	0.223414	0.104307
Ethylbenzene	11.4898	2.05E-05	11.4898
Styrene	0.0537415	1.30E-09	0.0537415
Methane	0	0	0
Carbon monoxide	0	0	0
Naphthalene	0	0	0
Biphenyl	0	0	0

3. Distillation column 3: D103

Chemsep Column
No of stages: 10
Feed stage: 3
Reflux Ratio: 2
Components in distillate: Styrene
Components in bottom: Naphthalene, Biphenyl
Mass flow of distillate: 24.5367 kg/s
Mass flow rate of bottom: 0.409373 kg/s
Total condenser and partial reboiler are used

Table 3.- Mass Flows in D103

Mass Flow (kg/s)	Feed	Top	Bottom
Water	0.00	0.00	0.00
Carbon dioxide	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00
Benzene	0.00	0.00	0.00
Toluene	0.00	0.00	0.00
Ethylbenzene	0.04	0.04	0.00
Styrene	24.53	24.49	0.03
Methane	0.00	0.00	0.00
Carbon monoxide	0.00	0.00	0.00
Naphthalene	0.19	0.00	0.19
Biphenyl	0.19	0.00	0.19

4. Distillation column 4: D104

   Shortcut Column

   Minimum reflux ratio: 2

   Minimum number of stages at infinite reflux: 8

   Chemsep Column

   No of stages: 16

   Feed stage: 8

   Reflux Ratio: 3

   Components in distillate: Benzene

   Components in bottom: Toluene

   Mass flow of distillate: 1.32 kg/s

   Mass flow rate of bottom: 0.15 kg/s

   Total condenser and partial reboiler are used.

   Table 4.- Mass Flows in D104

Mass flow (kg/s)	Feed	V Feed	L Feed	Top	Bottom
Water	0	0	0	0	0
Carbon dioxide	0	0	0	0	0
Hydrogen	0	0	0	0	0
Ethylene	0	0	0	0	0
Benzene	1.32008	0.00001	1.32008	1.31926	0.00082
Toluene	0.20643	0.00000	0.20643	0.00779	0.19864
Ethylbenzene	0.00004	0.00000	0.00004	0.00000	0.00004
Styrene	0	0	0	0	0
Methane	0	0	0	0	0
Carbon monoxide	0	0	0	0	0
Naphthalene	0	0	0	0	0
Biphenyl	0	0	0	0	0

5. Distillation column : D105

   Chemsep Column

   No of stages: 10

   Feed stage: 5

   Reflux Ratio: 1.5

   Components in distillate: Styrene

   Components in bottom: Anthracene, Naphthalene

   Mass flow of distillate: 0.18 kg/s

   Mass flow rate of bottom: 0.22 kg/s

   Total condenser and partial reboiler are used.

Table 5.- Mass Flows in D105

Mass flow (kg/s)	Feed	Top	Bottom
Water	0	0	0
Carbon dioxide	0	0	0
Hydrogen	0	0	0
Ethylene	0	0	0
Benzene	0	0	0
Toluene	0	0	0
Ethylbenzene	0	0	0
Styrene	0.0315343	0.0315326	1.72E-06
Methane	0	0	0
Carbon monoxide	0	0	0
Naphthalene	0.187992	0.127701	0.0602913
Biphenyl	0.189738	0.0079389	0.181799

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