# CHE654 – Plant Design Project #6
# Semester 1, 2024

# DESIGN OF A STYRENE PRODUCTION PROCESS FROM BENZENE VIA ETHYLBENZENE

Courtesy of National Programme on Technology Enhanced Learning (NPTEL)

## Introduction

Styrene, also known as ethenylbenzene, vinylbenzene, and phenylethene, is an organic compound with the chemical formula $C_6H_5CH=CH_2$. This derivative of benzene is a colorless oily liquid that evaporates easily and has a sweet smell, although high concentrations have a less pleasant odor. Styrene is the precursor to polystyrene and several copolymers. Styrene is also mainly used for making plastic toys and model kits. Moreover, housing for machines as well as refrigerator doors and air conditioner cases are made of styrene. Approximately 25 million tons (55 billion pounds) of styrene were produced in 2010.

Styrene can be manufactured from benzene and ethylene via ethylbenzene. The plant where you are employed has been buying styrene as a feedstock. Management is considering manufacturing styrene rather than purchasing it to increase profits. Someone has made a preliminary sketch for such a process and has submitted to the engineering department for consideration. Your group is assigned the problem of evaluating the sketch and recommending improvements in the preliminary design. Your job is to analyze a simplified styrene production process, to suggest profitable operating conditions, and to write a final report summarizing your findings. Note that optimization is <u>NOT</u> required in this design project.

**<u>Reactions</u>**

Alkylation of Benzene

- Benzene + Ethylene → Ethyl benzene
- Catalyst: $AlCl_3$ granules
- $C_2 H_5Cl$ provides hydrogen and chlorine free radicals
- Operating conditions: 95°C and 1 atm pressure
- Reaction is exothermic.

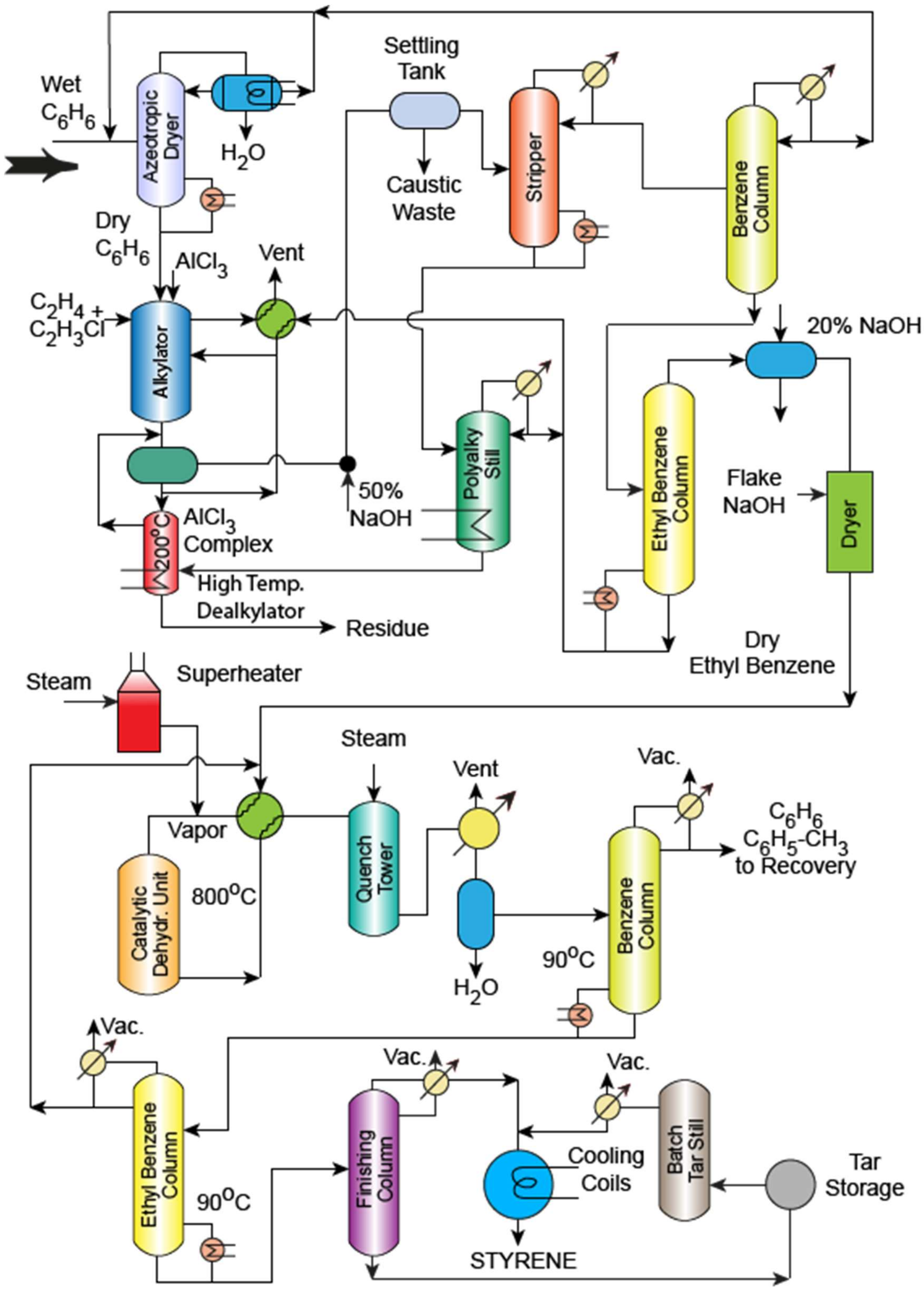
Dehydrogenation of ethylbenzene

- Ethylbenzene + Styrene + Hydrogen
- Reaction is endothermic
- Catalyst: SnO or FeO

- Operating conditions: 800°C.

**Process Technology**

The figure below shows a flowsheet of styrene from benzene and ethylene via ethylbenzene.



- The process consists of two separate reactor-separator-recycle networks in which one corresponds to the ethylbenzene flow sheet and the other corresponds to styrene flowsheet.

- We first present the flowsheet for ethylbenzene production.

- Benzene (wet) is sent first to an azeotropic distillation unit that separates water and produces dry Benzene. Dry Benzene is required so as to avoid unnecessary reactions in the alkylation reactor as well as damage to the catalyst as alumina can get formed.

- Dry Benzene + Ethylene + Ethyl chloride + $AlCl_3$ enter the alkylator catalyst.

- The reactor could be a jacketed tower where water is used as a cooling fluid in the jacket to control the reactor temperature.

- The reactor produces two products namely non-condensible gases and the liquid product in which $AlCl_3$ complex is available. This complex needs to be regenerated and sent back to the alkylator.

- The alkylator product is sent to a cooler which upon cooling to 40°C separates the aluminium chloride complex stream from the product stream. The other stream from the cooler is the ethylbenzene rich product stream.

- The aluminium chloride stream is partially recycled to the alkylator so as to maintain the required catalyst requirements. The other portion of the $AlCl_3$ complex is sent to a dealkylator unit in which the feed is heated to 200°C. By doing so, the polyethylbenzenes formed in the alkylator are converted to benzene and ethylbenzene (cracking reaction).

- The benzene and ethylbenzene are returned to the cooler.

- The delkylator produces a residue product consisting of tar + $AlCl_3$ mixture.

- From this mixture, $AlCl_3$ is recovered using water extraction as $AlCl_3$ is soluble in water. From there $AlCl_3$ is recovered from the water and returned back to the alkylation reactor.

- The product stream from the cooler consisting of ethylbenzene is mixed with 50 % NaOH to remove acidic impurities. Eventually, after settling waste is eliminated.

- The purified ethylbenzene then enters a stripper that separates ethylbenzene + benzene from the polyalkylbenzenes. The polyalkylbenzenes are sent to a polyalkyl still that separates the benzene + ethylbenzenes from the polyalkylbenzenes (bottom product). The polyalkyl still is operated under vacuum. The polyalkylbenzenes are fed to the dealkylator and the benzene + ethylbenzene rich stream is sent to a heat integrated exchanger that extracts heat from the vent gases and then eventually enters the alkylation reactor.

- The top product from the stripper is ethylbenzene + benzene and it enters a benzene column that separates wet benzene from crude ethylbenzene. The wet benzene is recycled to the azeotropic dryer where it is mixed with fresh wet benzene to enter the azeotropic dryer.

- The crude ethylbenzene is further purified in a fractionator where the bottom product (with benzene) is mixed with the top product of the polyalkyl still. Thereby, the stream enters the heat integrated exchanger.

- The ethylbenzene is further subjected to caustic wash and finally it is sent to a dryer to produce dry ethylbenzene.

- We now move to the dehydrogenation flowsheet.

- The ethylbenzene (dry) is heated with superheated steam to enter the catalytic dehydrogenator. Excess steam is used in this process. The feed pre-heating is carried out using the product vapor stream. The reaction is gas phase catalytic reaction.

- The vapor stream after cooling with the feed stream in a heat integrated exchanger is fed to a quench tower using steam quenching.

- After quenching, partial condensation of the quenched vapors produces three streams one being the vapor vent, the other being water and the third being the organic phase rich with styrene.

- The styrene rich stream is sent first to a benzene column to recover the benzene + toluene and this is sent to a benzene-toluene distillation column to recover benzene. The benzene is sent to the azeotropic distillation unit as a raw-material.

- The bottom product from the benzene column enters an ethylbenzene column which separates ethylbenzene from the styrene stream. The ethylbenzene stream is mixed with the dry ethylbenzene to enter the catalytic dehydrogenator.

- The bottom product from the ethylbenzene column is the styrene enriched stream and this is sent to the finishing column where styrene is further purified from unwanted impurities such as tar. The tar is further batch distilled to recover styrene from the tar. The styrene finishing column also produces styrene product. Both styrene products from batch still and styrene finishing column are mixed and cooled to store as styrene product.

- All three columns namely benzene, ethylbenzene and finishing columns are operated under vacuum.

**Technical Questions**

1. Explain how azeotropic distillation unit functions to convert wet benzene to dry benzene?

Ans: Wet benzene upon heating produces a heterogeneous azeotrope at the top and dry benzene at the bottom. Therefore, the unit upon condensation of the top vapors produces two streams namely water and benzene rich wet stream which is recycled back as the reflux stream.

2. Why is the benzene + ethylbenzene stream returned back to the cooler but not the alkylation reactor?

Ans: The alkylation reactor should be fed with very important chemicals only. It is possible that the temperatures prevailing in the dealkylator could enable the loss of polyalkylbenzenes to the vapor. Therefore, there is no point in feeding this stream to the alkylator. Instead the stream is sent to the cooler so that any polyalkylbenzenes could be condensed back and sent to the dealkylator again.

3. Why the $AlCl_3$ complex is partially returned to the reactor?

Ans: To maintain the required catalyst conditions. If not, then $AlCl_3$ fresh has to be provided to the reactor as $AlCl_3$ forms a complex with the hydrocarbons and would leave the alkylator along with the product streams.

4. Why do polyalkylbenzenes enter the ethylbenzene rich product?

Ans: This is the basic problem of the equilibrium separation factors of polyalkylbenzenes between the $AlCl_3$ complex rich product and the ethylbenzene rich product. Since sharp distribution of these compounds is not possible, polyalkylbenzenes get distributed between both these organic phases.

5. Why there are ethylbenzene + benzenes still available in the bottom product of the stripper?

Ans: The answer is same as that of question 3 i.e., the phase equilibrium limitations enable the availability of both benzene + ethylbenzene in the polyalkylbenzene stream.

6. Why the benzene is wet from the benzene column?

Ans: This is because caustic wash operation enabled the contact with water and some water will enter the organic phase due to phase equilibrium of water with the organic phase. This water therefore enters the benzene stream from the benzene column.

7. Why caustic wash followed by drying is carried out is carried out for the ethylbenzene stream?

Ans: Caustic wash removes any undesired impurities whereas dryer removes the water. Both water and acid are important compounds which if not eliminated contribute significantly to side reactions during the heating process with superheated steam. Therefore, totally dry and acid free conditions are targeted for ethylbenzene.

8. Why vacuum is used in the polyalkyl still unit?

   1. To enhance relative volatility of components that can be easily removed.

   2. To reduce dissociation of polyalkyl components in the column.

9. Why steam quenching but not water quenching is adopted?

Ans: Water quenching can give rise to additional reactions. Steam quenching does not allow condensation and hence is safe in that sense not to trigger any unwanted reactions of the styrene and ethylbenzene.

10. What gases are removed in the vent following quenching tower?

Ans: Gases such as hydrocarbons that are resultant of undesired cracking are removed as non-condensibles in the partial condenser. These are vented out.

11. Why tar consist of styrene?

Ans: Styrene being organic compound has affinity to get dissolved in the tar. Therefore, the batch still is used to extract styrene from the tar.

12. Why vacuum is used for the separation of benzene, toluene, ethylbenzene and styrene?

Ans: All these compounds are closely boiling systems. By going for vacuum distillation, we are able to enhance the relative volatility of the components and hence better separation. The increasing order of higher vacuum levels is applied for these three columns in series i.e., benzene column, ethylbenzene column and finishing column.

## Design of Heat Exchangers

A detailed design of at least one heat exchnager in the process is required for base-case conditions. For this heat exchanger design, the following information should be provided:

- Diameter of shell
- Number of tube and shell passes
- Number of tubes per pass
- Tube pitch and arrangement (triangular/square/..)
- Number of shell-side baffles, if any, and their arrangement (spacing, pitch, type)
- Diameter, tube-wall thickness, shell-wall thickness, and length of tubes
- Calculation of both shell- and tube-side film heat transfer coefficients
- Calculation of overall heat transfer coefficient (you may assume that there is no fouling on either side of the exchanger)
- Heat transfer area of the exchanger
- Shell-side and tube-side pressure drops (calculated, not estimated)
- Materials of construction
- Approximate cost of the exchanger

A detailed sketch of the exchanger should be included along with a set of comprehensive calculations in an appendix for the design of the heat exchanger. You should use ASPEN Exchanger Design & Rating (EDR) in the ASPEN Plus simulator to carry out the detailed design.

## Economic Analysis

When evaluating alternative cases, you should carry out an economic evaluation and profitability analysis based on a number of economic criteria such as payback period, internal rate of return, and cash flow analysis. In addition, the following objective function should be used. It is the equivalent annual operating cost (EAOC), and is defined as

EAOC = −(product value – feed cost – other operating costs – capital cost annuity)

A negative EAOC means there is a profit. It is desirable to minimize the EAOC; i.e., a large negative EAOC is very desirable, although you are not being asked to carry out optimization.

The costs for cumene (the product) and benzene (the feed) should be obtained from the *Chemical Marketing Reporter*, which is in the Evansdale Library. The "impure" propylene feed is $0.095/lb.

The capital cost annuity is an ***annual*** cost (like a car payment) associated with the ***one-time***, fixed cost of plant construction. The capital cost annuity is defined as follows:

$$capital\ cost\ annuity = FCI \frac{i(1+i)^n}{(1+i)^n - 1}$$

where *FCI* is the installed cost of all equipment; $i$ is the interest rate, $i = 0.15$; and $n$ is the plant life for accounting purposes, $n = 10$.

For detailed sizing, costing, and economic evaluation including profitability analysis, you may use the Aspen Process Economic Analyzer (formerly Aspen Icarus Process Evaluator) in Aspen Plus. However, it is also a good idea to independently verify the final numbers based on other sources such as cost data given below.

## Other Information

You should assume that a year equals 8,000 hours. This is about 330 days, which allows for periodic shut-down and maintenance.

## Final Comments

As with any open-ended problem; i.e., a problem with no single correct answer, the problem statement above is deliberately vague. You may need to fill in some missing data by doing a literature search, Internets search, or making assumptions. The possibility exists that as you work on this problem, your questions will require revisions and/or clarifications of the problem statement. You should be aware that these revisions/clarifications may be forthcoming.

Moreover, in some areas (e.g. sizing/costing) you are given more data and information than what is needed. You must exercise engineering judgment and decide what data to use. Also you should also seek additional data from the literature or Internet to verify some of the data, e.g. the prices of products and raw materials.

## References


1. Dryden C. E., *Outlines of Chemical Technology*, East-West Press, 2008.

2. Kirk R. E., Othmer D. F., *Encyclopedia of Chemical Technology*, John Wiley and Sons, 1999-2012.