



CHE654 – Plant Design Project #5 Semester 1, 2024



DESIGN OF BUTADIENE AND BENZENE PRODUCTION PROCESSES

Courtesy of National Programme on Technology Enhanced Learning (NPTEL)

Introduction

1,3-Butadiene is the organic compound with the formula $(\text{CH}_2=\text{CH})_2$. It is a colorless gas that is easily condensed to a liquid. It is important industrially as a monomer in the production of synthetic rubber. The molecule can be viewed as the union of two vinyl groups. It is the simplest conjugated diene. Although butadiene breaks down quickly in the atmosphere, it is nevertheless found in ambient air in urban and suburban areas as a consequence of its constant emission from motor vehicles. The name butadiene can also refer to the isomer, 1,2-butadiene, which is a cumulated diene with structure $\text{H}_2\text{C}=\text{C}=\text{CH}-\text{CH}_3$. This allene has no industrial significance.

Benzene is an organic chemical compound with the chemical formula C_6H_6 . The benzene molecule is composed of six carbon atoms joined in a ring with one hydrogen atom attached to each. As it contains only carbon and hydrogen atoms, benzene is classed as a hydrocarbon. Benzene is a natural constituent of crude oil and is one of the elementary petrochemicals. Due to the cyclic continuous pi bond between the carbon atoms, benzene is classed as an aromatic hydrocarbon, the second $[n]$ -annulene ($[6]$ -annulene). It is sometimes abbreviated PhH. Benzene is a colorless and highly flammable liquid with a sweet smell, and is responsible for the aroma around petrol (gas) stations. It is used primarily as a precursor to the manufacture of chemicals with more complex structure, such as ethylbenzene and cumene, of which billions of kilograms are produced annually. As benzene has a high octane number, aromatic derivatives like toluene and xylene typically comprise up to 25% of gasoline (petrol). Benzene itself has been limited to less than 1% in gasoline because it is a known human carcinogen. Most non-industrial applications have been limited as well for the same reason.

The plant where you are employed has been buying butadiene and benzene as feedstocks. Management is considering manufacturing the two compounds 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 simplified butadiene and benzene processes, to suggest profitable operating conditions, and to write a final report summarizing your findings. Note that optimization is NOT required in this design project.

Butadiene Manufacture

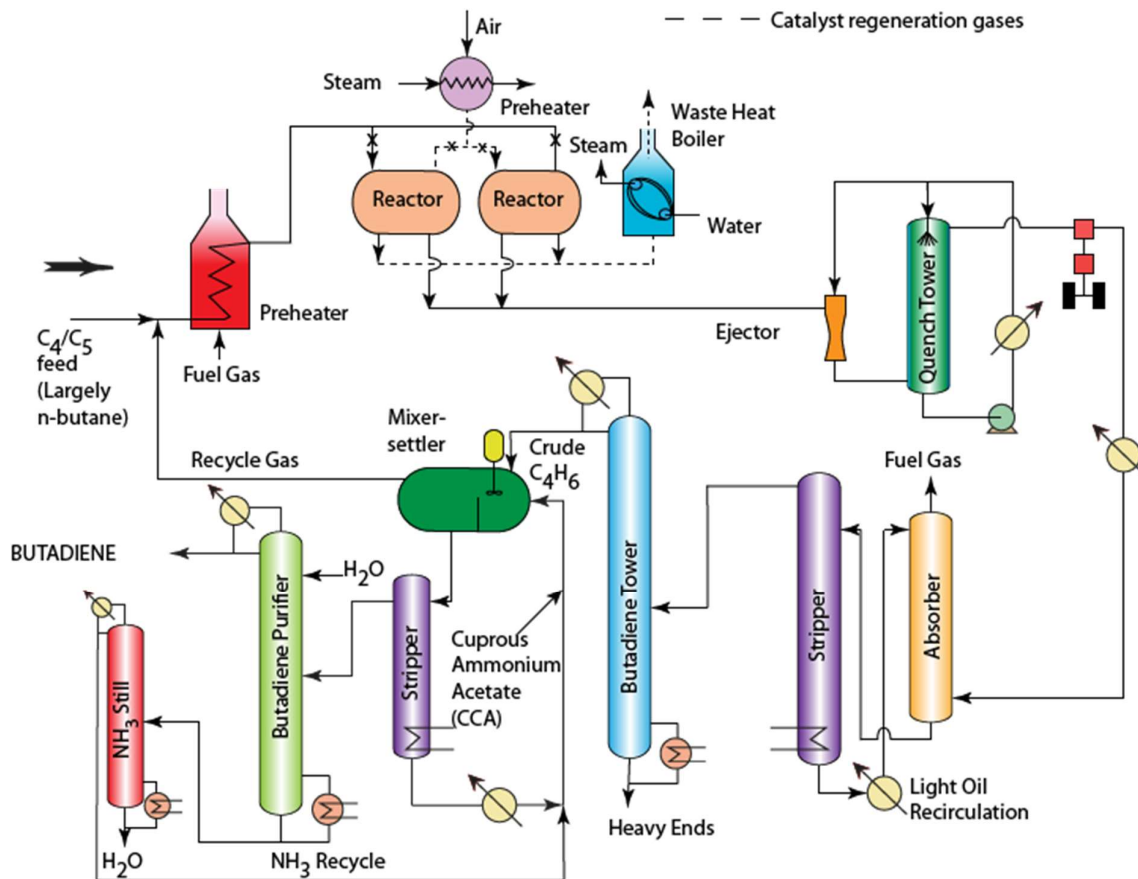
Reactions

- Main reaction: n-Butane \rightarrow Butadiene + Hydrogen.

- ❑ Side reaction: $n\text{-Butane} \rightarrow n\text{-Butylene} + \text{Hydrogen}$.
- ❑ Catalyst: Chromium oxide on alumina.
- ❑ Coke deposition is a very important issue. Therefore, catalyst regeneration needs to be carried out very frequently.
- ❑ Reaction is exothermic.
- ❑ Operating conditions: 650°C and 120-150 mm Hg (low pressure).
- ❑ Feed stock: $n\text{-Butane}$ with some isopentane from refinery processes.

Process Technology

The figure below shows a flowsheet of butadiene manufacture from $n\text{-butane}$.



- ❑ The process technology for Butadiene manufacture consists of a reactor-separator-recycle system.
- ❑ The separation network is extremely complex and involves quenching, absorption, distillation and extractive distillation process.

- ❑ First, the feed stock is pre-heated in a furnace along with unreacted gases that have been recovered in the process using the separator network.
- ❑ After pre-heating in a furnace to desired temperature, the gases enter the catalytic packed bed reactors loaded with the catalyst.
- ❑ After the specified residence time, the product is withdrawn and the feed to the unit is stopped. The product withdrawal and stoppage of the feed flow to the reactor unit is carried out using valves.
- ❑ The coked catalyst is subjected to combustion using pre-heated air. Air pre-heating is done using steam in an extended area heat exchanger equipment. Therefore, during regeneration, another set of valves operate to allow the pre-heated air in and enable the product withdrawal after the combustion.
- ❑ The pre-heated air not only removes the coke as CO_2 but increases the reactor temperature to 650°C .
- ❑ The flue gases are sent to a waste heat recovery boiler so as to generate steam from water.
- ❑ The entire operation of a feed entry, product withdrawal, pre-heated air entry and combustion gases withdrawal from the packed bed reactor corresponds to one single cycle.
- ❑ Since the above operation is a batch operation, to make the operation continuous in accordance to the separation network, two reactors are used and these reactors are operated in cyclic fashion i.e., when the first reactor is subjected to reaction, the second reactor is subjected to catalyst regeneration and vice-versa.
- ❑ The hot reactor outlet gases are sent to a quenching operation where light gas oil is used to quench the gases using a recirculating quenching tower.
- ❑ After product gases from the quenching tower are compressed and cooled to enter an absorber.
- ❑ In this absorber, naphtha is used as an absorbent to absorb all hydrocarbons except fuel gas.
- ❑ The absorbent + hydrocarbons enter a stripper that produces fresh naphtha and hydrocarbon mixture. The hydrocarbon mixture consists of unreacted feed stock and butadiene and some heavy ends.
- ❑ This mixture now enters a fractionator to separate the crude butadiene and heavy ends.
- ❑ The crude butadiene consists of butadiene and unreacted feed stock i.e., n-butane and isopentane. The separation of n-butane, other hydrocarbons with butadiene is one of the difficult separations and they cannot be separated using ordinary distillation. Therefore, a complicated route of separation is followed next that involves azeotropic distillation using ammonia.

- ❑ The crude butadiene is mixed with ammoniated cuprous ammonium acetate solution in a mixer settler. This solution is generated by absorbing ammonia into fresh cuprous ammonium acetate solution.
- ❑ The ammoniated cuprous ammonium acetate is sent to a mixer settler unit where the butadiene dissolves in the ammoniated solution. The gas from the mixer settler unit is recycled to mix with the feed stock and enter the pre-heater.
- ❑ The ammoniated cuprous ammonium acetate solution is thereby stripped to separate butadiene + ammonia from the ammonium acetate solution. The regenerated fresh solvent is allowed to absorb NH_3 and thereby enter the mixer-settler unit.
- ❑ The ammonia + butadiene mixture enters a fractionator fed with water. Here, water interacts with ammonia and generates the ammonium hydroxide product as the bottom product and butadiene is obtained as the top product.
- ❑ The ammonia solution is subjected to stripping to separate water and ammonia. The water is recycled back to the butadiene purifier and ammonia is allowed to get absorbed into the fresh cuprous ammonium acetate solution.
- ❑ This process is not followed in India. In India, it is manufactured from ethanol by catalytic cracking at $400\text{-}450^\circ\text{C}$ over metal oxide catalyst.

Technical Questions

1. Can the steam generated in the waste heat recovery boiler be sufficient to pre-heat the air if a principle of steam reuse is adopted?

Ans: From the basic principle of thermodynamics, somewhere heat needs to be added to the system. If we presume that the feed pre-heater heats the feed to 650°C (the desired temperature of the reactor) and the catalyst regeneration energizes the catalyst by 100°C (from 550 to 650°C), the flue gas should be able to generate some steam. However, it can be speculated that the steam generated will not be enough to meet the total air pre-heater requirements. Therefore, some make up steam will be always required.

2. Why is ammonia allowed to get absorbed into cuprous ammonium acetate?

Ans: Ammonia absorption into cuprous ammonium acetate facilitates maximum absorption of butadiene. This is because ammonia in many cases enhanced absorption factors by allowing chemical interaction between molecules which is better than just physical absorption.

3. Why is the fluid recirculated in the quench tower?

Ans: We are targeting gas quenching using a liquid in this process. Quenching a liquid with liquid is instantaneous but quenching a gas with a liquid needs considerable amount of time, and hold up time is very important. Therefore, fluid internal recirculation is required in the vapor quenching tower.

4. Why a cooler is used in the quenching tower?

Ans: The quenching operation increases the temperature of the fluid that is used for quenching. And we can see that the fluid is always circulated. Therefore, the purpose of quenching is to just cool the gas and don't absorb any of the components into itself. Therefore, to do so, the fluid shall be cooled in between.

5. Why compressor and cooler are at all required after quenching process?

Ans: The unit following quench tower is absorption. Absorption is favored at higher pressure and lower temperature. Therefore, both compressor and cooler are required to achieve these conditions of favourable absorption.

6. Why cooler is followed after compression but not vice versa?

Ans: In general, compression enables enhancement in the temperatures of the gas/vapour. This is because we don't usually follow adiabatic compression but we follow polytropic compression in reality. And polytropic compression will enable heating the gas/vapor. Therefore, cooling is used after compressor but not vice-versa. If cooler is used before compressor, then the gas entering absorber will be at a higher temperature and this is not favorable for absorption.

7. Explain in a more elaborate way what happens in the Butadiene purification fractionators?

Ans: The butadiene purification fractionator is fed with ammonia + Butadiene stream in which somehow ammonia should be recovered. Therefore, this unit is part of the azeotropic distillation that separates butadiene + ammonia as one of the products and eventually butadiene and ammonia are separated using water, as water absorbs ammonia instantaneously to form ammonium hydroxide. Eventually, it is also easy to strip the ammonia gas from aqueous ammonia solution.

8. Why we cannot separate butadiene-butane mixture using ordinary fractionation?

Ans: Their boiling points are very close and distillation requires large differences between boiling points of the components to be separated.

Benzene production using hydrodealkylation route

Reactions

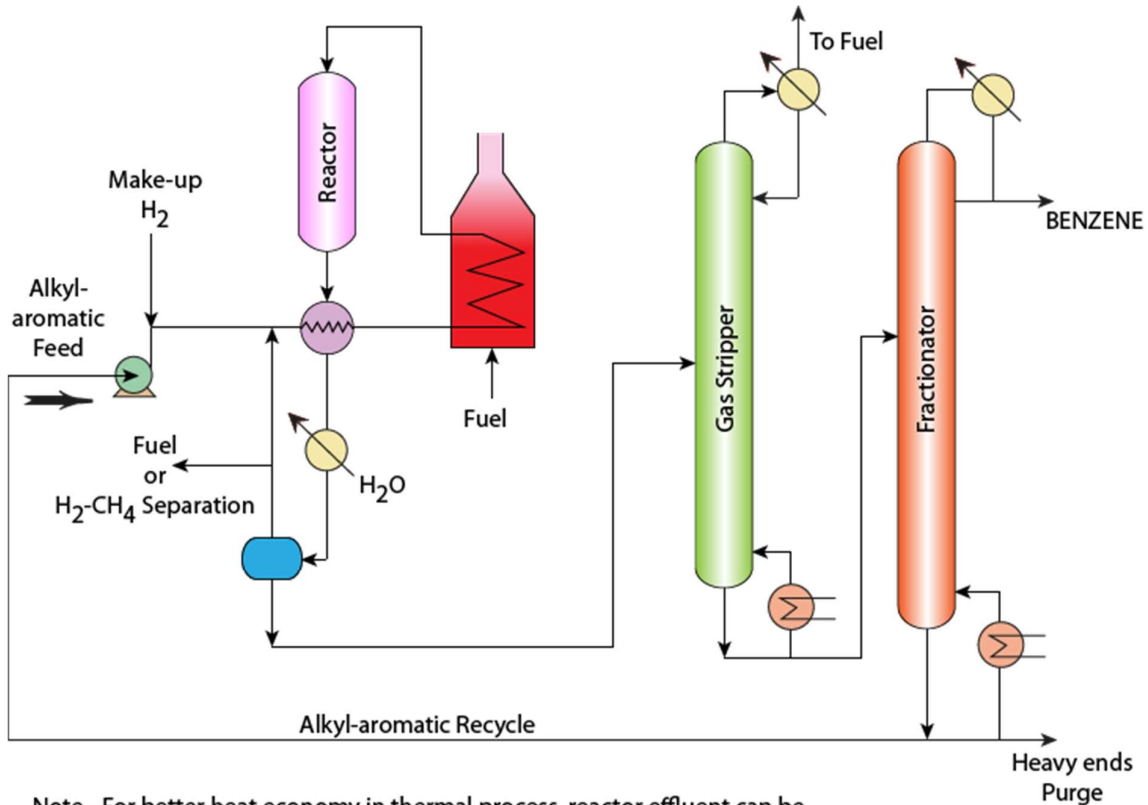
- Toluene does not have much market value.
- Therefore, Toluene is reacted with H_2 to produce Benzene and Methane
- Main reaction: $Toluene + H_2 \rightarrow Benzene + Methane$
- Reactor operating conditions: $600 - 650^\circ C$ and $35 - 40 atm$
- Catalyst: Chromia on porous carrier.
- Other reactions: $Alkyl aromatics + H_2 \rightarrow Benzene + Alkanes$

Side reactions

- ❑ Toluene \rightarrow Diphenyl + H₂
- ❑ Toluene + Benzene \rightarrow Methyl diphenyl
- ❑ Toluene + H₂ \rightarrow Alkanes (Cracking reaction)

Process Technology

The figure below shows a simplified flowsheet of benzene production using hydrodealkylation route.



Note - For better heat economy in thermal process, reactor effluent can be used for stripper and fractionator reboiler heat supply.

- ❑ The process corresponds to a simple reactor-separator-recycle system facilitated with heat integration.
- ❑ Alkyl-aromatics (toluenes and other higher order alkyl aromatics) along with makeup H₂ and recycle stream consisting of unreacted toluene is allowed to enter a feed pre-heater.
- ❑ The feed pre-heater increases the temperature of the reactants at the desired pressure.
- ❑ After the reaction, the reactor products are cooled using heat integration concept by exchanging heat with the cold feed stream. Further cooling of the stream is carried out using a water based cooler.

- ❑ The stream enters a phase separation unit where the fuel gas components such as H₂ and CH₄ are removed as vapor stream. The liquid stream consists of H₂, CH₄, Light ends, Benzene, Toluene, Diphenyl and other higher order aromatics.
- ❑ The vapor stream is partially purged and to a large extent recycled as the stream has good amount of H₂. The gas phase purge stream is for controlling the concentration of methane in the reactor.
- ❑ The liquid stream enters a gas stripper which removes the light ends as a gaseous product stream from the top tray. The bottom product is then sent to a fractionator.
- ❑ The fractionator separates benzene from all heavy ends. The heavy end product consisting of unreacted toluene, diphenyl etc. is largely sent back to the reactor by allowing mixing with the fresh feed.
- ❑ A purge stream is facilitated to purge components such as diphenyl in order to not allow their build up in the reactor.

Technical Questions

1. Despite removing H₂ and CH₄ from the phase separator, why again we remove them from the gas stripper unit?

Ans: This is due to the basic problem in the difficulty of sharp equilibrium factors which do not exist for these components. The equilibrium separation factors in a phase separator unit where the governing pressure and temperature dictate the distribution of components in the liquid and gas stream. Mostly methane and H₂ are removed as vapour stream in the unit. But still at the pertaining pressure and temperature of the phase separator, some lower order alkanes stay back in the liquid stream. Therefore, gas stripping is carried out to remove these.

2. Comment upon fuel efficiency in the process and possibilities to enhance it?

Ans: The process should indicate maximum fuel efficiency. This can be achieved by

- (1) Heat integration of feed and product streams to the reactor.
- (2) Reuse of fuel gas streams as a fuel in the pre-heating furnace.

If these two options are followed, then the process has maximum fuel efficiency and can be regarded to be very energy efficient.

3. Do you suggest to put one more distillation column for the heavy end compounds. If so why?

Ans: Yes, putting one more distillation column will separate toluene + diphenyl from other heavy end compounds. While diphenyl acts towards favoring forward reaction, the other heavy end compounds could tend to produce more coke during the reaction. Therefore, one more distillation unit to separate toluene+diphenyl from the heavy end compounds is recommendable.

4. Do you suggest any other alternative to eliminate the water cooler and even enhance the energy efficiency of the process?

Ans: Yes, it is possible, but existing temperatures of the gas stripper bottom sections need to be carefully analyzed. This is also due to the fact that phase separator operates at 450 psig and 100°F. Therefore, heat integration with gas stripper or fractionator reboilers can be beneficial and this way the process can be made even more energy efficient.

5. What is the basic problem of H₂ in the reactor?

Ans: Hydrogen causes embrittlement due to severe adsorption on the metal surface at higher pressures. Therefore, chrome steel is used to avoid these embrittlement problems as material of construction for the reactor.

6. Why is methane purged using the gas purge stream from the phase separator?

Ans: The reaction kinetics dictate the maximum concentration of methane in the gas stream entering the reactor. Therefore, to achieve maximum conversion, methane is purged.

Design of Heat Exchangers

A detailed design of at least one heat exchanger 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

$$\text{EAOC} = -(\text{product value} - \text{feed cost} - \text{other operating costs} - \text{capital cost annuity})$$

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:

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

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, Internet 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.