CHE654 – Plant Design Project #7
Semester 1, 2024

DESIGN OF A PHENOL PRODUCTION PROCESS FROM BENZENE

Courtesy of National Programme on Technology Enhanced Learning (NPTEL)

Introduction

Phenol is an aromatic organic compound with the molecular formula C_6H_5OH. It is a white crystalline solid that is volatile. The molecule consists of a phenyl group ($-C_6H_5$) bonded to a hydroxy group ($-OH$). It is mildly acidic and requires careful handling due to its propensity for causing chemical burns. Phenol was first extracted from coal tar, but today is produced on a large scale (about 7 billion kg/year) from petroleum. It is an important industrial commodity as a precursor to many materials and useful compounds. It is primarily used to synthesize plastics and related materials. Phenol and its chemical derivatives are essential for production of polycarbonates, epoxies, nylon, detergents, herbicides, and numerous pharmaceutical drugs. Phenol can be produced from many sources such as cumene, toluene, and benzene. Depending upon these raw materials, various chemical transformations and underlying physical principles apply.

Phenol can be manufactured from benzene using several ways

- Benzene hydrochlorination to form benzyl chloride followed by hydrolysis of benzyl chloride to form phenol.
- Benzene chlorination to form benzyl chloride which is transformed to sodium benzoate and eventually to phenol using NaOH and HCl.
- Benzene sulfonate process: In this process, benzene is convered to benzene sulfonate using sulphuric acid and eventually through neutralization, fusion and acidification, the benzene sulfonate is gradually transformed to phenol.
- In this project, we restrict our discussion to the manufacture of phenol from
  (1) Benzene hydrochlorination route
  (2) Benzene from chlorobenzene route

The plant where you are employed has been buying phenol as a feedstock. Management is considering manufacturing the compound 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 phenol production process using benzene as a raw material, to suggest profitable operating conditions, and to write a final report summarizing your findings. Note that optimization is NOT required in this design project.

Phenol Using Hydro Chlorination Route

Reactions

First reaction

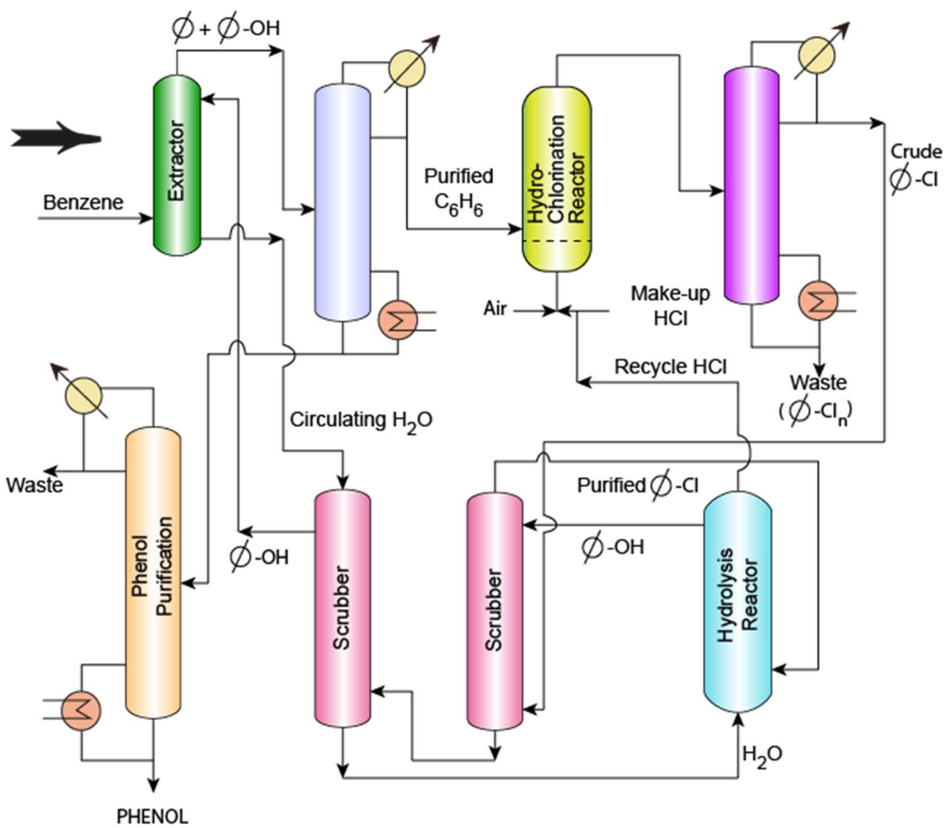
- ❑ Benzene + HCl + Oxygen → Benzyl chloride + Water
- ❑ Catalyst: $FeCl_3 + CuCl_2$
- ❑ Operating conditions: 240°C and atmospheric pressure

Second reaction

- ❑ Benzyl chloride + water → Phenol + HCl
- ❑ Catalyst: SiO_2
- ❑ Here, HCl is regenerated and will be recycled.
- ❑ Operating conditions: 350°C and atmospheric pressure

Process Technology

The figure below shows a flowsheet of phenol manufacture using hydro chlorination route.



- In this process, Benzene is used to extract phenol from phenol +water mixture. This unit is termed as an extraction unit (liquid liquid extraction principle). Therefore, this unit takes up fresh benzene and phenol + water mixture and produces two streams namely water stream (bottom product) and benzene + phenol stream (top product). The water stream is fed to a scrubber unit (i.e., Unit B that will be described later).

- Then onwards, the organic mixture is fed to a distillation column that produces purer benzene as the top product. The bottom product is phenol with other impurities.

- The bottom phenol rich product is sent to the phenol fractionator to obtain waste product as top product and pure phenol as bottom product.

- The purer benzene then enters the hydrochlorination reactor in which a mixture of HCl and O_2 is fed at 220°C. Under these conditions, Benzene will be also in vapor state.

- Therefore, the reactor is a gas solid reactor.

- The conversions are pretty low and not more than 20% of the benzene is converted to benzyl chloride.

- Eventually, the products are sent to two fractionators that separate unreacted benzene, crude benzyl chloride and poly benzyl chlorides as various products. The unreacted benzene is sent back to the hydrochlorination reactor as a recycle stream.

- The crude benzyl chloride then enters an absorber unit A where phenol is used to purify the benzyl chloride from other organic compounds (such as benzene and polybenzyl chlorides).

- The purified benzyl chloride stream then enters the hydrolysis reactor in which water is passed along with benzyl chloride over the silica catalyst. The reactor itself is a furnace with catalyst loaded in the tubes and hot fuel gases are circulated in the shell to obtain the desired higher temperature.

- Under these conditions, both reactants are in vapor state (with the benzyl chloride boiling point of 179°C) and therefore, the reaction is also a gas solid reaction.

- After hydrolysis reaction, the product vapors are sent to a partial condenser that separates the HCl from the organic phase.

- The HCl is recycled to the hydrochlorination reactor.

- The phenol rich product stream is sent as a solvent for the scrubber (unit A) that purifies crude benzyl chloride to purer benzyl chloride. The bottom product from the scrubber (i.e., unit A) enters another scrubber (unit B) that receives water from the extractor.

- The unit B enables washing of the phenol to remove any water soluble impurities. The water from the unit B enters the hydrolysis reactor.

Technical Questions

1. Discuss the merits of the process from waste minimization perspective?

Ans: In this flow sheet, the raw material itself is used as a solvent to extract the product. Also, one of the reactants (water) is used as another absorbent. The usage of raw materials and intermediates in the process as absorbents itself is very attractive from waste minimization perspective as waste water streams are not produced significantly. Also, the solvent used is benzene itself which reduces the complexity of using another solvent and subsequent safety related issues.

2. Comment upon the corrosion issues of the processes?

Ans: HCl is very corrosive and therefore, enough precaution shall be taken towards the plant and process design.

3. What impurities are removed in the unit B scrubber using water?

Ans: Benzyl chloride has limited solubility with water. Therefore, it is expected that benzyl chloride is dissolved to some extent in the unit B scrubber where benzyl chloride as an impurity in minor amounts can be removed from phenol.

4. Why do you think make up HCl is required?

Ans: Some HCl gets reacted to form poly benzyl chlorides. Some HCl gets lost as a vapor in various operations. Therefore, some make up HCl is definitely required in the process though, HCl is largely regenerated.

5. Compared to other Benzene based phenol production processes, what advantage this process has towards phenol production?

Ans: In this process, very little quantities of other raw materials are required. These are HCl. Air is inexpensive and is freely available. Therefore, the plant can be built easily as many other auxillary processes are not required provided benzene is available in large quantities in the vicinity. However, one basic drawback is that the fixed costs of units will be high in this case as HCl is involved.

Phenol from Chlorobenzene Route

Reactions

There are three reactions to convert benzene to phenol using chlorination route/

Chlorination

- Benzene + Cl_2 → monochloro benzene
- Operating temperature: 85°C
- Catalyst: Fe or $FeCl_3$ catalyst

Causticization

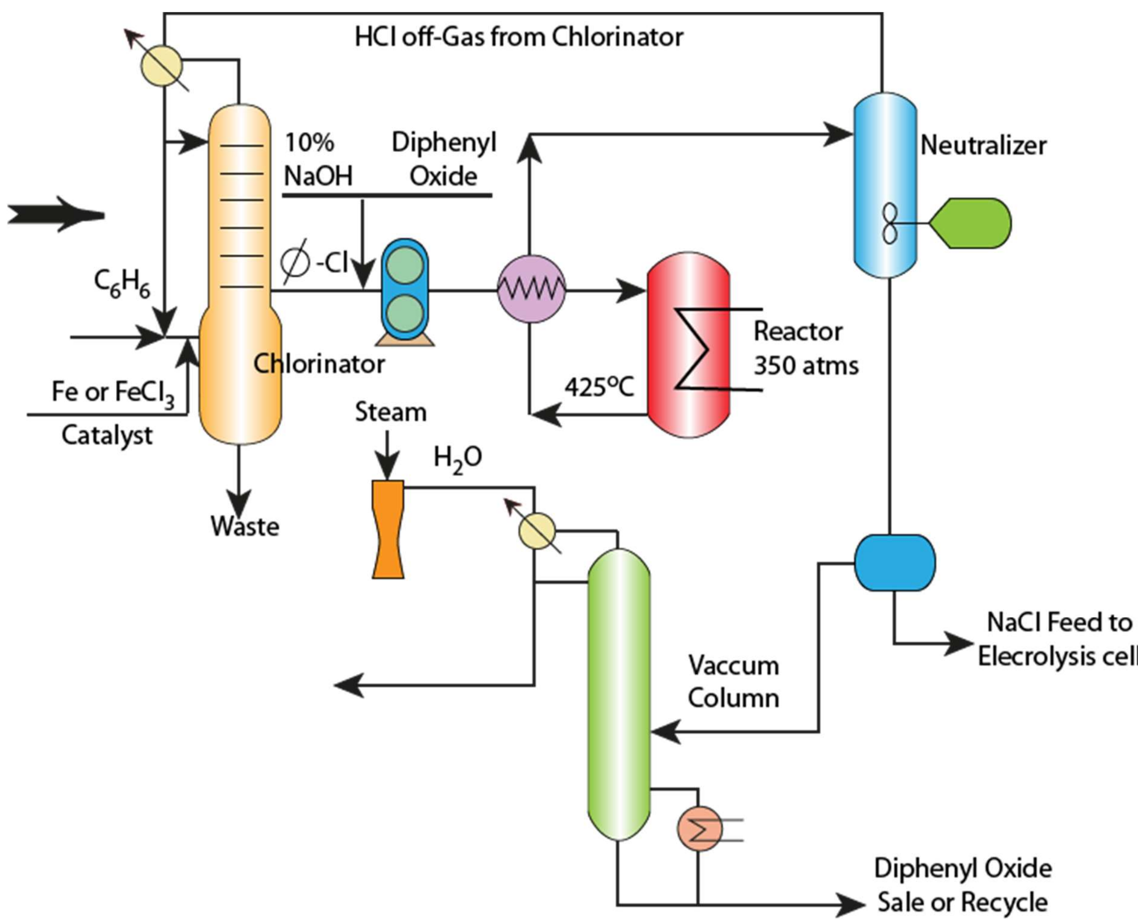
- ❑ Benzyl chloride + NaOH → sodium benzoate
- ❑ NaOH is in aqueous media
- ❑ Operating conditions: 425°C and 350 at
- ❑ Exothermic reaction

Hydrolysis

- ❑ Sodium benzoate + HCl (aq) → Phenol + NaCl (aq)
- ❑ Operating conditions: Nothing specific

<u>Process Technology</u>

The figure below shows a simplified flowsheet of phenol produced via chlorobenzene route.



- Benzene is first dried. Dry benzene and $FeCl_3$ catalyst enters the chlorination reactor.

- After the solid-gas-liquid reaction, the products are further heated up to enter a fractionator.

- The fractionator separates benzene as a top product and monochloro benzene as the bottom product. The top product also consists of HCl off gas that is obtained as the vapour stream from the partial condenser.

- The benzene is further cooled and sent back to the reactor and also as a reflux to the fractionator.

- The bottom product monochloro benzene is mixed with 10% NaOH solution and diphenyl oxide to enter a high pressure pump followed with heat integrated heat exchanger that pre-heats the feed to higher temperature.

- The feed then enters the causticization reactor which has cooling water tubes to control the temperature.

- The product stream is cooled using heat integrated exchanger and then enters a neutralizer that is fed with the HCl obtained from the fractionator partial condenser.

- After neutralization, the product phenol is separated from the aqueous phase using gravity settling principle.

- The organic layer rich in phenol is sent to a vacuum column to separate the phenol from diphenyl oxide (bottom product). The bottom product is partially recycled to enter the cauticization reactor.

Technical Questions

1. Why is diphenyl oxide added to the causticization reactor?

Ans: To suppress the formation of more diphenyl oxide at the causticization reactor.

2. How can you regenerate Cl_2 for this process?

Ans: Brine when subjected to electrolysis will produce Cl_2 and NaOH. Therefore, electrolytic process will be beneficial to produce Cl_2 and us e it to the requirements as well as produce excess NaOH and sell it too. This way, the process becomes more commercially attractive.

3. Can the chlorinator and the fractionators be integrated into a single unit where the bottom section is a reactor and the top section is a fractionator?

Ans: Yes, this is possible, as after chlorination the products are in vapor state and they can enter the trays above the reactor section of a single column. The heavier product in this case is the monochlorobenzene from fractionation perspective and this is the product as well. Therefore, integrating both reactor and separator in a single unit can reduce the costs significantly.

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:

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

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.