



**CHE654 – Plant Design Project #2**  
**Semester 1, 2024**



**DESIGN OF CUMENE AND ACRYLONITRILE PRODUCTION  
PROCESSES FROM PROPYLENE**

Courtesy of National Programme on Technology Enhanced Learning (NPTEL)

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## **Introduction**

Cumene (isopropylbenzene) is an organic compound that is based on an aromatic hydrocarbon with an aliphatic substitution. It is a constituent of crude oil and refined fuels. It is a flammable colorless liquid that has a boiling point of 152 °C. Nearly all the cumene that is produced as a pure compound on an industrial scale is converted to cumene hydroperoxide, which is an intermediate in the synthesis of other industrially important chemicals, primarily phenol and acetone.

Acrylonitrile is an organic compound with the formula  $\text{CH}_2\text{CHCN}$ . It is a colorless volatile liquid, although commercial samples can be yellow due to impurities. In terms of its molecular structure, it consists of a vinyl group linked to a nitrile. It is an important monomer for the manufacture of useful plastics such as polyacrylonitrile. It is reactive and toxic at low doses. Acrylonitrile was first synthesized by the French chemist Charles Moureu (1863–1929) in 1893.

Both cumene and acrylonitrile are very important compounds that are required for the manufacture of other downstream petrochemicals. Both compounds can be manufactured from propylene. The plant where you are employed has been buying cumene and acrylonitrile 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 cumene and acrylonitrile production 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.

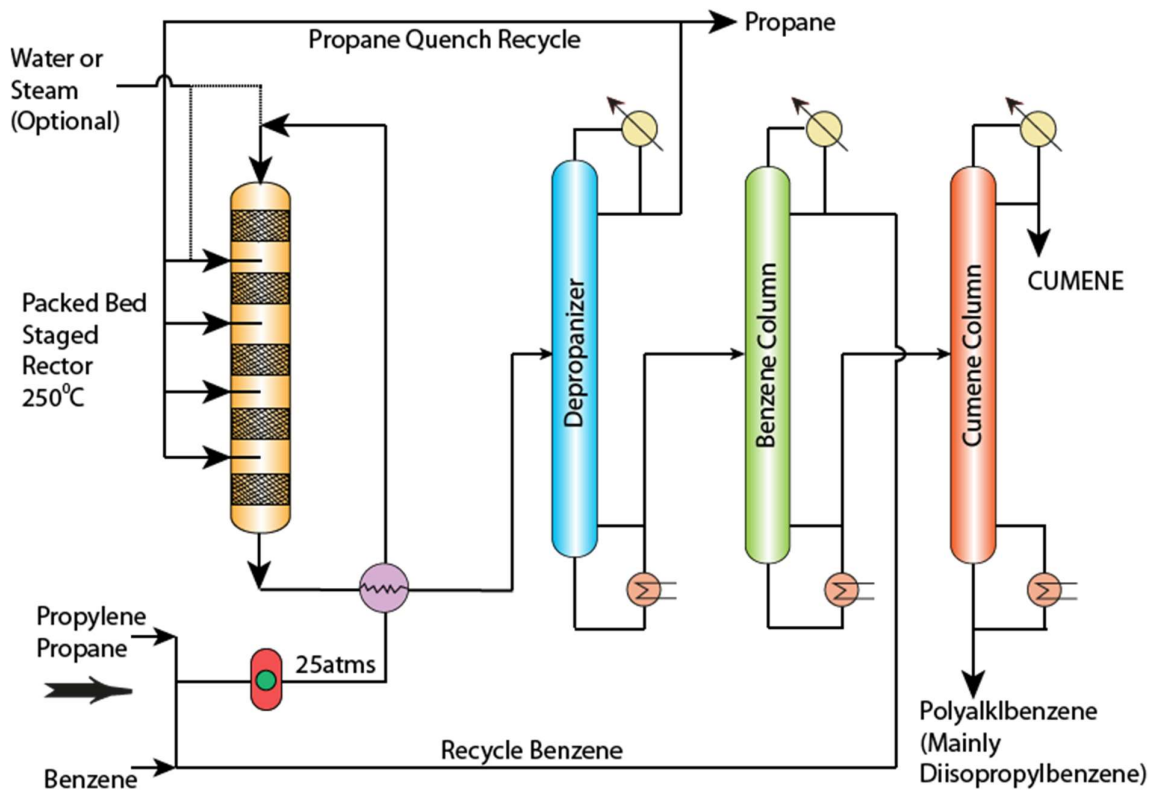
## **Cumene Manufacture**

### **Reactions**

- $\text{C}_6\text{H}_6 + \text{C}_3\text{H}_6 \rightarrow \text{C}_9\text{H}_{12}$
- The reaction is exothermic.
- Catalyst:  $\text{H}_3\text{PO}_4$  impregnated catalyst on porous carrier.
- Operating conditions: 25 atm pressure and 250°C temperature.

## Process Technology

The figure below shows a flowsheet of cumene manufacture from propylene.



- Propylene obtained from refinery processes as a mixture of propylene and propane.
- The mixture along with benzene is compressed to 25 atm.
- Eventually the mixture enters a heat integrated exchanger to heat the pre-heat the feed mixture.
- The feed mixture enters a packed bed reactor.
- The stream distribution in the packed bed reactor corresponds to cold shot arrangement i.e., cold propane from the distillation column in the process is added after every reactor with the product stream so that the temperature of the stream is controlled.
- Here, propylene is the limiting reactant and therefore, presumably all propylene undergoes conversion.
- Here, propane does not react but is a diluents or inert in the system. In that way it controls the reaction temperature.
- The reactor units are maintained at about 250°C.

- ❑ The product vapors are cooled using the heat integrated exchanger.
- ❑ The vapors then pass to a depropanizer which separates propane from the product mixture.
- ❑ The bottom product consisting of benzene, cumene and polyalkyl benzenes enters another distillation column which separates benzene from the mixture of cumene and polyalkyl benzene. The benzene stream is recycled to enter the compressor.
- ❑ The bottom product from the benzene column is sent to a cumene column which produces cumene as top product and poly alkyl benzene as bottom product.
- ❑ Therefore, the entire process technology is nothing but a simple reactor separator recycle arrangement.

### **Technical Questions**

1. What alternative reactor arrangement is possible if pure propylene feed is used?

Ans: When pure propylene is used, then there is no propane for quenching. Therefore, the packed bed reactor shall be provided a cooling jacket which can control the temperature of the reactor.

2. Comment on the sequence of distillation columns separating propane, benzene and cumene in series?

Ans: The distillation columns are so arranged so that lighter components are separated first followed by heavier components. Since no component is present which will decompose on long time heating, this arrangement is followed. If not, the component which can decompose upon long time heating will be separated first following by the lighter to heavier component sequence in the remaining components.

3. In what way propane quenching plays a role in the reactions?

Ans: Propane quenching reduces polymerization of cumene and formation of polyalkyl benzenes.

4. How can one suppress polyalkylbenzene formation?

Ans: By using high feed ratio of benzene to propylene and using propane as a diluent.

5. Is further heat integration not possible?

Ans: A further heat integration can be carried out using hot vapors in the distillation column to be as hot streams in the reboilers of various distillation columns.

6. In what way higher pressure in the product vapors from the reactor are beneficial for the depropanizer unit?

Ans: The depropanizer unit requires condensation of propane vapors in the condenser. Propane's boiling point is less than 0°C at 1 atm pressure. Therefore, higher pressures to the

extent of 25 atm will enhance propane boiling point to about 25 – 30°C for which cooling water can be used as the cooling media in the condenser. If not, refrigerant needs to be used and the refrigerant will require a refrigerating unit along with the process. This is much more expensive than using cooling water as the cooling media.

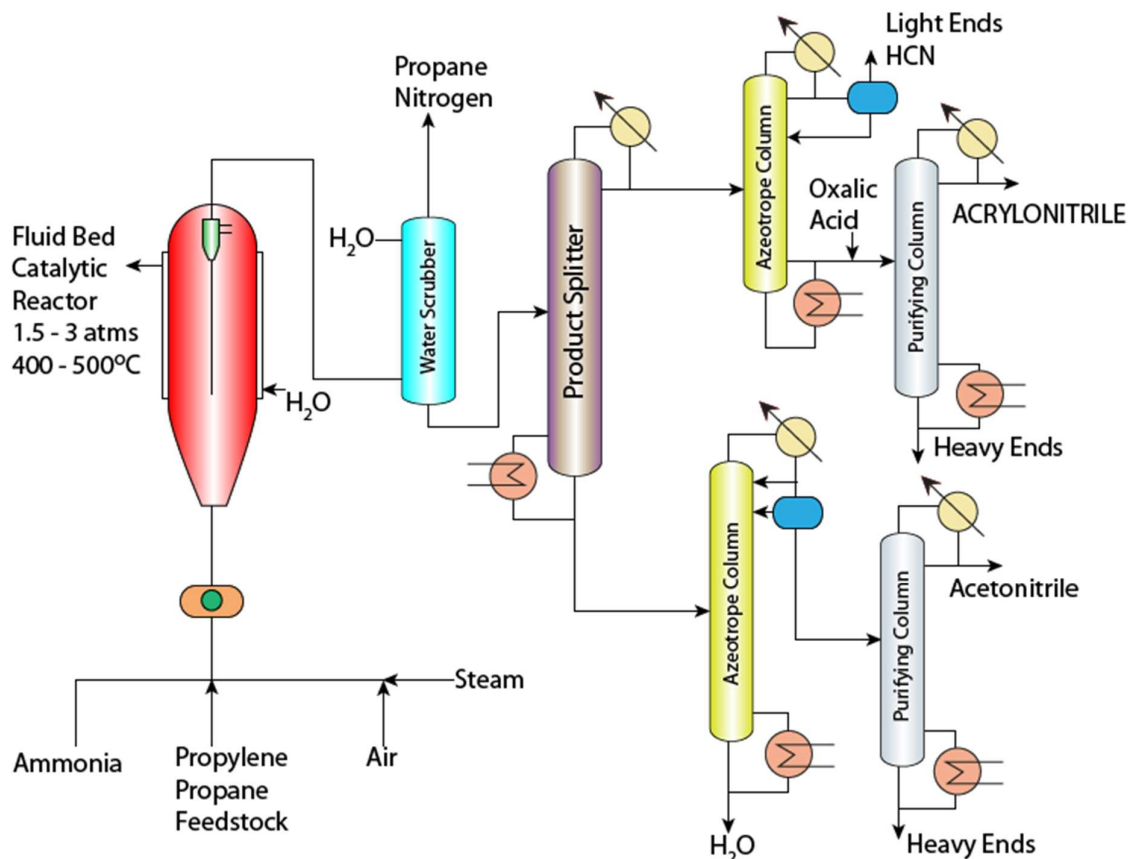
## Acrylonitrile Manufacture

### Reactions

- ❑  $C_3H_6 + NH_3 + O_2 \rightarrow C_3H_3N + H_2O$
- ❑ The reaction is exothermic.
- ❑ Stoichiometric ratio:  $C_3H_6 : NH_3 : O_2 = 1:1:1.5$ .
- ❑ Operating conditions: 1.5 – 3 atm pressure and 400 – 500°C.
- ❑ By products: Acetonitrile and Hydrogen cyanide from side reactions.
- ❑ Catalyst: Mo-Bi catalyst.

### Process Technology

The figure below shows a simplified flowsheet of the acrylonitrile manufacture from propylene.



- ❑ Propylene + Propane, Air and Ammonia, Steam are compressed to required pressure and are sent to the fluidized catalytic reactor consisting of the Mo-Bi spherical catalyst. The reactor is maintained at 400 – 500°C.
- ❑ Cyclone separator is also kept in the fluidized bed reactor in which catalyst and product gases are separated after fluidization. The contact time for fluidization is in the order of seconds.
- ❑ The product vapors then enter a water scrubber that does not absorb propane and nitrogen from the products. The products absorbed in the water include acrylonitrile, acetonitrile and other heavy ends.
- ❑ The very dilute acrylonitrile (about 3%) solution in water is sent to a fractionator. The fractionators separate acrylonitrile + heavy ends + HCN + light ends as a top product stream and acetonitrile + water + heavy ends as a bottom product.
- ❑ The top product then enters an extractive distillation column with water as extractant. The azeotropic distillation column vapor is partially condensed to obtain a vapor, aqueous and organic layer. The vapor consists of Light ends and HCN and is let out. The organic layer consists of acrylonitrile and heavy ends is sent for further purification. The aqueous layer is sent as a reflux to the azeotropic column. In other words, addition of water enabled the formation of a heterogeneous azeotropic mixture at the top.
- ❑ The bottom product from the azeotropic distillation column enters a product purification unit along with oxalic acid where acrylonitrile is further purified from heavy ends (+ oxalic acid) and is obtained as a 99.5% pure product.
- ❑ In similarity to this, the bottom product from the product splitter enters an azeotropic column which produces water as a bottom product. The total condenser in this column generates both aqueous and organic layers. The organic layer is rich in acetonitrile and heavy ends whereas the aqueous layer is sent back as a reflux to the azeotropic column.
- ❑ The bottom product from the acetonitrile azeotropic column enters a purification unit where distillation principle enables the separation of acetonitrile from the heavy ends.

### **Technical Questions**

1. Why is oxalic acid added in the acrylonitrile purification column?

Ans: One of the byproducts of the ammonoxidation of propylene are cyanohydrins. These organic compounds readily dissociate to form volatile compounds. These volatile compounds are severely polluting compounds. Therefore, to avoid this, oxalic acid is added to the purification column in order to form complex compounds with these cyanohydrins and these compounds eventually enter the heavy end products.

2. A careful analysis of the process flowsheet shown indicates that while absorption is favored at lower temperatures and higher pressures, exactly opposite conditions exist for the reactor outlet stream (at about 1 atm pressure and 400 – 500°C). What additional process modifications are suggested?

Ans: Cooling the vapor product stream from 400°C to about 50°C in a series of heat exchangers. Since vapor is involved, extended area exchangers will be beneficial. Heat integration with the reboilers of any of the distillation columns is also beneficial.

Pressurizing the vapor pressure to higher pressure and allowing it to enter the scrubber at the same temperature. This is beneficial but compressor costs will be enormous.

Therefore, in the light of the process costs, cooling the vapor stream is beneficial than compression to favor good absorption.

3. In certain processes for acrylonitrile production, cyanohydrins removal is desired. If so, what process modifications are suggested?

Ans: Cyanohydrins are in the bottom product obtained in the product splitter. Therefore, the bottom product can be sent to a reactor where cyanohydrins can be converted to acrolein and these acroleins can be separated and sent back to the ammonoxidation reactor (fluidized beds). In that case, oxalic acids are not used and the heavy ends will not also get produced significantly and therefore process topology will be somewhat different from what is being shown here. For further details upon how the process flowsheet changes please refer to Chemical Engineering Design (Book) by Sinnott where in Appendix these modifications have been explained thoroughly in the process description.

4. Is a partial condenser required in the acetonitrile azeotropic column?

Ans: No, the reason is that the bottom product from the product splitter consists of heavy ends, acetonitrile and water and does not consist of lighter ends and HCN. Therefore, a partial condenser is not required and a total condenser producing two separate liquid phase streams that separate upon gravity is required.

5. A feed stock heater is not shown in the process. However, reactor operating conditions indicate high temperature operation. How is the feed stock heated?

Ans: The heat for achieving the feed to desired temperature is provided by superheated steam that is mixed along with the feedstock. Typical feed molar composition is propylene 7, ammonia 8, steam 20 and air 65. Additional heat for the reaction is obtained from the highly exothermic reaction in the fluidized bed catalytic reactor.

6. What are the advantages of the fluidized catalytic reactor when compared to a packed bed reactor?

Ans: It is well known that the heat and mass transfer coefficients of gases are predominantly lower than those of the liquids. Therefore, fluidization principle effectively enhances bulk phase mass and heat transfer coefficients of the gas solid catalytic reaction. In other words, due to fluidization, less contact time that is required in the process, higher conversions can be achieved.

## **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.