CHE654 – Plant Design Project #1
Semester 1, 2024

DESIGN OF ISOPROPANOL AND ACETONE PRODUCTION PROCESSES FROM PROPYLENE

Courtesy of National Programme on Technology Enhanced Learning (NPTEL)

Introduction

Isopropyl alcohol (IUPAC name propan-2-ol; commonly called isopropanol or 2-propanol) is a compound with the chemical formula $CH_3CHOHCH_3$. It is a colorless, flammable chemical compound with a strong odor. As an isopropyl group linked to a hydroxyl group, it is the simplest example of a secondary alcohol, where the alcohol carbon atom is attached to two other carbon atoms. It is a structural isomer of 1-propanol and ethyl methyl ether. Isopropanol is used in the manufacture of a wide variety of industrial and household chemicals, and is a common ingredient in chemicals such as antiseptics, disinfectants and detergents. There may be many other uses of isopropanol, industrial as well as common uses. It finds use in pharmaceutical applications because of the low toxicity of any residues. Isopropanol is also used as a chemical intermediate in some industrial processes. It is also used as a gasoline additive.

Acetone, or propanone, is the organic compound with the formula $(CH_3)_2CO$. It is a colorless, volatile, flammable liquid and is the simplest and smallest ketone. Acetone is miscible with water and serves as an important solvent in its own right, typically for cleaning purposes in laboratories. About 6.7 million tons were produced worldwide in 2010, mainly for use as a solvent and production of methyl methacrylate and bisphenol A. It is a common building block in organic chemistry. Familiar household uses of acetone are as the active ingredient in nail polish remover and as paint thinner. Acetone is also used as a polar, aprotic solvent in a variety of organic reactions. One important property for which it is used as laboratory solvent is because does not form an azeotrope with water. Moreover, acetone is used in various medical and cosmetic applications. It also forms an important component in food additives and food packaging.

Acetone has VOC exempt status in the USA. Acetone is produced and disposed of in the human body through normal metabolic processes. It is normally present in blood and urine. People with diabetes produce it in larger amounts. Reproductive toxicity tests show that it has low potential to cause reproductive problems.

Isopropanol can be manufactured from hydration of propylene, and acetone can be produced using the dehydrogenation route of isopropanol. The plant where you are employed has been buying acetone as a feedstock. Management is considering manufacturing acetone 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 isopropanol and acetone 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.

Isopropanol Manufacture

Reactions

Sulfation: $CH_3CHCH_2 + H_2SO_4 \rightarrow (CH_3)_2 CH(OSO_3H)$ (Isopropyl acid sulphate).

Hydrolysis: Isopropyl sulphate + H_2O → Isopropanol + Sulfuric acid.

Thus sulphuric acid is regenerated in the process.

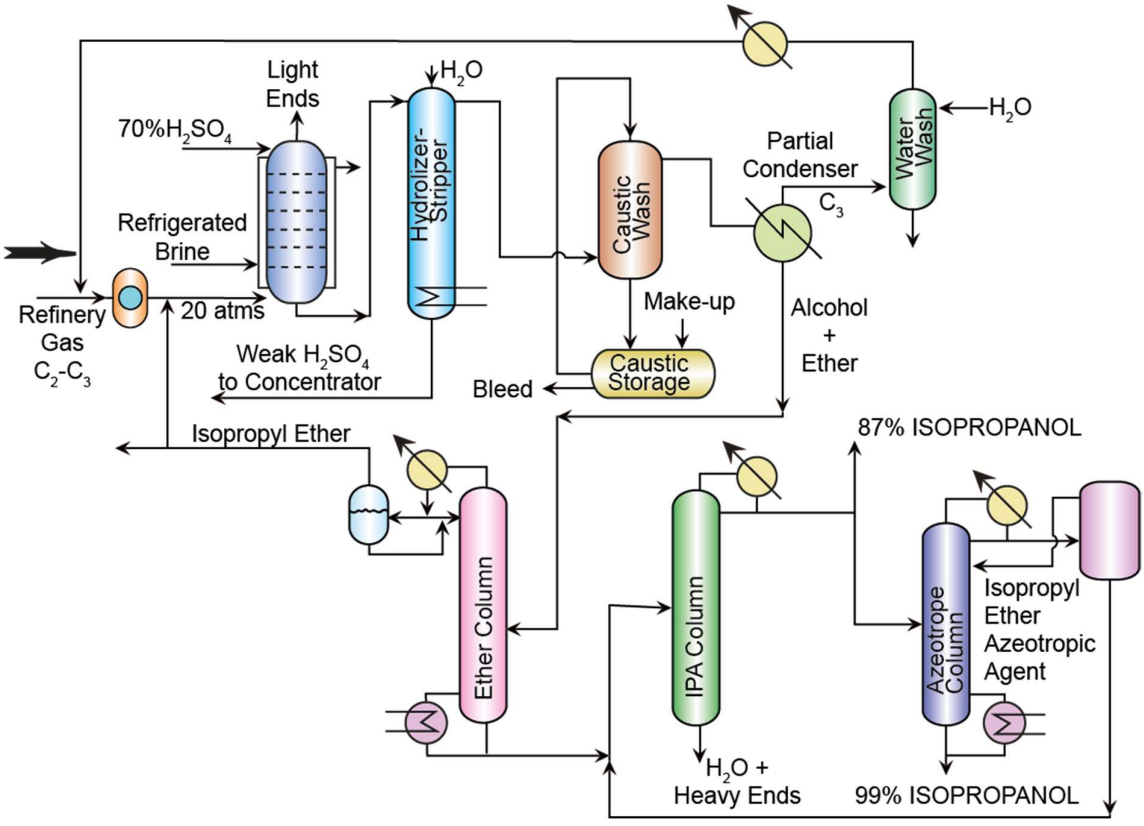
Side reaction: Disiopropyl sulphate + H_2O → Diisopropyl ether + Sulfuric acid.

Therefore, the primary reaction is a gas liquid reaction in which propylene is absorbed into a tray tower fed with sulphuric acid.

Operating conditions: Room temperature but 20 – 25 atms pressure. The reaction is highly exothermic.

Process Technology

The figure below shows a flowsheet of isopropanol manufacture.



- Either pure propylene or a mixture of Propylene and other C_2, C_3 components can be fed to a reactor.

- The hydrocarbon feed is compressed and fed to the reactor at about 20 – 25 atm pressure.

- Sulphuric acid of about 70% acid strength is fed in a countercurrent mode to the tray column where reactive absorption takes place. Here, sulfonation reaction takes place.

- The reaction is highly exothermic and therefore, refrigerated brine is used to control the temperature in the absorber. Jacketed arrangement will be preferred for the tray absorption column to circulate the refrigerated brine in the cooling jacket.

- After reaction, the unreacted light ends such as saturated components will leave the unit as the gas stream.

- The sulfonated product rich stream is then sent to a hydrolyzer cum stripper where isopropanol is produced and is vaporized due to existing stripper temperatures.

- The hydrolyzer is fed with water to facilitate the conversion of the sulfonate product.

- The isopropanol rich vapors then enter a caustic wash unit to remove the acidic impurities.

- The isopropanol rich vapors then enter a partial condenser which separates the unreacted propylene from the alcohol + ether mixture. Here, propylene is separated as the vapor and alcohol + ether is separated as the liquid stream.

- The separated propylene gas is once again subjected to water wash to remove soluble impurities (such as ethers and alcohols). Subsequently, pure propylene is sent to mix with the fresh feed stream. Before sending to the unit, the propylene is cooled to room temperature so as to have identification conditions as the fresh feed stock.

- The alcohol and ether enter an ether column that separates isopropyl ether which is returned to the reactor.

- The bottom product consisting of isopropyl alcohol and water is sent to an isopropyl alcohol column that produces water + heavy ends as the bottom product and 87% isopropanol-water azeotrope mixture as the top product.

- The azeotrope is sent to an azeotropic distillation column that uses isopropyl ether as a azeotropic agent to obtain 99 % isopropanol as the bottom product. The top product is a mixture of isopropyl ether and water. The top product is a low boiling azeotrope. This stream upon gravity settling will produce the isopropyl ether as the top product which is sent as a reflux stream to the azeotropic column. The bottom product is a mixture of isopropanol and water is recycled back to the isopropyl alcohol column along with the bottom product generated from the ether separating column.

Technical Questions

1. Why refrigerated brine is used in the sulfonation reactor?

Ans: The reaction temperature is room temperature (25 – 30˚C). Therefore, refrigerated fluid is used. Brine is used here, as refrigerated is antifreeze and can allow solution to reach lower temperatures without freezing problem.

2. Why a partial condenser but not total condenser is used to separate C_3 from alcohol + ether?

Ans: Apart from costs, the total condenser produces a single stream and this is of no use as propylene must be separated and sent as a gas back to the sulfonation reactor. All this is achieved in a single process unit by using partial condensation principle.

3. Why is isopropyl ether circulated back to the sulfonation reactor?

Ans: To suppress the side reaction and hence decomposition of sulfonation to less valued product.

4. Present the working principle of an azeotropic distillation column?

Ans: The azeotropic distillation column is fed with the azeotrope mixture and another component which forms a low boiling heterogenous azeotrope with the feed (azetropic mixture) components as one of the products and a purer compound as the other product. The low boiling azeotrope is then sent to a gravity settler that separates the heterogeneous phases into two products namely the azeotropic agent and an impure mixture of the original components. The impure mixture is actually fed to one of the distillation columns in the process flow sheet at a location that matches with the purity of the stream.

5. What happens to the water in which acid gets dissolved in the hydrolyzer cum stripper column?

Ans: Here, the stream is a weak acid stream that is fed to a multiple effect evaporator to concentrate the weak acid solution to a strong acid solution. The strong acid solution then can be used as one of the raw materials in the process.

6. Can you do heat integration for the partial condenser with the sulfonation reactor?

Ans: No, the reason is that sulfonation reaction is highly exotermic and heat needs to be quickly removed. This is not possible when vapors are used as the cooling stream as gas phase heat transfer coefficients are significantly lower than the liquid phase heat transfer coefficients.

7. Can a partial condenser be used for the ether column?

Ans: Yes, the reason is that there is no hard and fast rule that isopropyl ether be added in the liquid phase to the sulfonation reactor. In fact, it should be added as a vapor phase only and therefore, partial condenser should be used in place of total condenser to save costs as well as meet the process specifications.

Acetone manufacture from isopropanol

Reactions

Dehydrogenation of Isopropanol

Isopropanol → Acetone + H_2

Reaction pressure: 3 – 4 atm

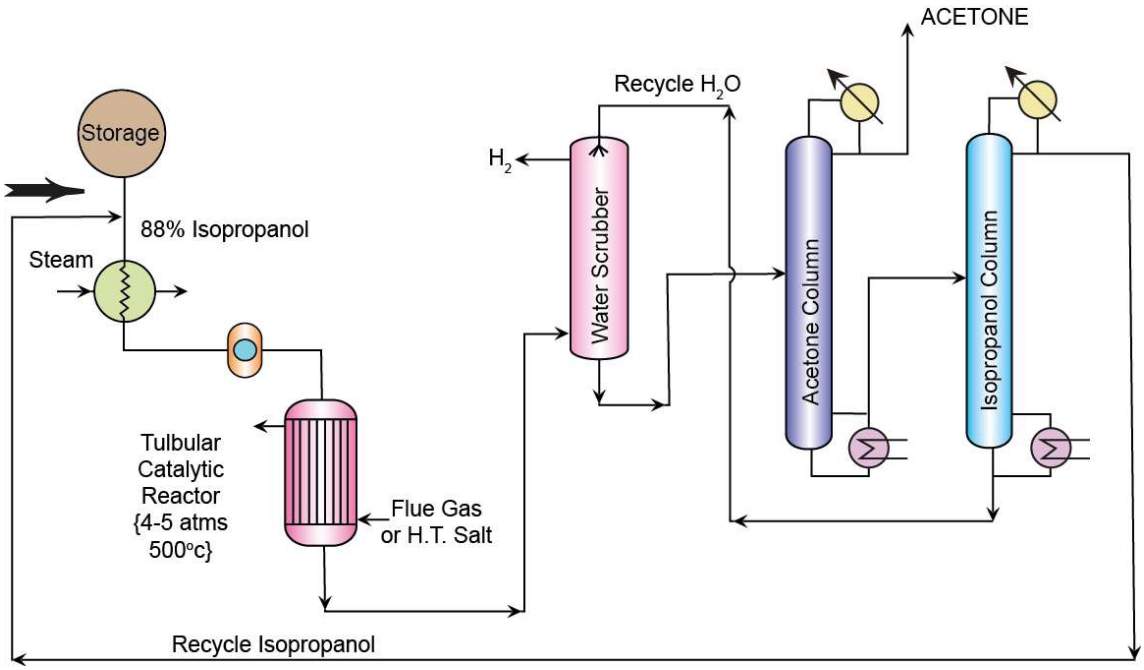
Reaction temperature: 400 – 500°C

Copper catalyst on porous carrier is used

Vapor phase reaction

Process Technology

The figure below shows a simplified flowsheet of the acetone manufacture from isopropanol.



- First, Isopropanol is heated using steam to vaporize the same.
- Then, Isopropanol is compressed to desired reactor pressure i.e., 4 – 5 atm.
- The compressed Isopropanol then enters a catalytic shell and tube reactor in the tube side. The tube is packed with the porous copper catalyst.

- The reactor is operated at 400 – 500°C using flue gas for heating. The flue gas is passed in the shell side of the shell and tube reactor.

- After reaction, the gases are condensed using cooling water condenser. The condensed isopropanol and acetone are sent for fractionation.

- The gases consisting of the remaining quantities of isopropanol and acetone are absorbed into water using a water scrubber.

- The acetone + isopropanol obtained from the condenser and water + isopropanol +acetone are sent to an acetone fractionator that separates acetone as the top product and isopropanol + water as bottom product.

- The bottom product isopropanol + water from the acetone fractionators is sent to a isoprpopanol column.

- This column produces water as the bottom product and isopropanol as the top product.

- The water is cooled using a water condenser and sent to the water scrubber as fresh water solvent.

Technical Questions

1. Is pure isopropanol required as feedstock in the reactor?

Ans: This question is asked due to the fact that isopropanol production process involves the formation of an azeotrope with 87% Isopropanol and 13% water. Therefore, if the azeotrope itself can be used as feedstock, then one can save azeotropic column costs if an acetone plant is constructed next to the isopropanol.

Yes, isopropanol azeotrope can be used as a feed stock. In this case, the water will not react and will condense in the condenser after the reactor.

2. Can't we feed the product gases directly to the water absorber eliminating the condenser?

Ans: The condenser removes the condensable components from the product vapors. If condenser is not used, then the hot vapors move to the absorber and absorber load and degree of separation should be pretty high and hence higher cost. Therefore, it's better to use the water cooling condenser.

3. Apply Le Chartlier principle and suggest what pressures be operated in the reactor. Eventually comment on the existing pressures?

Ans: If we apply Le Chartlier principle, dehydrogenation reaction is favored by lower pressures. However, higher pressures are used in this case. If the pressure of the system does not play a critical role in the conversion, then higher pressures are favored as they reduce the size of the reactor significantly for the throughput available. Also, higher pressures are favorable for absorption and reduce the water load in the absorption column.

4. Why is water from the isopropanol fractionators cooled and sent to the water absorber unit?

Ans: This is due to the fact that absorption is favored at lower temperature and higher pressure.

5. Why is isopropanol again sent to the compressor along with the feed?

Ans: The operating pressures of the absorber, acetone fractionator and isopropanol fractionators reduce sequentially as the stream progresses to the right side. Therefore, the last column produces the product with about atmospheric pressure only. Therefore, to bring it back to 5 atm as in the reactor conditions, the stream has to be compressed along with the feed stream.

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.