Lecture 25: Manufacture of Maleic Anhydride and DDT

25.1 Introduction

- In this last lecture for the petrochemicals module, we demonstrate the process technology for Maleic anhydride and DDT.
- Maleic anhydride is manufactured from benzene by butane oxidation.
- DDT is a pesticide and is manufactured from benzene, chlorine, and ethanol using sulphuric acid as a catalyst.
- We next present the process technology for maleic anhydride. Along with this compound, fumaric acid is also produced as another product.

25.2 Maleic anhydride & Fumaric acid

25.2.1 Reactions

- Benzene + O₂ (Air) → Maleic anhydride + H₂O + CO₂
- Reaction is exothermic
- Operating temperature is 400 – 500 °C
- Catalyst is V₂O₅
- For fumaric acid, the reaction is Maleic acid → Fumaric acid.
- Fumaric acid is an isomer of Maleic acid.
- HCl is used as a catalyst for the isomerisation reactor at normal pressure and temperature.

25.2.2 Process technology (Figure 25.1)
- The process technology is similar to phthalic anhydride production.
- Benzene or butane is first vaporized in excess air.
- Then the mixture enters the catalytic tubular reactor (with shell arrangement). The catalytic reactor is circulated with salt solution so as to absorb the heat generated using the reaction.
- The reactor products enter a waste steam recovery boiler where the boiler water is converted to steam.
- The product vapors eventually enter an integrated heat exchanger to exchange heat with the pre-heated feed stream.
- Eventually, the vapors are condensed followed with gravity settling to remove tar as a product in the gravity settling. The vapors then enter a water scrubber to obtain 40 % maleic acid solution. The leaving gases consist mainly of CO₂.
- The maleic acid from the absorber is partially sent to a dehydrator that removes water using azeotropic distillation principle. The purified maleic anhydride product is further sent to vacuum distillation to obtain the maleic anhydride product.
- The dilute maleic acid solution is partially sent to an isomerisation unit where HCl is used as the isomerisation catalyst.
- After reaction, the product is sent to a centrifuge that separates water from the fumaric acid.
- Eventually, fumaric acid is sent to a drier to obtain dry fumaric acid.

25.2.3 Uses:
Maleic anhydride can be used as a highly reactive and versatile raw material. It can be used in the manufacture of alkyd resins, which in turn are used for making paints and coatings. It can also be used in making agricultural chemicals like herbicides, pesticides and plant growth regulators.

25.2.4 Technical questions

1. Why is benzene separately vaporized in excess air?

Ans. To avoid the formation of explosive compositions, benzene is separately vaporized and then mixed with air. The lower flammability limit of benzene-air mixture is 1.35 % and the upper flammability limit of benzene is 6.35 %. Therefore, with such low levels of flammability limits, heating the benzene in hot process air can keep the process safe. Directly generating benzene vapors and mixing it with air is more dangerous.

2. Explain in brief how azeotropic distillation of maleic acid is carried out to generate maleic anhydride.

Ans. The aqueous maleic acid is fed to the azeotropic distillation column which is fed with an azeotropic agent such as xylene. The water is removed along with xylene as overhead vapors as a minimum boiling heterogenous azeotrope as the top product and the bottom product is the
maleic anhydride. The heterogeneous azeotrope can be easily separated from the xylene with gravity settling principle and the recovered xylene is fed back to the distillation column as the reflux stream.

3. Explain why waste steam recovery boiler is kept before heat integrated exchanger from the vapour products perspective

Ans. The reaction is highly exothermic and heating the feed to a high temperature is not desired. Had it been so, the waste steam recovery boiler would be kept after the heat integrated exchanger. This way, we generate good quality process steam from waste heat recovery boiler.

4. Explain how the usage of centrifuge is justified from process technology perspective

Ans. From physical property data, the solubility of maleic acid and fumaric acids are 68 g/100 ml water and 0.63 g/100 ml water respectively. This indicates that while maleic acid is soluble in water, fumaric acid is not. Therefore, after isomerisation reaction, the fumaric acid solids rich solution is sent to a centrifuge so as to separate the solids from the water. This clearly indicates how physical properties play an important role in choosing the separation process.

5. Can the process steam generated from the waste heat recovery boiler be also used for reboiler requirements in the azeotropic distillation unit, benzene vaporizer, vacuum distillation unit etc.?

Ans. Yes, this way we reduce the total utility requirements in the process. In fact the exact steam requirements (fresh) cannot be estimated unless we have a good idea of the total energy balances for the system.

6. Why is vacuum distillation required for maleic anhydride refining?

Ans. Maleic anhydride tends to polymerize upon aging and heating. Therefore, heating the maleic anhydride in vacuum conditions reduces the boiling point. Also, maleic anhydride is very corrosive and corrosiveness of any compound enhances with temperature. With all these limitations, vacuum distillation would suite the requirement.

25.3 DDT

25.3.1 Reactions

- DDT refers to Dichlorodiphenyltrichloroethane.
- DDT is produced by a reaction between monochlorobenzene and chloral in the presence of Oleum as catalyst.
  - Monochlorobenzene + Chloral → DDT + H₂O
- Therefore, to prepare DDT, first we need to prepare Chloral and purify it to the highest standard.
- Chloral is prepared by first forming chloral hydrate using chlorination of benzene route.
- The reaction for chloral is presented as
  \[ 4 \text{Cl}_2 + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{Cl}_3\text{CCH(OH)}_2 + 5 \text{HCl} \]
- Then chloral hydrate is allowed to distill in the presence of sulphuric acid which dessicates the chloral hydrate to chloral.

### 25.3.2 Process Technology

- In the process technology, we first discuss the process technology of chloral which is an important ingredient.
- Dry chlorine is first absorbed into ethanol at room temperature conditions. In this process, the alcohol turns to a syrupy fluid. The operation occurs in a chlorination tank which produces chloral hydrate and HCl.
- From the chlorination tank, HCl is separated by using partial condenser. The uncondensible HCl is sent for gas recovery using scrubbing. The liquid stream from the partial condenser is sent back to the chlorinator.
- The condensate from the chlorination tank is sent to a still, where distillation is facilitated in the presence of sulphuric acid which acts as a dessicant. Eventually, the still is operated at high temperature and for this purpose, steam is used for heating purposes. To control the operation, cooling water is also circulated in the jacket, as chloral hydrate conversion to chloral is a sensitive reaction.
- After the reaction, the batch still produces the waste acid as a product at the bottom and the clear chloral liquid at the top along with the vent gases.
- Eventually chloral is treated with lime to remove dissolved acidic impurities.
- The purified crude chloral is further sent to distillation in another still to remove chloral hydrates present in the stream. Therefore the second distillation unit is also operated in the presence of $\text{H}_2\text{SO}_4$. Vapors released during this step (from the partial condenser) are sent to the vent scrubber.
- Eventually, chloral is produced from the distillation unit and chloral hydrate is recycled back to the chloral hydrate converter to chloral.
- To manufacture DDT, purified chloral, monochlorobenzene, oleum are allowed to enter the DDT condensation unit.
- After condensation, the organic layer and spent acid are withdrawn. The organic layer consists of DDT and monochlorobenzene. This is first neutralized with soda ash.
- After reaction, the organic layer is sent to a dryer where the vapors generated from dryer enter a total condenser followed with gravity settling separator. The gravity settling unit separates monochlorobenzene from other organic impurities. The monochlorobenzene is recycled back to the condensation unit that is meant for preparing the DDT.
- The Dryer produces DDT powder which is sent for casting/pelletization process to obtain the DDT in either flakes or in pellets for sale.

With this flowsheet, we finish Module 2 in which process technology for good number of petrochemicals has been elaborated. We next move to the third module namely polymer technology.

### 25.3.3. Uses:

DDT is mainly used as a pesticide. DDT was the first of the modern insecticides. However, the use of this chemical has been restricted to some degree due to its harmful ill effects.

### 25.3.4 Technical questions

1. **Whyis the chloral hydrate converter fed with steam and water alternatively?**

   Ans. The chloral hydrate conversion to chloral takes good amount of time and switch type heating and cooling is required. Heating only with steam will enable faster decomposition of chloral which is very reactive and unstable. Therefore, the switch type heating is enabled in this case.
2. Why is air circulated in the DDT condensation unit?

Ans. In the DDT condensation unit, two liquids need to be thoroughly mixed. For this purpose, air is sparged so that interfacial area of the reactants enhances drastically due to the sparging effect.

3. DDT is a solid but the organic layer from the DDT condensation unit does not have any solid. Why?

Ans. DDT is soluble in most organic solvents but not in water. Therefore, upon drying, the liquid mass consisting of dissolved DDT in monochlorobenzene gets generated as a solid product.

4. Why are vapors released from the still despite knowing the fact that no HCl is produced from the still?

Ans. Due to the high temperature of the still, it is possible that some chloral hydrate decomposes to unwanted compounds such as HCl, chloroform and ethanol. These compounds will be non-condensible at the condenser operating temperatures and therefore, these are vented out.

5. Discuss what technology you would adopt to recover the H₂SO₄ from the spent solutions.

Ans. The sulphuric acid stream from the units will have higher concentrations of organics. Therefore, technology should be targeted that enables the recovery of these organics. Multiple effect evaporator appears to be suitable in this regard to concentrate the sulphuric acid as well as eliminate the organic impurities. The regenerated sulphuric acid with its regained original strength can be reused for the DDT condensation and chloral hydrate conversion operations.

References:

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