

PRODUCTION OF ISOAMYL ALCOHOL

There are two commercial processes that are widely used for the production of Isoamyl alcohol. They are,

- 1. CHLORINATION PROCESS.**
- 2. OXO PROCESS.**

1. CHLORINATION PROCESS:

Pentane Chlorination, while initially developed by Sharples and Rennsalt, is today used primarily overseas. But, here also Oxo plant construction is causing rapid obsolescence.

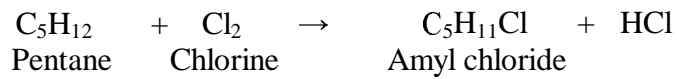
Pentane is dried over HCl, vaporized, and then mixed with chlorine in 15:1 ratio. The gas enters the furnace at 120⁰C, reacts and exits at 260⁰C. After prompt cooling, the reaction mixture is fractionated; producing HCl and amyl chloride. Unreacted pentanes are recycled. It is important to control the chlorine concentration and reaction severity closely to avoid the production of undesirable dichloropentanes.

The amyl chloride formed is hydrolyzed in an autoclave with aqueous caustic or sodium hydroxide in the presence of sodium oleate. Since the primary halides are difficult to hydrolyze directly, they are first esterified with 75-wt% of oleic acid, followed by saponification at 170⁰C and 14 atmospheres. Final alcohol workup is via steam distillation, followed by the fractionation of the isomers, if desired. The specific yield of each isomer obviously depends on the particular pentane, which is used as feed. Overall recovery is about 70% on the initial chloride.

A major material problem occurs in the tube furnace, where a special alloy of iron, copper and molybdenum is needed to handle the hot corrosive hydrocarbon/chlorine/HCl mixture.

Reactions:

1. Chlorination of Pentane:



2. Hydrolysis of Amyl chloride:



2. OXO PROCESS:

There are two main processes used commercially to produce higher alcohols via hydroformylation reaction. The first of the two processes was brought on steam by Ruhrchemie in Germany and Exxon in United States in the 1940's and is generally referred to as "High Pressure Cobalt Catalyst Technology". The active catalyst species is Cobalt Hydrocarbonyl, and a pressure of 200-300 atmospheres is required to maintain the stability of the catalyst. In the early 1960's, Shell commercialized a modern version of the Cobalt Catalyst Process. This technology is used on the basis of organophosphine ligands which allows lower operating pressure of about 30-100 atmospheres but at the expense of catalyst activity. The Shell technology is employed primarily in the production of linear primary alcohols, whereas the high pressure cobalt technology is frequently used in the production of branched alcohols.

1.1 HIGH PRESSURE COBALT PROCESS:

Several variations of the original High Pressure Cobalt Oxo Process have evolved over the years; however, the flow sequence essentially remains the same. There are four main processing steps. They are,

- (i) Oxonation or Oxo reaction or Hydroformylation,
- (ii) Catalyst recovery/ recycle or Decobalting,
- (iii) Hydrogenation , and
- (iv) Product Distillation/Purification.

Operations of the Oxonation and the Catalyst recovery sections are closely linked, and these are the main sections where companies like BASF and Kuhlmann have made enhancements to the original technology.

1.1.1 Hydroformylation or Oxo Reaction or Oxonation:

The hydroformylation reaction step is perhaps the most important economically because of high percentage of the total product cost associated with the olefin feed. Operating

conditions are selected to obtain the best economic combinations of desired product yield and minimum investment if factors affecting yield include temperature, pressure, contact time and catalyst concentration. Important investment considerations are pressure, reactor volume required per annual amount of product and material of construction. The reaction conditions selected and reactor design will vary to some extent with the type and number of olefin raw materials to be used. Two types of reactors for the hydroformylation reaction, they are: back mixed reactors where the composition of the reaction mixture approximates that of the product, and non back mixed or plug flow reactors, where the composition of the reaction mixture changes with reaction time. More than one reactor in series may be used. Typical of the former type are pot type reactors with mechanically driven agitators, which would be feasible for lower operation pressures. At higher pressures the problem of sealing the agitator shaft against pressure would make this design less preferable. If mechanical agitation is not used, mixing can be obtained from the synthesis gas rising from the liquid. Packing may be added or liquid may be recycled to improve back mixing. The plug flow reactors are usually long, narrow tubular reactors operated at high flow rates to provide gas-liquid mixing. The ability to remove high heat of reaction may limit the productivity of a reactor and various means are used. In back mixed reactors, cooling tubes may be inserted in the reaction zone or the liquid recycle may be cooled. In tubular reactors the heat is normally removed through reactor walls. The reactors are normally fabricated or lined with stainless steel to provide acceptable corrosion rates.

The type of olefin raw materials also influences the methods used to introduce the cobalt catalyst and the choice of catalyst. Cobalt soaps, such as naphthanate or oleate, are soluble in liquid olefins and can be conveniently fed in that manner. Cobalt salts or cobalt oxide may be slurried in the olefin feed or a suitable organic diluent. When the lower, gaseous olefins are used the catalyst may be fed as a solution as slurry in an inert diluent. The above methods are suitable for the formation of the active cobalt carbonyl catalyst in situ. If cobalt carbonyls are to be fed to the reactor, a separate, high pressure reactor is required to convert the cobalt slurry or solution in an inert diluent into cobalt carbonyl in

the presence of synthesis gas. External carbonyl generation is required if the hydroformylation reactor is operated at relatively mild temperatures and pressures.

1.1.2 Catalyst Removal and Recovery or Decobalting:

The techniques used to remove the cobalt catalyst from the crude liquid oxo product and recover it for reuse depend in part of the cobalt compound used as a catalyst feed, but are largely independent of whether in situ or external cobalt carbonyl formation is used because the same cobalt compound may be used for both methods and the crude oxo product contains carbonyls in either case. The cobalt catalyst can be recovered in 3 general forms they are

- i. As cobalt metal
- ii. As cobaltous ion and
- iii. As active catalyst

In the first two cases the cobalt carbonyl in the reactor product is decomposed by heat and/or aqueous acids. Thermal decobalting to cobalt metal can be accomplished by releasing the carbon monoxide pressure from the hot liquid. However, to facilitate the separation of the resulting solids from the crude product, steam or hot water is often used. In that manner, cobalt free organic phase can be decanted from the aqueous slurry. Because organic acids are formed in the hydroformylation steps as by products, steam decobalting is a combination of thermal and acid decobalting. The resulting solids are mixtures of cobalt metal, cobalt oxides, and cobalt salts. The use aqueous acids for decobalting is usually carried out at elevated temperatures. This technique requires good mixing to ensure contact between the two liquid phases to transfer the cobalt from the organic to the aqueous phase. Water soluble organic acids such as formic, acetic or Propionic may be used; inorganic acids such as sulphuric or phosphoric acid are also effective. The cobalt salts obtained from organic acid decobalting are sometimes recycled directly back to the oxo reactor. When inorganic acids are used, the salts are converted hydroxide or carbonate for recycle or for conversion into the preferred form of cobalt.

The strongly acidic properties of cobalt hydrocarbonyl are taken advantage of in two methods used to recycle active catalyst to the reactor. In one case aqueous solutions of cobaltous ions are used to remove the cobalt carbonyl from the organic phase by the formation of the cobalt salt, $\text{Co}(\text{Co}(\text{Co})_4)_2$. This salt has a very high solubility in water and allows the recycle of concentrated catalyst, part of which is in the carbonyl form. In the second case, the organic liquid is decobalted with an aqueous alkali at high pressures and temperatures to form the alkali metal salt of cobalt hydrocarbonyl. The volatile cobalt hydrocarbonyl is regenerated by contacting the aqueous solution with dilute mineral acid in the presence of a continuous flow of gas such as nitrogen or synthesis gas. The hydrocarbonyl is then transferred to the liquid olefin feed by contacting in an absorption tower. It is often desired to remove cobalt hydrocarbonyl from the oxo reactor vent gases to improve cobalt recovery and to avoid the deposition of cobalt in recycle compressors or other downstream equipments. The cobalt may be removed by thermal means or by scrubbing with aqueous caustic or an organic solvent.

1.1.3 Hydrogenation:

The alcohol oxo products are produced from the crude or semi refined, decobalted product by conventional hydrogenation processes. The type of process and feed purity depend to some extent on the molecular weight of the alcohol desired. The higher alcohols are rarely, if ever, prepared from a stream more highly refined than one from which hydrocarbons and residues have been removed. Either vapor phase or liquid phase hydrogenation may be used. In the former, the organic feed vaporized into a large volume of hot hydrogen and passed over the catalyst bed. A large hydrogen cycle flow is required. In the later, the liquid is fed directly to the catalyst bed, usually with preheat. Cocurrent upward flow, cocurrent downward flow, or counter current liquid and hydrogen flow may be used in the liquid phase process. In either of the processes the heat of reaction may be removed with a cooling fluid or by generating steam. Both internal and external cooling are used. The vapor phase process operates at low pressures and temperatures from 50° to 200°C . The liquid phase process operates at pressures from about 150 psig to 3500 psig at temperatures from 50° to 250°C .

The preferred catalysts are nickel, cobalt and molybdenum sulphide. The metallic catalyst normally prepared on an inert support such as kieselguhr, alumina or silica; other metals may be present as promoters. Quite often the catalysts are charged to the converter in the form of the metal oxide, followed by reduction in place with hydrogen to the metals. These catalysts are susceptible to poisoning by sulphur and chlorine containing compounds. A small bed of catalysts ahead of primary converter may be used to these contaminants. The molybdenum sulphide catalysts have the advantage of not being sensitive to sulphur poisoning, which is often desirable since the olefin raw material may contain appreciable amounts. Very complete hydrogenation is desirable because of the adverse effects of unhydrogenated, unsaturated and aldehydic compounds on the quality of the refined alcohol.

1.1.4 Product refining or Product distillation/purification:

Oxo products, both aldehydes and alcohols, are refined in conventional distillation equipment. For the lower aldehydes and alcohols, from C₂ to C₅, atmospheric distillations are used and the products can be isolated in high purity. Steam distillations or extractive distillations with water are sometimes employed. When aldehyde or alcohol isomers are to be separated, as in case with the butyl products, distillation columns with a great number of trays are required. Purification of higher alcohols derived from the olefin mixture is done under reduced pressure to minimize thermal degradation of the product.

The olefins and corresponding paraffins can be separated from the aldehydes and alcohols rather easily because of the difference in boiling point, but unhydrogenated aldehydes, the formates of the alcohols, and other impurities tend to codistill with the alcohol product. The aldehydes corresponding to higher boiling alcohols and the formates of lower boiling alcohols are very difficult to separate the distillation. Therefore, chemical treatments are often used to remove trace quantities of impurities which would cause colour formation in the manufacture of the esters for plasticizers. Caustic treatment will saponify the formates and will also reduce the sulphur contents. Sodium borohydride is used to reduce aldehydes and unsaturates. Treatment with mineral acids such as sulphuric or phosphoric acid is also used. This treatment produces coloured compounds

which would otherwise form during subsequent esterification and which can be separated by distillation.

The quality of the refined alcohol is often measured by contact with hot sulphuric acid for a specific period of time to check for colour development. The colour of the phthalate, prepared in the laboratory by a given procedure is also used as a measure of alcohol quality. Specifications for refined alcohols usually include purity, distillation range, acidity, aldehyde content, water content and colour. Unsaturation (iodine number) and ester content (saponification number) may also be included.

1.1.5 Byproducts:

Byproduct as defined here are co-products of limited usefulness, formed in the hydroformylation reaction and subsequent processing steps, and include all products other than the desired aldehydes and alcohols. As such, they represent a loss in efficiency for the process, and their formation is minimized as much as possible. Two types of byproducts are formed in the hydroformylation reactor, paraffins derived from hydrogenation starting olefin, and high boiling oxygenated compounds formed from condensation of the aldehydes and alcohols. Gaseous paraffins, mixed with the starting olefin, can be easily separated from the crude liquid product and can be recycled to the reactor if sufficient unreacted olefin is present, or can be used for fuel or returned to the refining area. Liquid olefin-paraffin mixtures can also be recycled or can be blended in to gasoline. Lower hydroformylation reaction temperatures reduce paraffin formation. The high boiling residues may contain aldol condensation products, acetals formed from the aldehyde and alcohol products. These oxo residues are usually about twice the molecular weight of aldehyde product. Smaller amounts byproducts are formed during hydrogenation. Minor amounts ethers may be formed from the alcohols in the presence of the catalyst. Some of the oxo residues are used as inexpensive solvents, but in general their utility is limited.

CHAPTER 4

MATERIAL BALANCE

The beginning of any design problem is to quantify the different streams involved in the process. This is done by formulating a material balance for the different units of the plant. The basis for the material balance is the product of **100 tons per day (TPD) of ISOAMYL ALCOHOL** at a purity of 99mol%. The mass/molar flow rates of different streams and their composition are given below.

Data Available:

Molecular weight of Isoamyl Alcohol= **88.15** kg/kmol.

Molecular weight of Valeraldehyde =**86.08** kg/kmol.

Molecular weight of Isobutylene = **56.00** kg/kmol.

Molecular weight of Carbon monoxide= **28.00** kg/kmol.

Molecular weight of Hydrogen = **2.00** kg/kmol.

Now,

$$\begin{aligned} 100 \text{ TPD of Isoamyl alcohol} &= \frac{100 \times 1000}{24 \times 88.15} \\ &= \underline{47.2679} \text{ kmol/hr.} \end{aligned}$$

$$= 4166.6667 \text{ kg/hr.}$$

Thus, 100 TPD Isoamyl alcohol = 47.2679 kmol/hr.

BASIS: 1 HOUR OPERATION.

From the stoichiometry of reactions, it is clear that 1mole of Isoamyl alcohol is produced by using 1 mole of Isobutylene.

Therefore, to produce 47.4679 kmol of Isoamyl alcohol amount of Isobutylene required is 47.2679 kmol or 2647.0024 kg. , provided the yield is 100%.

Thus, for a yield of 80%,

$$\begin{aligned} \text{Amount of Isobutylene required} &= \frac{47.3679}{0.80} \\ &= \underline{59.0849} \text{ kmol/hr.} \\ &= \underline{3303.7544} \text{ kg/hr.} \end{aligned}$$

Therefore, amount of Isobutylene actually required = 59.0849 kmol/hr.