

3. PROCESS SELECTION AND DETAILS

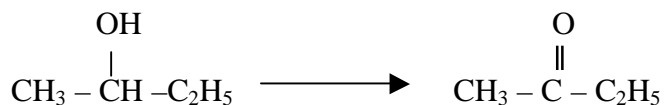
3.1 PROCESSES AVAILABLE:

There are a few processes listed below for the production of MEK.

- 1) Vapor phase dehydrogenation of 2- Butanol.
- 2) Liquid phase oxidation of n-Butane.
- 3) Direct oxidation of n-Butanes, Hoechst-Wacker process.
- 4) Direct oxidation of n-Butanes, Maruzen process.

VAPOR PHASE DEHYDROGENATION OF 2-BUTANOL:

MEK is prepared by vapor phase dehydrogenation of 2-butanol. A 2 step process from butanes, which are first hydrated to give 2-butanol, is used. The dehydrogenation of 2-butanol is an exothermic reaction (51 KJ/Kgmol). The reaction is as follows.



The equilibrium constant for 2-butanol can be calculated as follows:

$$\log K_p = -2790/T + 1.51 \cdot \log T + 1.856$$

Where T = reaction temperature, K

K_p = equilibrium constant, bar.

The MEK concentration in the reaction mixture increases and reaches its maximum at approximately 350°C. Copper, Zinc or Bronze are used as catalysts in gas phase dehydrogenation. Commercially used catalysts are reactivated by oxidation, after 3 to 6 months use. They have a life expectancy of several years.

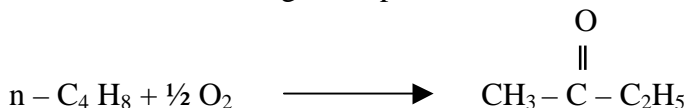
Sec-butyl alcohol is dehydrogenated in a multiple tube reactor, the reaction heat being supplied by heat transfer oil. The reaction products leave the reactor as gas and are split into crude MEK and hydrogen on cooling. The hydrogen is purified by further cooling. The crude MEK is separated from unreacted reactants and by-products by distillation.

LIQUID PHASE OXIDATION OF BUTANE:

MEK is produced as a by-product in the liquid phase oxidation of n-butane to acetic acid. Autoxidation of n-butane takes place in the liquid phase according to the radical mechanism yielding MEK as an intermediate and acetic acid as end product. MEK and acetic acid (mass ratio 0.2 : 1.0) are obtained by non-catalyzed liquid phase oxidation at 180°C and 53 bars with remixing. Continuous oxidation under plug flow conditions at 150°C, 65 bars and a residence time of 2- 7 minutes forms MEK and acetic acid at a mass ratio of 3:1. this process has slight economic advantage over the dehydrogenation of 2-butanol. But the key factor is availability and price of butane.

DIRECT OXIDATION OF N-BUTENES, HOECHST-WACKER PROCESS:

In direct oxidation of n-butenes by Hoechst-wacker process, oxygen is transferred in a homogenous phase on to n-butenes using redox salt pair, PdCl₂ / CuCl₂.



95% conversion of n-butenes can be obtained with the MEK selectivity of about 86%. The main disadvantage of this product is the formation of chlorinated butanones and b-butyraldehyde and corrosion caused due to free acids.

DIRECT OXIDATION N-BUTENES, MARUZEN PROCESS:

The Maruzen process is similar to the Hoechst-Wacker process except that oxygen is transferred by an aqueous solution of palladium sulfate and ferric sulfate. This method is attractive commercial route to get MEK via direct oxidation of n-butenes, but it is patented and very less information is available about this process. This process is generally not accepted due to formation of undesirable by products.

3.2 PROCESS SELECTION:

Commercially, MEK is predominantly produced by the catalytic dehydrogenation of SBA in vapor phase over ZnO or Brass catalyst. It can, however be produced by the selective direct oxidation of the olefin in a variety of processes, including the Hoechst-Wacker-type process employing a palladium(II) catalyst .

Most MEK (88%) is produced today by dehydrogenation of 2-butanol. 2-butanol can be easily produced by the hydration of n-butenes(from petrochemically produced C₄ raffinates). The remaining MEK is produced by process in which liquid butane is catalytically cracked giving both acetic acid and MEK.

The vapor phase dehydrogenation process gives high conversion of 2-butanol and high selectivity of MEK of about 95 mole%. Other advantages of this process include better yield, longer catalyst life, simple production separation and lower energy consumption.

MEK is produced as by product from liquid phase oxidation of n-butenes to acetic acid. The process has slight economic advantage over dehydrogenation of 2-butanol, but the key factor is the availability and price of n-butenes.

Of all the processes, it has been found that dehydrogenation of 2-butanol has more advantages and is more economical compared to other processes, so this process has been selected for design in following text.

3.3 PROCESS DETAILS:

The cold feed of 2-butanol will be pumped from the feed tank to a steam heater to a vertical thermosyphon vaporizer in which alcohol is vaporized. The thermosyphon vaporizer will be heated by reaction products discharged from the reactor. The wet alcohol vapor will be passed to a knock out drum to remove any entrained liquid. The liquid separated will be recycled and the dry alcohol will be fed to the reactor via super heaters heated by flue gas. The super heaters will be designed to raise the temperature of alcohol vapors to 500⁰C at which temperature the vapors enter the reactor.

The dehydrogenation reaction of SBA is as shown



The dehydrogenation reaction is endothermic and reversible and therefore a considerable amount of heat is to be supplied and hence, a multi-tube reactor is selected.

The gaseous reaction products discharged from the reactor at a minimum of 400⁰C will be passed on to the thermosyphon vaporizer in order to initiate the preheating of alcohol reactor feed. The reaction products will be cooled to near saturation in the vaporizer so that they will enter the water condenser at 150⁰C. There about 80% MEK and alcohol will be condensed and sent to the storage while the remainder will leave this unit as saturated vapor in non-condensable hydrogen.

This vapor will be fed to the bottom of the packed bed absorption column where MEK and 2-butanol will be absorbed in water. The water will be recycled from the extraction column and its rate will be controlled to provide an aqueous effluent containing 10% MEK. The hydrogen discharged from the top of the absorber will be dried and fed to the furnace.

The aqueous effluent from the absorber will be pumped into an extraction column where it will be contacted with 1,1,2-Trichloroethane to extract MEK and alcohol. In excess of about 95% of the MEK and alcohol will be extracted and remainder will be recirculated back to the absorber.

The trichloroethane extract phase will be pumped to a distillation unit for the separation unit for the separation of solvent, which is recycled. The distillate from this column will be MEK and alcohol, which will be, mixed liquid product form the condenser and this will be treated in a MEK product still for the purification of MEK. The alcohol discharged from the bottom of this column will be replaced back to alcohol feed tank. The MEK product will be cooled and stored.