

## MANUFACTURING PROCESS

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The basic principle behind the manufacture of Chlorobenzene is the chlorination of benzene with or without the presence of a catalyst (Friedel-Craft reaction). The products of such a reaction would be Chlorobenzene, dichlorobenzene, trichlorobenzene and the higher chlorinated benzenes. In actual practice in the industry, only Chlorobenzene and small amounts of dichlorobenzene are formed. The amounts of dichlorobenzene and higher substituted Chlorobenzene formed can be reduced greatly by using selective catalysts and modifying reaction conditions. Thus essentially chlorination of benzene can be considered as taking place in three pairs of two stages each:

- (1) Chlorination of benzene to monochlorobenzene and dichlorobenzene.
- (2) Chlorination of dichlorobenzene to trichlorobenzene and tetrachlorobenzenes.
- (3) Chlorination of tetrachlorobenzenes to pentachlorobenzenes and hexachlorobenzene.

Chlorination can be carried out either batch wise or continuously. When minimum formation of dichlorobenzenes is required then the latter procedure is followed. In the batch process, benzene is contained in a deep, iron or steel vessel, fitted with lead cooling coils. The chlorine feed-pipe enters at the bottom of the chlorinator and the catalyst is ferric chloride. The temperature is maintained at less than 45°C. HCl produced in the reaction can be recovered after separation from benzene by washing with a refrigerated solvent. At temperatures below 40°C, the rate of formation of dichlorobenzene is very low and this fact is used to suppress formation of dichlorobenzene in the continuous process. A typical continuous process plant consists of a series of small, externally cooled steel vessels containing the catalyst. Chlorine is supplied to

each vessel through suitably placed inlets and the temperature of the reaction is maintained between 20 - 40°C.

As the Chlorobenzene is formed, it leaves the chlorination zone at a speed that allows no further chlorination to take place. Unreacted benzene and Chlorobenzene are continuously separated by fractional distillation, returning the benzene to the chlorination stage and the efficiency of this process can be as high as 95%.

There are different ways in which the chlorination of benzene can be brought about and these form the different processes for the manufacture of Chlorobenzene. The first is called the Raschig Process. In this process, benzene is chlorinated by chlorine that has been produced in situ in the reactor by the catalytic oxidation of hydrogen chloride. A pre-heated mixture of benzene vapour, air, steam, and HCl, at ordinary pressure, is brought into contact at 220° - 260°C with a catalyst of copper oxide. 2% of the total benzene combusts, giving rise to about one quarter of the total heat output of the process. The disadvantage of this process is that the high temperature greatly favours high combustion rates of benzene and the reaction may become uncontrollable. Moreover the high costs of this vapour phase chlorination process in comparison with other available processes, allows it to be highly uneconomical for Chlorobenzene manufacture and thus renders it obsolete. In another process, chlorination of benzene is carried out in a quartz tube at 400 - 500°C. Here the principal product obtained is Chlorobenzene along with minor amounts of dichlorobenzene. Benzene has also been chlorinated in the gaseous phase at 425°C by means of nitrosylchloride. The process of Loeser and Schmidt, in which a mixture of benzene vapour, HCl, and air is reacted at 150 - 300°C in contact with a copper hydroxide-alumina catalyst (in the form of a fluidised mass), may be regarded as a variant of Raschig's Process. The disadvantages of all these processes are low efficiency and high temperature, which may make the reaction uncontrollable leading to formation

of higher Chlorobenzene. Based on all the above considerations, the continuous liquid phase chlorination of benzene at a temperature of about 40°C is best suited for production of large amounts of monochlorobenzene in the industry.

The process is economically viable too making it the most popular process being used in the industry for the manufacture of monochlorobenzene all over the world.

As already known, industrial chlorination of benzene is carried out in the liquid phase at moderate temperature with the help of a catalyst to produce monochlorobenzene and minor amounts of dichlorobenzene. Chlorobenzene and the o- and p-dichlorobenzene are the principal products. The reaction is a consecutive, competitive reaction. Liquid benzene is fed to a chlorinator operating at 2.4 bars. The feed enters at 25°C, at atmospheric pressure and also contains some water. Gaseous chlorine is fed to this tank, also at atmospheric pressure and at 25°C and is considered fully pure. There may be several chlorinators operating in series or parallel depending upon the degree of chlorination of benzene required. Ferric chloride is usually the catalyst. This can be added as a solution in benzene, or as iron turnings, or scrap that provides the ferric chloride in the chlorinator. Since the reaction is exothermic cooling is required to maintain the temperature at about 40°C. The HCl gas (90% of the HCl formed) leaving the reactor is first cooled to condense the impurities (benzene and chlorinated products) and then it is scrubbed in a scrubber using refrigerated Chlorobenzene. The crude chlorobenzene stream leaving the reactor is washed with NaOH solution (20 wt%; maintained slightly alkaline to protect downstream equipment from corrosion) in a pre-neutralizer. The product stream is free of HCl. The product is fed to a Benzene Recovery Column, which is a distillation column. Here the bottoms are almost 100 % pure chlorobenzene. The tops contain 98 % by weight of benzene and 2% chlorobenzene and all of the benzene is recycled to the benzene storage via a purifier. From the purifier the monochlorobenzene is sent to the refrigeration system. The bottoms from the

Benzene column contain monochlorobenzene and dichlorobenzene. This is fed to the chlorobenzene column, which is again a distillation column. This may contain 12 to 20 trays and is operated at a pressure ranging from 3–7 lb/in.<sup>2</sup> abs. The temperature in the chlorobenzene column may be between 100 - 120°C. Monochlorobenzene is the overhead distillate product of a purity of 99%. Dichlorobenzene is the bottom residue product of a purity of 97%.

The reactions involved in the process are as follows:

1.  $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$
2.  $C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$

Dichlorobenzene is assumed to be a para-isomer. Formation of trichloro isomers is neglected. When concentrations of dissolved chlorine remains essentially constant then reactions are first order.

$$r_b = -k_1 X_b$$

$$r_m = k_1 X_b - k_2 X_m$$

$$r_d = k_2 X_m$$

$$k_1 = 1 \times 10^{-4} \text{ s}^{-1} \quad \text{at } 55^\circ\text{C}$$

$$k_2 = 0.15 \times 10^{-4} \text{ s}^{-1} \quad \text{at } 55^\circ\text{C}$$

Where b = benzene, m = monochlorobenzene, d = dichlorobenzene