

Patent Application for a Process for the Manufacture
of Chlorinated Hydrocarbons

It has been found that saturated hydrocarbons or chlorinated hydrocarbons can be chlorinated in liquid phase with good yields and without the formation of undesired by-products if the starting material is mixed in the liquid phase with liquid chlorine (if necessary under pressure), in such a way that chlorination is avoided. The liquid mixture is then exposed to chemically active radiation, heat or chlorination catalysts or a combination of these conditions and thereby brought to reaction. In this way it is possible to chlorinate hydrocarbons which are gaseous under normal conditions - e.g. propane butane and isobutane. The quantity of chlorine to be used is also unlimited because the liquefied or liquid hydrocarbons or chlorinated hydrocarbons can be easily mixed with liquid chlorine in ratios of practical usefulness; pressure can be applied if necessary.

The amount of chlorine used is dependent on the product desired and the reactivity of the starting material. If hydrogen is to be replaced by chlorine in hydrocarbons or chlorinated hydrocarbons, it is recommended to use an excess of the material to be chlorinated in order to avoid overchlorination. The excess need not be as great, however, as in the chlorination in the gas phase. The entire amount of chlorine to be used can be mixed at once with the product to be chlorinated or the chlorine can be added stepwise during the course of the reaction. The process can be made continuous by having non-irradiated zones in the cycle system, and the chlorine is introduced in these non-irradiated zones. Higher chlorinated products are obtained correspondingly and stepwise chlorination can be carried out without separation of the chlorinating products after each step.

The continuous chlorination process in a closed system can be illustrated by the example of the chlorination of butane. The reaction is advantageously carried out in tubes or coils through which monochlorobutane is continuously recycled. The liquid mixture of butane and chlorine is introduced at one point of the system under conditions at which chlorination does not take place (at low temperature or under pressure). Catalysts or other agents which affect the reaction advantageously are arranged in the system. Catalysts can also be incorporated in the mixture of hydrocarbons and chlorine and subsequently exposed the mixture to conditions which result in reaction. The reacted material in mixture with the other compounds is removed at a suitable point in the system and fractionated in the usual way.

Chlorination can also be carried out in such a way that the reaction conditions are changed within the system itself. This can be accomplished by subdividing the system into several reaction zones and keeping the various reaction zones at different temperatures. The residence time in the different reaction zones can be changed in such a way that either very long reaction zones are provided or that the cross-section of the reaction vessels is changed so that a change in the residence time results. This is important because the chlorine concentration and especially the ratio of chlorinated product to non-chlorinated starting material changes continuously in the course of the reaction.

The amount of circulating liquid, the velocity and the dimensions of the reaction vessels are varied according to the quantity of starting materials introduced per unit of time. In order to obtain good mixing and dissipation of

the heat of reaction, it is advantageous to circulate the reaction mixture as fast as possible so that per hour a multiple of the amount of liquid present in the reactor passes through the system. The reaction is exothermic so that effective cooling is necessary at high-through-put rates.

By proper selection of the ratio of butane to chlorine it is possible to make either only monochlorobutane or in addition dichlorobutane. If much chlorine is used, part of the monochlorobutane in the reaction fluid will be chlorinated to dichlorobutane, whereas the butane feed will be converted to monochlorobutane. In this case, the liquid taken out of the system contains mono- and dichlorobutane besides non-reacted butane and hydrochloric acid. The butane obtained after separation of the HCl, together with the monochlorobutane, is recycled. In this way dichlorobutane is obtained from butane in one step and the dichlorobutane thus produced is free from higher chlorination products.

The pressure chosen for the reaction depends on the reaction temperature and should be selected in such a way that all reaction participants are liquid. Suitable temperatures range from -58°F. to 212°F.

Example: About 353 cubic feet of liquid, consisting of 66.7% isobutane, 22% isobutylchloride, 1.5% dichloroisobutane and 9.8% hydrochloric acid is circulated in a system of a capacity of about 84.5 gallons consisting of a tubular cooler with a cooling surface of about 140 sq.ft. and a reaction vessel of 6.9 feet length and a width of 7.9 inches; a quartz tube for a mercury vapor lamp is installed inside the reaction vessel.

A mixture of 715 pounds of isobutane and 165 pounds of liquid chlorine is pressed into the reactor and passed by the quartz lamp with a residence time of about 10 seconds. The heat of reaction is dissipated in the tubular cooler. At a temperature of about 86 - 104°F. the pressure is maintained at 147 psig. so that all reaction participants and reaction products are liquid and can be cycled in this form.

Eight hundred eighty (880) pounds of liquid are removed per hour from the reactor. In a pressure column 588 pounds of unreacted isobutane and 86 pounds of hydrochloric acid are removed by distillation. The hydrochloric acid is washed out with water and the isobutane is recycled after drying with potassium hydroxide. The residue from the pressure column is redistilled and yields 194 pounds of isobutylchloride. Thirteen point two (13.2) pounds of dichloroisobutane remains in the residue. At an hourly conversion of 128 pounds of isobutane the yield of isobutylchloride amounts to 95%.

Patent Claims

1. Process for the manufacture of chlorinated hydrocarbons by the chlorination of saturated hydrocarbons or chlorinated hydrocarbons in the liquid phase. The starting materials are mixed in the liquid phase, if necessary under pressure, with liquid chlorine under such conditions that no chlorination takes place and the mixture is reacted in the liquid phase at elevated pressure in the presence of agents beneficial to the reaction.
2. Process according to Claim 1 characterized by the introduction of the liquid mixture of the starting material at one or several points into the circulating liquid consisting of the chlorination product, reaction in the circulating liquid and removal of a quantity of the circulating liquid corresponding

to the quantity of starting material added and separation of the chlorination product from the mixture.

3. Process according to Claims 1 and 2 in which the reaction zone is subdivided into several zones in which the progress of the reaction can be controlled by various reaction conditions.