Water-to-Carbide Generation. This method, which has found only limited acceptance in the United States and Canada, has been used frequently in Europe. In this method, the rate of generation is simply regulated by the rate of water flow to the generator; hence, local undesirable hot spots may result, which may lead to hazardous overheating of the carbide mass and to the formation of polymers and other undesirable by-products. Water-to-carbide generation is generally used in small-size generators, such as in portable lamps, where the rate of generation and the heat of reaction are low and the mass of carbide involved is small.

Dry Generation. This water-to-carbide method, used in certain large-scale installations, has the advantage of being continuous and produces dry by-product lime which can be marketed as such or recycled to produce calcium carbide.

The dry process uses only about one pound of water per pound of carbide. Most of the heat of reaction is dissipated by vaporization of water. The reaction mass of dry lime and unreacted carbide must be continuously agitated to prevent hazardous localized overheating and formation of undesirable by-products. The acetylene is mechanically filtered to remove entrained lime dust. The lime is removed mechanically in a manner which prevents the escape of the gas.

Purification of Carbide Acetylene. The purity of carbide acetylene depends largely on the quality of the carbide employed and, to a much lesser degree, on the type and operation of the generator. Depending on the quality of the coke and lime used for the manufacture of the calcium carbide, a number of impurities are present in crude carbide acetylene. The nature and the amounts of the impurities in carbide acetylene are tabulated in Table 2.

Table 2. Impurities in Carbide Acetylene

Type	Amount, approx
phosphine	a few hundred ppm
divinyl sulfide	100 ppm (as H_2S)
ammonia	a few hundred ppm
oxygen	250 ppm or less
nitrogen	few tenths of a percent (<1.0)
arsine	3 ppm or less
methane, carbon dioxide, carbon monoxide, hydrogen	a few hundred ppm
silicon hydride (silane)	10 ppm or less
vinylacetylene	50 ppm
divinylacetylene	50 ppm
diacetylene	a few hundred ppm
propadiene ($CH_2=C=CH_2$), hexadiene, butadienyl, acetylene, methylacetylene	traces (variable according to carbide quality)

The total amount of impurities in acetylene, apart from water, manufactured from a standard U.S. grade of carbide, is generally less than 0.4%.

Purification of acetylene involves in principle the oxidation and hydration of phosphine to phosphoric acid, the neutralization and absorption of ammonia, and the oxidation of hydrogen sulfide and organic sulfur compounds. Depending on the type and amount of impurities, and on the end use of the gas, numerous agents and processes

are employed. These range from simply passing the gas over purifying media to multistep chemical treatments, and can be conducted as dry or wet processes.

The most commonly used dry methods employ oxidizing agents, such as chromic acid or chromates, hypochlorite, permanganate, and ferric salts, deposited on solid carriers, such as diatomaceous earth, arranged in beds or layers through which the gas is passed at ambient temperature. Some of the purifying media can be regenerated several times with diminishing effectiveness until they eventually lose their activity. Because of the high material and labor requirements, dry purification of acetylene is not practiced in the chemical industry where large volumes of gas have to be treated.

Large-scale acetylene installations exclusively employ continuous, wet purification processes. Elaborate purification methods have been developed in Europe, where on certain locations relatively low-grade carbide is used to generate acetylene of a lesser purity. Continuous purification processes are then employed whereby the gas is contacted in successive steps with water, dilute caustic solution, and chlorine–water or hypochlorite solution, followed in certain locations by a final treatment with activated carbon (5–7). Such an intensive purification of acetylene is also beneficial in cases where the gas is to be used in processes employing sensitive catalytic systems.

The chlorine–water purification is particularly effective on organic sulfur compounds. The chlorine concentration (about 1.3 g of chlorine per liter of solution) is rather critical; concentrations of less than one gram per liter are said to be of little effect, and concentrations of more than two grams of chlorine per liter lead to explosions due to the formation of monochloracetylene. Due to the presence of hypochlorous acid ($Cl_2 + H_2O \rightleftharpoons HCl + HOCl$), the action of this solution is mostly oxidative although undesirable chlorination side reactions cannot be entirely prevented. Small amounts of chloroform and tetrachlorodiethyl sulfoxide have been identified as by-products.

Manufacture from Hydrocarbons

Development of the modern processes for the manufacture of acetylene from hydrocarbons began in the 1920s when Badische Anilin- und Soda-Fabrik (BASF) initiated an intensive research program, based on Berthelot's early (1860) laboratory investigations on the conversion of low-molecular aliphatic hydrocarbons to acetylene by means of thermal cracking. BASF's development of the electric arc process led to the first commercial plant for the manufacture of acetylene from hydrocarbons. This plant was put into operation at Chemische Werke Huels in Germany in 1940. In the United States commercial manufacture of acetylene from hydrocarbons began in the early 1950s and is expanding rapidly. It has been estimated that, in the U.S., the 1963 hydrocarbon–acetylene capacity may increase to more than 700 million pounds per year compared with an estimated 1963 capacity of about 1125 million pounds per year of carbide–acetylene (8). All hydrocarbon–acetylene processes in operation or under development are thermal processes and differ essentially only in the manner in which the necessary energy for the reaction is supplied.

The method of producing acetylene by the thermal cracking of hydrocarbons takes advantage of the fact that, in contrast to the behavior of other hydrocarbons, the free energy of acetylene decreases at higher temperatures. At 1600°K or higher, acetylene is more stable than any other hydrocarbon. But even at these high temperatures, acetylene is less stable than its free elements and hence, the contact time at