ACETYLENE

1. Introduction

Acetylene, C_2H_2, is a highly reactive, commercially important hydrocarbon. It is used in metalworking (cutting and welding) and in chemical manufacture. Chemical usage has been shrinking due to the development of alternative routes to the same products based on cheaper raw materials. The reactivity of acetylene is related to its triple bond between carbon atoms and, as a consequence, its high positive free energy of formation. Because of its explosive nature, acetylene is generally used as it is produced without shipping or storage.

2. Physical Properties

The physical properties of acetylene [74-86-2] have been reviewed in detail (1). The triple point is at −80.55°C and 128 kPa (1.26 atm). The temperature of the solid under its vapor at 101 kPa (1 atm) is −83.8°C. The vapor pressure of the liquid at 20°C is 4406 kPa (43.5 atm). The critical temperature and pressure are 35.2°C and 6190 kPa (61.1 atm). The density of the gas at 20°C and 101 kPa is 1.0896 g/L. The specific heats of the gas, C_p and C_v (at 20°C and 101 kPa) are 43.91 and 35.45 J/mol · °C (10.49 and 8.47 cal/mol, °C), respectively. The heat of formation ΔH_f at 0°C is 227.1 kJ/mol (54.3 kcal/mol).

Tables and diagrams of thermodynamic properties have been given (1) and data on the solubility of acetylene in organic liquids in relation to temperature and pressure have been reviewed and correlated (1). The dissolving powers of some of the better solvents are compared in Table 1. The solubility in water at 20°C is 16.6 g/L at 1520 kPa (15.0 atm) and 1.23 g/L at 101 kPa. Acetylene forms a hydrate of approximate stoichiometry $C_2H_2 \cdot 6H_2O$. The dissociation pressure of the hydrate is 582 kPa (5.75 atm) at 0°C and 3343 kPa (33 atm) at 15°C. Its heat of formation at 0°C is 64.4 kJ/mol (15.4 kcal/mol) (1).

3. Chemical Properties

Acetylene is highly reactive due to its triple bond and high positive free energy of formation. Extensive reviews of acetylene chemistry are available (2–8). Important reactions involving acetylene are hydrogen replacements, additions to the triple bond, and additions by acetylene to other unsaturated systems. Moreover, acetylene undergoes polymerization and cyclization reactions. The formation of a metal acetylide is an example of hydrogen replacement, and hydrogenation, halogenation, hydrohalogenation, hydration, and vinylation are important addition

Table 1. **Solubility of Acetylene in Some Organic Liquids**

Solvent	CAS Registry Number	bp, °C	Acetylene solubility[a]
acetone	[67-64-1]	56.5	237
acetonitrile	[75-05-8]	81.6	238
N,N-dimethylformamide (DMF)	[68-12-2]	153	278
dimethyl sulfoxide	[67-68-5]	189	269
N-methyl-2-pyrrolidinone	[872-50-4]	202	213
γ-butyrolactone[b]	[96-48-0]	206	203

[a] g/L of solution at 15°C and 1520 kPa (15.0 atm) total pressure.
[b] Butanoic acid, 4-hydroxy-, lactone.

reactions. In the ethynylation reaction, acetylene adds to a carbonyl group (see ACETYLENE-DERIVED CHEMICALS).

Many of the reactions in which acetylene participates, as well as many properties of acetylene, can be understood in terms of the structure and bonding of acetylene. Acetylene is a linear molecule in which two of the atomic orbitals on the carbon are *sp* hybridized and two are involved in π bonds. The lengths and energies of the C—H σ bonds and $C{\equiv}C\sigma + 2\pi$ bonds are as follows:

Bond	Bond length, nm	Energy, kJ/mol
≡C—H	0.1059	506
—C≡C—	0.1205	837

The two filled π orbitals result in a greater concentration of electron density between the carbon atoms than exists in ethylene. The resulting diminution of electron density on the carbon atom makes acetylene more susceptible to nucleophilic attack than is ethylene. The electron-withdrawing power of the triple bond polarizes the C—H bond and makes the proton more acidic than the protons of ethylene or ethane. The pK_a of acetylene is 25 (9), and the acidic nature of acetylene accounts for its strong interaction with basic solvents in which acetylene is highly soluble (10,11). Acetylene forms hydrogen bonds with basic solvents (12), and as a result, the vapor pressures of such solutions deviate greatly from Raoult's law (13). The high concentration of electrons in the triple bond enables acetylene to behave as a Lewis base toward strong acids; it forms an adduct with HCl (14).

3.1. Metal Acetylides. The replacement of a hydrogen atom on acetylene by a metal atom under basic conditions results in the formation of metal acetylides that react with water in a highly exothermic manner to yield acetylene and the corresponding metal hydroxide. Certain metal acetylides can be prepared by reaction of the finely divided metal with acetylene in inert solvents such as xylene, dioxane, or tetrahydrofuran (THF) at temperatures of 38–45°C (15).

Acetylides of the alkali and alkaline-earth metals are formed by reaction of acetylene with the metal amide in anhydrous liquid ammonia.

$$C_2H_2 + MNH_2 \longrightarrow MC{\equiv}CH + NH_3$$

Aluminum triacetylide [61204-16-8] is formed from $AlCl_3$ and sodium acetylide [1066-26-8] in a mixture of dioxane and ethylbenzene at 70–75°C (16).

$$3\,NaC{\equiv}CH + AlCl_3 \longrightarrow Al(C{\equiv}CH)_3 + 3\,NaCl$$

Copper acetylides form under a variety of conditions (17–19). Cuprous acetylides are generally explosive, but their explosiveness is a function of the formation conditions and increases with the acidity of the starting cuprous solution. They are prepared by the reaction of cuprous salts with acetylene in liquid ammonia or by the reaction of cupric salts with acetylene in basic solution in the presence of a reducing agent such as hydroxylamine. Acetylides also form from copper oxides and salts produced by exposing copper to air, moisture, and acidic or basic conditions. For this reason, copper or brasses containing >66% copper or brazing materials containing silver or copper should not be used in an acetylene system. Silver and mercury form acetylides in a manner similar to copper.

Acetylene Grignard reagents, which are useful for further synthesis, are formed by the reaction of acetylene with an alkylmagnesium bromide.

$$C_2H_2 + 2\,RMgBr \longrightarrow BrMgC{\equiv}CMgBr + 2\,RH$$

With care, the monosubstituted Grignard reagent can be formed and it reacts with aldehydes and ketones to produce carbinols (see GRIGNARD REACTIONS).

3.2. Hydrogenation. Acetylene can be hydrogenated to ethylene and ethane. The reduction of acetylene occurs in an ammoniacal solution of chromous chloride (20) or in a solution of chromous salts in H_2SO_4 (20). The selective catalytic hydrogenation of acetylene to ethylene, which proceeds over supported Group 8–10% (VIII) metal catalysts, is of great industrial importance in the manufacture of ethylene by thermal pyrolysis of hydrocarbons (21–23). Nickel and palladium are the most commonly used catalysts. Partial hydrogenation to ethylene is possible because acetylene is adsorbed on the catalyst in preference to ethylene.

3.3. Halogenation and Hydrohalogenation. Halogens add to the triple bond of acetylene. $FeCl_3$ catalyzes the addition of Cl_2 to acetylene to form 1,1,2,2-tetrachloroethane, which is an intermediate in the production of the industrial solvents 1,2-dichloroethylene, trichloroethylene, and perchloroethylene (see CHLOROCARBONS AND CHLOROHYDROCARBONS). Acetylene can be chlorinated to 1,2-dichloroethylene directly using $FeCl_3$ as a catalyst and a large excess of acetylene. The compound *trans*-$C_2H_2Cl_2$ is formed from acetylene in solutions of $CuCl_2$, CuCl, and HCl (24–26). Bromine in solution or as a liquid adds to acetylene to form first 1,2-dibromoethylene and finally tetrabromoethylene. Iodine adds less readily and the reaction stops at 1,2-diiodoethylene. Hydrogen halides react with acetylene to form the corresponding vinyl halides. An example is the formation of vinyl chloride that is catalyzed by mercuric salts.

3.4. Hydration. Water adds to the triple bond to yield acetaldehyde via the formation of the unstable enol (see ACETALDEHYDE). The reaction has been carried out on a commercial scale using a solution process with $HgSO_4/H_2SO_4$ catalyst (27,28). The vapor-phase reaction has been reported at 250–400°C using a wide variety of catalysts (28) and even with no catalyst (29). Vapor-phase catalysts capable of converting acetic acid to acetone directly convert the steam–acetylene mixture to acetone (28,30,31).

$$2\,C_2H_2 + 3\,H_2O \longrightarrow CH_3COCH_3 + CO_2 + 2\,H_2$$

3.5. Addition of Hydrogen Cyanide. At one time the predominant commercial route to acrylonitrile was the addition of hydrogen cyanide to acetylene. The reaction can be conducted in the liquid (CuCl catalyst) or gas phase (basic catalyst at 400–600°C). This route has been completely replaced by the ammoxidation of propylene (SOHIO process) (see ACRYLONITRILE).

3.6. Vinylation. Acetylene adds weak acids across the triple bond to give a wide variety of vinyl derivatives. Alcohols or phenols give vinyl ethers and carboxylic acids yield vinyl esters (see VINYL POLYMERS).

$$\mathrm{ROH} + \mathrm{C_2H_2} \longrightarrow \mathrm{ROCH{=}CH_2}$$

$$\mathrm{RCOOH} + \mathrm{C_2H_2} \longrightarrow \mathrm{RCOOCH{=}CH_2}$$

Vinyl ethers are prepared in a solution process at 150–200°C with alkali metal hydroxide catalysts (32–34), although a vapor-phase process has been reported (35). A wide variety of vinyl ethers are produced commercially. Vinyl acetate has been manufactured from acetic acid and acetylene in a vapor-phase process using zinc acetate catalyst (36,37), but ethylene is the currently preferred raw material. Vinyl derivatives of amines, amides, and mercaptans can be made similarly. *N*-Vinyl-2-pyrrolidinone is a commercially important monomer prepared by vinylation of 2-pyrrolidinone using a base catalyst.

3.7. Ethynylation. Base-catalyzed addition of acetylene to carbonyl compounds to form -yn-ols and -yn-glycols (see ACETYLENE-DERIVED CHEMICALS) is a general and versatile reaction for the production of many commercially useful products. Finely divided KOH can be used in organic solvents or liquid ammonia. The latter system is widely used for the production of pharmaceuticals and perfumes. The primary commercial application of ethynylation is in the production of 2-butyne-1,4-diol from acetylene and formaldehyde using supported copper acetylide as catalyst in an aqueous liquid-filled system.

3.8. Polymerization and Cyclization. Acetylene polymerizes at elevated temperatures and pressures that do not exceed the explosive decomposition point. Beyond this point, acetylene explosively decomposes to carbon and hydrogen. At 600–700°C and atmospheric pressure, benzene and other aromatics are formed from acetylene on heavy-metal catalysts.

Cuprous salts catalyze the oligomerization of acetylene to vinylacetylene and divinylacetylene (38). The former compound is the raw material for the production of chloroprene monomer and polymers derived from it. Nickel catalysts with the appropriate ligands smoothly convert acetylene to benzene (39) or 1,3,5,7-cyclooctatetraene (40–42). Polymer formation accompanies these transition-metal catalyzed syntheses.

4. Explosive Behavior

4.1. Gaseous Acetylene. Commercially pure acetylene can decompose explosively (principally into carbon and hydrogen) under certain conditions of pressure and container size. It can be ignited, ie, a self-propagating decomposition flame can be established, by contact with a hot body, by an electrostatic spark, or by compression (shock) heating. Ignition is generally more likely the higher the pressure and the larger the cross-section of the container. The wire temperature required for ignition decreased from 1252 to 850°C with increasing

Table 2. **Ignition Energy of Gaseous Acetylene at Various Pressures**

pressure, kPa[a]	65	100	150	200	300	1000	2000
energy, J[b]	1200	100	10	2	0.3	0.002	0.0002

[a] To convert kPa to atm, divide by 101.3.

[b] To convert J to cal, divide by 4.184.

pressure from 170 to 2000 kPa (∼20 atm) (43) when a platinum or nickel resistance wire of 0.25-mm diameter and 25 or 75 mm length was heated gradually in pure acetylene; the pure acetylene was initially at room temperature in a tube 50 mm in diameter and 256 mm in length.

When the wall of the container is heated, ignition occurs at a temperature that depends on the material of the wall and the composition of any foreign particles that may be present. In clean steel pipe, acetylene at 235–2530 kPa (2.3–25 atm) ignites at 425–450°C (44,45). In rusted steel pipe, acetylene at 100–300 kPa ignites at 370°C (46). In steel pipe containing particles of rust, charcoal, alumina, or silica, acetylene at 200–2500 kPa ignites at 280–300°C (44). Copper oxide causes ignition at 250°C (47) and solid potassium hydroxide causes ignition at 170°C (44).

For local, short-duration heat sources, such as electrostatic sparks, the reported ignition energies for different pressures are on the orders of magnitude given in Table 2 (48–50).

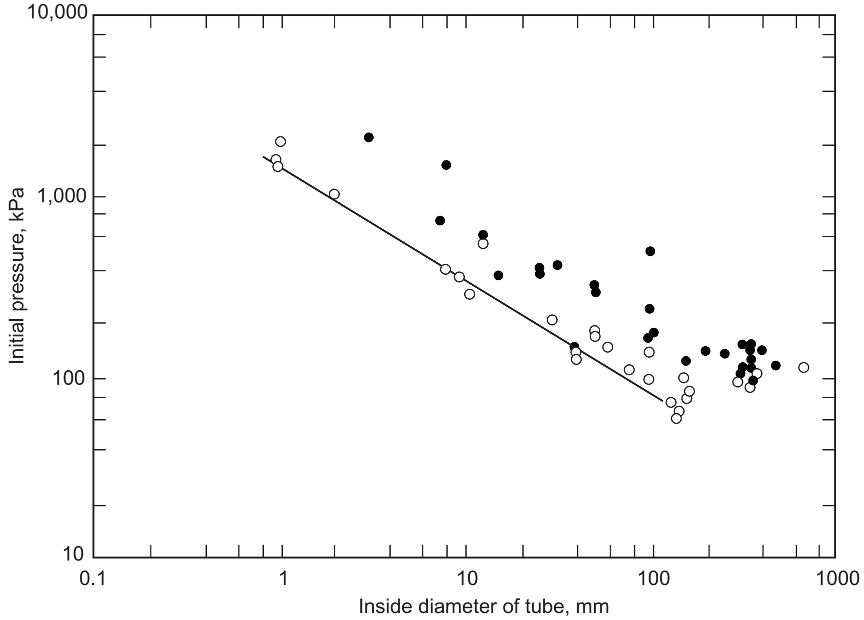

Fig. 1. Pressure required for propagation of decomposition flame through commercially pure acetylene free of solvent and water vapor in long horizontal pipes. Gas initially at room temperature; ignition by thermal nonshock sources. Curve shows approximate least pressure for propagation: (●), detonation, (○), deflagration (46,51–59). To convert kPa to atm, divide by 101.3.

Once a decomposition flame has formed, its propagation through acetylene in a pipe is favored by large diameter and high pressure. In a long pipe of given diameter, there is a pressure below which continued propagation of a flame, even though temporarily established, is very unlikely and may be impossible. In a pipe that is so short that heating by the ignition source raises the pressure, the required initial pressure is less than in a long pipe. Figure 1 shows pressures at which a flame travels through room temperature acetylene in long horizontal pipes of various diameters as the result of thermal (nonshock) ignition. The plotted points represent values reported in the literature (51–59) and the results of unpublished work (46). Many points representing detonation at higher pressures have been omitted. Propagation at pressures below atmospheric (101 kPa) require high energy ignition sources (100–1200 J or 24–287 cal). Pressure–diameter conditions near the curve, drawn at approximately the minimum pressure for propagation, tend to lead to deflagration rather than detonation, as indicated. However, the firing of a high explosive charge can cause a detonation wave to propagate at pressures even lower than those plotted as deflagrations, eg, 47 kPa in a 76-mm diameter tube and 80 kPa in a 13-mm diameter tube (60).

Deflagration flames in vessels and relatively short pipes usually propagate at an increasing velocity without becoming detonation waves, and develop pressures about ten times the initial pressure. In long pipes these flames usually become detonation waves. A slowly propagating deflagration flame in a long pipe occasionally neither accelerates nor dies out, but continues indefinitely. Decomposition flames in acetylene at pressures of 160–200 kPa in pipes of 50–150-mm diameter and 1500–6400 diameters in length have been observed to travel the full length at average velocities of 0.2 – 1 m/s (46). Generally, the velocity increases with increasing diameter. The pressure rises were <7 kPa (1 psi).

The calculated detonation velocity in room temperature acetylene at 810 kPa is 2053 m/s (61). Measured values are $\sim$1000 – 2070 m/s, independent of initial pressure but generally increasing with increasing diameter (46, 60–64). In a time estimated to be $\sim$6 s (65), an accidental fire-initiated decomposition flame in acetylene at $\sim$200 kPa in an extensive piping system traveled successively through 1830 m of 76–203-mm pipe, 8850 m of 203-mm pipe, and 760 m of 152-mm pipe.

The predetonation distance (the distance the decomposition flame travels before it becomes a detonation) depends primarily on the pressure and pipe diameter when acetylene in a long pipe is ignited by a thermal, nonshock source. Figure 2 shows reported experimental data for quiescent, room temperature acetylene in closed, horizontal pipes substantially longer than the predetonation distance (44,46,52,56,58,64,66,67). The predetonation distance may be much less if the gas is in turbulent flow or if the ignition source is a high explosive charge.

The pressure developed by decomposition of acetylene in a closed container depends not only on the initial pressure (or more precisely, density), but also on whether the flame propagates as a deflagration or a detonation, and on the length of the container. For acetylene at room temperature and pressure, the calculated explosion pressure ratio, $P_{\text{final}}/P_{\text{initial}}$, is $\sim$12 for deflagration and $\sim$20 for detonation (at the Chapman-Jouguet plane). At 800 kPa (7.93 atm) initial

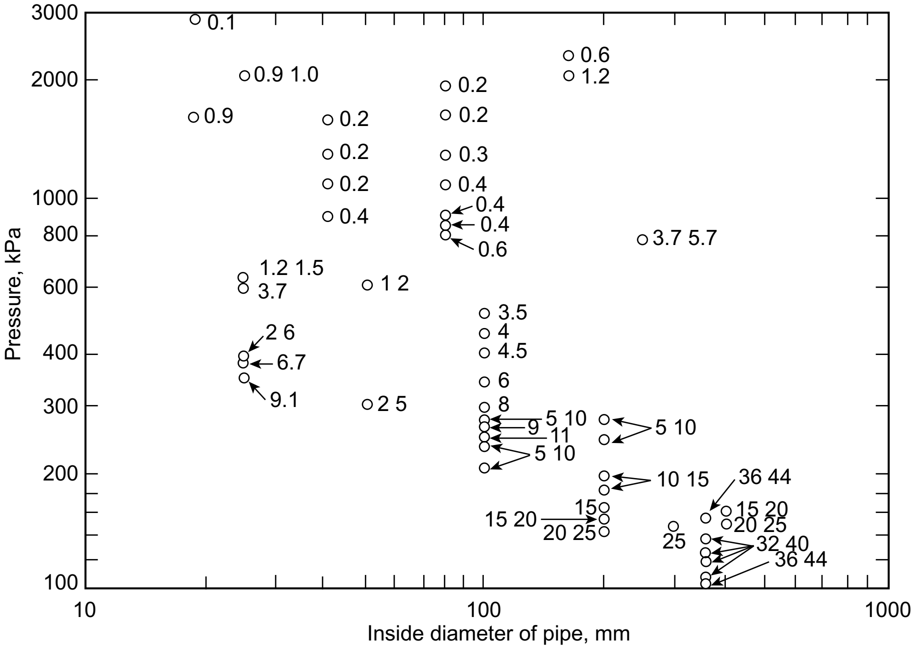

Fig. 2. Predetonation distances (in m) observed in acetylene at various pressures in horizontal pipes of various diameters. Gas quiescent, at room temperature, ignition by thermal nonshock sources (44,46,52,56,58,64,66,67). To convert kPa to atm, divide by 101.3.

pressure, the ratio is about the same for deflagration and 21.6 for detonation (61). The explosion pressure ratio for detonation refers to the pressure at the Chapman-Jouguet plane (of an ideal one-dimensional detonation wave) at which the heat-producing reaction has just come to equilibrium. This is the maximum effective pressure at the side wall of the pipe through which an established wave travels except at and near the end struck by the wave, where the pressure is increased by reflection. The calculated ratio, $P_{\text{reflected}}/P_{\text{initial}}$, for pressure developed by reflection of a detonation wave at the rigid end of a pipe is 48.5 for room temperature and pressure, and 52.5 for room temperature and 800-kPa initial pressure (46).

The measured explosion pressure ratio for deflagration in a container only a few diameters in length approaches the theoretical value; often it is ∼10. However, in a pipe hundreds or thousands of diameters in length, deflagration may cause very little pressure rise because only a small fraction of the contents is hot at any time.

Explosion pressure ratios that have been measured in experiments involving detonation vary over a wide range, and depend not only on the density of the acetylene through which the detonation wave travels, but on the location of the pressure sensor and its dynamic response. Unpublished Union Carbide work, using bursting diaphragms and bonded-strain gauge sensors, records values ranging from the theoretical reflected pressure ratio of ∼50–238. Russian work using crusher gauges indicates ratios as high as 658 (56,58). The Russian workers do not state whether the doubling effect of rapid rise inherent in the crusher gauge (68) was taken into account. The higher ratios have been indicated when the acetylene pressure has been only slightly above the minimum required for development of detonation. Evidently in these cases the acetylene in the far end of the pipe is compressed substantially while the flame moves at subsonic velocity toward it. The flame moves through acetylene at a density that is higher than the initial density after transition to detonation, particularly when the predetonation distance is a large fraction of the pipe length.

Flame Arresters. Propagation of a decomposition flame through acetylene in a piping system (by either deflagration or detonation) can be stopped by a hydraulic back pressure valve in which the acetylene is bubbled through water (65,69). It can also be stopped by filling the pipe with parallel tubes of smaller diameter, or randomly oriented Raschig rings (54,70–72). The small tubes should have a diameter less than that indicated (for the pressure to be used) by the curve of Figure 1, and the packed section should be long enough so that any decomposition products that are pushed through will not ignite the gas downstream. The presence of water or oil (on the walls or as mist) increases the effectiveness of the arrangement. Beds of granular ceramic material are effective with acetylene at cylinder pressure.

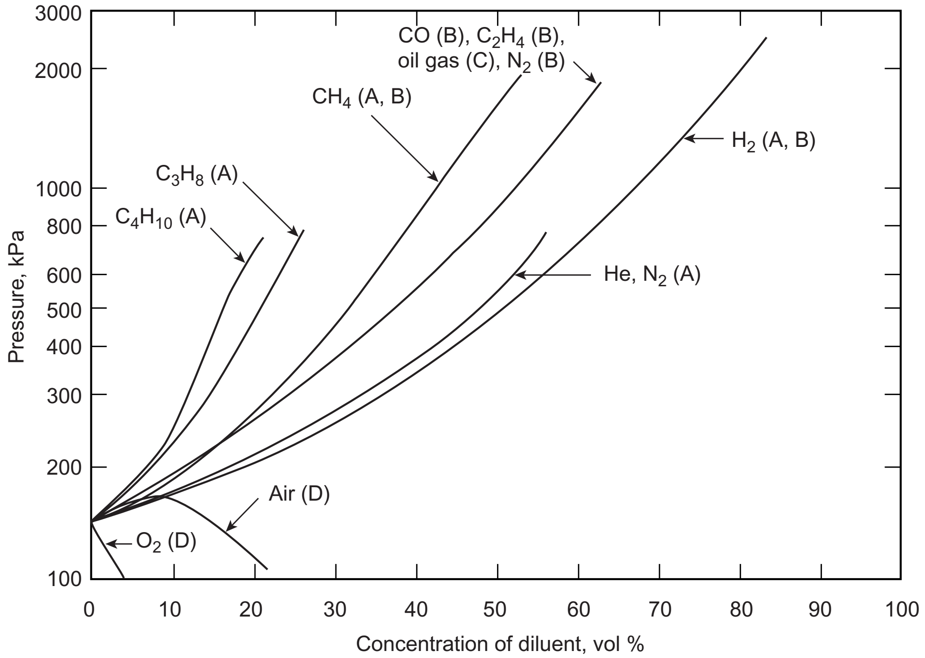

Fig. 3. Pressure required for ignition of mixtures of acetylene and a diluent gas (air, oxygen, butane, propane, methane, carbon monoxide, ethylene, oil gas, nitrogen, helium, or hydrogen) at room temperature. Initiation: fused resistance wire. Container: A, 50 mm dia × 305 mm length (73); B, 269 mm dia × 269 mm length (52); C, 102 mm dia × 254 mm length (74); and D, 120 mm dia sphere (75). To convert kPa to atm, divide by 101.3.

Ignition of Gaseous Acetylene Mixtures. The initial pressure required for ignition by fused resistance wire is given for several acetylene-diluent mixtures in Figure 3. Air in concentrations of less than ~13% inhibits ignition, but oxygen in any concentration promotes it. The data were obtained with relatively small containers and low ignition energies. With larger containers and higher ignition energies, the minimum pressure for ignition may be somewhat lower.

4.2. Acetylene—Air and Acetylene—Oxygen Mixtures.

The flammability range for acetylene–air at atmospheric pressure is ~2.5–80% acetylene in tubes wider than 50 mm. The range narrows to ~8–10% as the diameter is reduced to 0.8 mm. Ignition temperatures as low as 300°C have been reported for 30–75% acetylene mixtures with air and for 70–90% mixtures with oxygen. Ignition energies are lower for the mixtures than for pure acetylene; a spark energy of 0.02 mJ (200 erg) has been found sufficient to ignite a 7.7% acetylene–air mixture at atmospheric pressure and room temperature (76,77).

In acetylene–air mixtures, the normal mode of burning is deflagration in relatively short containers and detonation in pipes. In oxygen mixtures, detonation easily develops in both short and long containers. Measurements of predetonation distances of acetylene–oxygen at 100 kPa and 40°C in 25- and 50-mm diameter tubes 2.9 and 3.6 m long gave values of 25–35 mm for mixtures of 25–50% acetylene (78). For gas mixtures at atmospheric temperature and pressure, the maximum detonation velocity has been calculated to be 2020 m/s for acetylene–air (at 15% acetylene) (79) and 2944 – 2960 m/s for acetylene–oxygen (at 50% acetylene) (79,80). The corresponding explosion pressure ratios for detonations in mixtures of these compositions have been calculated to be 21.9–22.4 for acetylene–air (79,81) and 43.5–50.2 for acetylene–oxygen (79,80), both referring to the Chapman-Jouguet plane. The $P_{\text{reflected}}/P_{\text{initial}}$ ratios for the same mixtures are estimated to be ~ 50 for acetylene–air and 110 for acetylene–oxygen (46). Except for the detonation pressures of acetylene–air mixtures, these quantities have been measured and the results agree approximately with the calculated values (46).

Several studies of spherical and cylindrical detonation in acetylene–oxygen and acetylene–air mixtures have been reported (82,83). The combustion and oxidation of acetylene are reviewed extensively in Ref. 84. A study of the characteristics and destructive effects of detonations in mixtures of acetylene (and other hydrocarbons) with air and oxygen-enriched air in earthen tunnels and large steel pipe is reported in Ref. 81.

4.3. Liquid and Solid Acetylene.

Both the liquid and the solid have the properties of a high explosive when initiated by detonators or by detonation of adjoining gaseous acetylene (85). At temperatures near the freezing point neither form is easily made to explode by heat, impact, or friction, but initiation becomes easier as the temperature of the liquid is raised. Violent explosions result from exposure to mild thermal sources at temperatures approaching room temperature.

The minimum ignition energy of liquid acetylene under its vapor, when subjected to electrostatic sparks, has been found to depend on the temperature as indicated in Table 3 (86). Ignition appears to start in gas bubbles within the liquid.

Table 3. **Minimum Ignition Energy of Liquid Acetylene**

temperature, °C	−78	−50	−40	−35	−30	−27
vapor pressure, kPa[a]	145	537	779	931	1103	1234
minimum ignition energy, J[b]	>11	1.5	0.98–4.1	0.98	0.68	0.13

[a] To convert kPa to atm, divide by 101.3.

[b] To convert J to cal, divide by 4.184.

5. Manufacture from Hydrocarbons

Although acetylene production in Japan and Eastern Europe is still based on the calcium carbide process, the large producers in the United States and Western Europe now rely on hydrocarbons as the feedstock. Now >80% of the acetylene produced in the United States and Western Europe is derived from hydrocarbons, mainly natural gas or as a coproduct in the production of ethylene. In Russia ~40% of the acetylene produced is from natural gas.

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 weight aliphatic hydrocarbons to acetylene by means of thermal cracking. BASFs 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

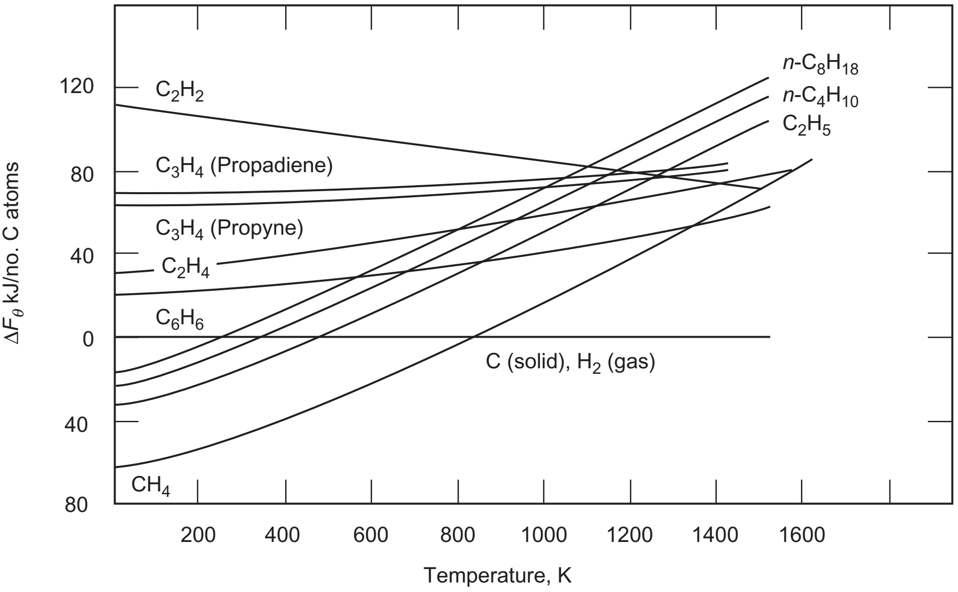

Fig. 4. Free energy of formation of several hydrocarbons. To convert kJ to kcal, divide by 4.184.

at Chemische Werke Hüls in Germany in 1940. In the United States, commercial manufacture of acetylene from hydrocarbons began in the early 1950s; expansion was rapid until the mid to late 1960s, when acetylene was gradually supplanted by cheaper ethylene as the main petrochemical intermediate.

5.1. Theory. The hydrocarbon to acetylene processes that have been developed to commercial or pilot-plant scale must recognize and take advantage of the unique thermodynamic properties of acetylene. As the free energy data shown in Figure 4 indicate, the common paraffinic and olefinic hydrocarbons are more stable than acetylene at ordinary temperatures. As the temperature is increased, the free energy of the paraffins and olefins become positive while that of the acetylene decreases, until at >1400 K acetylene is the most stable of the common hydrocarbons. However, it is also evident that, although it has the lowest free energy of the hydrocarbons at high temperature, it is still unstable in relation to its elements C and H_2. Thus it is necessary to heat the feedstock extremely fast to minimize its decomposition to its elements and, for a similar reason, the quench must be extremely rapid to avoid the decomposition of the acetylene product. Numerous acetylene production processes have been

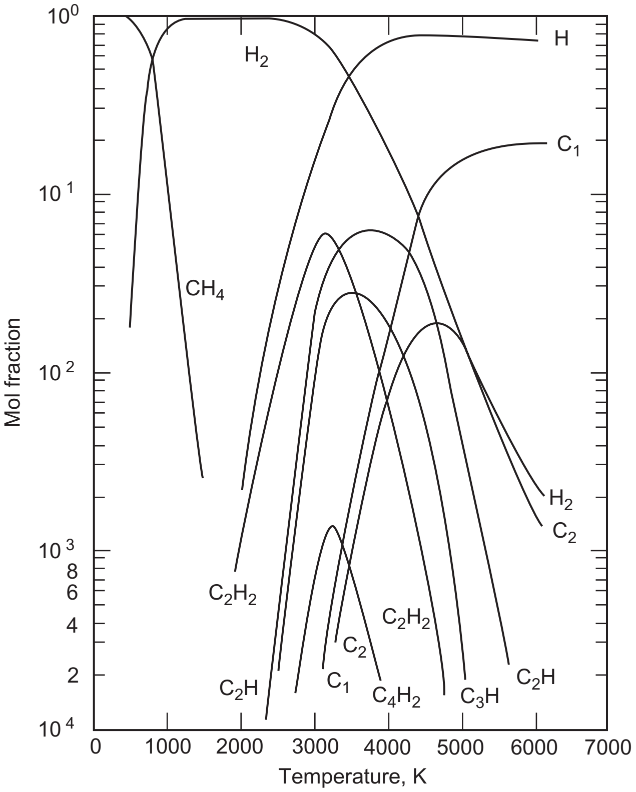

Fig. 5. Equilibrium diagram for carbon–hydrogen system at 101.3 kPa (1 atm). (C/H = 1/4).

developed, each in its own way and with varying degrees of success, accommodating the unique thermodynamics and pyrolysis kinetics of acetylene.

Examination of the equilibrium composition of the product gas mixture under relevant reactor conditions indicates the restrictive process conditions required to optimize the production process. Figure 5 illustrates the equilibrium composition for the carbon–hydrogen system with a C/H ratio of 1–4 at 101.3 kPa (1 atm) and at temperatures to 7000 K. This diagram is relevant to the pyrolysis of methane at atmospheric pressure. It is immediately evident that the hydrocarbon feedstock, CH_4, decomposes into its thermodynamically preferred state of C and H_2 at well <1000 K, whereas appreciable amounts of acetylene are not present until ~ 3000 K. Fortunately, the rate of the formation of acetylene is greater than the CH_4 decomposition rate. Thus it is important to heat the reactant as rapidly as possible to avoid decomposition of the feedstock to C and H_2 and to maximize the C_2H_2 formation. In a study to design an electric arc reactor (87) for producing acetylene from coal, it was found that the acetylene reaches equilibrium concentrations in <1 ms. Thus with rapid mixing and heating, it is possible to attain appreciable concentrations of acetylene with relatively little degradation of the feedstock to carbon.

Optimum reactor design and operating conditions can be further explored through equilibrium diagrams and computer models. The effects of feedstock composition pressures and temperature on the product composition have been explored in this manner in a study (87) in which in the added constraint that the heating would be rapid enough to preempt the degradation of the feedstock to carbon was imposed. Thus it was shown (Fig. 6) that at a C/H of 1–6 and at 51 kPa (0.5 atm), the concentration of acetylene at equilibrium conditions was as high as 16% and the temperature of peak concentration was 2000 K. Thus the process conditions of methane pyrolysis in excess hydrogen at reduced pressure are more promising than pyrolysis at atmospheric conditions as depicted in Figure 5.

Addressing the second step of the reaction, ie, the quench step, it is most important to quench the equilibrium mixture as quickly as possible in order to preserve the high acetylene concentration. In a study of the quenching mechanism (88), the acetylene-forming step was separated from the acetylene-preserving step by injecting known amounts of acetylene into a carbon-free plasma stream. The effect of various gases injected into the stream not only indicated the effectiveness of the quenching medium, but also revealed a great deal about the dynamics of the high temperature equilibrium composition. Hydrogen is much more effective in preserving the acetylene than the inert gases argon, helium, or nitrogen. Thus hydrogen injection allows recovery of as much as 90% of the acetylene, whereas with the other gases $<50\%$ of the acetylene was recovered. The observed effect of pressure was that in the 25–50 kPa (0.25–0.50 atm) range 85–90% of the acetylene is recovered, but at pressures between 50 and 100 kPa recovery decreases to 70%.

Because it was not possible to explain the differences in the effectiveness of hydrogen as compared to other gases on the basis of differences in their physical properties, ie, thermal conductivity, diffusivity, or heat capacity differences, their chemical properties were explored. To differentiate between the hydrogen

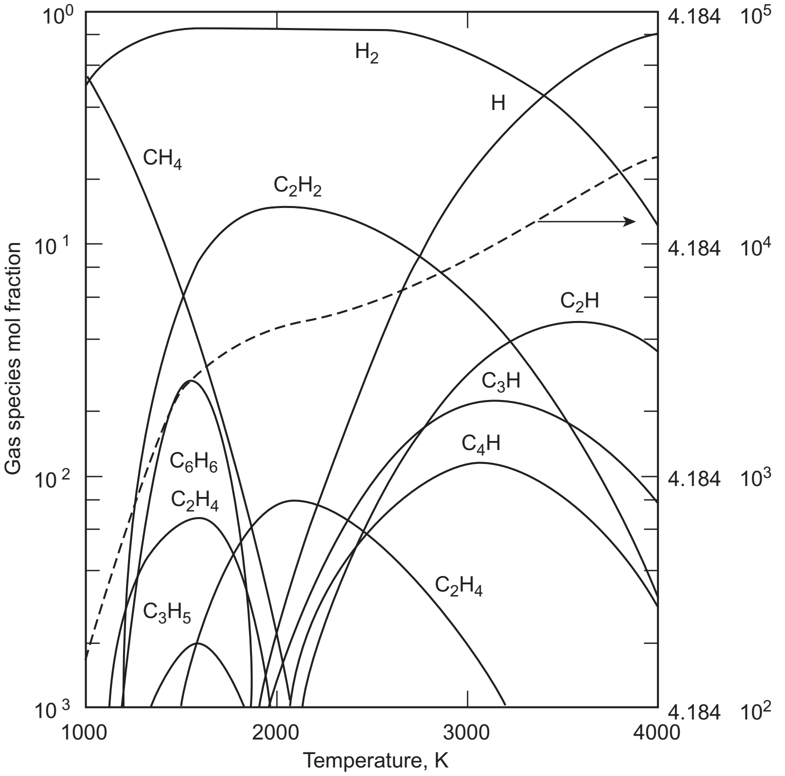

Fig. 6. Equilibrium diagram for carbon-hydrogen system at 51 kPa (0.5 atm). (C/H = 1/6). To convert J to cal, divide by 4.184.

atoms in the C_2H_2 molecules and those injected as the quench, deuterium gas was used as the quench. The data showed that although 90% of the acetylene was recovered, over 99% of the acetylene molecules had exchanged atoms with the deuterium quench to form C_2HD and C_2D_2.

To extend the study of the apparent decomposition recombination reaction, and specifically to determine if the carbon atoms exchange with other atoms in other acetylene molecules, tests using carbon isotopes were conducted. A mixture of 50% regular acetylene, $^{12}C_2H_2$, and 50% heavy acetylene, $^{13}C_2H_2$, was injected into the plasma stream. The results showed that, as before, 90% of the acetylene was recovered and that 97% of the acetylene molecules had exchanged carbon atoms.

These isotope exchange reactions not only provide an explanation for the effectiveness of hydrogen as a quench for the acetylene mixture, but also provide insight into the nature of the dynamic equilibrium present in hydrocarbon–hydrogen mixtures at high temperatures. The data indicate that essentially all of the acetylene molecules underwent total atom exchange, but because only a fraction of the energy required for decomposition of the C_2H_2 was supplied by the electric plasma, a chain or shuffle reaction is implied. The shuffle is initiated by the fragmentation of a relatively few C_2H_2 molecules into C_2H, C_2, CH, and H species. These fragments collide with C_2H_2 molecules, exchanging atoms and splitting off additional fragments. Allowing a residence time of 0.1 ms at an average plasma temperature of 3000 K, it can be estimated that each molecule undergoes $\sim 2 \times 10^4$ collisions. If an efficiency of 10% is assumed, each molecule experiences 2000 viable collisions in the first 2.5 cm of residency in the plasma stream. As the reaction mixture cools downstream, the number of collisions decrease and the chain reaction terminates as two CH fragments or a C_2H and H fragment collide to reform an acetylene molecule. Thus 90% of the acetylene is recovered but each C_2H_2 molecule has undergone some 2000 atom exchanges. As long as the exchanges occur between C and H species, high acetylene yield can be preserved. The introduction of inert species, A, He, or N_2, however, terminates the chain reaction and leads to acetylene degradation.

5.2. Process Technology. The processes designed to produce acetylene as the main product of a hydrocarbon feedstock are generally classified according to their energy source, ie, electricity or combustion. Using this classification, several processes that are now or have been operated commercially are listed in Table 4 and are described in the subsequent text. Two special cases, the production of acetylene by steam hydrocracking in oil refineries and the potentially commercial process of producing acetylene from coal, are also discussed.

Electric Discharge Processes. The synthetic rubber plant built by the I.G. Farbenindustrie during World War II at Hüls, contained the first successful commercial installation for the electric arc cracking of lower hydrocarbons to acetylene. The plant, with a capapcity of 200 t/day, was put into operation in August 1940.

The electric discharge processes can supply the necessary energy very rapidly and convert more of the hydrocarbons to acetylene than in regenerative or partial combustion processes. The electric arc provides energy at a very high

Table 4. **Acetylene Process Technology**

Energy source	Process designation	Feedstock	Typical cracked gas concentrations, mol% Acetylene	Ethylene
		Electricity		
electric arc	Hüls	natural gas	15	0.9
arc plasma	Hüls	crude oil	14	7
	Hoechst	naphtha	14	7
		Combustion		
partial comb.	BASF, SBA Montecatini	natural gas, naphtha	8	0.2
pyrolysis	Hoechst HTP, SBA	natural gas	11	15
	BASF submerged	naphtha, bunker C	6	6
	Flame Wulff	range of hydrocarbons	14	8
	Kureha	crude oil		8[a]

[a] Concentrations depend on severity of pyrolysis. At a high severity (~2000°C) acetylene/ethylene ratio is 1, but at lower severity acetylene concentration is reduced and ethylene is increased.

flux density so that the reaction time can be kept to a minimum (see FURNACES, ELECTRIC, ARC FURNACES).

There have been many variations in the design of electric arc reactors but only three have been commercialized. The most important is the installation at Hüls. The other commercial arc processes were those of Du Pont (89) (a high speed rotating arc) and a Romanian process that produced both ethylene and acetylene. However, the Du Pont process has been shut down since 1969.

Hydrocarbon, typically natural gas, is fed into the reactor to intersect with an electric arc struck between a graphite cathode and a metal (copper) anode. The arc temperatures are in the vicinity of 20,000 K inducing a net reaction temperature of ~1500°C. Residence time is a few milliseconds before the reaction temperature is drastically reduced by quenching with water. Just under 11 kW · h of energy is required per kilogram of acetylene produced. Low reactor pressure favors acetylene yield and the geometry of the anode tube affects the stability of the arc. The maximum theoretical concentration of acetylene in the cracked gas is 25% (75% hydrogen). The optimum obtained under laboratory conditions was 18.5 vol % with an energy expenditure of 13.5 kW · h/kg (90).

Hüls Arc Process. The design of the Hüls arc furnace is shown in Figure 7. The gaseous feedstock enters the furnace tangentially through a turbulence chamber, E, and passes with a rotary motion through pipe H (length ~1.5 m, diameter 85–105 mm). The arc, G, burns between the bell-shaped cathode, C, and the anode pipe, H (grounded). Due to the rotary motion of the gas, the starting points of the arc rotate within the hollow electrodes. The cathodic or anodic starting point of the arc can move upward or downward freely. With the exception of the insulator, D, all parts of the furnace are made of iron. The wall thickness of the electrodes is 10–20 min.

The arc is ~100 cm long and extends ~40–50 cm into the anode pipe. About 20 cm below the anodic starting point of the arc, cold hydrocarbons ($C \geq 2$) are introduced into the tube through several nozzles to prequench the hot (~1750 K) reaction gases. The quench feed becomes partly cracked (mainly to ethylene). Immediately below the anode pipe the hot reaction mixture is cooled to a temperature of ~450 K by means of a water spray, I. The electrodes are water jacketed. The cathode is insulated from the other parts of the furnace which are grounded (insulator D). The arc is started by means of an ignition electrode. The arc is operated at 8000 kW, 7000 V, and a direct current of 1150 A. Off-peak power is generally used (91).

The feed to the arc consists of a mixture of fresh hydrocarbons and recycle gas. Table 5 indicates the composition of a typical feedstock as well as the composition of the gas leaving the arc furnace.

Taking into account the purification losses, the following operating requirements are necessary in order to obtain 100 kg of purified acetylene: 200 kg hydrocarbons (feedstock plus quench), 1030 kW · h electric energy for the arc, 250 kW · h electric energy for the separation unit, and 150 kg steam.

The by-products amount to 49.5-kg ethylene, 29-kg carbon black, 15-kg residual oil, and 280-m^3 hydrogen.

A considerable amount of carbon is formed in the reactor in an arc process, but this can be greatly reduced by using an auxiliary gas as a heat carrier.

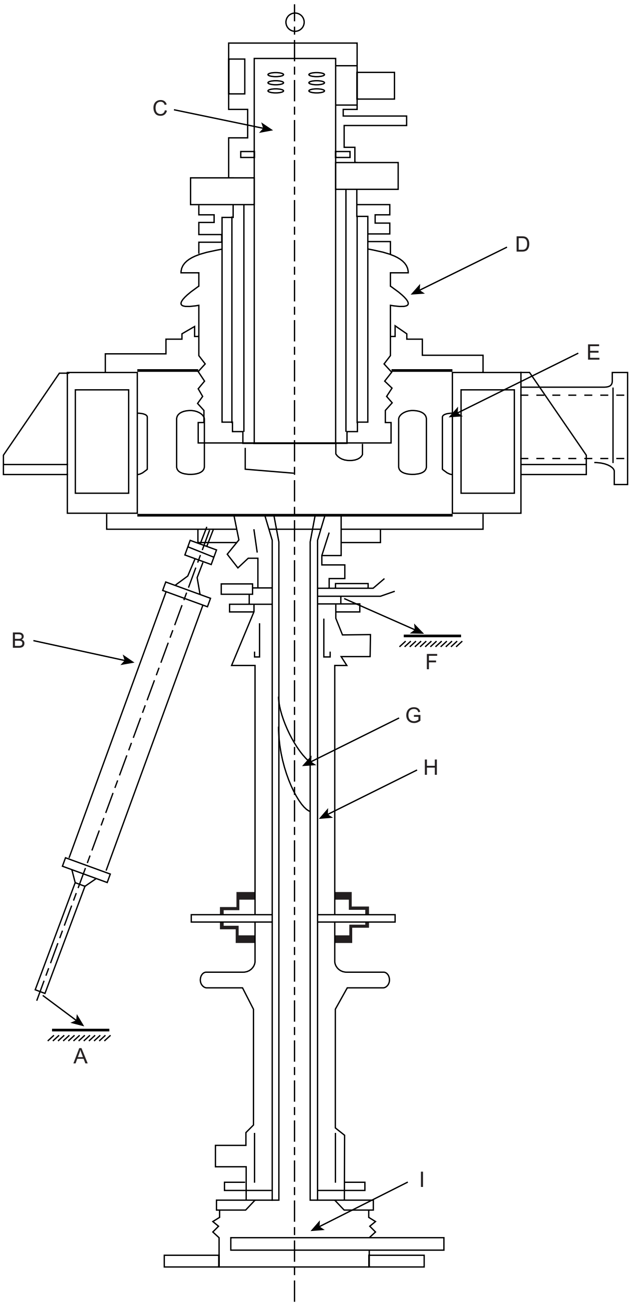

Fig. 7. Schematic drawing of a Hüls arc furnace. A, ground; B, ignition electrode; C, bell-shaped cathode; D, insulator; E, turbulence chamber; F, ground; G, arc; H, anode pipe; and I, water spray. Courtesy of Hüls AG.

Table 5. **Composition of Feedstock and Reaction Product, Arc Process**

Component	Feed gas, including recycle, vol %	Cracked gas,[a] vol %
C_2H_2	1.2	15.9
C_3H_4	1.0	1.0
C_4H_2	0.8	0.5
C_4H_4	0.7	0.5
C_2H_4	1.7	7.1
C_3H_6	2.3	0.9
C_4H_8	1.0	0.4
C_4H_6	0.4	0.3
CH_4	53.4	17.0
C_2H_6	10.2	1.2
C_3H_8	7.9	0.8
C_4H_{10}	12.5	2.1
C_5H_6	0.2	0.2
C_6H_6	0.4	0.4
C_7H_8		0.1
H_2	2.8	50.1
CO	0.8	0.7
N_2	2.7	0.8

[a] The cracked gas contains the products produced in the arc from the feedstock as well as the products obtained from the quench hydrocarbons. The liquid quench feed amounts to 120 kg/1000 kW·h and is composed of 25 kg C_3H_8 , 60 kg n-C_4H_{10}, and 35 kg iso-C_4H_{10}.

Hydrogen is a most suitable vehicle because of its ability to dissociate into very mobile reactive atoms. This type of processing is referred to as a plasma process and it has been developed to industrial scale, eg, the Hoechst WLP process. A very important feature of a plasma process is its ability to produce acetylene from heavy feedstocks (even from crude oil), without the excessive carbon formation of a straight arc process. The speed of mixing plasma and feedstock is critical (92).

Farbwerke Hoechst AG and Hüls AG have cooperated in the development of industrial-scale plasma units up to 10,000 kW (93). Yields of acetylene of 40–50 wt% with naphtha feedstock, and ∼27 wt% with crude oil feedstock, have been obtained. Acetylene concentration in the cracked gas is in the 10–15 vol% range.

Hoechst WLP Process. The Hoechst WLP process uses an electric arc-heated hydrogen plasma at 3500–4000 K; it was developed to industrial scale by Farbwerke Hoechst AG (94). Naphtha, or other liquid hydrocarbon, is injected axially into the hot plasma and 60% of the feedstock is converted to acetylene, ehtylene, hydrogen, soot, and other by-products in a residence time of 2–3 ms. Additional ethylene may be produced by a secondary injection of naphtha (Table 6, Case A), or by means of radial injection of the naphtha feed (Case B). The oil quenching also removes soot.

Hüls Plasma Process. In the Hüls plasma process, the hydrocarbon is injected tangentially into the hot hydrogen. In crude oil cracking, a residence time of 2–4 ms converts 20–30% of the crude (94). Crude oil data are given

Table 6. **Characteristic Data of Electric Plasma Processes**[a]

	Hoechst WLP process[b]		
Data	Case A	Case B	Hüls[c]
output, kW	10,000	9,000	8,500
naphtha input/100 kg acetylene, kg	192	250	
crude oil/100 kg acetylene, kg			367
quenching oil, kg	53	63	
products/100 kg acetylene,			
ethylene, kg	50	95	48
C_1–C_6 hydrocarbons, kg			82
hydrogen, m^3 (kg)	145 (13)	150 (13.5)	112 (10)
quenching oil, 20% carbon, kg	75	100	
crude oil residue with 20% carbon, kg			127
energy consumption/100 kg acetylene, kW·h	930	1,095	980
analysis of cracking gases, vol%			
C_2H_2	13.7	10.8	14.5
C_2H_4	6.4	9.8	6.5
yield ($C_2H_2 + C_2H_4$), wt %	78	78	56

[a] Ref. 93.

[b] Hydrogen plasma process using naphtha. Case A: secondary injection of naphtha; Case B: radial injection of the naphtha feed.

[c] Hydrogen plasma process using crude oil.

in Table 6, and data for naphtha and light hydrocarbon feeds are given in Table 7. In general, the arc processes achieve high temperatures easily, produce high yields of acetylene and few by-products, but can be handicapped by excessive carbon formation. On the strongly negative side are the high power consumption and the difficulty of controlling the arc geometry. Preheating the feed gas is one method to reduce cost in arc processes.

Electric arcs have been struck between grains of coal submerged in liquid hydrocarbons, such as kerosene and crude oil (95,96), to produce a gas with 30 vol% acetylene and 5–11 vol% ethylene (97). The energy consumption in those cases is about 9 kW · h/kg acetylene.

Flame or Partial Combustion Processes. In the combustion or flame processes, the necessary energy is imparted to the feedstock by the partial

Table 7. **Operational Results of the Hüls Plasma Process in the Cracking of Light Hydrocarbons**[a,b]

Data	Propane	*n*-Butane	Benzene	Naphtha
acetylene in the cracking gas, vol %	13.7	14.6	18.1	14.8
energy consumption, kW · h/100 kg C_2H_2	960	960	900	990
acetylene to ethylene ratio	2.2	1.7	18.0	1.8
carbon (rust) formation, kg/100 kg C_2H_2	2.3	3.1	44.5	6.1
yield ($C_2H_2 + C_2H_4$), wt %	61	61	56	54

[a] Courtesy of Applied Science Publishers Ltd.

[b] Ref. 93.

combustion of the hydrocarbon feed (one-stage process), or by the combustion of residual gas, or any other suitable fuel, and subsequent injection of the cracking stock into the hot combustion gases (two-stage process). A detailed discussion of the kinetics for the pyrolysis of methane for the production of acetylene by partial oxidation, and some conclusions as to reaction mechanism have been given (98).

There are several commercial versions of this partial combustion technique, including the widely used BASF process (formerly called the Sachsse process) and its various modifications with an overall similar design (99). Natural gas or other methane-rich feedstock is mixed with a limited amount of oxygen (insufficient for complete combustion), and fed through a specially designed distributor or burner to a single reaction zone in which ignition occurs. Preheating of the oxygen and methane, which is usually carried up to 500°C or above, supplies part of the energy and thus, by using less oxygen, reduces dilution of the acetylene by carbon oxides and hydrogen.

The design of the burner is of considerable importance (see COMBUSTION SCIENCE AND TECHNOLOGY). Combustion must be as brief and uniform as possible across the reaction chamber. Preignition, stability and blow-off of the flame, the possibility of backfiring through the ports of the burner head, and the deposition of carbon on the burner walls depend on the burner design and the velocities of the gas and the flame. The feasibility of partial combustion processes results from the high rates of reaction together with the relatively slow rate of decomposition of acetylene and hydrocarbon to carbon and hydrogen.

So-called tonnage oxygen, with a purity of 95–98%, is normally used as the oxidant. Although more expensive than air, its use gives several economic advantages, including a higher acetylene concentration in the cracked gas which results in lower purification costs. In addition, the plant off-gas obtained after separation of the acetylene contains high concentrations of hydrogen and carbon monoxide which, after further treatment, can be used for the synthesis of methanol or ammonia. The utilization of the off-gas is of considerable importance in establishing satisfactory economics for the partial combustion processes.

BASF Process. The basic design of the BASF process converter is shown in Figure 8. The burner is made of mild steel and is water cooled. The hydrocarbon feed can be methane, LPG, or naphtha, and these are separately preheated and mixed with oxygen. Self-ignition occurs if methane is preheated to 650°C and naphtha to 320°C. The oxygen and hydrocarbon feed are mixed in a venturi and passed to a burner block with >100 channels. The gas mixture speed in the channels is kept high enough to avoid backfiring but low enough to avoid blowout. The flame stability is enhanced by the addition of small amounts of oxygen flowing downward from the spaces between the channels. About one-third of the methane feed is cracked to acetylene and the remainder is burned.

The reaction gas is rapidly quenched with injected water at the point of optimum yield of acetylene, which happens to correspond with the point of maximum soot production. Coke will deposit on the walls of the burner and must be removed from time to time by a scraper.

The composition of the cracked gas with methane and naphtha and the plant feed and energy requirements are given in Table 8. The overall yield of acetylene based on methane is ∼24% (100). A single burner with methane

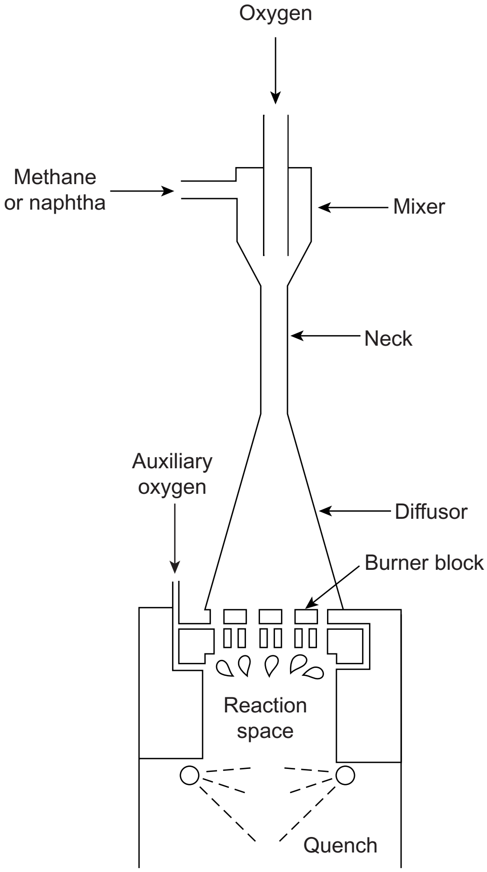

Fig. 8. BASF burner for the production of acetylene from methane or light naphtha (100). Courtesy of Verlag Chemie GmbH, Weinheim.

produces 25 t/d and with naphtha or LPG produces 30 t/d. The acetylene is purified by means of *N*-methylpyrrolidinone.

SBA Process. Two partial combustion processes have been developed by the Société Belge de l'Azote et des Produits Chimiques de Marly (located near Brussels). The first is a single-stage process using an entirely metallic converter. It produces 20–25 t/day of acetylene from methane, with an oxygen consumption of 4.6 kg/kg of acetylene produced. Methane and oxygen are preheated separately to 700°C and mixed. The oxygen is mixed with the methane through a series of holes in the internal shell. The volume flow rate of the mixed gas is set, using an inverted cone-shaped device, to that required at the point of ignition.

The flame-space walls are stainless steel and are water cooled. No mechanical coke scraper is required. A water quench cools the cracked gas stream rapidly at the point of maximum acetylene and this is followed by a secondary water quench. The primary quench point can be adjusted for variation in throughput, to accommodate the dependence of acetylene yield on residence time in the flame space.

Table 8. **BASF Process Consumptions and By-Product Yields and Cracked Gas Composition**[a,b]

Component	Methane	Naphtha
Feed and energy requirements		
hydrocarbon, kg/100 kg C_2H_2	410	430
oxygen, kg	490	430
N-methylpyrrolidinone, kg	0.5	0.5
electric energy consumption, kW · h	230	210
steam requirement, kg	450	450
residual gas, m^3	850	760
carbon, kg	5	30
Cracked gas, vol%		
C_2H_2	8.0	9.5
C_2H_4	0.2	0.2
CH_4	4.2	5.0
CO_2	3.4	3.8
CO	25.9	36.9
H_2	56.8	43.2
N_2	0.8	0.7
O_2	0.2	0.2
other hydrocarbons	0.5	0.7

[a] Courtesy of Verlag Chemie GmbH, Weinheim.
[b] Ref. 100.

Purification of the cracked gas is accomplished by water scrubbing, an electrostatic precipitator, and liquid ammonia absorption.

The SBA two-stage converter (Fig. 9) consists of two superimposed chambers. In the first (combustion) chamber, the combustion in oxygen of a hydrogen-rich gas is effected in the presence of superheated steam. By means of a special design, the combustion takes place with the formation of a ring of short flames, surrounded by steam. The energy required for pyrolysis is highly concentrated and thermal losses are reduced to a minimum (101). In the second (pyrolysis) chamber, the hydrocarbon feedstock is injected into the hot combustion gases. The reaction products are thoroughly quenched to avoid all parasitic reactions.

With this type of burner, a wide variety of raw materials, ranging from propane to naphtha, and heavier hydrocarbons containing 10–15 carbon atoms, can be used. In addition, the peculiar characteristics of the different raw materials that can be used enable the simultaneous production of acetylene and ethylene (and heavier olefins) in proportions which can be varied within wide limits without requiring basic modifications of the burner.

Montecatini Process. This partial combustion process operates at higher pressure, 405–608 kPa (4–6 atm), than the BASF and SBA processes. The burner dimensions are proportionately smaller. Because of the higher pressure, the danger of premature ignition of the methane–oxygen mixture is higher so that 2 vol% of steam is added to the gas mixture to alter the flammability limits.

The cracked gas composition is shown in Table 9 for the water quench operation (102). To produce 1800 m^3 of cracked gas, 1000 m^3 methane and 600 m^3 of oxygen are needed. If a naphtha quench is used, additional yields are

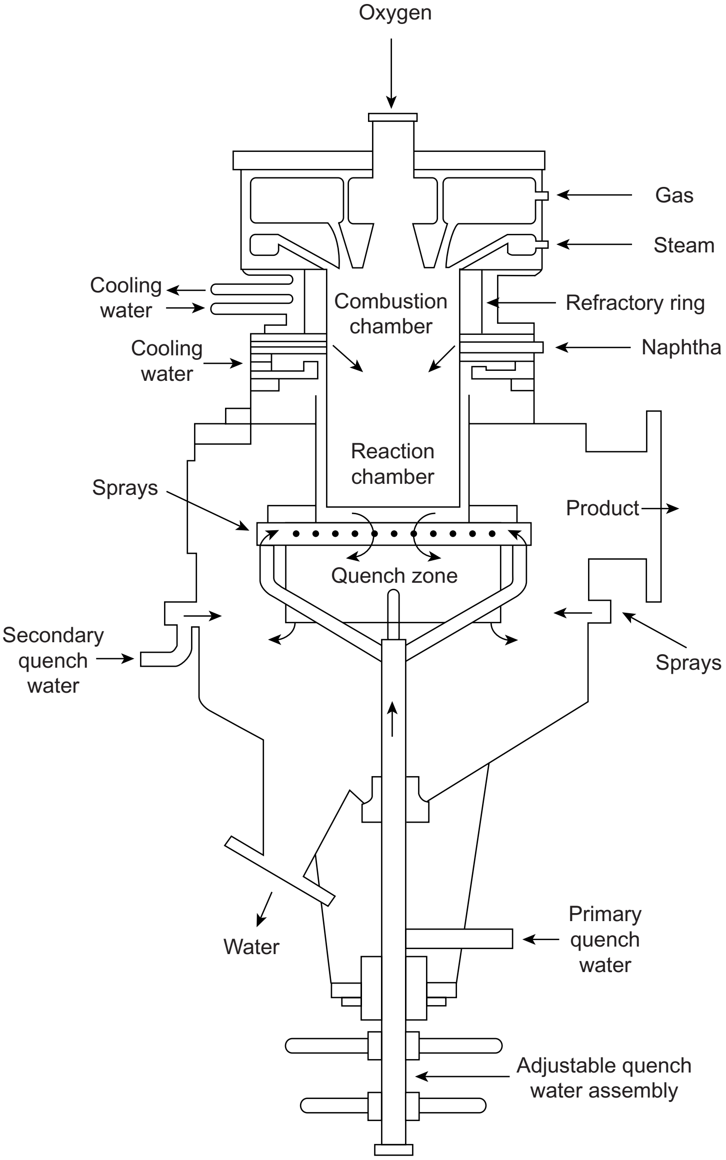

Fig. 9. SBA two-stage acetylene converter.

produced, consuming 130 kg of naphtha/1000 m^3 of methane (103). Purification of the acetylene is by methanol absorption.

Hoechst HTP Process. The two-stage HTP (high temperature pyrolysis) process was operated by Farbwerke Hoechst in Germany. The cracking stock for the HTP process can be any suitable hydrocarbon. With hydrocarbons higher than methane, the ratio of acetylene to ethylene can be varied over a range of 70:30–30:70. Total acetylene and ethylene yields, as wt% of the feed, are noted in Table 10.

Table 9. **Montecatini Process Cracked Gas Composition**[a]

Component	Composition, vol%	STP[b] m^3
C_2H_2	8.5	19.2
CO_2	3.8	2.6
CH_4	6.5	19.7
H_2	54.3	57.8
CO	25.2	9.8
C_2H_4 and higher hydrocarbons	1.7	31.2
Total	*100.0*	*140.3*

[a] Ref. 102.

[b] Per 100 kg of naphtha added.

The Hoechst burner is a water-cooled unit of all-metal construction. Fuel gas, which may be hydrogen, hydrocarbons, or off-gas from the process, is burned with oxygen in near stoichiometric amount in the combustion chamber. The hot combustion gases (tempered with dilution steam), together with the hydrocarbon feedstock injected, preferably as a vapor, enter the reaction zone where cracking of the feedstock takes place. Residence time in the reaction zone is very short, of the order of 1 ms. A rapid quench in specially designed equipment is effected to reduce the gas temperature below cracking temperatures.

BASF Submerged-Flame Process. This process can make acetylene from a wide range of feedstocks (naphtha to Bunker C oil) and, of course, crude oil itself. Oil is burned below the surface in an electrically ignited, oxygen-fed flame and quenching is immediate by the surrounding oil. The operating pressure is 900 kPa (9 bars) (100). The temperature of the oil is regulated at 200–250°C by circulation to a waste-heat boiler. The soot content of the oil is purged by burning it in the reactor. Crude oils with 12.4 wt% hydrogen can be cracked with a resulting soot level in the oil of 30%. Lower hydrogen content crudes can be handled by a separate purge of the oil to remove excess soot. An average composition of the cracked gas is shown in Table 11; it does not vary much with feedstock changes. The capcity of the commercial burner is 25 tons of acetylene and 30 tons of ethylene per day.

In summary, the bad features of partial combustion processes are the cost of oxygen and the dilution of the cracked gases with combustion products. Flame stability is always a potential problem. These features are more than offset by the inherent simplicity of the operation, which is the reason that partial combustion is the predominant process for manufacturing acetylene from hydrocarbons.

Table 10. **High Temperature Pyrolysis Process Yields**

Feed	Yield, wt%	Product
methane[a]	40.0	acetylene
butane	54.8	acetylene + ethylene (50:50)
light naphtha	54.0	acetylene + ethylene (30:70)
	50.0	acetylene + ethylene (70:30)

[a] Methane recycled.

Table 11. **BASF Submerged-Flame Process-Average Cracked Gas Composition**[a,b]

Component	Vol%
CH	43
H_2	29
CO_2	7
CH_4	4
C_2H_4	6.7
C_2H_2	6.2
C_3−plus higher hydrocarbons	4.0
H_2S	003−03

[a] Courtesy of Verlag Chemie GmbH, Weinheim.

[b] Ref. 100.

Regenerative Furnace Processes. The regenerative furnace processes supply the necessary energy for the cracking reaction by heat exchange with a solid refractory material. An alternating cycle operation is employed whereby the hydrocarbon feed is heated by the hot refractory mass to produce acetylene. Following this period, during which carbon and tars are deposited on the refractories, the process employs a combustion step in which the refractory mass is heated in an oxidizing atmosphere and the carbon and tar deposits are removed by burning. The refractories must resist both reducing and oxidizing atmosphere at ~1200°C. The refractories must also withstand the frequent and rapid heating and cooling cycles and abrasion in the case of moving refractory beds (pebbles).

Wulff Process. The regenerative technique is best exemplified by the Wulff process, licensed by Union Carbide Corp. The furnace consists basically of two masses of high purity alumina refractory tile having cylindrical channels for gas flow and separated by a central combustion space as shown in Figure 10. Its cyclic operation has four distinct steps, each of approximately 1 min in duration, the sequence being pyrolysis and heat in one direction followed by pyrolysis and heat in the other direction. Continuity of output is achieved by paired installations.

The regenerative nature of the Wulff operation permits the recovery of most of the sensible heat in the cracked gas. The gases leave the furnace at temperatures <425°C, thus obviating the need for special high temperature alloys in the switch valve and piping system.

This type of regenerative process runs at low pressure (just below atmospheric) and uses a considerable amount of dilution steam (two to three times the hydrocarbon feed). To crack methane, a reaction temperature of 1500°C must be reached, but higher hydrocarbons can be pyrolyzed to acetylene at lower temperatures, eg, 1200°C. Up to 15 vol% acetylene can be obtained in the cracked gas, but ethylene can also be produced at lower average cracking temperature and with lower acetylene yields. When cracking propane to acetylene and ethylene, the acetylene concentration in the cracked gases ranges from 14 to >16 mol%, and the ethylene concentration ranges from 8–13 mol% (104). Typical yields for acetylene plus ethylene (once-through cracking) on

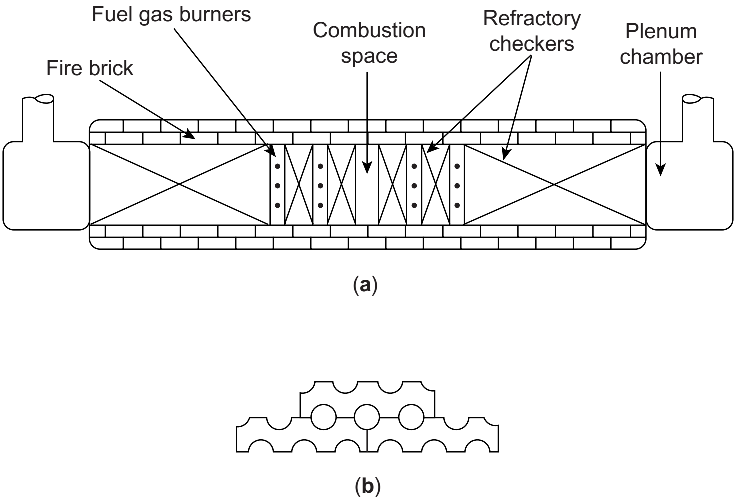

Fig. 10. (**a**) Wulff furnace design. (**b**) Checker detail of Wulff furnace refractory.

propane feed range from 51 to 59 wt% for acetylene to ethylene ratios of 3.5:1 and 1:3.5, respectively. Dimethylformamide (DM) is the purification solvent used (105).

Regenerative pyrolysis processing is very versatile; it can handle varied feedstocks and produce a range of ethylene to acetylene. The acetylene content of the cracked gases is high and this assists purification. On the other hand, the plant is relatively expensive and requires considerable maintenance because of the wear and tear on the refractory of cyclic operation.

Pyrolysis by Direct Firing. Pyrolysis of hydrocarbon in direct-fired tubes with steam dilution is practised extensively to make ethylene (qv). This technique is operated generally at the limits of metallurgy and at the maximum severity permissible (combination of time and temperature), while avoiding excessive coking rates inside the cracking tubes. The manufacture of acetylene requires even higher cracking temperatures. Such severe conditions normally induce an extreme rate of coking and an inoperable situation, If, however, the requisite high temperature can be reached without a high cracking severity and without excessively hot reactor walls, catastrophic coking rates can be avoided and useful operation is possible. Kureha Chemical Industries (Japan) developed a process based on this principle that operates at a level of pyrolysis and allows acceptable levels of acetylene production.

The unit Kureha operated at Nakoso to process 120,000 metric tons per year of naphtha produces a mix of acetylene and ethylene at a 1:1 ratio. Kureha's development work was directed toward producing ethylene from crude oil. Their work showed that at extreme operating conditions, 2000°C and short residence time, appreciable acetylene production was possible. In the process, crude oil or naphtha is sprayed with superheated steam into the specially designed reactor. The steam is superheated to 2000°C in refractory lined, pebble bed regenerative-type heaters. A pair of the heaters are used with countercurrent flows of combustion gas and steam to alternately heat the refractory and produce the superheated steam. In addition to the acetylene and ethylene products, the process produces a variety of by-products including pitch, tars, and oils rich in naphthalene. One of the important attributes of this type of reactor is its ability to produce variable quantities of ethylene as a coproduct by dropping the reaction temperature (106–108).

5.3. Separation and Purification of Hydrocarbon-Derived Acetylene. The pyrolysis of methane results in a cracked gas that is relatively low in acetylene content and that contains predominantly a mixture of hydrogen, nitrogen, carbon monoxide, carbon dioxide, unreacted hydrocarbons, acetylene, and higher homologues of acetylene. In cases where a higher hydrocarbon than methane is used as feedstock, the converter effluent also contains olefins (ethylene, propylene, propadiene, butadiene), aromatics (benzene, naphthalene), and miscellaneous higher hydrocarbons. Most acetylene processes produce significant amounts of carbon black and tars that have to be removed before the separation of acetylene from the gas mixture.

The isolation of the acetylene from the various converters presents a complicated problem. The unstable, explosive nature of acetylene imposes certain restrictions on the use of the efficient separation techniques developed for other hydrocarbon systems. The results of decomposition and detonation studies on acetylene and its mixtures with other gases indicate that operating conditions where the partial pressure of acetylene exceeds 103–207 kPa (15–30 psi) should be avoided. Similar limitations apply to the operating temperatures that should not exceed 95–105°C. Low temperatures may lead to the appearance of liquid or solid acetylene or its homologues with concomitant danger of unexpected decompositions. In view of these severe operating restrictions, it is not surprising that all commercial processes for the recovery of hydrocarbon-derived acetylene are based on absorption–desorption techniques using one or more selective solvents.

Of the many solvents proposed, only a few have found commercial application, including water (Hüls), anhydrous ammonia (SBA), chilled methanol (Montecatini), *N*-methylpyrrolidinone (BASF), butyrolactone, acetone, dimethylformamide, and hydrocarbon fractions.

The separation and purification of acetylene is further complicated by the presence in the pyrolysis gas of higher acetylenes which polymerize rather easily in solution. The removal of these constituents is a necessity, particularly in view of the utilization of the acetylene in chemical synthesis. This can be accomplished by scrubbing with small amounts of a suitable mineral oil or other organic solvent (SBA, Wulff) or by low temperature fractionation (Hüls). In the latter case, the concentrated, dry acetylene is cooled to the freezing point (195 K), whereby the higher acetylenes are liquefied and removed as a solution in methanol or benzene.

The carbon black (soot) produced in the partial combustion and electrical discharge processes is of rather small particle size and contains substantial amounts of higher (mostly aromatic) hydrocarbons which may render it hydrophobic, sticky, and difficult to remove by filtration. Electrostatic units, combined with water scrubbers, moving coke beds, and bag filters, are used for the removal of soot. The recovery is illustrated by the BASF separation and purification system (109). The bulk of the carbon in the reactor effluent is removed by a water scrubber (quencher). Residual carbon clean up is by electrostatic filtering in the case of methane feedstock, and by coke particles if the feed is naphtha. Carbon in the quench water is concentrated by flotation, then burned.

The BASF process uses *N*-methylpyrrolidinone as the solvent to purify acetylene in the cracked gas effluent. A low pressure prescrubbing is used to remove naphthalenes and higher acetylenes. The cracked gas is then compressed to 1 MPa (10 atm) and fed to the main absorption tower for acetylene removal. Light gases are removed from the top of this tower.

Stripping of acetylene from the solvent takes place at atmospheric pressure. Pure acetylene is removed from the side of the stripper; light impurities are removed overhead and recycled to the compressor. Higher acetylenes are removed from the side of a vacuum stripper with the acetylene overheads being recycled to the bottom of the acetylene stripper.

The gases leaving the purification system are scrubbed with water to recover solvent and a continuous small purge of solvent gets rid of polymers. The acetylene purity resulting from this system is 99%. The main impurities in the acetylene are carbon dioxide, propadiene, and a very small amount of vinylacetylene.

6. Manufacture From Calcium Carbide

Acetylene is generated by the chemical reaction between calcium carbide [75-20-7] and water with the release of 134 kJ/mol (900 Btu/lb of pure calcium carbide).

$$\mathrm{CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2}$$

Because of the exothermic reaction and the evolution of gas, the most important safety considerations in the design of acetylene generators are the avoidance of excessively high temperatures and high pressures. The heat of reaction must be dissipated rapidly and efficiently in order to avoid local overheating of the calcium carbide which, in the absence of sufficient water, may become incandescent and cause progressive decomposition of the acetylene and the development of explosive pressures. Maintaining temperatures $<150^\circ\mathrm{C}$ also minimizes polymerization of acetylene and other side reactions that may form undesirable contaminants. For protection against high pressures, industrial acetylene generators are equipped with pressure relief devices which do not allow the pressure to exceed 204.7 kPa (15 psig). This pressure is commonly accepted as a safe upper limit for operating the generator.

Most carbide acetylene processes are wet processes from which hydrated lime, $Ca(OH)_2$, is a by-product. The hydrated lime slurry is allowed to settle in a pond or tank after which the supernatant lime-water can be decanted and reused in the generator. Federal, state, and local legislation restrict the methods of storage and disposal of carbide lime hydrate and it has become increasingly important to find consumers for the by-product. The thickened hydrated lime is marketed for industrial wastewater treatment, neutralization of spent pickling acids, as a soil conditioner in road construction, and in the production of sand-lime bricks.

6.1. Carbide-to-Water Generation. This process is the one most widely used in the United States for generating acetylene from calcium carbide. Standards for the design and construction of acetylene-generating equipment using this technique have been developed over the years by the acetylene industry. Underwriters Laboratories, Inc. have generally accepted design criteria for acetylene generating equipment (110). A water capacity of 3.78 L (1 gal) per 0.454 kg of carbide and a gas-generating rate of 0.028 m^3 (1 ft^3) per hour per 0.454 kg of carbide hopper capacity is considered normal. These design criteria apply to gravity feed generators where it is possible to have an uncontrolled release of the entire carbide hopper contents into the generating chamber. Other high capacity generators (up to 283 m^3/h) are designed so that it is impossible to have uncontrolled feed of carbide (screw-feed type); therefore, the chamber water capacity can be reduced, the carbide hopper capacity can be increased, and the gas production capacity can be raised. These high capacity generators also must pass prescribed safety tests before sale.

There are two classes of acetylene generators: the low pressure generator which operates $<$108.2 kPa (15.7 psi), and the medium pressure generator which operates between 108.2 and 204.7 kPa (29.7 psi). The latter is more prevalent in the United States.

There are numerous variations in the design of commercially available carbide-to-water acetylene generators. Basically, however, they are practically identical in that they consist of a water vessel or reaction chamber, a carbide feed mechanism, and a carbide storage container that empties into the feed mechanism. The water vessel is equipped with a means of filling with water and draining the lime slurry. Agitation, either hand or power driven, is provided for keeping the lime hydrate and reacting carbide in suspension. Pressure gauges and relief devices are also incorporated in the generating chamber. The water shell or generating chamber in the more common generator supports the feed mechanism and the carbide hopper, which is also fitted with pressure gauges and safety relief valves. The valved gas outlet from the generator leads directly to a flash arrester that protects the equipment against flashbacks originating from acetylene-consuming equipment downstream. The gas in the high capacity generator, owing to the higher operating temperatures, is first cooled in a water scrubber, which is an integral part of the generator, before passing through the flash arrester. The continuous supply of cooling water in the scrubber is also a source of water for the reaction with carbide. Most commercial acetylene generators are fitted with either mechanical, pneumatic, or electrical interference mechanisms which for safety reasons enforce a prescribed sequence of procedures for the operator using the equipment. Some of these safety mechanisms are high and low water level shutdown, high temperature cut out, high acetylene pressure shutdown, and shutdown on loss of either electric or pneumatic power to the generator controls. All safety conditions must be satisfied before start-up or during operation.

The gas demand dictates the rate of acetylene generation that is satisfied by the rate of carbide feed. One method of feed of properly sized carbide, which is used in medium pressure generators, employs gravity flow controlled by a valve activated by a spring-loaded rubber diaphragm. The motion of the diaphragm reflects the change of internal generator pressure and is transmitted to the carbide feed valve which, in turn, either opens or closes as the pressure decreases or increases; the generator operating pressure is set by the spring load applied to the rubber diaphragm. High capacity generators are equipped with screw conveyors for carbide feed with either constant speed on–off operation or of the variable-speed close-pressure control type. The on–off type is controlled by a simple electric pressure switch which pneumatically signals the required feed-screw operation to match the gas demand and can have pressure fluctuations up to 128.9 kPa (18.7 psi) or less.

Carbide-to-water generators exhibit a noticeable temperature rise in the course of normal operation. In properly designed units employing the recommended ratio of water to carbide, the temperature rises 21–27°C and thus attains a temperature on the order of 60–65°C. In high capacity continuous generators, where water addition is through sprays in the cooling tower or the generating chamber, temperatures in the slurry are allowed to rise to 82.2°C. With this type of generator the lime slurry must be dumped periodically to avoid flooding and there is a certain amount of gas lost each time. Since the solubility of acetylene in lime slurry is greatly diminished at 71.1–82.2°C, the gas loss through solubility is minimized by operation at these elevated temperatures.

Carbide of proper size, such as 14 ND or 6 × 2 mm, is important to the trouble-free operation of carbide-to-water generators. Larger size carbide interferes with the proper closing of the carbide valve causing uncontrolled feed. In screw feeds, the carbide size is limited only to the clearance between the screw and its housing. Generators that do not have continuous paddle agitation or water sprays to submerge and wet the freshly introduced carbide must use oiled carbide to reduce the reaction rate. Otherwise, small size (6 × 2 mm) carbide, which reacts rapidly with water, can be carried to the surface by the evolved gas where, without sufficient dissipation of heat, it can become incandescent and may initiate explosive decomposition of acetylene. Low pressure generators use a large grade of carbide, 35 × 9 mm. The low pressure generator is no longer made in the United States; however, some are still in use after >40 years of service. Any generator equipped with effective water sprays or paddles can use mixtures of dust carbide. It is imperative that the dust be completely wetted; otherwise, islands of dust will float on the surface where they can become incandescent and initiate explosive acetylene decomposition.

6.2. Water-to-Carbide Generation. This method of acetylene production has found only limited acceptance in the United States and Canada but has been used frequently in Europe for small-scale generation. The rate of generation is regulated by the rate of water flow to the carbide. Hazardous hot spots may occur and overheating may lead to the formation of undesirable polymer by-products. This method is, therefore, used mainly in small acetylene generators such as portable lights or lamps where the generation rate is slow and the mass of carbide is small.

6.3. Dry Generator. This water-to-carbide acetylene generation method is used in certain large-scale operations. The dry process uses about a kilogram of water per kilogram of carbide and the heat of reaction is dissipated by the vaporization of the water. Absolute control of the addition of water is critical and the reacting mass of dry lime and unreacted carbide must be continuously mixed to prevent hazardous localized overheating and formation of undesirable polymer by-products. The gas stream is filtered to remove lime dust. The dry lime by-product is considered to be advantageous compared to the wet lime by-product. Lime from dry generators is very fine and requires storage in silos or protection from scattering by wind currents. Transport must be in closed containers, such as bags.

6.4. Purification of Carbide Acetylene. The purity of carbide acetylene depends largely on the quality of carbide employed and, to a much lesser degree, on the type of generator and its operation. Carbide quality in turn is affected by the impurities in the raw materials used in carbide production, specifically, the purity of the metallurgical coke and the limestone from which the lime is produced. The nature and amounts of impurities in carbide acetylene are shown in Table 12.

The maximum amount of impurities in U.S. Grade B acetylene (111) (Carbide Generated Acetylene) is 2% on a dry basis. This gas meets commercial requirements for acetylene used in cutting and welding (qv). Production of U.S. Grade A acetylene (111) used in sensitive chemical reactions requires further purification to reduce impurities to 0.5%. There are four main impurities: phosphine [7803-51-2], ammonia [7664-41-7], hydrogen sulfide [7783-06-4], and organic sulfides. The purification involves oxidation of phosphine to phosphoric acid, the neutralization and absorption of ammonia, and the oxidation of hydrogen sulfide and organic sulfur compounds. Many processes are employed depending on the type and amount of impurities and the end use of the gas. These wet or dry processes range from simply passing the gas over purifying media to multistep chemical treatments.

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 where large volumes of

Table 12. **Impurities in Carbide Acetylene**

Type	Amount, approx
PH_3	a few hundred ppm
$(CH_2{=}CH)_2S$	100 ppm (as H_2S)
NH_3	a few hundred ppm
O_2	250 ppm or less
N_2	few tenths of a percent (<1.0)
ArH_3	3 ppm or less
CH_4, CO_2, CO, H_2	a few hundred ppm
SiH_4	10 ppm or less
$CH_2{=}CH{-}C{\equiv}CH$	50 ppm
$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$	50 ppm
$HC{\equiv}C{-}C{\equiv}H$	a few hundred ppm
$(CH_2{=}C{=}CH_2)^a$	traces (variable according to carbide quality)

[a] And other dienes, eg, hexadiene and butadienylacetylene; also methylacetylene.

gas have to be treated. Large-scale acetylene installations exclusively employ continuous, wet purification processes. Elaborate continuous purification methods have been developed in Europe, where at certain locations relatively low grade carbide is used to generate acetylene of low purity; these involve successive contact with water, dilute caustic solution, and chlorine–water or hypochlorite solution, followed in certain locations by a final treatment with activated carbon (112–114). Such an intensive purification of acetylene is beneficial in cases where the gas is to be used in processes employing sensitive catalytic systems.

7. Coproduct Acetylene From Steam Cracking

In the steam cracking of petroleum liquids to produce olefine, mainly ethylene, small concentrations of acetylene are produced. Although the concentrations are small, the large capacities of the olefin plants result in appreciable quantities of coproduct acetylene which, in many cases, are sufficient to satisfy the modest growth in acetylene demand due to specialty chemicals such as 1,4-butanediol (see ACETYLENE-DERIVED CHEMICALS). Because specifications for polymer-grade ethylene limit the acetylene contamination to <5 ppm, the refinery operator must decide on whether to hydrogenate the contaminte acetylene to ethylene or to separate it as a by-product. The decision is influenced by the concentration of the acetylene, which is sensitive to the composition of the feedstock and the severity of the cracking conditions, and the availability of an over-the fence use because acetylene by its nature cannot be economically transported any distance or stored. If a convenient use is available, it is generally cost-effective to recover the acetylene and sell it as a by-product, since it generally attracts a higher price than the ethylene.

The quantity of coproduct acetylene produced is sensitive to both the feedstock and the severity of the cracking process. Naphtha, for example, is cracked at the most severe conditions and thus produces appreciable acetylene; up to 2.5 wt% of the ethylene content. On the other hand, gas oil must be processed at lower temperature to limit coking and thus produces less acetylene. Two industry trends are resulting in increased acetylene output: (*1*) the ethylene plant capacity has more than doubled, and (*2*) furnace operating conditios of higher temperature and shorter residence times have increased the cracking severity.

7.1. Acetylene Recovery Process.

A process to recover coproduct acetylene developed by Linde AG (Fig. 11), and reduced to practice in 11 commercial plants, comprises three sections: acetylene absorption, ethylene stripper, and acetylene stripper.

Acetylene Absorption. The gaseous feedstock containing the C_2 hydrocarbons is introduced into the acetylene absorption tower at a pressure range of 0.6–3 MPa (6–30 bar) depending on availability within the process design of the olefin plant. The absorption takes place in a countercurrent lean solvent flow, which is preferably DMF and with less frequency *N*-methylpyrrolidinone (NMP). The overhead gas fraction is partially condensed against refrigerant to avoid any solvent losses. The acetylene absorption tower is designed from thermodynamic and hydraulic points of view to minimize the acetylene content in the

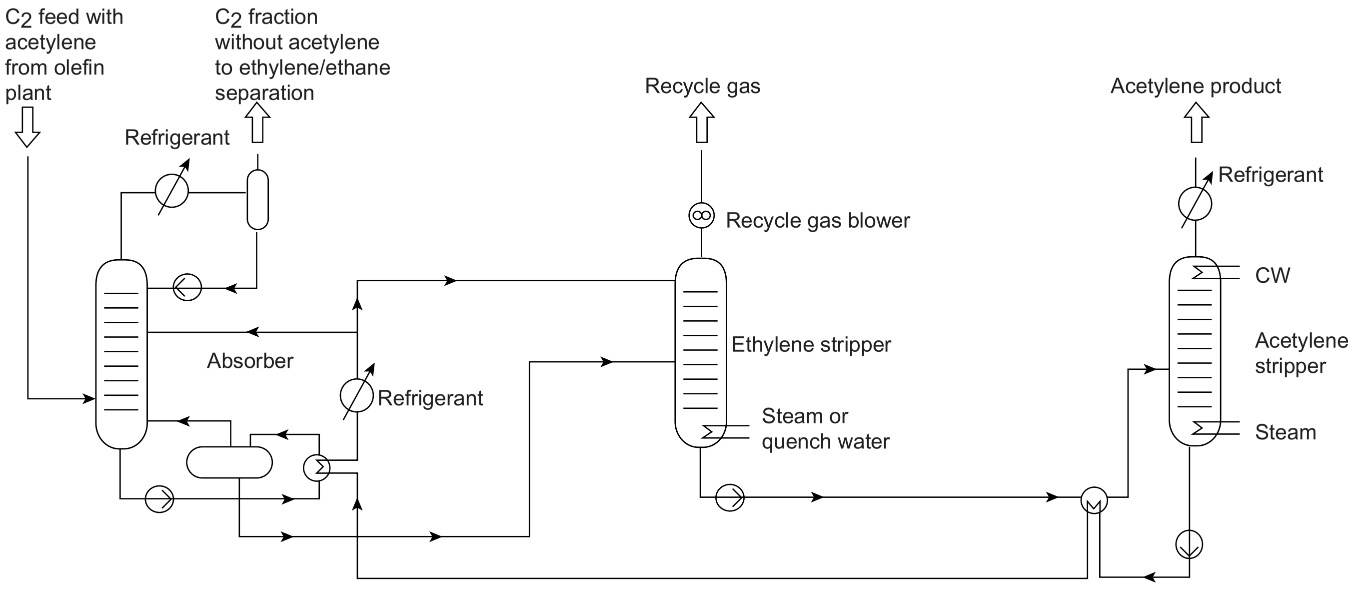

Fig. 11. Linde AG acetylene recovery unit for acetylene absorption, ethylene stripping, and acetylene stripping. CW = cooling water. Courtesy of P. Cl. Haehn, Linde AG.

overhead product (<0.2 ppm) and the recycle flow rate to the cracked gas compressor in the olefin plant ($<2\%$).

Elthylene Stripping. The acetylene absorber bottom product is routed to the ethylene stripper, which operates at low pressure. In the bottom part of this tower, the loaded solvent is stripped by heat input according to the purity specifications of the acetylene product. A lean dimethylformamide fraction is routed to the top of the upper part for selective absorption of acetylene. This feature reduces the acetylene content in the recycle gas to its minimum (typically 1%). The overhead gas fraction is recycled to the cracked gas compression of the olefin plant for the recovery of the ethylene.

Acetylene Stripping. The loaded solvent with acetylene and traces of other basically olefinic components is pumped to the acetylene stripper tower for the delivery of the acetylene product in the overhead (typically 99.9% purity minimum). Solvent traces can be eliminated by chilling or water washing depending on downstream process requirements. The bottom product (lean solvent) is pumped back to the acetylene absorber and ethylene stripper towers after exchanging the maximum possible amount of its energy within the recovery process of economic reasons. The recovery process uses commercial solvents ithout the addition of an antifoaming agent. The applied solvents are not corrosive or fouling.

8. Acetylene from Coal

Coal, considered a solid hydrocarbon with a generic formula of $CH_{0.8}$, was explored by numerous workers (115–122) as a feedstock for the production of acetylene. Initially, the motivation for this work was to expand the market for the use of coal in the chemical process industry, and later when it was projected that the cost of ethylene would increase appreciably if pretroleum resources were depleted or constrained.

Acetylene traditionally has been made from coal (coke) via the calcium carbide process. However, laboratory and bench-scale experiments have demonstrated the technical feasibility of producing the acetylene by the direct pyrolysis of coal. Researchers in Great Britain (115,119), India (116), and Japan (118) reported appreciable yields of acetylene from the pyrolysis of coal in a hydrogen-enhanced argon plasma. In subsequent work (120), it was shown that the yields could be dramatically increased through the use of a pure hydrogen plasma.

Based on the bench-scale data, two coal-to-acetylene processes were taken to the pilot-plant level. These were the AVCO and Hüls arc-coal processes. The Avco process development centered on identifying fundamental process relationships (120). Preliminary data analysis was simplified by first combining two of three independent variables, power and gas flow, into a single enthaply term. The variation of the important criteria, specific energy requirements (SER), concentration, and yield with enthalpy are indicated in Figure 12. As the plots show, minimum SER is achieved at an enthalpy of $\sim$5300 kW/(m^3/s) (2.5 kW/cfm), whereas maximum acetylene concentrations and yield are obtained at about 7400 kW/(m^3/s) (3.5 kW/cfm). An operating enthalpy between these two values

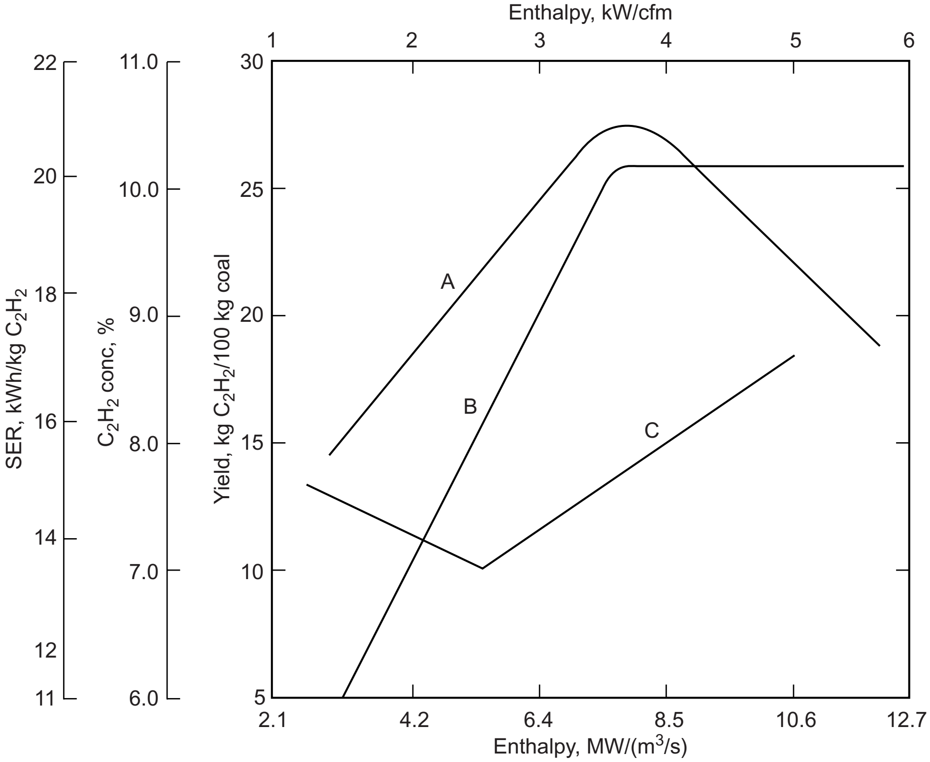

Fig. 12. Critical process parameters as a function of gas enthalpy where A is yield, B is concentration, and C is the specific energy requirement (SER).

should, therefore, be optimum. Based on the results of this work and the need to demonstrate the process at sufficient size to judge industrial applicability, AVCO built and operated a 1 MW reactor in 1979–1982. This project was jointly funded by the U.S. Department of Energy (121).

The AVCO reactor design is called a rotating arc reactor. In this design (Fig. 13), the arc is spread out radially from a center cathode to the walls that serve as the anode. In order to ensure temperature uniformity of the gas as well as the reactor wall, the arc is rotated using a magnetic field. The coal, which has been ground to conventional power plant grind, ie, 80% through a 74 μm (200 mesh) screen, is suspended in a hydrogen carrier gas and is fed through the top of the arc-coal reactor. The acetylene formed in the arc region is stabilized by rapidly quenching the gas stream to below 1400 K using a variety of quench media (hydrogen, methane, coal, hydrocarbons, water, etc).

The overall energy efficiency of the arc reactor is greatly enhanced by using a two-stage approach, ie, by using a chemically active quench in which further acetylene is produced. The active quench takes advantage of the latent heat of the gas below the arc to form additional acetylene. Two quench materials inverstigated were additional coal and a hydrocarbon (propane). In each case, the additional feed was injected below the arc reactor zone. Included in these experiments was a secondary water quench to freeze the acetylene yield.

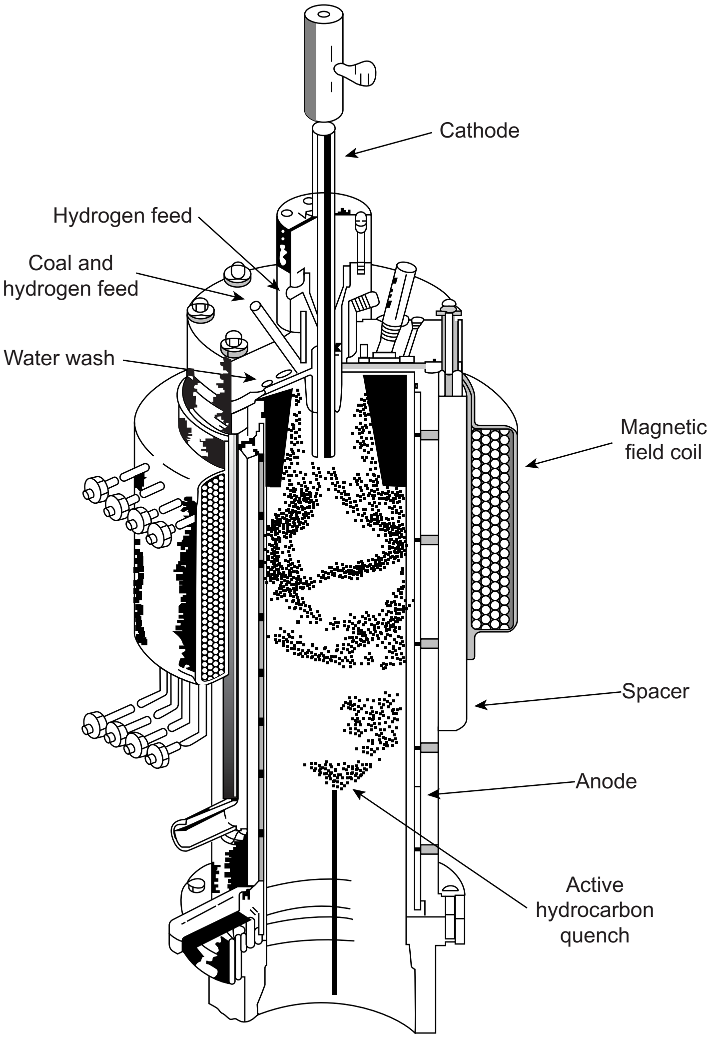

Fig. 13. AVCO rotating arc reactor.

An analytical model of the process has been developed to expedite process improvements and to aid in scaling the reactor to larger capacities. The theoretical results compare favorably with the experimental data, thereby lending validity to the application of the model to predicting directions for process improvement. The model can predict temperature and compositional changes within the reactor as functions of time, power, coal feed, gas flows, and reaction kinetics. It therefore can be used to project optimum residence time, reactor size, power level, gas and solid flow rates, and the nature, composition, and position of the reactor quench stream.

The economics of the arc-coal process is sensitive to the electric power consumed to produce a kilogram of acetylene. Early plant economic assessments indicated that the arc power consumption ($\mathrm{SER} = \mathrm{kW} \cdot \mathrm{h/kg}C_2H_2$ must be below

13.2. The coal feedcoal quench experiments yielded a 9.0 SER with data that indicated a further reduction to below 6.0 with certain process improvements. In the propane quench experiment, ethylene as well as acetylene is produced. The combined process SER was 6.2 with a C_2H_2/C_2H_4 production ratio of 3:2. Economic analysis was completed utilizing the achieved acetylene yields, and an acetylene price ~35% lower than the price of ethylene was projected.

In subsequent work at Hüls (122) similar results were obtained. That is, using German coals it was also found that the magnetically rotated arc was the preferred reactor design and that the product mixture could be enriched through the use of a hydrocarbon quench. In this two-stage reactor, a SER of 11.5 kW · h/kg C_2H_2 was achieved, but it was projected that this could be reduced through further development work.

9. Shipment and Handling

The design of equipment for the handling and use of acetylene must take into consideration the possibility of acetylene decompositions. The design parameters must consider various factors, namely, pressure, temperature, source of ignitions, and ultimate pressures which may result from a decomposition. Decompositions do not occur spontaneously but must have a source of ignition. Decompositions in small vessels and short piping systems used at moderate pressures of 103 kPa (15 psi) result in a maximum pressure not greater than ~12 times the initial pressure (1240 kPa or 180 psi), in this example. Theoretically, during constant volume deflagration at ~100 – 500 kPa (1–5 atm) without loss of heat, the pressure rises to 11.5–12 times the initial pressure. The minimum acetylene pressure at which a deflagration flame can propagate throughout a long tube of any diameter has been determined experimentally. As a typical example, acetylene deflagrates in a 2.54-cm inside diameter tube at pressures above 241 kPa (35 psi) and a detonation does not develop. In pipelines of considerable lengths and of diameter sufficient to permit a true detonation to develop, the maximum pressure developed is ~50 times the initial pressure. Thus, the maximum pressure expected in a 2.54-cm inside diameter tubing at 277 kPa (40 psi) is 13.8 MPa (277 kPa × 50). In long pipelines, an effect called cascading may develop in which case the maximum pressure may be several hundred times the initial pressure.

Exact design criteria on equipment for handling acetylene is not readily available because of the great number of factors involved. However, recommendations have been made concerning the equipment, piping, compressors, flash arresters, and proper materials (69,123–125).

9.1. Acetylene in Cylinders. Acetylene cylinders are constructed to stabilize acetylene and, thereby, safely avoid the hazard of a detonation (126). Cylinders constructed for other gases do not have the same features and it is extremely important that such cylinders not be charged with acetylene. Likewise, acetylene cylinders should not be charged with other gases, even though they are capable of containing those gases up to the service pressure of the cylinder. The basic feature of an acetylene cylinder that is different from all other cylinders is that it is entirely filled with a monolithic porous mass. It is this monolithic mass that stabilizes the acetylene and permits its safe shipment. The monolithic mass is a unique technical development because it must have high porosity (up to 92%) to be economical and yet possess sufficient strength that it will not break down, crack, or crumble during many years of service. Thus whereas the porous mass completely fills the interior of the cylinder, it occupies only ~10% of the total volume. There is a slight clearance between the outside surface of the filler mass and the inside surface of the pressure shell, through which the acetylene flows to the valve for discharge. After the cylinder has been manufactured, a specified quantity of solvent is added, usually acetone. Acetone dissolves many times its own volume of acetylene and its purpose is to increase the amount of acetylene that may be safely charged and shipped. The acetylene is, therefore, not a free gas but is in solution. The solubility of acetylene in acetone increases with rising pressure and with diminishing temperature. Thus a pressure gauge attached to an acetylene cylinder reads the solution pressure and is not a direct measure of the amount of acetylene contained. The pressure is greatly affected by changes in cylinder temperature. For example, the gauge pressure of a cylinder may be 1590 kPa (230 psi) when the temperature is 21°C, and <692 kPa (100 psi) at -17.7°C without any acetylene having been withdrawn. It is therefore obvious that the contents of an acetylene cylinder, unlike oxygen or nitrogen cylinders, cannot be determined accurately by pressure gauge readings alone. Acetylene cylinder contents can, however, be accurately measured by weight, and it is on this basis that cylinder charging operations are conducted. Weight of acetylene can be converted into standard volume (atmospheric pressure, and 21°C) by the factor of 0.906 L/kg (14.7 ft^3/lb).

Acetylene cylinders are fitted with safety devices to release the acetylene in the event of fire. Cylinders manufactured in the United States are equipped with safety devices which contain a fusible metal that melts at 100°C. In large cylinders the safety devices are in the form of a replaceable, threaded steel plug with a core of fusible metal. Small cylinders (0.28 and 1.12 m^3; 10 and 40 ft^3, respectively) may have the fusible metal in passages in the cylinder valve.

The most common sizes of acetylene cylinders are those with nominal capacities of 0.28, 1.12, 2.80, 8.4, and 11.2 m^3 (10, 40, 100, 300, and 400 ft^3). The largest size produced in any quantity is about 28.0 m^3 (1000 ft^3) capacity and is commonly referred to as a lighthouse cylinder because of its use in lighting buoys, etc, for marine navigation purposes.

The manufacture and shipping of acetylene cylinders in the United States are in compliance with the specifications and regulations of the Department of Transportation (127). The specifications are verified by the Bureau of Explosives of the American Association of Railroads. DOT-8 and DOT-8AL specify the requirements for manufacture and testing of steel shell, porous mass, and quantity of acetone (therefore, acetylene) which may be charged. These regulations specify such things as the chemical analysis and physical properties of the shell material, certain critical fabrication limits, heat treatment and the tests which must be conducted on each cylinder, as well as destructive sampling tests. To be a legal article of commerce, each cylinder must bear the following markings: DOT Specification (for 8AL), serial number, registered symbol, inspector symbol, date of manufacture, and tare weight. The cylinder must be registered with the Bureau of Explosives through a manufacturing report which also includes the test results for that group of cylinders.

The tare weight (sometimes called stencil weight because it is cut into the cylinder metal) is the total weight of the cylinder and contents, but does not include a removable valve protection cap, if such is used. The saturation gas part of the tare weight is a calculated number which allows for the 11.4 g of acetylene required to saturate each 453.6 g of contained acetone at atmospheric pressure. The correct tare weight is an absolute necessity to the safe charging of acetylene cylinders.

The specifications set the maximum vol% of solvent that may be added to the cylinder shell (measured by its water capacity). The volume of solvent also varies with the capacity of the cylinder. Cylinders in the 90–92% porosity range with a capacity >9.1 kg of water may contain a maximum acetone charge of 43.4%, whereas those with 9.1 kg or less water capacity may contain up to 41.8 vol %. The first category of cylinders are normally referred to as welding cylinders and the latter as small tanks (those with 0.28 and 1.12 m^3 acetylene capacity).

The volume of acetylene that may be charged is limited by the DOT regulations to the amount that would produce an equilibrium pressure of 1833 kPa (266 psi) at 21°C. This maximum ratio by weight is 0.58 units of acetylene per unit of acetone. Welding cylinders designed and charged to these limits have a liquid-full temperature of ~65.5°C and the small tanks have a liquid-full temperature of ~79.4°C. The liquid-full temperature represents the point at which the liquid (acetylene–acetone) has expanded to completely fill the container. The DOT regulations specify that an acetylene cylinder shall not be filled and shipped at a pressure that would exceed the equivalent pressure of 1833 kPa at 21°C. A cylinder designed to the limits indicated above and charged to 1833 kPa at 21°C would have a pressure of ~2142 kPa (311 psi) at 32°C.

The DOT regulations also stipulate that prior to manufacture of cylinders of new design, or with substantially modified design, prototype cylinders must pass a set of Designed Qualification Tests administered by the Bureau of Explosives. These tests include a drop test to show that the porous mass will not compact, break down, or disintegrate during normal use; a flash test to show that the porous mass–acetone–shell combination will extinguish a flash that enters the cylinder (this requirement is the heart of acetylene cylinder design); a fire test to show the adequacy of the safety devices; and an impact test to show that the full charge of acetylene is stable under conditions such as falling off a fast-moving truck.

After a design has proved to be satisfactory by passing these tests, the regulations require inspection during manufacture to make certain that the cylinders produced are of equal quality.

Filling Cylinders with Acetylene. The filling and shipping of acetylene cylinders are subject to the regulations of the U.S. Department of Transportation. To completely charge acetylene cylinders in a reasonable period of time requires compression of acetylene to pressures >1833 kPa, usually in the range of 2074–2419 kPa (300–350 psi). Because acetylene at these pressures detonates, if a source of ignition is present, the cylinder charging plant must be carefully designed and constructed taking into account all of the safety hazards. The acetylene industry has prepared a basic set of guidelines (125).

Many factors must be taken into account in the charging operation, such as the rate of charging, cooling during charging, and interstage cooling of the gas to remove as much water as possible prior to the final drying. Water reduces the quantity of acetylene which may safely be carried, because the solubility of acetylene in water is less than in acetone. Other important factors include the mechanical reliability of the cylinder, valves and safety devices, the residual acetylene, and the presence of sufficient acetone to maintain the 0.58 ratio of acetylene/solvent. The charging of acetylene cylinders can be hazardous and should only be undertaken with the consent of the owner and by persons having full knowledge of the subject (128).

10. Economic Aspects

The relative economics of acetylene for chemical uses from calcium carbide and from hydrocarbon partial combustion or arc processes have swung rather clearly in favor of the hydrocarbon-based processes. Even more economically attractive is the acetylene produced as an unavoidable by-product in the manufacture of ethylene (qv). The economics apply to chemical uses, not industrial gases where calcium carbide does have advantages of scale that overcome its higher production cost. However, the key economic factor in the use of acetylene is the lower price of alternative materials which have decreased or eliminated some of the largest outlets for acetylene. Acetylene's triple bond inherently consumes more energy of formation than olefins; thus acetylene is more expensive. There seems no likelihood of reversing the decline in acetylene usage unless there is a change in raw material costs or more by-product acetylene is recovered.

Most by-product acetylene from ethylene production is hydrogenated to ethylene in the course of separation and purification of ethylene. In this process, however, acetylene can be recovered economically by solvent absorption instead of hydrogenation. Commercial recovery processes based on acetone dimethylformamide, or *N*-methylpyrrolidinone have a long history of successful operation. This represents a small volume for an economically scale derivatives unit.

The average price of pipeline shipments of acetylene in the United States in 2001 ranged from \$0.63 to \$0.80/kg. The range of prices due to the different sources of the acetylene can only be roughly estimated since each process has by-products and coproducts which may be credited or debited in more than one way. However (129), the relative prices of acetylene by the three primary categories of process may be calculated to be 2:1.5:1 g from calcium carbide, from hydrocarbon partial combustion, and for by-product acetylene, respectively. Pricing of the by-product acetylene from ethylene production at a value equivalent to ethylene plus recovery costs could reverse the trend away from acetylene-based processes. There is a commercial swing toward this objective as high cost calcium carbide sources are shut down.

Acetylene from calcium carbide can be advantageous in that calcium carbide may be shipped to the point of acetylene usage and acetylene generated on the spot. This avoids the necessity for low pressure, low pressure-drop gaseous acetylene pipelines, or high pressure cylinders for shipping acetylene. The carbide route is the preferred method of operation for most industrial gas

Table 13. **U.S. Producers of Acetylene and their Capacitities**[a]

Producer	Capacity, $\times 10^6$ kg ($\times 10^6$ lb)
BASF, Geismar, La.	45.4 (100)
Borden Chemicals, Geismar, La.	90.7 (200)
Carbide-Graphite Group, Calvert City, Ky, and Louisville, Ky.	34.0 (75)
ChevronPhillips, Cedar Bayou, Tex.	9.1 (20)
Dow, Seadrift, Tx.	5.4 (12)
Dow, Taft, La.	11.3 (25)
Dow, Texas City, Tex.	6.8 (15)
Equistar, LaPorte, Tex.	11.3 (25)
Rohm and Haas, Deer Park, Tex.	27.2 (60)
Total	*241.2 (532)*

[a] From Ref. 130.

operations. It is well suited to small-scale consumers. The high cost of acetylene in industrial gas applications reflects these scale, handling, and shipping factors.

Table 13 lists the producers of acetylene in the United States and their capacities. The capacity does not include industrial gas producers manufacturing acetylene from calcium carbide. The majority of the capacity is targeted for chemical use (~96%). This use includes acetylene black and supply to the industrial gas market. Most of the U.S. capacity, ~68%, is based on natural gas, 18% is based on ethylene coproduct, and 14% on calcium carbide (130).

In 2000, consumption of acetylene in the United States and Western Europe was 400×10^3t. Thirty-six percent was used for producing acetylenic chemicals (1,4-butanediol, vinyl ether, and *N*-vinyl-2-pyrrolidone), 27% was used to produce vinyl acetate monomer and vinyl chloride monomer. Consumption is expected to decline at a rate of 5% until 2005 in the U.S. Consumption is expected to decline slightly in Western Europe and to remain unchanged in Japan (131). For the year 2004, a demand of 98.4×10^6 kg (217×10^6 lb) is expected (130). Nearly all acetylene is consumed at the production site (131).

1,4-Butanediol accounts for ~90% of the demand for acetylene for producing acetylene chemicals. This demand is growing at a rate of 5%. Strong demand is for downstream intermediates, tetrahydrofuran and γ-butyolactone. A major use for butanediol is in resins for the automotive industry. The market for vinyl chloride is weak due to a soft market for poly(vinyl chloride) (130).

11. Analytical Methods

11.1. General Methods.

Traces of acetylene can be detected by passing the gas through Ilosvay's solution that contains a cuprous salt in ammoniacal solution. The presence of acetylene is indicated by a pink or red coloration caused by the formation of cuprous acetylide, Cu_2C_2. The same method can be used for the quantitative determination of acetylene in parts per billion concentrations; the copper acetylide is measured colorimetrically (132).

The preferred quantitative determination of traces of acetylene is gas chromatography, which permits an accurate analysis of quantities <1 ppm. This procedure has been highly developed for air pollution studies (133) (see AIR POLLUTION CONTROL METHODS). Other physical methods, such as infrared and mass spectroscopy, have been widely used to determine acetylene in various mixtures.

Acetylene can be determined volumetrically by absorption in fuming sulfuric acid (or more conveniently in sulfuric acid activated with silver sulfate); or by reaction with silver nitrate in solution and titration of the nitric acid formed:

$$\mathrm{HC{\equiv}CH + 3\,AgNO_3 \longrightarrow (AgC{\equiv}CAg)AgNO_3 + 2\,HNO_3}$$

The precipitated acetylide must be decomposed with hydrochloric acid after the titration as a safety measure. Concentrated solutions of silver nitrate or silver perchlorate form soluble complexes of silver acetylide (134). Ammonia and hydrogen sulfide interfere with the silver nitrate method, which is less accurate than the sulfuric acid absorption method. Acetylene and monosubstituted acetylenes may also be determined by means of potassium mercuric iodide and potassium hydroxide in methanol solution by back-titration of the excess potassium hydroxide (135).

$$\mathrm{2\,RC{\equiv}CH + K_2HgI_4 + 2\,KOH \longrightarrow (RC{\equiv}C)_2Hg + 4\,KI + 2\,H_2O}$$

11.2. Acetylene Derived from Calcium Carbide. The analysis of acetylene derived from calcium carbide includes the determination of phosphorus, sulfur, and nitrogen compounds that are always present in the crude gas. Gas chromatographic methods that are accurate and convenient have been developed for phosphine, arsine, hydrogen sulfide, and ammonia (136). Chemically, the quantitative determination of phosphorus and sulfur can be achieved by oxidation with calcium or sodium hypochlorite. Phosphine and hydrogen sulfide present in the gas are oxidized to phosphate and sulfate and are measured gravimetrically as phosphomolybdate and barium sulfate, respectively. Ammonia is determined by the Nessler method after absorption in dilute hydrochloric acid. Oxygen, if present, can be determined by gas chromatography or by paramagnetic oxygen analyzer. It can also be determined chemically by absorption in alkaline pyrogallol after the acetylene has been removed by fuming sulfuric acid (20%) or it can be determined electrometrically after removal of interfering impurities. Qualitatively, hydrogen sulfide and phosphine can be detected in concentrations as low as 10 ppm by the brown to black discoloration of moist silver nitrate paper.

11.3. Acetylene Derived from Hydrocarbons. The analysis of purified hydrocarbon-derived acetylene is primarily concerned with the determination of other unsaturated hydrocarbons and inert gases. Besides chemical analysis, physical analytical methods are employed such as gas chromatography, infrared (ir), ultraviolet (uv), and mass spectroscopy. In industrial practice, gas chromatography is the most widely used tool for the analysis of acetylene. Satisfactory separation of acetylene from its impurities can be achieved using 50–80 mesh Porapak N programmed from 50–100°C at 4°C/min.

12. Health and Safety Aspects

Acetylene has a faint ethereal odor. Commercial-grade acetylene has a garliclike odor. The odor threshold is 657.2 mg/m^3 (137).

The NIOSH REL for acetylene is 2500 ppm as a ceiling. OSHA and ACGIH treat acetylene as a simple asphyxiant (137).

13. Uses

Acetylene is used primarily as a raw material for the synthesis of a variety of organic chemicals (see ACETYLENE-DERIVED CHEMICALS). In the United States, this accounts for ~90% of acetylene usage and most of the remainder is used for metal welding or cutting. The chemical markets for acetylene are shrinking as ways are found to substitute lower cost olefins and paraffins for the acetylene, with some products now completely derived from olefinic starting materials.

13.1. Chemical Uses. In Europe, products such as ethylene, acetaldehyde, acetic acid, acetone, butadiene, and isoprene have been manufactured from acetylene at one time. Wartime shortages or raw material restrictions were the basis for the choice of process. Coking coal was readily available in Europe and acetylene was easily accessible via calcium carbide.

The principal chemical markets for acetylene at present are its uses in the preparation of vinyl chloride, and 1,4-butanediol. Polymers from these monomers reach the consumer in the form of surface coatings (paints, film, sheets, or textiles), containers, pipe, electrical wire insulation, adhesives, and many other products that total billions of kilograms. The acetylene routes to these monomers were once dominant but have been largely displaced by newer processes based on olefinic starting materials.

Vinyl chloride (chloroethene) was a significant market for acetylene (see VINYL POLYMERS), but is soft at present. The reaction of acetylene and hydrogen chloride is carried out in the vapor phase at 150–250°C over a mercuric chloride catalyst. The acetylene route is usually coupled with an ethylene chlorination unit so that the hydrogen chloride derived from cracking dichloroethane can be consumed in the reaction with acetylene. Thus one mole each of ethylene, acetylene, and chlorine give 2 mol of vinyl chloride with a minimum of by-products. The oxychlorination of ethylene, however, eliminates by-product hydrogen chloride and thus much of the incentive for using the acetylene-based process. Hard cracking of hydrocarbons to a 1:1 molar mixture of ethylene and acetylene for use as feedstock for vinyl chloride production is done primarily outside the United States.

Vinyl acetate (ethnyl acetate) is produced in the vapor-phase reaction at 180–200°C of acetylene and acetic acid over a cadmium, zinc, or mercury acetate catalyst. However, the palladium-catalyzed reaction of ethylene and acetic acid has displaced most of the commercial acetylene-based units (see ACETYLENE-DERIVED CHEMICALS; VINYL POLYMERS).

Minor amounts of acetylene are used to produce chlorinated ethylenes. Trichloroethylene (trichloroethane) and perchloroethylene (tetrachloroethene) are prepared by successive chlorinations and dehydrochlorinations (see

CHLOROCARBONS AND CHLOROHYDROCARBONS). The chlorinations take place in the liquid phase using uv radiation and the dehydrochlorinations use calcium hydroxide in an aqueous medium at 70–100°C. Dehydrochlorination can also be carried out thermally (330–700°C) or catalytically (300–500°C).

Tetrachloroethylene can be prepared directly from tetrachloroethane by a high temperature chlorination or, more simply, by passing acetylene and chlorine over a catalyst at 250–400°C or by controlled combustion of the mixture without a catalyst at 600–950°C (138). Oxychlorination of ethylene and ethane has displaced most of this use of acetylene.

Acetylene is condensed with carbonyl compounds to give a wide variety of products, some of which are the substrates for the preparation of families of derivatives. The most commercially significant reaction is the condensation of acetylene with formaldehyde. The reaction does not proceed well with base catalysis which works well with other carbonyl compounds and it was discovered by Reppe (139) that acetylene under pressure [304 kPa (3 atm), or above] reacts smoothly with formaldehyde at 100°C in the presence of a copper acetylide complex catalyst. The reaction can be controlled to give either propargyl alcohol or butynediol (see ACETYLENE-DERIVED CHEMICALS). 2-Butyne-1, 4-diol, its hydroxyethyl ethers, and propargyl alcohol are used as corrosion inhibitors. 2,3-Dibromo-2-butene-1,4-diol is used as a flame retardant in polyurethane and other polymer systems (see BROMINE COMPOUNDS; FLAME RETARDANTS).

Much more important is the hydrogenation product of butynediol, 1, 4-butanediol [110-63-4]. The intermediate 2-butene-1,4-diol is also commercially available but has found few uses. 1,4-Butanediol, however, is used widely in polyurethanes and is of increasing interest for the preparation of thermoplastic polyesters, especially the terephthalate. Butanediol is also used as the starting material for a further series of chemicals including tetrahydrofuran, γ-butyrolactone, 2-pyrrolidinone, NMP, and *N*-vinylpyrrolidinone (see ACETYLENE-DERIVED CHEMICALS). The 1,4-butanediol market essentially represents the only growing demand for acetylene as a feedstock. This demand accounted for 90% demand for acetylene in 2001 (130).

A small amount of acetylene is used in condensations with carbonyl compounds other than formaldehyde. The principal uses for the resulting acetylenic alcohols are as intermediates in the synthesis of vitamins (qv).

Another small-scale use for acetylene is in the preparation of vinyl ethers from alcohols, including polyols and phenols. A base such as sodium or potassium hydroxide is used as catalyst in a liquid-phase high pressure reaction at 120–180°C. This general reaction is also a product of the acetylene research done at I. G. Farbenindustries by J. W. Reppe. A wide variety of alcohols can be vinylated, but only a few have achieved any commercial use. The most important is methyl vinyl ether (methoxyethene), which is used as a monomer and comonomer with maleic anhydride (Gantrez resins, GAF) for the preparation of adhesives, coatings, and detergents, as well as starting materials for further synthesis.

Acetylene black is prepared by the partial combustion of acetylene and has specialty uses in batteries.

Vinyl fluoride (fluoroethene), is manufactured from the catalyzed addition of hydrogen fluoride to acetylene. It is used to prepare poly(vinyl fluoride) which was found use in highly weather-resistant films (Tedlar film, Du Pont). Poly(vinylidene fluoride) also is used in weather-resistant coatings (see FLUORINE COMPOUNDS, ORGANIC). The monomer can be prepared from acetylene, hydrogen fluoride, and chlorine but other nonacetylenic routes are available.

At one time, the only commercial route to 2-chloro-1,3-butadiene (chloroprene), the monomer for neoprene, was from acetylene (see ELASTOMERS, SYNTHETIC, SURVEY). In the United States, Du Pont operated two plants in which acetylene was dimerized to vinylacetylene with a cuprous chloride catalyst and the vinyl acetylene reacted with hydrogen chloride to give 2-chloro-1, 3-butadiene. This process was replaced in 1970 with a butadiene-based process in which butadiene is chlorinated and dehydrochlorinated to yield the desired product (see CHLOROCARBONS AND CHLOROHYDROCARBONS).

13.2. Fuel Uses. At one time acetylene was widely used for home, street, and industrial lighting. These applications disappeared with the advent of electrical lighting during the 1920s. However, one of the first fuel uses for acetylen, metalworking with the oxyacetylene flame, continues to consume a significant amount of acetylene (140).

Fusion welding is the process of uniting metallic parts by heating the surfaces of the portions to be joined until the metal flows. Many electrical and chemical means are used to provide the heat for various welding processes, but the oxyacetylene flame remains the preferred choice of the gas welding processes. Cheaper fuels are available, such as propane and butane, but they do not reach the high flame temperature (3200°C) or achieve acetylene's combustion intensity (product of the burning velocity and the heating value of the fuel). The cheaper fuels are reserved for use in specialized applications where their properties are applicable. The oxyacetylene flame can be used in joining most meals and thus has a versatility advantage (see WELDING).

Large quantities of acetylene are used in metal cutting, which involves the combustion and melting of the metal; the oxyacetylene flame supplies the heat to initiate the process. Acetylene seems to have the advantage over other fuels because of the need for less oxygen and a shorter preheat time. Although oxyacetylene cutting is used in the field for construction and demolition, most cutting operations are performed in steel mills or fabricating shops.

Other uses of oxyacetylene flames in mill operations are in building up or hardfacing metal, lancing (piercing a hole in a metal mass), and a variety of metal cleaning procedures. A minor but interesting fuel use of acetylene is in flame spectrophotometry where oxygen and nitrous oxide are used as oxidants in procedures for a wide variety of the elements.

An internal combustion engine adapted to use an environmentally clean multifuel composition, comprising acetylene as a primary fuel and a combustible fuel, such as one or ore fluids selected from an alcohol such as ethanol, methanol or any other alcohol or alcohols from the group comprising C_1-C_{12} carbon chains, ethers such as from the group comprising dimethyl ether, diethyl ether, methyl *tert*-butyl ether, ethyl *tert*-butyl ether, *tert*-amyl methyl ether, diisopropyl ether, etc., low molecular weight esters such as from the group comprising methyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, ethyl malate, and butyl malate, or other suitable combustible fluid such as mineral spirits, as a secondary fuel for operatively preventing early ignition and knock arising from the primary fuel has been described (141).

13.3. Other. In a new strategy called "click" chemistry recently developed ar Scripps Research Institute, reactive molecular building blocks are designed to click together selectively and covalently. The expanded strategy is the use of chemical and biological receptor structures as templates to guide the formation of click products.

The reactive building blocks that are focused on at present have azide and acetylene groups that combine readily with each other (when in close proximity to each other) to from triazoles. Triazoles have been prepared that can inhibit the disease-associated enzyme, acetylcholinesterase. Acetylcholinesterase is a crucial enzyme in the mammalian nervous system and a current target for drugs to alleviate Alzheimer's disease (142).

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