Acetylene

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

Acetylene [*74-86-2*] is the simplest hydrocarbon with a triple bond. In the days before oil gained widespread acceptance as the main feedstock of chemical industry, acetylene was the predominant building block of industrial organic chemistry. The calcium carbide process was the sole route for acetylene production until 1940, when thermal cracking processes using methane and other hydrocarbons were introduced. At first, these processes used an electric arc; then, in the 1950s, partial oxidation and regenerative processes were developed.

However, along with the expansion of the petroleum industry there was a changeover from coal chemistry to petrochemistry, in the 1940s in the United States and in the 1950s in Europe. As a consequence, acetylene lost its competitive position to the much cheaper and more readily available naphtha-derived ethylene and other olefins. This competition between acetylene and

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ethylene as feedstocks for chemical industry has been much discussed in the 1960s and 1970s [1, 2]. The few hopes, such as BASF's contribution to the submerged flame process, Hoechst's crude oil cracking (HTP), or Hüls' plasma process, have not halted the clear trend toward ethylene as a basic chemical. With the first oil price explosion in 1973, the development of crude cracking processes suffered a setback, and the new processes, such as the Kureha/Union Carbide process, DOW's PCC process (PCC = partial combustion cracking), or the Kureha/Chiyoda/Union Carbide ACR process (ACR = advanced cracking reactor), raise little hope for a comeback of acetylene chemistry. Acetylene production peaked in the United States at 480000 t in the 1960s, and in Germany at 350000 t in the early 1970s [3]. Since then, acetylene production has decreased steadily. In both countries the losses were principally in carbide-derived acetylene; in fact, Germany has produced acetylene for chemical purposes almost exclusively from natural gas and petrochemical sources since 1975.

All acetylene processes, including carbide processes, are high-temperature processes, requiring a large amount of energy. They differ essentially only in the manner in which the necessary energy is generated and transferred. They can be classified into three groups: partial combustion processes, electrothermic processes, and processes using heat carriers. Finally, the use of byproduct acetylene from olefin plants is economically viable in many cases. For each group of acetylene processes several variants have been developed using various feedstocks and techniques. Today, only three processes remain for the commercial production of acetylene: the *calcium carbide route*, in which the carbide is produced electrically, the *arc process*, and the *partial oxidation of natural gas*. Other once popular processes have become uneconomical as the price of naphtha has increased.

Some processes were shelved in the experimental or pilot-plant stage as the importance of acetylene declined. However, other new processes involving the use of coal, sulfur-containing crude oil, or residues as feedstocks for acetylene production are in the pilot-plant stage.

However, the position of acetylene in chemical industry may improve because of the variety of valuable products to which acetylene can be converted with known technology and high yields.

2. Physical Properties

Due to the carbon–carbon triple bond and the high positive energy of formation, acetylene is an unstable, highly reactive unsaturated hydrocarbon. The C – C triple bond and C – H σ bond lengths are 0.1205 and 0.1059 nm, respectively. For the electronic structure of acetylene and a molecular orbital description, see [4]. The acidity of acetylene ($pK_a = 25$) permits the formation of acetylides (see Section 3.2). For comparison the pK_a value of ethylene is 44 and that of acetone 20.

Under normal conditions acetylene is a colorless, nontoxic but narcotic gas; it is slightly lighter than air. The main physical properties are listed in Table 1. The critical temperature and pressure are 308.32 K and 6.139 MPa. The triple point at 128.3 kPa is 192.4 K. The vapor pressure curve for acetylene is shown in Figure 1.

Table 1. Physical properties of acetylene [5–8]

Molecular mass	26.0379
Critical temperature	308.32 K (35.17 °C)
Critical pressure	6.139 MPa
Critical volume	0.113 m^3/kmol
Triple point	192.4 K (– 80.75 °C)
Triple point pressure	128.3 kPa
Normal sublimation point and normal boiling point	189.15 K (– 84.0 °C)
Crystal transition point	133.0 K (– 140.15 °C)
Enthalpy of transition	2.54 kJ/mol
Density	760.2 kg/m^3 (131 K) 764.3 kg/m^3 (141 K)
Density (liquid C_2H_2)	465.2 kg/m^3 (273.15 K)
Density (gaseous C_2H_2 at 1 bar)	1.095 kg/m^3 (288.15 K)
Molecular volume (0 °C, 1.013 bar)	22.223 m^3/kmol
Enthalpy of vaporization (calculated)	10.65 kJ/mol (273.15 K)
Enthalpy of sublimation	21.168 kJ/mol (5.55 K)
Enthalpy of formation	227.5 ± 1.0 kJ/mol (298.15 K)
Gibbs free energy of formation	209.2 ± 1.0 kJ/mol (298.15 K)
Entropy of formation	200.8 J mol^{-1} K^{-1} (298.15 K)
Enthalpy of combustion	−1255.6 kJ/mol (298.15 K)
Higher heating value	50 400 kJ/kg
Lower heating value	48 700 kJ/kg
Vapor pressure	2.6633 MPa (273.15 K)
Thermal conductivity	0.0184 W m^{-1} K^{-1} (0 °C, 1.013 bar)
Heat capacity (ideal gas state)	43.990 J mol^{-1} K^{-1} (298.15 K)

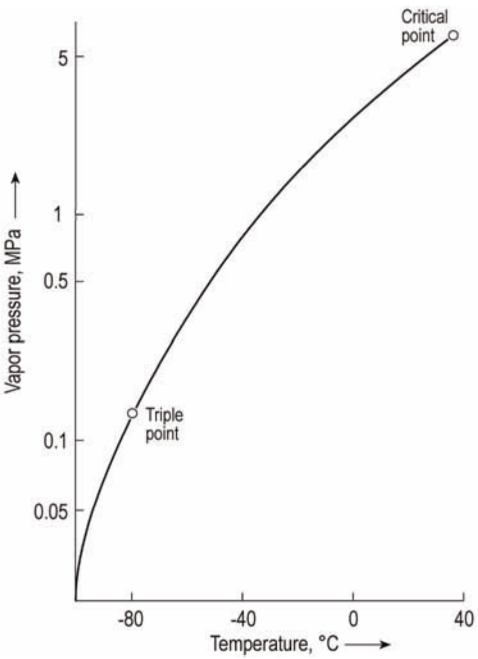


Figure 1. Vapor pressure of acetylene [5, 6]

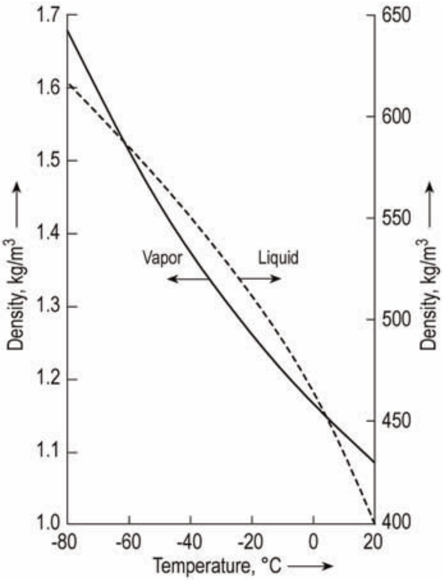


Figure 2. Density of acetylene vapor (at 1.013 bar) and liquid

The formation of acetylene is strongly endothermic ($\Delta H_f = +\ 227.5$ kJ/mol at 298.15 K).

Self-decomposition can be initiated when certain pressure limits above atmospheric pressure are exceeded (for details see Section 5.1).

The crystalline structure of solid acetylene changes at − 140.15 °C from a cubic to an orthorhombic phase. The heat of reaction for this phase change is 2.54 kJ/mol [7]; two different values for the enthalpy of fusion are reported in the literature [5, 6]. Figure 2 shows the density of liquid and gaseous acetylene.

Details about flame properties, decomposition, and safety measures are given in Chapter 5.

Solubility coefficients of acetylene in organic solvents are listed in Table 2 [9]. Further solubility data are available as Bunsen absorption coefficients α (20 °C, m^3 (STP) m^{-3} atm^{-1}), as solubilities (g/kg of solvent), and for different pressures (see [10]). The solubilities of acetylene at infinite dilution are shown in Figure 3 for water, methanol, DMF, and *N*-methyl-2-pyrrolidone (NMP) [*872-50-4*]. Figure 4 shows the solubility of acetylene in acetone for various partial pressures and temperatures. While at 20 °C and 1.013 bar 27.9 g (51.0 g) acetylene can be dissolved in 1 kg acetone (DMF) at 20.26 bar 689.0 g (628.0 g) can be dissolved in the same amount of solvent [129]. The heat of solution depends on the concentration of acetylene in the solvent: dissolving 0.5 kg of acetylene in 1 kg of solvent generates 293 kJ for acetone and 335 kJ for DMF. For details on the influence of

Table 2. Solubility coefficients of C_2H_2 in various solvents (in mol kg^{-1} bar^{-1}) [9]

Solvent	C_2H_2 pressure, bar	− 20 °C	25 °C
Methanol	0.98	1.979	0.569
Ethanol	0.98	0.851	0.318
n-Butanol	0.245 – 0.657		0.237
1,2-Dichloroethane	0.4–1.05	0.569	0.218
Carbon tetrachloride	0.98	0.164	0.075
n-Hexane	6.90	0.523	0.264
n-Octane	0.196 – 14.71	0.205	0.146 (0° C)
Benzene	0.98		0.225
Toluene	0.98	0.619	0.214
Xylene (tech.)	0.98	0.528	0.189
4-Methyl-1,3-dioxolan-2-one (propylene carbonate)	0.98	1.137	0.350
Tri-*n*-butylphosphate	0–0.4	2.366	0.614
Methyl acetate	0.98	2.912	0.878
Triethylene glycol	0.98		0.205
Acetone	0.98	4.231	1.069
N-Methyl-2-pyrrolidone	0.98	5.687	1.319
N,*N*-Dimethylformamide	0.98	5.096	1.501
Dimethyl sulfoxide	0.98		1.001
Ammonia	0.98	7.052	2.229

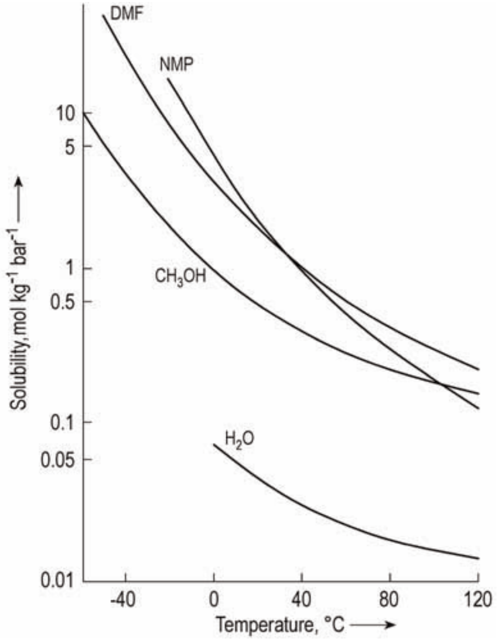


Figure 3. Solubility of acetylene in various solvents at infinite dilution

water, of partial pressure, and deviations from Henry's law, see [9, 10]. Only at temperatures above 25 °C and pressures < ca. 10 bar the solubility of acetylene in acetone follows Henry's law. At higher pressures the solubility increases more rapidly than predicted by Henry's law [130]. The temperature dependence of the solubility of acetylene in DMF at infinite dilution is compared with those of ethylene and ethane in Figure 5 (see also [9, 11] for selectivities).

The solubility of acetylene in water at 25 °C is 0.042 mol L^{-1} bar^{-1}. Under pressure of acetylene (e.g., > 0.5 MPa at 0 °C) and at temperatures between 268 and 283 K, waxy hydrates of the composition $C_2H_2 \cdot (H_2O)_{\sim 5.8}$ are formed [9, 10]. The hydrates can block equipment; shock waves may initiate self-decomposition.

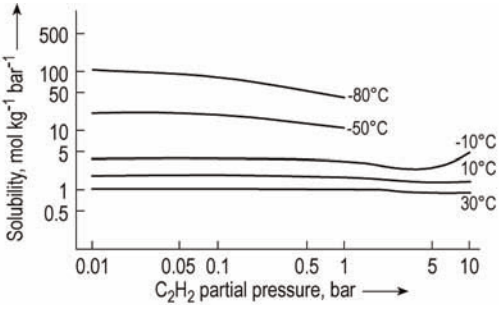


Figure 4. Solubility of acetylene in acetone [9]

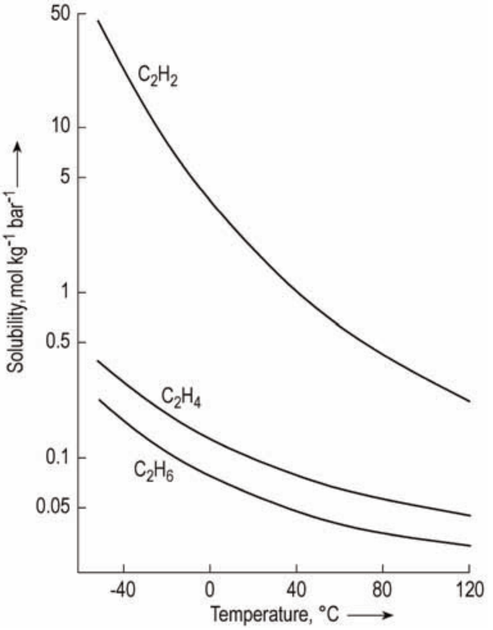


Figure 5. Solubility of C_2 hydrocarbons in DMF at infinite dilution

Liquid oxygen dissolves only traces of acetylene (5.5 ppm at 90 K [12]); the solubilities of ethylene and ethane in oxygen are much higher (factor of 350 and 2280, respectively). The prepurification of the process air in air separation plants with molecular sieves removes acetylene to < 1 ppb provided there is no breakthrough of carbon dioxide. This fact guarantees a safe operation of the downstream equipment [13].

Typical adsorption isotherms of acetylene are shown in Figure 6 for molecular sieves, activated carbon and silica gel at 25 °C [14]; additional information for activated carbon is summarized in [15].

3. Chemical Properties

Because of its strongly unsaturated character and high positive free energy of formation, acetylene reacts readily with many elements and compounds. As a result acetylene is used as raw material for a great variety of substances. Important are addition reactions, hydrogen replacements, polymerization, and cyclization.

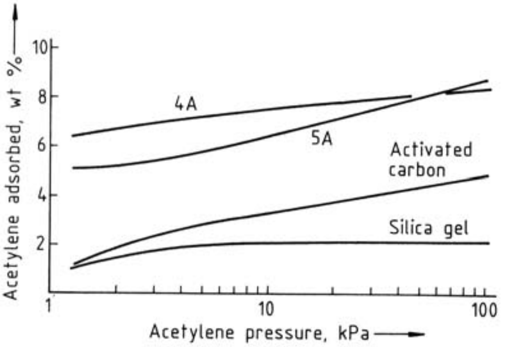


Figure 6. Adsorption isotherms for acetylene on 4A and 5A molecular sieves, activated carbon, and silica gel at 25 °C [14]

Acetylene is more susceptible to nucleophilic attack than, for instance, ethylene. In addition, the polarized C-H bond makes acetylene acidic (pK_a = 25) [16]. Because of this acidity, acetylene is very soluble in basic solvents [17, 18], forming hydrogen bonds with them [19]. Therefore, the vapor pressures of such solutions cannot be described by Raoult's law [20].

The development of the acetylene pressure reactions by W. Reppe (1892 – 1969), BASF Ludwigshafen (Germany) [21–23] began modern acetylene chemistry. The most interesting groups of reactions are vinylation, ethynylation, carbonylation, and cyclic and linear polymerization.

3.1. Industrially Important Reactions

Vinylation Reactions and Products [24]. Vinylation is the addition of compounds with a mobile hydrogen atom, such as water, alcohols, thiols, amines, and organic and inorganic acids, to acetylene to form vinyl compounds chiefly used for polymerization.

The two types of vinylation reactions are *heterovinylation* and the less usual *C vinylation.* In the former, the hydrogen atom originates from the heteroatoms O, S, and N, whereas C vinylation occurs when the mobile hydrogen atom is directly bound to a carbon atom. Examples of C vinylation are dimerization and trimerization of acetylene, the synthesis of acrylonitrile from acetylene and hydrogen cyanide, and the addition of acetylene to unsaturated hydrocarbons with activated hydrogen atoms, such as cyclopentadiene, indene, fluorene, and anthracene.

The first industrial vinylation products were acetaldehyde, vinyl chloride, and vinyl acetate. Many other products followed.

Some examples of industrial vinylation processes are given below:

Acetaldehyde [75-07-0] (→ Acetaldehyde):

$$HC \equiv CH + H_2O \rightarrow CH_3CHO$$

Catalyst: acidic solutions of mercury salts, such as $HgSO_4$ in H_2SO_4. Liquid-phase reaction at 92 °C.

Vinyl Chloride [75-01-4] (→ Chloroethanes and Chloroethylenes):

$$HC \equiv CH + HCl \rightarrow CH_2 = CHCl$$

Catalyst: $HgCl_2$ on coal. Gas-phase reaction at 150 – 180 °C.

Vinyl Acetate [108-05-04] (→ Vinyl Esters):

$$HC \equiv CH + CH_3COOH \rightarrow CH_2 = CHOOCCH_3$$

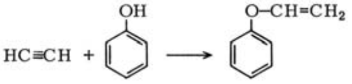
Catalyst: cadmium, zinc, or mercury salts on coal. Gas-phase reaction at 180 – 200 °C.

Vinyl Ethers (→ Vinyl Ethers), conjectured reaction steps:

$$ROH + KOH \xrightarrow{-H_2O} ROK \xrightarrow{C_2H_2} RO{-}CH{=}CHK$$
$$RO{-}CH{=}CHK + ROH \rightarrow RO{-}CH{=}CH_2 + ROK$$

where R is an alkyl group. Reaction temperature of 120 – 150 °C; pressure high enough to avoid boiling the alcohol used, e.g., 2 MPa with methanol to produce methyl vinyl ether (acetylene pressure reaction).

Vinyl Phenyl Ether [766-94-9], vinylation with KOH catalyst:



Vinyl Sulfides, KOH catalyst:

$$HC \equiv CH + RSH \rightarrow CH_2 = CH{-}S{-}R$$

Vinyl Esters of Higher Carboxylic Acids:

$$HC \equiv CH + R{-}COOH \rightarrow RCOO{-}CH = CH_2$$

Catalyst: zinc or cadmium salts. Liquid-phase reaction.

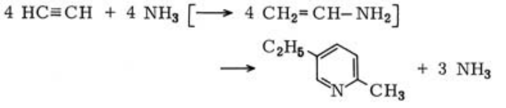
Vinyl Amines, vinylation with zinc or cadmium compounds as catalyst:

$$R^1R^2NH + HC \equiv CH \rightarrow R^1R^2N{-}CH = CH_2$$

where R^1 and R^2 are alkyl groups.

N-Vinylcarbazole [*1484-13-5*], vinylation of carbazole in a solvent, e.g., *N*-methylpyrrolidone, at 180 °C.

Vinylation of Ammonia, complex Co and Ni salts as catalysts, reaction temperature of 95 °C:



Vinylation of Acid Amides, potassium salt of the amide as catalyst:

$$HC \equiv CH + RCO{-}NH_2 \rightarrow RCO{-}NH{-}CH = CH_2$$

N-Vinyl-2-pyrrolidone [*88-12-0*], vinylation of 2-pyrrolidone with the potassium salt of the pyrrolidone as catalyst.

Acrylonitrile [107-13-1], C-vinylation of HCN in aqueous hydrochloric acid with CuCl and NH_4Cl catalyst:

$$HC \equiv CH + HCN \rightarrow H_2C = CH{-}CN$$

Ethynylation Reactions and Products

[25]. Ethynylation is the addition of carbonyl compounds to acetylene with the triple bond remaining intact. Reppe found that heavy metal acetylides (see Section 3.2), especially the copper(I) acetylide of composition $Cu_2C_2 \cdot 2\ H_2O \cdot 2\ C_2H_2$, are suitable catalysts for the reaction of aldehydes with acetylene. Alkaline catalysts are more effective than copper acetylide for the ethynylation of ketones. The generalized reaction scheme for ethynylation is:

$$HC \equiv CH + RCOR' \rightarrow HC \equiv C{-}C(OH)RR'$$

where R and R′ are alkyl groups or H.

The most important products from ethynylation are propargyl alcohol and butynediol.

Propargyl Alcohol, 2-propyn-1-ol [*107-19-7*] (→ Alcohols, Aliphatic):

$$CH \equiv CH + HCHO \rightarrow HC \equiv CCH_2OH$$

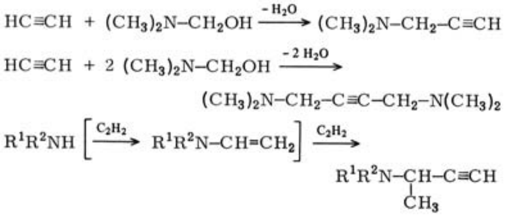
Catalyst: $Cu_2C_2 \cdot 2\ H_2O \cdot 2\ C_2H_2$.

Butynediol, 2-butyne-1,4-diol [*110-65-6*] (→ Butanediols, Butenediol, and Butynediol):

$$HC \equiv CH + 2\ HCHO \rightarrow HOCH_2C \equiv CCH_2OH$$

Catalyst: $Cu_2C_2 \cdot 2\ H_2O \cdot 2\ C_2H_2$.

Other examples of ethynylation are the reactions of aminoalkanol and secondary amines with acetylene:



$$HC{\equiv}CH + (CH_3)_2N{-}CH_2OH \xrightarrow{-H_2O} (CH_3)_2N{-}CH_2{-}C{\equiv}CH$$

$$HC{\equiv}CH + 2\ (CH_3)_2N{-}CH_2OH \xrightarrow{-2\,H_2O} (CH_3)_2N{-}CH_2{-}C{\equiv}C{-}CH_2{-}N(CH_3)_2$$

$$R^1R^2NH \left[\xrightarrow{C_2H_2} R^1R^2N{-}CH{=}CH_2\right] \xrightarrow{C_2H_2} R^1R^2N{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}C{\equiv}CH$$

Carbonylation Reactions and Products

[26]. Carbonylation is the reaction of acetylene and carbon monoxide with a compound having a mobile hydrogen atom, such as water, alcohols, thiols, or amines. These reactions are catalyzed by metal carbonyls, e.g., nickel carbonyl, $Ni(CO)_4$ [*13463-39-3*]. Instead of metal carbonyls, the halides of metals that can form carbonyls can also be used.

Acrylic Acid [79-10-7] (→ Acrylic Acid and Derivatives):

$$HC \equiv CH + CO + H_2O \rightarrow CH_2 = CH{-}COOH$$

The reaction of acetylene with water or alcohols and carbon monoxide using $Ni(CO)_4$ catalyst was first reported by W. Reppe [26]. If water is replaced by thiols, amines, or carboxylic acids, then thioesters of acrylic acid, acrylic amides, or carboxylic acid anhydrides are obtained.

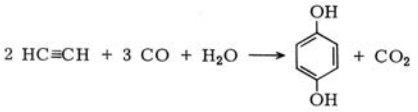
Ethyl Acrylate [140-88-5] (→ Acrylic Acid and Derivatives):

$$\begin{aligned} &4\ C_2H_2 + 4\ C_2H_5OH + Ni(CO)_4 + 2\ HCl \\ &\rightarrow 4\ \ CH_2 = CHOOC_2H_5 + H_2 + NiCl_2 \end{aligned} \tag{1}$$

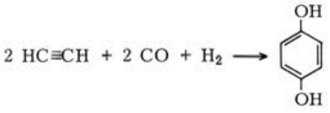
$$C_2H_2 + C_2H_5OH + CO \rightarrow CH_2 = CHCOOC_2H_5 \tag{2}$$

Catalyst: nickel salts. Reaction temperature: 30 – 50 °C. The process starts with the stoichiometric reaction (1); afterwards, most of the acrylate is formed by the catalytic reaction (2). The nickel chloride formed in the stoichiometric reaction (1) is recovered and recycled for carbonyl synthesis.

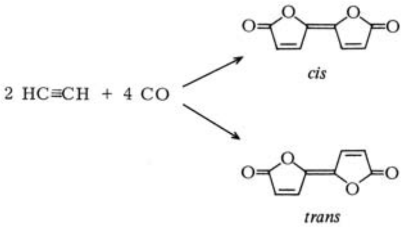
Hydroquinone [123-31-9] is formed in a suitable solvent, e.g., dioxane, at 170 °C and 70 MPa [27]. The catalyst is $Fe(CO)_5$:



Hydroquinone is formed at 0 – 100 °C and 5 – 35 MPa if a ruthenium carbonyl compound is used as catalyst [28]:



Bifurandiones: The reaction of acetylene and CO in the presence of octacarbonyldicobalt, $(CO)_3Co-(CO)_2-Co(CO)_3$ [*10210-68-1*], forms a cis–trans mixture of bifurandione. The reaction is carried out under pressure (20 – 100 MPa) at temperatures of about 100 °C [29]:



New aspects of such CO insertion reactions have been reported [30].

Cyclization and Polymerization of Acetylene In the presence of suitable catalysts, acetylene can react with itself to form cyclic and linear polymers.

Cyclization was first observed by BERTHELOT, who polymerized acetylene to a mixture of aromatic compounds including benzene and naphthalene. In 1940, REPPE synthesized 1,3,5,7-cyclooctatetraene [*629-20-9*] with a 70 % yield at an only slightly elevated pressure:

Reaction temperature of 65 – 115 °C, pressure of 1.5 – 2.5 MPa, $Ni(CN)_2$ catalyst.

The reaction is carried out in anhydrous tetrahydrofuran. The byproducts are mostly benzene (about 15 %), chain oligomers of acetylene of the empirical formulas $C_{10}H_{10}$ and $C_{12}H_{12}$, and a black insoluble mass, called niprene after the nickel catalyst.

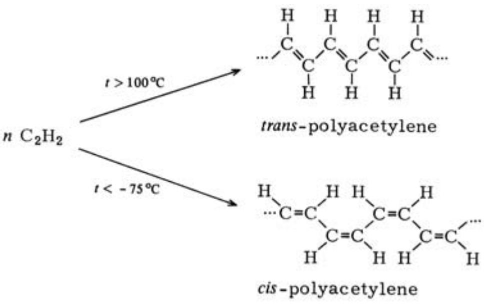
If dicarbonylbis(triphenylphosphine)nickel [*13007-90-4*], $Ni(CO)_2[(C_6H_5)_3P]_2$, is used as catalyst, the cyclization products are benzene (88 % yield) and styrene (12 % yield). The reaction is carried out in benzene at 65 – 75 °C and 1.5 MPa [31, 32].

Linear polymerization of acetylene occurs in the presence of a copper (I) salt such as CuCl in hydrochloric acid. Reaction products are vinylacetylene, divinylacetylene, etc. [33]:

$$HC \equiv CH + HC \equiv CH \rightarrow H_2C = CH-C \equiv CH$$

A particular polymerization product, known as *cuprene*, is formed when acetylene is heated to 225 °C in contact with copper sponge. Cuprene is chemically inert, corklike in texture, and yellow to dark brown.

Polyacetylene [34, 35] is formed with Ziegler–Natta catalysts, e.g., a mixture of triethylaluminum, $Al(C_2H_5)_3$, and titanium tetrabutoxide, $Ti(n\text{-}OC_4H_9)_4$, at 10^{-2} to 1 MPa:



Polymerization can be carried out in an auxiliary inert liquid, such as an aliphatic oil or petroleum ether. The monomer can also be copolymerized in the gas phase.

Polyacetylene is a low-density sponge-like material consisting of fibrils with diameters of 20 – 50 nm. The ratio *cis*- to *trans*-polyacetylene depends on the reaction temperature.

Polyacetylene doped with electron acceptors (I_2, AsF_5), electron donors (Na, K), or protonic dopants ($HClO_4$, H_2SO_4) is highly conductive and has the properties of a one-dimensional metal [35].

3.2. Other Reactions; Derivatives

Metal Acetylides [36]. The hydrogen atoms of the acetylene molecule can be replaced by metal atoms (M) to yield metal acetylides. Alkali and alkaline-earth acetylides can be prepared via the metal amide in anhydrous liquid ammonia:

$$C_2H_2 + MNH_2 \rightarrow MC_2H + NH_3$$

The direct reaction of the acetylene with a molten metal, such as sodium, or with a finely divided metal in an inert solvent, such as xylene, tetrahydrofuran, or dioxane, at a temperature of about 40 °C, is also possible:

$$2\ M + C_2H_2 \rightarrow M_2C_2 + H_2$$

The very explosive copper acetylides, e.g., $Cu_2C_2 \cdot H_2O$, can be obtained by reaction of copper(I) salts with acetylene in liquid ammonia or by reaction of copper(II) salts with acetylene in basic solution in the presence of a reducing agent such as hydroxylamine. Copper acetylides can also form from copper oxides and other copper salts. For this reason copper plumbing should be avoided in acetylene systems.

Silver, gold, and mercury acetylides, which can be prepared in a similar manner, are also explosive.

In sharp contrast to the highly explosive $Cu_2C_2 \cdot H_2O$, the catalyst used for the synthesis of butynediol, $Cu_2C_2 \cdot 2\ H_2O \cdot 2\ C_2H_2$, is not as sensitive to shock or ignition.

Halogenation. The addition of chlorine to acetylene in the presence of $FeCl_3$ yields 1,1,2,2-tetrachloroethane [*79-34-5*], an intermediate in the production of the solvents 1,2-dichloroethylene [*540-59-0*], trichloroethylene [*79-01-6*], and perchloroethylene [*127-18-4*].

Bromine and iodine can also be added to acetylene. The addition of iodine to acetylene stops with formation of 1,2-diiodoethylene.

Hydrogenation. Acetylene can be hydrogenated, partly or completely, in the presence of Pt, Pd, or Ni catalysts, giving ethylene or ethane.

Organic Silicon Compounds [37, 38]. The addition of silanes, such as $HSiCl_3$, can be carried out in the liquid phase using platinum or platinum compounds as catalysts:

$$HC \equiv CH + HSiCl_3 \rightarrow CH_2 = CH{-}SiCl_3$$

Oxidation. At ambient temperature acetylene is not attacked by oxygen; however, it can form explosive mixtures with air or oxygen (see Chap. 5). The explosions are initiated by heat or ignition. With oxidizing agents such as ozone or chromic acid, acetylene gives formic acid, carbon dioxide, and other oxidation products. The reaction of acetylene with dilute ozone yields glyoxal.

Hydrates. At temperatures below ca. 15 °C, under pressure, hydrates of the composition $C_2H_2 \cdot 6\ H_2O$ are formed (see Section 2).

Chloroacetylenes [39]

Monochloroacetylene, $HC{\equiv}CCl$, M_r 60.49, *bp* −32 to −30 °C, a gas with nauseating odor that irritates the mucous membranes, is obtained by reaction of 1,2-dichloroethylene with alcoholic NaOH in the presence of $Hg(CN)_2$. It ignites in the presence of traces of oxygen. In air it explodes violently. Chloroacetylene is very poisonous.

Dichloroacetylene, $ClC{\equiv}CCl$, M_r 94.93, *mp* − 66 to − 64.2 °C, a colorless oil of unpleasant odor, explodes in the presence of air or on heating. It is obtained from acetylene in strongly alkaline potassium hypochlorite solution [40] or by reaction of trichloroethylene vapor with caustic alkali.

4. Production

4.1. Thermodynamic and Kinetic Aspects

The production of acetylene from hydrocarbons, e.g.,

$$2\,CH_4 \rightleftharpoons C_2H_2 + 3\,H_2 \quad \Delta H\,(298\,K) = 376.4\,kJ/mol$$

requires very high temperatures and very short reaction times. The main reasons for the extreme conditions are the temperature dependence of the thermodynamic properties (molar enthalpy of formation, ΔH_f, and molar free energy of formation, ΔG_f) of the hydrocarbons; the position of the chemical equilibria under the reaction conditions; and the kinetics of the reaction.

Thermodynamic data relevant to the hydrocarbon–acetylene system are shown in Table 3 and Figure 7. These data show clearly that at normal temperatures acetylene is highly unstable compared to the other hydrocarbons. However, Figure 7 also shows that the free energy of acetylene decreases as temperature increases, whereas the free energies of the other hydrocarbons increase. Above about 1230 °C, acetylene is more stable than the other hydrocarbons. The temperature at which the acetylene line intersects an other line in Figure 7 is higher the shorter the chain length of the hydrocarbons. Acetylene production from methane requires higher reaction temperatures than production from heavier hydrocarbons.

The equilibrium curve for the methane reaction as a function of temperature (Fig. 8) shows that acetylene formation only becomes apparent above 1000 K (730 °C). Therefore, a very large energy input, applied at high temperature, is required.

However, even at these high temperatures acetylene is still less stable than its component elements, carbon und hydrogen (see Fig. 7). In fact, the large difference in free energy between acetylene and its component elements favors the decomposition of acetylene to carbon and hydrogen up to temperatures of about 4200 K.

Table 3. Standard molar enthalpies of formation and Gibbs free energy of formation at 298 K

	ΔH_f (kJ/mol)	ΔG_f (kJ/mol)
C (s)	0	0
H_2 (g)	0	0
CH_4 (g)	− 74.81	− 50.82
C_2H_2 (g)	+226.90	+209.30
C_2H_4 (g)	+ 52.30	+ 68.15
C_2H_6 (g)	− 84.64	− 32.90
C_3H_6 (g)	+ 20.43	+ 62.75
C_3H_8 (g)	−103.90	− 23.48
n-C_4H_{10} (g)	−126.11	− 17.10

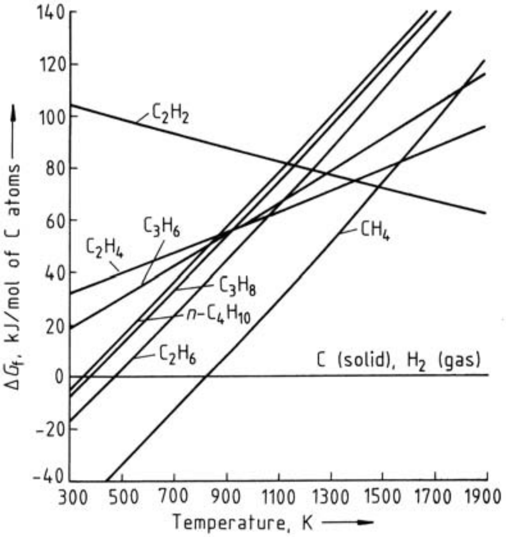


Figure 7. Gibbs free energy of formation per carbon atom of several hydrocarbons as a function of temperature

$$C_2H_2 \rightarrow 2\,C(s) + H_2\,(g) - \Delta G_f\,(298\,K) = -209.3\,kJ/mol$$

Thus cracking and recombination of the hydrocarbons and decomposition of acetylene compete. To achieve reasonable acetylene yields and to avoid the thermodynamically favorable decomposition into the elements, rapid quenching of acetylene produced in the cracking reaction is necessary. In practice, the residence time at high temperature is between 0.1 and 10 ms.

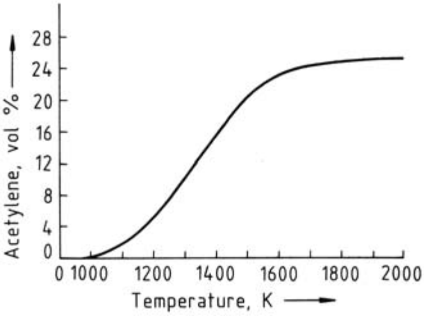


Figure 8. Equilibrium curve for the methane cracking reaction, $2\,CH_4 \rightleftharpoons C_2H_2 + 3\,H_2$

Higher temperatures also increase the rate of conversion of acetylene to byproducts. Again, the residence time must be sufficiently short to prevent this.

In the case of cracking by partial oxidation, the combustion reaction of the hydrocarbon supplies the energy necessary for the production of acetylene from the other part of the hydrocarbon feed:

$$CH_4+O_2 \rightarrow CO+H_2+H_2O \quad \Delta H \ (298\ K) = -277.53\ kJ/mol$$

$$CO+H_2O \rightarrow CO_2+H_2 \quad \Delta H \ (298\ K) = -41.19\ kJ/mol$$

From these reaction enthalpies, the amount of oxygen needed to produce the high reaction temperature can be calculated. Therefore, in addition to the short residence time, the correct methane : oxygen ratio, which also determines the reaction temperature, is essential to obtain good acetylene yields.

4.2. Partial Combustion Processes

In this group of processes, part of the feed is burnt to reach the reaction temperature and supply the heat of reaction. The necessary energy is produced where it is needed. Almost all carbon-containing raw materials can be used as feedstocks: methane, ethane, natural gas liquids (NGL), liquefied petroleum gas (LPG), naphtha, vacuum gas oil, residues, and even coal or coke. Natural gas is especially suitable because it is available in many parts of the world. Only under the conditions of acetylene synthesis can methane be transformed into another hydrocarbon in a single process step, and this is the essential reason for using the thermodynamically unfavorable acetylene synthesis.

The partial combustion processes for light hydrocarbons, from methane to naphtha, all follow similar schemes. The feed and a certain amount of oxygen are preheated separately and introduced into a burner. There they pass through a mixing zone and a burner block into the reaction zone, where they are ignited. On leaving the reaction zone the product mixture is cooled rapidly, either by water or oil. Cooling by water is easier, and more common, but it is thermally less efficient than cooling by oil. Alternatively, the gases can be cooled with light hydrocarbon liquids, which leads to additional acetylene and ethylene formation between 1500 and 800 °C. These processes are usually called *two-step processes*.

Burner design is very important for all partial combustion processes. The residence time of the gas in the reaction zone must be very short, on the order of a few milliseconds, and it should be as uniform as possible for all parts of the gas. Flow velocity within the reaction zone is fixed within narrow limits by the requirements of high yield and the avoidance of preignition, flame separation from the burner block, and coke depositions. A survey of the processes operating according to these principles is given in [7, 41]. Only the BASF process is described here in detail, because it is the most widely used process for the partial combustion of natural gas.

The *submerged flame process*, SFP, was developed by BASF with the aim of producing acetylene from crude oil or its heavy fractions, and thus to be independent of the more expensive refined oil products used in olefin chemistry. One unit of this kind was built in Italy, but it became uneconomic and was shut down after a year of operation [42]. Nevertheless, the process is described in some detail below because of its simple cracking section, because of the simultaneous formation of acetylene and ethylene, and because of its high thermal efficiency and its high degree of carbon conversion (perhaps of even greater importance in the future).

The *partial combustion carbide process*, also developed by BASF, uses coke, oxygen, and lime as feed. It was developed in the 1950s to reestablish the competitive position of carbide in the face of the new acetylene processes on a petrochemical–natural gas basis. Some attention is given here to the basics of this process, although it has never gone beyond the pilot-plant stage. When petrochemical feedstocks become scarce, this process may have a place in a future coalbased chemistry because it has a higher degree of carbon conversion and a higher thermal efficiency than the electric carbide process.

All these acetylene processes based on partial combustion yield a number of byproducts, such as hydrogen and/or carbon monoxide, which may cause problems if acetylene is the only product desired. Within a complex chemical plant, however, these may be converted to synthesis gas, pure hydrogen, and pure CO and can actually improve the economics of acetylene production.

4.2.1. BASF Process (Sachsse-Bartholome)

The BASF process for the production of acetylene from natural gas has been known since 1950 [43]. Worldwide, some 13 plants used this process in 1983, a total capacity of about 400000 t/a. All use a water quench, except the plant in Ludwigshafen (Germany) operated with an oil quench [44].

The basic idea of partial combustion involves a flame reaction on a premixed feed of hydrocarbon and oxygen. In this way the rate of hydrocarbon conversion is made independent of the gas-mixing rate, which is governed by diffusion. Only then can the residence time in the reaction zone be made much smaller than the average decay time of acetylene. The separate preheating of the reactants to the highest temperature possible before introduction into the burner reduces the consumption of oxygen and the hydrocarbon within the burner. It also causes a higher flame propagation speed and therefore a higher mass flow within the acetylene burner.

The smallest, but most important, part of a partial oxidation acetylene plant is the burner, Figure 9. Its design is nearly identical in the two process variants (i.e., oil and water quench).

At the top of the burner, the preheated reactants, (600 °C in the case of methane) must be mixed (c) so rapidly that there are no domains with a high oxygen concentration. Such domains cause preignition before the reactants are introduced into the reaction zone (g). In fact, the reaction mixture ignites after an induction time depending on the hydrocarbon used as feed and on the preheat temperature, on the order of a few tenths of a second. The maximum preheat temperature is lower for higher hydrocarbons than for methane. Backmixing of the gas between the mixing and the reaction zones is avoided by the diffuser (e), a tube which connects the mixing zone and the burner block (f). Because of its smooth surface and the small opening angle the reaction feed is decelerated gently and backmixing does not occur.

The burner block (f) consists of a water-cooled steel plate with a large number of small channels. The flow velocity through these channels is substantially higher than the flame propagation speed, so that the flame below the burner block cannot backfire into the diffuser. The lower side of the burner block has small openings between the channels through which additional oxygen is fed into the reaction mixture. At these openings small flames form and initiate the flame reaction. The strong turbulence below the burner block stabilizes the flame.

Under unfavorable conditions the flame may appear above the burner block. In this case the oxygen feed must be shut off immediately and replaced by nitrogen. This extinguishes the preignition before it can cause any damage to the equipment. Such preignitions can result from a momentary shift in the oxygen : hydrocarbon ratio or the entrainment of small particles of pyrophoric iron formed from rust in the preheaters.

As mentioned above, the hot gas leaves the reaction chamber within a few milliseconds and passes through sprays of water or oil, which cool the gas almost instantaneously, to about 80 °C in the case of water or 200 – 250 °C in the case of oil. The quench system consists of a set of nozzles that are fed by three annular tubes below the reaction chamber.

The concentrations of the major constituents of the cracked gas depend on the oxygen : hydrocarbon ratio in the feed as shown in Figure 10. As the oxygen supply is increased, the acetylene concentration increases until it passes through a smooth maximum. At the same time there is an increase in the volume of the cracked gas. Thus maximum acetylene production is attained when a little more oxygen is used than the amount required for maximum acetylene concentration in the cracked gas. This is clear from the consumption of natural gas per ton of acetylene produced and the reduction in unconverted methane. When the oxygen : hydrocarbon ratio is too low, the reaction time is insufficient for complete conversion of oxygen, and the cracked gas contains free oxygen. Free oxygen can be tolerated only up to a certain concentration. When the oxygen : hydrocarbon ratio is too high, the increased velocity of flame propagation exceeds the flow velocity in the channels of the burner block, leading to preignitions.

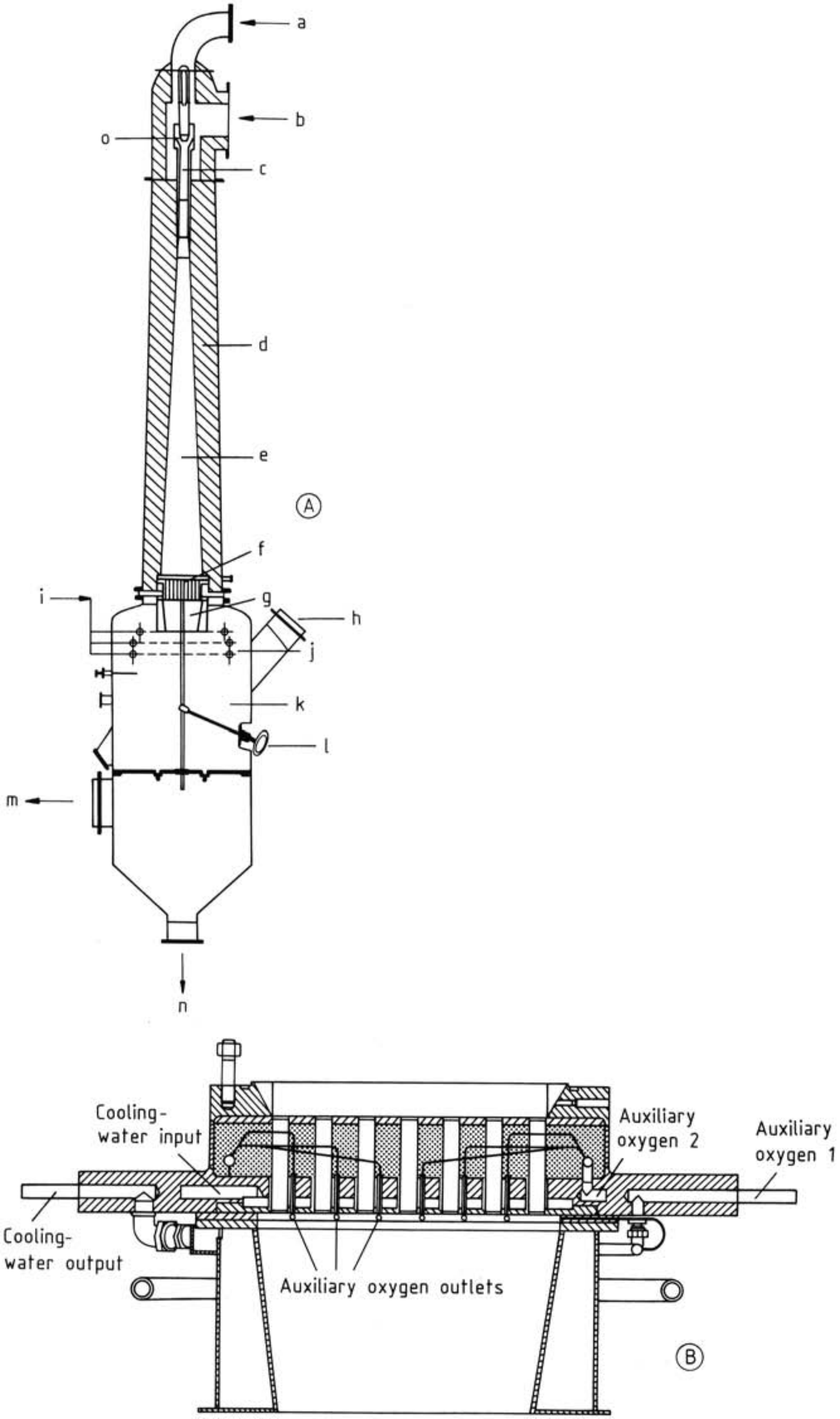


Figure 9. BASF acetylene burner
A) The burner: a) Oxygen: b) Hydrocarbon; c) Mixer; d) Concrete lining; e) Diffuser; f) Burner block; g) Reaction chamber; h) Rupture disk; i) Quench-medium inlet; j) Quench rings; k) Quench chamber; l) Manual scraper; m) Cracked-gas outlet; n) Quench-medium outlet. B) The burner block

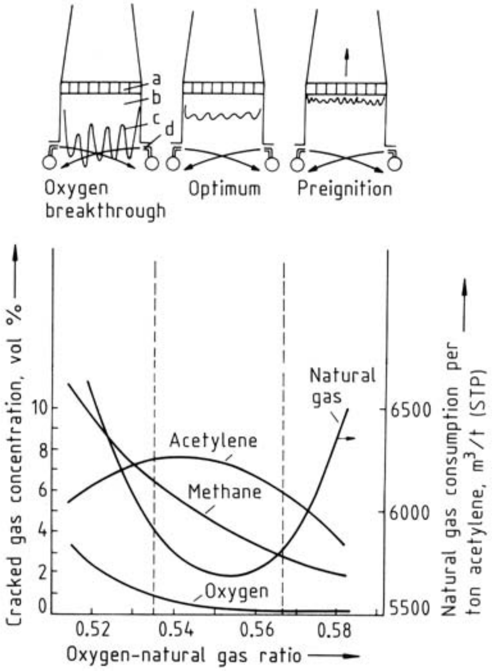


Figure 10. Burner characteristics a) Burner block; b) Reaction chamber; c) Flame front; d) Quench-medium inlet

Coke deposits in the reaction chamber have to be removed from time to time with a manual or an automatic scraper. Normally, a burner produces 25 t of acetylene per day from natural gas and 30 t per day from liquid feedstocks.

Acetylene Water Quench Process (AWP), Soot Removal (Fig. 11). After quenching with water the cracked gas leaves the burner (b) at 80 – 90 °C. A certain amount of soot is formed in the reaction chamber in spite of the very short reaction time. When natural gas is used as a feedstock, the soot is 50 kg per ton of acetylene, with LPG feedstock it is 250 kg, and with naphtha it is 350 kg. The soot is partly removed from the gas by the quench, then by washing with recirculated water in a cooling column (c), and by passing the gas through an electrofilter (d). After cooling and soot removal, the gas has a pressure slightly above atmospheric, a temperature of about 30 °C, and a soot content of about 1 mg/m^3. The water effluents from the quench system, the cooling column, and the electrofilter carry the washed-out soot. Some gas remains attached to the soot, causing it to float when the soot-containing water flows slowly through basin decanters (e). The upper soot layer, which contains 4 – 8 wt % of carbon, depending on the feedstock, is scraped off the water surface and incinerated.

Acetylene Oil Quench Process (AOP), Soot Removal (Fig. 12). In this process the cracked gas is quenched with oil sprays and leaves the burner at 200 – 250 °C. The oil absorbs the heat from the gas and then passes through waste heat boilers before returning to the quench. The

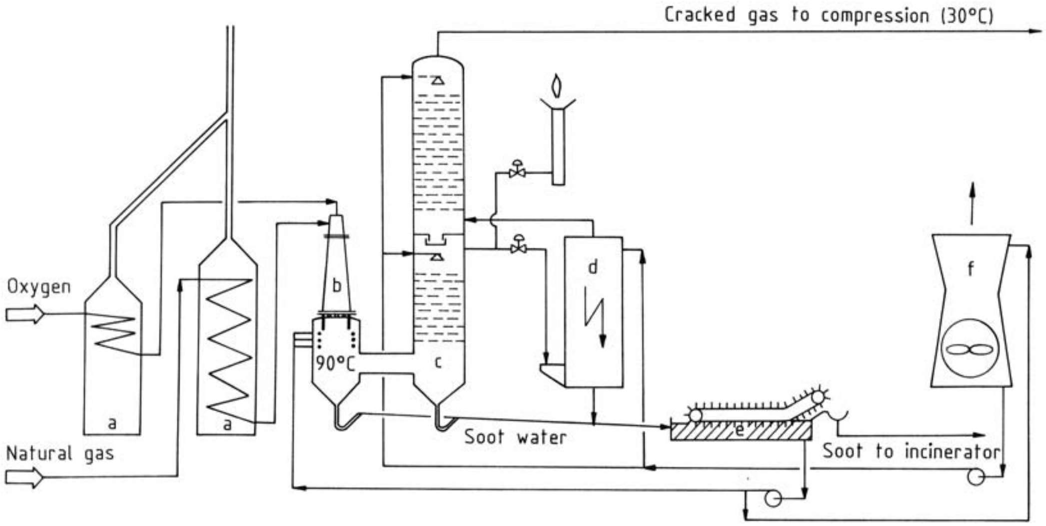


Figure 11. Acetylene water quench process (AWP) a) Preheaters; b) Acetylene burner; c) Cooling column; d) Electrofilter; e) Soot decanter; f) Cooling tower

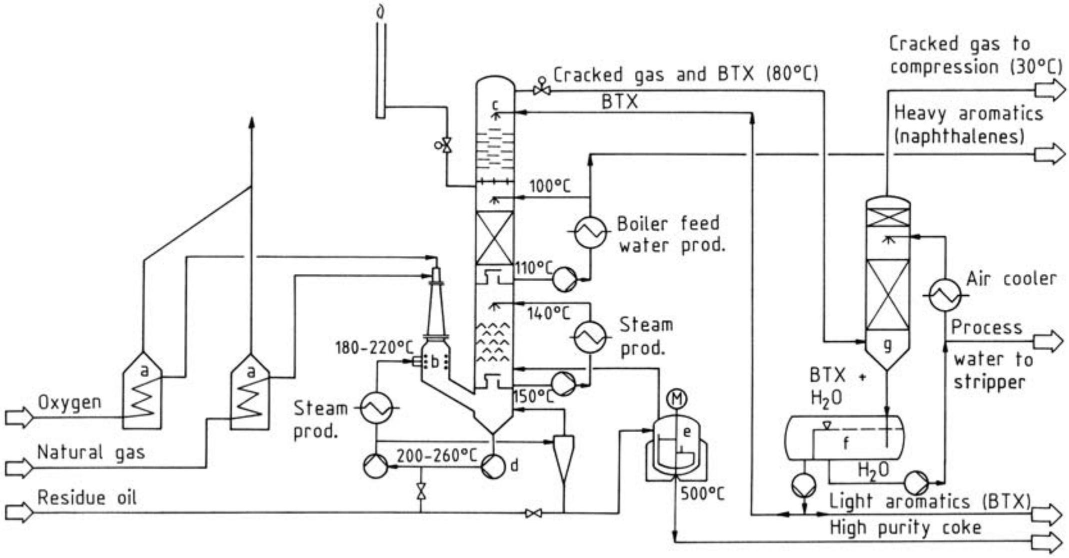


Figure 12. Acetylene oil quench process (AOP) a) Preheaters; b) Acetylene burner; c) Burner column; d) Mill pump; e) Coker; f) Decanter; g) Final cooler

sensible heat of the cracked gas represents more than 15 % of the heating value of the feedstock. The pressure of the generated steam depends on the process configuration and can reach 15 bar (1.5 MPa).

Unlike the water quench process, where the scraped coke deposits sink to the bottom of the quench chamber and are easily removed, in the oil quench the coke deposits do not settle immediately. In order to prevent plugs in the quench nozzles a mill pump (d) is installed immediately underneath the burner column.

The coke and soot content in the quench circuit is kept near 25 % by sending a fraction of the coke-containing oil to externally heated, stirred kettles (coker (e)). In the kettles the volatile matter evaporates very quickly, leading to fluidization of the coke bed. The vapor is returned to the burner column, while the soot is agglomerated. A fine-grained coke is withdrawn from the bottom of the coker.

Because of the cracking losses in the quench a certain amount of quench oil has to be added continuously to the process. This makeup oil is at least 0.15 to 0.3 t per ton of acetylene, depending on the stability of the oil used. When residual oil from steam crackers is used, it can be desirable to add up to 1 t of oil per ton of acetylene, because the excess oil is partially converted to light aromatic hydrocarbons.

The cracked gas leaving the quench is cooled in a burner column (c), where there are additional oil circuits for the production of 3-bar steam and for boiler feedwater preheat. At the top of the column a small amount of a low-boiling oil (BTX = benzene, toluene, and xylene) is added to prevent deposit-forming aromatics (mainly naphthalene) from passing downstream into other parts of the plant. The cracked gas, which has to be compressed before separation, is cooled further (g) by water. At this stage most of the BTX condenses and is separated from the water in a large decanter (f).

Table 4 shows the cracked gas compositions for the BASF acetylene oil quench process when natural gas, liquid petroleum gas (LPG), or naphtha is used as feedstock. The water quench process gives very similar compositions. The relative amounts of hydrogen and carbon monoxide formed depend on the hydrogen : carbon ratio of the feedstock used. Even when naphtha is used, almost no ethylene forms. This is because the reaction takes place above 1200 °C where the formation of ethylene is thermodynamically impossible. Only a prequench with additional naphtha or LPG produces additional acetylene

Table 4. BASF acetylene oil quench process, cracked gas composition (vol %)

Component [a]	Raw material (ΔH, kJ/mol)		
	Methane (400)	LPG (325)	Naphtha (230)
H_2	56.5	46.4	42.7
CH_4	5.2	5.0	4.9
C_2H_4	0.3	0.4	0.5
C_2H_2	7.5	8.2	8.8
C_{3+} [b]	0.5	0.6	0.7
CO	25.8	35.0	37.9
CO_2	3.2	3.4	3.5
O_2	0.2	0.2	0.2
Inerts		balance	

[a] Dry gas, water, and aromatic compounds condensed out;
[b] Hydrocarbons with three or more carbon atoms.

and ethylene at intermediate temperatures, as in the case of two-step processes. The higher hydrocarbons require a somewhat lower reaction temperature than methane and have a less endothermic heat of reaction: oxygen consumption per ton of acetylene is lower for the higher hydrocarbons in spite of the lower preheating temperature.

Comparison of Oil Quench and Water Quench Processes The advantage of the oil quench process is obvious: the heat recovery in the form of steam makes the overall thermal efficiency in relation to primary energy input rather high. If the thermal efficiency for the production of electricity is 33 %, over 70 % of the net heating value of the overall primary energy input is recovered in the form of products and steam. A comparison between the oil quench and water quench (see Table 6) shows that the oil quench requires a net heating value input of 300 – 330 GJ per ton of acetylene, of which 82 GJ (27 – 25 %) is lost, whereas the water quench requires a 288 GJ input, of which 113 GJ (39 %) is lost.

Acetylene Recovery Liquid acetylene is a dangerous product, even at low temperatures. Separation of the cracked gas by cryogenic processes such as those used in olefin production is clearly ruled out. One exception to this rule is the acetylene recovery unit of the submerged flame process (Section 4.2.3) [45], in which all hydrocarbons except methane are condensed at −165 C. Otherwise, acetylene is recovered by *selective* absorption into a solvent. This procedure is economical only when the cracked gas is compressed. The upper limit for the pressure is determined by the danger of explosions, and as a rule the partial pressure of acetylene should be kept below 1.4 bar (0.14 MPa).

The solubility of acetylene in the solvents used is between 15 and 35 m^3 (STP) per cubic meter of solvent under process conditions. The dissolved gas is recovered by depressurizing the solvent and by vapor stripping at higher temperatures. All solvents used commercially, *N*-methylpyrrolidone (NMP), methanol, ammonia, and dimethylformamide (DMF), are miscible with water. They are recovered from the gas streams leaving the plant by water scrubbing and distillation.

The kinetics of acetylene formation always lead to the formation of higher homologues of acetylene as byproducts [46], mainly diacetylene, but also methylacetylene, vinylacetylene, and others. These compounds polymerize very easily and must be removed from the cracked gas as soon as possible. Because they are much more soluble in the solvents than acetylene, scrubbing the cracked gas with a small amount of solvent before it enters the acetylene recovery stages is sufficient.

Absorption Section (Fig. 13). Acetylene recovery is illustrated here by the BASF process. *N*-Methylpyrrolidone is used to separate the cracked gas into three streams:

1. Higher homologues of acetylene and aromatics, the most soluble part of the cracked gas. (This is a small stream of gas, which is diluted with crude synthesis gas for safety reasons and is used as fuel.)
2. Product acetylene, less soluble than the higher acetylenes, but much more soluble than the remainder of the gas
3. Crude synthesis gas (off-gas), mainly hydrogen and carbon monoxide

In the prescrubber (b) the cracked gas is brought into contact with a small amount of solvent for removal of nearly all the aromatic compounds and C_4 and higher acetylenes except vinylacetylene. This is done after the compression of the gas if screw compressors are used but before compression if turbo compressors are

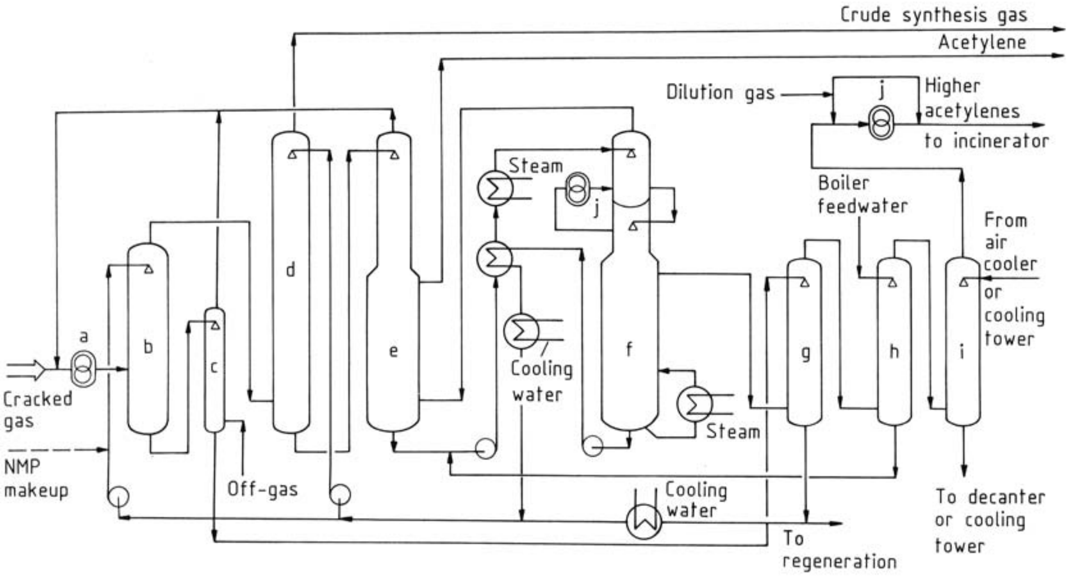


Figure 13. BASF acetylene process — *N*-methylpyrrolidone absorption section a) Compressor; b) Prescrubber; c) Acetylene stripper; d) Main scrubber; e) Stripper; f) Vacuum column; g) Vacuum stripper; h) Side column; i) Condenser; j) Vacuum pumps

used because turbo compressors cannot tolerate deposits on their rotors. In the main scrubber (d) the gas is brought into contact with a much larger amount of *N*-methylpyrrolidone (NMP), which dissolves all the acetylene, the remaining homologues, and some carbon dioxide. Crude synthesis gas (off-gas) leaves at the top of the column.

The NMP solution is degassed in several steps in which the pressure is reduced and the temperature increased. The stripper (e) operates at pressures and temperatures slightly above ambient. In this tower, the solution is put in contact with a countercurrent gas stream from the subsequent degassing step (f). This leads to the evolution of carbon dioxide, the least soluble of the dissolved gases, at the top of the stripper. The carbon dioxide is recycled to the suction side of the compression and thereby is shifted into the crude synthesis gas. The acetylene product is withdrawn as a side stream from the stripper. The *N*-methylpyrrolidone solution is then completely degassed (f) in two further steps at 110 – 120 °C, first at atmospheric, then at reduced pressure. Vinylacetylene, methylacetylene, and excess process water are withdrawn as bleed streams from the vacuum column (f). The water content of the solvent is controlled by the reboiling rate in the vacuum column. At the bottom of the vacuum column, degassing is completed, and the solvent is cooled and returned to the main scrubber (d).

The small amount of solvent from the prescrubber (b) is stripped with crude synthesis gas for recovery of the dissolved acetylene, the overhead gas being recycled to the suction side of the compressor. The solvent is then degassed completely in the vacuum stripper (g), a column which also accepts the bleed stream from the vacuum column (f) containing the excess process water together with some higher acetylenes. The overhead vapor of the vacuum stripper contains the higher acetylenes, water, and some NMP vapor. In a side column (h) the NMP is recovered by scrubbing with a small amount of water, which is recycled to the main solvent stream. The gas is cooled (i) by direct contact with water from a cooling circuit to condense most of the water vapor. The higher acetylenes are diluted with crude synthesis gas before they enter and after they leave the vacuum pump (j). The diluted higher acetylenes, which are now at a pressure slightly above atmospheric, can be used as fuel gas, e.g., for soot incineration.

In order to minimize the polymer content of the solvent, about 2 % of the circulating flow is withdrawn continuously from the vacuum stripper circuit and distilled under reduced pressure, leaving the polymers as a practically dry cake for disposal.

The acetylene product from the process as described above has a purity of about 98.4 %, the remainder consisting mainly of propadiene, methylacetylene, and nitrogen. For most applications the purity is increased to 99.7 % by scrubbing with sulfuric acid and sodium hydroxide solutions. Table 5 compares the compositions of crude and purified acetylene. Table 6 compares the consumption and product yields per ton of acetylene for the oil quench process with those for the water quench process.

4.2.2. Other Partial Combustion Processes

The main features of the BASF process described in detail above are common to all partial oxidation processes. Therefore only the differences between the BASF acetylene burner and burners used in the *Montecatini* and the *SBA processes* [41, 47] are described. These two processes have also attained some importance. The details of the acetylene recovery process depend on the properties of the solvent, but here too the basic principles are the same for all processes.

Montecatini Process. The Montecatini burner [48] has the same main components as the BASF burner: mixing unit, gas distributor, reaction chamber, and quench. The essential difference is the pressure for acetylene synthesis, which can be as high as several bar. This saves compression energy, improves heat recovery from the quench water, which is obtained at 125 °C, and is claimed to make soot removal easier because the cracked gas is scrubbed with water above 100 °C. Although it is well known [7] that acetylene decomposition is accelerated under pressure at high temperatures (> 1000 °C), the acetylene yield is comparable to that obtained at atmospheric pressure because of the short residence time in the reactor. Methanol is used at cryogenic temperatures for acetylene recovery. The main steps of the gas separation are absorption of higher acetylenes and of aromatics, absorption of acetylene, stripping of coabsorbed impurities, and desorption of acetylene.

Table 5. Purity of the acetylene from the BASF process

Component	Crude acetylene, vol %	Purified acetylene, vol %
Acetylene	ca. 98.42	99.70
Propadiene	0.43	0.016
Propyne	0.75	traces
Vinylacetylene	0.05	0
1,3-Butadiene	0.05	0
Pentanes	0.01	0.01
Carbon dioxide	ca. 0.10	0
Nitrogen	ca. 0.30	0.30

SBA Process (of the Société Belge de l'Azote). The SBA burner [49] has the same main components as the other processes. However, it has a telescope-like reaction chamber and a device for shifting the quench up and down. Thus it is possible to adjust the length of the reaction zone for optimum residence time at any throughput. The walls of the reaction chamber are sprayed with demineralized water to prevent coke deposits. This eliminates the need to scrape the reaction chamber periodically. Acetylene recovery is carried out with several scrubbing liquids – kerosene, aqueous ammonia, caustic soda, and liquid ammonia, each with its own circuit. After soot is separated from the gas in an electrofilter, higher hydrocarbons are absorbed in kerosene or gas oil. Carbon dioxide is scrubbed in two steps, first with aqueous ammonia and then with caustic soda solution. The acetylene product is absorbed into anhydrous ammonia and must be scrubbed with water after desorption. All the ammonia–water mixtures are separated in a common distillation unit. This recovery scheme leads to exact separation of the various cracked gas components.

Additional Remarks The Montecatini and SBA processes can also be operated with two-stage burners. A prequench with light hydrocarbons cools the cracked gas to about 800 °C. After a residence time at this intermediate temperature the gas is cooled down with water. In this way the heat content of the hot gases is used for further cracking of hydrocarbons to yield extra acetylene and olefins. The presence of additional components in the cracked gas requires more process steps in the gas separation units.

4.2.3. Submerged Flame Process

The submerged flame process (SFP) of BASF attracted considerable interest up to 1973 as a

Table 6. BASF acetylene process, consumption and product yields per ton of acetylene

Consumption and product yields	Oil quench	Water quench
Feed and energy requirements		
Natural gas, 36 000 kJ/m^3(STP) (LHV) [a]	5833 m^3 = 210 GJ	5694 m^3 = 205 GJ
Oxygen, 0.55 kWh/m^3(STP) [b]	3400 m^3 = 20.4 GJ	3400 m^3 = 20.4 GJ
Fuel gas	= 12.0 GJ	= 18.0 GJ
Residue oil minimum (surplus)	0.3 (1.0) t = 12.0 (40.0) GJ	
Sulfuric acid	160 kg	160 kg
Sodium hydroxide	5 kg	5 kg
N-Methylpyrrolidone	5 kg	5 kg
Electric energy [b]	3200 kWh = 34.9 GJ	3100 kWh = 33.8 GJ
Steam, 4 bar	5.0 t = 11.7 GJ	4.5 t = 10.5 GJ
Energy input	301.0 (329.0) GJ	287.7 GJ
Product yields		
Acetylene, 48650 kJ/kg (LHV)	1.0 t = 48.6 GJ	1.0 t = 48.6 GJ
Crude synthesis gas, 12100 kJ/m^3(STP) (LHV)	10600 m^3 = 128.3 GJ	10150 m^3 = 122.8 GJ
Coke (with residue surplus), 35 500 kJ/kg	0.3 (0.46) t = 10.7 (16.3) GJ	–
BTX (with residue surplus), 40 250 kJ/kg (LHV)	0.05 (0.12) t = 2.0 (4.8) GJ	–
Naphthalenes (with residue surplus), 38770 kJ/kg (LHV)	0.0 (0.41) t = – (15.9) GJ	–
Steam (up to 15 bar)	13.0 (14.0) t = 30.3 (32.6) GJ	1.5 t = 3.5 GJ
Energy output	219.9 (246.5) GJ	174.9 GJ
Thermal efficiency	73.0 (74.9) %	60.8 %
Energy losses, absolute per ton acetylene	81.1 (82.5) GJ	112.8 GJ

[a] If the natural gas contains inerts and higher hydrocarbons, the required input will remain approximately the same on a heating value basis (LHV = low heating value), but the cracked gas analyses and the crude synthesis gas analyses will differ slightly.

[b] Thermal efficiency of electricity production is assumed to be 33 %.

partial combustion process for the production of acetylene, ethylene, C_3, and C_4 hydrocarbons, and synthesis gas from feedstock of crude oil and residues, such as Bunker C oil and vacuum residue [44, 45]. Although it was abandoned at the end of 1973, the need to make the most economic use of raw materials has renewed interest in this process [50].

Oxygen compressed to 16 bar (1.6 MPa) feeds a flame that is submerged in the oil. The oil surrounding the flame is partially burnt to obtain the necessary reaction temperature and also acts as the quenching medium. This process differs from the partial oxidation processes using natural gas and lighter hydrocarbons in five main respects:

1. Crude oil can be gasified without the formation of residues, and the process can be operated under certain conditions with heavy fuel oil.
2. All the soot formed is consumed when crude oil feedstock is used, eliminating all the problems associated with the storage, disposal, or utilization of acetylene soot.
3. The heat of reaction is removed by steam generation at 8 bar (0.8 MPa).
4. The process is operated at 9 bar (0.9 MPa) so that the oxygen is the only compressed stream. The cracked gas is formed at a pressure sufficient for economic separation.
5. The design of the cracking unit is greatly simplified because the reaction feed, fuel, and quenching medium are identical.

The process is described in detail in the literature cited; therefore, only general overviews of the cracking unit (Fig. 14) and the separation unit (Fig. 15) are shown here. The capacities of a submerged flame burner for acetylene and ethylene are 1 t/h and 1.15 t/h, respectively. To produce these quantities, 5000 m^3 (STP) of oxygen and 8 – 10 t of oil are required per hour. The cracked gas shows the following average composition (vol %, the components grouped as streams leaving the separation unit):

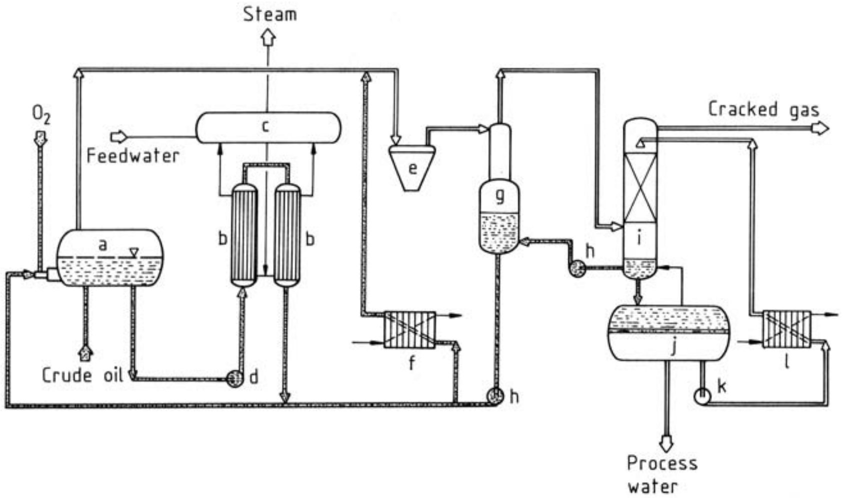


Figure 14. Submerged flame process (SFP) – cracking unit a) Reactor; b) Oil cooler; c) Steam generator; d) Oil recycle pump; e) Scrubber; f) Naphtha cooler; g) Naphtha separator; h) Naphtha pump; i) Spray cooler; j) Separating vessel; k) Recycle-water pump; l) Recycle-water cooler

Main products	
Acetylene	6.2
Ethylene	6.5
Crude synthesis gas	
Carbon monoxide	42.0
Hydrogen	29.0
Methane	4.0
Inerts	0.6
Other hydrocarbons	
Ethane	0.5
Propane	0.1
Propene	1.2
Propadiene, propyne	0.7
1,3-Butadiene	0.5
Other C_4 and C_{5+}[a] hydrocarbons	1.5
Remainder	
Carbon dioxide	7.0
Hydrogen sulfide	0.05 – 0.5
Carbon oxide sulfide	0.03 – 0.3

[a] C_{5+}, five or more carbons

Unlike all other processes the submerged flame process uses low temperatures (–165 °C) to separate the off-gas, consisting of carbon monoxide, hydrogen, and methane, from the C_2 and higher hydrocarbons. On account of the acetylene in the condensed phase, extensive decomposition tests have been carried out. Whereas the cracking unit (Fig. 14) and the amine scrubbing unit have been tested by Soc. Ital. Serie Acetica Sintetica, Milan, on a commercial scale, the remaining purification units (Fig. 15) have not. However, the experience obtained with a pilot plant indicates that major difficulties are not to be expected.

The submerged flame process may become competitive because of its ability to use crude oil and especially residues and because of its low losses on the primary energy input.

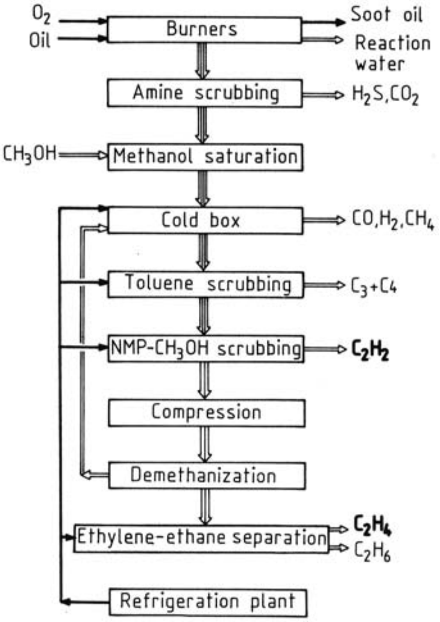


Figure 15. Submerged flame process — purification unit

4.2.4. Partial Combustion Carbide Process

Calcium carbide production from lime and coal requires a large high-temperature heat input (see Section 4.3.4). In the thermal process some of the coal must be burnt to attain the necessary reaction temperature and supply the heat of reaction. The thermal carbide process was developed by BASF [7, 51] from 1950 to 1958 to eliminate the input of electrical energy necessary in the classic carbide process. Starting in 1954, a large pilot plant, with a nominal carbide capacity of 70 t/d, was operated, but in 1958 the more economical petrochemical acetylene production halted further development. Carbide production is just one way of converting coal chemically; other methods include pyrolysis, hydrogenation, and gasification. The question arises as to the conditions under which a thermal carbide process using oxygen can compete with the electric carbide process. The biggest drawback of carbide production in a shaft furnace (Fig. 16) compared to the electric carbide process is the lack of commercial-scale operational experience. Specific disadvantages are greater susceptibility to disruption because of plugging of the furnace feed, more stringent specifications for the raw materials, more handling of solids, and the large amount of byproduct. There are two main advantages:

1. A thermal efficiency of about 50 % versus about 30 % for the electrothermal process if the thermal efficiency of electricity production is 33 %
2. Carbon monoxide production, which is desirable because carbon monoxide can be converted to synthesis gas by the water-gas shift reaction (→ Gas Production, 3. Gas Treating)

If the carbon monoxide is converted to synthesis gas and the electrical energy is produced from fossil fuels, production costs are about one third lower for the thermal process than for the electrical process [52] based on the pilot-plant consumption data (Table 7).

4.3. Electrothermic Processes

Because calcium carbide is produced electrothermally, the production of acetylene from this material also is discussed in this group of processes (Section 4.3.4).

Electrothermic processes have the following advantages over partial oxidation:

- The energy requirement for the formation of acetylene can be made independent of the hydrocarbons used as feedstock.
- Hydrocarbon consumption can be reduced by 50 %.
- Provided that electrical energy is available under favorable conditions (nuclear power, hydroelectric power, cheap coal) and/or the availability of hydrocarbons is limited, electrothermic processes are more economical.

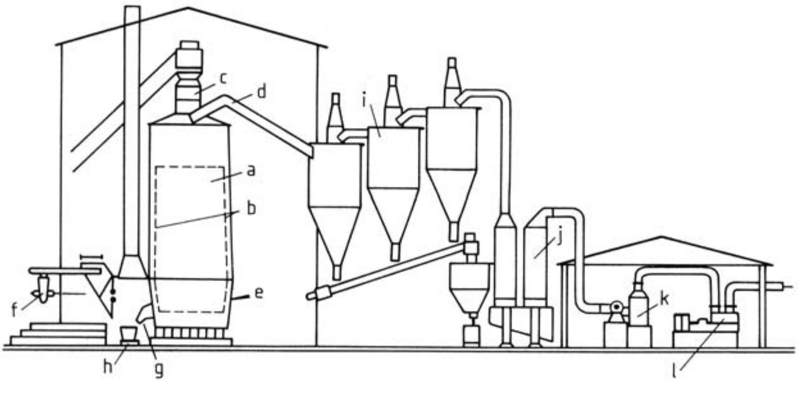


Figure 16. Partial combustion carbide process a) Carbide furnace; b) Refractory brick lining; c) Charging hopper; d) Gas outlet; e) Oxygen jet; f) Tapping burner; g) Tapping chute; h) Bogey; i) Cyclone; j) Washing column; k) Desintegrator; l) Compressor

Table 7. Partial combustion carbide process, consumption and product yields per ton acetylene

Raw materials	
Coke, dry (88 % C)	5700 kg
Lime (92 % CaO)	3140 kg
Oxygen (98 %) 3560 m^3 (STP)	5090 kg
Total consumption	13 930 kg
Products	
Carbide (80.5 %)	2850 kg ≙ 1000 kg acetylene
Carbon monoxide 7980 m^3 (STP) (CO 95.5, H_2 2.0, N_2 2.0, CO_2 0.5 vol %)	9975 kg
Dust	900 kg
Losses	205 kg
Total products	13 930 kg

In the case of acetylene formation, the electric-arc process offers optimal conditions for the endothermic reaction at high temperatures.

The development of the electric-arc process for cracking light hydrocarbons to acetylene began in 1925 in Germany. The acetylene was to be used as feedstock for butadiene production. In 1940, the first commercial plant was put on stream at Chemische Werke Hüls in Marl, Germany. The Hüls process has since been improved , and the capacity raised, but it retaired the original principles [53].

Feedstock for electric-arc processes may be gaseous or liquid hydrocarbons or even solids such as coal. The design of the arc furnace and the purification section for the cracked products have to be adapted to the different feedstocks. For gaseous or gasified hydrocarbons the classical one-step process is used: the arc burns directly in the gas being cracked. For liquid and solid feeds, a one- or two-step process may be used. In the two-step process hydrogen is first heated in the arc furnace, and then liquid or solid feed is injected into the hydrogen plasma [54]. Figure 17 shows both types of arc furnaces. Because of hydrogen formation during the cracking reaction, the arc burns in a hydrogen atmosphere in both processes. The conductivity and the high rate of ion–electron recombination for hydrogen mean that arcs above a certain length cannot be operated with alternating current at normal frequency and high voltage. All commercial plants therefore run on direct current.

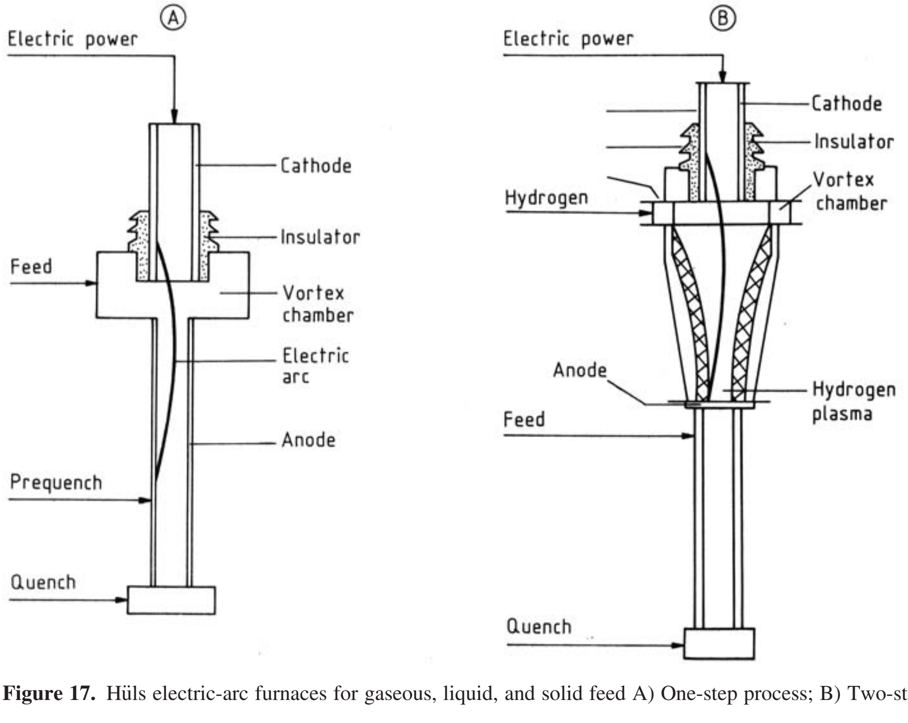


Figure 17. Hüls electric-arc furnaces for gaseous, liquid, and solid feed A) One-step process; B) Two-step process

4.3.1. Production from Gaseous and/or Gasified Hydrocarbons (Hüls Arc Process)

The plant for the Hüls arc process includes the arc furnace section itself (Fig. 17 A), which is operated at a pressure of 1.2 bar, and a low and high pressure purification system.

Arc Furnace. A cathode, a vortex chamber, and an anode make up the arc furnace. Cathode and anode are water-jacketed tubes of carbon steel 0.8 m and 1.5 m long, respectively, and with inner diameters of 150 and 100 mm, respectively. The arc burns between cathode and anode with a length of about 1.2 m and with a current of 1200 A. The cathode is connected to the high-voltage side of the rectifier (7.1 kV) and electrically isolated from the other parts of the furnace. Between cathode and anode is the vortex chamber. The gas is injected into it tangentially at a specific velocity to stabilize the arc by creating a vortex. The arc burns in the dead zone, and the striking points of the arc on the electrodes are forced into a rapid rotation so that they only burn for fractions of a millisecond at one point, which gives the electrodes a lifetime up to 1000 h. Temperatures reach 20 000 °C in the center of the arc. Because of the tangential flow of the gas, the arc is surrounded by a sharply decreasing coaxial temperature field, and the temperatures at the wall of the electrode are only 600 °C. Thermal losses are therefore limited to less than 10 % of the electrical power input of 8.5 MW.

The residence time of the gas in the arc furnace is a few milliseconds. In this interval, the hydrocarbons are cracked, mainly into acetylene, ethylene, hydrogen, and soot. At the end of the arc furnace, the gases are still at a temperature of about 1800 °C. The high heat content of this gas can be exploited for additional ethylene production by means of a prequench with liquid hydrocarbons. This lowers the temperature to about 1200 °C. Because acetylene rapidly decomposes into soot and hydrogen at these temperatures, the gases must be quenched immediately with water to about 200 °C, i.e., a quench rate of 10^6 °C/s must be achieved.

The *specific energy requirement* (SER) and the acetylene yield depend on the geometry and dimensions of the furnace and electrodes, the velocity distribution of the gas, and the kind of hydrocarbon to be cracked. Once the furnace has been designed, only the hydrocarbons can be varied.

Process Without Prequench. Figure 18 shows acetylene and ethylene yields and the specific energy requirement (SER) of various saturated hydrocarbons under constant conditions without prequench. Methane shows the highest SER and acetylene yield, but the lowest ethylene yield. As the chain length is increased, both acetylene yield and SER decline, corresponding to the declining heat of acetylene formation from the various hydrocarbons.

Normally, pure hydrocarbons are not available. The results obtained from mixtures of hydrocarbons can be expressed as a function of the carbon number, which is the number of moles of carbon atoms bound in hydrocarbons per mole of the gaseous mixture. Figure 19 shows specific amounts of acetylene, ethylene, and hydrogen formed and of hydrocarbon consumed as a function of carbon number. This function enables the Hüls process to be optimized within certain limits, for example, for hydrogen output in relation to acetylene production.

Process with Prequench. Cracking in the prequench section is essentially an ultrasevere steam cracking process. The kind and amount of hydrocarbons used for the prequench can be varied. Figure 20 shows the specific product yield for different prequench rates for feeding methane to the arc furnace and propane to the prequench. Acetylene and hydrogen yields are unaffected, whereas ethylene shows a slight

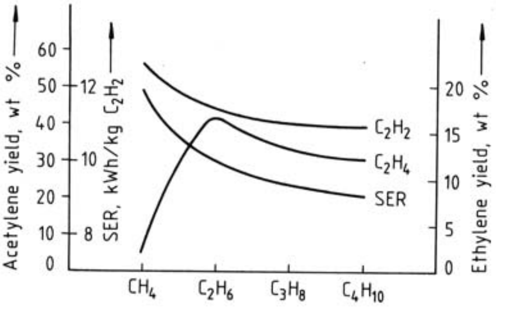


Figure 18. Acetylene yield, ethylene yield, and energy consumption for various hydrocarbons in the Hüls arc process

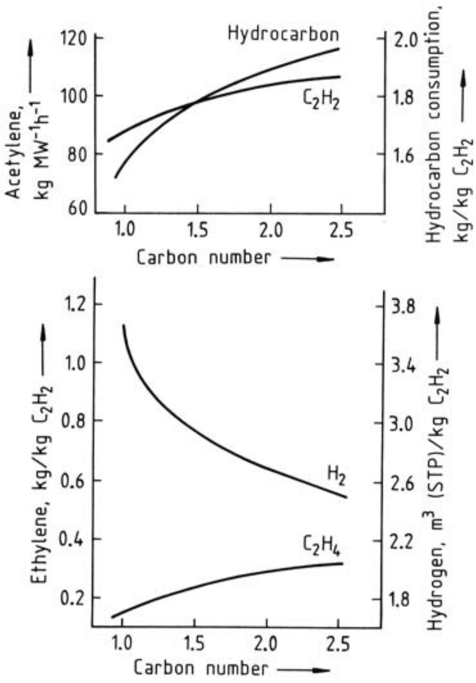


Figure 19. Specific values for acetylene and hydrogen formation

maximum and declines when the temperature is not sufficient at a given residence time. Propene shows a steady increase, and the $C_3 : C_2$ ratio is below 0.25. The relative ethylene yield from various hydrocarbons is as follows: ethane 100, propane 75, *n*-butane 72, isobutane 24, 1-butene 53.

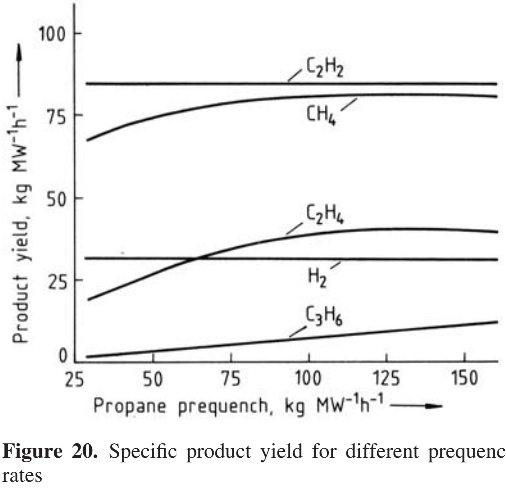


Figure 20. Specific product yield for different prequench rates

Oil Quench Because the gas temperature of the furnace gas after prequench is on the order of 1200 °C, an oil quench system has been developed to regain about 80 % of the sensible heat content of the furnace gas as steam by heat exchange. The soot–oil mixture formed can be upgraded to a sulfur- and ash-free high-grade petroleum coke. Figure 21 shows the Hüls system with oil quench.

The Purification System The process of purification depends on the type of the quench system. In the case of water quenching, 80 % of the carbon black is removed by cyclones as dry carbon black, the remaining 20 % as soot in water-operated spray towers. In a combined oil–water scrubbing system, aromatic compounds are removed and benzene, toluene, and xylene (BTX) are recovered in a distillation process.

Figure 22 shows the principle separation and purification steps for the furnace gas. The gas leaves the first three purification sections with a carbon black content of 3 mg/m^3 and is compressed by four-stage reciprocating compressors to 19 bar (1.9 MPa). The gas is washed in towers with water in a countercurrent flow. At the bottom of the tower, the water is saturated with acetylene, whereas the overhead gas contains less than 0.05 vol % acetylene. The acetylene–water solution is decompressed in four stages. Gas from the first decompression stage returns to the compressor to improve selectivity. The last two stages operate at 0.2 and 0.05 bar (20 and 5 kPa). The gas still contains about 10 vol % of higher acetylenes, which are removed by a cryogenic process. The higher acetylenes are liquefied, diluted with flux oil, stripped, and returned to the arc furnace together with spent hydrocarbon. A more selective solvent such as *N*-methylpyrrolidone or dimethylformamide is preferred to the water wash.

Linde and Hüls have designed an appropriate purification system. Hydrogen and ethylene are separated by well-known technology, such as the cryogenic process or pressure-swing adsorption (see → Adsorption).

Process Data Hüls operates its plant with a mixture of natural gas, refinery gas, and liquefied petroleum gas. The carbon number varies between one and two. Table 8 shows a typical analysis of feed gas and cracked gas.

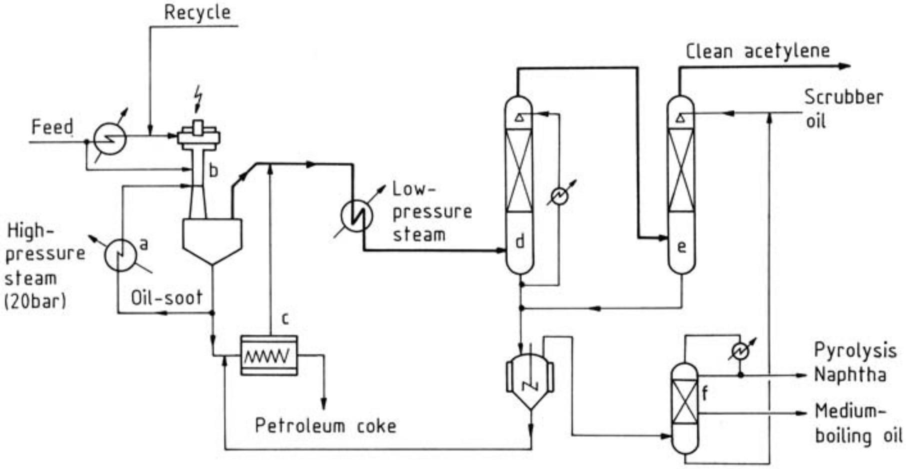


Figure 21. Process with oil quench system a) Heat recovery; b) Arc furnace; c) Oil recovery; d) Separation of medium-boiling compounds; e) Separation of low-boiling compounds; f) Oil regeneration

The Hüls plant has 19 arc furnaces, the number operated depending on the electricity supply. The arc furnaces can be started up and shut down immediately. Two large gas holders provide a storage volume of 350 000 m^3 so that the purification section operates on permanent load and there is a dependable supply of products, even if the arc furnace section is operated at higher or lower load.

The plant has an annual capacity of 120 000 t acetylene, 50 000 t ethylene, 400×10^6 m^3 (STP) hydrogen, 54 000 t carbon black and soot, and 9600 t aromatic compounds. The energy consumption is 1.5×10^6 MW h/a.

Specific data for consumption of hydrocarbons and energy and the production of byproducts per ton of acetylene produced are as follows:

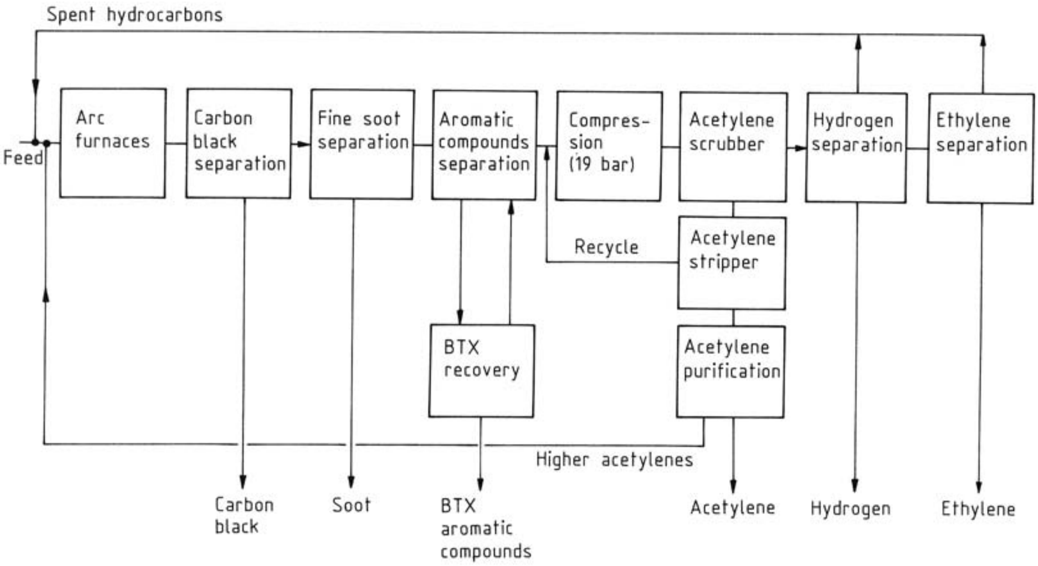


Figure 22. Principal separation and purification steps for the furnace gas of the Hüls arc process

Table 8. Typical analysis of feed and cracked gas

	Feed gas, vol %	Cracked gas, vol %
C_2H_2	0.4	15.5
C_3H_4	1.4	0.4
C_4H_2	1.2	0.3
C_4H_4	1.7	0.4
C_2H_4	0.8	6.9
C_3H_6	3.6	1.0
Allene	0.4	0.2
C_4H_8	1.0	0.2
C_4H_6	0.9	0.2
C_5H_6	0.6	0.2
C_6H_6	0.5	0.5
CH_4	64.6	13.8
C_2H_6	7.5	0.4
C_3H_8	3.6	0.3
C_4H_{10}	4.6	1.0
C_5H_{12}	0.5	0.1
H_2	4.5	57.6
CO	0.5	0.6
O_2	0.1	0.0
N_2	1.6	0.4

Hydrocarbons to the arc furnace	1.8 t
Hydrocarbons for prequench	0.7 t
Energy for the arc furnace	9800 kW h
Energy for gas purification	2500 kW h
Ethylene	0.42 t
Hydrogen	3300 m^3 (STP)
Carbon black and soot	0.45 t
Aromatics	0.08 t
Residue	0.12 t
Heating gas	0.12 t

4.3.2. Production from Liquid Hydrocarbons (Plasma Arc Process)

Two different plasma furnaces, each with the appropriate reactor for the cracking of liquid hydrocarbons, were developed by Hoechst and Chemische Werke Hüls in close cooperation. Both units were tested on an industrial scale at a power level of 8 – 10 MW [55]. However, neither process has actually come into use for acetylene production on account of the economics.

The scheme of the plasma generator used by Hüls is shown in Figure 17 B. The unit consists of three parts: the arc furnace, the reactor, and the quench system. The arc burns over a length of 1.6 m at 7 kV d.c. and 1.2 kA, resulting in a power input of 8.5 MW. It is stabilized by hydrogen injected tangentially through the vortex chamber. The thermal efficiency of the furnace is ca. 88 % of the electrical power input. The hydrogen plasma jet passing through the anode nozzle has an energy density of 3.5 kW h/m^3(STP), corresponding to an average temperature of 3500 K. The liquid hydrocarbons (e.g., crude oil) to be cracked are injected into the cylindrical reactor to achieve good mixing with the plasma jet and to avoid the formation of carbonaceous deposits on the wall. Within several milliseconds the hydrocarbons are heated and cracked to acetylene, ethylene, hydrogen, soot, and other byproducts before the mixture is quenched with oil to 300 °C. The acetylene ratio can be adjusted by varying the residence time. By operation of an oil quench with the high-boiling residue of the crude oil, 80 % of the sensible heat content of the cracked gas can be recovered as steam. The soot is taken up by the quench oil and is removed from the system as an oil–soot dispersion having 20 % soot concentration. The unconverted vaporized fractions of the oil are condensed in oil scrubbers at a lower temperature, simultaneously cleaning the gas of the aromatic components and fine soot. These oil fractions are recycled to the reactor and the quench system, respectively.

Tests were carried out with a variety of hydrocarbons from propane to naphtha, but mainly with crude oil and residue oils. The cracking results depend on the chemical nature of the feed. Consumption figures and yields for various feedstocks are given in [55]. For high-boiling petroleum fractions, the acetylene and ethylene yields increase with the content of low-boiling components in the feed (see Fig. 23). Consumption and byproduct yields per ton of acetylene for a Libyan crude oil are summarized below:

Consumption	
Crude oil consumed	3.5 t
Power (d.c.)	10500 kW h
Byproducts	
Ethylene	0.46 t
Hydrogen (99.9 %)	1100 m^3 (STP)
Fuel gas	0.74 t
Soot – oil mixture (20 % soot)	1.2 t

Hoechst used a high-intensity three-phase a.c. arc furnace at 1.4 kV and 4.2 kA, giving a power input of 10 MW [55]. The thermal efficiency was

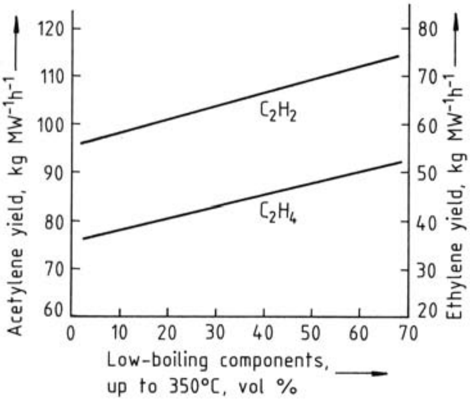


Figure 23. Acetylene and ethylene yields as a function of the low-boiling components

90 %. Because of the high amperage the graphite electrodes had to be replenished continually. The generator was lined with graphite. Different reactor designs for ethylene: acetylene ratios of 0.5 and 1.0 were developed by varying the mixing intensity of the hydrogen plasma jet with the liquid hydrocarbon. The tests were carried out with naphtha feed (see Table 9). The cracked gas was quenched with residue oil, in a manner similar to that described in the Hüls process.

The acetylene concentration in the Hüls process and the Hoechst process was ca. 14 vol % so that in principle the same acetylene separation process can be used as described above for the arc process.

4.3.3. Production from Coal (Arc Coal Process)

Numerous laboratory tests for the conversion of coal to acetylene using the arc or plasma processes have been carried out since the early 1960s [56]. The results can be summarized as follows:

- Acetylene yields up to 30 % can be obtained.
- Because of the rapid heating of the coal in the plasma jet, a higher total gas yield can be achieved than is indicated by the volatiles of the coal measured under standard conditions.
- Hydrogen (instead of argon) plasma gas considerably increases the acetylene yield.

Table 9. Consumption and yield per ton of acetylene for the Hoechst arc process and naphtha feed for different reactor designs

	Low ethylene yield	High ethylene yield
Consumption		
Naphtha	1.92 t	2.50 t
Quench oil	0.53 t	0.63 t
Energy(2-phase a.c.)	9300 kW h	10500 kW h
Byproducts		
Ethylene	0.5 t	0.95 t
Hydrogen	1450 m^3 (STP)	1500 m^3 (STP)
Soot–oilmixture (20 % soot)	0.75 t	1.00 t

The AVCO arc furnace (Fig. 24) consists of a water-cooled tungsten-tip cathode and a water-cooled anode [57]. The arc is stabilized by a magnetic field surrounding the anode, forcing the anode striking point of the arc to rotate rapidly and so avoiding burnthrough. The dried and finely ground coal is injected by means of a hydrogen gas flow around the cathode. Additional gas without coal is introduced around the cathode and at the anode as a sheath. On passing the arc zone the coal particles are heated up rapidly. The volatiles are released and are cracked to acetylene and byproducts, leaving a residue of fine coke particles covered with soot. After a residence time of some milliseconds the gas–coke mixture is quenched rapidly with water or gases. The use of a prequench system similar to that of the Hüls arc process was also tested. The

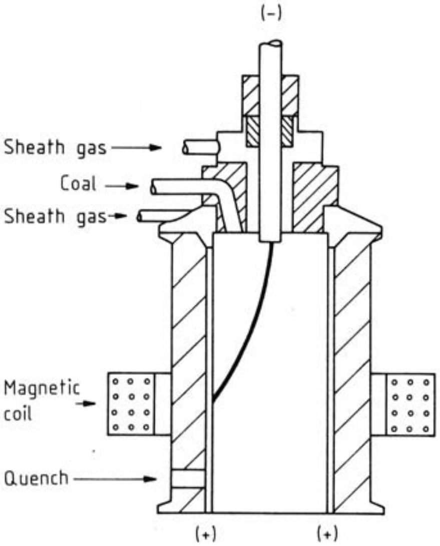


Figure 24. Principal scheme of the AVCO plasma furnace for the pyrolysis of coal

system pressure can be varied between 0.2 and 1.0 bar (20 and 100 kPa).

Hüls' pilot plant uses the same plasma furnace as for the crude oil cracking, but with 500 kW of power [58]. The dried and ground coal is injected into the plasma jet, and the coal is cracked to acetylene and byproducts in the reactor. The reactor effluent can be prequenched with hydrocarbons for ethylene production or is directly quenched with water or oil. Char and higher boiling components are separated by cyclones and scrubbers, respectively. The problem in the reactor design is to achieve thorough and rapid mixing of the coal with the plasma jet and to avoid forming carbonaceous deposits on the wall. Smaller amounts of deposits can be removed by periodic wash cycles with water. Operation times of 2.5 h by AVCO and 5 h by Hüls have been reported.

Experiments published by Hüls and AVCO show that at the optimal residence time the energy density of the plasma jet, the specific power, and the pressure all greatly affect the acetylene yield (Fig. 25 and Fig. 26). Other parameters affecting the yield are the amounts of volatiles in the coal and the particle size. The lowest figures for the specific energy consumption published by AVCO are of the order of 27 – 37 % based on water-free coal.

In addition to acetylene, the exit gas contains considerable amounts of CO, depending on the oxygen content of the coal. Because nitrogen and sulfur are present in the coal, other byproducts are HCN, CS_2, COS, and mercaptans. The gas separation system is therefore designed accordingly [59]. Depending on the hydrogen content of the coal, the process is either self-sufficient in hydrogen or has a slight surplus. The total gas yield of the coal based on a volatile content in the coal of 33 % is up to 50 %. Thus 50 % of the coal remains as char. Tests with a view to using this char in the rubber industry have been unsuccessful so far. Thus the char can be used only for gasification or as a fuel.

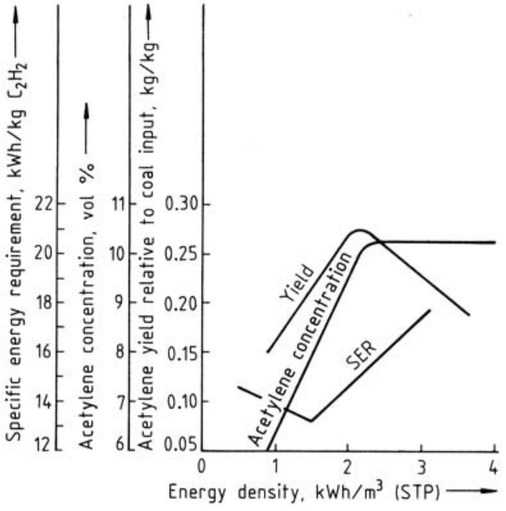


Figure 25. Effect of the energy density of the plasma on the cracking of coal (AVCO)

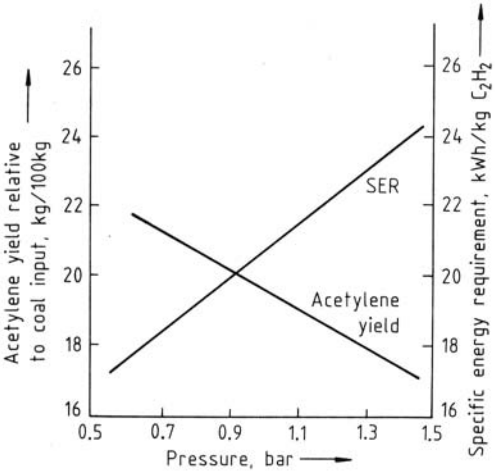


Figure 26. Acetylene yield and specific energy requirement as a function of pressure (Hüls)

In all the processes under development, the production of ethylene from coal requires several process steps (Fig. 27), resulting in a high capital demand for a production plant. In contrast, the acetylene production from coal arc pyrolysis is straightforward, leading to lower investment costs. Demonstration units on a higher power level are therefore scheduled by both AVCO and Hüls.

4.3.4. Production from Calcium Carbide

At present, the generation of acetylene from calcium carbide (→ Calcium Carbide) is of primary importance for welding and for the production of carbon for batteries. The particular raw-material situation and the use of special processes are two common reasons for continu-

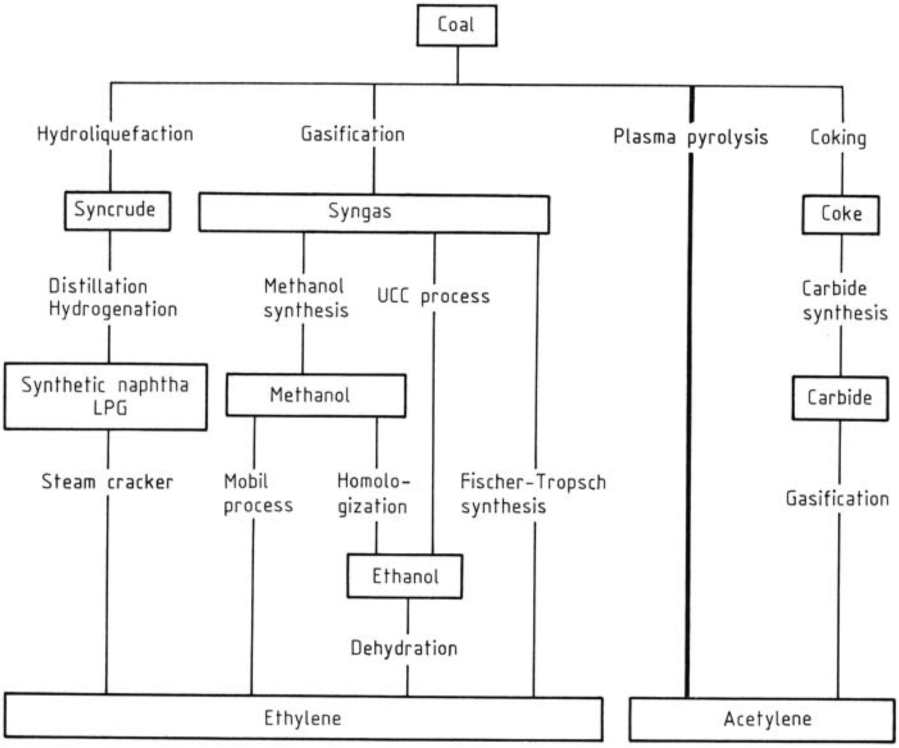


Figure 27. Alternative routes from coal to ethylene and acetylene

ing to use acetylene generated from carbide in the chemical industry.

The reaction of calcium carbide and water to form acetylene and calcium hydroxide is highly exothermic:

$$CaC_2+2\ H_2O\rightarrow C_2H_2+Ca(OH)_2\quad \Delta\ H=-129\ \text{kJ/mol}$$

The acetylene generator used for commercial production must therefore be designed to allow dissipation of the heat of reaction. In the event of inadequate heat dissipation, for example, when gasification proceeds with insufficient water, the carbide may become red-hot. Under certain circumstances (including increasing pressure), this may cause the thermodynamically unstable acetylene to decompose into carbon and hydrogen. (For safety precautions see Chap. 5.) Carbide for the production of acetylene is used in the following grain sizes (mm): 2 – 4, 4 – 7, 7 – 15, 15 – 25, 25 – 50, 50 – 80. This classification is virtually identical in most countries: DIN 53922 (Germany); BS 642:1965 (United Kingdom); JIS K 1901 – 1978 (Japan); Federal Specification 0–6–101 b/GEN CHG NOT 3 (United States). In addition, grain size 0 – 3 is used for the dry generation of acetylene.

Pure calcium carbide has a yield number of 372.66. This means that the gasification of 1 kg of carbide yields 372.66 L acetylene at 15 °C and 1013 mbar (101.3 kPa). Commercially available carbide has a yield number of 260 – 300.

A distinction is made between two groups of acetylene generators (with continuous rates of production greater than 10 m^3 acetylene per hour): the wet type and the dry type.

In *wet generators*, the acetylene is converted with a large water excess. In most cases, a lime slurry containing 10 – 20 wt % calcium hydroxide is obtained. The heat of reaction increases the temperature of the generator water and is removed from the reactor with the lime slurry.

In *dry generators*, the water mixed with the carbide is just sufficient for chemical reaction and for dissipating the heat of reaction. The calcium hydroxide is obtained in the form of a dry, easily pourable powder having a residual moisture content of 1 – 6 %. The heat of reaction is dissipated by evaporation of part of the generator water.

Generators are classified according to their working pressure as either low or medium pressure. This classification is governed by the regulations concerning acetylene plants and calcium carbide storage facilities (*Acetylenverordnung*) [60] issued by Deutscher Acetylenausschuß (German acetylene committee) and the associated technical rules for acetylene plants and calcium carbide storage facilities *TRAC* (*Technische Regeln für Acetylenanlagen und Calciumcarbidlager*) [61]. The *Acetylenverordnung* and *TRAC* constitute a comprehensive set of rules for handling acetylene. Recommendations in other countries (e.g., United States) deal only with some aspects, such as safety precautions [62].

Low-pressure generators are designed for a maximum allowable working pressure of 0.2 bar. They must be rated for an internal pressure of at least 1 bar. Lower pressure ratings are possible if proof is given in each particular case that the generator can withstand the expected stress (maximum working pressure, water filling, agitator, etc.; *TRAC 201*).

Medium-pressure generators have a maximum allowable working pressure of 1.5 bar. They must be rated for an internal pressure of 24 bar. A design pressure of 5 bar suffices whenever the generators are equipped with rupture disks of a defined size and specified response pressure (3 – 4.5 bar, *TRAC 201*).

4.3.4.1. Wet Generators

Wet generators are used primarily for the production of small amounts of acetylene, e.g., for welding purposes. Wet generators work by one of three different principles [63]:

1. The *carbide-to-water principle,* where the carbide is mixed with a large excess of water at a rate corresponding to the gas withdrawal rate. Most generators work by this principle.
2. The *water-to-carbide principle* (drawer type generators), where water is added at a controlled rate to the carbide, which is held in a replaceable container (drawer).
3. The *contact principle* (basket generators), where the carbide, which is held in a basket, is immersed into the generator water. This type is designed so that the water drifts off the basket as a result of the gas pressure at low gas withdrawal rates and, conversely, returns to the basket when gas withdrawal rates increase.

Medium-Pressure Generators The Messer Griesheim MF 1009 is a typical carbide-to-water generator (Fig. 28).

The carbide skip (a) is filled with carbide of the 4 – 7 grain size. The skip is connected by gas-tight gates to the hopper (b) and is purged of air by nitrogen or acetylene. The carbide drops into the hopper (b) and is fed continuously by the feeding system (c) to the gasification chamber (d). The gasification chamber contains water up to a level defined by the generator capacity and is equipped with an agitator (e) for whirling the lime slurry. The heat evolved in gasification heats the generator water. For continuous operation the water temperature must not exceed 90 °C; therefore, fresh water is admitted continuously to the gasification chamber. If the defined water level is exceeded, the slurry valve (f), controlled by a float, opens, allowing the excess water and the lime slurry to be discharged from the generator.

The acetylene generated collects above the water and is withdrawn. The feeding system

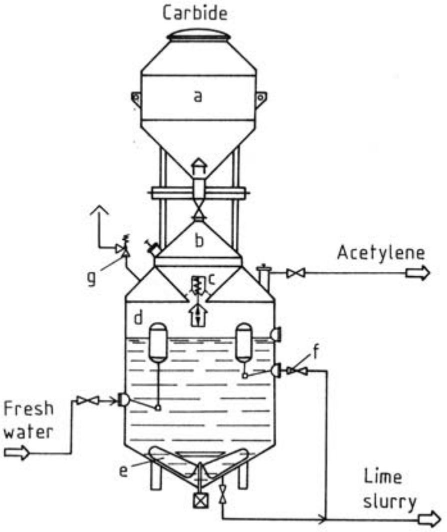


Figure 28. Medium-pressure wet generator a) Carbide skip; b) Hopper; c) Feeding system; d) Gasification chamber; e) Agitator; f) Slurry valve, g) Safety device

(c) is controlled by the gas pressure, i.e., the rate at which carbide drops into the gasification chamber varies directly with the rate of gas withdrawal.

The carbide stock in the hopper (b) is sufficient for about one hour, but the skip (a) can be refilled with carbide and replaced on the hopper so that continuous operation is possible. The wet generator described has a continuous hourly output of 75 m^3 of acetylene. The skip holds 1000 kg of carbide.

Low-Pressure Generators. The working principle of the low-pressure carbide-to-water generators is very similar to that of the medium-pressure carbide-to-water generator described above. In most cases, a downstream acetylene holder, normally of the floating gas bell type, is provided. In contrast to the medium-pressure generator, in which the carbide feed rate is controlled by the acetylene gas pressure, the feed rate in the low-pressure generator is controlled by the position of the bell in the acetylene holder, i.e., by the gas quantity.

Products. The acetylene generated in the wet generator can be used for welding, often without further purification. In certain cases, coke- or gravel-filled purifiers or a wet scrubber are connected downstream from the generator for separating solid or liquid particles. Before it is fed to a synthesis unit, the acetylene must be purified chemically (see Section 4.3.4.3).

The lime slurry formed is fed into pits. Here, the calcium hydroxide settles in the form of a lime dough containing 35 – 75 wt % water (wet lime, carbide lime dough). This dough is used as carbide lime.

4.3.4.2. Dry Generators

Dry generators are mainly used for the production of large quantities of acetylene for chemical synthesis.

Compared to the wet generator, the primary advantage of the dry generator is that the dry calcium hydroxide formed as a byproduct can be used in other processes more easily, more cheaply, and in a more diversified way than the lime slurry obtained in the wet generator [64]. Moreover, lime recycling into the carbide production process is only possible with dry calcium hydroxide.

A high gasification rate and the elimination of the risk of overheating were originally the most important criteria for the design of dry generators. Early designs of dry generators worked by continuous renewal of the reaction surfaces of coarse carbide with the aid of rotating drums, blades, vibrating screens, and similar equipment.

Typical examples are the early generator of Shawinigan Chemicals [65] and the Piesteritz dry generator [66].

Although a number of factors affect the gasification rate of carbide, e.g., density, porosity, and crystalline structure, above all it is the specific surface that affects the carbide gasification rate the most. Hence, dry generators work with finely ground carbide (0 – 3 mm), which gasifies in a fraction of the time needed for coarse carbide. The result is a high space–time yield.

A typical application of this principle is the large-scale *Knapsack dry generator*, which was developed at the Knapsack works of Hoechst. This type of generator is used worldwide and is described in more detail below (Fig. 29).

Carbide of the grain size 0 – 3 falls from the chain conveyor (a) into the subdivided feed bin (b). The chain conveyor is loaded with material

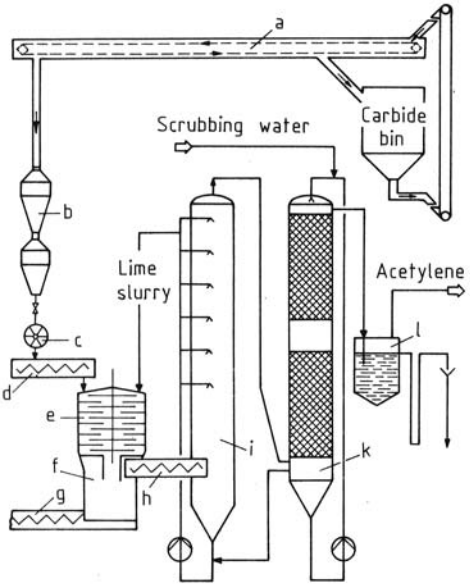


Figure 29. Knapsack dry generator a) Chain conveyor; b) Feed bin; c) Star wheel; d) Carbide feed screw; e) Generator; f) Lime lockhopper; g) Lime discharge screw; h) Lime scraper; i) First scrubbing tower; k) Second scrubbing tower; l) Dip seal

from the carbide bin. Because of the recirculating stream of carbide the feed bin (b) is full at all times. The carbide layer in the feed bin (b) acts as a gas seal between the generator and the carbide conveying system.

The carbide is fed to the generator (e) via the star wheel (c) and the carbide feed screw (d). The largest generator of this kind built to date has a diameter of 3.5 m and an overall height of approximately 8.0 m. The generator has up to 13 circular trays. These are so designed as to leave alternate annular gaps on the shell side and at the central agitator shaft. The agitator shaft moves stirrer paddles across the trays.

The carbide first reaches the uppermost tray where the generator water is also admitted. The reaction mixture consisting of carbide, water, and calcium hydroxide is pushed by the stirrer paddles towards the outer edge, drops on to the second tray, returns towards the center, etc. When it reaches the last tray, the carbide has been fully gasified. The calcium hydroxide, which still contains up to 6 % water, drops into the lime lockhopper (f). Here, a lime layer two meters deep serves as the gas closure between generator and lime conveying system. The lime is withdrawn continuously.

The gas leaving the generator through the lime scraper consists of 25 % acetylene and ca. 75 % water vapor. The water vapor is the result of dissipating the major portion of the reaction heat. Depending on the generator load, up to several hundred kilograms of lime hydrate dust are carried along with the acetylene. The lime scraper (h) retains the major portion of this dust and returns it to the generator. The remainder is sent together with the gas into the first scrubbing tower (i). Here, lime slurry is sprayed into the hot acetylene gas (ca. 90 °C) to scrub out the lime dust; part of the water vapor condenses because of the simultaneous cooling. In the second scrubbing tower (k), the acetylene is sprayed with atomized water to cool the gas below 40 °C; additional water vapor condenses here. Any ammonia still present in the gas is also removed.

The acetylene leaves the generator via the dip seal (l). It still contains certain impurities in the form of sulfur and phosphorus compounds.

The Knapsack dry generator is suitable for a carbide throughput of 15 t/h, corresponding to an acetylene quantity of 3750 m^3/h. During this process, about 17.5 t of calcium hydroxide per hour are obtained. The pressure in this low-pressure generator amounts to approximately 1.15 bar (115 kPa).

The dry generator of Shawinigan Chemicals, Montreal [67], also processes finely ground carbide and has a variety of applications. It consists of several superimposed troughs. Carbide and water are fed into the uppermost trough. The reacting mixture, which is constantly kept in motion by blades, flows over a weir onto the trough below, etc. At the uppermost trough, water is admitted at such a rate that carbide-free calcium hydroxide can be withdrawn at the lowermost trough. The generated acetylene is purified in two scrubbing towers and cooled.

The calcium hydroxide formed (carbide lime) has a wide range of applications, e.g., in the building industry (for preparing mortar, cement, etc.), in the chemical industry (for neutralization and for recycling to the carbide furnace), in agriculture (as fertilizer), and for water purification and waste water treatment [64].

4.3.4.3. Acetylene Purification

During the gasification of carbide with water, gaseous compounds become mixed with the acetylene, and these must be removed because they have a harmful effect on the downstream chemical synthesis processes. The impurities are mainly sulfur and phosphorus compounds. They can be removed by one of the following purification processes.

In the first process, *dilute chlorinated water* is used as the oxidizing agent. The chlorine concentration of the water is limited to 1.5 g/L to prevent the formation of unstable chlorine compounds, which present an explosion hazard. The chlorine scrubbing step is followed by a caustic soda scrubber to remove the hydrogen chloride formed during the oxidation process. The disadvantage of this purification process is that considerable quantities of scrubbing water are produced.

The second process uses 98 % *sulfuric acid* as the oxidizing agent [68]. Because very small quantities of sulfuric acid are admitted, it is difficult to dissipate the heats of absorption and reaction. Heating the acetylene results in increased formation and settling of polymerization products in the purification stage. For this reason the gas requires additional cooling in the event that the acetylene contains appreciable quantities of impurities. Moreover, it is recommended that a second scrubbing tower be kept on standby if a high onstream factor is desired (e.g., 91 % ≙ 8000 h/a operating time).

The sulfuric acid scrubber is followed by a caustic soda scrubber, in which the sulfur dioxide formed during oxidation is removed.

The main advantage of this purification method is that virtually no waste water is obtained. The small amount of polluted, highly concentrated sulfuric acid can be used, for example, in fertilizer plants.

These two purification processes yield the following acetylene purities (by volume):

Acetylene	> 99.5 %
Sulfur, as H_2S	< 10 ppm
Phosphorus, as H_3P	< 10 ppm

As a result of the extremely good sorption properties of the concentrated sulfuric acid, very pure acetylene can be expected.

4.4. Other Cracking Processes

4.4.1. Thermal Cracking By Heat Carriers

Well-known processes using heat carriers, such as the Wulff and Hoechst high-temperature pyrolysis (HTP) processes, are no longer used because they require refined petrochemical feedstocks such as naphtha and liquid petroleum gas. The Wulff process uses refractory material as the heat carrier, whereas the Hoechst HTP process uses hot combustion gases.

Newer processes, which are able to convert crude and heavy distillates into olefins and considerable amounts of acetylene, are still in the pilot-plant stage. These processes include the advanced cracking reactor process developed by Kureha, Chiyoda, and Union Carbide, using high-temperature superheated steam, and Dow's partial combustion cracking process, using hot combustion gases produced from oxygen and fuel oil as the heat carrier.

Wulff Process [69, 70, p. 58]. This process is based on indirect heat transfer, an approach fundamentally different from the partial-oxidation and electric-arc processes. The hydrocarbon feed is cracked in refractory ovens previously heated by combustion gas. After cracking, the products are quenched outside the reactor. Soot formation is a serious problem because the feed cannot be heated as rapidly as in the partial-oxidation or arc processes. This problem can be diminished by using a feed with a higher hydrogen:carbon ratio. However, methane is not suitable because of the high temperature and high heat of reaction required, resulting in a low conversion rate. Thus the best feed for the Wulff process is ethane or propane.

Hoechst High-Temperature Pyrolysis (HTP) Process (Fig. 30) [1, 70, p. 55, 71]. This is a two-stage process. In the first stage, heat is produced in the burner by the combustion of residual cracked gas from the acetylene recovery section (CO, H_2, CH_4) with oxygen. Immediately after combustion, the temperature is about 2700 °C; this is moderated to about 2300 °C by the injection of steam before the reactor is entered. In the second stage, the feedstock naphtha is injected, and the adiabatic cracking reaction takes place. A final temperature of about 1300 °C is reached: This determines the

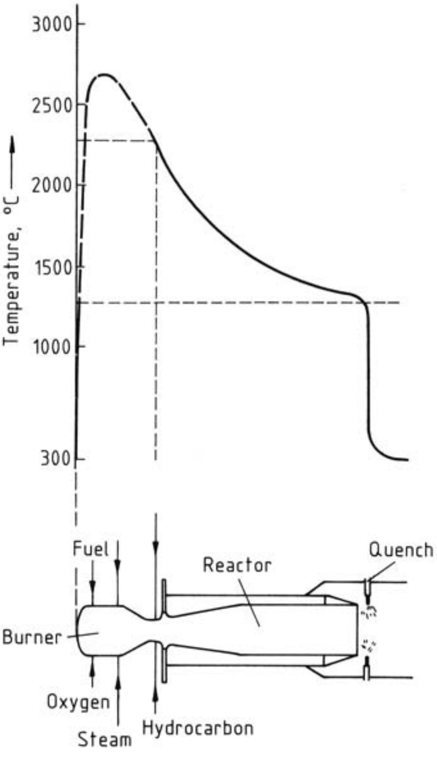


Figure 30. High-temperature pyrolysis (HTP) process

cracked gas composition. By varying the feed rate of naphtha the acetylene–ethylene ratio can be altered from 30 : 70 to 70 : 30. However, thermodynamic and economic considerations show that the optimum ratio is 40 : 60.

After a reaction time of a few milliseconds the cracked gas is quenched to approximately 250 °C by the injection of cracked oil from the process. The oil absorbs heat from the cracked gas and is passed through waste heat boilers, raising the steam pressure. No soot is formed in this process, even when crude oil is used as feed because of the high steam content of the carrier gas.

After the oil crisis of 1973 the process became uneconomical in spite of its high thermal efficiency, and in 1976 it was shut down after 15 years of operation. However, one unit is still running in Czechoslovakia.

Kureha, Chiyoda, Union Carbide Advanced Cracking Reactor (ACR) Process [72]. To avoid dependence on oil refineries or gas processors for the supply of feedstocks, processes for directly cracking crude oil have been developed by various companies for the production of olefins. Some of these processes operate at reaction temperatures intermediate between those of the usual crack processes for olefins and those for acetylene. The ACR process (Fig. 31) uses a multi-port burner to produce a heat carrier gas of 2000 °C by the combustion of $H_2 - CH_4$ mixtures with oxygen in the presence of steam preheated to 800 °C.

The oil to be cracked is introduced through nozzles into the stream of carrier gas and passes into an advanced cracking reactor, where the reaction takes place adiabatically at 5 bar (0.5 MPa). The initial temperature is 1600 °C; the final temperature at the exit of the reactor is 700 – 900 °C after a residence time of 10 – 30 ms. The cracked gas is quenched by oil in an Ozaki quench cooler (Fig. 32), where steam production up to 120 bar (12 MPa) is possible. This particular boiler design was developed for a high heat transfer rate without coke formation on the exchanger surfaces. Yields reported for Arabian light crude oil are 11.2 wt % hydrogen and methane, 40.7 wt % olefins, and 4.2 wt % acetylene. The acetylene yield is about ten times higher than in usual olefin processes.

Dow Partial Combustion Cracking (PCC) Process [72]. The basic idea of this process is to reduce coking and soot formation considerably when heavy feeds are cracked and when hydrogen is present in the reaction mixture. The PCC process (Fig. 33), which accepts crude oil and heavy residue as feedstock, attains a high partial pressure of hydrogen in the reaction zone by recycling the quench oil (produced in the process) to the burner where it is partially oxidized to

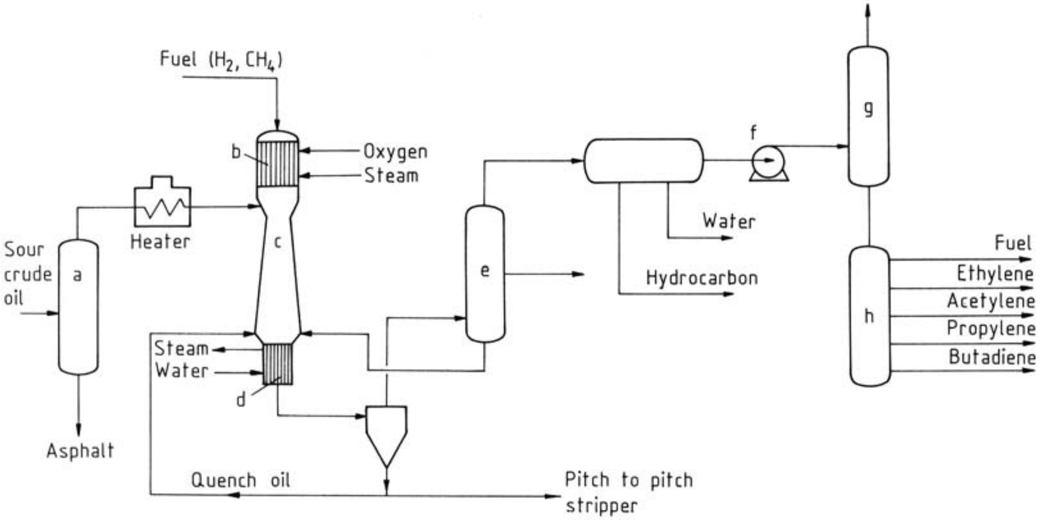


Figure 31. Advanced cracking reactor process (ACR) a) Crude distillation column; b) Burner; c) Advanced cracking reactor; d) Ozaki quench cooler; e) Oil gasoline fractionator; f) Compressor; g) Acid gas removal column; h) Gas separator

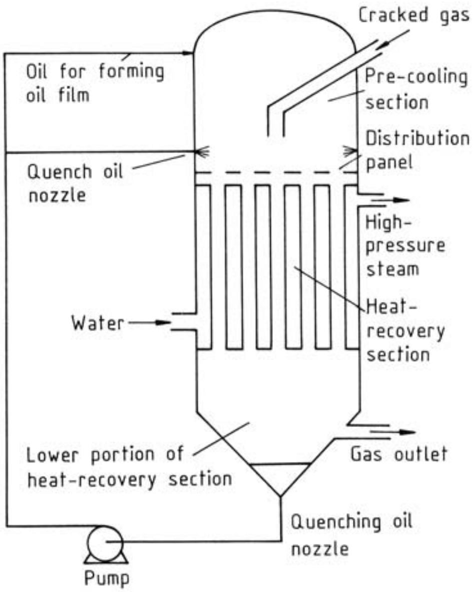


Figure 32. Ozaki quench cooler

yield synthesis gas. Thus there is no need to find a use for the quench oil as in the case of the ACR process. Starting from residual oil boiling above 343 °C, yields are given as 12.4 wt % methane, about 38 wt % alkenes, and 2.5 wt % acetylene. This is seven to eight times more acetylene than that obtained from a steam cracker, but less than the acetylene yield of the ACR process, because of a residence time in the reaction zone which is three to ten times longer.

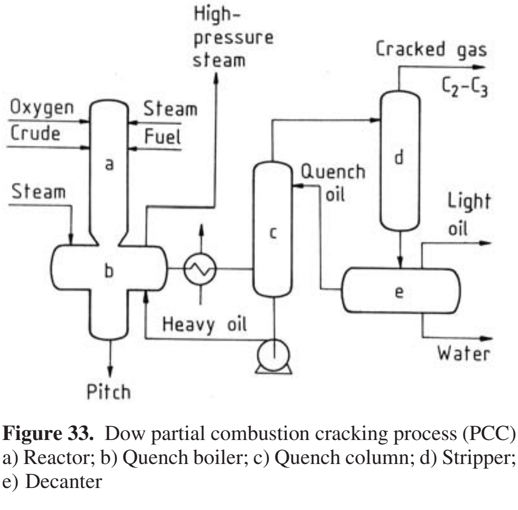


Figure 33. Dow partial combustion cracking process (PCC)
a) Reactor; b) Quench boiler; c) Quench column; d) Stripper; e) Decanter

4.4.2. Acetylene as a Byproduct of Steam Cracking

In a steam cracker saturated hydrocarbons are converted to olefinic products such as ethylene and propene. Besides these desired components, acetylene and many other products are formed in the cracking process (Fig. 36). The concentration of acetylene depends on the type of feed, the residence time, and temperature (cracking severity: expressed as conversion or propene/ethylene ratio P/E). Typical data are given in Table 10. The acetylene concentration in the off-gas from the furnace varies between 0.25 and 1.35 wt %. In certain cases of propane and butane cracking the the raw gas can contain up to 2.1 wt % acetylene with corresponding very low amounts of propyne and propadiene. The corresponding content of acetylene in the C_2 fraction is about 0.4 – 2.5 wt %. An ethylene plant producing 400 000 t/a ethylene produces 4500 – 11 000 t/a acetylene. The acetylene is removed by catalytic selective hydrogenation or solvent extraction. Today the dominating acetylene removal process is selective hydrogenation.

Acetylene Hydrogenation Most ethylene plants are equipped with a hydrogenation unit. Acetylene is converted selectively to ethylene on a Pd-doped catalyst. Whereas in the past mainly Ni catalysts were used, today Pd catalysts are doped with other metals such as silver to improve selectivity [73]. Typical process conditions are temperatures of about 40 – 120 °C, pressures of 15 – 40 bar and space velocities of 1000 – 120 000 kg L^{-1} h^{-1}. Depending on the type of feed and the plant, there are several process options:

1. Front-end hydrogenation (C_{2-} stream containing H_2, CO, methane, C_2H_2, C_2H_4 and C_2H_6)
2. Raw-gas hydrogenation (hydrogenation before C_2/C_3 separation, stream containing H_2, CO and all hydrocarbons of the raw gas after cracked gas compression).This variant of front-end hydrogenation is only used in gas crackers where the content of C_{3+} hydrocarbons is comparable low.
3. Tail-end hydrogenation (pure C_2 stream containing C_2H_2, C_2H_4, and C_2H_6; separate addition of an equimolar amount of hydrogen is necessary)

Table 10. Yields of unsaturated components (wt %) in raw gas from steam cracking

Feedstock	Cracking severity	Acetylene	Propyne	Propadiene
Ethane	65 % convers.	0.4 – 0.50	0.04	0.02
LPG	90 % convers.	0.65 – 1.35	0.63	0.35
Full-range naphtha	P/E: 0.4	0.9 – 1.05	0.81	0.54
Full-range naphtha	P/E: 0.53	0.5 – 0.70	0.68	0.50
Full-range naphtha	P/E: 0.65	0.25 – 0.42	0.46	0.38
Atmospheric gas oil	P/E: 0.55	0.40	0.34	0.29
Hydrocracker residue	P/E: 0.55	0.50	0.36	0.31

Typical specifications for acetylene content in the ethylene product are < 2 ppm with a tendency to further reduction to < 1 ppm.

General aspects of the process and the catalyst requirements are reviewed in [74–76] (see also → Ethylene, Section 5.3.2.2.).

Acetylene Recovery Acetylene is extracted from the C_2 fraction of the steam cracker. The solvent must fulfil the following criteria:

- Melting point lower than the dew point of the feed gas
- High solubility of acetylene at a temperature near the dew point of the C_2 fraction
- High acetylene selectivity ([9, 11])
- High chemical and thermal stability
- No foaming tendency due to traces of hydrocarbons
- Low toxicity
- Low vapor pressure at the operating temperature

After testing many solvents, including DMF, NMP, and acetone, the most suitable solvent for such a process proved to be DMF. The solubility of acetylene as a function of temperature is shown in Figure 5.

The process for the recovery of high-purity acetylene is shown in Figure 34 [77]. The gaseous C_2 mixture, consisting of ethylene, ethane, and acetylene, is fed to the acetylene absorber; the gas stream is contacted with counterflowing lean DMF at a pressure of 0.8 – 3.0 MPa. The process is suitable for the full pressure range prevailing in any of the known ethylene processes. The entire acetylene and some of the ethylene and ethane are dissolved by the solvent. Water and carbon monoxide decrease the solubility of acetylene. Furthermore, water causes hydrolysis of DMF, resulting in additional formation of carbon monoxide. Entrainment of DMF at the top of the column is avoided by a reflux stream. The purified C_2 fraction, containing < 1 ppm of acetylene, is fed to the C_2 splitter. The rich

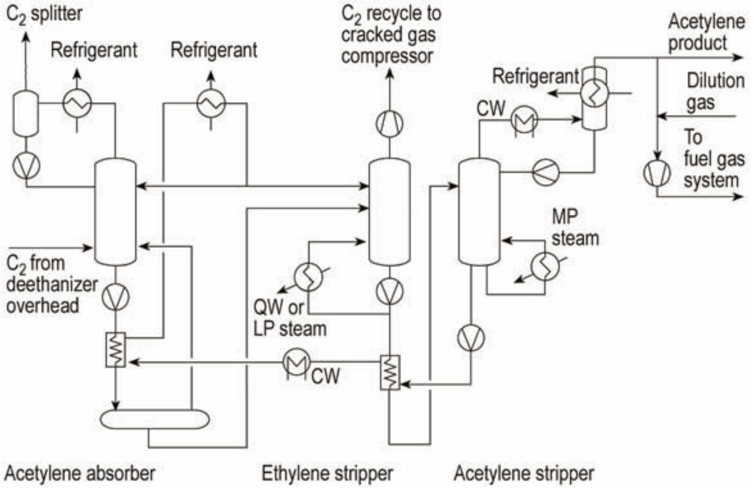


Figure 34. Acetylene recovery process [77]

Table 11. Material balance (mol %) for an acetylene recovery process operating on the C_2 fraction from a plant producing 400 000 t/a C_2H_4 (Linde) [78]

	Gas to absorber	Purified gas	Recycle gas	Product C_2H_2
Methane	trace	trace		
Acetylene	2	1 ppm	4	99.8
Ethylene	82	83.5	85.7	0.2
Ethane	16	16.5	10	trace
C_3	trace	trace	0.3	trace
DMF		1 ppm	trace	trace
Temperature, K	252	249	255	258
Pressure, MPa	2	1.98	0.11	0.12
Flow rate, kmol/h	2186	2126	17.5	52.5

solvent stream is sent to the ethylene stripper, which operates slightly above atmospheric pressure. Ethylene and ethane are stripped off and recycled to the first stage of the cracked gas compression. Any acetylene entrained with the overhead gas is recovered by washing with cold solvent at the top of the stripper. In the acetylene stripper, pure acetylene is isolated from the top of the column. After cooling and heat recovery, the acetylene-free solvent is recycled to the absorber and ethylene stripper. The acetylene product has a purity of $> 99.8\,\%$ and a DMF content of less than 50 ppm and is available at 10 kPa and ambient temperature.

The material balance and the utilities consumption of an acetylene recovery unit are listed in Tables 11 and 12. At present, more than 112 000 t/a of petrochemical acetylene from twelve olefin plants worldwide is recovered by this technology. With a big drop in the total acetylene market in 2001, the market decreased on average by 6.8 % per year from 1998 to 2003, and only a marginal growth rate is expected until 2009 (max. 2 % per year) [134]. For this reason during the last five years (2006) no new acetylene recovery facilities have been erected. Only some existing plants were expanded. In North America, for example, there are currently only two major companies producing acetylene as byproduct of ethylene production, i.e., Dow Chemical in Taft, LA, and Petroment at Varennes in Canada [135]. Figure 35 shows an industrial plant with a design capacity of 14 400 t/a of high-purity acetylene.

Table 12. Consumption of utilities for an acetylene recovery process operating on the C_2 fraction from a plant producing 400 000 t/a C_2H_4 (Linde) [78]

DMF, kg/h	1.3
Heating steam, t/h	3.9
Cooling water, m^3/h	100
Electrical energy, kW	125
Refrigerant, GJ/h	6.3
Quench water, GJ/h	3.1
Plot area, m × m	15 × 40

A material balance for ethylene plant outputs including acetylene extraction or hydrogenation is shown in Figure 36 [79]. The economic evaluation shows that petrochemical acetylene remains attractive even if the price of ethylene is doubled. It is economical to retrofit acetylene absorption in an existing olefin plant equipped with a catalytic hydrogenation. Isolation of acetylene obtained as an unavoidable byproduct of ethylene production is the economically most attractive route to cover acetylene demand.

A similar process is available for propyne (see → Propyne)

5. Safety Precautions, Transportation, and Storage

General literature is given in [10, 80, 81].

5.1. General Safety Factors and Safety Measures

Decomposition and Combustion. Acetylene is thermodynamically unstable under normal conditions. Decomposition into carbon and hydrogen can achieve temperatures of about 3100 °C, but due to formation of other products, the temperature reached adiabatically is 2800 – 2900 °C. The decomposition can be initiated by heat of reaction, by contact with a hot body, by an electrostatic spark, by compression heating, or by a shock wave. The decomposition induced by heating the wall of the container or pipe is very

Figure 35. Acetylene recovery plant (name plate capacity: 14 400 t/a of high-purity acetylene)

sensitive to the pressure, the size and shape of the container or the diameter of the pipe, the material of the container, and traces of impurities or other components. Solid particles such as rust, charcoal, alumina, and silica can lower the ignition temperature compared to clean steel pipe.

Decomposition gives rise to different scenarios:

- Working range I (deflagration): a flame produced by decomposition or combustion and propagates at a velocity below the velocity of sound into the unconverted gas (pressure rises simultaneously in front of and behind the flame front)
- Working range III (detonation): the flame propagates at ultrasonic velocity into the unconverted gas (shock wave between low pressure in the unconverted gas and high pressure in the converted gas)
- Working range II (intermediate between I and III): often the propagation velocity of a deflagration is not constant (it increases with increasing density, temperature, and turbulence), and therefore a change from deflagration to detonation is observed

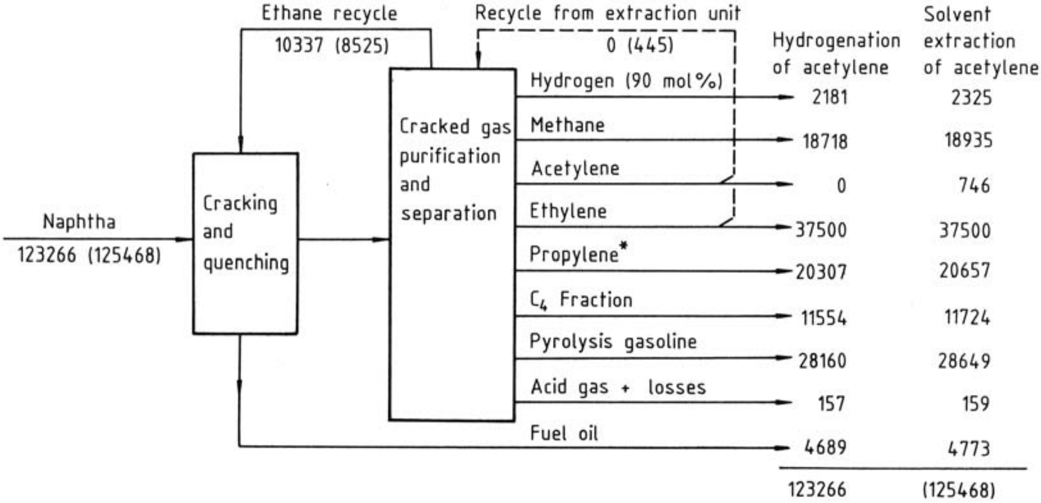


Figure 36. Material balances of a 300 000 t/a ethylene plant equipped with either C_2 hydrogenation or acetylene extraction (all rates in kg/h, the numbers in parentheses are for the solvent extraction process) [79] * Chemical grade

As consequence, design criteria for piping and other components are proposed for the different working ranges and depend on the diameter of the pipe. Limit lines for deflagration and detonation are given in [82] on the basis of the work of Sargent [83]. An extended Sargent diagram is shown in Figure 37.

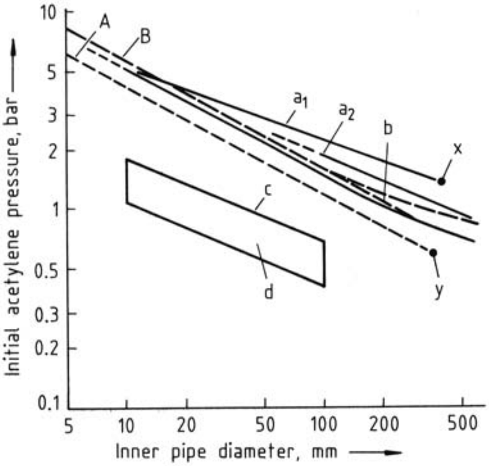


Figure 37. Detonability limits of acetylene [83, 88]
A) Deflagration limit; B) Detonation limit
Detonation limits: a) Thermal ignition in a plain pipe (a_1 melting wire, 20 – 80 J; a_2 detonator cup, ≈2400 J); b) Thermal ignition plus orifice; c) Ignition by chemical reaction in a shock wave; d) Range of possible quasi-detonation depending on ignition energy of shock wave; x) and y) Limiting ignition pressure for thermal ignition with melting Pt wire and with detonator cup, respectively

The limits are influenced by the method of ignition (e.g., melting wire or a detonator cap). Changing the method of ignition from a melting Pt wire (Reppe) to the exploding wire ignitor (ignition energy ca. 70 J) used by BAM resulted in lower stability pressures for acetylene mixtures [84] and pure acetylene [85] (Table 13). A description of the experimental setup can be found in [133].

Mixtures of acetylene with methane have higher stability pressures than those with nitrogen or hydrogen. The phlegmatizing influence of foreign gases increases in the order $H_2 < N_2 < CO_2 < NH_3$, which corresponds to the heat capacities of these gases [133]. For C_2H_2 – C_2H_4 mixtures the stability pressure rises with increasing ethylene fraction. However, a significant effect can be observed only at C_2H_2 contents

Table 13. Stability pressure (bar) of acetylene and acetylene mixtures for two methods of ignition and pressure increase [84, 85]

Mixture	Ignition method		p_{ex}/p_a [a]
	Reppe	BAM	(BAM)
100 % C_2H_2	1.4	0.8	
90 % C_2H_2/10 % N_2	1.8	1.0	8.6
90 % C_2H_2/10 % CH_4	2.1	1.0	7.2
90 % C_2H_2/10 % H_2	1.6	0.9	6.9
50 % C_2H_2/50 % N_2	9.0	3.6	6.3
50 % C_2H_2/50 % CH_4	14.7	12.9	
50 % C_2H_2/50 % H_2	4.7	2.5	5.5

[a] p_{ex}/p_a: ratio of maximum pressure to pressure before ignition.

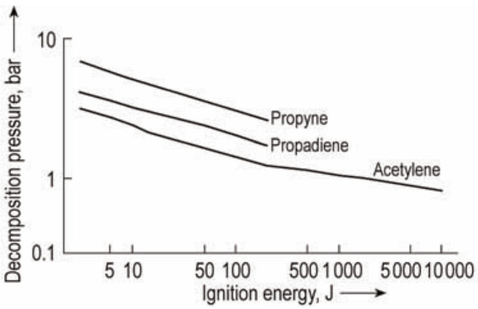


Figure 38. Decomposition pressure versus ignition energy for unsaturated hydrocarbons

< 50 % [133]. Further information on the effect of additional gases on acetylene decomposition is given in [86]. The dependence of stability pressure on the energy of the ignition source has led to ongoing discussion about its relevance for industrial design and operations [87].

Figure 38 shows the decomposition pressure of acetylene, propyne, and propadiene as function of ignition energy. This relationship is the basis for the safe design of processes for the recovery of acetylenic components (see Section 4.4.2 and → Propyne). Additional investigations have been published on the dependence of deflagration pressure on the flow in pipes [88] and the decomposition of high-pressure acetylene in branched piping [89]. Solid acetylene is not critical with regard to decomposition, provided it is the only material involved [7]. In liquid oxygen, solid acetylene can readily ignite on mechanical impact and react violently [90]. Recommendations for equipment used in gas welding and cutting technology, such as rubber hoses, safety devices, and flame arresters, are given in [91–93].

Combustion of Acetylene in Oxygen (Air)

The reaction of acetylene and oxygen at 25 °C and 1 bar to form water and CO_2 generates 1255.6 kJ/mol. Temperatures of around 3100 °C can be reached. Figure 39 shows flame temperatures and flame front velocities for mixtures of oxygen with hydrocarbons [94].

Acetylene allows the highest temperatures and flame front velocities to be attained. The maximum temperature is very sensitive to the mixing ratio, which also determines whether a reducing, neutral, or oxidizing flame exists (Fig. 40).

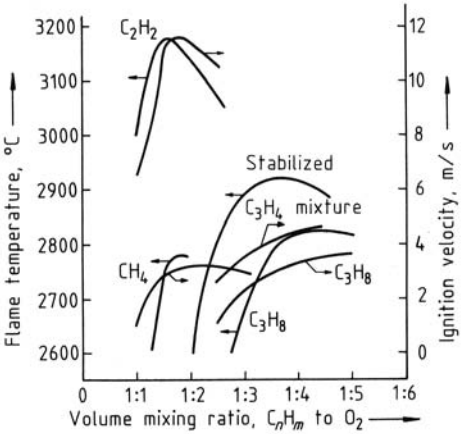


Figure 39. Flame temperatures and ignition velocities of acetylene–oxygen mixtures and mixtures of other hydrocarbons with oxygen

Fundamental safety data for acetylene–air and acetylene–oxygen mixtures are listed in Table 14. At atmospheric pressure and 25 °C mixtures of 2.4 – 93.0 vol % acetylene in oxygen are explosive; the possibility of self-decomposition at high acetylene must also be taken into account. A large explosion at Acetylene Services Company (ASCO) in the USA in 2005 was caused by accumulation of acetylene in the water-pipe system. Most probably the contact of

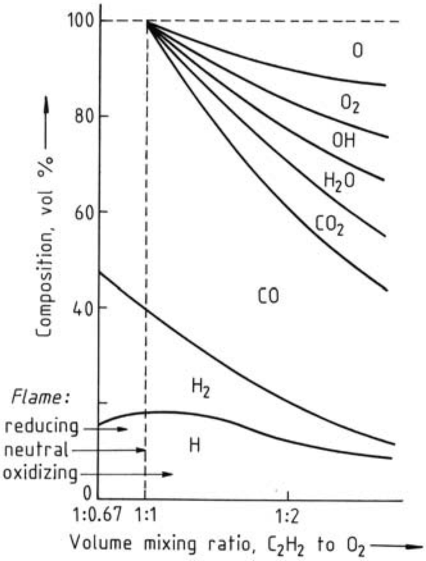


Figure 40. Chemical composition of an oxygen–acetylene flame at its tip versus mixing ratio

Table 14. Fundamental safety data for acetylene–air and acetylene–oxygen mixtures

	Air	Oxygen
Lower flammability limit, vol %	2.5	2.4
Upper flammability limit, vol %	82	93
Flame temperature[a], K	2863	3343
Flame front velocity, m/s	1.46	7.6
Increase of pressure (deflagration)	11	50
Detonation velocity, m/s	2300	2900

[a] Stoichiometric mixture.

acetylene with the hot surface of a propane heater caused the explosion [95]. A comparison of C_2H_2 deflagration and $C_2H_2 - O_2$ explosion with TNT explosion is given in [96].

Handling of Acetylene. For pure acetylene the prescribed safety instructions, for example, the *Technische Regeln für Acetylenanlagen und Calciumcarbidlager* (Technical regulations for acetylene plants and calcium carbide depots), *TRAC,* [97], have to be strictly followed. The former *Acetylenverordnung* (Decree about acetylene) [53] in Germany has been replaced by the more general *Betriebssicherheitsverordnung* (Decree about safety in plants) [97] as of January 1, 2003. However, it is not possible to formulate general safety instructions for the great variety of chemical processes with acetylene as reaction component under diverse reaction conditions.

Both handling acetylene and experiments with it necessitate critical examination of sources of possible danger. The literature cited can only serve as an aid to decisions on precautions. The safety regulations mentioned above have been determined in experiments with well-defined apparatus dimensions (length, diameter, geometry). For other dimensions they can only serve as an indication of explosive behavior and should not be considered as rigid limits. The development of economical chemical processes involving acetylene at elevated pressures or under other hazardous conditions calls for decomposition tests for the crucial stages where decomposition could occur. This must be done in close cooperation with official testing institutions, such as the Bundesanstalt für Materialprüfung (BAM) in Germany.

In general, the following rules should be observed in handling acetylene:

- Temperature and pressure must be selected so as to avoid liquefaction of acetylene.
- Reactions of acetylene in solvents or with liquid reaction components must be carried out at such acetylene concentrations that explosive decomposition of the acetylene in the liquid phase cannot occur. In many cases this condition is fulfilled at an acetylene loading below 100 m^3 (STP) per cubic meter of solvent. Higher loadings are only permitted if additional precautions are taken, such as filling the volumes containing the liquid with steel packings. The formation of a separate gas phase has to be avoided.
- The technical rules (such as *TRAC* [97]) are valid for pure gaseous acetylene. If an inert gas, such as nitrogen, is added to the acetylene, higher acetylene partial pressures are permitted.
- In the design of apparatus the partial pressure of acetylene should be selected so that the minimum distance to the decomposition limit is about 20 %. The apparatus should be designed to withstand pressures (1) 12-fold the initial pressure for pure acetylene systems or (2) the initial pressure plus 12-fold the acetylene partial pressure for mixtures and solutions.
- Formation of hydrates (see Chap. 2) under pressure must be avoided because this leads to obstructions in the apparatus and pipelines. The melting point of these compounds is in the range 0 –13 °C; therefore, pressurized acetylene containing water has to be kept above 15 °C.

In addition to the measures for building construction, electrical installations, fire protection, purging, and leak detection, acetylene plants and distribution systems are provided with flame traps and flashback and release valves and locks [98, 99]. Flame traps consist either of tubes immersed into water-filled cylinders (wet trap) or cylinders filled with a packing of high surface area to decelerate the decomposition. A wet arrester, which is used for an acetylene distributing line, is shown in Figure 41. Suitable materials for dry-trap packings are sinter metals, ceramic beads (e.g., Raschig rings), bundles of small tubes, and corrugated metal foils [100, 101].

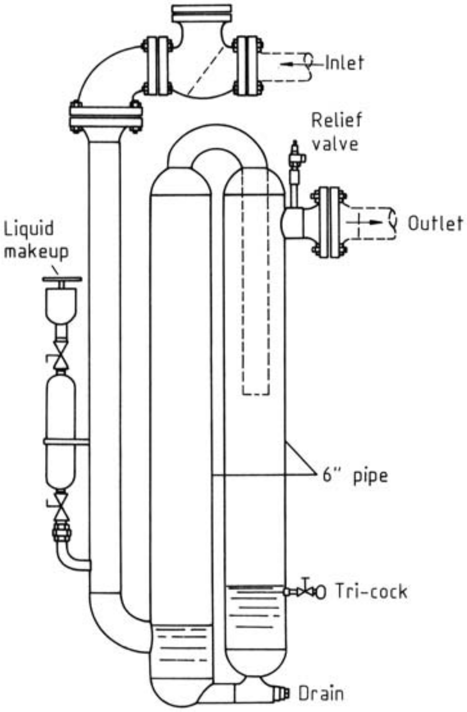


Figure 41. Hydraulic flame trap for acetylene lines (Union Carbide), [102]

Tapping points for acetylene distribution units which meet the German *TRAC* rules include a nonreturn valve to avoid intrusion of air from downstream, a sinter-metal flame trap, and a thermo- or pressure-sensitive spring lock. The last closes if a flame is stopped by the trap but still burns outside of the flame trap. Detailed information is given in [98].

Transportation in Pipelines Acetylene is occasionally transported in pipelines. Figure 42 shows the safety components of an acetylene pipeline between Burghausen and Gendorf, Federal Republic of Germany. The pipeline was operated until 1976 without incident. Its length is 8 km, and the pipes are 300 mm in diameter. Design pressure was 100 bar, although operation pressure was only 2 bar at the inlet and 1.25 bar at the outlet. The pipeline was provided with rupture disks, which open to atmosphere in case of decomposition. Quick closing valves are initiated simultaneously to protect both upstream and downstream equipment. At each end, part of the pipeline is filled with tube bundles to stop propagation of any acetylene decomposition. The flame traps consist of 600-mm-diameter U's filled with Raschig rings.

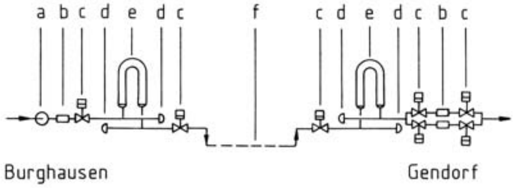


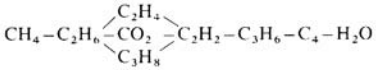
Figure 42. The 8 km acetylene pipeline from the Marathon refinery, Burghausen, to Farbwerke Hoechst, Gendorf, Federal Republic of Germany [103] a) Compressor; b) Control points; c) Automatic quick-closing valves; d) Rupture disks to atmosphere; e) Flame traps; f) Pipeline

A report [102] is available on an acetylene-decomposition event in a pipeline system, which demonstrates the need for safety measures. Instead of transportation of pure acetylene, pipeline transportation of acetylene solutions in acetone was proposed as safer [103]. In the United States, transportation of acetylene solutions in liquid ammonia was considered for existing ammonia distribution systems [104].

Hazardous Acetylene Traces in Low-Temperature Processes Acetylene is the most dangerous component in gas mixtures processed in low-temperature plants. In air separators, for example, acetylene can be suspended in liquid oxygen as a solid or as a segregated liquid phase that is quite unstable and tends to uncontrollable and violent decomposition. (The solubility of acetylene in liquid oxygen is low, see Chap. 2) Therefore much attention must be given to checking for and removing acetylene in low-temperature separation plants.

Normally air contains some acetylene, up to 0.3 mL/m^3. In industrial areas, especially in the proximity of petrochemical plants, higher concentrations (up to 1 mL/m^3) can occur. Without any measures, acetylene in the feed air of an air separator would be enriched in the cold section of the unit.

In modern air separators alternating molecular sieve adsorbers are used. The adsorbers obey the following breakthrough sequence:



$$CH_4-C_2H_6 \begin{array}{c} \diagup C_2H_4 \diagdown \\ - CO_2 - \\ \diagdown C_3H_8 \diagup \end{array} C_2H_2-C_3H_6-C_4-H_2O$$

To avoid acetylene breakthrough the adsorber is operated for sufficient CO_2 removal and is regenerated when the CO_2 concentration at the adsorber outlet starts to increase. Further details are given in [105–109].

Another possible way to remove acetylene and other combustible air contaminants is catalytic oxidation prior to the separation [107, 110]. This method, being expensive, is rarely used.

All air separators are provided with routine analysis systems for acetylene (→ Oxygen). Routine analysis concentrates on the liquid oxygen of the main condenser [111].

The removal of acetylene in cracked gas separation is treated in Section 4.4.2. The processing of other acetylene-containing gases, e.g., coke-oven gas, by low-temperature separation is described in [112].

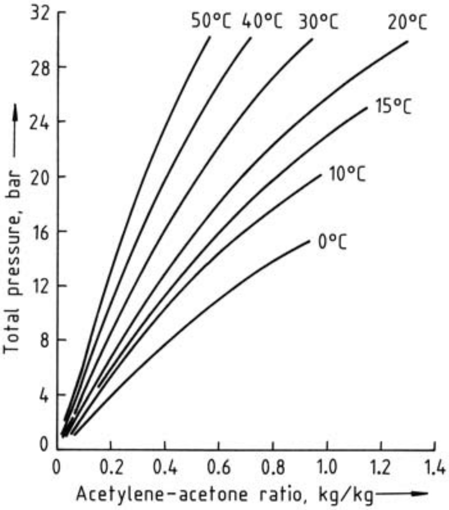


Figure 43. Total pressure of acetylene solution in acetone as a function of acetylene : acetone ratio and temperature [7]

5.2. Acetylene Storage in Cylinders

Because of its tendency to deflagrate or to detonate, acetylene cannot be compressed and stored in gas cylinders like other gases. At the end of the 19th century attempts to store acetylene under high pressure or liquefied led to fatal detonations in the USA, Paris, and Berlin.

For desensitizing, acetylene stored in gas cylinders is dissolved in a solvent in which the acetylene is very soluble. This solvent is dispersed in a porous solid that completely fills the gas cylinder. As well as giving better solvent distribution the porous material arrests any local acetylene decomposition induced, for instance, by flashback.

Acetone and dimethylformamide are the preferred solvents for acetylene in cylinders. An advantage of dimethylformamide is its lower vapor pressure, resulting in lower solvent losses during acetylene discharge. A disadvantage is its higher toxicity. The total pressure of an acetone-containing acetylene cylinder depends on the acetylene : acetone ratio and on temperature as is shown in Figure 43. Deviations from the plotted curves resulting in higher pressures are caused by the porous filling of the gas cylinder, which absorbs acetone, changing the effective acetylene : acetone ratio [113].

Impurities in the acetylene decrease the dissolving capacity of the acetone. Figure 44 shows the effect of moisture on acetylene solubility. As a result, acetylene produced from calcium carbide and water has to be dried.

Calcium carbide-based acetylene contains further impurities that have to be scrubbed out to avoid decreased solubility in acetone. Examples are divinyl sulfide and phosphine: 1 wt % divinyl sulfide in the acetone reduces the acetylene solubility from 35 g/kg to 31 g/kg at 20 °C and an acetylene pressure of 0.1 MPa. Further values, also for phosphine, are given in [114, 115]. The impurities have to be scrubbed

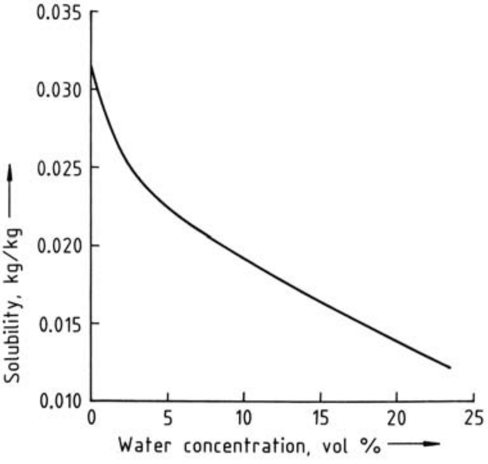


Figure 44. Solubility of acetylene in water-containing acetone at 25 °C and $p_{C_2H_2} = 1$ bar (0.1 MPa) [114]

out to residual concentrations of 0.5 g of phosphorus and 0.1 g of sulfur per cubic meter of acetylene.

During acetylene production from calcium carbide, disperse calcium hydroxide (0.1 – 1.0 μm) is produced. This contaminates the product gas. The calcium hydroxide present in acetylene filled into acetone-containing gas cylinders catalyzes aldol condensation of the solvent and reduces the solubility for acetylene:

$$2\ (CH_3)_2CO \rightarrow (CH_3)_2COHCH_2COCH_3 \quad \text{diacetone alcohol}$$

Therefore, the solids content of calcium carbide-based acetylene for filling acetone-containing gas cylinders must be kept below 0.1 mg/m^3 [114, 116].

The gas cylinders have to be filled with definite amounts of acetylene and solvent. Commercial-grade, seamless gas cylinders which meet specified standards (in Germany, DIN 4664) may be filled with the amounts listed in Table 15.

The amounts are fixed by regulations for handling pressurized gases [118]. Corresponding regulations in the United States have been issued by the Department of Transportation [119].

To determine maximum acetylene filling of gas cylinders, extensive ignition, impact, and heating tests have been worked out [120, 121].

The porous material in the acetylene gas cylinders must satisfy the following requirements: no interaction with the cylinder material, acetylene, or acetone and suitable mechanical properties, such as sufficient impact resistance. Suitable materials include pumiceous compounds, silica, charcoal, asbestos fiber, and alkaline carbonates. The porosity of these materials varies between 70 and 80 % [114, 122]. Modern monolithic materials are made preferably from silica, lime, and glass fiber. The mixtures are suspended in water to obtain a pasty material which is filled into the gas cylinders. The material is hardened at about 200 °C and subsequently dried and activated at 350 – 400 °C. A porosity of about 90 % is obtained.

Any porous material to be used for acetylene cylinders has to be examined and approved by competent authorities. The examination includes the determination of the maximum acetylene and solvent filling, the maximum filling pressure, and ignition and impact testing. Table 16 lists three porous materials approved for use in Germany. Figure 45 shows a photograph of “Linde M1” magnified 1 : 10000, clearly revealing the porous structure of such materials.

Methods for examining the materials have been standardized by CPI (Commission Permanente Internat. de l’Acétylène, de la Soudure Autogène et des Industries qui s’y rattachent, Paris) and ISO (International Organization for Standardization) [122].

Discharging acetylene from a gas cylinder leads to acetone losses because the partial pressure of acetone at 15 °C ranges from 0.14 bar at 15 bar total pressure to 0.18 bar at 1 bar total pressure. Solvent loss has to be replaced when an acetylene cylinder is reloaded. Further details concerning acetylene cylinders, porous materials, and valves can be found in [129].

6. Uses and Economic Aspects

6.1. Use in Metal Processing

Acetylene has many applications in the processing of metals and other materials. This is

Table 15. Permitted acetylene and acetone filling of seamless gas cylinders (satisfying German standards and safety rules) [117]

Gas cylinder			Acetone filling, kg			Acetylene filling, kg
Vol. of gas cylinder, L	Outer diameter, mm	Length, mm	Minimum	Maximum		
				General	Exceptional	
3	140	300	0.789	0.8625	0.9375	0.4725
5	140	460	1.315	1.4375	1.5625	0.7875
10	140	850	2.630	2.8750	3.125	1.575
20	204	810	5.260	5.750	6.250	3.150
27	204	1040	7.101	7.7625	8.4375	4.2525
40	204	500	10.520	11.50	12.50	6.30
40	229	1210	10.520	11.50	12.50	6.30

Table 16. Examples of approved silica-based porous materials in German acetylene cylinders [122] (for seamless 40-L cylinders satisfying DIN 4664, Blatt 2)

Material		Approved filling			
Type	Origin [a]	Acetylene[b], kg	Acetone[c], kg	Acetylene : acetone, kg/kg	Maximum pressure[d], bar
Linde M1	Linde, Munich	8.0	12.7	0.63	19
AGA 2	AGA, Hamburg	8.0	12.4	0.645	19
SIAD 2	SIAD, Sabbio	8.0	12.4	0.645	19

[a] Approval only when porous filling is prepared at place of origin;
[b] Maximum;
[c] Desired value;
[d] Gage, at 15 °C.

because of the high flame temperature and propagation velocity resulting in high energy densities and rapid heat transfer to the piece being worked. Examinations at Linde showed that for extreme oblique sections the efficiency using acetylene is up to 50 % higher than using propane as fuel gas [131]. The properties of an oxyacetylene flame given here supplement those in Section 5.1.

The temperature profile of an oxyacetylene flame consists of a hotter primary flame and a scattered secondary flame. The highest flame temperature is at the tip of the primary flame (Fig. 46). For material processing the primary flame is the more important.

The heating efficiency of the primary flame is the product of the volume-based heat released by the primary flame and the propagation velocity. This is plotted in Figure 47 for the oxyacetylene

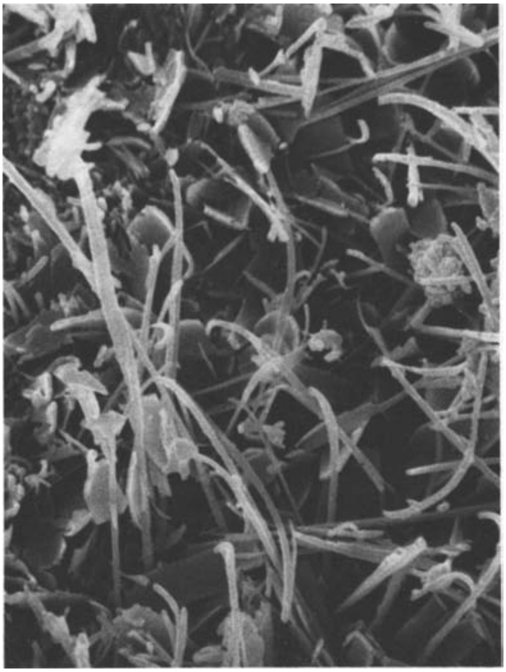


Figure 45. Porous silica material Linde M1 for acetylene cylinders (magnification 1 : 10 000)

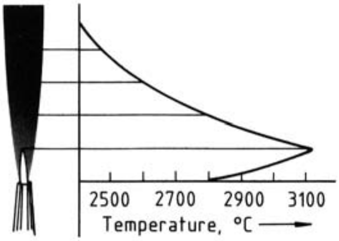


Figure 46. Temperature profile of an oxyacetylene flame

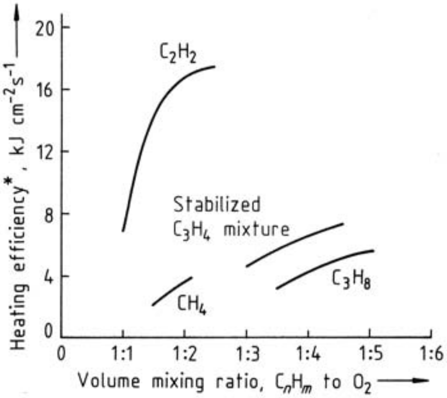


Figure 47. Heating efficiency of acetylene–oxygen mixtures and mixtures of other hydrocarbons with oxygen * based on area of primary flame cone

Table 17. Heat transfer in welding [123]

Gas temperature, K	Welding temperature, K					
	800		1200		1600	
	Q_S	Q_K	Q_S	Q_K	Q_S	Q_K
1000	2.3	13.4				
2000	3.8	55.4	3.4	37.0	2.3	18.5
3000	4.0	83.2	3.8	68.0	3.6	50.4

[a] Q_S, heat transfer by radiation (kJ cm^{-2} h^{-1});

[b] Q_K, heat transfer by convection (kJ cm^{-2}h^{-1}) at a gas velocity of 50 m/s

flame and some other flames. The heat transferred in welding is generated by radiation, convection, and thermal conduction (see Table 17). The heat transfer is promoted by a high temperature gradient between flame and workpiece.

Oxidizing, neutral, or reducing (carburizing) flames can be obtained by varying the oxygen : acetylene ratio (Fig. 40). For steel, alumina, and copper welding usually neutral or slightly reducing flames are used, whereas oxidizing flames are preferred for brass welding, cutting, pickling, and surface hardening [124]. Acetylene is burned with oxygen in single torches or in bundles of torches, the chief components of which are the connections for acetylene and oxygen, regulating valves, a mixing chamber (usually of the injection type), a flashback protection element, and a nozzle adapted to the specific applications [125, 126].

Oxyacetylene flames are used in welding, cutting, brazing, soldering, surfacing, flame spraying, heating, hardening, straightening, cleaning, pickling, rust removal, and decarbonizing.

Acetylene–air flames are occasionally used for tin brazing, hot air welding of thermoplastics, glassworking, and paint removal [125], although the convenience and safety of fuels such as propane or butane has displaced acetylene in those applications. Soft and hard soldering, flame hardening, and flame tempering are important applications for the softer acetylene–air flame. For acetylene–air mixtures, self-aspirating Bunsen-type and acetylene–compressed air burners are used.

The different uses of oxyacetylene and acetylene–air flames in metal working, the procedures, and the equipment are comprehensively described in [7] and [127]; other sources of information for oxyacetylene flame properties in welding are [123, 124], and [128].

6.2. Use as Raw Material in Chemical Industry

Because of the diversity of acetylene chemistry (see Section 3.1), acetylene has been used as a starting material for a great variety of industrially important products. These are summarized, together with their applications, in Figure 48.

Between 1960 and 1970, when worldwide acetylene production peaked, most of the products listed in Figure 48 were produced via acetylene. The competition between acetylene and the olefins since the 1970s (see Section 6.3) has resulted in substitution of ethylene and propene for acetylene, especially in the production of acetaldehyde and acrylonitrile. At present, acetylene is used mainly for the production of vinyl chloride, vinyl acetate, and other vinyl esters; acrylic acid; acetylene black; and acetylenic chemicals such as 1,4-butynediol and acetylenic alcohols. For the acetylenic chemicals the acetylene route is either the only commercial production process available or the predominant process. Vinyl chloride, vinyl acetate, and acrylic acid, formerly the main products from acetylene, are produced today mainly from ethylene and propene in most countries. However, acetylene demand for vinyl chloride monomer has grown 15.9% per year in China since 1997 and further calcium carbide-based production units are being erected from 2008 to 2013 in China.

China is by far the largest producer and consumer of acetylene, consuming more than 80% of the acetylene produced worldwide [132].

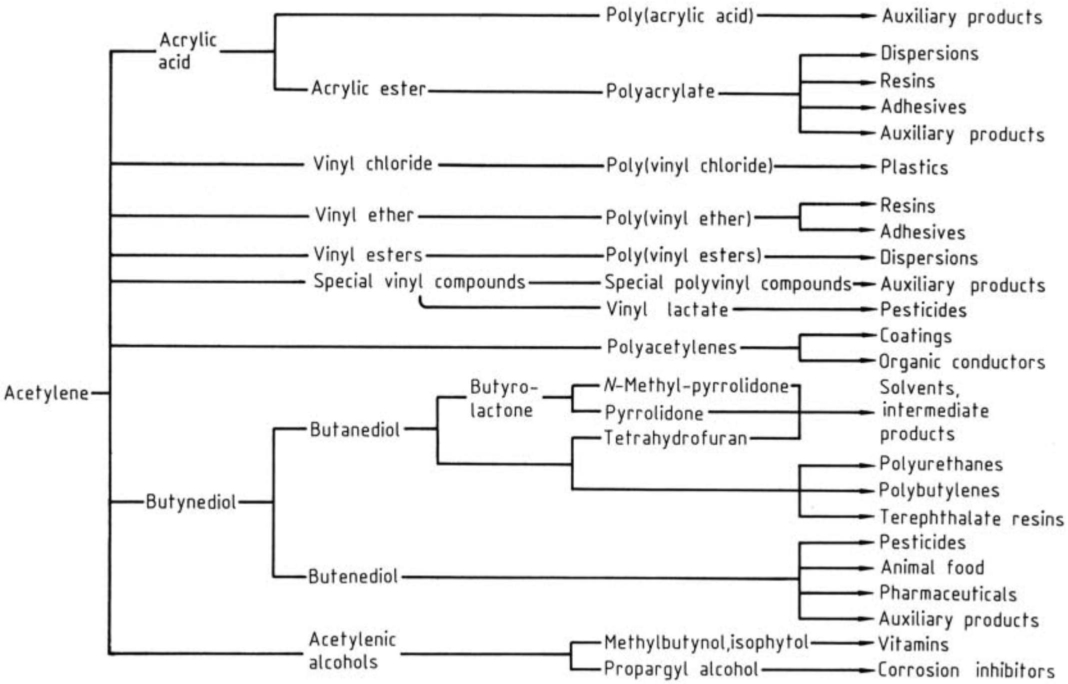


Figure 48. Acetylene as a starting material for industrial products

6.3. Competitive Position of Acetylene as Chemical Feedstock

Today, acetylene plays an important role only in the production of the acetylenic chemicals. The fact that acetylene production has not decreased further seems to indicate that the competition from the olefins is no longer as strong as it was. The main reason for this is that European olefin chemistry depends on refinery products, which have become more expensive than natural gas, the main feedstock for acetylene. Another contributing factor is that acetylene is produced only in old plants, which have low capital costs.

In addition, process improvements, such as an increase in thermal efficiency and optimum use of byproducts by other plants, can make acetylene more competitive. The position of acetylene in chemical industry may be advanced because of the variety of valuable products to which it can be converted in high yields with known technology. Acetylene must compete with ethylene for the production of vinyl chloride and vinyl acetate, and for the production of acrylic acid and its esters it must compete with propene.

7. Toxicology and Occupational Health

Pure acetylene is a simple asphyxiant. When generated from calcium carbide, acetylene is frequently contaminated with arsine, hydrogen sulfide, or phosphine, and exposure to this impure acetylene has often resulted in serious consequences. Commercial acetylene no longer contains these impurities and is therefore less harmful [136].

The lowest published lethal concentration for rats is 9 vol% [137]. Dogs are less sensitive: 80 vol% acetylene in the air is necessary to produce a narcosis accompanied by an increased blood pressure and a decreased pulse frequency (stimulation of vasomotor and vagus centers) [138]. In humans, the inhalation of air containing 10 vol% acetylene has a slight intoxicating effect, marked intoxication occurs at 20 vol%, incoordination at 30 vol%, and unconsciousness within 5 min on exposure to 35 vol%. Inhaling 35 vol. % for 5 – 10 min or 10 vol% for 30 – 60 min is lethal. Symptoms of intoxication are excitement, coma, cyanosis, weak and irregular pulse, and memory failure [139–141].

There is no evidence that *repeated exposure* to tolerable levels of acetylene has effects deleterious to health [142]. Inhalation of air with 33 vol % of acetylene by humans led to unconsciousness within 6 min, but when the experiment was repeated within the week the susceptibility to acetylene decreased: 9 min were required on the second exposure and more than 33 min on the third exposure to produce unconsciousness [138].

Acetylene does not irritate the mucous membranes [136]. Neither threshold limit value (TLV) nor a MAK has been established. The standard air concentration allowed for OSHA and NIOSH is 2500 ppm [140].

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