Kirk-Othmer Encyclopedia of Chemical Technology.

ACETYLENE FROM HYDROCARBONS

1. Manufacture From Hydrocarbons

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

Development of the modern processes for the manufacture of acetylene from hydrocarbons began in the 1920s when Badische Anilin- und Soda-Fabrik (BASF) initiated an intensive research program based on Berthelot's early (1860) laboratory investigations on the conversion of low molecular weight aliphatic hydrocarbons to acetylene by means of thermal cracking. BASF's development of the electric arc process led to the first commercial plant for the manufacture of acetylene from hydrocarbons. This plant was put into operation at Chemische Werke Hüls in Germany in 1940. In the United States, commercial manufacture of acetylene from hydrocarbons began in the early 1950s; expansion was rapid until the mid to late 1960s, when acetylene was gradually supplanted by cheaper ethylene as the main petrochemical intermediate.

1.1. Theory

The hydrocarbon to acetylene processes that have been developed to commercial or pilot-plant scale must recognize and take advantage of the unique thermodynamic properties of acetylene. As the free energy data shown in Figure 1 indicate, the common paraffinic and olefinic hydrocarbons are more stable than acetylene at ordinary temperatures. As the temperature is increased, the free energy of the paraffins and olefins become positive while that of the acetylene decreases, until at >1400 K acetylene is the most stable of the common hydrocarbons. However, it is also evident that, although it has the lowest free energy of the hydrocarbons at high temperature, it is still unstable in relation to its elements C and H_2. Thus it is necessary to heat the feedstock extremely fast to minimize its decomposition to its elements and, for a similar reason, the quench must be extremely rapid to avoid the decomposition of the acetylene product. Numerous acetylene production processes have been developed, each in its own way and with varying degrees of success, accommodating the unique thermodynamics and pyrolysis kinetics of acetylene.

Examination of the equilibrium composition of the product gas mixture under relevant reactor conditions indicates the restrictive process conditions required to optimize the production process. Figure 2 illustrates the equilibrium composition for the carbon–hydrogen system with a C/H ratio of 1 to 4 at 101.3 kPa (1 atm) and at temperatures to 7000 K. This diagram is relevant to the pyrolysis of methane at atmospheric pressure. It is immediately evident that the hydrocarbon feedstock, CH_4, decomposes into its thermodynamically preferred state of C and H_2 at well below 1000 K, whereas appreciable amounts of acetylene are not present until about 3000 K. Fortunately, the rate of the formation of acetylene is greater than the CH_4 decomposition rate. Thus

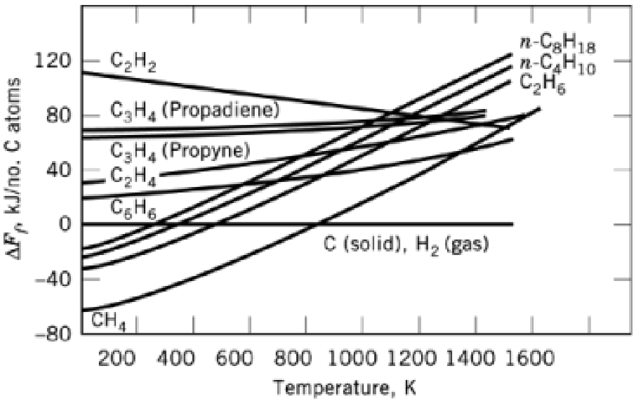

Fig. 1. Free energy of formation of several hydrocarbons. To convert kJ to kcal, divide by 4.184.

it is important to heat the reactant as rapidly as possible to avoid decomposition of the feedstock to C and H_2 and to maximize the C_2H_2 formation. In a study to design an electric arc reactor (1) for producing acetylene from coal, it was found that the acetylene reaches equilibrium concentrations in less than 1 millisecond. Thus with rapid mixing and heating, it is possible to attain appreciable concentrations of acetylene with relatively little degradation of the feedstock to carbon.

Optimum reactor design and operating conditions can be further explored through equilibrium diagrams and computer models. The effects of feedstock composition pressures and temperature on the product composition have been explored in this manner in a study (1) in which the added constraint that the heating would be rapid enough to preempt the degradation of the feedstock to carbon was imposed. Thus it was shown (Fig. 3) that at aC/H of 1 to 6 and at 51 kPa (0.5 atm), the concentration of acetylene at equilibrium conditions was as high as 16% and the temperature of peak concentration was 2000 K. Thus the process conditions of methane pyrolysis in excess hydrogen at reduced pressure are more promising than pyrolysis at atmospheric conditions as depicted in Figure 2.

Addressing the second step of the reaction, ie, the quench step, it is most important to quench the equilibrium mixture as quickly as possible in order to preserve the high acetylene concentration. In a study of the quenching mechanism (2), the acetylene-forming step was separated from the acetylene-preserving step by injecting known amounts of acetylene into a carbon-free plasma stream. The effect of various gases injected into the stream not only indicated the effectiveness of the quenching medium, but also revealed a great deal about the dynamics of the high temperature equilibrium composition. Hydrogen is much more effective in preserving the acetylene than the inert gases argon, helium, or nitrogen. Thus hydrogen injection allows recovery of as much as 90% of the acetylene, whereas with the other gases less than 50% of the acetylene was recovered. The observed effect of pressure was that in the 25–50 kPa (0.25–0.50 atm) range 85–90% of the acetylene is recovered, but at pressures between 50 and 100 kPa recovery decreases to 70%.

Because it was not possible to explain the differences in the effectiveness of hydrogen as compared to other gases on the basis of differences in their physical properties, ie, thermal conductivity, diffusivity, or heat capacity differences, their chemical properties were explored. To differentiate between the hydrogen atoms in the C_2H_2 molecules and those injected as the quench, deuterium gas was used as the quench. The data showed that although 90% of the acetylene was recovered, over 99% of the acetylene molecules had exchanged atoms with the deuterium quench to form C_2HD and C_2D_2.

To extend the study of the apparent decomposition recombination reaction, and specifically to determine if the carbon atoms exchange with other atoms in other acetylene molecules, tests using carbon isotopes were conducted. A mixture of 50% regular acetylene, $^{12}C_2H_2$, and 50% heavy acetylene, $^{13}C_2H_2$, was injected into

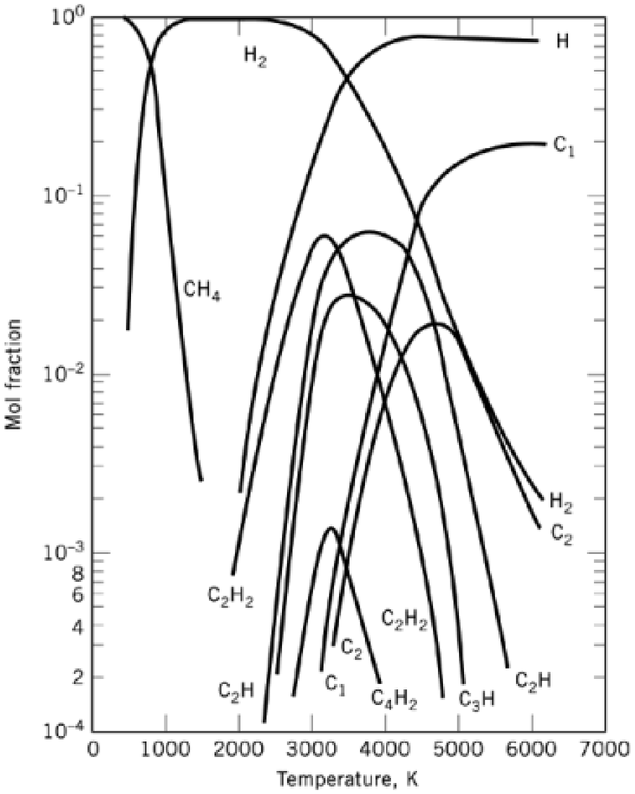

Fig. 2. Equilibrium diagram for carbon–hydrogen system at 101.3 kPa (1 atm). (C/H=1/4).

the plasma stream. The results showed that, as before, 90% of the acetylene was recovered and that 97% of the acetylene molecules had exchanged carbon atoms.

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

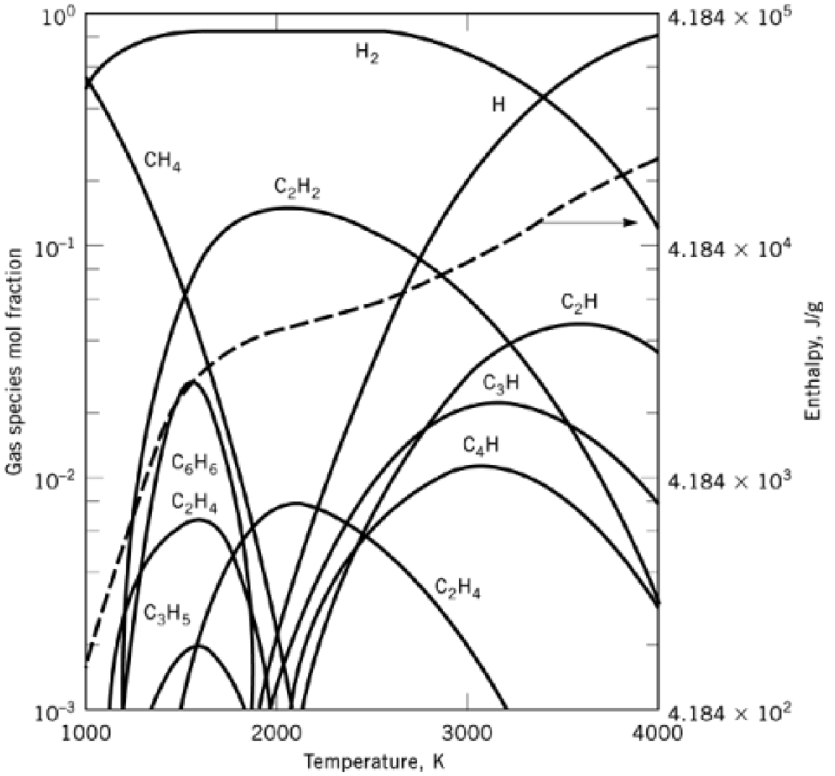

Fig. 3. Equilibrium diagram for carbon–hydrogen system at 51 kPa (0.5 atm). (C/H=1/6). To convert J to cal, divide by 4.184

1.2. Process Technology

The processes designed to produce acetylene as the main product of a hydrocarbon feedstock are generally classified according to their energy source, ie, electricity or combustion. Using this classification, several processes that are now or have been operated commercially are listed in Table 1 and are described in the subsequent text. Two special cases, the production of acetylene by steam hydrocracking in oil refineries and the potentially commercial process of producing acetylene from coal, are also discussed.

1.2.1. Electric Discharge Processes

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

The electric discharge processes can supply the necessary energy very rapidly and convert more of the hydrocarbons to acetylene than in regenerative or partial combustion processes. The electric arc provides energy at a very high flux density so that the reaction time can be kept to a minimum (see Furnaces, electric; arc furnaces).

There have been many variations in the design of electric arc reactors but only three have been commercialized. The most important is the installation at Hüls. The other commercial arc processes were those of Du Pont (3) (a high speed rotating arc) and a Romanian process that produced both ethylene and acetylene. The

Table 1. Acetylene Process Technology

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

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

Hüls process and the Romanian process (at Borzesti, Romania) are still operating, but the Du Pont process has been shut down since 1969.

Hydrocarbon, typically natural gas, is fed into the reactor to intersect with an electric arc struck between a graphite cathode and a metal (copper) anode. The arc temperatures are in the vicinity of 20,000 K inducing a net reaction temperature of about 1500°C. Residence time is a few milliseconds before the reaction temperature is drastically reduced by quenching with water. Just under $11\ kW\cdot h$ of energy is required per kg of acetylene produced. Low reactor pressure favors acetylene yield and the geometry of the anode tube affects the stability of the arc. The maximum theoretical concentration of acetylene in the cracked gas is 25% (75% hydrogen). The optimum obtained under laboratory conditions was 18.5 vol % with an energy expenditure of 13.5 kWh/kg (4).

1.2.1.1. Hüls Arc Process. The design of the Hüls arc furnace is shown in Figure 4. The gaseous feedstock enters the furnace tangentially through a turbulence chamber, E, and passes with a rotary motion through pipe H (length approx 1.5 m, diameter 85–105 mm). The arc, G, burns between the bell-shaped cathode, C, and the anode pipe, H (grounded). Due to the rotary motion of the gas, the starting points of the arc rotate within the hollow electrodes. The cathodic or anodic starting point of the arc can move upward or downward freely. With the exception of the insulator, D, all parts of the furnace are made of iron. The wall thickness of the electrodes is 10–20 mm.

The arc is about 100 cm long and extends about 40–50 cm into the anode pipe. About 20 cm below the anodic starting point of the arc, cold hydrocarbons ($C \geq 2$) are introduced into the tube through several nozzles to prequench the hot (about 1750 K) reaction gases. The quench feed becomes partly cracked (mainly to ethylene). Immediately below the anode pipe the hot reaction mixture is cooled to a temperature of about 450 K by means of a water spray, I. The electrodes are water-jacketed. The cathode is insulated from the other parts of the furnace which are grounded (insulator D). The arc is started by means of an ignition electrode. The arc is operated at 8000 kW, 7000 V, and a direct current of 1150 A. Off-peak power is generally used (5).

The feed to the arc consists of a mixture of fresh hydrocarbons and recycle gas. Table 2 indicates the composition of a typical feedstock as well as the composition of the gas leaving the arc furnace.

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

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

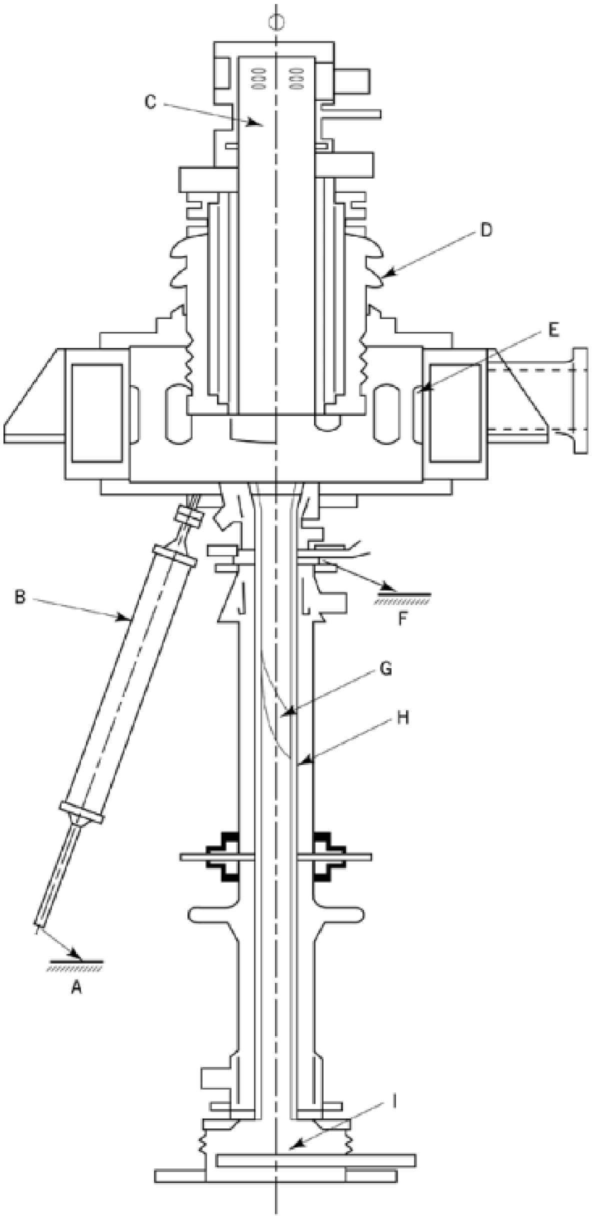

Fig. 4. Schematic drawing of a Häls arc furnace. A, ground; B, ignition electrode; C, bell-shaped cathode; D, insulator; E, turbulence chamber; F, ground; G, arc; H, anode pipe; and I, water spray.(Courtesy of Hüls AG.)

A considerable amount of carbon is formed in the reactor in an arc process, but this can be greatly reduced by using an auxiliary gas as a heat carrier. Hydrogen is a most suitable vehicle because of its ability to dissociate into very mobile reactive atoms. This type of processing is referred to as a plasma process and it has been developed to industrial scale, eg, the Hoechst WLP process. A very important feature of a plasma

Table 2. Composition of Feedstock and Reaction Product, Arc Process

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

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

process is its ability to produce acetylene from heavy feedstocks (even from crude oil), without the excessive carbon formation of a straight arc process. The speed of mixing plasma and feedstock is critical (6).

Farbwerke Hoechst AG and Hüls AG have cooperated in the development of industrial-scale plasma units up to 10,000 kW (7). Yields of acetylene of 40–50 wt % with naphtha feedstock, and about 27 wt % with crude oil feedstock, have been obtained. Acetylene concentration in the cracked gas is in the 10–15 vol % range.

1.2.1.2. Hoechst WLP Process. The Hoechst WLP process uses an electric arc-heated hydrogen plasma at 3500–4000 K; it was developed to industrial scale by Farbwerke Hoechst AG (8). Naphtha, or other liquid hydrocarbon, is injected axially into the hot plasma and 60% of the feedstock is converted to acetylene, ethylene, hydrogen, soot, and other by-products in a residence time of 2–3 milliseconds. Additional ethylene may be produced by a secondary injection of naphtha (Table 3, Case A), or by means of radial injection of the naphtha feed (Case B). The oil quenching also removes soot.

1.2.1.3. Hüls Plasma Process. In the Hüls plasma process, the hydrocarbon is injected tangentially into the hot hydrogen. In crude oil cracking, a residence time of 2–4 ms converts 20–30% of the crude (8). Crude oil data are given in Table 3, and data for naphtha and light hydrocarbon feeds are given in Table 4. In general, the arc processes achieve high temperatures easily, produce high yields of acetylene and few by-products, but can be handicapped by excessive carbon formation. On the strongly negative side are the high power consumption and the difficulty of controlling the arc geometry. Preheating the feed gas is one method to reduce cost in arc processes.

Electric arcs have been struck between grains of coal submerged in liquid hydrocarbons, such as kerosene and crude oil (9, 10), to produce a gas with 30 vol % acetylene and 5–11 vol % ethylene (11). The energy consumption in those cases is about 9 kWh/kg acetylene.

1.2.2. Flame or Partial Combustion Processes

In the combustion or flame processes, the necessary energy is imparted to the feedstock by the partial combustion of the hydrocarbon feed (one-stage process), or by the combustion of residual gas, or any other suitable fuel,

Table 3. Characteristic Data of Electric Plasma Processes[a]

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

[a] Ref. 7.

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

[c] Hydrogen plasma process using crude oil.

Table 4. Operational Results of the Hüls Plasma Process in the Cracking of Light Hydrocarbons[a, b]

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

[a] Courtesy of Applied Science Publishers Ltd.

[b] Ref. 7.

and subsequent injection of the cracking stock into the hot combustion gases (two-stage process). A detailed discussion of the kinetics for the pyrolysis of methane for the production of acetylene by partial oxidation, and some conclusions as to reaction mechanism have been given (12).

There are several commercial versions of this partial combustion technique, including the widely used BASF process (formerly called the Sachsse process) and its various modifications with an overall similar design (13). Natural gas or other methane-rich feedstock is mixed with a limited amount of oxygen (insufficient for complete combustion), and fed through a specially designed distributor or burner to a single reaction zone in which ignition occurs. Preheating of the oxygen and methane, which is usually carried up to 500°C or above, supplies part of the energy and thus, by using less oxygen, reduces dilution of the acetylene by carbon oxides and hydrogen.

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

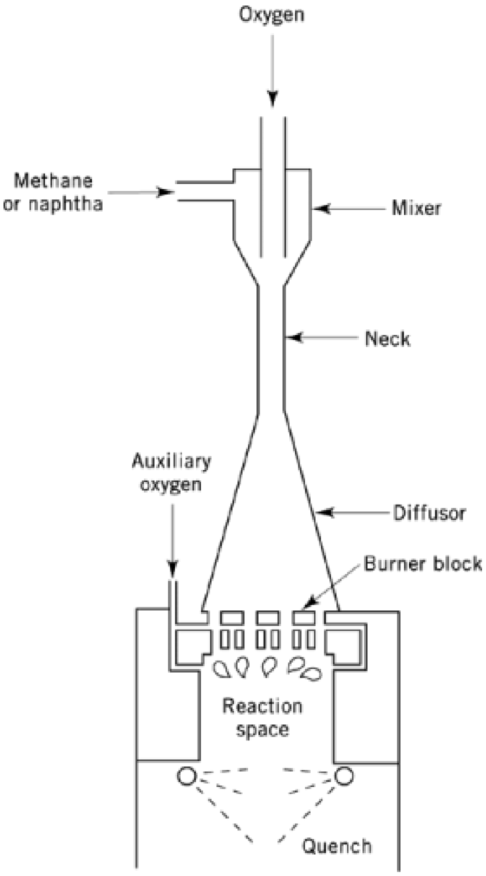

Fig. 5. BASF burner for the production of acetylene from methane or light naphtha (14).(Courtesy of Verlag Chemie GmbH, Weinheim.)

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

1.2.3. BASF Process

The basic design of the BASF process converter is shown in Figure 5. The burner is made of mild steel and is water-cooled. The hydrocarbon feed can be methane, LPG, or naphtha, and these are separately preheated and mixed with oxygen. Self-ignition occurs if methane is preheated to 650°C and naphtha to 320°C. The oxygen and hydrocarbon feed are mixed in a venturi and passed to a burner block with more than 100 channels. The gas mixture speed in the channels is kept high enough to avoid backfiring but low enough to avoid blowout. The flame stability is enhanced by the addition of small amounts of oxygen flowing downward from the spaces between the channels. About one-third of the methane feed is cracked to acetylene and the remainder is burned.

Table 5. BASF Process Consumptions and By-Product Yields and Cracked Gas Composition[a, b]

Component	Methane	Naphtha
Feed and energy requirements		
hydrocarbon, kg/100 kg C_2H_2	410	430
oxygen, kg	490	430
N-methylpyrrolidinone, kg	0.5	0.5
electric energy consumption, kWh	230	210
steam requirement, kg	450	450
residual gas, m^3	850	760
carbon, kg	5	30
Cracked gas, vol %		
C_2H_2	8.0	9.3
C_2H_4	0.2	0.2
CH_4	4.2	5.0
CO_2	3.4	3.8
CO	25.9	36.9
H_2	56.8	43.2
N_2	0.8	0.7
O_2	0.2	0.2
other hydrocarbons	0.5	0.7

[a] Courtesy of Verlag Chemie GmbH, Weinheim.
[b] Ref. 14.

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

The composition of the cracked gas with methane and naphtha and the plant feed and energy requirements are given in Table 5. The overall yield of acetylene based on methane is about 24% (14). A single burner with methane produces 25 t/d and with naphtha or LPG produces 30 t/d. The acetylene is purified by means of *N*-methylpyrrolidinone.

1.2.4. SBA Process

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

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

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

The SBA two-stage converter (Fig. 6) consists of two superimposed chambers. In the first (combustion) chamber, the combustion in oxygen of a hydrogen-rich gas is effected in the presence of superheated steam. By means of a special design, the combustion takes place with the formation of a ring of short flames, surrounded by steam. The energy required for pyrolysis is highly concentrated and thermal losses are reduced to a minimum

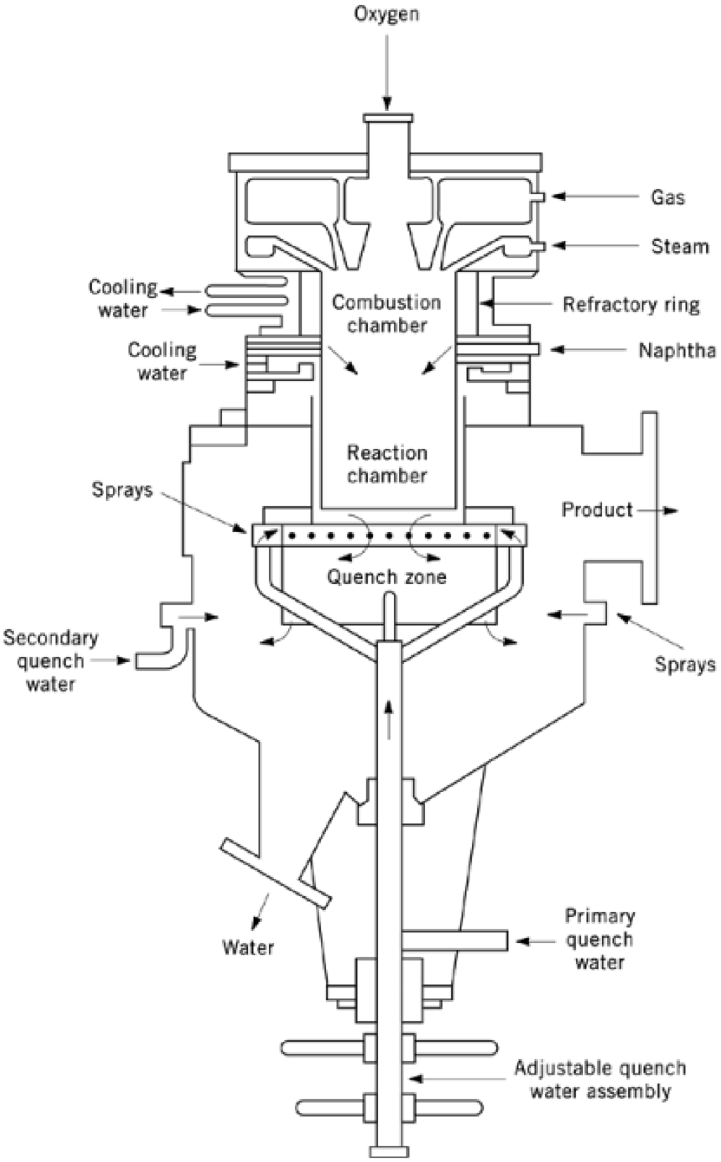

Fig. 6. SBA two-stage acetylene converter.

(15). In the second (pyrolysis) chamber, the hydrocarbon feedstock is injected into the hot combustion gases. The reaction products are thoroughly quenched to avoid all parasitic reactions.

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

Table 6. Montecatini Process Cracked Gas Composition[a]

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

[a] Ref. 16.

[b] Per 100 kg of naphtha added.

Table 7. High Temperature Pyrolysis Process Yields

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

[a] Methane recycled.

1.2.5. Montecatini Process

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

The cracked gas composition is shown in Table 6 for the water quench operation (16). One thousand cubic meters of methane and 600 m^3 of oxygen produce 1800 m^3 of cracked gas. If a naphtha quench is used, additional yields are produced, consuming 130 kg of naphtha/1000 m^3 of methane (17). The volume and distribution of this additional yield is shown in Table 6. Purification of the acetylene is by methanol absorption.

1.2.6. Hoechst HTP Process

The two-stage HTP (high temperature pyrolysis) process was operated by Farbwerke Hoechst in Germany. The cracking stock for the HTP process can be any suitable hydrocarbon. With hydrocarbons higher than methane, the ratio of acetylene to ethylene can be varied over a range of 70:30 to 30:70. Total acetylene and ethylene yields, as wt % of the feed, are noted in Table 7.

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

1.2.7. BASF Submerged-Flame Process

This process can make acetylene from a wide range of feedstocks (naphtha to Bunker C oil) and, of course, crude oil itself. Oil is burned below the surface in an electrically ignited, oxygen-fed flame and quenching is immediate by the surrounding oil. The operating pressure is 900 kPa (9 bars) (14). The temperature of the oil is regulated at 200–250°C by circulation to a waste-heat boiler. The soot content of the oil is purged by burning

Table 8. BASF Submerged-Flame Process-Average Cracked Gas Composition[a, b]

Component	Vol %
CO	43
H_2	29
CO_2	7
CH_4	4
C_2H_4	6.7
C_2H_2	6.2
C_3–plus higher hydrocarbons	4.0
H_2S	0.03–0.3

[a] Courtesy of Verlag Chemie GmbH, Weinheim.
[b] Ref. 14.

it in the reactor. Crude oils with 12.4 wt % hydrogen can be cracked with a resulting soot level in the oil of 30%. Lower hydrogen content crudes can be handled by a separate purge of the oil to remove excess soot. An average composition of the cracked gas is shown in Table 8; it does not vary much with feedstock changes. The capacity of the commercial burner is 25 tons of acetylene and 30 tons of ethylene per day.

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

1.2.8. Regenerative Furnace Processes

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

1.2.9. Wulff Process

The regenerative technique is best exemplified by the Wulff process, licensed by Union Carbide Corp. The furnace consists basically of two masses of high purity alumina refractory tile having cylindrical channels for gas flow and separated by a central combustion space as shown in Figure 7. Its cyclic operation has four distinct steps, each of approximately 1 min in duration, the sequence being pyrolysis and heat in one direction followed by pyrolysis and heat in the other direction. Continuity of output is achieved by paired installations.

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

This type of regenerative process runs at low pressure (just below atmospheric) and uses a considerable amount of dilution steam (two to three times the hydrocarbon feed). To crack methane, a reaction temperature of 1500°C must be reached, but higher hydrocarbons can be pyrolyzed to acetylene at lower temperatures, eg, 1200°C. Up to 15 vol % acetylene can be obtained in the cracked gas, but ethylene can also be produced at lower average cracking temperatures and with lower acetylene yields. When cracking propane to acetylene and ethylene, the acetylene concentration in the cracked gases ranges from 14 to greater than 16 mol %, and the ethylene concentration ranges from 8 to 13 mol % (18). Typical yields for acetylene plus ethylene

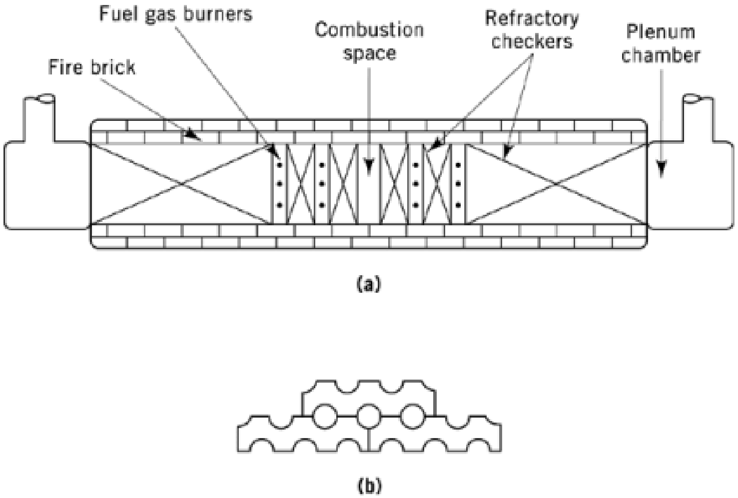

Fig. 7. (**a**) Wulff furnace design. (**b**) Checker detail of Wulff furnace refractory.

(once-through cracking) on propane feed range from 51 to 59 wt % for acetylene to ethylene ratios of 3.5:1 and 1:3.5, respectively. Dimethylformamide is the purification solvent used (19).

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

1.2.10. Pyrolysis by Direct Firing

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

The unit Kureha operated at Nakoso to process 120,000 metric tons per year of naphtha produces a mix of acetylene and ethylene at a 1:1 ratio. Kureha's development work was directed toward producing ethylene from crude oil. Their work showed that at extreme operating conditions, 2000°C and short residence time, appreciable acetylene production was possible. In the process, crude oil or naphtha is sprayed with superheated steam into the specially designed reactor. The steam is superheated to 2000°C in refractory lined, pebble bed regenerative-type heaters. A pair of the heaters are used with countercurrent flows of combustion gas and steam to alternately heat the refractory and produce the superheated steam. In addition to the acetylene and ethylene products, the process produces a variety of by-products including pitch, tars, and oils rich in naphthalene. One of the important attributes of this type of reactor is its ability to produce variable quantities of ethylene as a coproduct by dropping the reaction temperature (20–22).

1.3. Separation and Purification of Hydrocarbon-Derived Acetylene

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

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

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

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

The carbon black (soot) produced in the partial combustion and electrical discharge processes is of rather small particle size and contains substantial amounts of higher (mostly aromatic) hydrocarbons which may render it hydrophobic, sticky, and difficult to remove by filtration. Electrostatic units, combined with water scrubbers, moving coke beds, and bag filters, are used for the removal of soot. The recovery is illustrated by the BASF separation and purification system (23). The bulk of the carbon in the reactor effluent is removed by a water scrubber (quencher). Residual carbon clean-up is by electrostatic filtering in the case of methane feedstock, and by coke particles if the feed is naphtha. Carbon in the quench water is concentrated by flotation, then burned.

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

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

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

2. Coproduct Acetylene from Steam Cracking

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

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

Worldwide, approximately $180,000\ \text{t/yr}$ acetylene product is recovered as a by-product within olefin plants. This source of acetylene is expected to increase as plant capacity and furnace temperature increase. The recovery may include compression and transfer of the acetylene product via pipelines directly to the downstream consumer.

2.1. Acetylene Recovery Process

A process to recover coproduct acetylene developed by Linde AG (Fig. 8), and reduced to practice in 11 commercial plants, comprises three sections: acetylene absorption, ethylene stripper, and acetylene stripper.

2.1.1. Acetylene Absorption

The gaseous feedstock containing the C_2 hydrocarbons is introduced into the acetylene absorption tower at a pressure range of 0.6–3 MPa (6–30 bar) depending on availability within the process design of the olefin plant. The absorption takes place in a countercurrent lean solvent flow, which is preferably dimethylformamide (DMF) and with less frequency *N*-methylpyrrolidinone (NMP). The overhead gas fraction is partially condensed against refrigerant to avoid any solvent losses. The acetylene absorption tower is designed from thermodynamic and hydraulic points of view to minimize the acetylene content in the overhead product (less than 0.2 ppm) and the recycle flow rate to the cracked gas compressor in the olefin plant (less than 2%).

2.1.2. Ethylene Stripping

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

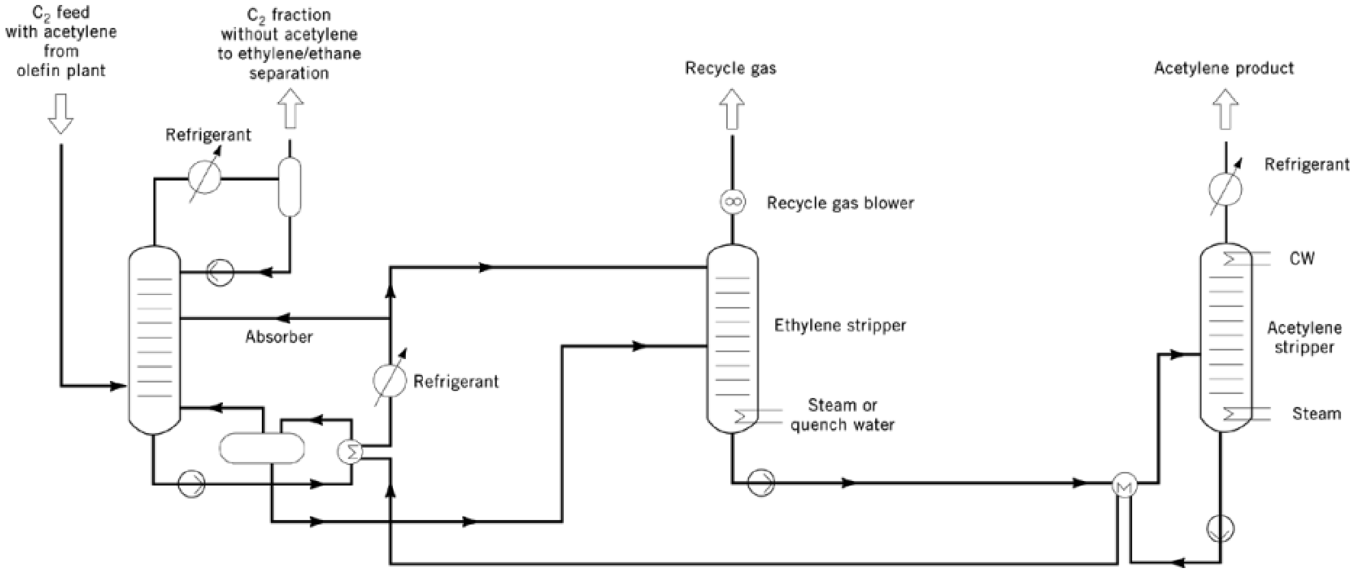

Fig. 8. Linde AG acetylene recovery unit for acetylene absorption, ethylene stripping, and acetylene stripping. CW=cooling water .(Courtesy of P. Cl. Haehn, Linde AG.)

2.1.3. Acetylene Stripping

The loaded solvent with acetylene and traces of other basically olefinic components is pumped to the acetylene stripper tower for the delivery of the acetylene product in the overhead (typically 99.9% purity minimum). Solvent traces can be eliminated by chilling or water washing depending on downstream process requirements. The bottom product (lean solvent) is pumped back to the acetylene absorber and ethylene stripper towers after exchanging the maximum possible amount of its energy within the recovery process for economic reasons. The recovery process uses commercial solvents without the addition of an antifoaming agent. The applied solvents are not corrosive or fouling.

3. Acetylene from Coal

Coal, considered a solid hydrocarbon with a generic formula of $CH_{0.8}$, was explored by numerous workers (24–31) as a feedstock for the production of acetylene. Initially, the motivation for this work was to expand the market for the use of coal in the chemical process industry, and later when it was projected that the cost of ethylene would increase appreciably if pretroleum resources were depleted or constrained.

Acetylene traditionally has been made from coal (coke) via the calcium carbide process. However, laboratory and bench-scale experiments have demonstrated the technical feasibility of producing the acetylene by the direct pyrolysis of coal. Researchers in Great Britain (24, 28), India (25), and Japan (27) reported appreciable yields of acetylene from the pyrolysis of coal in a hydrogen-enhanced argon plasma. In subsequent work (29), it was shown that the yields could be dramatically increased through the use of a pure hydrogen plasma.

Based on the bench-scale data, two coal-to-acetylene processes were taken to the pilot-plant level. These were the AVCO and Hüls arc-coal processes. The Avco process development centered on identifying fundamental process relationships (29). Preliminary data analysis was simplified by first combining two of three independent variables, power and gas flow, into a single enthalpy term. The variation of the important criteria, specific

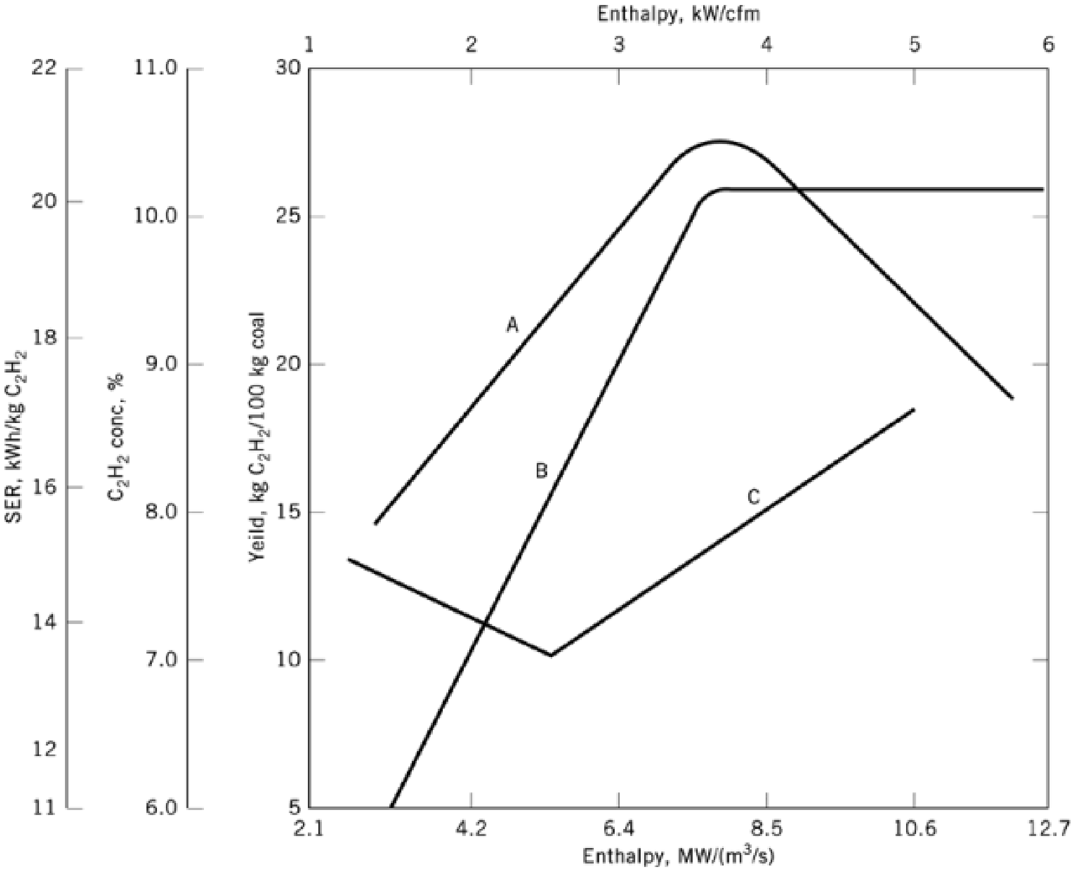

Fig. 9. Critical process parameters as a function of gas enthalpy where A is yield, B is concentration, and C is the specific energy requirement (SER).

energy requirements (SER), concentration, and yield with enthalpy are indicated in Figure 9. As the plots show, minimum SER is achieved at an enthalpy of about 5300 kW/(m^3/s) (2.5 kW/cfm), whereas maximum acetylene concentrations and yield are obtained at about 7400 kW/(m^3/s) (3.5 kW/cfm). An operating enthalpy between these two values should, therefore, be optimum. Based on the results of this work and the need to demonstrate the process at sufficient size to judge industrial applicability, AVCO built and operated a 1 MW reactor in 1979–1982. This project was jointly funded by the U.S. Department of Energy (30).

The AVCO reactor design is called a rotating arc reactor. In this design (Fig. 10), the arc is spread out radially from a center cathode to the walls which serve as the anode. In order to ensure temperature uniformity of the gas as well as the reactor wall, the arc is rotated using a magnetic field. The coal, which has been ground to conventional power plant grind, ie, 80% through a 74 μm (200 mesh) screen, is suspended in a hydrogen carrier gas and is fed through the top of the arc-coal reactor. The acetylene formed in the arc region is stabilized by rapidly quenching the gas stream to below 1400 K using a variety of quench media (hydrogen, methane, coal, hydrocarbons, water, etc).

The overall energy efficiency of the arc reactor is greatly enhanced by using a two-stage approach, ie, by using a chemically active quench in which further acetylene is produced. The active quench takes advantage of the latent heat of the gas below the arc to form additional acetylene. Two quench materials investigated

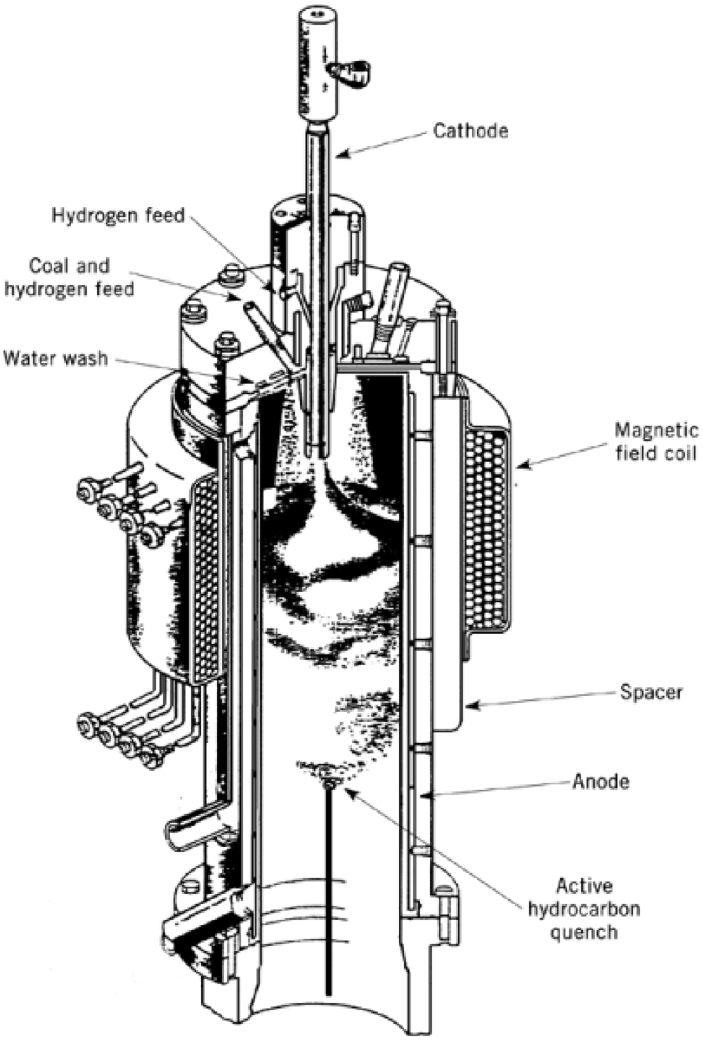

Fig. 10. AVCO rotating arc reactor.

were additional coal and a hydrocarbon (propane). In each case, the additional feed was injected below the arc reactor zone. Included in these experiments was a secondary water quench to freeze the acetylene yield.

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

The economics of the arc-coal process is sensitive to the electric power consumed to produce a kilogram of acetylene. Early plant economic assessments indicated that the arc power consumption (SER = $kw{\cdot}h/kgC_2H_2$) must be below 13.2. The coal feedcoal quench experiments yielded a 9.0 SER with data that indicated a further reduction to below 6.0 with certain process improvements. In the propane quench experiment, ethylene as well as acetylene is produced. The combined process SER was 6.2 with a C_2H_2/C_2H_4 production ratio of 3 to 2. Economic analysis was completed utilizing the achieved acetylene yields, and an acetylene price approximately 35% lower than the price of ethylene was projected.

In subsequent work at Hüls (31) similar results were obtained. That is, using German coals it was also found that the magnetically rotated arc was the preferred reactor design and that the product mixture could be enriched through the use of a hydrocarbon quench. In this two-stage reactor a SER of 11.5 kW·h/kg C_2H_2 was achieved, but it was projected that this could be reduced through further development work.

4. Uses

Acetylene is used primarily as a raw material for the synthesis of a variety of organic chemicals (see Acetylene-derived chemicals). In the United States, this accounts for about 80% of acetylene usage and most of the remainder is used for metal welding or cutting. The chemical markets for acetylene are shrinking as ways are found to substitute lower cost olefins and paraffins for the acetylene, with some products now completely derived from olefinic starting materials. Metalworking applications, however, have held up better than chemical uses.

4.1. Chemical Uses

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

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

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

Vinyl acetate (ethenyl acetate) is produced in the vapor-phase reaction at 180–200°C of acetylene and acetic acid over a cadmium, zinc, or mercury acetate catalyst. However, the palladium-catalyzed reaction of ethylene and acetic acid has displaced most of the commercial acetylene-based units (see Acetylene-derived chemicals; Vinyl polymers). Current production is dependent on the use of low cost by-product acetylene from ethylene plants or from low cost hydrocarbon feeds.

Minor amounts of acetylene are used to produce chlorinated ethylenes. Trichloroethylene (trichloroethene) and perchloroethylene (tetrachloroethene) are prepared by successive chlorinations and dehydrochlorinations (see Chlorocarbons and chlorohydrocarbons). The chlorinations take place in the liquid phase using uv radiation and the dehydrochlorinations use calcium hydroxide in an aqueous medium at 70–100°C. Dehydrochlorination can also be carried out thermally (330–700°C) or catalytically (300–500°C).

Tetrachloroethylene can be prepared directly from tetrachloroethane by a high temperature chlorination or, more simply, by passing acetylene and chlorine over a catalyst at 250–400°C or by controlled combustion of the mixture without a catalyst at 600–950°C (32). Oxychlorination of ethylene and ethane has displaced most of this use of acetylene.

Acetylene is condensed with carbonyl compounds to give a wide variety of products, some of which are the substrates for the preparation of families of derivatives. The most commercially significant reaction is the condensation of acetylene with formaldehyde. The reaction does not proceed well with base catalysis which works well with other carbonyl compounds and it was discovered by Reppe (33) that acetylene under pressure (304 kPa (3 atm), or above) reacts smoothly with formaldehyde at 100°C in the presence of a copper acetylide complex catalyst. The reaction can be controlled to give either propargyl alcohol or butynediol (see Acetylene-derived chemicals). 2-Butyne-1,4-diol, its hydroxyethyl ethers, and propargyl alcohol are used as corrosion inhibitors. 2,3-Dibromo-2-butene-1,4-diol is used as a flame retardant in polyurethane and other polymer systems (see Bromine compounds; Flame retardants).

Much more important is the hydrogenation product of butynediol, 1,4-butanediol [110-63-4]. The intermediate 2-butene-1,4-diol is also commercially available but has found few uses. 1,4-Butanediol, however, is used widely in polyurethanes and is of increasing interest for the preparation of thermoplastic polyesters, especially the terephthalate. Butanediol is also used as the starting material for a further series of chemicals including tetrahydrofuran, γ-butyrolactone, 2-pyrrolidinone, *N*-methylpyrrolidinone, and *N*-vinylpyrrolidinone (see Acetylene-derived chemicals). The 1,4-butanediol market essentially represents the only growing demand for acetylene as a feedstock. This demand is reported (34) as growing from 54,000 metric tons of acetylene in 1989 to a projected level of 88,000 metric tons in 1994.

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

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

Acetylene black is prepared by the partial combustion of acetylene and has specialty uses in batteries. Only about 3500 t/yr are produced in the United States.

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

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

4.2. Fuel Uses

At one time acetylene was widely used for home, street, and industrial lighting. These applications disappeared with the advent of electrical lighting during the 1920s. However, one of the first fuel uses for acetylene, metalworking with the oxyacetylene flame, continues to consume a significant amount of acetylene (35).

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

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

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

5. Economic Aspects

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

Most by-product acetylene from ethylene production is hydrogenated to ethylene in the course of separation and purification of ethylene. In this process, however, acetylene can be recovered economically by solvent absorption instead of hydrogenation. Commercial recovery processes based on acetone, dimethylformamide, or *N*-methylpyrrolidinone have a long history of successful operation. The difficulty in using this relatively low cost acetylene is that each $450,000\ \text{t/yr}$ world-scale ethylene plant only produces from $7000-9000\ \text{t/yr}$ of acetylene. This is a small volume for an economically scaled derivatives unit.

The average price of pipeline shipments of acetylene in the United States in 1990 was $\$0.86/\text{kg}$. In comparison, the average price of ethylene was about $\$0.53/\text{kg}$. The range of prices due to the different sources of the acetylene can only be roughly estimated since each process has by-products and coproducts which may be credited or debited in more than one way. However (36), the relative prices of acetylene by the three primary categories of process may be calculated to be 2:1.5:1 g from calcium carbide, from hydrocarbon partial combustion, and for by-product acetylene, respectively. Pricing of the by-product acetylene from ethylene production at a value equivalent to ethylene plus recovery costs could reverse the trend away from

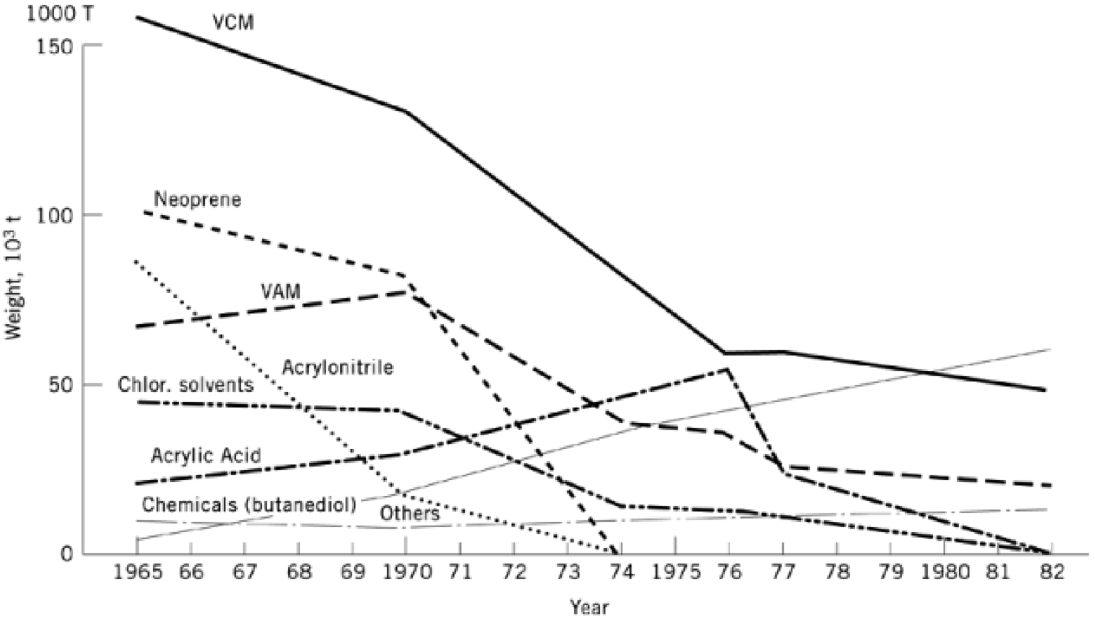

Fig. 11. Acetylene for chemical us in the United States (37). Courtesy of Chem Systems. Total consumption for specified years in 10^3 t as follows: 1965, 478; 1970, 385; 1974, 195; 1976, 174; 1977, 142; and 1982, 109–116.

acetylene-based processes. There is a commercial swing toward this objective as high cost calcium carbide sources are shut down.

Acetylene from calcium carbide can be advantageous in that calcium carbide may be shipped to the point of acetylene usage and acetylene generated on the spot. This avoids the necessity for low pressure, low pressure-drop gaseous acetylene pipelines, or high pressure cylinders for shipping acetylene. The carbide route is the preferred method of operation for most industrial gas operations. It is well suited to small-scale consumers. The high cost of acetylene in industrial gas applications reflects these scale, handling, and shipping factors.

5.1. Supply and Demand

5.1.1. United States

The demand for acetylene generally peaked between 1965 and 1970, then declined dramatically until the early 1980s, and has been slowly increasing at between 2 and 4% per year since. The dramatic decline was related to increased availability of low cost ethylene, an alternative feedstock for many chemicals, and the recent increase is due to the modest growth of acetylenic chemicals, particularly 1,4-butanediol.

In the United States, the acetylene production exceeded 450, 000 t/yr between 1963 and 1970, but then declined until it hit a minimum production level below 150, 000 t/yr in 1982. Of this production, about 40,000 t were dedicated to industrial use, ie, welding, etc. Thus only slightly more than 100,000 t were produced for the chemical process industry. Figure 11 illustrates the 17-year decline in acetylene production and indicates the reduced derivative demand to which the accumulated decline is attributed (37).

As Figure 11 also shows, the only acetylene derivatives to sustain growth during this period were the so-called acetylenic chemicals. These include 1,4-butanediol, vinyl ethers, *N*-vinyl-2-pyrrolidinone, and butanediol. Of these, 1,4-butanediol, a principal feed for tetrahydrofuran, accounts for over 90% of the acetylenic chemicals demand (38).

Table 9. Plants Producing Acetylene in the United States, 1991

Operator/location	Process	Feedstock	Capacity, 10^3 t/yr	Market
Borden-BASF Geismar, La.	BASF part. ox.	natural gas	90	VCM and 1,4-butanediol
Carbon-Graphite Group Calvert City, Ky.		calcium carbide	34	acetylenic chemicals
Chevron Cedar Bayou, Tex.	ethylene coproduct	petroleum	8	acetylene black
Rohm and Haas Deer Park, Tex.	BASF part. ox.	natural gas	25	1,4-butanediol
Quantum Chemical Deer Park, Tex.	ethylene coproduct	petroleum	14[a]	1,4-butanediol
Union Carbide Seadrift, Tex.	ethylene coproduct	petroleum	6	acetylenic chemicals
Taft, La.	ethylene coproduct	petroleum	5	industrial gas
Texas City, Tex.	ethylene coproduct	petroleum	8	acetylenic chemicals

[a] Estimated.

In 1984, acetylene production received a significant influx with the increase of capacity at the Borden Co. plant in Geismar, Louisiana. This influx provided an additional 33, 000 t/yr, which were absorbed by the vinyl chloride monomer (VCM) and acetylenic chemicals market. Acetylene demand has exhibited a modest growth rate of about 2% per year since 1984. In fact, demand exceeded production by about 10,000 t in 1987. This imbalance has generally been corrected by added capacity, particularly by the Quantum Chemical Co. plant at Deer Park, Texas, which came on line in 1991.

The U.S. Department of Commerce estimates total production of about 163,000 t in 1990. Other estimates based on demand data indicate that it was as high as 175,000 t. With demand and supply in balance, it is estimated that in 1997 the demand will be 185,000 t. The distribution in product demand is projected to be the following: 1,4-butanediol and other acetylenic chemicals (45%), vinyl chloride monomer (45%), acetylene black (5%), and industrial use (5%).

In 1991, U.S. plant capacity for producing acetylene was estimated at 176, 000 t/yr. Of this capacity, 66% was based on natural gas, 19% on calcium carbide, and 15% on ethylene coproduct processing. Plants currently producing acetylene in the United States are listed in Table 9.

It is difficult to indicate a representative price for acetylene because it is generally produced either for captive use or on contract. The price seems to be dictated mainly by the price movement of ethylene, often a coproduct as well as an alternative feedstock competing with acetylene. That is, in 1981 when ethylene was $0.55 per kg, acetylene was $1.12 per kg; and when in 1987 the price of ethylene dropped to $0.31 per kg, acetylene dropped to $0.68 per kg.

5.1.2. Western Europe

Acetylene demand in Western Europe exceeds by far that of any other geographical region. Prior to the unification of Germany in 1990, acetylene consumption in Western Europe was estimated to be 430, 000 t/yr; with the addition of 280,000 t of consumption attributed to the former German Democratic Republic, total consumption increased to 710,000 t.

Table 10 lists the acetylene-producing plants in Western Europe as of 1991. Of the 782,000 t of annual capacity, 48% is produced from natural gas, 46% from calcium carbide, 4% from naphtha, and 2% as ethylene coproduct.

Of the estimated 710,000 t consumed in 1990, 25% was used to produce vinyl chloride [75-01-4] monomer (VCM), 14% for vinyl acetate [108-05-4] monomer (VAM), 23% for butanediol, 14% for industrial use, and the balance to produce other products such as acrylic acid, synthetic rubber, chlorinated solvents, and acetylene black. The demand for PVC is expected to decrease as legislation limiting its use in packaging is pending. Consequently, VCM consumption will also suffer.

Table 10. Plants Producing Acetylene in Western Europe, 1991

Location/operator	Process	Feedstock	Capacity, 10^3 t/yr	Market
Germany				
BASF	part. ox.	natural gas	85	acrylics and
	coproduct	petroleum	6	acetylenic chemicals
Hoechst AG	calcium carbide		6	acetylene black
Hüls	electric arc	natural gas	130	VCM and acetylenic chemicals
former GDR plants	calcium carbide		350	synthetic rubber VAM, VCM
Italy				
EniChem Anic Sol	part. ox.	natural gas	70	VCM
Montedipe	part. ox.	natural gas	41	VAM and tetra-chloroethane
Netherlands				
DSM NV	coproduct	petroleum	2	captive
Shell	coproduct	petroleum	9	captive
Switzerland				
Lonze AG	Montecatini	naphtha	30	acetaldehyde and acetylenic chemicals
Austria				
Donan Chemic AG	calcium carbide		3	captive
France				
Rhône-Poulenc	BASF	natural gas	50	VAM

Table 11. Production of Acetylene in Eastern Europe

Country	Feedstock	Capacity, 10^3 t/yr	Market
Bulgaria	CaC_2	11.6	VCM
Czechoslovakia	CaC_2	20	VAM, VCM acetic acid
Hungary	CaC_2	5.4	VCM
Poland	CaC_2	123	VCM, acetaldehyde
Rumania	natural gas	155	VCM, VAM acetic acid and acetylenic chemicals
former Soviet Union states	natural gas and CaC_2	270	VAM, VCM, acetic acid, acetaldehyde
Yugoslavia	Ca_2C	12.6	VCM

Growth in the use of acetylene for the production of 1,4-butanediol is projected to continue at the rate of about 5% per year. However, competition from a new technology based on maleic anhydride may impact the use of acetylene in this market.

5.1.3. Eastern Europe

Production of acetylene in Eastern Europe is dominated by the capacity of states of the former Soviet Union. In 1990, production from Eastern Europe amounted to between 530,000 and $535,000$ t/yr, with 51% provided by the states of the former Soviet Union. Of the balance, Poland with 23% and Rumania with 17% are the main producers. Table 11 indicates the capacity levels of each of the countries of Eastern Europe.

5.1.4. Japan and China

During the 1980s, acetylene demand in Japan suffered a significant decline. Chemical use declined from over 100,000 to 42,000 t, acetylene black production declined from 20,000 to less than 10,000 t, and industrial use went from 42,000 to 30,000 t. Thus, based on 1990 estimates, Japan has an excess capacity for acetylene production with capabilities for $247,000$ t/yr and a demand of only 82,000 t.

Almost all (98%) of the acetylene produced in Japan is based on the calcium carbide process, with only about 2% being produced as a coproduct of ethylene production. The reliance on calcium carbide and its attractions for small users can be partially related to market demand. Thus, only a single plant with a maximum annual capacity of 89,000 t, operated by Danki Kagaku Koggs KK, is dedicated to the chemical process industry. Two smaller plants are dedicated to the production of acetylene black, but 64 plants with annual capacities generally less than 5000 t serve the industrial acetylene needs, ie, metals cutting and welding.

Very little data are readily available on China's supply and demand situation. It is known, however, that they rely almost entirely on calcium carbidey for acetylene production and that there are numerous low capacity plants, a situation that is probably not too different from that of Japan.

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