

PERP Program – Acetylene Production Technologies

New Report Alert

June 2007

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Acetylene Production Technologies (05/06S9)***. To view the table of contents or order this report, please click on the link below: <http://www.chemsystems.com/reports/index.cfm?catID=2>

Introduction

A number of high temperature processes for the production of acetylene have been commercialized via cracking reactions in the 1,000 to 1,600°C temperature range, or synthesis reactions at temperatures above 1,600°C. The most important process routes are:

- Partial oxidation: Methane, LPG, or light gasoline are pyrolyzed to cracked gases containing acetylene.
- Steam cracker acetylene: 1 to 2 percent of acetylene, related to the severity of operating conditions, is produced in ethylene steam crackers. The acetylene can be hydrogenated to ethylene or recovered by separation using a solvent.
- Electric arc or plasma arc: Cracking of light hydrocarbons in an electric arc.
- Calcium carbide: Acetylene is generated by the reaction of calcium carbide and water.

Partial Oxidation Processes

Partial oxidation or combustion processes consist of those in which the necessary energy needed to supply the reaction heat is provided by burning a portion of the hydrocarbon feed or by combustion of residual gas. Carbon feedstock can come from a wide range of materials, including natural gas, ethane, natural gas liquids, naphtha, and liquefied petroleum gas.

There are several oxidation processes that have been commercialized, including:

- BASF (Sachsse-Bartholomé)
- Montecatini
- SBA (Societe Belge de l'Azote)

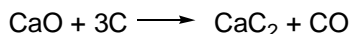
The main features of the processes are similar. The peculiarities in the burner design are the major differences. In each of the processes, oxygen and the hydrocarbon feed are preheated separately to greater than 1,400°C, mixed, and then ignited in a burner.

The process requires extremely short residence times of the reaction materials of from 10^{-2} to 10^{-3} seconds, low partial pressure of the acetylene and rapid quenching of the gases formed. Upon pyrolysis and partial oxidation, acetylene is obtained in the form of a gas mixture, the so-called cracking gas. The cracking gas normally comprises from about 5 to 20 percent by volume of acetylene. The acetylene is extracted from the cracking gas by *N*-methyl pyrrolidone, dimethylformamide, kerosene, methanol or acetone and subsequently purified further.

The design and operation of the burner are critical to the success of the process, and much development work by several companies has been directed toward improving the yield of acetylene achieved. The concentrations of the major constituents of the cracked gas depend on the oxygen to hydrocarbon ratio in the feed. As the oxygen supply is increased, the acetylene concentration increases until it reaches a maximum. At the same time, there is an increase in the volume of the cracked gas. Maximum acetylene production is achieved when a little more oxygen is used than is required for maximum acetylene concentration in the cracked gas.

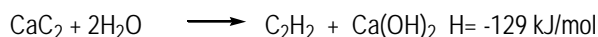
Calcium Carbide Process

The classical commercial route to acetylene is the calcium carbide route in which lime is reduced by carbon (in the form of coke) in an electric furnace to yield calcium carbide:



Q207_00101.0006.4124-1.cdx

The calcium carbide is then hydrolyzed to produce acetylene:



Q207_00101.0006.4124-1.cdx

There are two principal methods for producing acetylene from calcium carbide, based on the type of generator used. In the wet generator, the reaction takes place in a cylindrical water shell attached below a carbide feed hopper. A large excess of water is used as the carbide is fed into the water reservoir at a controlled rate until the reaction is complete. Calcium hydroxide byproduct is obtained as a slurry containing 10 to 20 percent hydroxide.

For larger scale plants, the dry generation design is more common. This design features a continuous feed of carbide mixed with enough water to complete the reaction and serve to dissipate the reaction exotherm. Typically, 1 kg of water is used per kg of carbide. The reaction heat is dissipated by water evaporation, leaving a pourable powder calcium hydroxide with moisture content of 1-6 percent.

Both processes yield acetylene of 99.6 volume percent purity after a light scrubbing.

Calcium carbide technology suffers from high energy costs, which have contributed to its decline in importance since the 1960s. However, we are seeing a rebirth of this technology in China, especially coal to VCM. The high exotherm reaction heat requires the use of specialized equipment to meet safety requirements. Improvements to the technology have dealt with eliminating or controlling rapid heat dissipation associated with local overheating of the calcium carbide, which can raise the acetylene pressure and cause rupture of the vessel and release of the acetylene.

The furnace may be of the open type, in which the CO burns to CO₂ when it contacts the air above the charge; semi closed, in which the mix is fed around the electrode openings in the primary furnace cover resulting in mix seals; or closed type, in which the gas is collected from the furnace and is either used as fuel or flared, depending on the capacity of the furnace and the intended applications of the furnace gas, but environmental regulations strongly favor the closed furnace design.

Acetylene Recovery from Steam Crackers

Conditions in ethylene-producing steam cracking tubular furnaces are such that the cracked gas leaving the quench system contains acetylene. The quantity of acetylene produced is a function of the severity of cracking: more acetylene is produced as the severity increases. Light naphtha is cracked at the highest severity and therefore produces the most acetylene. Gas oil, conversely, must be cracked at low severity to reduce coking in the tubes and, therefore, produces very little acetylene. Table 1 indicates typical production rates of acetylene for various steam cracker feeds.

Table 1
Production of Acetylene for Various Steam Cracker Feeds
(Pound acetylene per pound ethylene)

30/70 Ethane/propane	0.0095
C5-350° Light Arabian naphtha	0.022
430°-750° Light Arabian gas oil	0.0065

Acetylene specifications for polymer grade ethylene are generally less than 5 ppm maximum and, therefore, an efficient means of separating it from the ethylene product is essential. Removal by fractionation is not economical since ethane, the other major component present in the final purification stages of an ethylene plant, and acetylene form azeotropes, which persist at low pressures. A frequent method of overcoming this difficulty is to provide a selective catalytic hydrogenation stage at a convenient point in the purification train to convert the acetylene to ethane and ethylene. Alternatively, the acetylene can be separated by absorption in a selective solvent such as acetone, dimethyl acetamide, dimethyl formamide (DMF), or *N*-methyl pyrrolidone. To be attractive, the recovery of acetylene from steam crackers must bring in greater revenues than would be realized by hydrogenating it and increasing the production of ethylene.

The acetylene recover plant can be put at the front or back end of the fractionation train. More processes offered for license favor the back end location where the pressure is 300-350 psig.

Normally, about 99.5 percent of the acetylene is recovered leaving only traces in the ethylene leaving the absorber. These traces are usually removed in a trim hydrogenation converter to ensure that process upsets in the absorption system do not cause excessive acetylene concentrations in the product ethylene.

Electric Arc Technology

An electric arc discharge can be used to supply the necessary energy to convert hydrocarbons to acetylene at a very high flux and short reaction time. Feedstocks to an electric arc can be gaseous or liquid hydrocarbons or solid in the form of coal.

Development work for production from hydrocarbons was started in Germany in the 1920s by BASF. This work was eventually continued by Chemische Werke Hüls, which used the technology commercially in Marl, Germany.

In an actual electric arc zone, the temperatures are between 10,000 and 20,000°K, which place the gases in a plasma state. In plasma chemistry there are two basic design arrangements. In the one stage arrangement, the feed materials to be converted flow through the electrical discharge zone as the carrier gas or with a carrier gas. In the two stage arrangement, a carrier gas flows through the discharge zone and the feed material is injected into the hot plasma jet and converted. Both designs were developed for gaseous, liquid or solid feed stocks or combinations.

The production of acetylene from a hydrocarbon requires several conditions: large quantities of energy at high temperature due to the high enthalpy of formation, limitation of residence time to a

few milliseconds necessitating high heat transfer rates, and a high rate of quench to avoid decomposition of the acetylene formed into unwanted byproducts.

The Hüls electric arc plant started in 1939. By 1965, the plant had been expanded to a capacity of 130,000 metric tons per year of acetylene, 60,000 metric tons of ethylene, and 350 million cubic meters of hydrogen from 19 furnaces. In order to operate the plant more economically, Hüls installed gas holders to store the product so that gas could be processed at night during non-peak power rate periods, lowering the unit cost of power consumption. The thermal efficiency of the furnace is about 95 percent.

Economics

Nexant assessed the cost of production economics for the four acetylene technologies discussed above at capacities that are representative of actual plant capacities:

- Coal-based calcium carbide at 215 KTA (coal to coke; coke to calcium carbide and carbide to acetylene cost of production sheets are included)
- Via ethylene steam cracker at 7 KTA (valued at loss of potential ethylene sales)
- Natural gas-based partial oxidation 50 KTA (two scenarios: syngas @ chemical value and syngas @ fuel value)
- LPG-based electric arc process at 35 KTA

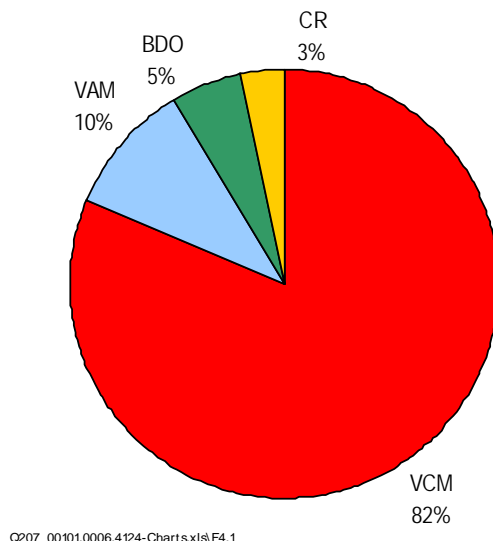
Commercial Analysis

Acetylene was once a major raw material used for the production of synthetic chemicals such as vinyl chloride, vinyl acetate, acrylonitrile and acetaldehyde. In the mid 1960s, however, acetylene use began to be replaced by ethylene produced from low cost petroleum. Today, the major chemical applications for acetylene are for the production of vinyl chloride monomer (VCM) and 1,4 butanediol. Non-chemical applications include welding and cutting of metals and the production of carbon for batteries.

In the United States, the majority of acetylene produced is used as chemical feedstock. It is difficult to transport and is usually used, in large quantity as in chemical use, at or near its production site because of acetylene's high flammability and combustion heat. Acetylene's limitations as a freely marketable product makes accurate demand and production estimates difficult.

Global acetylene consumption for chemical derivatives is driven by VCM production (82% of total), with lesser amounts for the production of vinyl acetate (VAM), 1,4-butanediol (BDO), and chloroprene rubber (CR), as shown in Figure 1.

Figure 1 – Estimated Acetylene Chemical End-Use Pattern, 2006



=====

Copyright© by Nexant, Inc. 2007. All Rights Reserved.

Nexant, Inc. (www.nexant.com) is a leading management consultancy to the global energy, chemical, and related industries. For over 38 years, Nexant's *ChemSystems Solutions* has helped clients increase business value through assistance in all aspects of business strategy, including business intelligence, project feasibility and implementation, operational improvement, portfolio planning, and growth through M&A activities. Nexant has its main offices in San Francisco (California), White Plains (New York), and London (UK), and satellite offices worldwide.

These reports are for the exclusive use of the purchasing company or its subsidiaries, from Nexant, Inc., 44 South Broadway, 5th Floor, White Plains, New York 10601-4425 U.S.A. For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: <http://www.chemsystems.com>.