BASF and Acetylene – 70 Years of Reppe Chemistry – Long-Standing Reliability and Promising Future – and now, the only Natural Gas Based Clean Technology for Acetylene Production

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Abstract

Acetylene is still an attractive intermediate synthesis component because carbon in methane from natural gas comes at a lower price than carbon in naphtha from crude oil or coal. Acetylene can be understood as a product of C-C coupling and functionalization. Beginning in the 1950s, BASF developed the partial oxidation (Pox) process, in addition to the electric arc process dating from the 1930s and the submerged flame process. The originally developed Pox process came along with severe emissions of hydrocarbons to the environment. Nowadays it is extremely important to have a clean, environmentally friendly technology. So in the 1990s a closed water-quench process was developed and built in the United States. The presentation focuses on the ways of making acetylene, the use of acetylene and BASF's closed water-quench process based on natural gas. This process will be presented including some important safety aspects. The process is available for licensing.

Introduction

Today BASF looks back on more then 70 years of experience with acetylene chemistry and production. Up to the early 1960s carbide was the source for acetylene. At that time BASF operated a carbide plant at the Ludwigshafen site. In 1921, Walter Reppe joined BASF and started working at the main laboratory. He became interested in acetylene as early as 1928.

Acetylene a Basic Chemical: "Reppe Chemistry"

Up to 1940 Walter Reppe developed the acetylene chemistry. He first focused on the safe handling of acetylene. Up to his work it was not possible to handle acetylene at pressures above 1.4 bar(abs) due to its deflagration and detonation properties. He studied these properties comprehensively and developed several countermeasures to avoid these safety risks. This was the basis for developing vinylation, ethynylation, carbonylation and cyclization reactions. Starting during the 1960s, the acetylene chemistry was partly substituted by petrochemistry, but several processes survived. For some basic chemicals acetylene is still an attractive feedstock. BASF still produces several chemicals on the basis of acetylene, including 1,4-butanediol, vinylpyrrolidone and Koresin. For vinyl chloride (China) and vinyl acetate, too, acetylene remains a very attractive feedstock.

At the Ludwigshafen site a 1,4-butanediol plant was built in 1940 for what was then a huge annual capacity of 20,000 tons. The target was to produce the important chemicals butadiene and buna for tires. The butadiene/buna plant was destroyed by air attacks in 1943. For a long time after that, up to the 1960s in fact, the 1,4-butanediol plant operated only at low capacity, for tetrahydrofuran (THF) and polyurethanes only. Then the demand for 1,4-butanediol increased continuously. The current capacity of the plant is 190,000 tons per year, and in 2008 4 million tons of BDO were produced. Several parts of the equipment used in the plant of the 1940s are still in operation today. Now most of the 1,4-butanediol goes to PolyTHF (PTHF), the key raw material for spandex fibers. In this field, too, BASF has its own technology and operates plants worldwide. PTHF can be produced in several molecular weights from 250 up to 2000.

Another typical old "Reppe product" is Koresin. This is a tackifier for high-performance truck and car tires. Koresin is a resin produced from acetylene and p-t-butyl phenol. BASF has been manufacturing Koresin since 1939. Currently the capacity is being increased and a second train will be finished in 2014.

How to Make Acetylene

There are several routes to produce acetylene. A lot of energy is always needed because acetylene is a high-calorific molecule. Acetylene shows a heat of formation of 227 kJ/mol in comparison to ethylene, at 52 kJ/mol, or ethane, at -85 kJ/mol. So during synthesis energy must be added to the system. This can be done in several ways. One is the BASF partial oxidation process developed by Sachsse and Bartholomé, another one the Montecatini process operated by Lonza. Here the energy is generated by oxidation of a part of the feedstock.

Another way to put in the energy is directly by an electric arc. This process is applied at the Ashland plant at Marl. By the way, the electric arc process was also invented by BASF in the 1930s. Then, not to forget, acetylene might also be a minor steam-cracker byproduct. There the acetylene can be separated or hydrogenated selectively to ethylene. A still very important source for acetylene, and currently the biggest source especially in China, is calcium carbide. During calcium carbide production the energy is brought into the system by electricity. The second step of adding water to the carbide to produce acetylene is easy and needs no further energy for reaction.

Now let us focus on BASF's partial oxidation process that Sachsse and Bartholomé developed during the 1950s. Nowadays the typical feedstock is natural gas, the main component of which is methane. Around 60% of the methane is partially oxidized by pure oxygen to carbon monoxide and hydrogen. The hydrogen produced is also partially oxidized to water. This provides the energy to build acetylene at temperatures of around 1500-1600°C. Acetylene is a metastable molecule, so if it resides at such high temperatures for too long a time, it will continue to react quantitatively to produce soot. The cracked gas stream must consequently be cooled down after a sufficient, but not excessive residence time. This time is in the range of a couple of milliseconds. The remaining methane is around 4% and the oxygen is nearly quantitatively consumed to less than 0.5 vol.% in the cracked gas stream. This is done in a burner that converts a premixed stream of natural gas and oxygen after both feed streams have been heated to around 600°C in the mixing unit. The mixing unit assures perfect mixing and distribution of the reaction mixture over the burner block. The gas speed before the burner block is around 25 m/s, and the gas passes the tubes in the burner at more than 150 m/s to avoid flash back. The flame downstream of the burner plate is stabilized by oxygen pilot flames. The reactions take place in the main flame, and they are stopped in the quench after leaving the fire room.

The burner characteristics show a maximum of acetylene concentration in the cracked gas of around 8 vol.% in the region of 0.54 to 0.56 oxygen to natural gas ratio. In this region a sufficient conversion of methane occurs.

The Closed Water-Quench Process

The core part of the burner has been discussed in the previous section on "How to Make Acetylene."

A water-quench plant has three main parts, the cracked gas generation, compression and separation sections. In the generation section the cracked gas is produced, containing mainly acetylene, carbon monoxide, hydrogen, residual methane and minor amounts of higher acetylenes and aromatics. Some of the soot formed in the reaction and water is separated here too. The next step is the compression up to around 10 bars. This step also removes the rest of the soot from the gas stream in the closed water-quench process.

The separation section of the plant follows next, where the acetylene is separated from the acetylene off-gas (AOG) and a higher acetylene stream.

The AOG stream contains all the carbon monoxide, hydrogen, carbon dioxide and further inerts. Applications for the AOG stream will be discussed later. Typical components in the higher acetylene stream are the dangerous components like diacetylene, vinyl acetylene and propadiene. The way to handle such a stream in a safe way will be discussed later.

The next part focuses on an overview of and the differences between the old open water-quench process and the new closed water-quench process. Now let's have a closer look at the process. After the natural gas and the oxygen have been separately preheated and mixed, the gas stream passes the burner. The cracked gas from the burner is quenched down to around 90°C in the cooling column. The old open water-quench process needs electrofilters to remove the soot from the cracked gas stream and soot decanters to separate the soot from the process water. The soot decanters and the open cooling tower are the source of the serious organic components emissions of the open water-quench process.

With a small increase of the oxygen to natural gas ratio, lower amounts of higher acetylenes and soot are built at a reasonably high acetylene yield. Due to this, in the closed water-quench process the electrofilters and the soot decanters can be omitted and the cooling water system can be operated in a closed loop. Modern feed-forward control makes it possible to omit the cracked-gas holder before the compression. The remaining soot in the cracked gas is separated by the cracked gas compressors. The soot in the waste water can be separated easily by flocculation and filtration. Also, now three burners are connected to one cracked gas column instead of having separate cracked gas columns for each burner as in the old open water-quench process. These are the main advantages of the closed water-quench process.

The next point is a short overview on the cracked gas separation section. Here the acetylene is separated from the acetylene off-gas (AOG) and the higher acetylenes after compression to around 10 bar. In the first column, the pre-scrubber, mainly the diacetylene is removed by a low amount of NMP (n-methyl-pyrrolidone). From this solution acetylene is stripped off in the acetylene stripper by means of AOG. In the following main scrubber the acetylene is absorbed entirely in NMP, and the AOG goes over-head and leaves the plant. Then the acetylene-containing NMP from the main scrubber is flashed to the stripper. The first flash gas is carbon dioxide and small amounts of acetylene. This top product of the stripper is recycled to the cracked gas before the compressors. That's why the carbon dioxide goes to the AOG, the top product of the main absorber. Counter-current to the acetylene from the thermal degasser the acetylene is desorbed from the NMP and withdrawn in the side stream of the stripper. In the vacuum column water and higher acetylenes are separated and withdrawn by a vapor side stream. The top product, a highly acetylene-rich gas, is fed through the thermal degasser to the bottom of the stripper to remove acetylene from the NMP from the main scrubber. In the higher acetylenes section the first step in the vacuum stripper is to remove water and the diacetylene from the NMP stream coming from the acetylene stripper. The overhead stream is washed with water in the side column to remove NMP. The last step before the higher acetylenes compression is the condensation of water in the condenser.

Safety aspects of the process

A not impossible scenario is that a 25mm nozzle in the vacuum section is ruptured during normal operation, e.g., during maintenance work with a mobile crane. As a consequence of this, sucking in of around 320 kg of air and the vacuum pumps running with 3000 Nm^3 leads to a non-acceptable oxygen concentration of 1.7 vol.%. At oxygen levels larger than 1 vol.%, the famous Sargent diagrams are no longer valid, the decomposition barriers are no longer working and instead of deflagration detonation may occur. A look at the triangle diagrams of nitrogen, oxygen and acetylene shows the dependency on the total pressure. There is a region out of the explosion range only in vacuum conditions. But at ambient or elevated pressure the risk of explosion must always be taken into account. This very critical scenario must be detected in SIL 3 quality and the countermeasures of dilution and flaring must be provided in that quality as well.

An always very interesting safety aspect is the handling of the higher acetylenes.

To evaluate the limiting pressure such mixtures BASF uses the Le Chatelier formula for explosion limits. This is the reciprocal value of the sum of the quotients of the molar fraction in the mixture and the decomposition pressure of each component. A typical mixture contains 34 vol.% acetylene, 2 vol.% methylacetylene, 11 vol.% vinylacetylene and 53 vol.% diacetylene. This gives a limiting critical deflagration pressure of 0.3 bars(abs). Hence such a mixture can be handled safely at a pressure lower than this critical deflagration pressure.

The vacuum section in the plant works at 200 mbar(abs) and in addition to this there is a dilution by steam. So there the condition is pretty much on the safe side. For further use of this stream it must be compressed to a slightly elevated pressure, in our case 1.15 bar(abs.). Now the gas stream is diluted before and after the compressor by dilution gas. This may be natural gas in SIL 3 quality, for example. With a dilution of 82 vol.% dilution gas in the gas stream the safe side is reached with a deflagration pressure of around 1.8 bar(abs.).

Plant Set-up
The typical plant size of a closed water-quench plant is 50,000 t/a acetylene. This plant consists of 6 burners arranged in 2 trains, 2 cracked gas compressors and one common separation unit.
The main advantages of this process:

- Meets international emission standards
- Higher purity of acetylene and syngas
- Advanced process control
- Shared global safety concept with customers
- Less personnel required
- ~20% lower investment costs (for 50,000 t/a)
- Experienced BASF engineering

Usage of the acetylene off-gas
Another important economic issue is the use of the AOG, which contains around 75% of the carbon of the natural gas feed. The first choice is to make methanol or chemical use of carbon monoxide and hydrogen. Verbund integration with methanol and acetic acid to make vinyl acetate is another option. Here also acetylene is used for the final product vinyl acetate. Alternatively, the AOG may be fed to a fertilizer plant. The last possibility, which is not recommended, is to burn the AOG and use only the fuel value.

Summary
From the current standpoint acetylene is today, and will be in the future, an attractive basic chemical. The main advantage is the use of natural gas or coal as a base feedstock for the carbide route instead of naphtha. For a bundle of specialty products and several large products acetylene is still the only reasonable intermediate feedstock. BASF has now more than 70 years of experience in producing and handling acetylene in a safe and economical way. The BASF closed water-quench process currently offers the only proven and clean access to acetylene based on natural gas. This process can be built worldwide and meets all emission and safety standards.

Acknowledgement

References
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