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PLANT OF CHEMISCHE WERKE HULS

HULS, GERMANY

Reported by
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on behalf of the

U. S. Technical Industrial Intelligence Committee

[1945]

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Personnel of Team

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INSPECTION OF SYNTHETIC RUBBER PLANT OF CHEMISCHE WERKE HULS, HULS, GERMANY

Date of Inspection: April 11, 1945

Object: This target is primarily a synthetic rubber plant using, as one of the principal materials, acetylene manufactured from natural gas. The investigation of this target was undertaken by the Oil Team to obtain the information available on the production of acetylene and other products from natural gas.

Condition of the Target: The plant was found practically intact, the only damage being from shellfire at the time the plant was captured, and apparently had not been bombed.

Acetylene Plant: The acetylene plant was designed to operate on a gas from the Scholven hydrogenation works, containing 70% methane, 25% ethane and 5% propane. Due to the bombing of the Scholven works, natural gas containing 90% methane, 2% ethane, 8% nitrogen, with some H_2S and CO_2 was substituted as feed stock.

The gas is purified to remove H_2S with Alkazid and sodium hydroxide. The gas, under a few inches of water pressure, is then passed through an iron arc. The gas from the arc has the following composition:

Carbon monoxide	0.9%
Oxygen	0.2%
Acetylene	16.8%
Ethylene	3.9%
Paraffins, mostly CH_4	24.9%
Hydrogen	50.7%
Nitrogen	2.5%

The gas at the outlet of the arc is cooled to 150°C. by direct water injection and passes to a second water contacting tower. The carbon black produced is removed by cyclone separators and bag filters. The tar polymers are next removed by an oil scrubber using a low temperature tar oil; the HCN is removed by water washing and the H_2S then removed by a luxmasse (Fe_2O_3) treatment. The gas is then stored in a gas holder for charge to the acetylene separation plant.

The gas mixture is compressed to 18 atms in four stages with interstage cooling to prevent excessive heating which would cause explosion difficulties, and then contacted with water. The acetylene is dissolved in the water under these conditions, and then is flashed from the water in four stages. In the first stage, the water is flashed to 2 atms pressure where a gas containing the absorbed hydrocarbons and some acetylene is removed and recycled to the suction of the compressors. In the second stage, the water is flashed to atmospheric pressure and a 93% pure acetylene obtained. In the third and fourth stages the water is flashed to 80% and 95% vacuum respectively. The acetylene mixture from the three final stages contains 95-96% acetylene, the remainder being hydrogen, nitrogen and ethane.

The unabsorbed gas from the water contactor contains 55% hydrogen, 20-35% total hydrocarbon, including 3-5% of ethylene, and 8-10% nitrogen with a small amount of carbon monoxide. This gas is processed in two Linde units for the production of pure hydrogen and ethylene. In the first Linde unit, the gas, under 17 atms. pressure, is separated into three streams: ethane-ethylene, methane, and hydrogen. A temperature of 205°C. is obtained for the separation of the hydrogen from the methane by boiling pure nitrogen under vacuum. The hydrogen stream containing 0.0001% CO and 98-99% hydrogen is used for the hydrogenation of acetylene to ethylene as will be explained later. The methane stream is returned to the arc unit. The ethane-ethylene stream is charged to a second Linde unit where pure ethylene is separated. The ethane is returned to the arc unit.

The natural gas consumption is 120,000 tons per year. Each 100 kgs. of raw gas produces 45 kgs. of acetylene, 9.2 kgs. of ethylene, 5.3 kgs. of carbon black and 142.5 cu.m. of pure hydrogen.

The plant consists of 14 arcs with 12 arcs running at any one time. One arc consumes 7000 kw. and produces 700-800 kgs. of acetylene per hour. The cost of manufacturing acetylene by this process is reported to be 25-30 pfennings per kg. of 95-96% acetylene. The following is the consumption of utilities per 100 kgs. of acetylene produced:

(1) Electric Power:

(a)	Arc Unit	1008 Kw.
(b)	Separation Unit	220 Kw.
(c)	Low Voltage Users	7 Kw.
(2)	Water	40 cu.m.
(3)	Steam	0
(4)	Coke-oven gas (4300 Cal/cu.m.)	2.7 cu.m.

160 men per shift are employed to make 6.3 tons of acetylene per hour. 30 men are employed in the arc building, 50 men on the gas purification and carbon black unit, 40 men on the compressors and scrubbers, and 40 men on the Linde plant.

The plant started construction in 1938 and was in operation in 1940. The cost of the entire plant was 80,000,000 marks. The Linde plant cost 30,000,000 marks. The maintenance cost is not included in the 160 men mentioned above, but was said to amount to about 2½% per year of the investment cost.

The ideal gas for charge to the arc units would be pure ethene, but a gas of about $C_{1.5}$ is the most practical feed stock. With the Scholven gas containing 70% methane, about 800 kgs. of acetylene is produced per arc, while with the natural gas containing 90% methane, about 700 kgs. of acetylene is obtained.

A sketch of the arc is attached as Figure 1.

The gas enters the upper section of the arc through a tangential arrangement to produce a swirling motion in the arc tube proper so that the arc will not remain at one point for sufficient time to burn through the tube. The arc tube proper is an iron pipe of 90 mm. inside diameter and 1 meter in length. A water jacket is provided around this tube to prevent excessive burning of the tube. The arc is struck by a starting mechanism which is immediately withdrawn. The iron arc tube has a life of 150 hours and then is removed and discarded. It is necessary to shut down the arc every 1-3 days for cleaning out the carbon black. Two arcs are used in connection with

with one water-washing system in order that the arc tube can be cleaned or changed without materially affecting the output of the plant.

Ethylene Oxide Plant: Ethylene oxide is produced by reaction of ethylene with hypochlorous acid followed by treatment with lime. 1600 tons per month of ethylene oxide is processed at 200°C. and 20 atms. with water to produce ethylene glycol. Di-glycol is produced by recycling the glycol through the same reactor.

Acetophenone Plant: Acetophenone is manufactured by the direct oxidation of ethyl benzene with air in the presence of a cobalt-copper catalyst at 60°C. The reaction is carried out in the liquid phase at atmospheric pressure using a theoretical amount of air. The reaction is stopped at 30-50% conversion, the ultimate conversion being 70-80%. The acetophenone was to be shipped elsewhere for chlorination to chloroacetophenone.

Acetylene Hydrogenation Plant: At Hüls, the production of ethylene was not sufficient for a balanced operation, and the hydrogenation of a part of the acetylene to ethylene was carried out. The acetylene was hydrogenated using 50% excess hydrogen at atmospheric pressure and 200°C. over a palladium on silica gel catalyst, containing 0.01% Pd. The catalyst was arranged in three beds of 3 meters diameter and about 33 cm. in depth per bed. 2 mols of steam were added to 1 mol of total gas at the inlet of the reactor, and water was introduced between the catalyst beds to control the temperature so as not to exceed 200°C. The catalyst life is approximately six months. The catalyst is then removed from the reactor and regenerated by oxidizing with air at 500°C. Each reactor produces 170 tons of ethylene per month. Four reactors were normally in operation, each reactor containing 3.6 cu.m. of catalyst. The palladium catalyst is very selective for hydrogenation of acetylenes to double bonds, the efficiency being 85% in the case of ethylene production, the remainder of the product being ethane and normal butane.

Ethylbenzene Plant: The plant produced 1500-2000 tons of 98% pure ethylbenzene per month. The reaction is carried out in the presence of $AlCl_3$ as catalyst,

using a temperature of 90°C and a ratio of benzene to ethylene of 2:1. The sludge formed is drawn off at the bottom of the reactor and recycled together with fresh benzene entering at the side of the enamel-lined reactor, while the ethylene is introduced at the bottom. Fresh aluminum chloride is fed from the top of the reactor through a tube, leading to the bottom of the reactor. The product is taken off at the top and is fractionated to give unreacted benzene, ethylbenzene and higher ethylbenzenes. The ratio of mono to higher ethylbenzenes produced is 2:1. Diethylbenzene is shipped to aviation gasoline blending stations under the code name of "Kybol." The aluminum chloride consumption is 3% by weight of the ethylbenzene produced.

Comments: Since this plant is primarily a rubber and chemical target, no attempt was made to obtain detailed information on the processes since it was felt that such detailed information would be obtained when the target was investigated by the other groups. Samples of the various catalysts used in the plant were obtained, however, for evaluation. No documents were removed from the plant and a more complete report on this plant will not be submitted by the Oil Team since such a report would be duplication of effort of the other teams.

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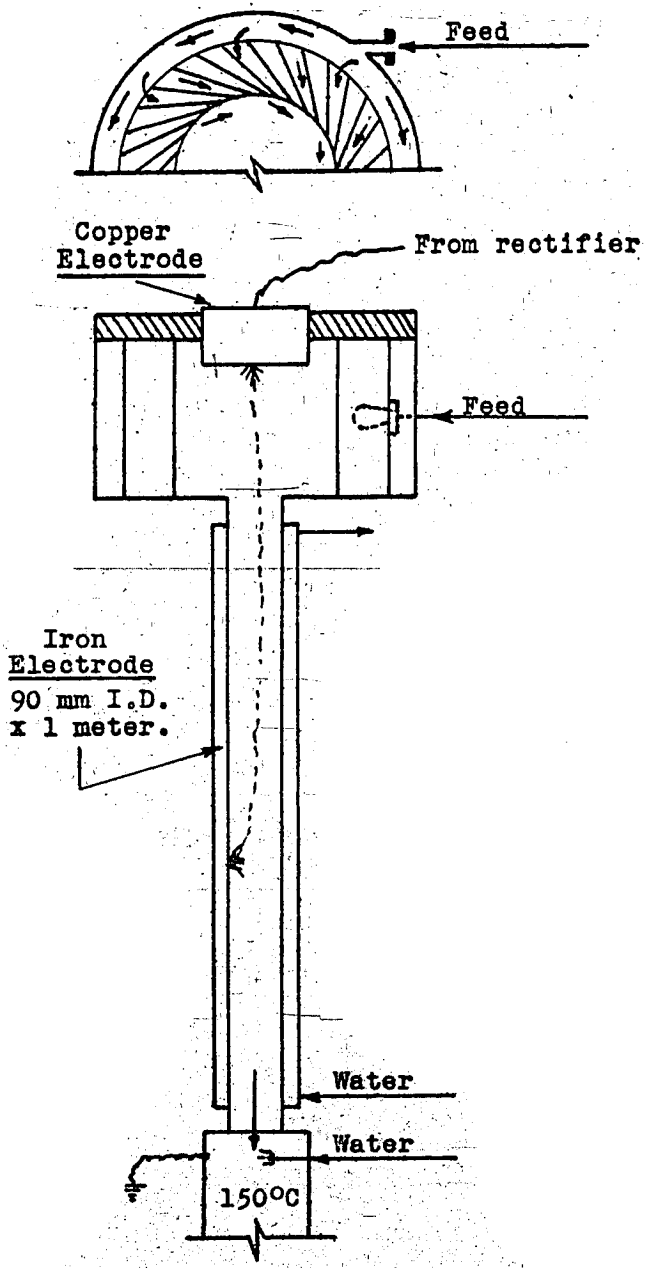

ARC ARRANGEMENT - ARC ACETYLENE PROCESS

FIGURE NO. 1

A4878 Fosh & Cross Ltd., London.