United States Patent

Brunner et al.

[15] **3,686,344**

[45] **Aug. 22, 1972**

[54] **PRODUCTION OF ACETYLENE**

[72] Inventors: **Erwin Brunner**, Ludwigshafen; **Rolf Platz**, Mannheim; **Kurt Taglieber**; **Kurt Weinfurter**, both of Ludwigshafen, all of Germany

[73] Assignee: **Badische Anilin- & Soda-Fabrik Aktiengesellschaft**, Ludwigshafen (Rhine), Rhineland Pfalz, Germany

[22] Filed: **June 22, 1970**

[21] Appl. No.: **47,964**

[30] **Foreign Application Priority Data**

July 7, 1969 Germany..........P 19 34 304.5

[52] **U.S. Cl.**........................**260/679 A,** 55/64, 62/20

[51] **Int. Cl.**..**C07c 11/24**

[58] **Field of Search**..........................260/679, 679 A; 62/10–12, 17, 20; 55/64, 42

[56] **References Cited**

UNITED STATES PATENTS

3,026,969	3/1962	Braconier et al.	183/115
2,894,602	7/1959	Fauser	62/17
3,405,192	10/1968	Kruis et al.	260/679
3,531,915	10/1970	Nagel et al.	55/32
3,174,292	3/1965	Kasbobm et al.	62/17

FOREIGN PATENTS OR APPLICATIONS

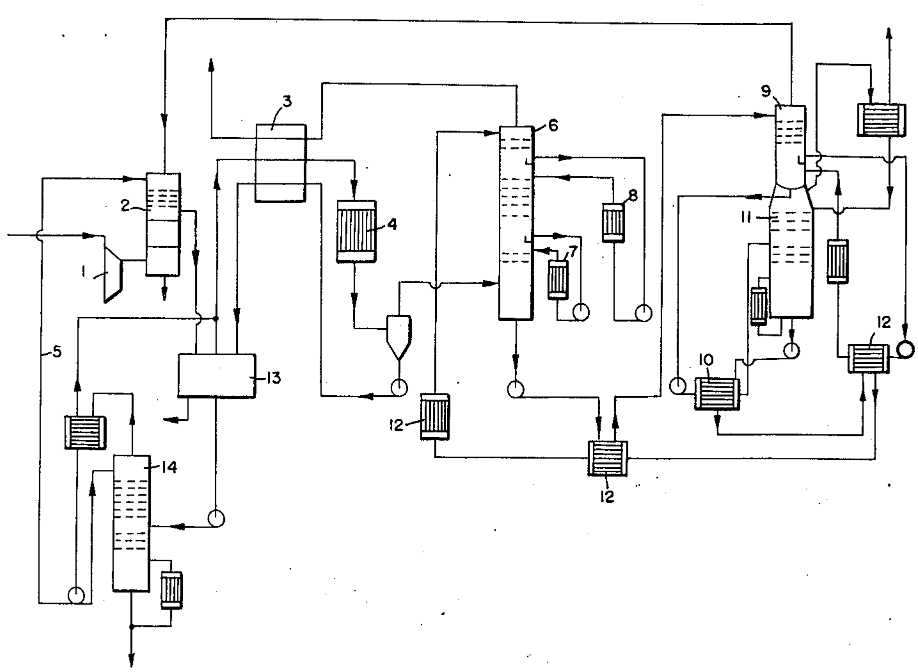
573,349	3/1959	Canada	55/64
834,419	5/1960	Great Britain	260/679 A

Primary Examiner—Delbert E. Gantz
Assistant Examiner—J. Nelson
Attorney—Johnston, Root, O'Keeffe, Keil, Thompson & Shurtleff

[57] **ABSTRACT**

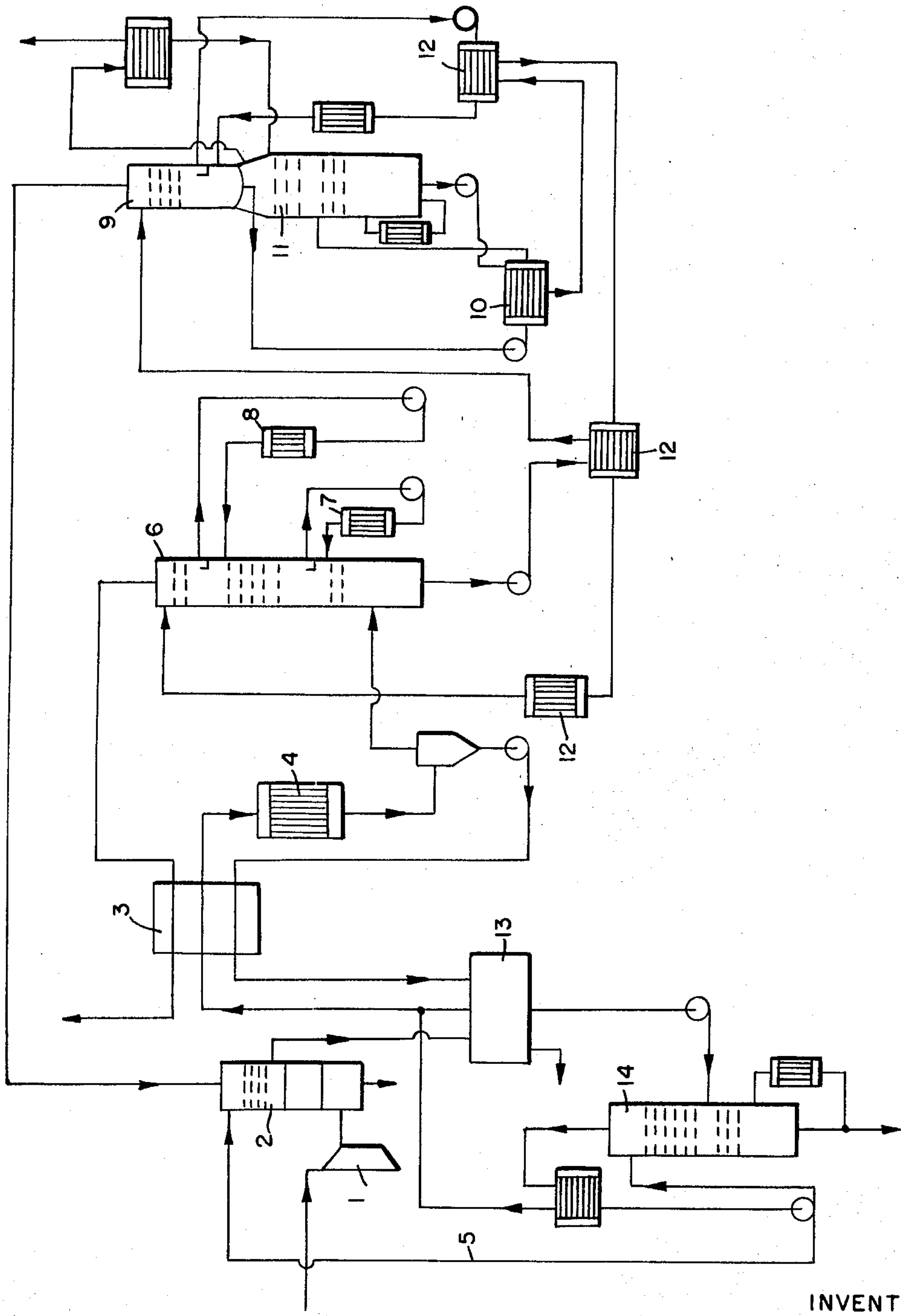
Production of pure acetylene from a cracked gas obtained by cracking gaseous hydrocarbons, the process comprising a number of steps wherein the higher C_3 to C_5 hydrocarbons remaining in the crude acetylene are washed out with an organic solvent such as toluene.

3 Claims, 1 Drawing Figure



PATENTED AUG 22 1972

3,686,344



INVENTORS:

ERWIN BRUNNER
ROLF PLATZ
KURT TAGLIEBER
KURT WEINFURTER

BY

Johnston, Root, O'Keeffe, Keil, Thompson & Shurtleff

ATT'YS

PRODUCTION OF ACETYLENE

This invention relates to a process for the production of acetylene by thermal cracking of methane, in particular natural gas, and working up the cracked gas by removing CO_2 and washing the acetylene with a selective solvent, whereupon the crude acetylene thus obtained is further purified by a combined condensation and washing step.

It is well known that thermal cracking of hydrocarbons immediately followed by quenching of the cracked gas gives a gas mixture consisting of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, acetylene and hydrocarbons of more than two carbon atoms. Thermal cracking processes for the production of such acetylene-containing gas mixtures are described, for example, in Chemie-Ing-Techn., 26, No. 5, 253 (1954), British Pat. Specification No. 834,419 (1960) and German Pat. Specification No. 1,063,595.

In the commercially most commonly used process for thermally cracking methane there is produced a cracked gas from which the acetylene may be recovered in known manner in a gas wash using a solvent showing selectivity for acetylene. A particularly suitable solvent for this purpose is N-methyl pyrrolidone. The crude acetylene thus obtained still contains impurities consisting of hydrocarbons, especially hydrocarbons of from three to five carbon atoms.

This crude acetylene, which also contains some hydrocarbons having more than five carbon atoms, is in many cases unsuitable for further processing, since the impurities may cause undesirable side-reactions.

It is thus an object of the invention to produce an acetylene not suffering from the above disadvantages from natural gas by a combination of steps embracing thermally cracking the natural gas and working up the cracked gas thus obtained.

This object is achieved by conventional cracking of natural gas, washing the thus obtained cracked gas with a solvent showeing selectivity for acetylene and subsequently purifying the resulting crude acetylene in a further washing stage, in which, however, the inorganic reagents and absorbents used as washing liquors in known processes are replaced by certain organic solvents.

We have now found that pure acetylene may be produced in an advantageous manner by a combination of the following steps:

a. thermally cracking natural gas in known manner;

b. subsequently washing the acetylene with a solvent showing selectivity for the dissolution of acetylene and recovering a crude acetylene still containing hydrocarbons of more than 2 carbon atoms and possibly water;

c. cooling the crude acetylene to temperatures ranging from approximately −10° to −30° C and thereby substantially condensing out hydrocarbons of five or more carbon atoms;

d. treating the thus partially purified crude acetylene with a countercurrent wash at temperatures between approximately −20° and −40° C to wash out substantially all of the hydrocarbons still accompanying the acetylene using an organic washing liquor having a boiling range of from 50° to 150° C and a freezing point below −40° C;

e. heating the washing liquor laden with the extracted hydrocarbons and acetylene to temperatures ranging from approximately 0° to 40° C and recovering dissolved acetylene in a degasifier and recycling the recovered acetylene to the crude acetylene; and

f. distilling the washings after removal of said acetylene so as to produce bottoms consisting of pure washing liquor and an overhead product consisting of the extracted hydrocarbons.

If the crude acetylene to be purified in step (c) contains moisture, care must be taken to avoid the deposition of ice when the crude acetylene is chilled to −10° to −30° C, since this would eventually choke the condensing apparatus.

We have also found that this may be simply achieved by loading the water-containing crude acetylene with methanol vapor such that a liquid mixture consisting of higher hydrocarbons, methanol and water is condensed out in the condensation step, separating the condensate in a separating vessel into a hydrocarbon phase and a methanol/water phase containing traces of hydrocarbons and acetylene, separating the latter phase in a distillation column into water as bottoms and methanol as overhead product, and recycling the desorbed acetylene together with non-condensed methanol vapor to the condensation stage.

In a special embodiment of the invention the moisture-containing crude acetylene recovered from the N-methyl pyrrolidone wash may be washed, not with methanol but with anhydrous N-methyl pyrrolidone. This is particularly advantageous because no additional washing liquor need be introduced between the selective wash and the toluene wash.

Specifically, the novel method of producing pure acetylene is carried out by thermally cracking natural gas by the aforementioned process described in Chemie-Ing.-Techn. loc. cit., to produce a cracked gas containing the following components, in percentages by volume:

H_2	56.3	C_2H_4	0.25
CO	25.4	propadiene	0.028
CO_2	2.8	propyne	0.065
inert gases (N_2, Ar)	2.1	butadiene	0.002
CH_4	4.5	vinyl acetylene	0.041
C_2H_2	8.1	diacetylene	0.284
C_2H_6	0.005	higher aromatics	0.125

The acetylene is washed out of the cracked gas in known manner with a suitable solvent, such as dimethyl formamide, butyro lactone, tetraethyl glycol dimethyl ether and, preferably, N-methyl pyrrolidone. This wash is described in detail in Chemie-Ing.-Techn., loc. cit. The N-methyl pyrrolidone wash is expediently carried out by initially treating the cracked gas in a pre-washing stage using N-methyl pyrrolidone as washing liquor in order to remove the highly soluble diacetylene.

The acetylene is washed out in the washing column proper. Pressures between 5 and 20 atmospheres absolute, preferably between 10 and 15 atmospheres absolute, and temperatures ranging from 10° to 50° C are used. More sparingly soluble components which are also dissolved in the cracked gas stream are stripped in a countercurrent column by rising acetylene, using a column pressure preferably 1 to 2 atmospheres absolute.

The solvent is then regenerated in a vacuum column at pressures between 0.15 and 0.3 atmospheres absolute, in which the bottoms temperature is from 100° to 140° C and preferably from 110° to 120° C.

The washing stage described above produces a moist crude acetylene having, for example, the following composition:

C_2H_2	96.5% by volume	propyne	0.43% by volume
CO_2	0.1% by volume	butadiene	0.02% by volume
inert gases	0.05% by volume	vinyl acetylene	0.04% by volume
(N_2, Ar)		diacetylene	0.01% by volume
propadiene	0.35% by volume	H_2O	2.5% by volume

This crude acetylene is compressed to a pressure of not more than 1.7 atmospheres absolute in a blower (**1**, FIG. 1) and is cooled to a temperature of from approximately −10° to −30° C, preferably about −28° C, in heat exchangers, for example a combination of three different heat exchangers. The first heat exchanger of such a combination is advantageously a packed, water-irrigated direct cooler **2**, which also acts as a decomposition barrier for the acetylene. In the second heat exchanger **3** of the combination the gas is cooled countercurrently with condensate and pure acetylene, whilst the residual heat is removed in the third heat exchanger **4** by refrigerants.

The crude acetylene normally contains water vapor, and to avoid choking the condenser it is necessary to prevent the water vapor from freezing out before the crude acetylene enters the final heat exchanger, in which cooling to below 0°C is effected. This may be achieved by washing the crude acetylene with methanol or anhydrous N-methyl pyrrolidone before it enters the condenser, as may be effected, for example, in a small washer attached to direct cooler **2**.

The hydrocarbons of from three to five carbon atoms accompanying the partially purified acetylene coming from the condensation stage are removed in a countercurrent wash **6** by means of an organic washing liquor. Suitable washing liquors are, preferably, weakly polar organic liquids which are inert under the reaction conditions, have a boiling range above 80° C and a freezing point below −40° C, and low viscosity in the temperature range −20° to −40° C. Such organic liquids are, for example, aliphatic or aromatic hydrocarbons free from functional groups. Specific examples are n-heptane, n-octane, m-xylene, di-n-butyl ether and preferably toluene. Mixtures of such compounds are also eminently suitable. A preferred embodiment of the invention has been illustrated and is described in the accompanying drawing.

The wash with the organic liquid boiling above 80° C is carried out in conventional apparatus, for example a washing column, the crude acetylene entering at the bottom, whilst the organic liquid trickles down countercurrently. As usual, the dimensions of this washing column are such that as many hydrocarbons as possible are washed out. The heat of solution which is liberated during the countercurrent wash is conveniently removed in intermediate coolers **7**,**8**. There is thus obtained, at the top of the washing column, a purified acetylene which contains, apart from CO_2 (0.02 percent by volume) and indifferent gases (particularly nitrogen and noble gases) (0.06 percent by volume), only 0.001 percent by volume of C_3 to C_5 hydrocarbons and 0.1 percent by volume of the organic washing liquor.

The laden organic liquor leaving the washing column as bottoms is heated to approximately 0° to 20° C and degasified to recover dissolved acetylene, conveniently in a countercurrent tower **9**. The gas obtained contains about 75 mole percent of acetylene and is recycled to the crude acetylene entering heat exchanger **2**. The washings leaving the countercurrent tower are then heated to about 100° C in a heat exchanger **10** and then passed to a fractionating column **11**. The overhead product consists essentially of C_3 to C_5 hydrocarbons and contains about 0.4 mole percent of acetylene.

The regenerated organic washing liquor is cooled in conventional heat exchangers **12** and recycled to the washing column.

The methanol entrained as vapor from apparatus **2** is preferably recovered. To this end, water is added to the condensate obtained by cooling the crude acetylene in the separator, and separated in a separating vessel **13** into a water/methanol phase and a hydrocarbon phase. Liberated acetylene is recycled via a degasifying pipe to the second heat exchanger of the cooler combination.

Methanol is isolated from the methanol/water phase, conveniently by distillation in a column **14**, and is re-used in the condensation stage. Liberated acetylene and a portion of non-condensed methanol vapor are also recycled to the crude acetylene stream.

Where the moist crude acetylene is dried with anhydrous N-methyl pyrrolidone instead of methanol, the N-methyl pyrrolidone/water mixture obtained in separating vessel **13** is passed to the countercurrent tower used for the N-methyl pyrrolidone wash. This part of the wash is not shown in FIG. **1**.

The process according to the invention is particularly suited for the production of pure acetylene from cracked gases as obtained by cracking gaseous hydrocarbons such as natural gas.

We claim:

1. A process for the production of pure acetylene which comprises the following steps:
   a. thermally cracking a gaseous hydrocarbon in the presence of oxygen with subsequent quenching under conditions conducivee to the formation of acetylene;
   b. washing the gaseous effluent from step (a) with an organic liquid showing selectivity for the absorption of acetylene and selected from the group consisting of dimethyl formamide, butyrolactone, tetraethyl dimethyl glycol ether and N-methylpyrrolidone, and recovering from said organic liquid a crude acetylene containing hydrocarbons of three to more carbon atoms and traces of water;
   c. cooling said crude acetylene to temperatures ranging from −10° to −30° C. and thereby freezing out hydrocarbons of more than five carbon atoms from said crude acetylene;
   d. removing from the gaseous effluent from step (c) substantially all of the hydrocarbons containing three to five carbon atoms accompanying the acetylene by washing the crude acetylene obtained from step (c) with toluene;
   e. recovering dissolved acetylene from the toluene obtained from step (d) by heating said toluene to temperatures ranging from 0° to 40° C. and recycling the recovered acetylene to the gaseous effluent from step (b); and
   f. distilling the toluene wash liquid obtained from step (e), thereby producing an overhead product

consisting of hydrocarbons and a bottoms product consisting of pure toluene which is recycled to step (d) as fresh wash liquid.

2. A process as claimed in claim 1 for the purification of water-containing crude acetylene, which comprises the steps of

ca. loading the gaseous effluent from step (b) with methanol vapor and condensing out of said laden effluent a liquid mixture comprising methanol, water and a hydrocarbon mixture consisting essentially of hydrocarbons of more than five carbon atoms,

cb. separating the liquid effluent from step (ca) in a separating vessel into a hydrocarbon phase and a methanol/water phase still containing traces of hydrocarbons and acetylene,

cc. distilling said methanol/water phase to give water as the bottoms product and methanol as the overhead product, and

cd. recycling desorbed acetylene obtained from step (cc), said desorbed acetylene being laden with methanol vapor not condensed in said step (cc), to the condensation step (ca).

3. A process as claimed in claim 1 wherein said gaseous hydrocarbon is natural gas consisting essentially of methane.

* * * * *