March 27, 1962 F. F. A. BRACONIER ET AL 3,026,969

GAS TREATING PROCESS

Filed Sept. 9, 1959 2 Sheets-Sheet 1

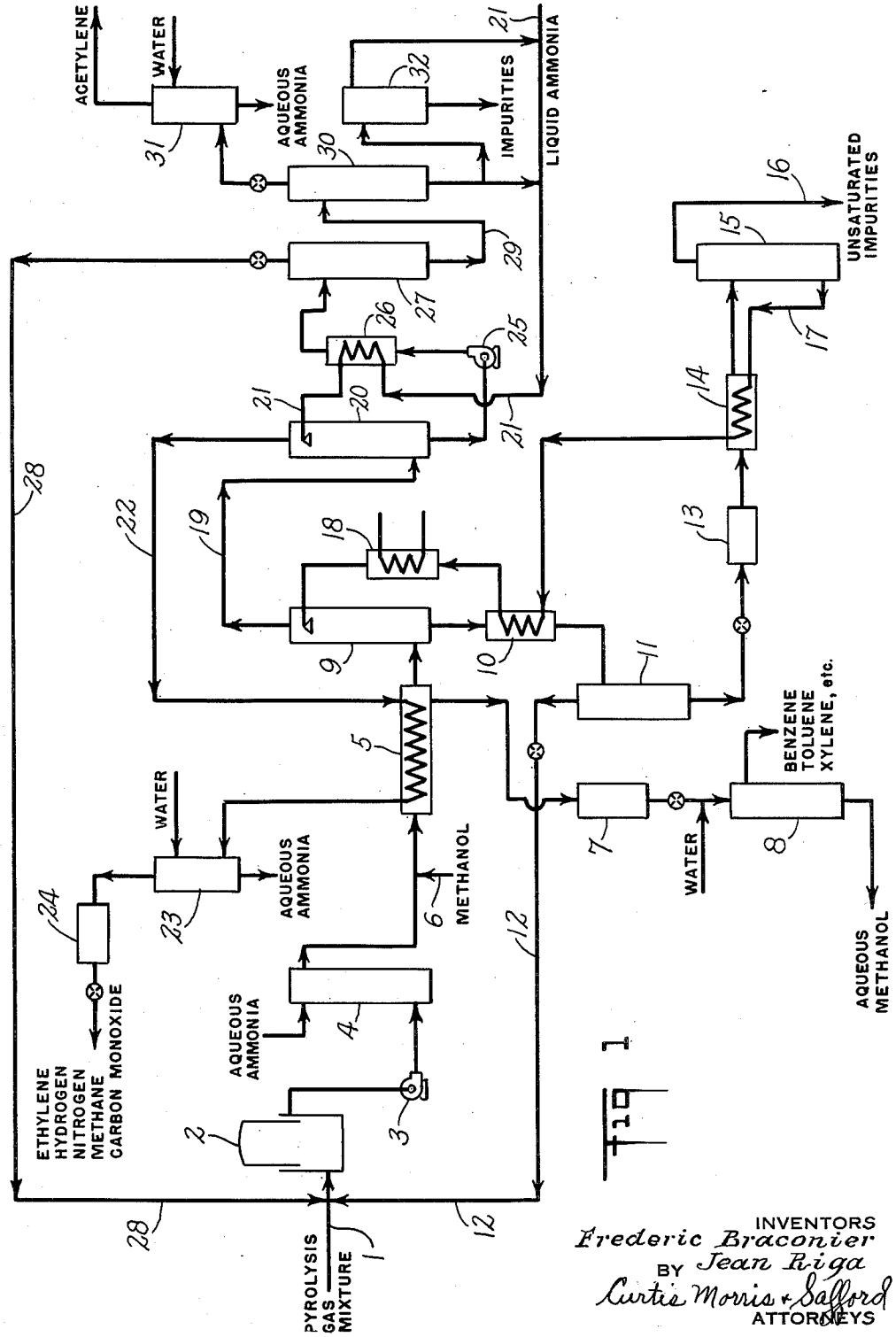


FIG. 1

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Fig 3

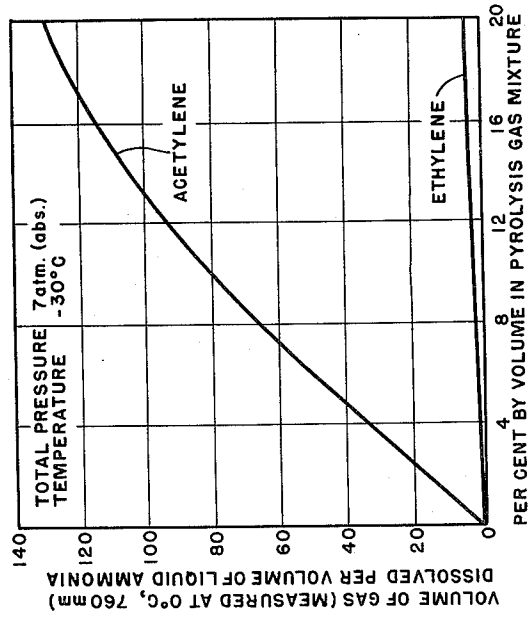
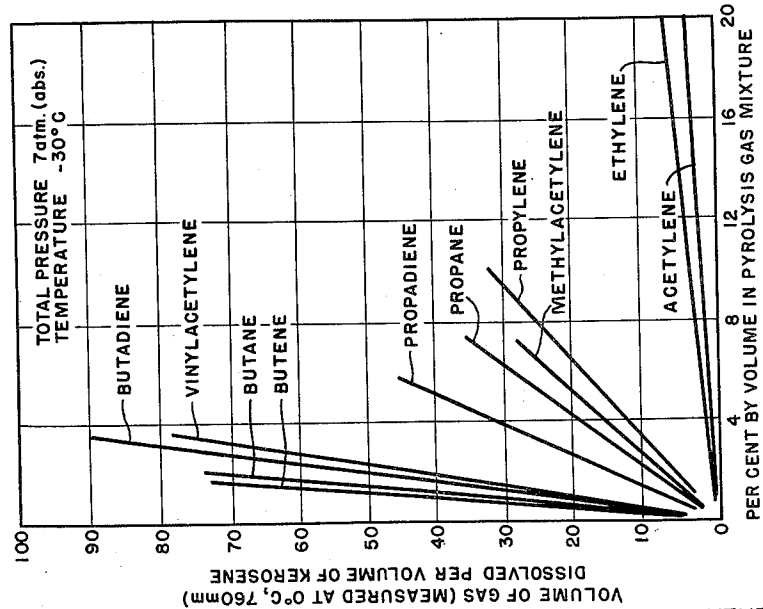


Fig 2



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GAS TREATING PROCESS

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6 Claims. (Cl. 183—115)

This invention relates to a process for treating gases, and relates particularly to a process for the separation of acetylene from gas mixtures containing the same.

It is known in the art that unsaturated hydrocarbons, particularly acetylene and olefines, may be prepared from more saturated hydrocarbons by subjecting the latter to a thermal treatment, e.g. by injecting the hydrocarbons into the hot gases formed by one or more flames fed preferably with oxygen and hydrogen (or other hydrogen-rich fuel gas), or by partial combustion of gaseous hydrocarbons. In addition to acetylene and olefines, other unsaturated compounds are formed during these reactions, for example diacetylene, methylacetylene and other higher acetylene homologues as well as propadiene, butadiene, and the like.

The acetylene is diluted with these other unsaturated compounds, which are impurities from which acetylene is to be separated with a high yield and in a sufficiently pure state to be used in chemical reactions. For example, acetylene is useful in the synthesis of unsaturated monomeric substances such as vinyl compounds, which in turn are polymerized to form many useful polymers.

The process generally used for concentrating and purifying acetylene contained in gases obtained by the thermal decomposition of hydrocarbons comprises essentially:

(*a*) removing impurities from the pyrolysis gas by washing the latter with a solvent for the impurities but in which acetylene is not very soluble. This first operation will be defined hereafter as a pre-purification operation;

(*b*) treating the pre-purified gas with a selective solvent for acetylene. This second operation, thus, concentrates acetylene contained in the pre-purified gas.

It is known in the art to remove impurities from acetylene during the pre-purification by washing the pyrolysis gases with liquid hydrocarbons in which acetylene is not very soluble, the washing being carried out in one or more steps according to the hydrocarbon used in the washing step and the degree of purity subsequently desired for the concentrated acetylene. However, the washing process is not completely satisfactory on an industrial scale generally using mixtures of different hydrocarbon fractions, some of which have a low boiling point, as washing hydrocarbons. Thus, for instance, the same hydrocarbons as those subjected to the pyrolysis are sometimes used for washing the gases. A substantial amount of the volatile light hydrocarbon fractions are often entrained in the non-dissolved gas during the washing operation. The entrained portion of washing liquid later causes trouble during the selective solution of acetylene.

Apparently it would be advantageous to use a mixture of hydrocarbon fractions having a high boiling point as the pre-purification liquid solvent. However, tests effected with different solvent mixtures have shown that the pre-purification solvent has a dissolving power for impurities which increases as the molecular weight of the liquid approaches the relatively low molecular weight of the impurities to be dissolved. Consequently, an ideal pre-purification solvent combines two substantially incompatible properties, namely a low volatility and a low

molecular weight. In addition, the pre-purification solvent advantageously has other properties which facilitate an efficient and safe purification.

For example, the impurities present in the pyrolysis gases readily yield polymers which are dangerous to handle and which has a tendency to form deposits in the pipes and the apparatus used for treating the gases, which deposits are liable rapidly to block the apparatus. It is thus desirable to use a washing liquid in which such polymers remain dissolved. Also, in order to avoid costly recyclings and to make the pre-purification operations easier, the washing liquid desirably should dissolve only a minimum of acetylene and ethylene. The solvent is preferably also one which is readily regenerated and easily handled.

In addition, to obtain a particularly efficient combination of the acetylene pre-purification and concentration operations, the small proportions of impurities not dissolved by the first, pre-purification, solvent are desirably retained by the second, acetylene concentrating, solvent and remain dissolved in said second solvent when the latter is treated to free pure acetylene. It is thus highly advantageous to have two "complementary" solvents.

These many conditions are fulfilled in the process of the present invention, which comprises carrying out the pre-purification of a pyrolysis gas by washing said gas with kerosene (a mixture of hydrocarbon fractions boiling between about 175° and about 225° C. and having an average molecular weight of about 180), and then carrying out the final concentration of acetylene by treating the pre-purified gas with anhydrous liquid ammonia. Acetylene dissolved in the anhydrous ammonia is finally recovered by degasification of the solution, e.g. by distillation.

Kerosene effects the removal of substantially all the unsaturated impurities contained in the pyrolysis gas, and the subsequent concentration of acetylene contained in the prepurified gas is made substantially easier. A smaller quantity of concentrating solvent can be used per volume of prepurified pyrolysis gas, and regeneration of the solvent is easier.

As the selective acetylene solvent, it is particularly advantageous to use liquid ammonia. It has been observed that the small proportion of impurities not completely removed with kerosene are readily separated from acetylene by the treatment of the pyrolysis gas with ammonia, the boiling point of which is between that of acetylene and said impurities. Selective solvents for acetylene, other than liquid ammonia, do not present this particularly interesting advantage. In the same way, if other solvents are substituted for kerosene during the pre-purification steps, impurities are left in the pyrolysis gas and form, with liquid ammonia, azeotropes having boiling points in the neighborhood of that of acetylene. Thus kerosene and liquid ammonia are particularly advantageous "complementary" solvents.

Carbon dioxide, which yields ammonium carbamate with ammonia, and some pyrolysis gas components which may be readily condensed and may otherwise be solidified and block the purification apparatus at the low temperature used for extracting acetylene, are advantageously removed before the treatment with kerosene and ammonia.

The process herein described for extracting acetylene and ethylene in a substantially pure state from pyrolysis gases comprises the following steps:

(1) treating the pyrolysis gas, advantageously previously freed from carbon black and tar, to remove carbon dioxide therefrom;

(2) drying and cooling the pyrolysis gas to fix the

saturation water and to remove those hydrocarbons which may be readily condensed;

(3) pre-purifying the pyrolysis gas by washing with kerosene at a low temperature selectively to dissolve the higher acetylene homologues and other unsaturated hydrocarbons, while only dissolving a small fraction of acetylene and ethylene;

(4) concentrating acetylene contained in the pre-purified gas by dissolving the acetylene contained in said gas in liquid ammonia at a low temperature, and then distillating the ammoniacal solution of acetylene to free pure acetylene therefrom.

This process is advantageous in that it is particularly adaptable to the treatment of pyrolysis gases having varying compositions. The following Table 1 gives, by way of example, analyses of two pyrolysis gases showing the complexity of these gaseous mixtures and the variation of the content of the components. The indicated figures are percent by volume.

TABLE 1

Components of the pyrolysis gas	By partial combustion of methane	By pyrolysis of naphtha
Acetylene	8.1	8.5
Ethylene	0.3	16.2
Methane	4.8	14.1
Ethane		0.5
Methylacetylene	0.13	0.8
Propadiene	0.04	
Propylene		1.3
Diacetylene	0.1	0.05
Vinylacetylene	0.03	0.45
Butadiene		0.6
Butenes		0.2
Cyclopentadiene		0.35
Pentadiene		0.05
Benzene		0.5
Toluene		0.1
Phenylacetylene		0.1

The hydrocarbon components of the exemplary gas mixtures are seen to be principally acetylene, ethylene, alkanes, arylanes, and unsaturated aliphatic, alicyclic and arylaliphatic hydrocarbons having more than two carbon atoms. The remainder of these gases consists mainly of hydrogen, carbon monoxide, carbon dioxide and nitrogen.

A better understanding of the invention and its many advantages can be had by referring to the accompanying drawings, in which:

FIG. 1 is a flow diagram of a gas treating process; and

FIGS. 2 and 3 respectively show the solubilities of various hydrocarbons in kerosene and in liquid ammonia.

Referring now to FIG. 1, pyrolysis gas, advantageously freed from carbon black, tar and other easily condensable components, is fed through a conduit **1** into a gasometer **2**. The gas is then passed through a compressor **3**, and is then introduced at a pressure of a few atmospheres into a column **4** in which carbon dioxide is removed. This operation avoids the formation of ammonium carbamate which is not very soluble in the liquid ammonia used for dissolving acetylene. Carbon dioxide may be removed by any of the methods known in the art, e.g. by washing the gas with ammoniacal solutions. The pyrolysis gas, freed from carbon dioxide, is then dried and cooled in a heat-exchanger **5** by heat-exchange with the gas leaving a column **20** in which acetylene is dissolved in liquid ammonia.

To avoid frosting of the drying apparatus, methanol is injected into the pyrolysis gas through conduit **6** before said gas enters the exchanger **5**. The condensing liquid is collected in a tank **7** and is eventually subjected to an expansion, when working under pressure. The condensate contains water mixed therewith, whereby two layers are formed in decanting vessel **8**. The lower layer consists of an aqueous methanol solution and the upper layer consists substantially of a mixture of benzene, toluene, and xylene, etc.

After leaving the exchanger **5** at a temperature of from −10° to −30° C., the pyrolysis gas is washed in a column **9** with kerosene cooled to from about −10° to about −40° C., under a pressure from 1 to 10 atm., preferably from 5 to 10 atm. By this washing, the gas is freed from substantially all acetylene homologues and other unsaturated impurities, which impurities are retained in the washing liquid in a dissolved state.

At the same time small amounts of acetylene and ethylene may be absorbed. These gases are recovered by reheating the kerosene to a temperature from about 10° to about 30° C. by passing it through a heat-exchanger **10** and then by partially expanding it in a column **11**. In this way, the small proportions of acetylene and ethylene contained in the kerosene are freed and this gas mixture is advantageously recycled, e.g. to gasometer **2** through a conduit **12**.

So freed from acetylene and ethylene, the kerosene is regenerated by degasifying the dissolved impurities. For degasifying, the kerosene is further expanded, or reheated slightly, or freed from the dissolved compounds by means of an inert gas, or subjected to a combination of these processes. Preferably, the kerosene is expanded down to a pressure in the neighborhood of atmospheric pressure and is then heated to a temperature from about 100° to about 120° C. by passing it through a reheater **13** and a heat-exchanger **14**. The kerosene is then subjected to entrainment with an inert gas in column **15**. As an inert gas, steam may advantageously be used, in which case column **15** is advantageously kept at a temperature higher than the dew point of the steam at the pressure used, to avoid any condensation of steam in the kerosene. The temperature may conveniently be maintained by a jacket of steam under pressure surrounding the whole length of column **15**. The impurities dissolved in kerosene are entrained with the inert gas from column **15** and are discharged through a conduit **16**. Hot regenerated kerosene is returned to the pyrolysis gas washing column **9** through conduit **17** by successively passing through heat exchanger **14** and **10**, in which it is cooled and serves to heat impure kerosene coming from the washing column **9**, and is then passed through another heat exchanger **18**, where it is further cooled.

The pre-purified gas, cooled from about −10° to about −40° C., leaves column **9** and enters a conduit **19** leading to column **20**, where acetylene is selectively dissolved in anhydrous liquid ammonia fed through a conduit **21**. The cooling produced by vaporisation of the ammonia determines the thermal equilibrium of column **20**, which is at a temperature of from about −10° to about −70° C. The vaporisation is caused by the passage of the pyrolysis gas through the liquid ammonia. The selective dissolution of acetylene in the ammonia is advantageously carried out at a pressure from 1 to 10 atm., or from 1 to 20 atm., preferably from 5 to 10 atm.

The remaining gas, freed from acetylene, cooled, and saturated with ammonia, leaves the column **20** through a conduit **22**. After having passed through heat exchanger **5**, where it cools the pyrolysis gas to be purified, said gas is then freed from the accompanying ammonia, e.g. preferably by washing with water in column **23**, and then it is returned to a fractionating unit **24**. The gas consists substantially of ethylene, hydrogen, methane, carbon monoxide and nitrogen, said components being separated by fractionating in unit **24**. In this way, very pure ethylene is recovered and may be used directly in chemical syntheses.

Liquid ammonia containing dissolved acetylene is recovered at the bottom of column **20**, and then, after having been compressed in compressor **25**, and after having passed through a cold recovering heat-exchanger **26**, is fed to a column **27**. In this column the whole of the dissolved ethylene, together with a small fraction of dissolved acetylene, is recovered by degasifying the ammonia

either by partial expansion or by heating or by both processes combined. After separation from any entrained ammonia, e.g. by washing with water, this ethylene and acetylene mixture is then returned through a conduit 28 to the purification circuit, i.e. to the gasometer 2 for the pyrolysis gas. It is also possible to return said mixture directly to washing column 20. Liquid ammonia containing acetylene and no ethylene is sent through a conduit 29 to a column 30, where acetylene is evolved, e.g. by heating at a low temperature. The acetylene, accompanied by gaseous ammonia, leaves column 30 and enters column 31 where ammonia is removed, e.g. by washing. Substantially pure acetylene is thereby obtained at the top of said column 31. According to the subsequent utilisation conditions, said pure acetylene may be substantially at atmospheric pressure or at a higher pressure.

The liquid anhydrous ammonia drawn off at the bottom of column 30 contains no more acetylene but does contain a small proportion of the impurities which were not removed during the prepurification in column 9. The major portion of liquid ammonia is returned to the washing column 20 through conduit 21. The remainder is distilled in column 32 to separate said impurities, purified ammonia being also returned to the washing column 20 through conduit 21.

The process of this invention may be used on all gases obtained from the thermal treatment of hydrocarbons, either by partial combustion or by pyrolysis in hot combustion bases. It is particularly advantageous when applied to a pyrolysis gas obtained by injecting a liquid hydrocarbon into hot combustion gases. Before being injected in the pyrolysis chamber, said liquid hydrocarbon is advantageously gasified and preheated to a high temperature. During said preheating, it is advantageous to protect said hydrocarbon thermally by mixing it with steam, as known in the art. In the present invention, by entraining with steam the impurities dissolved in the kerosene used, there is obtainable, at the outlet 16 of column 15, a mixture of impurities and steam which may be mixed with the hydrocarbon to be pyrolysed. By this means, the steam may be used both as an inert gas carrying the impurities and as a diluent for the hydrocarbon to be pyrolysed. In addition, full use is made of the impurities as raw material, since they yield acetylene on thermal decomposition.

The process of this invention is also advantageous in that the gaseous mixture entering the fractionation unit 24 may be separated into different fractions, e.g. ethylene, methane, mixtures of carbon monoxide and hydrogen, and residual gas. The methane and residual gas fractions, with amounts of carbon monoxide and hydrogen, are particularly interesting gases, and can be used to produce, by combustion, the hot gases into which the hydrocarbon to be pyrolysed is injected. The remainder of the mixture of carbon monoxide and hydrogen is a high-grade product suitable for use in the synthesis of ammonia and methanol, for example.

Comparative tests have shown that it is generally more economical to pre-purify the pyrolysis gas under pressure. For instance, under a pressure of about 10 atmospheres and at a temperature from −20° to −30° C., the unsaturated impurities in acetylene are very soluble in kerosene and solvent entrainment due to the action of vapour tension is negligible. Also, in addition to the reduction in space required for the unit, by working under pressure the kerosene through-put and the costs for the recovery of the impurities dissolved by this solvent may be substantially reduced for a given purity of acetylene. Further, if it is advantageous after the separation of acetylene to compress (e.g. to about 15 atmospheres) the gas leaving column 20 before it enters the fractionation unit 24, the energy consumed by the process is smaller when working at superatmospheric pressure than when working at atmospheric pressure.

It is also advantageous to work under pressure in the absorption column 20, since the latter, which is thermally self-regulation by partial vaporization of ammonia, is then equilibrated at temperatures higher than those obtained with said column under atmospheric pressure. Thus, under atmospheric pressure the temperature reached is from −60° to −70° C., while at a pressure of about 7 atmospheres the temperature is stabilized at −25° to −35° C., whence a very substantial reduction of the cold losses is obtained.

In FIG. 2 of the accompanying drawings there are given the solubilities, at 7 atmospheres and −30° C., of several major components of the pyrolysis gas in kerosene as a function of their proportions by volume in the pyrolysis gas. FIG. 2 shows that kerosene is a very good solvent for the C_4 and C_3 hydrocarbons (particularly the C_4 hydrocarbons). However it also appears from FIG. 2 that kerosene is a poor solvent for the C_2 hydrocarbons, namely acetylene and ethylene.

FIG. 3 compares the solubilities of acetylene and ethylene in liquid ammonia according to their proportions by volume in the pyrolysis gas. The solubility data are given for a pressure of 7 atmospheres and a temperature of −30° C. Anhydrous liquid ammonia is advantageously employed as a complementary solvent to kerosene in the production of pure acetylene because anhydrous liquid ammonia is a good solvent for acetylene and the portion of the impurities which are not retained by kerosene, and is also a poor solvent for ethylene.

It has been observed that the small amount of ethylene dissolved, together with all the acetylene, in the liquid ammonia may be readily separated by a partial degasifying of the ammoniacal solution. Ethylene, together with some ammonia and acetylene, is preferentially removed from the solution, which then contains only acetylene and small amounts of other impurities. The ethylene removed is advantageously returned to the treatment cycle of the pyrolysis gas. Due to the low solubility of ethylene in ammonia, the ammonia always dissolves only the same small saturation concentration of ethylene in circulating between columns 20 and 27. Consequently, when running the installation, substantially the total amout of ethylene contained in the fresh pyrolysis gas is contained in the gaseous mixture leaving the top of the absorption column 20 and returning to the fractionation unit 24.

At the bottom of column 27, there is drawn off liquid ammonia which contains only dissolved acetylene and some impurities which are not retained during the treatment of the pyrolysis gas with kerosene. These various impurities are readily separated by distillation, since, under the pressures employed, the boiling point of ammonia is between that of acetylene and those of the impurities. After expansion, the acetylene and ammonia enter column 31, where ammonia is removed, e.g. by washing, so that very pure acetylene leaves the top of column 31.

The mixture of acetylene and ammonia leaving column 30 preferably has a composition such that, at the pressures and temperatures employed, no explosive reaction is likely to occur. Systematic tests have shown that to meet safety requirements the gaseous mixture of acetylene and ammonia should preferably contain about equal portions by weight of the constituents (about 50 percent by weight of acetylene and about 50 percent by weight of ammonia) at a pressure of, for example, approximately 16 atmospheres and at a temperature of −30° C. Similarly, the gaseous mixture of acetylene, ethylene and ammonia entering the top of column 27 preferably contains about 50 percent by weight of ammonia and 50 percent by weight of acetylene and ethylene.

The following example illustrates the invention by description of the treatment of a pyrolysis gas obtained by injecting naphtha into hot combustion gases, but is not to be taken as limiting the process of the invention to this embodiment.

Example

The pyrolysis gas (1000 m.³ measured at 0° C. and 760 mm. Hg), freed from carbon black, tar and other condensable components, has the composition indicated in Table 2. Said pyrolysis gas is introduced into the gasometer **2**, after having been mixed with the recycled gases, fed through conduits **12** and **28**, coming respectively from the column **11** for expanding the solution of impurities in kerosene and the column **27**, in which ethylene dissolved in the ammoniacal acetylene solution is removed from solution.

The gaseous mixture coming from gasometer **2** is compresed to 10 atmospheres by means of compressor **3**, and carbon dioxide is then removed in column **4** with the gas at an average pressure of 9.5 atmospheres. The removal is advantageously carried out by washing the gas with an aqueous ammonia solution obtained by the recovery of the ammonia vapours entrained in the product gases during the subsequent absorption step with ammonia. A small proportion of methanol is introduced into the carbon dioxide free gas to avoid frosting of the heat exchanger **5**, into which the gas is next introduced to dry it and to remove condensable components therefrom. These components are principally cyclic hydrocarbons. In exchanger **5**, the gas is cooled intensively by cold gas coming from the treatment step with liquid ammonia. The liquid fraction formed in the exchanger **5** is recovered in vessel **7** and then, after expansion to atmospheric pressure and addition of water, is separated into phases in the decanting vessel **8**. The lower layer is an aqueous methanol solution and the upper layer consists substantially of benzene, toluene and cyclopentadiene. For 1 ton of concentrated acetylene recovered at the end of the treatment (at the top of column **31**), 105 kg. cyclopentadiene, 320 kg. benzene and 70 kg. toluene are recovered.

When leaving exchanger **5**, the gas has the composition given in the appropriate column of Table 2. This gas (942 m.³) is introduced at the bottom of column **9**, where it is washed with kerosene. 2.680 kg. of kerosene are introduced through the top of the washing column **9** at a temperature of −28.5° C. The pre-purification washing is effected under a pressure of 8.13 atmospheres. A solution of impurities in kerosene is drawn off at the bottom of column **9** at a temperature of −18.5° C. After heat exchange with purified and recycled kerosene in the exchanger **10**, this solution of impurities in kerosene is expanded in column **11**. In said expansion, small amounts of acetylene and ethylene dissolved by the kerosene are freed and are then returned to the beginning of the purification cycle through conduit **12**. After reheating in heater **13** and exchanger **14**, the expanded kerosene is introduced into column **15**, in which the impurities are removed by distillation and vapour entrainment, said impurities being then recovered through conduit **16**. At the top of column **15**, the temperature is approximately 120° C. The impurities are returned to the pyrolysis furnace, where they represent approximately 10 percent of the weight of the naphtha subjected to the pyrolysis. Purified kerosene is returned to column **9** after having been cooled down to a temperature of −28.5° C. by passing through the exchangers **14** and **10** and after having been additionally cooled in exchanger **18**, the refrigeration therefor being supplied from an external source.

The pre-purified gas (818 m.³) leaving the top of the washing column **9** passes through conduit **19** to column **20**, in which it is washed with anhydrous liquid ammonia for selectively dissolving acetylene. Before entering said column **20**, the gas has the composition indicated in Table 2. For dissolving acetylene in column **20**, 984 kg. of anhydrous liquid ammonia having a temperature of −27° C. are used. The pressure in said column is 7.6 atmospheres. The solution of acetylene in ammonia drawn off at the bottom of column **20** has a temperature of −35° C. The residual gas (742 m.³) undissolved by ammonia and having the composition given in Table 2 passes through conduit **22** and exchanger **5** to the water washing column **23** (for fixing the ammonia vapors entrained by the gas). It then enters the fractionating unit **24** at a pressure of 7 atmospheres. This gas is separated into several fractions, namely ethylene, methane and a mixture of hydrogen and carbon monoxide, said fractions being obtained in pure state and directly available for chemical synthesis purposes. The ammonia solution drawn off at the bottom of column **20** contains acetylene and ethylene together with a small proportion of impurities, which are not retained by kerosene during the pre-purification. After having been compressed to 18 atmospheres by compressor **25**, and after having partially cooled the ammonia entering the column **20**, this acetylene solution enters column **27**, in which dissolved ethylene is freed by heating and partial expansion down to 16 atmospheres. This ethylene is returned to gasometer **2**. A solution of acetylene in ammonia is recovered at the bottom of column **27**, said ammonia being sent through conduit **29** to column **30** where the acetylene is freed. The degasifying of the solution is carried out at a pressure of 16 atmospheres and at a temperature of −30° C. (at the top of column **30**). A gaseous mixture of substantially equal parts by weight of acetylene and ammonia is obtained. Finally, to obtain pure acetylene, this gas mixture is washed with water to remove ammonia. The resulting acetylene (77.4 m.³) is in a particularly pure state (99.6 percent). The composition of the final product is given in Table 2. The ammonia recovered at the bottom of column **30** is returned to column **20**. It still contains small quantities of acetylene which are partially removed by distilling a portion of said ammonia in column **32**.

TABLE 2

Components (mole percent)	Pyrolysis gas (entering conduit 1)	Dried, CO_2-free gas entering column 9)	Prepurified gas (leaving column 9)	Residual impurity gas (column 20)	Final product
Acetylene	8.02	9.36	9.80	0.12	99.62
Ethylene	15.57	19.0	18.86	20.78	0.11
Hydrogen	30.17	32.2	36.93	40.91	-------
Nitrogen	0.28	0.30	0.34	0.38	-------
Carbon monoxide CO	13.87	14.95	16.98	18.81	-------
Carbon dioxide CO_2	13.02	-------	-------	-------	-------
Methane	12.84	14.09	15.71	17.40	-------
Ethane		1.26	1.02	1.13	-------
Methylacetylene + propadiene		2.24	0.04	0.02	0.25
Propylene		4.69	0.31	0.34	0.02
Diacetylene		0.12	-------	-------	-------
Vinylacetylene		0.60	-------	-------	-------
Butadiene		0.81	-------	-------	-------
Butene		0.15	-------	-------	-------
Butane	6.23 (total)	0.02	-------	-------	-------
Cyclopentadiene		0.12	-------	-------	-------
Pentadiene			-------	-------	-------
Pentene		0.04 (total)	-------	-------	-------
Pentane			-------	-------	-------
Benzene		0.03	-------	-------	-------
Cyclohexane		0.01	-------	-------	-------
Toluene		0.01	-------	-------	-------

Although specific embodiments of the invention have been herein shown and described, it is to be understood that they are illustrative and are not to be construed as limiting the scope and spirit of the invention.

We claim:

1. The method of separating substantially pure acetylene from a gaseous mixture of hydrocarbons containing the same and produced by the pyrolysis of hydrocarbons, which method comprises compressing said gas mixture to a pressure above atmospheric pressure, washing the compressed gas with a kerosene fraction of hydrocarbons boiling between about 175° and 225° C., washing the kerosene-washed compressed gas with liquid ammonia selectively to dissolve acetylene, and degasify-

ing the resulting ammonia solution to recover acetylene therefrom.

2. The method of separating substantially pure acetylene from a gaseous mixture containing the same and produced by pyrolysis of hydrocarbons, which method comprises washing said gaseous mixture at a temperature between −10° C. and about −40° C. with a kerosene mixture of hydrocarbon fractions boiling between 175° and 225° C., washing the kerosene-washed mixture with liquid ammonia at a temperature between about −10° C. and −70° C. selectively to dissolve acetylene, and degasifying the resulting ammonia solution to recover acetylene.

3. The method of separating substantially pure acetylene from a gaseous mixture containing the same and produced by pyrolysis of hydrocarbons, which method comprises removing carbon dioxide from said gas mixture, washing the carbon dioxide-free gas with a kerosene fraction of hydrocarbons boiling between about 175° and 225° C., said gas being at a pressure between one atmosphere and about ten atmospheres and at a temperature between about −10° C. and about −40° C., next washing with kerosene-washed gas with liquid ammonia, said gas being at a pressure between one atmosphere and about 20 atmospheres and at a temperature between about −10° C. and about −70° C., whereby acetylene is preferentially dissolved in said ammonia, and then distilling the resulting ammonia solution to recover acetylene therefrom.

4. The method of separating substantially pure acetylene from a gaseous mixture containing the same and produced by the pyrolysis of hydrocarbons, which method comprises removing carbon dioxide from said gaseous mixture, cooling the remaining gases to condense less volatile components therefrom, dissolving out unsaturated components having more than two carbon atoms with a kerosene mixture of hydrocarbon fractions boiling between about 175° and 225° C., washing the residue with liquid ammonia selectively to dissolve acetylene therefrom, and degasifying the resulting ammonia solution to recover acetylene.

5. The method of separating substantially pure acetylene from a gaseous mixture containing the same and produced by the pyrolysis of hydrocarbons, which method comprises washing said mixture under pressure with kerosene to dissolve out from said mixture unsaturated hydrocarbon components having more than two carbon atoms, whereby an acetylene enriched gas phase and a kerosene solution of said unsaturated components results, reducing the pressure on said kerosene solution, heating said solution and contacting said solution with steam to remove said unsaturated components from the solution, incorporating the resultant mixture of steam and unsaturated components with hydrocarbons for pyrolysis, washing said acetylene-enriched gas phase with liquid ammonia selectively to dissolve acetylene, and distilling said ammonia solution to recover acetylene therefrom.

6. The method of separating acetylene from a gaseous pyrolysis mixture including acetylene, ethylene, other saturated and unsaturated aliphatic and aromatic hydrocarbons having more than two carbon atoms and inorganic gases including hydrogen, carbon dioxide, carbon monoxide and nitrogen, which method comprises washing said gaseous mixture with aqueous ammonia to remove carbon dioxide therefrom, cooling the residual gases to condense therefrom said aromatic hydrocarbons and a portion of said unsaturated hydrocarbons having more than two carbon atoms, washing the residual gases with a kerosene hydrocarbon solvent fraction of hydrocarbons boiling between about 175° and 225° C. to dissolve substantially all the remaining unsaturated hydrocarbons having more than two carbon atoms, washing the residual gases with liquid ammonia to dissolve acetylene and to leave a gaseous residue consisting essentially of ethylene and saturated aliphatic hydrocarbons and inorganic gases, distilling the resulting ammonia solution to remove acetylene therefrom, and washing the distilled gases with water to remove ammonia therefrom, whereby a substantially pure acetylene product is obtained.

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