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ACETYLENE RECOVERY

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This invention relates to an improved method for recovering acetylene from gas mixtures, and in particular concerns a process wherein acetylene-containing gases are contacted or scrubbed with certain organic liquids in which acetylene is highly soluble. It further concerns new and useful solutions of acetylene dissolved in such organic liquids.

In the production of acetylene by the cracking or partial oxidation of hydrocarbons at high temperatures, the acetylene product is invariably obtained in admixture with various other gaseous products of the reaction, e. g. oxides of carbon, hydrogen, unsaturated hydrocarbons other than acetylene, etc. Unreacted components of the feed gas, e. g. nitrogen and hydrocabrons, are also present. The concentration of acetylene in the product gas seldom exceeds 10 per cent by volume and is usually of the order of 3 to 6 per cent by volume. Various methods for recovering the acetylene in substantially pure form from the product gas have been proposed. The majority of such methods involve scrubbing the gas with a selective solvent for the acetylene component, and thereafter stripping or boiling the acetylene away from the solvent. When such method is applied to the treatment of large volumes of gas containing only small amounts of acetylene, it is essential that the solvent, in addition to having high solvent power for acetylene, also have as high a boiling point as possible in order to minimize solvent loss. Thus, acetone, despite its high solvent power for acetylene, cannot economically be employed for scrubbing acetylene cut of dilute gas mixtures because of its normally high vapor pressure. Other criteria for suitable solvents include low viscosity, chemical stability, and inertness with respect to the components of the gas mixture to be treated. A wide variety of compounds have been proposed for use as solvents for the recovery of acetylene, e. g., glycol ethers and esters, gylcol ether-esters, mono- and poly-ketones, polybasic acid esters, aliphatic lactones, carbonate esters, polyglycols and their ethers and esters, dialkyl formamides, tetralkyl ureas, etc. However, all of such previously proposed solvents have unduly high vapor pressures or leave much to be desired in the way of solvent power for acetylene, and many lack selectivity with respect to hydrocarbons other than acetylene.

It is accordingly an object of the present invention to provide solvents better adapted than those heretofore known for use in recovering acetylene from mixed gases.

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Another object is to provide compounds having exceptionally high solvent power for acetylene coupled with low vapor pressure and low solvent power for the gases with which acetylene is normally contaminated.

Another object is to provide concentrated solutions of acetylene in organic solvents.

A further object is to provide an improved method for recovering acetylene from gas mixtures, particularly those obtained in hydrocarbon cracking or partial oxidation processes.

Other objects will be apparent from the following description of the invention, and various advantages not specifically referred to herein will be apparent to those skilled in the art upon employment of the invention in practice.

I have now found that the above and related objects may be realized through the use of the formyl or acetyl derivatives of certain heterocyclic compounds as solvents for acetylene. More particularly, I have found that the N-formyl and N-acetyl derivatives of certain nitrogen-containing heterocyclic compounds have very high solvent power for acetylene coupled with very low vapor pressure at ordinary pressures, and are highly selective with respect to a wide variety of gases, including those with which acetylene is ordinarily associated. Such solvents are inert with respect to acetylene and the gases normally associated therewith and are relatively inexpensive. The invention thus consists in the method for recovering acetylene from gas mixtures containing the same which comprises scrubbing said mixtures with a liquid essentially comprising at least one member of the herein defined class of chemical compounds, whereby the acetylene is selectively dissolved or absorbed in said liquid, and in solutions of acetylene dissolved in said liquid.

The heterocyclic compounds which are employed as acetylene solvents in accordance with the invention are N-formyl-pyrrolidine, N-acetylpyrrodlidine, N-formyl-piperidine and N-acetyl-piperidine. Of these compounds, the two pyrrolidine derivatives are preferred by reason of their somewhat greater solvent power for acetylene and their somewhat better selectivity with respect to other hydrocarbon gases. All of such compounds are high-boiling, relatively mobile liquids which are inert with respect to acetylene and the gases with which it is usually contaminated. In the practice of the present invention these compounds are usually employed in substantially pure form, but if desired they may be employed in admixture with one another or in

combination with another liquid which may or may not be a solvent for acetylene.

The formyl compounds of the present class are conveniently prepared simply by adding formic acid to the heterocyclic compound, and heating the mixture gently until reaction is complete. Usually a small excess of the formic acid is employed, and if desired the reaction may be carried out in the presence of an inert reaction solvent. Upon completion of the reaction the product may be isolated and purified by fractional distillation. The acetyl compounds are prepared in the same general manner except that acetic anhydride or an acetyl halide is substituted for the formic acid.

The following example is illustrative of the preparation of the compounds of the present class, but is not to be construed as limiting the invention:

Approximately 43.7 parts by weight (0.95 mole) of formic acid are slowly added with stirring to 66 parts by weight (0.93 mole) of pyrrolidine. An exothermic reaction occurrs accompanied by a rise in temperature to about 125° C. Upon completion of the addition of the formic acid, the reaction mixture is heated at about 125° C. for about 20 minutes, after which it is fractionally distilled to recover the N-formyl-pyrrolidine product. The latter is obtained as a substantially colorless liquid distilling at 84.4°–85.0° C. under 8 mm. pressure and having a density of about 1.0880 g./ml. at 24° C. N-formyl-piperidine is prepared in a similar manner. It distills at about 81.7° C. under 5 mm. pressure, and has a density of about 1.0397 g./ml. at 24° C. N-acetyl-pyrrolidine is prepared by substituting acetic anhydride for the formic acid in the foregoing synthesis, and is found to distill at about 73.9° C. under 5 mm. pressure and to have a density of about 1.009 g./ml. at 24° C. N-acetyl-piperidine is similarly prepared, and is found to distill at about 80.6°–81.1° C. under 5 mm. pressure and to have a density of about 1.010 g./ml. at 24° C.

The following table presents a comparison of the solubility of acetylene in the solvents of the present class with the solubility in a number of other compounds which have been suggested for use as acetylene solvents:

Solvent	Boiling Point, ° C.	C_2H_2 Solubility, Vol./Vol. at 1 atm.
N-Formyl-pyrrolidine	84.4–85.0 at 8 mm	21.4 at 23.8° C.
N-Acetyl-pyrrolidine	73.9 at 5 mm	24.4 at 23.7 °C.
N-Formyl-piperidine	81.7 at 5 mm	15.0 at 24.0° C.
N-Acetyl-piperidine	80.6–81.1 at 5 mm	20.8 at 23.8° C.
Diethyl Oxalate	185 at 760 mm	12 at 20° C.
Butyrolactone	206 at 760 mm	15 at 27° C.
Pentanedione-2,4	139 at 746 mm	7.5 at 30° C.
Dimethyl tetraethylene glycol.	276 at 750 mm	11.4
Acetone	56.5 at 760 mm	13.1 at 25° C.

In addition to their high boiling points and excellent solvent power for acetylene, the compounds of the present class are very poor solvents for the gases with which acetylene is usually contaminated. Of such contaminating gases, ethylene is usually one of the most difficult to separate by reason of its analagous unsaturated character and molecular weight. The following table presents a comparison of the solubilities of acetylene and ethylene in the solvents of the present class, and the ratio of acetylene solubility to ethylene solubility:

Solvent	C_2H_2 Solubility, Vol./Vol. at 1 atm.	C_2H_4 Solubility, Vol./Vol. at 1 atm.	Ratio C_2H_2/C_2H_4 Solubilities
N-Formyl-pyrrolidine	21.4 at 23.8° C.	1.40 at 25° C.	15.3/1
N-Acetyl-pyrrolidine	24.4 at 23.7° C.	2.40 at 24.2° C.	10.2/1
N-Formyl-piperidine	15.0 at 24.0° C.	1.40 at 24.1° C.	10.2/1
N-Acetyl-piperidine	20.8 at 23.8° C.	2.88 at 23.8° C.	7.2/1

As will be apparent from the foregoing, the properties of the compounds of the present class render these compounds exceptionally well adapted for use as solvents for extracting acetylene from gas mixtures comprising only relatively small amounts of the same. Such extraction process consists essentially in scrubbing the mixed gas with the solvent, whereby the acetylene is preferentially absorbed, separating the rich solvent from the non-absorbed gas, and thereafter treating the rich solvent to recover the acetylene therefrom. The initial scrubbing step may be carried out in the conventional manner in conventional equipment, e. g., a bubble-cap or packed absorption tower operating on the countercurrent principle. The operation may be carried out at atmospheric, subatmospheric or superatmospheric pressure with superatmospheric pressures of the order of about 20 to about 200 lbs./sq. in. being particularly suitable. The solution of acetylene in the solvents of the present class closely follows Henry's law in that the weight of acetylene dissolved by a given weight of solvent increases substantially linearly with the partial pressure of the acetylene. Since the solubility of the acetylene varies indirectly with temperature, the absorption or scrubbing operation is advantageously carried out at as low a temperature as can conveniently or economically be maintained. When the present process is applied to the recovery of acetylene from the effluent gas of a high temperature hydrocarbon cracking or partial oxidation process, such gas is preferably first cooled to a temperature below 100° C. to condense out the water vapor, after which it is passed to the absorption or scrubbing step of the present process with or without compression. As a general rule, it is preferred to effect the absorption or scrubbing step at an absolute pressure between about 50 and about 150 lbs./sq. in. and at a temperature between about 10° and about 100° C.

Desorption of the acetylene from the rich solvent may likewise be effected in any of the conventional ways employing conventional equipment. Since the desorption operation is the reverse of that carried out in the absorption or scrubbing step, it is favored by elevated temperatures and/or low partial pressures of acetylene. Preferably, both of these factors are combined, i. e., the rich solvent is heated under partial vacuum until substantially all of the acetylene is driven off. Alternatively, it may be gas stripped at ordinary or elevated temperatures. The stripping gas should be one which can readily be separated from the acetylene by condensation or other means. Because of their very low solubilities in the solvents of the present class, the vapors of

condensible saturated hydrocarbons such as pentane, hexane, heptane, octane, etc. are well adapted for use as stripping gases.

The following example illustrates the use of the solvents of the present class in recovering acetylene from a gas mixture in accordance with the invention, but is not to be construed as limiting the same.

Example II

A typical product gas obtained from the high temperature partial oxidation of natural gas has the following composition on a dry basis:

	Percent by volume
Acetylene	3.6
Nitrogen	42.8
Hydrogen	42.0
Carbon dioxide	0.5
Carbon monoxide	5.7
Ethylene	0.4
Methane	5.0
	100.0

This gas is compressed to about 90 lbs./sq. in., and is passed upwardly through a bubble-cap absorption tower countercurrent to a descending stream of N-formyl-pyrrolidine. The liquid-to-gas ratio is maintained at about 0.70 lb./cu. ft. The acetylene-rich solvent withdrawn from the bottom of the tower is passed to a distillation column wherein it is heated to about 50° C. under 10 mm. pressure to drive off the dissolved acetylene. The lean solvent withdrawn from the bottom of the column is cooled and recycled back to the top of the absorption tower. The gas taken from the top of the distillation column contains about 95 per cent of acetylene. If desired, it may be further purified by a second solvent extraction operation carried out with the same or a different acetylene solvent.

While the invention has been described above primarily as a new and useful process for recovering acetylene from gaseous mixtures comprising the same, it will be apparent that it further comprises new solutions of acetylene which are useful in the art. For example, acetylene may advantageously be stored and/or shipped in the form of a solution in one or a mixture of the present solvents in the same way as acetone solutions of acetylene are commonly employed for the same purpose. As will be apparent from the table above, the solubility of acetylene in N-acetyl-pyrrolidine, for example, is almost twice as great as the solubility of acetylene in acetone. Accordingly, shipping a given volume of acetylene in the form of a solution in N-acetyl-pyrrolidine involves the transportation of only about half as much solution as is required when acetone is employed as the solvent.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the steps

or materials employed provided the methods or compositions stated by any of the following claims, or the equivalent of such stated methods or compositions, be employed or obtained.

I, therefore, particularly point out and distinctly claim as my invention:

1. The process for recovering acetylene from a gas containing the same in admixture with ethylene which comprises scrubbing said gas with a solvent essentially comprising a compound selected from the class consisting of N-formyl-pyrrolidine, N-acetyl-pyrrolidine, N-formyl-piperidine, and N-acetyl piperidine.

2. The process of claim 1 wherein the solvent essentially comprises N-formyl-pyrrolidine.

3. The process of claim 1 wherein the solvent essentially comprises N-acetyl-pyrrolidine.

4. The process of claim 1 wherein the solvent essentially comprises N-formyl-piperidine.

5. The process of claim 1 wherein the solvent essentially comprises N-acetyl-piperidine.

6. The process for recovering acetylene from a gas containing the same in admixture with ethylene which comprises scrubbing said gas with a solvent essentially comprising a compound selected from the class consisting of N-formyl-pyrrolidine, N-acetyl-pyrrolidine, N-formyl-piperidine, and N-acetyl piperidine, said scrubbing being carried out at a pressure between about 20 and about 200 lbs./sq.in. and at a temperature between about 10° C. and about 100° C., separating the solvent containing dissolved acetylene from non-absorbed gases, and recovering acetylene from the separated solvent.

7. The process of claim 6 wherein the acetylene is recovered from the separated solvent by heating said solvent under partial vacuum.

8. The process of claim 6 wherein the acetylene is recovered from the separated solvent by stripping said solvent with a condensible vapor of a saturated hydrocarbon.

9. A composition of matter essentially comprising a solution of acetylene in a solvent essentially comprising a compound selected from the class consisting of N-formyl-pyrrolidine, N-acetyl-pyrrolidine, N-formyl-piperdine, and N-acetyl-piperidine.

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