April 1, 1941. R. L. HASCHE 2,236,534

MANUFACTURE OF ACETYLENE, INCLUDING RECYCLING

Filed July 10, 1937 2 Sheets-Sheet 1

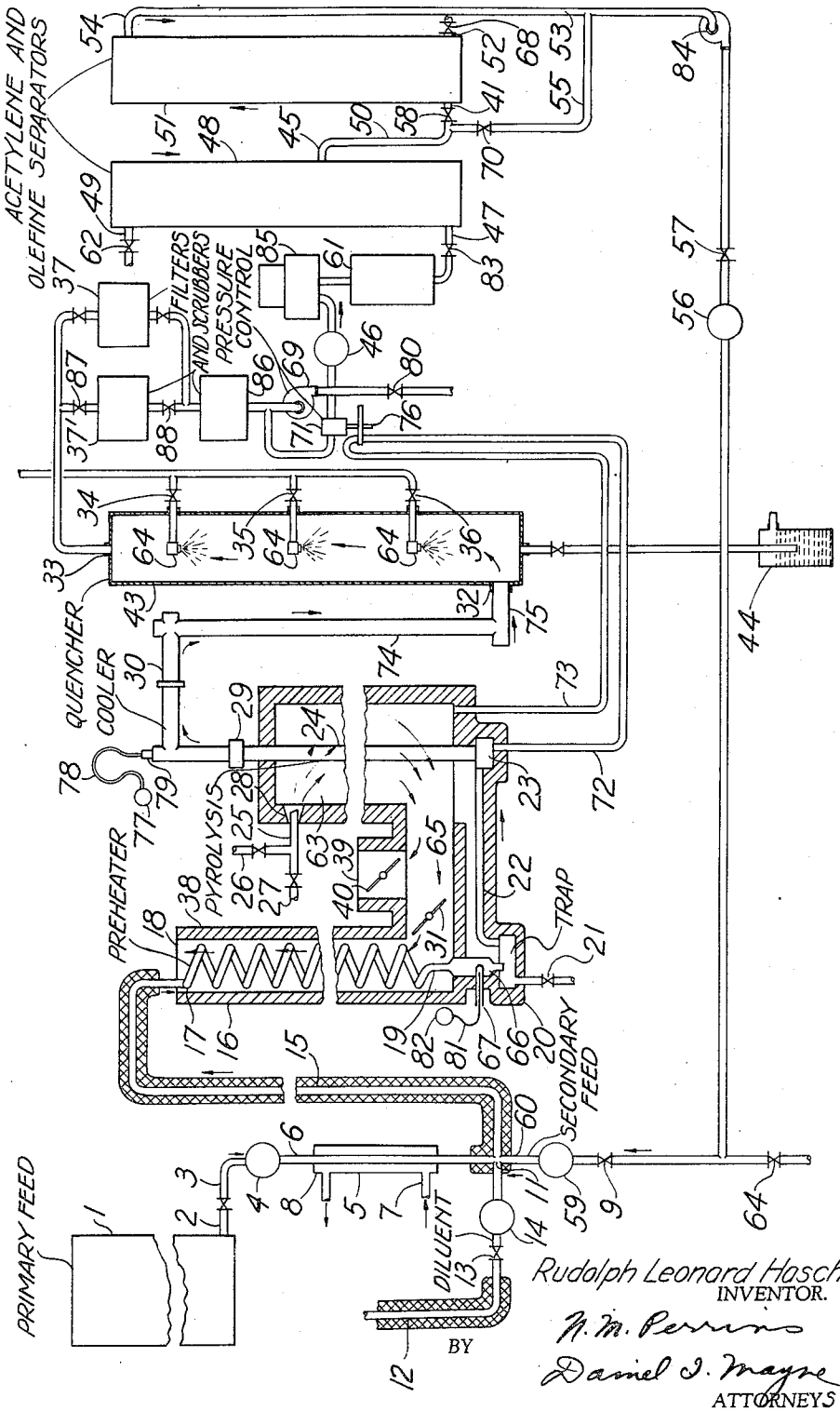


FIG. 1

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Filed July 10, 1937 2 Sheets-Sheet 2

FIG. 2

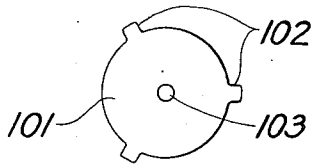


FIG. 4

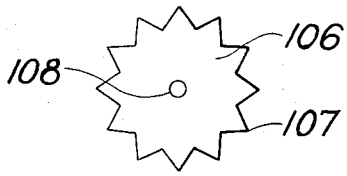


FIG. 3

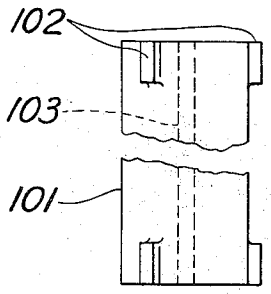


FIG. 5

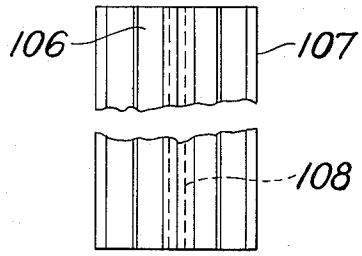
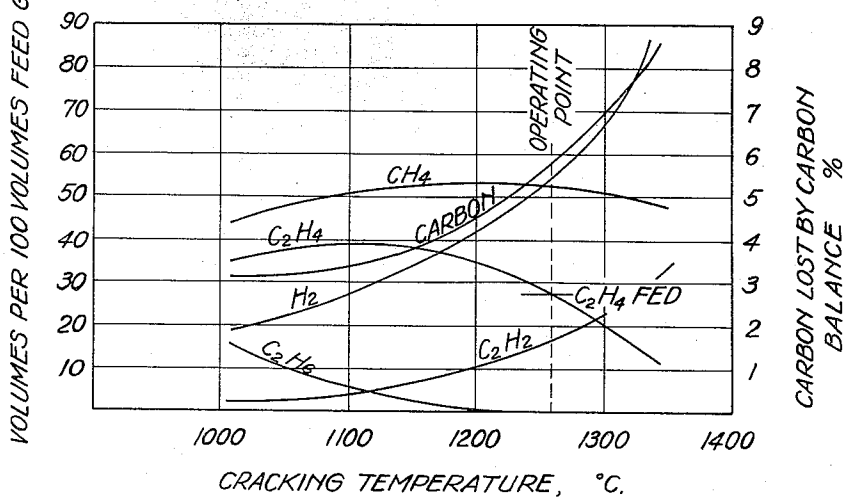


FIG. 6



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UNITED STATES PATENT OFFICE

2,236,534

MANUFACTURE OF ACETYLENE, INCLUDING RECYCLING

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Application July 10, 1937, Serial No. 153,042

10 Claims. (Cl. 260—679)

This invention relates to a process of making acetylene, or a gas containing acetylene, together with numerous by-products to be named and characterized herein. More particularly it relates to a pyrolysis process for making acetylene and by-products more economically than has heretofore been known.

While my process resembles that of Wulff, U. S. 1,880,309, in which a suitable raw material, mixed with a preponderant proportion of diluent, is cracked for a yield of acetylene and other products, increased economy of my process, however, is due to application of results of extensive investigation of a number of important factors of operation. That I have attained such increased economy is shown in the fact that I present herein results of work on a large scale, whereas in published literature hitherto, there is information only on laboratory experiments.

This invention has for one object to provide a method of producing approximately maximum yields of acetylenic, plus olefinic hydrocarbons rather than the production of maximum acetylenic yields alone. Still another object is to provide a pyrolysis process which permits the use of a smaller proportion of diluent than formerly thought necessary. A still further object is to provide a pyrolysis process in which there is considerable preheating before final pyrolysis, thus producing improved performance and increased capacity. A still further object is to provide a high temperature pyrolysis process in which there is a definite relationship between the heating surfaces and volume heated. A still further object is to provide a high temperature pyrolysis process in which there is definite expansion ratio between the materials pyrolyzed and the products obtained.

Still another object is to provide a pyrolysis process in which there may be recirculation through the pyrolysis equipment of a chosen part of the products which have been previously formed therein. Still another object is to provide a high temperature pyrolysis process employing diluents in which an improved method of dilution is carried out. Another object is to provide a high temperature process for the production of acetylenic hydrocarbons from raw materials which may contain more or less sulphur components. A still further object is to provide a process for producing acetylenic and ethylenic hydrocarbons in equipment which may be comprised in part of eighth group metals. Other objects will appear hereinafter.

In the following matter it will be clearly brought out how the aforementioned improvements of the art of cracking to produce acetylene effect their several economies. Furthermore, there will also be set out many other new facts of much value in the production of acetylene by this principle. It will be evident also, that the advantages of operating according to my process may be applied by those skilled in the art, to raw materials and diluents considerably different from those preferred herein, and with materials of construction and design of equipment considerably different from what are disclosed in this invention, all without departing from the principle of it.

This application is in some parts related to my copending application 153,044, entitled "Manufacture of acetylene."

For a more complete understanding of my invention, reference is made to the attached drawings.

Referring to the accompanying drawings, Fig. 1 is a diagrammatic representation in the nature of a flow sheet of equipment that will serve to illustrate the process in general. Figs. 2 and 4 are side elevation views of fillers or corebusters which may be contained in my pyrolysis tube **24**. Figs. 3 and 5 are end views respectively of the aforementioned fillers or corebusters. Fig. 6 is a graph showing a relationship between the feed, composition, temperature and other factors.

A preferred raw material for my process consists of a gas containing at least a substantial proportion of a normally gaseous paraffin or olefin hydrocarbon or of any composition of normally gaseous paraffin and/or olefin hydrocarbons. What is not hydrocarbon in the raw material, is relatively indifferent gas such as hydrogen, nitrogen, carbon monoxide, and the like of fixed gases. The hydrocarbon in the raw material may contain, besides what has just been specified, also various amounts of normally liquid hydrocarbons. Suitable raw material will henceforth be called simply raw material, or stock.

Raw material may consist either of externally secured suitable raw material, or of such material secured from my own process by recirculation, or of both as in my preferred method of operation.

For the purposes of obtaining an understanding of my process in its entirety, reference is made to Fig. 1 and the following description. In Fig. 1, the primary stock to be used in making acetylene and other products, is supplied from the container **1**. Force required for putting it in flow may be available from the natural pressure of stock in the container **1**, or from superposed gaseous pressure above the liquid therein, or by any other suitable means, such as by introducing a pump into the line **2**. In the line **2** is a valve **3** for regulating the rate of flow. Following valve **3** is a flow meter **4**, followed in turn by a heater **5**. The said heater is preferably put in use if the primary stock tends to condense. The heater **5** may operate in the conventional manner by admitting at **7** a heating medium about

the tube 6. At the pipe juncture 11 the primary stock joins with diluent furnished under pressure through the pipe 12, preferably in superheated vapor form. Valve 13 serves to adjust the rate of flow of the diluent, and 14 is a flow meter in the line. The pipe 60 also makes communication with the point of juncture 11 for admitting secondary stock in a manner to be described.

Raw material and diluent become intimately mixed in the pipe 15 which carries the feed to the preheater 16. This preheater comprises a housing 38 and a heating coil 17 that receives the feed from pipe 15. The heating medium for the feed in coil 17 may be flue gas in countercurrent, coming from the cracking furnace 42 operating in conjunction. Flue gases forming in the combustion chamber 63 of the said furnace, pass into a duct 65, and may be divided into two streams by manipulation of the two dampers 31 and 40, which therefore serve as means for controlling the degree of preheat for the feed in coil 17. From the coil 17 the feed passes into the pipe 19, in which there may be a chamber as at 66. Integral therewith is a thermocouple well 67, where the degree of preheat of the feed may be determined by the thermocouple 81 indicating at the pyrometer 82. If a chamber is not desired, then the thermocouple well is integral with the pipe 19 which leads directly to the trap 20. The purpose of this trap is to catch oils and tars that form when the feed consists of heavy oils. Any accumulation in trap 20 may be drained at will through valve 21. I refer to any accumulations at this point as "heavy components."

Feed that does not condense in the trap 20, continues through pipe 22, and enters the cracking tube 24 through a fitting 23. The cracking tube 24 is heated by one or more burners as at 25, supplied with fuel and air respectively through valves 26 and 27 for regulating the degree of temperature in the said cracking tube. Preferably there are at least two such burners, disposed to give the most uniform possible heating of the said tube. Cracked mixture leaves the tube 24, passes through a fitting 29, and enters pipes 30, 74, and 75 which convey it to the quencher 43, which it enters at a point 32. The said pipes 30, 74 and 75 are preferably water-jacketed or otherwise cooled, while in fact both fittings 23 and 29 are of cooled design, for purposes to be brought out in full later. 79 indicates a point of entry for a thermocouple 78 used for testing at different levels within the tube 24, temperatures indicated on the pyrometer 77.

While I have indicated the use of temperature-measuring instruments, flow meters and the like, at various points in my apparatus, it is to be understood that my invention is not limited to such construction or use of such instruments and various other instruments may be employed or attached to my apparatus at different points.

The quencher 43 is preferably a tower fitted with liquid connections such as 34, 35, and 36, each of these having a valve as indicated for adjustment, and a spray device 64 within the tower in operating relation to the said liquid connection and valve. The cracked mixture, cooled by the pipe 30, on entering tower 43, at 32, is suddenly chilled by the water or other liquid sprays within, to a temperature at which acetylene and ethylene are stable. At the same time the diluent, if of boiling point substantially higher than that of the final gas temperature in the tower, will for the most part be condensed. Together with such diluent, will be removed from the cracked mixture, the greater part of any oil and asphalt or tar vapors, particles of solid organic matter, and particles of carbon that the said mixture contains as a result of the cracking operation in tube 24. Such material removed from the gas, for the most part is liquid, making possible its removal from the tower at will, through the trap 44.

Cooled cracked gas, after quenching, rises and makes exit from tower 43 at a point 33, containing some residual diluent, and residues also of liquid and solid by-products. Cracked gas will be so termed herein till reaching the point 47 of the tower 48, regardless of intermediate changes in its character. Cracked gas may thus pass alternately through two filters 37, where are removed most of the remaining particles of oil and asphalt fog, and particles of solid organic matter and carbon. Much of this deposit in the filters may be removed by steaming, hence, filtration is carried out in one filter while steaming the other. Steam connections are not shown, nor will alternate operation of the filters be detailed. After filtering, the cracked gas may enter an oil scrubber 86 which removes from the gas traces of the same kinds of deposits caught by the filters 37. The said scrubber is not detailed, but circulates an oil that makes intimate contact with the gas in a conventional manner and takes to itself further heavy impurities in the cracked gas.

On leaving the oil scrubber 86 the cracked gas enters the suction end of the pump 69, whose full function is to be explained later. 71 is a valve for by-passing part of the discharge of pump 69. The said valve 71 is operated by pressures in chambers 23 and 63 communicating through pipes 72 and 73, respectively. The purpose of this valve 71 is to maintain a desired ratio between the pressures in the chambers 23 and 63. From the exit end of the pump 69, the cracked gas passes through a meter 46, a gas holder 85, and then preferably through a dryer 61 for removing traces of any diluent for the most part condensed in the quencher 43.

After drying and otherwise treating as above described, the materials enter a diagrammatically indicated unit or tower 48 at a point 47 where preferably are removed from the products acetylene (and any other components which it is desired to retain) as well as ethylene or other olefines. Stripped gas then makes exit from unit 48 at a point 49, and may be conducted through 62 to the furnace for the heating thereof. The acetylene plus ethylene may leave the unit at, for example, a point 45, and through pipe 50 enters another unit or tower 51 at a point 41. Here may be separated or otherwise treated the two gases, acetylene leaving the said unit at a point 52. From the point 54 the ethylene (with or without other materials) enters pipe 53, and passes through pump 84 and meter 56. It is to be understood that the units 48 and 51 may comprise one or more towers, absorbers or the like, and that I do not wish to be restricted to the particular construction shown which is shown merely for illustrating my invention.

If unit 48, instead of removing from the cracked gas acetylene plus ethylene, removes only ethylene, it is then obvious that the gas leaving the point 49 of the tower 48 will include the acetylene produced, and will therefore be handled for utilization of the said acetylene in ways known to the art. Then ethylene alone will issue from the point 45 of the unit 48, and

it need not go through unit 51. Instead, it is allowed to go through pipe 55 so as to enter pipe 53 and be handled as though it had come from unit 51.

It should be repeated that Fig. 1 does not show each of the units of the process in its exact form, but diagrammatically. While it is preferred to employ an apparatus arrangement in accordance with Fig. 1, my process may also be carried out in other apparatus such as that shown in the various Wulff Patents 1,880,308, 1,880,309 and others. It is also desired to set forth that the speed of passage, diluents, etc., employed in my process may also be more or less in accordance with the teachings set forth in the Wulff patents.

Referring now to towers 48 and 51, it follows also, that besides ethylene, any other suitable raw materials such as methane to be found in the cracked gas may be extracted according to known art, and recycled.

After the secondary stock has passed through meter 56, it may be allowed to pass through valve 64 to be saved in a gas holder for use later as a primary stock in my process. I prefer, however, to circulate some or all of it as secondary stock, allowing it therefore to pass through valve 9 and the meter 59, so that it may enter pipe 60 which communicates with the point of juncture where is mixed the original primary stock with its diluent. In the case of such recirculation, then, necessarily the raw material to be cracked consists of primary and secondary stock, mixed in the proportion as indicated on the meters 4 and 59. It is clear that each of the said stocks at will may be analyzed so as to determine, in connection with the meter readings, the exact composition of the raw material resulting from them.

As pointed out, Figs. 2–5 show construction which may be contained in my pyrolysis tube 24. This construction serves to improve the pyrolysis process by facilitating heat transfer as well as producing a definite area ratio within the pyrolysis chamber. Construction may be of a number of types, for example, one type of corebuster may comprise a cylindrical refractory unit 101. This unit will have positioned on it at various points, lugs 102 which serve to more or less center the corebuster within the device for the reception of a pyrometer unit or other mechanism. If desired, a construction such as shown in Figs. 4 and 5 may be employed. This construction includes a refractory unit 106 having thereon the protrusions 107 which serve to position the corebuster within the pyrolysis tube. In general, this modification is more or less of a star-shaped design and as already pointed out, may contain a passageway 108 for the reception of temperature-recording instruments.

As indicated in the preceding description, one feature of my invention relates to the recirculation of certain materials. In order that the benefits of this step may be better appreciated at the onset, I set forth hereinafter certain comparisons.

In Tables I and II are shown comparative results obtained in cracking butane with and without recirculation of ethylene and methane. It is to be noted that by recirculating all of the ethylene at the proper operating temperature there is no more ethylene formed during the cracking operation. The same is true to approximately the same degree with methane. The net results of this recirculation as shown in the tables is to practically double the yield of acetylene from the butane fed.

TABLE I

Cracking butane with recirculation of ethylene and methane

	Vols./100 vols. of feed	
	Feed gas	Cracked gas
Butane	26.2	
Acetylene		27.4
Ethylene	29.5	29.5
Methane	44.3	62.0
Hydrogen		76.5
Benzene		1.0
Carbon monoxide		8.7
Carbon dioxide		1.5

Yield of C_2H_2=50.3% (calculated on basis of butane fed).

TABLE II

Cracking butane without recirculation of ethylene and methane

	Vols./100 vols of feed	
	Feed gas	Cracked gas
Butane	100	
Acetylene		55
Ethylene		56.7
Methane		86.0
Hydrogen		162.0
Benzene		1.2
Carbon monoxide		12.0
Carbon dioxide		3.0

Yield of C_2H_2=27.5% (calculated on basis of butane fed).

The operation of my process, with variations, is preferably carried out in the following manner, reference being had to the accompanying drawings, principally Fig. 1. And, hereunder, in the absence of specific statement to the contrary, operation and discussion of the process will assume substantially atmospheric pressure in the cracking tube 24. All of the valves would be closed in container 1. The various mechanism in my apparatus would be set in operation, that is, fuel and air pressure would be supplied to the burners, filter material, oil scrubbing medium and cooling medium would be supplied to the various parts. The pyrolysis tube and preheater would be heated. The various spray valves 34, 35 and 36 are open. The valve 71 would be adjusted so that the pressure exterior of pyrolysis unit 24 would be about equal to the pressure in the interior thereof (or at some other predetermined relationship) for minimizing leakage or controlling or inducing leakage in a particular direction. Steam or other diluent materials (see the Wulff patent) may be allowed to proceed from the valve 13. When the apparatus has obtained the desired temperature, material to be pyrolyzed may be fed in from container 1 through the various conduits. Heat may be applied at 6 if desired, for vaporizing the material if it is a liquid which is to be pyrolyzed. The proper proportions of materials, of course, may be obtained by regulation of the valves and notation of the flow through the respective meters. Any materials produced in the preheater may be collected in the chamber 66 and trap 28 and may be removed through valve conduit 21.

While my process forms acetylene at so high a temperature as usually to require a refractory tube in the final treatment, still much of the load

of heating can be taken off the said tube through the use of high preheat in less expensive equipment. Further than that, I find that the changes that occur in the feed as a result of the preheating, can be very beneficial if they are controlled. In other words, certain reactions possible in the feed during preheat are useful, and others are not.

The feed, thus preheated in the coil 17, and whether or not modified in chemical constitution thereby, proceeds then to the fitting 23, which is now already hot and does not condense diluent. From there it courses through the cracking tube 24 where are formed the acetylene and by-products to be recovered. If, with acetylene so forming, the temperature of the tube as indicated on the pyrometer 77 is not as desired, suitable adjustment of the valves 26 and 27 of the burners 25 will bring the said temperature to the value preferred. Unless otherwise noted, in subsequent mention of maximum cracking tube-temperature, the said temperature will be that found along the axis of the tube 24 for a given set of operating conditions, and in the manner and with the apparatus hereinbefore described, particularly in reference to Fig. 1.

Feed having been cracked in the tube 24, then becomes a mixture of cracked primary stock and diluent, including by-products of such cracking as for instance organic condensation products and carbon that may also form. Included in the said mixture are any products of reaction of diluent with the primary stock or with any of the products it forms in the tube 24. This mixture of gas as described in the present paragraph has been termed cracked mixture, and will so be called herein. And while the mixture is given this name, it is nevertheless to be understood that there may be a certain amount of physical and chemical change in the mixture between the point that it leaves the tube 24 and enters the quencher 43 which fixes its composition. Such change as may occur is due to the time required in traversing the path between the said points, which delays the complete quenching of the stream. The said path is water-jacketed or otherwise cooled (as with refrigerants) to chill the cracked mixture as rapidly as possible from the instant of exit from the tube 24. To this end even the fitting 29 may be water-jacketed. Thus I may choose to drop the temperature of the cracked mixture very rapidly to any predetermined point before letting it proceed to the quencher 43.

Normally the water-cooled piping that conveys the cracked mixture to the quencher 43 is too short to condense diluent, hence (except for any heavy oil or asphalt or carbon deposited), the cracked mixture as such enters the tower 43 for quenching. Here is condensed normally all the diluent, as well as any normally liquid or solid organic compounds to be found in the cracked mixture just before quenching. In addition, a certain amount of free carbon may be washed from the said mixture. Residual gas leaving the tower is normally moist with water and any diluent of similar boiling point that may have been present. The said gas may also have appreciable residues of oil and asphalt vapors, and at times also carbon in fine form. And though these tend to drop out in further handling of the said gas from the tower 43, it will herein be called cracked gas, from the point that it issues from tower 43 to the point at which it enters tower 48 at the point 47.

Cracked gas leaving the said tower 43 may be further cleaned of solid and liquid contaminants in the filter 37, which preferably is a bed of coke through which the gas must pass. After leaving filter 37, the cracked gas is thoroughly washed with an oil scrubber 85 in which is circulated an oil for contacting the gas, that is suitable for dissolving from the said cracked gas, further quantities of contaminant such as the filter 37 removes less efficiently. After leaving the scrubber 86, the cracked gas is picked up by pump 69, and ejected to the atmosphere through valve 80 when starting the operation. The adjustment of the stud 76 on the by-pass valve 71 is now made so as to hold preferably the same pressure within chamber 23 as within the combustion zone 63. Valve 71 of course performs this function by relieving suction on the pump 69 through the by-pass line in which it operates. Higher or lower pressure may also be produced.

When the cracking of feed has continued for a length of time sufficient to secure a satisfactory and steady analysis of cracked gas issuing from the valve 80 under the chosen conditions of operation finally set up. To this end are opened valves 83, 62, 58, 57, and 68, and the pump 84 is set in operation. Then valve 80 is manipulated to force cracked gas into the gas holder 85, and adjusted so as to hold the gas holder always partly full. Then valve 64 is opened to cause a flow of gases through the towers 48 and 51, and valve 80 is again adjusted to maintain a quantity of gas in the gas holder 85. Valve 64 is then further opened, increasing the flow of gases in the towers 48 and 51. These operations with valves 64 and 80 are repeated till at last valve 80 is closed, and valve 64 is open at a point that will still hold a quantity of gas in the gas holder 85. According to the actual manner of operation of the towers 48 and 51, these are set in action and adjusted till satisfactory results are evident from the purity of ethylene and acetylene issuing respectively from the valves 64 and 68, and from the leanness of stripped gas as to ethylene and acetylene issuing from the valve 62. At this point, I may recirculate ethylene by opening valve 9 so as to admit ethylene to the pipe juncture 11 where it will mix with diluent and primary stock from container 1 as before described. As valve 9 is then admitting ethylene to the system for recirculation, valve 64 is adjusted to relieve only what ethylene is not passed through the said valve 9, for otherwise the process of separation may be disturbed, or the purity of the ethylene may drop. And if all the ethylene produced is recirculated in this manner, then obviously valve 64 should be closed. It will also be obvious from Fig. 1 that the pump 84 of need would have a delivery pressure convenient to the niceties of control as to recirculation, and sufficient to exceed easily the pressure in the pipe juncture 11 where the mixing is to take place.

In the material immediately foregoing, the separation of acetylene from the cracked gas is described as carried out with the towers 48 and 51 together. It is to be understood that these parts described as towers may comprise one or more towers, absorber, or other type unit. And it is herewith repeated that the system of separation is only illustrative. While I have described principally the separation of ethylene for recirculation as secondary stock, the said system of separation may well include other raw material to be

found in my cracked gas as seen from Table III. Hence, in the following matter reference may be had largely to secondary stock rather than ethylene as secondary stock.

Such diluent as may have been of boiling point too low to be condensed in the quencher **43**, will pass out of the separation system still in the stripped gas leaving as at point **49**. According to the type of diluent, it may be removed from the said stripped gas in ways known to the art, either for increasing the value of the stripped gas, or for recovery of the diluent as in repeated use. If the stripped gas also contains acetylene at the said point of exit **49**, of course that too is recovered for use as may be desired. The stripped gas resulting may very well be used as fuel for firing the cracking furnace **42**, as I elect to do.

It is to be recalled here that valves **62**, **68** and **64** preferably are to be connected to forms of apparatus (not shown) respectively suitable for utilizing in any chosen way or ways, each of the gases issuing from the said valves.

When recirculating secondary stock in the operation of my process, it is evident that additional raw material is being added to assist in forming the feed to the cracking tube **24**, disturbing the steady state established without the secondary stock. Olefins in the said stock make a considerable difference in the performance of the raw material, as will herein be set forth. Accordingly, when recirculating ethylene, or olefins generally I secure a higher yield.

Figure 6 shows the volumes of cracked constituents formed at various temperatures in the cracking operation, and it is to be noted that there is a definite optimum operating point for a given composition of recycled feed. That optimum condition for the feed composition given in Table I is shown by the vertical line to be about 1255° C. and corresponds to the point where the ethylene in the cracked gas totals the same volume as the ethylene in the feed.

There is a different composition of cracked gas for each operating temperature, residence time and dilution, and hence, I may elect to operate below or above the equilibrium point. Maximum temperature registered in the corebuster during each test is recorded in degrees centigrade, as are all records of temperature herein. Butane, ethylene and steam used for dilution are all measured in standard cubic feet, and rates of flow in cubic feet per minute, for convenience abbreviated C. F. and C. F. M. So for all primary and secondary stock and any diluent herein. A standard cubic foot of gas represents the quantity of a gas in such a volume at 25° C. and one atmosphere absolute pressure, and will so be understood herein. The weight of such a volume of a given gas or gas mixture, is assumed to be equal to the molecular weight, or average molecular weight, in pounds, divided by 384. And while steam is of course non-existent in those conditions, still the hypothetical volume is herein computed by extrapolation as though it did exist, and behaved like a fixed gas such as nitrogen. In order to establish without possible doubt the meaning of one standard cubic foot of steam, it will be assumed herein that such a unit of steam weighs 18/384=0.0468 pound avoirdupois, arrived at exactly as for gases. The same formula is herein to be applied to other diluents and other normally liquid substances according to their molecular weights. The care exercised in this paragraph in establishing units and factors of conversion is due to the ease with which confusion can creep in, and to the fact that for purposes of testing variables relating to my process, it is better to speak in terms of volumes rather than weights, while for purposes of elucidating economies, the converse practice is more convenient.

Further, the item "Dil." signifies dilution or extent of dilution, expressed as the ratio of rate of flow of diluent to that of stock being cracked, each expressed in C. F. M. The item "Exp." signifies expansion or the number of cubic feet of cracked gas formed from one cubic foot of stock cracked. Gas analysis is given in percent by volume, and likewise in the claims the percents are by volume.

In order to generally illustrate the operation of some features of my process, I shall take butane as an example of raw materials for cracking. Cracking butane at a temperature of around 1300° C. will yield a cracked gas analysis about 12% acetylene, 22% ethylene and 29% methane. If the same material is cracked at a higher temperature, a somewhat higher percentage of acetylene, around 15–16% is obtainable, and the ethylene will drop to 10–11%. Although the processes under consideration are for the production of acetylene and the higher temperature produced 15–16% acetylene, I have found that the former conditions producing an apparently smaller yield of acetylene, when operated in accordance with my invention, provide improved acetylene production for a number of reasons. That is, more moderate temperatures can be used and a greater yield of acetylene obtained from the same quantity of raw materials.

According to my process, the cracked gas after being cooled is then treated by absorption or liquefaction or other ways of which there are a large number described in the prior art to obtain acetylenic and ethylenic components. In my process, cracked gas is preferably concentrated by extraction with a solvent to obtain a gas which contains about 65% acetylene, 20% ethylene and 7% methane, and the balance carbon monoxide and nitrogen. This concentrated gas mixture may be removed from the solvent by reducing the pressure.

The aforementioned gas containing about 65% acetylene and 20% ethylene may be chemically treated, reacted or otherwise processed for removing acetylene and the resultant gas containing about 65% ethylene together with some methane and the like is returned and either cracked separately or mixed with fresh butane and recracked. If the ethylene containing gases are cracked separately, this may be done by positioning another furnace of the type shown in Fig. 1 parallel with the aforementioned apparatus. Cracking the ethylene component described in this example, separately, will yield about 21% acetylene and 9% ethylene. By using my improved process of cracking to maximum acetylenic and olefinic components, rather than maximum acetylene, followed preferably by the recirculation of the olefinic components with new saturated hydrocarbon feed, I have obtained a number of advantages. For example, the cracking temperatures can be kept lower than in the case where a maximum acetylene content is required. The size of the equipment involved in my process is less. The subsequent treatment of the produced acetylene and ethylene, removes various impurities which might subsequently lead to difficulties, fouling catalysts and the like, depending upon the uses to which the acetylene might be put. The

recycling of ethylene leads to savings in raw material cost not obtainable by cracking to maximum acetylene. My recirculation process also allows a minimum raw material cost and the simplest type of conversion plant making it unnecessary to dispose of ethylene and other materials produced by converting them to various chemicals such as ethyl alcohol, acids and the like. In my process the materials including ethylene go into the production of acetylene.

As apparent from the preceding description, my assembly and cracking procedure differs considerably from what the prior art has taught as to the production of acetylene. In the prior art it is said that progressively higher temperatures with correspondingly briefer periods produce constantly greater yields. I have found, however, that I am able to secure a still higher yield than produced in the prior art without going to such extreme conditions of operation. Hence, I crack under conditions that will produce a maximum of acetylenic and olefinic hydrocarbons which may be relatively mild conditions, not only because of the limit of some of the present acetylene equipment but because I find that considerable of the ethylene will survive the operation. Then I extract or otherwise separate and recirculate the ethylene.

I find that for securing a cracked gas from butane that shows a maximum yield of acetylene plus ethylene, regardless of the dilution, that preferably there is required an expansion of from three to about 4.2. Also, I may elect to operate at a slightly higher expansion ratio than that stated, largely to the end of increasing the concentration of acetylene in the cracked gas to the extent of making more efficient the subsequent extraction of the acetylene therefrom. I may also at times choose to operate in such a way as to eliminate all content of olefines other than ethylene in the cracked gas. The utility of this particular feature lies in the value of bringing into employment the extraction of ethylene by chemical methods which are very efficient but do not function to as great advantage in the presence of higher olefines. To this end, therefore, I may at times operate at an expansion ratio of 4.2 and slightly above.

Having explained the relationship of expansion to analysis and yield, for purposes of more clearly illustrating what has been said in this respect, reference is made to the following table with butane at a dilution of 12:

TABLE III

Relation of butane expansion to yield

Expansion	C_2H_2	Yield, vols., per 100 vols.	
		C_2H_4	Total
2.68	16.1	106	122
3.15	28.0	113	141
3.49	41	105	146
3.65	49	94	143
3.92	61	79	140
4.00	64	75	139

It will be noted in the foregoing table that the yields are carried by volume rather than weight. The reason for this is that perfect conversion of ethylene would give 100 acetylene by volume but not by weight.

Thus far I have illustrated my cracking operation primarily with butane as the raw material. However, numerous other raw materials may be handled as described, with butane.

But while I have discovered that my process is economically operable at a dilution as low as 3, this dilution is so low as to give a rather rapid accumulation of tar, while in fact it provides quite an excess of fuel for the furnace. Hence, I prefer to use a higher dilution, of say about 5 to 8 for ordinary purposes and at times up to 18, when using a raw material containing only minor proportions of ethylene. For ethylene I incline to the use of lower dilutions in comparison to my other raw materials. With methane I incline in one of two directions. Either I convert in the preheater at dilutions of from 20 to 40, extensively to ethylene, after which I handle the feed as ethylene-rich, or I do not so convert in the preheater, and use dilutions of from 3 to 6, together with cracking temperatures of from 1300° C. to 1600° C. Ethylene should have an expansion of about 1.7 to 2.1 while the range of 1150° C. to 1400° C. should be suitable. Methane should have an expansion of 1.4 to 2.2, while temperatures required to crack it are considerably higher than for remaining raw materials, as just indicated.

Thus far I have illustrated the cracking operation of my process with butane as the raw material, suggesting temperature and expansion ranges within which it should be cracked. And while in the preceding paragraph I have indicated that but for methane, the remainder of my raw materials can be handled within the same temperature range, each of the said raw materials has its own particularly suited range of expansion, just as in the heating operations analyzed earlier herein. For approximately maximum yield of acetylene plus ethylene from each of these, the range of expansion should be; for propane, 2.6 to 3.6, preferably 3.0; for ethane, 2.1 to 2.9, preferably, 2.5; for methane, 1.6 to 2.2, preferably 1.9. For the olefins, expansion should be set slightly lower than the corresponding paraffins. For mixtures of any of the materials herewith listed, expansion should be computed as though each component expanded alone according to the figures above given. Thus, an arithmetic average that takes into consideration the volumetric analysis of the raw material mixture, will given the favored range of expansion.

For most raw materials I assume a temperature rise of the feed or the stream, from 95° C. to 1350° C. For this temperature it may be stated that the residence period for my 4-inch tube may lie between 0.12 and 0.002 second, though ordinarily within the limits of 0.02 to 0.004 second. In general the residence period is shorter for hydrocarbons of lower molecular weight, and for higher dilutions with any given raw material. Ethylene requires slightly more time than would be figured say for ethane, but its operating range and preferred range both are within the limits set out in this paragraph.

In respect to residence period generally including all raw materials at their most suitable dilution and suitable tube and corebuster relationships a time value is probably less than one-hundredth of a second. However, other periods of time described in the several Wulff patents aforementioned may be employed.

In order to still further improve my process the butane or other materials fed through the cracking operation are preferably free of sulphur or if sulphur-containing stock is employed, then the proportion of steam or other diluent is preferably reduced or some reduced pressure secured

by pump 69, employed. It is also possible to remove sulphur, mercaptans or other such impurities by an alkaline wash or other similar treatment well-known in the art. It is to be noted also that the diluent steam has a loosening effect on any carbon which might tend to be deposited in the apparatus. Carbon dioxide also has a similar effect and accordingly may be similarly used.

While in the construction of the preheater, it is preferred to use any of the various heat-resisting alloy steels such chromium steels, chrome-aluminum, chrome-molybdenum, chrome-tungsten steel, all of which are described in the prior art, I also may employ various heat-resisting chromium nickel alloys such as chromium-nickel steels. When operating my process in this respect, either with preheater tubes containing substantial nickel or feed containing sulphur, I employ less steam as a diluent or substitute therefor a more nearly inert diluent, if not a certain measure of reduced pressure and temperature. I may also elect to use a combination, of tubes with a moderate amount of nickel together with less steam or inert diluent or a measure of reduced pressure. I may also prove operation under the aforementioned conditions by introducing at least a part of the steam diluent immediately after the preheater rather than as above described.

In heating my pyrolysis tubes it is most advantageous to use a fuel of high hydrogen content because, for example, hydrogen has a very high speed of combustion, thus localizing the heat. I find that in my process described herein, the gas from which ethylene and acetylene have been removed contains a large quantity of hydrogen. For example, the gas removed through valve 62 in my process may contain more than 50% hydrogen and this may be conducted as fuel to burner 28.

In the particular apparatus which I have shown in Fig. 1, I am also able to obtain an improved heating not only by virtue of the use of the fuel just described, but also, by means of the units shown in Figs. 2–5, inclusive, I am able to obtain an area ratio within my pyrolysis apparatus of any value between about 12–600. This area ratio is expressed in square feet per cubic foot. For instance, if the tube is 1.75 inches internal diameter without a corebuster, the ratio might be

$$\frac{48}{1.75}=27.4$$

However, if a corebuster is present the sum of the internal areas expressed is divided by the net volume bounded by said areas.

Also produced in my process may be varying amounts of benzol, naphthalene and the like which are separated in the filters and oil scrubbers already described in detail herein.

From the preceding it is apparent that I have devised a novel method for producing acetylene. By my process I am able to obtain considerably more acetylene from a unit of raw material than has heretofore been produced. In addition, my process is considerably more economic because of various savings incurred. That is, I am able to employ lower temperatures which involves savings in heating and extends the life of my apparatus.

From the preceding it is apparent that my invention is susceptible of modification, hence, I do not wish to be restricted excepting insofar as necessitated by the prior art and the spirit of the appended claims.

What I claim and desire to secure by Letters Patent of the United States is:

1. A process for the manufacture of acetylene, which comprises subjecting a saturated hydrocarbon capable of conversion to acetylene and ethylene, to a pyrolysis treatment, conducting the pyrolysis treatment at a temperature between about 800° C. and 1450° C. for a residence period of less than $\frac{1}{10}$th of a second to obtain a gaseous mixture containing more than 5% acetylene together with an ethylene content at least 50% greater than the acetylene content, subjecting the mixture to treatment for separating an ethylene component and returning at least a major part of the ethylene component together with further saturated hydrocarbon to the aforementioned pyrolysis treatment.

2. A process for the manufacture of acetylene, which comprises mixing a paraffinic hydrocarbon having from 2–7 carbon atoms with steam in a dilution ratio between about 3–18, preheating the mixture, separating heavy components present in the materials conducted from the preheating, further heating the mixture to a temperature higher than the preheating, said heating and preheating being within the temperature range of 700° C.–1600° C. and for a period of less than a second, for obtaining a gas mixture containing greater than 6% acetylene together with an olefine content at least 50% greater than the acetylene content, treating the mixture to separate an olefine and conducting at least the major part of the separated olefine together with further paraffinic hydrocarbon to the aforementioned pyrolysis treatment.

3. A process for the production of acetylene from saturated hydrocarbons, which comprises diluting the hydrocarbon with steam and ethylene, heating the mixture at temperatures between 700° C. and 1600° C. for less than a few seconds in heating zones having area ratios between about 30 and 400, to form a gas mixture containing at least 6% acetylene together with a larger amount of ethylene, spray cooling, recovering and separating acetylene and ethylene, and subjecting at least a part of the ethylene together with saturated hydrocarbons to further pyrolysis under the aforesaid heating conditions.

4. A method for starting and operating a process for the manufacture of acetylene in a pyrolysis unit, which comprises supplying heat to the unit, passing a diluent therethrough, supplying the unit with an organic compound capable of forming acetylene and olefines, pyrolyzing the organic compound under conditions which cause substantial aggregate yields of acetylene and olefines in which the content of each is greater than 10% by volume, separating and recovering acetylene and olefines, thereby leaving a gas rich in hydrogen and after the process has been in operation for a fraction of an hour, recycling to the pyrolysis step at least the major part of the olefines produced, and burning hydrogen for heating the unit.

5. A process for the manufacture of acetylene, which comprises mixing material essentially comprised of non-acetylenic hydrocarbons suitable for decomposition to acetylene and ethylene, with a diluent, subjecting the mixture to a rapid pyrolysis treatment of less than a few seconds duration, at temperatures substantially greater than 700° C., but less than 1600° C., for producing a gaseous mixture containing at least 10% by

volume each of acetylene and ethylene, the ethylene content being greater than the acetylene content, cooling and purifying the gaseous mixture, treating the mixture to recover and separate acetylene and ethylene components and recycling, in the presence of further non-acetylenic hydrocarbons as aforedescribed, the ethylene components so separated, to further rapid pyrolysis between 700° C.–1600° C. for the manufacture of a gaseous mixture containing acetylene in the presence of a larger volume of ethylene.

6. In a process for the manufacture of acetylene by pyrolysis of hydrocarbons at high temperatures where heretofore a mixture of olefines and acetylene had been obtained in which the acetylene content has been larger than the olefine content, the improvement steps which comprise subjecting a paraffinic hydrocarbon having more than 2 carbon atoms to a pyrolysis treatment for a fraction of a second at a temperature between about 800° C. and 1600° C., said paraffinic hydrocarbon also having present therewith a content of olefines of a magnitude of approximately from one-half to twice the amount of olefines which would be produced from the paraffinic hydrocarbons by the pyrolysis treatment if no olefines had been present therein, and by said improvements obtaining a gas mixture containing at least 10% each by volume of acetylene and olefines, the olefine content being larger than the acetylene content, separating and returning sufficient of these olefines to said pyrolysis to give said content of olefine mixed with said paraffinic hydrocarbon.

7. A process for the production of acetylene from non-acetylenic hydrocarbon materials decomposable into acetylene and ethylene, and largely comprised of saturated hydrocarbons, which comprises diluting the hydrocarbons with water vapor and ethylene, pyrolyzing the resultant mixture at a temperature in excess of 700° C. but less than 1600° C. and for a heating period of less than one second to obtain a gaseous mixture containing more than 4% by volume of acetylene together with an ethylene content larger than said acetylene content present therewith, separating the acetylene and ethylene content and subjecting at least a major part of said ethylene content to a further pyrolysis treatment in the presence of other non-acetylenic hydrocarbons as aforementioned, for the production of acetylene under said temperatures and for said heating period.

8. A method for starting and operating a process for the manufacture of acetylene in a pyrolysis unit, which comprises supplying heat to the unit, passing a diluent therethrough, substantially continuously supplying the unit with a feed largely comprised of saturated hydrocarbons capable of forming acetylene and olefines, pyrolyzing said feed under conditions including heating at temperatures between 800° C.–1600° C. for less than one second, which causes the production of a substantial aggregate yield of acetylene and olefines in which the content of each is greater than 10% by volume, separating and recovering acetylene and olefines and thereafter recycling to the pyrolysis step substantially all of the olefines separated.

9. A process for the manufacture of acetylene from a hydrocarbon feed-mixture which is comprised of more than 50% of saturated hydrocarbons, the remainder of the mixture including at least 10% of olefines, which comprises cracking said mixture for less than one second at temperatures within the range of 800°–1600° C. to obtain a cracked gas in which there is more than 10% by volume of each of the components acetylene and olefine, separating at least the bulk of the olefine component and returning it to the process for forming said hydrocarbon mixture.

10. A process for the production of acetylene from non-acetylenic hydrocarbons suitable for decomposition to acetylene and ethylene, which comprises diluting the hydrocarbon with steam and ethylene, heating the mixture at temperatures between 700° C. and 1600° C. for less than a few seconds in heating zones having area ratios between about 30 and 400, to form a gas mixture containing at least 6% acetylene together with a larger amount of ethylene, rapidly cooling this gas mixture, recovering and separating acetylene and ethylene, and subjecting at least a part of the ethylene together with said non-acetylenic hydrocarbon to pyrolysis under the aforesaid heating conditions.

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