

1

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PYROLYSIS OF HYDROCARBONS

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This application is a continuation-in-part application of application Serial No. 73,435, filed December 2, 1960, entitled "Selective Pyrolysis of Methane to Acetylene and Hydrogen", now issued as U.S. Patent No. 3,156,733.

This invention relates generally to the pyrolysis of hydrocarbons preferably diluted or admixed with hydrogen to give relatively uncontaminated mixtures of acetylene and hydrogen as the sole gaseous products. More particularly, the present invention relates to an improved pyrolytic method of obtaining acetylene and hydrogen as essentially the only products of pyrolysis of non-aromatic hydrocarbons having from two to ten carbon atoms by employing a combination of carefully controlled and critical operating conditions.

The pyrolysis of the higher hydrocarbons to acetylene, hydrogen and other products by other methods is well known to the art. Heretofore, however, the isolation of acetylene and/or hydrogen in a relatively pure state from gaseous products prepared by pyrolytic procedures, has required elaborate separation and product recovery techniques. Thus, previously known straight pyrolytic procedures such as the Wulff and Ruhrchemie processes have yielded from these hydrocarbons, in addition to acetylene and hydrogen, the full range of products theoretically obtainable by the pyrolytic decomposition of the hydrocarbon. The extraneous products are produced in amounts sufficient to require laborious isolation and recovery procedures in order to make the process commercially practical. Thus, for example, the pyrolysis of propane yields substantial amounts of propylene and ethylene in addition to methane, hydrogen, acetylene and the higher acetylenes.

Modified processes, such as the partial combustion of the hydrocarbons yield, in addition to the aforementioned organic by-products such as olefins, methane and higher molecular weight hydrocarbons of a saturated, olefinic or acetylenic nature, substantial amounts of the undesirable, carbon monoxide, water and carbon dioxide.

A process employing electrical energy has been in commercial operation at the acetylene plant of Chemische Werke Huls in Germany. This process employs an electric arc for heating the gaseous hydrocarbon feed. In this reactor, it is not precisely known at what temperature the acetylene actually forms from the hydrocarbon; however, it is known that the core of the arc burns at about 3000° C. while at the end of the reactor tube the temperature is between 1600 and 2000° C. It is readily apparent that while a portion of the reacting feed gases is subjected to arc temperature, i.e., around 3000° C., a substantial portion bypasses this hottest part of the arc and is pyrolyzed at substantially lower temperatures. Consequently, the over-all process involves an essentially uncontrolled time-temperature pyrolysis. On the one hand the high temperatures leads to the production of higher acetylenic hydrocarbons such as diacetylene and other alkynes in substantial amounts, and at the same time, the lower temperatures leave a considerable portion of incompletely pyrolyzed hydrocarbon feed in the effluent gases.

The presence of these contaminates and the elaborate procedures required for their effective separation from the acetylene and hydrogen products, makes isolation and re-

2

covery the most expensive phases of the presently known pyrolytic processes.

Although it has been reported that at temperatures above 1500° C., pressures well below 100 mm. Hg. abs. are necessary for satisfactory operation with methane, it has been found that pyrolysis processes performed at partial pressures of methane of 100 mm. Hg abs. and higher were operable and useful up to and exceeding 1900° C.; also if practiced according to certain critical and controlled conditions, there results substantial improvements in both selectivity and yield of acetylene. As an improvement, it has also been found that mixtures of methane and hydrogen also give high yields of acetylene.

However, a gas containing substantially pure methane is sometimes not available as a feed stock. In addition, it may be desired to crack non-aromatic hydrocarbons other than those consisting mostly of methane either as pure feed or in admixture with each other and/or with methane. It was therefore believed desirable to study the reaction of higher hydrocarbon pyrolysis in an effort to achieve advantageous yields and conversion, and at the same time to extend the process to the pyrolysis of saturated hydrocarbons other than methane.

For example, such non-aromatic hydrocarbons as ethane, propane, the butanes, the heptanes, and the like, ethylene, propylene, butenes, and higher olefins and cyclohexane, and mixtures thereof can be advantageously used in this newly discovered process.

In the past it was found difficult to operate a reactor for the cracking of hydrocarbons of molecular weights greater than methane to give acetylene. Further, under conditions whereby such reactions were operable, large amounts of methane and hydrocarbons both saturated and unsaturated other than acetylene, were obtained.

In order to make the reaction easier to operate, it was decided to try the addition of hydrogen to feed in order to suppress coke formation. Unexpectedly, the cracking process became operable over a much wider range of operating conditions, and also, very unexpectedly, the yield of by-product hydrocarbons such as methane, olefins and the like decreased to the point of disappearance.

Thus, it has now been discovered that, under the controlled conditions of the pyrolysis of methane or methane-hydrogen mixtures the use of hydrogen as a diluent can be extended to the pyrolysis of heavier hydrocarbons using controlled time-temperature relations. The heavier hydrocarbons used must be volatile or capable of being volatilized. It has further been found that in addition to the required critical reactor zone hold up time and temperature limits, the overall hydrogen to carbon ratio of the feed hydrocarbons is critical and must be closely controlled to achieve the desired results.

While it is not intended in any way to limit the advantages of the invention to a theory, one explanation of the effectiveness of hydrogen, may be that, during the initial stage of hydrocarbon pyrolysis, the formation of coke is suppressed by the presence of hydrogen, which is of course not present at the start of the reaction when pure hydrocarbons are used as feed. However, there may be other better explanations such as increased heat transfer rates or other changes in the physical nature of the system. Also, the effect of hydrogen on free radical reactions yielding coke may be the reason for the surprising improvements observed when hydrogen rather than other inert diluents is used. At present there is no theory to account for the disappearance of the by-products by use of hydrogen dilution.

When used in the selective, high temperature process, the control of the hydrogen to carbon ratio has another unique advantage; i.e., the process itself produces acetylene and essentially pure hydrogen containing small

amounts of methane; methane is also hydrogen rich relative to other hydrocarbons. Thus, after the removal of acetylene from the process effluent gas, no elaborate separation procedure is necessary for the removal of acetylene from the process effluent gas, no elaborate separation procedure is necessary for the removal or recovery of any other hydrocarbons from this gas. That is, can be recycled directly to dilute the hydrocarbon feed in an amount necessary to give a hydrogen to carbon ratio which is within the limits required to yield the outstanding results of this invention.

It is considered that the process of the invention can be operated under conditions in which the limits of the effective ratio of hydrogen to carbon are from 6 to 30. This critical ratio is defined in greater detail hereinafter.

The process of the invention can also be operated so that the effluent gases from the reactor, after removal of acetylenes, will consist of essentially pure hydrogen. For example, if the hydrogen to carbon ratio is chosen in the upper ranges of the limits, that is from 15 to 30, then the effluent gas, after removal of acetylenes consists of up to 98% hydrogen with methane as the only principal contaminant. Another alternate method is to first pyrolyze a stream wherein the hydrogen to carbon ratio is in the lower ranges of the limit, that is, from 6 to 20. This will yield an effluent which, after the removal of acetylene hydrocarbons has a hydrogen to carbon ratio in the upper ranges of the limits. This product stream, after acetylene removal, can if desired, be further processed in a second reactor to yield a second effluent stream consisting of essentially pure hydrogen and acetylene.

However, it is not necessary to restrict the operation of the process to use of pure hydrogen as a diluent. For example, if it is desired to use the hydrogen produced by this process in the manufacture of ammonia, a mixture containing up to one part nitrogen, either free or combined, for every three parts of hydrogen (the total hydrogen in the feed plus that expected from pyrolysis) can be employed. Such a mixture has obvious advantages, if the feed to the ammonia process is purified from trace impurities by means of a liquid nitrogen wash, since effluent hydrogen from such a wash step would naturally contain some nitrogen. In a similar fashion, if the hydrogen were to be used for methanol manufacture, carbon monoxide, carbon dioxide, or other gases containing oxygen or their mixtures or compounds with each other would be operable. If pure hydrogen is not a desired by-product of the pyrolysis process, relatively large amounts of diluents, up to about 35% can be tolerated. These diluents could be nitrogen, carbon monoxide, carbon dioxide, water and the like. In one mode of operation a hydrocarbon-hydrogen mixture can be partially burned to bring the gas up to required temperature and then the mixture further heated so that the pyrolysis process is essentially isothermal rather than adiabatic. Since a large proportion of the heat requirement is consumed by the pyrolysis reactions, if additional heat is not added after pyrolysis begins, the temperature of the reaction zone will fall rapidly as, for example, is the case in the Sachsse process.

The process of this invention comprises introducing a mixture of at least one non-aromatic hydrocarbon and hydrogen preferably continuously into a reaction zone wherein the maximum temperature within the effective reaction zone is above 1400° C.; withdrawing the effluent from said reaction zone and, at the point of withdrawal, quenching the effluent to a temperature of 600° C. or less; lower quench temperatures are operable, e.g., 350° C. or less. The hydrocarbon used may have two to ten carbon atoms. Since the gas is primarily being heated during its passage through the reactor, and is being heated and cracked during its passage through the effective reaction zone, the temperature of the gas reaches a maximum temperature during its passage through the reaction zone at a point prior to the quench. It is this maximum

temperature which is said to characterize the reaction and which is referred to as the maximum reaction zone temperature. Maximum temperatures within the reaction zone of 1450° C. to 2000° C. are generally preferred while a carefully controlled maximum temperature within the range of about 1500° C. to 1800° C. affords optimum yields of desired products in addition to relative freedom from contaminants.

The space velocity, Sv, is stated as:

$$Sv = V_f / V_r$$

where,

V_f = flow rate of feed gases, ft.³/sec. measured at 0° C. and 760 mm. Hg abs. and

V_r = reaction zone volume, ft.³

However, in this improved process since the feed gas is not a pure hydrocarbon or mixture of hydrocarbons, but a mixture of hydrocarbons with hydrogen, a new term hereafter referred to as effective space velocity has been defined as follows:

Effective space velocity

$$Se = S_v = \text{sec.}^{-1} \text{ atm.}^{-1} \frac{P}{P}$$

wherein P is the total reactor pressure in atmosphere absolute. For purposes of this application, including the claims, the foregoing formula for effective space velocity is the definition of the effective space velocity for the reaction zone.

The range of effective space velocity which can be employed over the temperature and hydrogen to carbon ratio, as defined above is 1.0 to 400 sec.⁻¹ atm.⁻¹, and is preferably in the range 2.5 to 300 sec.⁻¹ atm.⁻¹.

It is especially necessary in this selective pyrolysis to define carefully the reaction zone in which the principal part of the pyrolysis reaction occurs, and to which defined zone it is in fact desired to confine the pyrolysis reaction. The beginning of the reaction zone is taken to be that point at which the temperature of the reacting gases first reaches a level of about 250° C. below the maximum temperature in the reactor; the end of the reaction zone is considered to be the point of quenching or start of quenching. In the reaction zone as so defined, the gas temperature is estimated to be within 100° C. of the wall temperature. Thus a substantially isothermal pyrolysis reaction zone is obtained considering the relatively high temperature level of the zone.

This "isothermal reaction zone" is very important. If substantial amounts of decomposition of the feed occur prior to this reaction zone, a tenacious carbon deposit forms in this part of the reactor causing increased pressure drop and decreased acetylene yields. In fact, operation may be stopped entirely because of blockage. On the other hand, if substantial reaction occurs within the quench zone, soot will form due to acetylene degradation. This carbon, which is soft, represents a loss in yield. It does not necessarily produce blockage of the reactor and is usually carried out of the reactor zone with the gas as soot.

It will be evident from the relatively short time afforded the reacting gas within the reaction zone that the aforesaid maximum temperatures must be attained in a very abbreviated and critical time period. It will also be apparent that descent of the gas to temperatures substantially below the maximum involves rapid quenching in time periods commensurate with the abbreviated time in the reaction zone. Such quenching or cooling should be effected instantaneously and preferably to a temperature of 300° C. or less. Normally, however, rapid cooling to a temperature of at least 600° C. or less is desirable. By virtue of such cooling, undesirable reactions such as decomposition, hydrogenation or polymerization of the product acetylene is avoided. Cooling of the products to ambient temperatures may then, if desired, proceed at a somewhat slower and more conventional rate. To

achieve the high rate of initial cooling, injection of cold gas or liquid into the product gas is normally employed. It is, of course, preferred that the gas or liquid entrained or admixed with the hot product gases for cooling be of such a nature that it does not contaminate the product stream with gases which are difficult to remove, which difficulty would thus negate certain advantages of the invention. This is especially true in cases where pure hydrogen is a desired by-product. The effluent can be quenched for instance through a De Laval nozzle so as to secure a rapid drop in temperature. The high velocity effluent gases thus attained can then be mixed with water or another quenching medium, or, they can be passed through a turbine to extract a portion of their energy.

The pressure employed within the reaction zone is essentially atmospheric, but pressures from 130 mm. Hg. abs. up to five atmospheres abs. can be employed, five atmospheres being a convenient pressure level in commercial recovery operations. Yields will vary with hydrogen dilution. Where reaction zone pressures, other than atmospheric are employed, an effective hydrogen to carbon ratio as previously described, can be used to define the effect of pressures on the extent of hydrogen dilution desired.

The feed material to the reactor for the production of acetylene need not be any one pure hydrocarbon, i.e., prior to hydrogen dilution. Commercial sources of hydrocarbons of 2 to 10 carbon atoms and containing mixtures of paraffinic, alicyclic, olefinic and other types of non-aromatic hydrocarbons are suitable as feedstocks as long as they can be volatilized into a hydrogen stream under the conditions of the process. If pure hydrocarbons of this type are available these would also be suitable feedstocks. Varying amounts of gases such as nitrogen can also be present in the feed stream and/or in the hydrogen dilution stream. Small amounts of gases such as for example, oxygen, carbon monoxide and carbon dioxide may also be present. The aforementioned contaminants will show up in the product stream as nitrogen and/or carbon monoxide and water. Although these cannot be used to advantage in subsequent reactions with hydrogen, they have little or no effect on the yields of acetylene and affect only the purity of the hydrogen obtained.

When hydrocarbons of higher molecular weight than methane, i.e., of 2 to 10 carbon atoms content, are subjected to temperatures within the range of the process of this invention, the products of such pyrolysis normally include methane as is well known. In the process of this cracking of methane itself, and the decomposition of methane so formed proceeds to the formation of acetylene and hydrogen when carried out under the herein described conditions. The decomposition of hydrocarbons heavier than methane proceeds more rapidly than the cracking of methane itself, and the decomposition of methane is in fact the rate controlling step in the overall decomposition of the heavier hydrocarbons to acetylene and hydrogen. Thus, at effective space velocities, Se , nearer the lower end of the operable range, i.e., near $0.5 \text{ atm.}^{-1} \text{ sec.}^{-1}$, complete decomposition of the feed hydrocarbon to hydrogen and acetylene is approached. However, it has been found that if conditions are such that there is complete decomposition to acetylene of the methane produced the process is accompanied by the simultaneous decomposition of acetylene already produced with resultant more or less sacrifice in the overall yields of acetylene. Thus it has been found necessary to operate in the upper levels of the temperature range and nearer the upper levels of the effective space velocity range to achieve high acetylene yields while simultaneously limiting methane production to relatively small amounts. This is the preferred method of operation for the process using the higher hydrocarbons as feed.

Further, in the past, it has been found that at desirable levels of reactor pressure, it is very difficult to operate

with hydrocarbon feeds of higher molecular weight than methane, because the rate of coke and tar formation is relatively very high with these feeds. This has not been found to be the case in this process. Even hydrocarbons which are normally liquid can be successfully employed without undue formations of tar.

One embodiment of the invention is described herein below.

In carrying out the process a carefully metered hydrocarbon feed, suitably diluted with hydrogen, is caused to pass through an electrically heated reaction chamber and is rapidly quenched. Thus, for example, the maximum temperature within the reaction zone will be for example, about 1750°C . The hydrocarbon feed and the hydrogen diluent are withdrawn from storage, metered, and passed through suitable control valves. At this point, the desired concentration of the hydrogen diluent is provided by a metered amount of hydrogen being incorporated into the feed stream of hydrocarbon. The pressure of the feed material is measured and the feed stream proceeds to the electrically heated reactor. Alternately, the hydrocarbon stream and hydrogen diluent would be metered separately and passed as separate streams into the reactor, i.e., the gas feed entering the furnace can be a pre-mixed stream of hydrogen and hydrocarbon or the components can be fed separately. The latter is more desirable where the hydrocarbon is of high molecular weight so that it must be vaporized by the addition of heat to bring it to the gaseous state at the temperature and pressure conditions at the reactor inlet.

The hydrocarbon containing feed passes through the length of the reactor zone and thereby into contact with the thermocouple which measures temperatures within the reactor. The thermocouple arrangement is for example composed of an alumina thermocouple protection tube and a platinum-platinum-10% rhodium thermocouple protection tube. This thermocouple protection tube is disposed within and along the length of the larger reactor tube. The thermocouple is employed to measure a longitudinal temperature profile. This profile can be measured in two ways i.e., with the thermocouple and/or with the pyrometer. However, above 1650°C ., only the pyrometer is used. The profiles, so obtained establish the extent of the reaction zone. The thermocouple protection tube is maintained within the reactor tube is made of alumina and positioned within the graphite resistance element designed to use a low voltage electrical current up to 3 k.v.a., thus providing sufficient heat to effect the maximum temperature within the reactor tube. The anulus positioned between the large diameter reactor tube and the smaller diameter thermocouple protection tube thus constitutes the reactor cross section.

Successive cylindrical walls of insulation material are positioned about the graphite heating element. Thus, for example refractory walls of zirconia and aluminum silicate, together with an intermediate radiation shield of stainless steel and a furnace wall of copper, are desirably employed. The outer wall of the reactor is desirably water cooled. A window is preferably positioned in the outer wall of the reactor to permit, if desired, observation by an optical pyrometer sighting on the reactor tube (through a slit in the graphite resistance element), thus providing means for determining the temperature thereof.

Upon leaving the reaction zone, the gaseous effluent stream enters the quenching chamber where rapid cooling of the hot product gas to a temperature in the range of at least 600°C . down to 300°C . or less is caused to occur as described above. As noted earlier, quenching is effected most desirably at this point by cold fluid injection, either gaseous or liquid. In this particular system, using hydrocarbon and hydrogen as a feed mixture the hot effluent product gases are quenched with a portion of the effluent which has been withdrawn, cooled and recycled by the recycle pumps to the quench chamber. This is one preferred method for cooling. Additional

cooling may be achieved by water cooling of the outer metallic surface of the quenching chamber. Analysis of the gaseous components in the product effluent is accomplished by gas chromatograph and/or mass spectroscopy.

It will be evident, that any suitable systems and reactors may be employed for the practice of this invention so long as they provide for adequate heat transfer rates into the gaseous feed phase for controlling the temperatures in the reaction zone, and adequate and immediate quenching of the reaction following the reaction zone of the reactor.

Suitable devices may include among others those containing a reactor formed of: a space between narrow, heated channels of high temperature refractories; a space between regularly disposed heated rods of carbon or high temperature refractory; or a space between previously heated small particles in a moving stream, as well as the type of annulus reactor employed in the present description of the invention.

The decomposition of hydrocarbons higher than methane within the temperature range specified occurs very fast relative to the rate of decomposition of methane. This is true whether it results from the decomposition of the higher hydrocarbons or their subsequent decomposition products or whether it is the initial feed. Therefore, higher hydrocarbons can be cracked to a product gas which consists substantially of methane, acetylene and hydrogen. However, within the range of hydrogen to carbon ratios useful in this process, it is only at the low end of the temperature range and/or as the higher values of the effective space velocity, Se , are approached that substantial amounts of methane are obtained. Even under these conditions, by-products other than methane are minimal.

By operating within the appropriate hydrogen to carbon ratio and toward the lower end of the range specified for Se , or toward the upper range specified for the temperatures, it is possible to crack the methane in the feed or that formed as a decomposition product of the heavier hydrocarbons. Thus, a product gas can be obtained consisting substantially of acetylene and hydrogen, with the total of all other hydrocarbons, including methane generally less than 5% to 7% (volume).

It has been found that, for instance, at 1650°, the conversion of methane to acetylene per pass reaches a maximum at about 90% methane conversion. Also, it was shown that this maximum occurred at lower methane conversion as the temperature decreased below 1650° C. and at higher methane conversions as the temperature increased above 1650° C.

Under the conditions of hydrogen to carbon ratio, Se and temperature as disclosed, feed disappearance, inclusive of any methane present in the feed, is in a range of 95 to 100%. In fact, with practically all feed mixtures within the range of hydrogen to carbon ratios, the maximum in feed conversion to acetylene occurs as Se substantially lower than that required to give 100% feed disappearance. To achieve the maximum conversion of feed hydrocarbon to acetylene per pass, it is necessary to pyrolyze a substantial portion of the methane present whether this methane is present in the feed or from the pyrolysis of heavier hydrocarbons. Thus the maximum conversion of hydrocarbon to acetylene per pass will occur at values of Se substantially lower than those required to give complete hydrocarbon feed disappearance, exclusive of methane in the feed. An example illustrative of, but not intended to be limitative thereof of the concentrations of methane attainable is at a hydrogen to carbon ratio of 8.21 at 1750° C., this maximum will occur when the methane concentration is in the range of 0.2 to 2.5 volume percent. In general, increasing the maximum reaction temperature will move this maximum to even lower ranges of methane concentration, and conversely,

decreasing the temperature below 1750° C. will move this maximum into a higher methane concentration range. Also, increasing the hydrogen to carbon ratio will, at a given temperature, decrease the methane concentration at which this peak occurs.

The most common solid substance to be removed from the product effluent by a solids trap, is carbon in the form of small flakes formed in the reactor as a product of the pyrolysis. Soot in the effluent gas is trapped in the oil system of the compressors. Only minute amounts of condensible liquid product have been found and therefore no provision for handling such product has been considered necessary.

Any suitable pumping system may be employed. Thus, a main pump may be employed to draw the feed and hydrogen diluent and product gases through the reactor and the quenching chamber. A recycle pump may be employed to recycle a part of the product through a cooler and back to the quenching chamber for the rapid and immediate cooling of the newly produced effluent product leaving the reactor. In addition, if desired, a gas sampling system may be provided downstream of the main pump and will include a volumetric gas meter and gas sample valve.

Considerable data was obtained in the many experimental runs carried out to study the operating conditions using hydrogen as a diluent for the heavier hydrocarbon feeds. In these runs, it is to be noted that the hydrocarbon disappearance is affected by the "effective space velocity," Se , for a given temperature. The conversion to acetylene will vary somewhat depending upon the rate of temperature increase prior to the maximum temperature and the rate of temperature decrease in the quenching zone. In every instance, the examples represent conditions easily attainable by conventional techniques of operating within the conditions of the process.

The following examples taken from the large number of aforementioned runs are intended only to be illustrative of the invention but not in any way limitative thereof. In each example, the term C_O , C_A , C_E , C_M and Y_A which appear are defined as follows:

Equivalent hydrocarbon is that single hydrocarbon which at the same mole percent in the feed as the summation of all percentages of hydrocarbons present in the feed would yield, per 100 mols of feed, the same number of atoms of hydrogen and of carbon as are present in the feed (exclusive of hydrogen molecules present in the gas). For complicated mixtures of hydrocarbons such as the commercial naphthas, it is only necessary to know the empirical formula and the average molecular weight of the mixture. Then for pure hydrocarbon diluted with hydrogen:

C_O =moles of hydrocarbon disappearing per 100 moles of hydrocarbon fed per pass, called "Disappearance."

If more than one hydrocarbon is present in the feed, then

C_O =disappearance of lowest molecular weight hydrocarbon, C_O^1 is for next highest molecular weight, C_O^2 is for the next highest, etc.

C_A =moles of equivalent hydrocarbon converted to acetylene, per 100 moles of equivalent hydrocarbon fed, per pass, called "Once Thru Acetylene Yield"

C_E =moles equivalent hydrocarbon converted to ethylene per 100 moles of equivalent hydrocarbon fed, per pass, called "Once Thru Ethylene Yield"

C_M =moles of equivalent hydrocarbon converted to methane per 100 moles equivalent hydrocarbon fed, per pass, called "Once Thru Methane Yield"

Y_A =
$$\frac{\text{moles of equivalent hydrocarbon converted to acetylene, per pass}}{100 \text{ moles of equivalent hydrocarbon converted, per pass, called "Acetylene Selectivity"}}$$

When pure hydrocarbons are fed, the word, "hydrocarbon" should be substituted for the words, "equivalent hydrocarbon."

Further, the product analyses do not include other hydrocarbons some of which appeared in all runs, but to the extent generally of less than 0.5% (mole) each, and which, in total, are generally about 1% (mole) or less. Diluents, other than hydrogen, and solid carbon are also not shown.

It should be noted that as long as some hydrogen is used to dilute the feed, pressure reduction is feasible along with hydrogen dilution, but only to the extent of the about 77% of the total hydrogen dilution. Further, the vacuum is not as effective as hydrogen dilution. For purposes of calculating an effective H/C ratio only, generally, 2 mm. Hg of vacuum are taken as being equivalent to 1 mm. Hg hydrogen dilution. Thus, at pressures other than atmospheric, an effective hydrogen to carbon ratio $(H/C)_{\text{eff.}}$ is employed when the vacuum dilution of the hydrocarbon is used with hydrogen dilution. For, example, for mixtures of paraffinic hydrocarbons

$$(H/C)_{\text{eff.}} = \frac{(1-P) + P[\Sigma X(2n+2) + (1-\Sigma X)2]}{P[\Sigma X(n)]}$$

where X = mole fraction of a particular hydrocarbon species in the feed

n = carbon atoms per molecule for that species

P = reactor pressure in atmospheres (abs.)

At 1.0 atm. abs. pressure, the actual and effective hydrogen to carbon ratios are identical since $(1-P)=0$. For hydrocarbons other than paraffins, the ratio of hydrogen to carbon in the particular hydrocarbon is substituted for the term $(2n+2)$, in the equation. For example, for olefins, $C=n$, $H=2n$; therefore, in the summation, use $[X(2n)]$ for olefin terms.

For complicated mixtures of hydrocarbons, the average molecule weight and hydrogen to carbon ratio of an equivalent hydrocarbon, as previously defined, are used; thus,

$$(H/C)_{\text{eff.}} = \frac{(1-P) + P[(X_{\text{eq.}})(H \text{ atoms/mole equiv. HC}) + (1-X)2]}{P[X(C \text{ atoms/mole equiv. HC})]}$$

The range of $(H/C)_{\text{eff.}}$ for the conditions of temperature, pressure and Se of the process, is from 6 to 30; and preferably, from 7 to 25.

The temperature stated in each of the following examples is the maximum temperature observed in the reaction zone, in each case, and all analyses presented are given in mole percents.

Example 1

A gas mixture wherein the H/C is 7.3/1 consisting of 81.2% hydrogen, 18.6% ethane and about 0.2% methane was passed continuously through a pyrolysis reactor of the type described hereinabove. The reaction zone is taken as that zone which starts at a temperature about 250° C. below the maximum temperature observed in the reaction zone, and ends at the point of quench. The volume of the reaction zone is V_r ; the space velocity, S_p , is taken as the total flow of gas measured at 0° C., 760 mm. Hg abs. pressure in cubic feet/sec., fed to this defined reaction zone, divided by the reaction zone volume in cubic feet. "Effective space velocity," S_e is taken as:

$$S_e = \frac{S_p}{P} = \text{sec.}^{-1} \text{ atm.}^{-1}$$

where P is the total reactor pressure in atmospheres. In this example, $P=1$ atm. abs.

The maximum temperature observed in the reactor is

1766° C. $Se=10.6 \text{ sec.}^{-1} \text{ atm.}^{-1}$. Under these operating conditions, the effluent gas had the following analysis:

Component:	Percent
Hydrogen -----	86.17
Methane -----	0.81
Ethylene -----	0.94
Acetylene -----	11.03

98.95

Under these conditions, therefore, the once through results are:

$C_O=99.06$ Disappearance
$C_A=79.32$ Once Thru Acetylene Yield
$C_E=6.76$ Once Thru Ethylene Yield
$C_M=2.49$ Once Thru Methane Yield
$Y_A=80.07$ Acetylene Selectivity

Example 2

A gas mixture wherein the H/C ratio was 11.2/1 consisting of 89.65% H_2 , 10.35% C_2H_6 and no methane was passed through the reactor. The maximum temperature in the reaction zone was 1635° C. The pressure was substantially atmospheric. $Se=52 \text{ sec.}^{-1} \text{ atm.}^{-1}$. Under these conditions, the effluent gas had the following analysis:

Hydrogen -----	90.46
Methane -----	1.87
Ethylene -----	0.24
Acetylene -----	7.17

99.74

corresponding to:

$C_O=100$ Disappearance
$C_A=81.85$ Once Thru Acetylene Yield
$C_E=2.70$ Once Thru Ethylene Yield
$C_M=10.65$ Once Thru Methane Yield
$Y_A=81.85$ Acetylene Selectivity

Example 3

A gas mixture wherein the H/C ratio was 3.86/1 consisting of 46.3% hydrogen, 53.6% ethane, and a trace of methane was passed through the reactor at 204 mm. Hg absolute pressure (0.269 atm. absolute). The effective H/C ratio is 6.39.

The maximum temperature in the reaction zone was 1750° C. $Se, 48.4 \text{ sec.}^{-1} \text{ atm.}^{-1}$. Under these conditions, the effluent gas had the following analysis:

Hydrogen -----	73.21
Methane -----	2.65
Ethylene -----	4.05
Acetylene -----	18.25

98.16

which corresponds to:

$C_O=100$ Disappearance
$C_A=65.8$ Once Thru Acetylene Yield
$C_E=14.60$ Once Thru Ethylene Yield
$C_M=4.67$ Once Thru Methane Yield
$Y_A=65.8$ Acetylene Selectivity

Example 4

A gas mixture wherein the H/C ratio was 9.43 consisting of 82.28% hydrogen, 8.50% methane and 9.21% ethane, was passed through the reactor at 784.3 mm. Hg abs. (1.032 atm. abs.) The effective hydrogen to carbon ratio is:

$$(H/C)_{\text{eff.}} = \frac{(1-P) + P[\Sigma X(2n+2) + (1-\Sigma X)2]}{P[\Sigma X(n)]} = \frac{(1-1.032) + 1.032[0.085(4) + 0.0921(6) + (1-0.085-0.9021)2]}{1.032[0.085(1) + 0.0921(2)]} = 8.99$$

The maximum reaction zone temperature was 1643° C., and Se , 18.0 sec.⁻¹ atm.⁻¹. Under these conditions, the product gas had the following analysis:

Hydrogen	88.79
Methane	2.03
Ethylene	0.39
Acetylene	8.41
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	99.62

which corresponds to:

$C_O=70.43$ (Methane Disappearance)
 $C_O^1=100$ (Ethane Disappearance)
 $C_A=77.37$ Once Thru Acetylene Yields
 $C_E=3.59$ Once Thru Ethylene Yields
 $Y_A=87.19$ Acetylene Selectivity

Example 4A

Under otherwise the same conditions as described in Example 4, but with the maximum temperature in the reaction zone at 1775° C., and $Se=32.4$ sec.⁻¹ atm.⁻¹, the product gas has the following analysis:

Hydrogen	89.83
Methane	0.65
Ethylene	0.30
Acetylene	8.84
	<hr/>
	99.62

which corresponds to:

$C_O=90.34$ Methane Disappearance
 $C_O^1=100$ Ethane Disappearance
 $C_A=82.53\%$ Once Thru Acetylene Yield
 $C_E=2.77\%$ Once Thru Ethylene Yield
 $Y_A=85.68\%$ Acetylene Selectivity

Example 4B

Under otherwise the same conditions as in Example 4A, but with the maximum temperature in the reaction zone at 1790° C., and with $Se=18.7$ sec.⁻¹ atm.⁻¹, the product gas had the following analysis:

Hydrogen	90.34
Methane	0.23
Ethylene	0.40
Acetylene	8.09
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	99.06

which corresponds to:

$C_O=96.54$ (Methane Disappearance)
 $C_O^1=100$ (Ethane Disappearance)
 $C_A=75.82$ Once Thru Acetylene Yield
 $C_E=3.72$ Once Thru Ethylene Yield
 $Y_A=76.83$ Acetylene Selectivity

Example 5

A gas mixture wherein the H/C ratio was 7.00 consisting of 67.76% hydrogen, 24.42% CH₄ and 7.80% ethane was passed through the reactor at about 140 mm. Hg absolute (0.185); the (H/C)_{eff.} is 19.1. The maximum reaction zone temperature was 1715° C., and $Se=48.5$ sec.⁻¹ atm.⁻¹. Under these conditions, the product gas had the following analysis:

Hydrogen	83.25
Methane	5.42
Ethylene	0.33
Acetylene	10.48
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	99.48

which corresponds to:

$C_O=70.69$ Methane Disappearance
 $C_O^1=100$ Ethane Disappearance
 $C_A=69.18$ Once Thru Acetylene Yield
 $C_E=2.18$ Once Thru Ethylene Yield
 $Y_A=86.28$ Acetylene Selectivity

Example 5A

Under otherwise the same conditions as in Example 5, but with the maximum reaction zone temperature at 1750° C., the product gas analyzed as follows:

Hydrogen	84.50
Methane	3.77
Ethylene	0.23
Acetylene	10.92
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	99.42

which corresponds to:

$C_O=79.25$ Methane Disappearance
 $C_O^1=100$ Ethane Disappearance
 $C_A=73.35$ Once Thru Acetylene Yield
 $C_E=1.54$ Once Thru Ethylene Yield
 $Y_A=85.32$ Acetylene Selectivity

Example 5B

As in Example 5A, but with the maximum reaction zone temperature at 1795° C., the product gas analyzed as follows:

Hydrogen	85.40
Methane	2.09
Ethylene	0.19
Acetylene	11.65
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	99.33

which corresponds to:

$C_O=88.30$ Methane Disappearance
 $C_O^1=100$ Ethane Disappearance
 $C_A=79.60$ Once Thru Acetylene Yield
 $C_E=1.30$ Once Thru Ethylene Yield
 $Y_A=86.43$ Acetylene Selectivity

Example 6

With the gas mixture of Example 5, but at about 165 mm. Hg abs. (0.217 atm. abs.) the (H/C)_{eff.}=15.9. The maximum reaction zone temperature was 1680° C. and $Se=101$ sec.⁻¹ atm.⁻¹. Under these conditions, the product gas analyzed as follows:

Hydrogen	75.60
Methane	14.00
Ethylene	0.54
Acetylene	9.37
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	99.51

which corresponds to:

$C_O=30.4$ Methane Disappearance
 $C_O^1=100$ Ethane Disappearance
 $C_A=56.8$ Once Thru Acetylene Yield
 $C_E=3.3$ Once Thru Ethylene Yield
 $Y_A=93.2$ Acetylene Selectivity

Example 6A

With the gas mixture of Example 5, but at 785 mm. Hg abs. (1.032 atm. abs.), the (H/C)_{eff.}=6.90. The maximum reaction zone temperature was 1700° C. and $Se=28.3$ sec.⁻¹ atm.⁻¹. Under these conditions, the product gas had the following analysis:

Hydrogen	84.92
Methane	3.64
Ethylene	0.42
Acetylene	10.58
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	99.56

which corresponds to:

$C_O=80$ Methane Disappearance
 $C_O^1=100$ Ethane Disappearance
 $C_A=70.96$ Once Thru Acetylene Yield
 $C_E=2.82$ Once Thru Ethylene Yield
 $Y_A=82.06$ Acetylene Selectivity

13

Example 7

A gas mixture with a (H/C) ratio of 7.88 consisting of 88.56% hydrogen, 11.18% propane and 0.26% ethane was passed through the reaction zone. The maximum temperature in the reaction zone was 1780° C., and $Se=43.0 \text{ sec.}^{-1} \text{ atm.}^{-1}$. The pressure was 722 mm. Hg abs. (0.95 atm. abs.) corresponding to $(H/C)_{\text{eff.}}=8.14$. Under these conditions, the product gas analyzed as follows:

Hydrogen -----	89.44
Methane -----	1.44
Ethylene -----	0.31
Acetylene -----	8.55
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	99.74

which corresponds to:

$C_O=98.00$ Propane Disappearance
 $C_A=65.95$ Once Thru Acetylene Yield
 $C_E=2.39$ Once Thru Ethylene Yield
 $C_M=4.40$ Once Thru Methane Yield
 $Y_A=67.27$ Acetylene Selectivity

Example 8

A gas mixture with a (H/C) ratio of 6.74 consisting of 85.92% hydrogen and 14.08% propane was passed through the reaction zone. The maximum temperature in the reaction zone was 1561° C., and $Se=122 \text{ sec.}^{-1} \text{ atm.}^{-1}$. The pressure was 204 mm. Hg abs. (0.269) corresponding to $(H/C)_{\text{eff.}}=13.2$. Under these conditions, the product gas analyzed as follows:

Hydrogen -----	79.78
Methane -----	6.76
Ethylene -----	0.72
Acetylene -----	11.81
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	99.07

which corresponds to:

$C_O=98.97$ Propane Disappearance
 $C_A=73.49$ Once Thru Acetylene Yield
 $C_E=4.48$ Once Thru Ethylene Yield
 $C_M=21.03$ Once Thru Methane Yield
 $Y_A=74.25$ Acetylene Selectivity

Example 8A

A substantially the same condition as Example 8, but with the maximum temperature at 1604° C. and $Se=64.9 \text{ sec.}^{-1} \text{ atm.}^{-1}$, the product gas analyzed as follows:

Hydrogen -----	83.48
Methane -----	2.46
Ethylene -----	0.16
Acetylene -----	13.03
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	99.13

which corresponds to:

$C_O=98.73$ Propane Disappearance
 $C_A=85.00$ Once Thru Acetylene Yield
 $C_E=1.04$ Once Thru Ethylene Yield
 $C_M=8.02$ Once Thru Methane Yield
 $Y_A=86.09$ Acetylene Selectivity

Example 9

A gas mixture with a (H/C) ratio of 11.25 consisting of 92.8% hydrogen and 7.2% propane was passed through the reaction zone. The maximum temperature in the reaction zone was 1670° C. and $Se=62.5 \text{ sec.}^{-1} \text{ atm.}^{-1}$. The pressure in the reaction zone was 79.9 mm. Hg abs. (1.048 atm. abs.) corresponding to $(H/C)_{\text{eff.}}=10.38$.

14

Under these conditions, the product gas analyzed as follows:

Hydrogen -----	90.30
Methane -----	2.28
Ethylene -----	0.29
Acetylene -----	6.75
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	99.62

which corresponds to:

$C_O=100$ Propane Disappearance
 $C_A=74.0$ Once Thru Acetylene Yield
 $C_E=3.2$ Once Thru Ethylene Yield
 $C_M=12.5$ Once Thru Methane Yield
 $Y_A=74.0$ Acetylene Selectivity

Example 10

A gas mixture with a (H/C) ratio of 21.15 consisting of 98.51% hydrogen and 1.49% heptane was passed through the reaction zone. The maximum temperature in the reaction zone was 1638° C. and $Se=42.3 \text{ sec.}^{-1} \text{ atm.}^{-1}$. The pressure in the reaction zone was 770 mm. Hg abs. (1.017 atm. abs.) corresponding to $(H/C)_{\text{eff.}}=20.8$. Under these conditions, the product gas analyzed as follows:

Hydrogen -----	94.48
Methane -----	1.18
Ethylene -----	0.22
Acetylene -----	4.03
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	99.91

which corresponds to:

$C_O=100$ Heptane Disappearance
 $C_A=84.17$ Once Thru Acetylene Yield
 $C_E=4.59$ Once Thru Ethylene Yield
 $C_M=12.32$ Once Thru Methane Yield
 $Y_A=84.17$ Acetylene Selectivity

While there are above disclosed but a limited number of embodiments of the invention herein presented, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed.

What is claimed is:

1. A process for the pyrolysis of mixtures containing substantially non-aromatic hydrocarbons having 2 to 10 carbon atoms admixed with hydrogen which comprises heating said mixture of hydrocarbons and hydrogen within a substantially isothermal pyrolysis reactor zone at a maximum temperature within said reaction zone of at least 1450° C. up to 2000° C., the effective space velocity of said mixture through said reaction zone being within the range 1.0 to 400 $\text{sec.}^{-1} \text{ atm.}^{-1}$.

2. A process for the pyrolysis of mixtures containing at least 65 mole percent of at least one non-aromatic hydrocarbon having from 2 to 10 carbon atoms and hydrogen to produce acetylene and hydrogen which comprises heating the mixture of hydrocarbon and hydrogen within a substantially isothermal pyrolysis reactor zone at a maximum temperature within said reaction zone of at least 1450° C. up to 2000° C., the effective space velocity of said mixture through said reaction zone being within the range 1.0 to 400 $\text{sec.}^{-1} \text{ atm.}^{-1}$, the effective hydrogen to carbon ratio in said mixture of hydrocarbon and hydrogen being from 6.0 to 30.0.

3. A process for the pyrolysis of a mixture of non-aromatic hydrocarbons having from 2 to 10 carbon atoms and hydrogen to produce acetylene and hydrogen which comprises heating said mixture of hydrocarbons and hydrogen within a pyrolysis reactor zone at a maximum temperature within the reaction zone of said reactor of at least 1450° C. up to 2000° C., the effective space velocity of said mixture through said reaction zone being within the range 1.0 to 400 $\text{sec.}^{-1} \text{ atm.}^{-1}$, the beginning of the pyrolysis reactor zone being defined as that point at which

15

the temperature of the reacting gases first reaches a temperature level of about 250° C. below the maximum temperature and the end of said zone being defined as the point of quenching of the product gases.

4. The process defined in claim 3, in which the product gases are rapidly quenched to a temperature of at least 600° C.

5. A process for the pyrolysis of mixtures of hydrogen and non-aromatic hydrocarbons having from 2 to 10 carbon atoms to produce acetylene which comprises heating a mixture of hydrogen and said hydrocarbons having an effective hydrogen to carbon atomic ratio in the range 6.0 to 30.0, within a substantially isothermal pyrolysis reactor at a maximum temperature within said reaction zone of at least 1450° C. to 2000° C., the effective space velocity through said reaction zone being in the range of 2.5 to 300 sec.⁻¹ atm.⁻¹.

6. A process for the isothermal pyrolysis of non-aromatic hydrocarbons having 2 to 10 carbon atoms, to produce acetylene and hydrogen which comprises heating a mixture of hydrogen, hydrocarbons and inert gases within a pyrolysis reactor at a maximum temperature within the reaction zone of said reactor of at least 1450° C. up to 2000° C., the effective space velocity of said mixture through said reaction zone being in the range of 2.5 to 300 sec.⁻¹ atm.⁻¹, and thereafter rapidly quenching the product gases to a temperature of at least 600° C.

16

matic hydrocarbons having 2 to 10 carbon atoms, to produce acetylene and hydrogen which comprises heating a mixture of hydrogen, hydrocarbons and inert gases within a pyrolysis reactor at a maximum temperature within the reaction zone of said reactor of at least 1450° C. up to 2000° C., the effective space velocity of said mixture through said reaction zone being in the range of 2.5 to 300 sec.⁻¹ atm.⁻¹, and thereafter rapidly quenching the product gases to a temperature of at least 600° C.

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