June 12, 1956 H. J. HEPP 2,750,420

CONVERSION OF HYDROCARBONS

Filed April 29, 1953 2 Sheets-Sheet 1

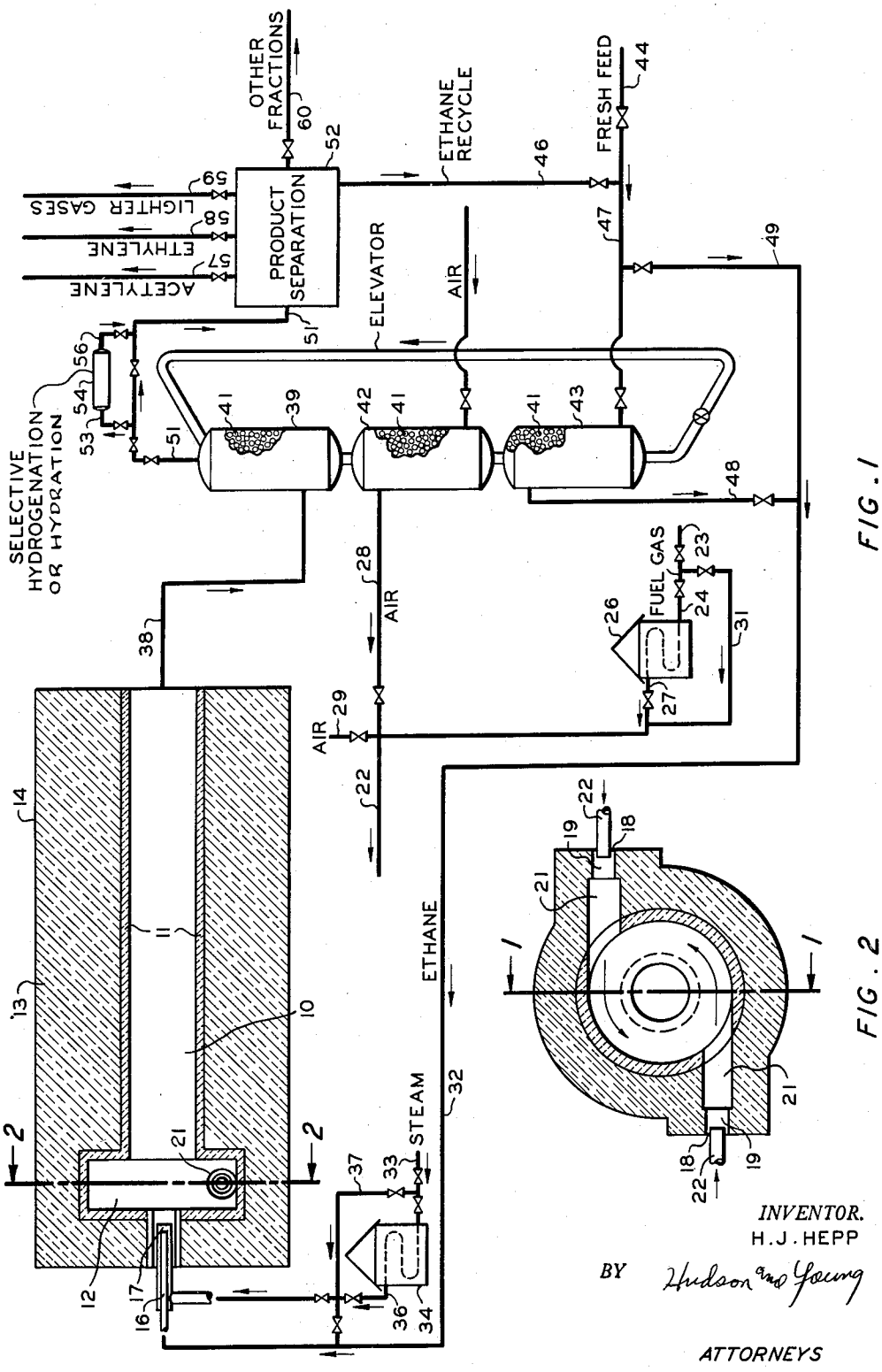


FIG. 1

FIG. 2

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Filed April 29, 1953 2 Sheets-Sheet 2

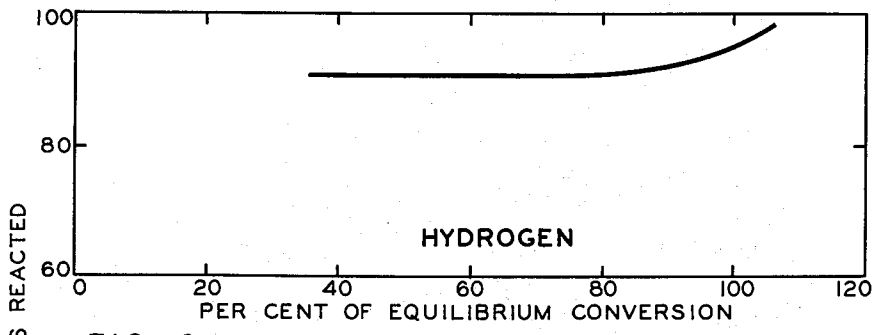


FIG. 3

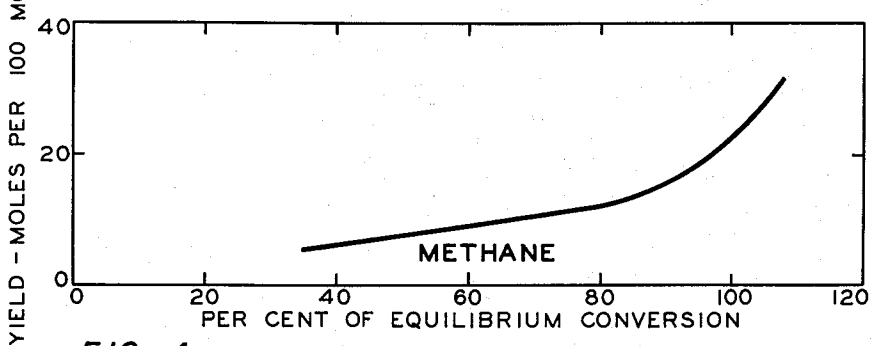


FIG. 4

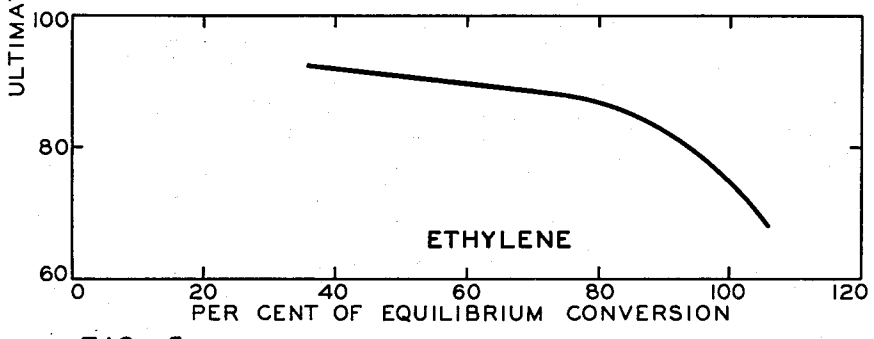


FIG. 5

YIELD OF LIGHT PRODUCTS IN ETHANE PYROLYSIS

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2,750,420

CONVERSION OF HYDROCARBONS

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Application April 29, 1953, Serial No. 351,780

21 Claims. (Cl. 260—605)

This invention relates to the pyrolysis of hydrocarbons. In one aspect this invention relates to the manufacture of aromatic hydrocarbons, olefins and acetylenes. In another aspect this invention relates to a hydrocarbon pyrolysis process wherein pyrolysis effluents are promptly quenched and efficient heat exchange is effected between pyrolysis effluent product and one or more gas streams to be introduced into the pyrolysis zone. In another aspect this invention relates to a hydrocarbon pyrolysis process wherein over-reacting and carbon deposition and formation, are substantially completely prevented. In still another aspect this invention relates to the pyrolysis of hydrocarbons in a tangential burner reactor wherein a hydrocarbon feed stream is heated to pyrolysis temperature in a combustion zone while in initial contact with hot combustion gases and while surrounded by a steam annulus to prevent direct exposure of the feed stream to peak radiant heat temperatures therein, thereby preventing substantially "shock" heating of the feed with concomitant over reacting of feed and accompanying undesired reactions or degradation of desired products. In still another aspect this invention relates to the pyrolysis of ethane to produce ethylene in high yield, under selected conditions preventing carbon formation and polymerization of ethylene product.

This application is a continuation-in-part of my copending application Serial No. 106,183 filed July 22, 1949, now abandoned.

A number of cracking methods have been proposed for conversion of hydrocarbons to olefins and aromatic hydrocarbon product, from various hydrocarbon stocks. Many of these proposed methods involve thermally treating the hydrocarbon stock in cracking-tubes disposed in a conventional gas-fired furnace. Normally, these processes are conducted at temperatures below about 1500° F., in view of operating difficulties that occur at higher temperatures, as a result of excessive carbon deposition and cracking-tube failure. Such a temperature limitation is disadvantageous from the standpoint of producing certain valuable olefins, acetylenes and aromatic hydrocarbon products.

This invention is concerned with a process for the pyrolysis of hydrocarbon stocks at temperatures usually above 1200° F. and as high as 3000° F. or higher, wherein over-reacting of hydrocarbon reactants, and carbon formation are greatly minimized, and wherein valuable pyrolysis products may be formed in high yields.

An object of this invention is to provide a process for the pyrolysis of hydrocarbons.

Another object is to provide a process for the pyrolysis of ethane to produce ethylene, wherein carbon formation and polymerization of ethylene pyrolysis product is substantially prevented.

Another object is to provide valuable aromatic hydrocarbons, diolefins, olefins, and acetylenes, as hydrocarbon pyrolysis products.

Another object is to prevent carbon formation and deposition from occurring during a hydrocarbon pyrolysis process.

Another object is to provide for heating a hydrocarbon pyrolysis feed stock to pyrolysis temperature, in a manner to prevent concomitant carbon deposition.

Another object is to provide a hydrocarbon pyrolysis process wherein over-reacting of hydrocarbon reactants, carbon formation and undesirable side reactions, particularly polymerization of olefin product, are substantially prevented.

Another object is to provide for the pyrolysis of hydrocarbons at temperatures as high as 3000° F., to produce valuable pyrolysis products in high and efficient yield.

Another object is to provide for the pyrolysis of selected hydrocarbon stocks boiling in the gas oil range, and higher, to produce low-boiling olefins, and hydrocarbons boiling in the gasoline boiling range.

Another object is to provide for the pyrolysis of saturated normally gaseous hydrocarbons.

Another object is to provide for conserving heat utilized in a hydrocarbon pyrolysis process.

Other objects will be apparent, to one skilled in the art, from the accompanying discussion and disclosure.

My invention provides for pyrolysis of hydrocarbons in a tangential-burner-reactor, of the type described hereafter, at temperatures generally higher than those employed in ordinary tube-cracking processes, under conditions greatly minimizing loss of hydrocarbon reactant to carbon and tar formation, and to undesirable side reactions, and preventing deposition of any such carbonaceous materials in the pyrolysis reaction zone.

In accordance with my invention I have provided a process for the pyrolysis of hydrocarbons to produce predominantly aromatic, acetylenic, and olefinic products with no substantial undesired reaction or degradation of desired products taking place, comprising passing a hydrocarbon axially into a first cylindrical zone; annularly passing steam into said first cylindrical zone to form a steam annulus about said hydrocarbon; introducing a combustible fuel gas mixture tangentially into said first cylindrical zone and burning same therein about said steam annulus to generate combustion gas at a hydrocarbon pyrolyzing temperature; passing said hydrocarbon axially through said first cylindrical zone separated from said combustion gas therein by said annulus of steam; passing said hydrocarbon, said steam, and said combustion gas from the said first cylindrical zone into a second cylindrical zone having a smaller diameter than, and adjacent to said first cylindrical zone; in said second cylindrical zone transferring heat from said combustion gas to said hydrocarbon to pyrolyze said hydrocarbon, and recovering a pyrolysis product from said second cylindrical zone. In accordance with a narrower concept of my invention, ethane is pyrolyzed under conditions providing for its pyrolysis within a specified decomposition range, defined hereinafter, by which the ethane is converted to ethylene and hydrogen in high yield with substantially no carbon formation or polymerization of ethylene product taking place. In accordance with still another concept of this invention, sensible heat carried from the pyrolysis zone is transferred from the pyrolysis zone effluent to incoming hydrocarbon feed and a combustion-supporting oxygen-containing gas, in a novel multiple zone pebble heat exchanger, in which pebbles are first heated in contact with pyrolysis effluent gas in a first pebble zone, are then contacted in a second pebble zone in heat exchange relation with an oxygen-containing gas to be preheated for supporting combustion in the combustion zone, and finally contacted in a third pebble zone in heat exchange relation with hydrocarbon reactants to be preheated.

Pyrolysis temperature is regulated by appropriate selection of proportions of components of the combustible fuel

mixture, acetylenic products being formed in relatively high yield at pyrolysis temperatures above about 2000° F. and olefinic products being formed in relatively high yield at temperatures below about 2000° F.

Any suitable feed stock for hydrocarbon pyrolysis can be converted in accordance with my process and can be introduced into the above described first cylindrical zone as a gas or as a liquid, the latter preferably in atomized form.

I have found that by employing a steam annulus in the described manner, it is possible to focus heat of radiation in the combustion zone in a direction toward the hydrocarbon feed to heat the said feed at a requisite high temperature and in a shorter time than possible heretofore without "shock" heating the feed and obtaining, concomitantly, undesirable side reactions. Thus hydrocarbon feed passed through the combustion zone is protected from direct contact with hot combustion gases therein and thereby from peak radiant heat temperature therein, by the surrounding steam annulus which absorbs the inwardly directed heat radiation from the flame to prevent shock heating the hydrocarbon feed.

In the said second pyrolysis zone, mixing of hydrocarbon reactant, combustion gas, and steam is substantially instantaneous and pyrolysis is effected at a substantially uniform temperature level throughout the pyrolysis zone. Operating in this manner, over-cracking of portions of the hydrocarbon stream with concomitant carbon formation and deposition is prevented, during the time that the hydrocarbon reactant is being heated to pyrolysis temperature, and mixing is substantially instantaneous, so that the pyrolysis reaction is uniformly effected throughout the pyrolysis mixture with very little, if any, carbon formation and/or undesirable side reaction taking place.

In one form of this invention my process is carried out in a tangential-burner-reactor, or furnace system, which comprises two cylindrical sections, one of which may be termed a combustion section and the other a reaction or pyrolysis section. The two sections are adjacent each other, preferably coaxial and preferably disposed horizontally. The combustion section is positioned upstream from the pyrolysis section and has a shorter length and a larger diameter as compared to the adjacently disposed pyrolysis section, and preferably it has a diameter greater than its own length. In the practice of one form of my invention in conjunction with such a burner-reactor, a combustible fuel gas mixture is passed tangentially into the combustion chamber, by "tangentially" it being meant herein introduction of gas into the combustion section in a direction tangent its inner side wall with the predominating direction of motion being preferably perpendicular to the longitudinal axis of the combustion chamber, while at the same time a hydrocarbon pyrolysis feed stream is introduced axially into the combustion chamber, together with steam introduced as a surrounding annulus therefor. The tangentially introduced combustible mixture is burned in the combustion chamber and is introduced thereinto at a velocity sufficiently high that combustion gas thus formed, travels along an inward spiral path in the combustion section. Axially introduced hydrocarbon travels through the combustion zone into the adjacent pyrolysis zone, separated from hot combustion gas and protected from peak radiant heat temperatures therein, by the steam annulus. Quick mixing of hydrocarbon reactant, combustion gas, and steam, is effected in the pyrolysis zone and pyrolysis takes place in a very short time at a temperature concomitantly uniform throughout the pyrolysis reaction mixture. In this way, very little carbon formation and undesirable side reacting takes place, either during the time that the hydrocarbon reactant is brought to pyrolysis temperature in the combustion zone, or during the time which the pyrolysis takes place.

Pyrolysis effluent is quenched in a novel pebble heat exchanger of the type already briefly discussed. Such a pebble heat exchanger comprises a series of substantially vertically extending chambers often in vertical alignment with each other. These pebble chambers are insulated and are connected by relatively narrow insulated conduits, or throats. Generally, three such pebble chambers are employed, the topmost of which may be referred to as the quench zone, the middle chamber as the oxygen preheating zone, and the bottommost chamber as the hydrocarbon reactant preheating zone. A contiguous mass of particulate contacting material, often referred to as pebbles, fills the topmost, middle and bottom zones and the interconnecting throats, and flows downwardly through these zones by force of gravity. Pebbles are discharged from the bottom zone at a controlled rate, returned usually by elevating means, to a pebble inlet in the upper portion of the top zone and introduced thereinto. A contiguous moving pebble mass thereby fills the top, middle, and lower pebble zones and the interconnecting zones or throats, at all times.

The term "pebble" as used in this specification denotes any solid refractory material in flowable form, size or strength which will flow readily by gravity through the various pebble zones of the pebble heat exchanger apparatus. Pebbles are preferably substantially spherical and are about $\frac{1}{32}$ of an inch to 1 inch in diameter the preferred range being about $\frac{1}{4}$ inch to $\frac{1}{2}$ inch.

Pyrolysis zone effluent is quenched in heat exchange relation with relatively cool pebbles in the topmost pebble zone. Quenched product gas is withdrawn and further processed for recovery of selected pyrolysis product fractions. Some pebbles, subsequent to contact with product in the pebble quench zone may bear a slight deposit of carbonaceous material imparted from suspension in the pyrolysis product. Oxygen-containing gas is preheated in the middle pebble zone in heat exchange relation with pebbles previously heated in the quench zone, at the same time burning free any carbon retained on the pebble surfaces. Hydrocarbon pyrolysis feed, or, if desired, the hydrocarbon fuel component of the combustible gas mixture, is preheated in the bottom pebble zone in contact with pebbles previously contacted with oxygen-containing gas in the middle zone. Pebbles thus cooled by transfer of heat to oxygen-combustion supporting gas and to hydrocarbon pyrolysis feed or combustion feed, are withdrawn from the bottom pebble zone and elevated and introduced, i. e. recycled, into the topmost pebble zone.

My invention is illustrated by the accompanying diagrammatic drawings. However, it is to be understood that various modifications of the illustrated process and apparatus may be made and still remain within the scope of my invention. Figure 1 includes a section in elevation of a tangential-burner-reactor embodying my invention and taken on the line 1—1 of Figure 2, and a diagrammatic view of the pebble heat exchanger apparatus, together with other apparatus, used in practicing a preferred embodiment of this invention. Figure 2 is a cross sectional view of the tangential-burner-reactor taken on line 2—2 of Figure 1. Figures 3, 4 and 5 are curves illustrating product yields in connection with ethane pyrolysis, discussed hereafter.

Referring to Figure 1, elongated reaction section **10** is lined with highly refractory material **11**, such as corundum brick, silica brick, mullite brick, zirconia brick, millimanite brick, or similar suitable materials resistant to high temperatures developed therein. Upstream from and adjacent to section **10** is combustion section **12**, coaxial with section **10**. Section **12** is also lined with lining material **11** already described. Lined sections **10** and **12** are surrounded by a layer of insulating material **13** and the whole is contained in an outer steel shell **14**. Combustion section **12** preferably has a rela-

tively large diameter in comparison with its length while the reverse is true of reaction section **10**.

In the upstream, or inlet end of combustion zone **12**, is hydrocarbon feed inlet conduit **16** arranged axially so that hydrocarbon feed introduced therethrough will pass through section **12** and enter section **10**, axially. Surrounding conduit **16** is a coaxial, larger steam inlet conduit **17**. The arrangement of conduits **16** and **17** defines an annular space through which steam may be axially passed into chamber **12**. Steam passed through line **17** enters zone **12** annularly disposed about hydrocarbon reactant stream introduced through line **16**. If desired, steam may be introduced as an annulus about the incoming hydrocarbon stream in any other manner, such as for example through a plurality of inlets disposed peripherally about an axial hydrocarbon inlet. With reference to Figure 2, in combustion zone **12**, are arranged inlets **18** which are so disposed that gas may be passed therethrough into combustion zone **12** in a direct tangent to its inner side wall, with the predominating direction of flow preferably athwart the longitudinal axis of zone **12**. Each tangential gas inlet **18** may consist of a small conduit **19** joining a larger conduit or tunnel **21**, which latter terminates as an opening into chamber **12**. An inlet pipe **22** extends part-way into conduit **19**. As mentioned hereinbefore, the tangential gas inlet assembly is so arranged that gas enters chamber **12** in a direction tangent its cylindrical side wall at the point of inlet. Most of the tangentially introduced gas is burned within tunnels **21** to maintain a steady flame.

In a preferred operation of the process of my invention, a combustible fuel gas mixture, such as natural gas and air, is preheated and charged to tangential burner **18**. This may be done by introducing fuel gas from line **23** through line **24** to preheater **26** wherein it may be heated to a selected preheat temperature preferably not higher than 1200° F. Preheated fuel gas is withdrawn from preheater **26** through line **27** and passed to line **22** for admixture therein with air from line **28** and/or **29**, and subsequent burning in combustion zone **12**. Fuel gas in any desired proportion may be introduced into line **22** through line **31**, without preheat. Air, preheated in the manner described hereafter, may be introduced into line **22** through line **28**. Air in any desired proportion may be introduced into line **22** from line **29**, without preheat. When the air and fuel gas are to be mixed prior to introduction into the combustion zone, the allowable preheat temperature is limited by the ignition temperature of the gas mixture, since otherwise there is danger of flashback to the mixing zone. When fuel and air preheat temperatures are employed, which would cause the temperature of a resulting fuel-air mixture to be above its ignition temperature, the separate preheated air and fuel streams should be discharged directly into the burner so as to avoid flash-back. Thus, in that event, air from lines **28** and/or **29** and fuel gas from line **27** should each discharge separately into conduit **19**. It is however to be understood that such separate introduction of fuel components into the combustion section **12** can be carried out at any time if desired. Preheating either air or fuel gas, or both, may be dispensed with in part or entirely, when desired, in which case lines **31** and **29** may be the partial or sole source of fuel gas and air respectively. The resulting air-fuel gas combustible mixture in line **22** is introduced into conduits **19** and into tunnels **21**, and burned. Combustible gas is introduced through line **22** into chamber **12** at a rate sufficiently high that a steady flame is maintained during the burning, and that combustion gas thus formed therein follows an inward spiral path.

Ethane, preferably preheated in the manner described hereafter, is passed from line **32** into line **16** and charged axially into combustion chamber **12**. Preheating may be dispensed with in part or completely, as will be discussed hereafter. Simultaneously, steam is preheated and introduced axially into combustion zone **12**, annularly disposed about ethane entering zone **12** through line **16**. Steam thus added is passed from line **33** and preheated in preheater **34** to a temperature usually within the range of 500 to 1000° F. Preheating of steam may be dispensed with if desired. Preheated steam in zone **34** is withdrawn through line **36** and passed into line **17**. When steam preheating is dispensed with, steam from line **33** may be passed to line **17** through line **37**. Ethane from line **16** enters zone **12**, surrounded by an annulus of steam and is passed through zone **12** separated from the combustion gas therein by that steam annulus. During the residence of ethane in zone **12**, the steam annulus absorbs the high temperature heat radiation, thus effectively slowing the transfer of heat to ethane, and preventing over-cracking of portions thereof, which would result in an unduly large amount of coke deposition. Combustion gas, steam, and ethane passed from zone **12** into zone **10**, mix substantially instantaneously in zone **10** to provide a uniform temperature level throughout the pyrolysis reaction mixture, thus preventing uneven reaction temperatures and concomitantly high yields of tars, and the like.

Temperature is regulated in zone **10** by selection of the particular fuel gas to be burned, the quantity of that gas which is burned, the fuel-air ratio, and/or the ratio of axial hydrocarbon feed to total tangential gas feed. Obviously, a higher B. t. u. gas, or a larger quantity of such fuel gas burned, provides heat for development of higher temperatures than are obtained when burning a low B. t. u. content gas or a smaller quantity thereof. Any suitable fuel gas may be used, and the amount burned may be selected in accordance with the pyrolysis temperature to be developed in pyrolysis zone **10**.

Pyrolysis effluent is withdrawn from zone **10** through line **38** and introduced into the lower portion of pebble quench zone **39** of a pebble heat exchange apparatus of the type already described, and passed countercurrently therein in heat exchange relation with a portion of relatively cool down-flowing pebble mass **41**. Pyrolysis product gas, quenched in zone **39**, e. g., 700–1500° F. is withdrawn through line **51** for purification and recovery of selected pyrolysis product fractions, described hereafter.

Air to be preheated for use in combustion in zone **12**, is introduced into a lower portion of pebble preheat zone **42** of the pebble heat exchanger and contacted countercurrently therein with downwardly flowing pebbles previously heated in zone **39**, and generally bearing some carbon. Air is introduced into zone **42** in an amount in excess of that required for combustion in zone **12**, to burn free any carbonaceous deposits therein on the pebble surfaces. Air is withdrawn from an upper portion of zone **42**, through line **28** at a temperature in the range of 500 to 1000° F. and passed into line **22**. Ethane to be preheated, from lines **44** and **46** discussed hereafter, is introduced through line **47** into the lower portion of pyrolysis feed preheat zone **43** of the pebble heat exchanger and therein countercurrently contacted in heat exchange relation with pebbles, previously contacted with oxygen in zone **42**. Ethane is preheated in zone **43** to a temperature not exceeding 1200° F., preferably from 700 to 1000° F., and is withdrawn from zone **43** through line **48** and passed into line **32**. When it is desired to dispense with ethane preheat, ethane from line **44** may be passed directly to line **32** through line **49**.

Quenched pyrolysis product in line **51** is passed into product separation means **52** which may comprise any combination of product recovery steps, not individually illustrated, but which are well known to those skilled in the art for recovering product fractions from the product gas in line **51**. Such a combination of recovery equipment may include cooling, absorption, adsorption, fractionation, and the like. Separation zone **52** may comprise for example a direct water quench, an oil adsorption step for separating butanes and heavier from the quenched product gas, an adsorption step utilizing a moving charcoal bed for separation of methane and lighter products from the residual product of oil adsorp-

tion, and fractionation equipment for separating ethane, ethylene, propane, propylene, butanes and butenes from the charcoal absorbate. Among various well known solvents for recovering acetylene from gases that may be used in zone **52**, are acetone, water, or acetic acid. When pyrolysis conditions are employed which provide for the formation of trace quantities of acetylene, or quantities otherwise uneconomically recovered in zone **52**, acetylene present in the gas in line **51** may be passed through line **53** into selective hydrogenation zone **54** wherein acetylene may be selectively hydrogenated to ethylene and/or ethane in accordance with well-known methods for such selective hydrogenation. If desired, hydration of acetylene to acetaldehyde may be employed instead of selective hydrogenation. Effluent from zone **54**, substantially free of acetylene, may be withdrawn through line **56**, returned to line **51**, and passed on into zone **52**.

From product separation zone **52**, acetylene, when produced in desired yields for recovery may be withdrawn through line **57**, ethylene may be withdrawn through line **58**, residual gases, i. e. methane and hydrogen through line **59**, other selected fractions through line **60**, and unreacted ethane through line **46**. Unreacted ethane may be passed into line **47** and recycled to combustion zone **12** either through pebble preheater zone **43** or directly through line **32**.

For convenience and clarity certain apparatus such as pumps, surge tanks, accumulators, valves, etc. have not been shown in the drawing. Obviously, such modifications of the present invention may be practiced without departing from the scope of the invention.

In the general practice of my invention I prefer to introduce air to the combustion step, in an amount less than the stoichiometric equivalent of oxygen required for completely burning the fuel gas. Generally, I prefer to employ from 70–90 per cent of that stoichiometric amount. However, in those instances wherein the endothermic heat requirement of the pyrolysis reaction is sufficiently high that an undesirable temperature decrease occurs across the pyrolysis zone, it is often desirable to introduce air in an amount in excess of that stoichiometric equivalent of oxygen, sufficiently great to burn as much as 10 per cent of the hydrocarbon feed, so that such a portion of the feed stock is burned to produce heat in sufficient amount to lessen or entirely prevent the undesired temperature drop. Steam may be added with the oxygen-containing gas to reduce flame temperature. In some instances, it is desirable to burn a theoretical fuel-air mixture, adding steam to the burner as required to reduce flame temperature.

I have found that in cracking ethane to produce ethylene, only in a narrow range of the decomposition, $C_2H_6 \leftrightharpoons C_2H_4+H_2$, is it possible to obtain high "per pass" ethane conversion together with concomitantly high ultimate product yields, and low yields of undesirable side reaction product.

The optimum decomposition range in ethane cracking for ethylene production varies with both the temperature and pressure, increasing with the temperature and decreasing with the pressure. I have found it possible to define the optimum decomposition range in terms of the equilibrium, $C_2H_6 \leftrightharpoons C_2H_4+H_2$. The interrelation of reaction temperature, pressure, and time, necessary to produce ethane conversion in the desired decomposition range is as follows: $t=(2.303/k)[100/(100-AE)]$, where A is a constant having a value in the range of 0.8 to 0.95, E is the per cent of ethane dissociated at equilibrium at reaction temperature and pressure, t is reaction time in seconds, and k is the first order reaction velocity constant. The value of E at reaction temperature and pressure may be determined from the interrelations, $\log (Pe^2/(1-2e))=6.35-12{,}375/(T+460)$ and $E=100e/(1-e)$, wherein T is the reaction temperature in degrees F., P is reaction pressure in atmospheres, e is the mol fraction of ethylene in the equilibrium mixture, and k is determined by the relation,

$$\log k=14.02-27{,}423/(T+460)$$

Preferably, the above interrelations are applied when employing a temperature within the limits of 1200–2000° F. and a pressure within the limits of 1 to 100 p. s. i. a. However, it is to be understood that other pressures and temperatures may be utilized when desired.

I have discovered that excessive coke and tar formation experienced in ethane cracking, results in a large part from driving the ethane conversion beyond the equilibrium ethane dissociation. Ethane dissociations higher than permitted by the $C_2H_6 \leftrightharpoons C_2H_4+H_2$ equilibrium, at the existing temperature-pressure conditions are readily obtained, because the ethylene product polymerizes with resultant rapid increase in coke and tar formation. I have found that by limiting ethane cracking to the range of 80–95 per cent of the equilibrium dissociation over the temperature and pressure ranges usually employed in ethane cracking, i. e. temperatures from 1200 to 2000° F. and pressures up to 100 p. s. i. a., carbon and coke formation may be substantially avoided; and furthermore, when operating under these conditions, cracking capacity of available equipment is increased, and product purification and recovery costs are minimized. Conversions lower than 80 per cent of the equilibrium conversion result in low daily ethylene production, high ethane recycle and increased ethylene recovery costs. Conversions above 95 per cent of equilibrium conversion result in decreased yields of ethylene and larger yields of tar and coke with attendant process operating difficulties. It is to be understood, however, that conversions below 80 per cent of the equilibrium conversion may be utilized when desired.

The effect of lowering the yield of ethylene and increasing the yield of methane and hydrogen by increasing the ethane conversion to a level higher than 95 per cent of the equilibrium conversion is illustrated by the curves of Figures 3, 4 and 5.

Although my invention has been illustrated in terms of using air in the combustion zone, it is to be understood that oxygen of any purity, such as commercial grade purity, i. e., 90–95 per cent or any free oxygen-containing gas suitable for supporting such combustion may be employed, if desired.

The amount of steam to be added axially as an annulus about the hydrocarbon feed stream entering the combustion zone may be regulated, in accordance with the amount of protection that is required, which in turn may be regulated by varying the thickness of the protecting steam annulus, as determined by trial. Usually a thickness of from 0.5 to 5 inches is sufficient, and may be regulated by the selection of the steam inlet conduit of the proper diameter so that the annulus of steam surrounding the incoming hydrocarbon stream entering the combustion zone has the required thickness.

The linear velocity of the incoming steam is preferably the same as the velocity of the hydrocarbon reactant stream, although the steam annulus may be introduced at a linear velocity somewhat higher than that of the hydrocarbon stream. Such practice is usually not preferred in view of the tendency for mixing of steam and hydrocarbon to occur before those gases are passed completely through the combustion zone, in which case some overreacting might occur. Generally, I prefer to introduce hydrocarbon and steam axially into the combustion zone each at substantially the same linear velocity, within the limits of about 500–1500 ft./sec.

While my process has been illustrated in terms of ethane pyrolysis, other feed stocks may be selected from over a wide boiling range, particularly natural gas and normally gaseous paraffins, gas oils, selected fractions boiling in the gas oil range, or heavier materials. Obviously, specific conditions of temperature, pressure, and

time, may be selected by one skilled in the art in accordance with the particular feed stock and degree of conversion sought, to produce the desired product.

The pyrolysis product may vary considerably, dependent upon the time and temperature conditions chosen. For example, acetylene may be made as a major product of ethane cracking by suitably increasing pyrolysis temperature to 2000° F. or above. Similarly, the process may be utilized to produce aromatic hydrocarbons by the proper choice of time-temperature conditions, or to produce higher boiling olefins by a suitable choice of both time-temperature and charge stock, e. g., paraffin wax.

My invention is illustrated by the following example. The reactants, their proportions, and other specific ingredients are presented as being typical and should not be construed to limit the invention unduly.

Example

Fresh ethane feed is introduced axially into a combustion zone of a tangential burner-reactor at the rate of 6560 pounds per hour, together with 3440 pounds per hour of recycled ethane. The total feed is preheated to 1200° F. Steam, preheated to 1200° F., is also added axially into the same combustion zone at a rate of 5200 pounds per hour, through an inlet pipe concentrically disposed about the ethane inlet pipe. Natural gas is introduced tangentially into the same combustion zone and burned at the rate of 9400 C. F. H. in admixture with air, preheated at 1200° F., and introduced at the rate of 186,000 C. F. H. Ethane and combustion gas, together with steam as a separating annulus are passed axially through the combustion zone into the adjacent pyrolysis zone. Reaction temperature in the pyrolysis zone, under these conditions is 1800° F., and contact time is 0.05 second. Total effluent is produced at the rate of 399,570 C. F. H. and comprises the following products, in the proportions indicated.

	Cu. ft./hr.
N_2	147,200
CO	11,500
CO_2	11,500
H_2O	37,900
H_2	69,600
CH_4	8,040
C_2H_2	1,000
C_2H_4	67,900
C_2H_6	43,400
C_3+	1,530
	399,570

Ethane unreacted in the pyrolysis zone is recycled.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawings, and appended claims to the invention, the essence of which is a process for the pyrolysis of hydrocarbons comprising the steps of passing a hydrocarbon axially into a first cylindrical zone; annularly passing steam into said first cylindrical zone to form a steam annulus about said hydrocarbon; introducing a combustible fuel gas mixture tangentially into said first cylindrical zone and burning same therein about said steam annulus to generate combustion gas at a hydrocarbon pyrolyzing temperature; passing said hydrocarbon axially through said first cylindrical zone separated from said combustion gas therein by said annulus of steam; passing said hydrocarbon, said steam, and said combustion gas from said first cylindrical zone into a second cylindrical zone having a smaller diameter than, and adjacent to said first cylindrical zone; in said second cylindrical zone transferring heat from said combustion gas to said hydrocarbon to pyrolyze said hydrocarbon; and for recovering a pyrolysis product from said second cylindrical zone; another concept providing for recovery of sensible heat carried from the pyrolysis zone and return of same to the pyrolysis zone, employing a novel multiple zone pebble heat exchanger in which pebbles are first heated in contact with pyrolysis effluent gas in a first pebble zone, are then contacted in a second pebble zone in heat exchange relation with an oxygen-containing gas to be preheated for supporting combustion in the combustion zone, and are finally contacted in a third pebble zone in heat exchange relation with hydrocarbon reactants to be preheated; still another concept providing for pyrolysis of ethane under correlated time-temperature conditions for effecting the pyrolysis of ethane within the range of 80–95 per cent of its equilibrium dissociation to ethylene plus hydrogen, whereby ethylene and hydrogen are produced in high yield with no substantial undesired reactions, degradation or polymerization of ethylene product taking place.

I claim:

1. A process for the pyrolysis of a normally gaseous hydrocarbon, comprising preheating such a hydrocarbon in the manner described hereafter, axially introducing a stream of hydrocarbon thus preheated into a first cylindrical zone having a diameter greater than its length at a linear velocity within the limits of 500 to 1500 ft./sec., introducing a stream of steam into said first cylindrical zone annularly disposed about said hydrocarbon stream so that the resulting steam annulus has an initial thickness of from 0.5 to 5 inches and in a volume ratio to said hydrocarbon within the limits of 0.25:1 to 1:1 and at a linear velocity substantially the same as that of said hydrocarbon stream, preheating natural gas to a temperature not higher than 1200° F., preheating oxygen to a temperature not higher than 1000° F. in the manner described hereafter, introducing oxygen and natural gas thus preheated as a combustible fuel gas mixture containing oxygen in an amount within the range of 70–90 per cent of the stoichiometric equivalent of oxygen necessary for completely burning said natural gas in said first cylindrical zone in a direction tangent to its inner side wall with the predominating component of motion of said combustible mixture perpendicular to the longitudinal axis of said first cylindrical zone, burning said natural gas in said first cylindrical zone and maintaining said burning in a steady flame, passing resulting combustion gas therein in an inward spiral path, passing said axially introduced hydrocarbon stream through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said first cylindrical zone into a second cylindrical zone longer than, coaxial with, and adjacent said first cylindrical zone, maintaining said first cylindrical zone and said second cylindrical zone at an absolute pressure within the limits of from 1 to 50 p. s. i. g., regulating the amount of natural gas burned to produce heat to maintain the temperature of said hydrocarbon stream in said second cylindrical zone to within a range of 1500 to 3000° F. by transfer of heat from said combustion gas, quickly mixing normally gaseous hydrocarbon and combustion gas in said second cylindrical zone and maintaining said combustion gas and said hydrocarbon in uniform admixture for a contact time within the range of 0.005 to 1.0 seconds, passing effluent from said second cylindrical zone into a first and topmost zone of a pebble heat exchange system comprising a plurality of substantially vertically extending zones filled with a contiguous downwardly moving mass of pebbles, in said first zone quenching said effluent in heat exchange relation with pebbles, in said preheating of oxygen passing oxygen through a second zone of said heat exchange system disposed below said first zone in heat exchange relation with pebbles previously heated in said first pebble zone, in said preheating of normally gaseous hydrocarbon passing same through a third zone of said pebble heat exchange system disposed below said second zone in heat exchange relation with pebbles previously contacted with oxygen, withdrawing oxygen from said second pebble zone at a temperature not higher than 1000° F. and passing same to said first cylindrical zone as a component of said com-

bustible mixture, withdrawing normally gaseous hydrocarbon from said third zone at a temperature not higher than 1200° F., and introducing same axially into said first cylindrical zone as pyrolysis hydrocarbon feed, withdrawing quenched hydrocarbon pyrolysis effluent from said first pebble zone and passing same to a product separation means and therein separating selected product fractions, and recovering a hydrocarbon thus separated as a product of the process.

2. The process of claim 1, wherein the pyrolysis temperature is above 2000° F. and acetylene is the chief product of the process.

3. The process of claim 1 wherein the pyrolysis temperature is less than 2000° F. and ethylene is the chief product of the process.

4. A process for the pyrolysis of ethane to produce ethylene and hydrogen, which comprises passing ethane axially into a first cylindrical zone having a diameter greater than its length, passing steam into said first cylindrical zone annularly disposed about said ethane so that the resulting steam annulus has an initial thickness of from 0.5 to 5 inches, introducing a combustible fuel gas mixture tangentially into said first cylindrical zone and burning same therein, passing combustion gas along an inward spiral path in said first cylindrical zone, passing said ethane axially through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing ethane, steam and combustion gas from said first cylindrical zone into a second cylindrical zone longer than, having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, regulating said burning to produce heat to maintain said ethane in said second cylindrical zone at a selected pyrolysis temperature within the range of 1200 to 2000° F., maintaining said first cylindrical zone and said second cylindrical zone at a pressure within the limits of 1 to 100 p. s. i. a., regulating contact time of said ethane in said second cylindrical zone in accordance with the interrelation, $t=(2.303/k)\log[100/(100-AE)]$, where t is the reaction time in seconds, k is the reaction velocity constant at the specified temperature within said 1200 to 2000° F. range, E is the extent of dissociation of ethane at equilibrium at the same temperature, and A is a numerical value in the range of 0.80 to 0.95, passing effluent from said second cylindrical zone and separating a selected pyrolysis product fraction therefrom, and recovering said fraction as a product of the process.

5. The process of claim 4 wherein said combustible fuel gas mixture contains oxygen in an amount in excess of the stoichiometric equivalent of oxygen necessary for burning fuel gas therein.

6. A process for cracking ethane to produce ethylene and hydrogen, which comprises passing ethane axially into a first cylindrical zone having a diameter greater than its length, passing steam into said first cylindrical zone annularly disposed about said ethane, so that the resulting steam annulus has an initial thickness of from 0.5 to 5 inches, introducing a combustible fuel gas mixture tangentially into said first cylindrical zone and burning same therein, passing combustion gas along an inward spiral path in said first cylindrical zone, passing said ethane axially through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing ethane, steam and combustion gas from said first cylindrical zone into a second cylindrical zone longer than, having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, regulating said burning to produce heat to maintain said ethane in said second cylindrical zone at a selected cracking temperature within the range of 1200 to 2000° F., maintaining said first cylindrical zone and said second cylindrical zone at a pressure within the limits of 1 to 100 p. s. i. a., in said second cylindrical zone effecting said cracking to the extent of from 80 to 95 per cent of equilibrium dissociation of ethane, passing effluent from said second cylindrical zone and separating a selected pyrolysis product fraction therefrom, and recovering said fraction as a product of the process.

7. A hydrocarbon pyrolysis process comprising passing a gaseous hydrocarbon pyrolysis feed stream axially into a first cylindrical zone, passing a stream of steam into said first cylindrical zone annularly disposed about said gaseous hydrocarbon stream, introducing a combustible fuel gas mixture into said first cylindrical zone tangentially to its inner side wall with the predominating component of motion perpendicular to the longitudinal axis of said zone, burning said combustible gas mixture in said first cylindrical zone while introducing said combustible gas thereinto at a velocity sufficiently high that combustion gas formed follows an inward spiral path, passing said hydrocarbon stream axially through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing hydrocarbon, combustion gas, and steam from said first cylindrical zone into a second cylindrical zone longer than, having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, regulating said burning to produce heat to maintain a pyrolysis temperature of said hydrocarbon stream in said second cylindrical zone by transfer of heat from said combustion gas, in said second cylindrical zone quickly mixing said combustion gas and said hydrocarbon gas and pyrolyzing said hydrocarbon at a temperature in the range of 1500 to 3000° F. for a contact time within the range of 0.001 to 1.0 second, passing effluent from said second cylindrical zone through a first pebble zone in heat exchange relation with a continuous mass of pebbles cooler than said effluent, passing an oxygen-containing gas through a second pebble zone in heat exchange relation with pebbles previously heated in said first pebble zone and hotter than said oxygen-containing gas, passing hydrocarbon pyrolysis feed stock through a third zone in heat exchange relation with pebbles hotter than said hydrocarbon and previously contacted with said oxygen-containing gas, passing oxygen-containing gas from said second pebble zone into said first cylindrical zone as a component of said combustible mixture, passing hydrocarbon pyrolysis feed stock from said third pebble zone axially into said first cylindrical zone, passing pyrolysis product from said first pebble zone to a product separation means, and recovering an unsaturated hydrocarbon fraction as a product of the process.

8. A hydrocarbon pyrolysis process comprising passing a gaseous hydrocarbon stream axially into a first cylindrical zone, passing a stream of steam into said first cylindrical zone annularly disposed about said gaseous hydrocarbon stream, introducing a combustible fuel gas mixture tangentially into said first cylindrical zone and burning same therein, passing combustion gas along an inward spiral path in said first cylindrical zone, passing said hydrocarbon stream axially through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said first cylindrical zone into a second cylindrical zone longer than, having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, regulating said burning to produce heat to maintain said hydrocarbon in said second cylindrical zone at a temperature within the limits of 1500 to 3000° F. by transfer of heat from said combustion gas, maintaining said hydrocarbon gas in said second cylindrical zone for a contact time within the range of from 0.005 to 1.0 second, and recovering from an effluent from said second cylindrical zone an unsaturated hydrocarbon fraction as a product of the process.

9. A hydrocarbon pyrolysis process comprising passing a gaseous hydrocarbon stream axially into a first cylindrical zone having a diameter greater than its length, passing steam into said first cylindrical zone annularly disposed about said gaseous hydrocarbon stream, tangentially introducing a combustible fuel gas mixture into

said first cylindrical zone, burning said combustible gas in said first cylindrical zone, passing said hydrocarbon stream axially through said first cylindrical zone separated from combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said first cylindrical zone into a second cylindrical zone having a smaller diameter than, and adjacent said first cylindrical zone, in said second cylindrical zone transferring heat from said combustion gas to said hydrocarbon to pyrolyze said hydrocarbon, passing effluent from said second cylindrical zone, and recovering selected pyrolysis product fractions from said effluent.

10. A hydrocarbon pyrolysis process comprising passing a gaseous hydrocarbon pyrolysis feed stream into a first cylindrical zone, passing a stream of steam into said first cylindrical zone annularly disposed about said gaseous hydrocarbon stream in a volume ratio to said hydrocarbon within the limits of 0.25:1 to 1:1 and at a linear velocity substantially the same as the linear velocity of said hydrocarbon stream axially introduced, introducing a combustible fuel gas mixture into said first cylindrical zone, burning said combustible gas in said first cylindrical zone, passing said hydrocarbon stream axially through said first cylindrical zone separated from combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said first cylindrical zone into a second cylindrical zone having a smaller diameter than, and adjacent said first zone, in said second cylindrical zone transferring heat from said combustion gas to said hydrocarbon to pyrolyze said hydrocarbon, passing effluent from said second cylindrical zone, and recovering selected pyrolysis product fractions from said effluent.

11. A hydrocarbon pyrolysis process comprising passing a gaseous hydrocarbon pyrolysis feed stream into a first cylindrical zone having a diameter greater than its length, passing steam into said first cylindrical zone annularly disposed about said gaseous hydrocarbon stream in a volume ratio to said hydrocarbon within the limits of 0.25:1 to 1:1 and at a linear velocity substantially the same as that of said hydrocarbon stream, introducing oxygen and a fuel gas admixed in a mole stoichiometric ratio of oxygen to fuel gas below that necessary for completely burning said fuel gas into said first cylindrical zone in a direction tangent to its inner side wall with the predominating component of motion perpendicular to the longitudinal axis of said zone, burning said fuel gas in said first cylindrical zone, maintaining a steady flame in said first cylindrical zone, passing combustion gas in said first cylindrical zone along an inward spiral path, passing said hydrocarbon stream axially through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said cylindrical zone into a second cylindrical zone, longer than, having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, regulating said burning to produce heat to maintain said hydrocarbon at a pyrolysis temperature within the limits of 1500 to 3000° F. and maintaining said hydrocarbon at such a pyrolysis temperature for a contact time within the range of 0.005 to 1.0 second, passing effluent from said second cylindrical zone to a separation means and therein separating selected pyrolysis product fractions therefrom, and recovering a selected fraction thus separated from said effluent as a product of the process.

12. A hydrocarbon pyrolysis process comprising passing a gaseous hydrocarbon stream axially into a first cylindrical zone, passing steam into said first cylindrical zone annularly disposed about said gaseous hydrocarbon, tangentially introducing a combustible fuel gas mixture into said first cylindrical zone, burning said combustible gas in said first cylindrical zone, passing said hydrocarbon stream axially through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said first cylindrical zone into a second cylindrical zone having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, in said second cylindrical zone transferring heat from said combustion gas to said hydrocarbon to effect hydrocarbon pyrolysis, passing effluents from said second cylindrical zone directly into a first and topmost pebble zone of a pebble heat exchange system comprising a plurality of substantially vertically extending zones filled with a contiguous downwardly moving mass of pebbles, in said first pebble zone quenching said effluent in heat exchange relation with pebbles, passing an oxygen-containing gas through a second zone of said heat exchange system disposed below said first zone in heat exchange relation with pebbles previously heated in said first pebble zone, from said second pebble zone withdrawing said oxygen-containing gas thus preheated and passing same to said first cylindrical zone as a component of said combustible mixture, through a third zone of said pebble heat exchange system disposed below said second pebble zone passing a hydrocarbon stock in heat exchange relation with pebbles previously contacted with said oxygen-containing gas, from said third pebble zone withdrawing hydrocarbon stock thus preheated and axially introducing same as said gaseous hydrocarbon steam into said first cylindrical zone, and withdrawing quenched hydrocarbon pyrolysis effluent from said first pebble zone and separating same into selected product fractions.

13. A hydrocarbon pyrolysis process comprising passing a pyrolysis feed stream consisting essentially of a gaseous hydrocarbon stock axially into a first cylindrical zone having a diameter greater than its length, passing a stream of steam into said first cylindrical zone annularly disposed about said gaseous hydrocarbon stream so that the resulting steam annulus has an initial thickness of from 0.5 to 5 inches, introducing a combustible fuel gas mixture tangentially into said first cylindrical zone, burning said fuel gas in said first cylindrical zone and maintaining said burning in a steady flame, passing said flame and combustion gas along an inward spiral path in said first cylindrical zone adjacent the inner wall thereof, passing said hydrocarbon stream axially through said first cylindrical zone separated from spirally moving flame and combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said first cylindrical zone into a second cylindrical zone longer than, having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, regulating said burning to produce heat to maintain said hydrocarbon in said second cylindrical zone at a temperature within the limits of 1500 to 3000° F. by transfer of heat from said combustion gas, maintaining said hydrocarbon gas in said cylindrical zone for a contact time within the range of from 0.005 and 1.0 second, and recovering from an effluent of said second cylindrical zone an unsaturated hydrocarbon fraction as a product of the process.

14. A pyrolysis process, comprising passing hydrocarbon axially into a first cylindrical zone; annularly passing steam into said first cylindrical zone to form a steam annulus about said hydrocarbon; introducing a combustible fuel gas mixture tangentially into said first cylindrical zone and burning same therein about said steam annulus to generate combustion gas at a hydrocarbon pyrolyzing temperature; passing said hydrocarbon axially through said first cylindrical zone separated from said combustion gas therein by said annulus of steam; passing said hydrocarbon, said steam, and said combustion gas from said first cylindrical zone into a second cylindrical zone having a smaller diameter than, and adjacent to said first cylindrical zone; in said second cylindrical zone transferring heat from said combustion gas to said hydrocarbon to pyrolyze said hydrocarbon, and recovering a pyrolysis product from said second cylindrical zone.

15. A hydrocarbon pyrolysis process comprising pass-

ing a gaseous hydrocarbon stream axially into and through a first cylindrical zone; annularly passing steam into said first cylindrical zone to form a steam annulus about said gaseous hydrocarbon stream, tangentially introducing a combustible fuel gas mixture into said first cylindrical zone and burning same therein about said steam annulus to generate combustion gas at a temperature at which it can cause pyrolysis of said hydrocarbon; passing said hydrocarbon stream axially through said first cylindrical zone separated from hot combustion gas therein by said steam annulus; passing said hydrocarbon, said steam, and said combustion gas from said first cylindrical zone into a second cylindrical zone longer than, having a smaller diameter than, coaxial with, and adjacent to said first cylindrical zone; regulating said burning to produce heat to maintain said hydrocarbon in said second cylindrical zone at a pyrolysis temperature within the range 1200–3000° F. by transfer of heat from said combustion gas; and recovering a pyrolysis product from said second cylindrical zone.

16. A process for the pyrolysis of a normally gaseous hydrocarbon comprising preheating such a hydrocarbon in the manner described hereafter, axially introducing a stream of hydrocarbon thus preheated into a first cylindrical zone at a linear velocity within the limits of 500 to 1500 ft./sec., introducing a stream of steam into said first cylindrical zone annularly disposed about said hydrocarbon stream in a volume ratio to said hydrocarbon within the limits of 0.25:1 to 1:1 and at a linear velocity substantially the same as that of said hydrocarbon stream, preheating natural gas to a temperature not higher than 1200° F., preheating oxygen to a temperature not higher than 1000° F. in the manner described hereafter, introducing oxygen and natural gas thus preheated as a combustible fuel gas mixture containing oxygen in an amount within the range of 70–90 per cent of the stoichiometric equivalent of oxygen necessary for completely burning said natural gas in said first cylindrical zone in a direction tangent to its inner side wall with the predominating component of motion of said combustible mixture perpendicular to the longitudinal axis of said first cylindrical zone, burning said natural gas in said first cylindrical zone and maintaining said burning in a steady flame, passing resulting combustion gas therein in an inward spiral path, passing said axially introduced hydrocarbon stream through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing hydrocarbon, steam, and combustion gas from said first cylindrical zone into a second cylindrical zone longer than, coaxial with, and adjacent said first cylindrical zone, maintaining said first cylindrical zone and said second cylindrical zone at an absolute pressure within the limits of from 1 to 50 p. s. i. g., regulating the amount of natural gas burned to produce heat to maintain the temperature of said hydrocarbon stream in said second cylindrical zone to within a range of 1500 to 3000° F. by transfer of heat from said combustion gas, quickly mixing normally gaseous hydrocarbon and combustion gas in said second cylindrical zone and maintaining said combustion gas and said hydrocarbon in uniform admixture for a contact time within the range of 0.005 to 1.0 second, passing effluent from said second cylindrical zone into a first and topmost zone of a pebble heat exchange system comprising a plurality of substantially vertically extending zones filled with a contiguous downwardly moving mass of pebbles, in said first zone quenching said effluent in heat exchange relation which pebbles, in said preheating of oxygen passing oxygen through a second zone of said heat exchange system disposed below said first zone in heat exchange relation with pebbles previously heated in said first pebble zone, in said preheating of normally gaseous hydrocarbon passing same through a third zone of said pebble heat exchange system disposed below said second zone in heat exchange relation with pebbles previously contacted with oxygen, withdrawing oxygen from said second pebble zone at a temperature not higher than 1000° F. and passing same to said first cylindrical zone as a component of said combustible mixture, withdrawing normally gaseous hydrocarbon from said third zone at a temperature not higher than 1200° F. and introducing same axially into said first cylindrical zone as pyrolysis hydrocarbon feed, withdrawing quenched hydrocarbon pyrolysis effluent from said first pebble zone and passing same to a product separation means and therein separating selected hydrocarbon product fractions, and recovering a hydrocarbon thus separated as a product of the process.

17. A process for cracking ethane to produce ethylene and hydrogen, which comprises passing ethane axially into a first cylindrical zone, passing steam into said first cylindrical zone annularly disposed about said ethane, introducing a combustible fuel gas mixture tangentially into said first cylindrical zone and burning same therein, passing combustion gas along an inward spiral path in said first cylindrical zone, passing said ethane axially through said first cylindrical zone separated from hot combustion gas therein by an annulus of said steam, passing ethane, steam and combustion gas from said first cylindrical zone into a second cylindrical zone longer than, having a smaller diameter than, coaxial with, and adjacent said first cylindrical zone, regulating said burning to produce heat to maintain said ethane in said second cylindrical zone at a selected cracking temperature within the range of 1200 to 2000° F., maintaining said first cylindrical zone and said second cylindrical zone at a pressure within the limits of 1 to 100 p. s. i. a., in said second cylindrical zone effecting said cracking to the extent of from 80 to 95 per cent of equilibrium dissociation of ethane, passing effluent from said second cylindrical zone and separating a selected pyrolysis product fraction therefrom, and recovering said fraction as a product of the process.

18. The process of claim 12 wherein acetylene in said quenched hydrocarbon pyrolysis effluent is selectively removed prior to separation of said effluent into said selective product fractions.

19. The process of claim 18 wherein said acetylene is selectively hydrogenated to form a less saturated hydrocarbon.

20. The process of claim 18 wherein said acetylene is selectively hydrated to form acetaldehyde.

21. In the pyrolysis of a hydrocarbon, wherein hydrocarbon feed is passed through a combustion zone in contact with hot combustion gas produced therein, as a pyrolysis heat source, and pyrolysis product is subsequently withdrawn from the pyrolysis system in admixture with said combustion gas, the improvement comprising introducing steam into said combustion zone as an annulus about said hydrocarbon feed and passing said hydrocarbon feed through said combustion zone separated from said combustion gas by said annulus of steam, withdrawing an admixture of steam, combustion gas and pyrolysis product from the pyrolysis system, and recovering pyrolysis product.

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