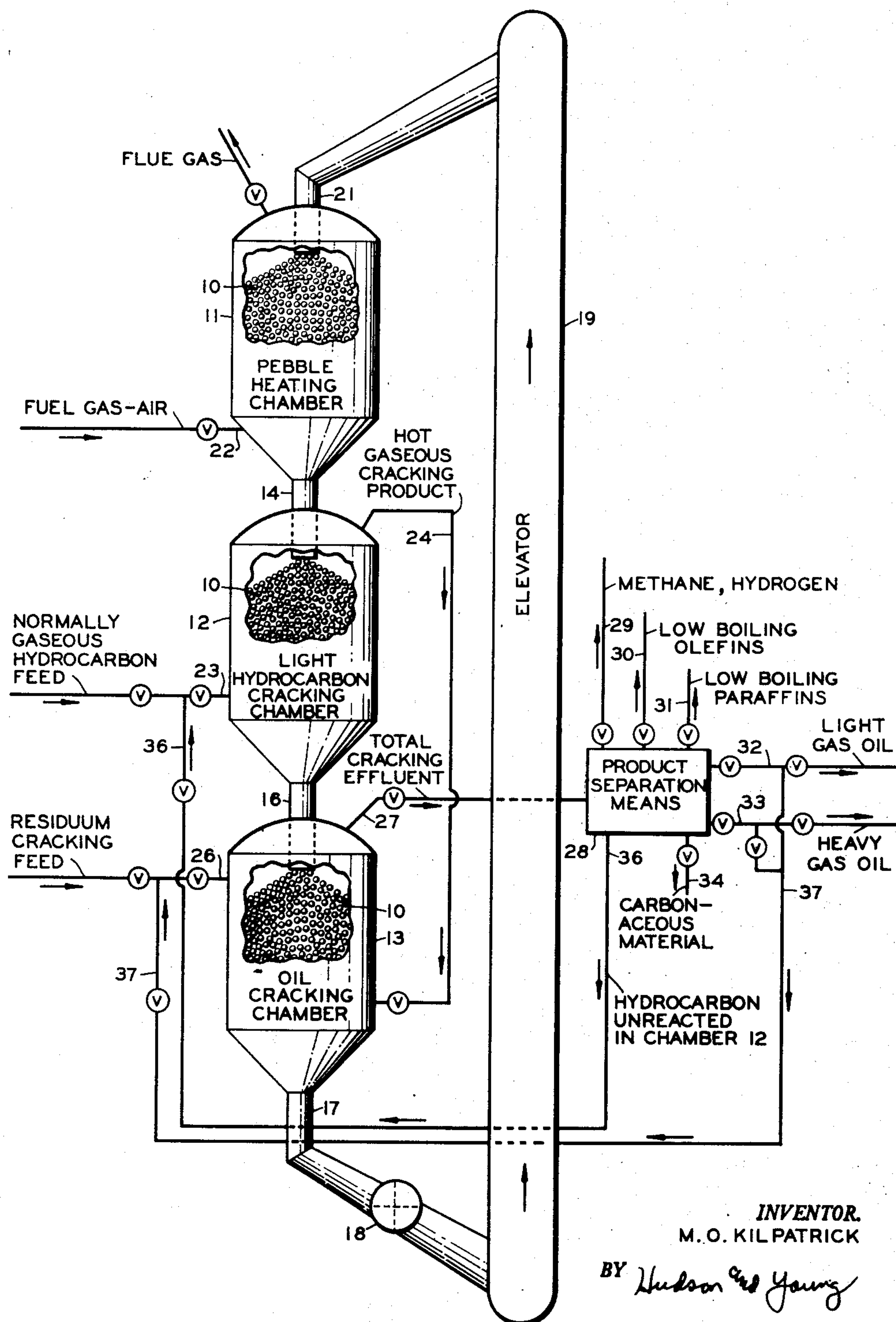


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M. O. KILPATRICK
HYDROCARBON CONVERSION

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HYDROCARBON CONVERSION

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This invention relates to the conversion of hydrocarbons. In one embodiment this invention relates to a combination conversion process for reacting low-boiling hydrocarbons and higher boiling hydrocarbons in a single conversion system. In another embodiment this invention relates to a combination process for cracking normally gaseous hydrocarbons and oil residuum stocks.

Hydrocarbon oil residuum stocks are by-product heavy residual or bottoms fractions obtained from distillation of crude petroleum, or resulting from certain refining operations. When further treatment of these stocks is attempted such as distillation or cracking, or the like, excessive decomposition of the heavy material to carbon or carbon-rich materials generally occurs, resulting in the rapid accumulation of carbonaceous deposits in the treating system and necessitating shut-down of equipment after short operating periods. Such short operating periods are uneconomical from the standpoint not only of the cost of shutting down and subsequently starting up, but also with respect to the time and manpower requirements for removing the carbonaceous deposits and for readying the equipment for start-up.

Various processes have been proposed in the art for the thermal conversion, or cracking, of light hydrocarbons, particularly normally gaseous hydrocarbons. Such a conversion reaction is highly endothermic and requires a large input of heat at high temperature. Cracking effluent is withdrawn from the conversion zone and cooled prior to recovery of the desired products formed. Although this type of operation is suitable in many instances, the heat carried from the conversion system in the effluent is often inefficiently recovered.

The use of pebble heater apparatus has been proposed by many workers in the art as providing numerous advantages over other known means for cracking hydrocarbons, particularly for the reason that high cracking temperatures can be provided together with accurately controlled contact times to provide the desired cracking product in selectively high yield.

The term "pebble," as used throughout the specification, denotes any solid refractory material of flowable form and size that can be utilized to carry heat from one zone to another. Pebbles are preferably substantially spherical and are about $\frac{3}{8}$ inch to 1 inch in diameter, the preferred range being about $\frac{1}{4}$ to $\frac{1}{2}$ inch. Pebbles are formed of a refractory material which will

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withstand temperatures at least as high as the highest temperature obtained in the pebble heating chamber, and must be capable also of withstanding temperature changes within the apparatus. Refractory materials, such as metal alloys, ceramics, and other satisfactory materials, can be utilized to form pebbles. Silicon carbide, alumina, periclase, thoria, beryllia, Stellite, zirconia, and mullite, may be satisfactorily used to form such pebbles or may be used in admixture with each other or with other materials. Pebbles formed of such materials, when properly fired, serve very well at high temperatures. Some pebbles withstand temperatures up to about 3500° F. Pebbles which are used may be either inert or catalytic as used in any selected process.

A pebble heater system, or pebble heater apparatus, as it is often referred to, usually comprises a series of substantially vertically extending zones, often in vertical alignment with each other and connected by relatively narrow interconnecting zones or throats. Generally, the top or upper zone is employed as a pebble heating zone or chamber, and the succeeding lower zones as conversion zones, cooling zones, or the like, as required in the specific process. A combustion zone or chamber is often positioned adjacent or in close proximity to the sides of the lower portion of the pebble heating zone, and hot combustion gas formed in the combustion chamber is passed through the mass of pebbles in the pebble heating zone in heat exchange relation with the cooler pebbles therein. A hot gas source other than a combustion chamber is sometimes employed.

My process can be used to convert normally liquid hydrocarbons, i. e., pentanes and higher boiling hydrocarbons, preferably light gas oils and high boiling hydrocarbon materials such as heavy gas oils, fuel oils, crude residua, and the like. Production of aromatics and olefins, particularly ethylene, is high when ethane and/or propane are cracked in the first cracking zone, and a heavy gas oil, fuel oil, or crude residuum is converted in the second cracking zone in accordance with the process of my invention; these oils each having a boiling range preferably above 700° F.

With reference to the attached drawing, one embodiment of the process of my invention will be specifically disclosed. The figure is a diagrammatic illustration of one form of apparatus in which my process can be practiced. It is to be understood that this flow diagram is diagrammatic only and can be altered in many respects

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by those skilled in the art, and yet remain within the scope of my invention.

Referring to the figure, a fluent mass of pebbles 10 substantially filling pebble heating chamber 11, light hydrocarbon cracking chamber 12, and oil cracking chamber 13, and interconnecting throats 14 and 16, is passed by gravity through these chambers and through pebble outlet conduit 17 in the bottom of chamber 13, and through pebble flow control means, or star valve 18, to elevator 19. Elevator 19 transfers pebbles from valve 18 to pebble inlet conduit 21 in the top of chamber 11, for recirculation through the pebble system. By regulation of valve 18, a moving contiguous column of pebbles is maintained throughout the apparatus from conduit 21 to star valve 18.

A combustible fuel-oxygen mixture, such as a mixture of natural gas and air, is introduced into pebble heating chamber 11 through line 22 and burned therein on the surfaces of pebbles in pebble mass 10. Sufficient free oxygen is present in the combustible gas mixture introduced through line 22 for the purpose of burning carbonaceous matter from the surfaces of pebbles reintroduced by elevating means 19, into chamber 11, as described hereafter. Hot combustion gas formed from burning the combustible fuel mixture in chamber 11 is passed upwardly there-through in countercurrent flow to, and heat exchange relation with pebbles, to heat them to a temperature above a predetermined cracking temperature required in cracking chamber 12. Generally, the cracking temperature in chamber 12 is within the limits of from 1300 to 2200° F., and the temperature to which pebbles are heated in chamber 11 is generally from 100 to 300° F. above that cracking temperature.

A normally gaseous hydrocarbon to be cracked in chamber 12 is introduced thereinto at a point in a lower portion, through line 23 and contacted in countercurrent flow relation with pebbles in mass 10 previously heated in chamber 11. In this manner, hydrocarbon feed from line 23 is heated in chamber 12 to the requisite cracking temperature, and converted to cracking-product. Pebbles thus contacted with hydrocarbons in chamber 12 are cooled, as a result of the heat exchange, to a temperature generally from 200 to 800° F. below the temperature at which they are introduced into chamber 12. Hot gaseous cracking product is withdrawn from chamber 12 at a point in an upper portion thereof through line 24 and introduced into chamber 13 at a point in a lower portion thereof and contacted in countercurrent flow, and heat exchange relation with pebbles in mass 10, previously utilized in chamber 12 and cooled as already described. Hydrocarbon oil cracking feed is introduced into chamber 13 through line 26 and contacted therein in concurrent flow relation with pebbles in mass 10. Operating in this manner, heat carried from chamber 12 in the gaseous effluent is utilized in cracking chamber 13 to heat pebbles and oil therein, to a requisite temperature, to crack the oil. Hot effluent from chamber 12 is thereby quickly quenched. Furthermore, the partial pressure of oil vapors formed in chamber 13 is reduced by the presence of effluent gases from chamber 12, and the amount of coke formation in chamber 13 is minimized, thus providing for an increase in the efficiency of the oil cracking reaction.

A contiguous mass of flowable particulate contact material, or pebbles, fills the pebble heating zone and each of the succeeding zones together

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with the interconnecting zones or throats, and flows downwardly through these zones by gravity. Pebbles are discharged from the bottom of the lowermost zone of the series, at a controlled rate, and returned, usually by elevating means, into the upper portion of the pebble heating zone.

Pebble heater apparatus is generally employed in the thermal treatment or conversion of hydrocarbon materials. Operation of such a pebble system generally involves circulating a contiguous pebble mass through the entire series of pebble zones, including the interconnecting throats. That portion of the pebble mass descending through the heating chamber is heated to a suitable predetermined temperature above a desired conversion temperature in heat exchange relation with combustion gas or other hot gases from any desired source. Pebbles are often heated in the heating chamber to temperatures as high as from 2,000 to 3,000° F., and in some cases higher, dependent upon the temperature requirements of the subsequent treating steps. The pebbles thus heated are contacted directly with one or more materials to be treated in one or more zones of the pebble heating system under suitable time and temperature conditions to effect the desired treatment. The pebble mass, having given up heat to the material or materials treated, descends through the bottom of the lowermost pebble zone, and is fed to an elevator for further handling, generally for transfer to an inlet at the top of the pebble heating chamber for reheating and recirculation through the system.

In introducing an oil residuum feed into contact with a mass of pebbles, great difficulty is experienced in uniformly contacting all the pebbles in the mass, so that each pebble is coated with oil. Instead, disproportionately large amounts of oil reach only a relatively small part of the hot pebble mass, with the result that a considerable amount of the oil thus introduced moves as a free flowing liquid through a limited portion of the pebble mass, while the uncontacted portion of the pebble mass passes through the system unutilized. Considerable coking of the free-flowing oil to form carbonaceous by-products takes place, thus reducing efficiency of the conversion to a level not economically feasible. Furthermore, agglomeration of pebbles and carbonaceous by-product thus formed takes place with the result that pebble circulation through the pebble system is impaired, and often stopped entirely. Agglomeration of carbonaceous matter and pebbles is, of course, undesirable, since the pebble system must then be shut down for an extended period for removal of the agglomerate and for readying the equipment for re-start-up.

My invention is concerned with a combination process for converting normally gaseous hydrocarbon materials and normally liquid hydrocarbon materials, and with the utilization of a contiguous mass of solid particulate heat transfer materials moving through a plurality of contacting chambers, in carrying out such a process. My invention provides for an economic recovery of heat carried in the effluent from a normally gaseous hydrocarbon cracking zone, and for utilization of that cracking effluent in distributing a heavier hydrocarbon feed uniformly onto the surfaces of solids particles in a hydrocarbon conversion zone.

An object of my invention is to provide for the conversion of hydrocarbons.

Another object is to provide a combination process for converting low-boiling normally gas-

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eous hydrocarbon materials and higher boiling normally liquid hydrocarbon materials, and for the utilization of a pebble heater system in conducting such a combination process.

It is another object to provide a combination thermal conversion process for the conversion of low-boiling hydrocarbons, such as methane, ethane, propane, and butanes, and higher boiling normally liquid hydrocarbon materials, such as gas oils, fuel oils, crude residuum, and the like.

It is another object to provide a process for cracking oil residuum stocks in a pebble heater system and for continuously removing carbon and carbon-rich materials from the system, formed therein as by-products of the cracking.

Another object is to provide a process for cracking an oil residuum in a pebble heater system, wherein oil is introduced into contact with pebbles in a manner that it uniformly coats the pebbles, and carbonaceous by-product of said conversion is continuously removed from the pebble system, on the pebble surfaces.

Another object is to provide for an efficient recovery of heat carried in a gaseous effluent from a hydrocarbon cracking chamber.

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

In accordance with one embodiment of my invention, normally gaseous hydrocarbon materials and higher boiling normally liquid hydrocarbon materials are cracked in a pebble heater system comprising a pebble heating zone, a first cracking zone positioned below the pebble heating zone, and a second cracking zone positioned below the first cracking zone; a contiguous mass of pebbles is passed by gravity through the series of downwardly extending zones, thus filling the system with a contiguous moving mass of pebbles. Pebbles in the pebble heating zone are heated in any desired manner, preferably by introducing a combustible fuel-oxygen mixture into the heating zone and then burning it, and passing the resulting hot combustion gas upwardly through the pebbles to heat them to a temperature, above a cracking temperature required in the first cracking zone.

In the first cracking zone, that portion of the pebble mass previously heated in the pebble heating zone is contacted with a normally gaseous hydrocarbon, to heat that hydrocarbon to a cracking temperature, and to crack it. Pebbles in the first cracking zone lose heat to the cracking reaction and are concomitantly cooled to a temperature generally from 200 to 800° F. lower than their maximum initial temperature. Gaseous effluent from the first cracking zone, referred to hereafter as hot gaseous cracking product, is discharged at about the maximum cracking temperature therein, generally within the limits of 1300 and 2200° F. A hydrocarbon oil to be cracked, is introduced into the second cracking zone and passed concurrently therein with that portion of the pebble mass, previously utilized in the first cracking zone. The temperature of pebbles thus entering the second cracking zone is too low to provide heat at the necessary high temperature for cracking the oil contacted therewith, which oil-cracking temperatures are generally from about 800 to 1400° F., or in some cases higher. High temperature heat for cracking the oil in the second cracking zone is provided by passing hot gaseous cracking product, withdrawn from the first cracking zone, into the second cracking zone, in heat exchange and

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countercurrent flow relation with oil and pebbles therein. The temperature of hot cracking product withdrawn from the first cracking zone is from 200 to 800° F. higher than the temperature of pebbles introduced into the second cracking zone, and the temperature of the resulting pebble-hot gaseous cracking product mixture therein is above the required temperature for cracking the oil. The oil in the second cracking zone is heated to its cracking temperature in heat exchange relation with the resulting hot pebble-cracking product mixture, and cracked. Effluent products from the pebble heater system are withdrawn from the second cracking zone and passed to a conventional product recovery system for separation and recovery of desired cracking product.

Preferred low-boiling normally gaseous hydrocarbons which can be converted or cracked in the process of my invention are paraffinic hydrocarbons having from 1 to 4 carbon atoms in the molecule, as methane, ethane, propane, and butanes. Ethane and/or propane can be respectively converted to ethylene and/or ethylene and propylene at high temperatures, low pressures, and short contact times. Methane conversion to produce hydrogen under similar conditions of time, pressure, and higher temperature is readily accomplished.

Total cracking effluent, i. e., total cracking product, formed both in chambers 12 and 13 is withdrawn from chamber 13 through effluent line 27 and passed to product separation means 28 comprising distillation equipment, solvent extraction equipment, storage, and the like, well-known in the art for conducting a separation and recovery of products from such a cracking effluent as withdrawn from chamber 13 through line 27, and not individually illustrated. From product separation means 28 are withdrawn a light gas fraction comprising methane and hydrogen through line 29, low-boiling olefins such as ethylene, propylene, butylene, or mixtures thereof through line 30, low-boiling paraffins through line 31 including any unreacted feed to chamber 12, a light gas oil fraction through line 32, and a heavier gas oil fraction through line 33. Any small carbonaceous particles and any high-boiling by-product materials suspended in the gaseous effluent in line 27 are separated in zone 28 and withdrawn through line 34. If desired, unreacted feed to chamber 12 can be separated in zone 28 and withdrawn through line 36 instead of through line 31, and recycled to line 23 for return to cracking chamber 12. Similarly, if desired, an oil cracking stock recovered in chamber 28 and withdrawn through either lines 32 or 33, or both, can be recycled for further cracking to chamber 13 through line 26, from line 37.

In the operation of the process of my invention, oil introduced into chamber 13 is caused to uniformly coat the surfaces of pebbles contacted therewith as a result of the turbulence and intermingling in chamber 13 of gases from line 24, with pebbles and oil. Any oil tending to flow downwardly as a free liquid through chamber 13 is "blown" among pebbles in the mass 10 therein until oil thus introduced has finally contacted a sufficient portion of the pebble mass 10 to uniformly coat the pebble surfaces. As provided by my process, agglomeration of the type discussed is prevented, for the reason that no large chunks or bodies of carbon are formed and accordingly, the process is maintained over long operating pe-

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riods as desired without interruption resulting from coking in chamber 13.

Upon initial contact of oil with pebbles in chamber 13, some of the lowest boiling components of the oil may be immediately vaporized, in which case these vapors are withdrawn along with cracking product through line 27. Heavier oil components remaining on the hot pebble surfaces are converted as the pebble mass moves downwardly through chamber 13 as a function of the increased residence time in the pebble mass. As the pebble mass moves downwardly in chamber 13, the more refractory feed components remaining on the pebble surface are gradually converted to desired product as a function of the prolonged residence time. Finally, as pebbles approach the pebble discharge point, i. e. discharge conduit 17, the refractory carbonaceous by-product remaining on the surfaces is substantially "dry" as a result of the reaction of substantially all reactive components on the pebble surfaces to form cracking product. Pebbles introduced into elevator 19 carry the "dry" carbonaceous matter from the conversion chamber, adhered to their surfaces, and are recycled to heating chamber 11 where they are reheated and burned free of the adhered carbonaceous matter, as discussed above, and then recirculated through the pebble system.

I find that when regulating the ratio of pebbles introduced into chamber 13 to oil feed introduced thereinto through line 26, in a manner that the amount of oil introduced does not exceed the maximum amount that can be coked to dryness in chamber 13, no agglomeration takes place. Such a ratio is, of course, dependent upon the type of oil feed utilized, as well as the characteristics of the specific pebble material utilized, such as pebble surface, specific heat, and the like. In general, however, I find that by regulating the weight ratio of pebbles to oil feed introduced into chamber 13 to a value equal at least to 14:1, adequate pebble surface is available for absorbing the total oil introduced, and for preventing the occurrence of free flowing liquid through the pebble mass with the concomitant undesirable coking and agglomeration. Any higher weight ratio of pebbles to oil may be employed. However, I find that when employing such a weight ratio exceeding about 30:1, the heat from the cracked gases is not efficiently utilized.

My process provides numerous advantages in addition to those above discussed. In the first place, heat carried from the cracking chamber 12 in gaseous effluent through line 24 is generally utilized in various heat exchange steps, often in an inefficient manner. However, as provided by my invention, that heat is efficiently utilized to heat pebbles and oil in chamber 13, and thereby to crack the oil feed to the desired cracking product. The hot gaseous product from chamber 12 is not only quenched, but reduces the partial pressure of the oil vapors in chamber 13 and causes the oil and pebbles to be uniformly contacted as a result of the "blowing" effect of the countercurrently flowing gases distributing the oil among the mass until no more free flowing oil is present. In this manner, carbonaceous by-product inherently formed in such a cracking reaction in chamber 13 is uniformly deposited on the pebble surfaces and is continuously and completely carried from chamber 13 and introduced into heating chamber 11, being further utilized as fuel, in chamber 11, to provide the required hot heat exchange gases therein. Or-

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dinarily, carbonaceous by-product formed in cracking heavy oils is not further usable. Inherently, with the utilization of carbonaceous by-product in this manner, pebbles are reconditioned, i. e. burned free of carbon, and reheated, for recirculation through the pebble system to maintain the combination cracking process of my invention on a continuous basis over an operating period of any desired duration.

My invention provides for increased yields of oil cracking product by virtue of the uniform pebble-oil coating that takes place as above described. The more refractory oil feed components can be reacted as a function of the prolonged residence time of the feed coated pebbles in the cracking chamber, so that the only carbonaceous by-product remaining is the dry by-product, having a high content of elemental carbon.

In conducting the process of my invention, I can crack ethane in cracking chamber 12 at a pressure of from 5 to 40 p. s. i. a., a temperature of from 1300 to 2200° F., preferably 1500 to 1900° F., and for a contact time of from 0.001 to 1 second, preferably from 0.05 to 0.2 second. If propane, or propane and ethane are cracked in chamber 12, similar conditions can be employed, as for example, a pressure of from 5 to 40, more preferably from 5 to 25 p. s. i. a., a temperature of from 1200 to 2000° F., more preferably from about 1400 to 1800° F., and a contact time of from 0.02 to 0.15 second, preferably 0.07 to 0.5 second. Similar, but somewhat milder conditions can be employed in chamber 12 when cracking butanes, as for example, a temperature within the limits of about 1000 to 1600° F., a pressure of from 5 to 40 p. s. i. a., and a contact time of from 0.01 to 0.10 second.

In the conversion of the oil feed in cracking chamber 13, I prefer an operating pressure of from 5 to 40, preferably from 5 to 25 p. s. i. g., a temperature of from 950 to 1600° F., preferably 1100 to 1400° F., and a reaction time of from 0.2 to 3.5 seconds, preferably from 1 to 2 seconds.

Although I have indicated product separation means 28 diagrammatically, it is to be understood that zone 28 includes means for quenching the combined effluents discharged from chamber 13 through conduit 27 to a temperature of 900° F. or less, preferably to a lower temperature within the limits of 525 to 725° F.

Advantages of this invention are illustrated in the following example. The reactants and their proportions and their specific ingredients are presented as being typical and should not be construed to limit the invention unduly. The example is presented with reference to the attached drawing.

Ethane is introduced into cracking chamber 12 and cracked at a rate of 70,000 standard cubic feet per hour at a temperature of 1850° F. for a contact time of 0.05 second. A 10 degree API reduced crude is preheated to a temperature of 900° F. and introduced into chamber 13 at a point in an upper portion thereof at a rate of 680 barrels per day. Pebbles are passed by gravity through the oil cracking chamber 13 in a weight ratio to reduced crude introduced thereinto of about 20:1. Total gaseous effluent is withdrawn from the ethane cracking chamber 12 and introduced into the oil cracking chamber 13 at a point in the lower portion thereof and passed countercurrently therein with respect to oil and pebbles. The temperature of total gaseous effluent thus introduced into

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chamber 13 is about 1800° F., and pebbles introduced thereinto are at a temperature of about 1000° F. Pebbles and oil are heated in heat exchange relation with hot gases from chamber 12 to a temperature of 1250° F. The reaction time is 1.5 seconds.

The ethane conversion in chamber 12 is maintained at a pressure slightly higher than that of the oil conversion in chamber 13, the latter taking place at about 2 p. s. i. g. Pebbles discharged from the oil cracking chamber 13 are at a temperature of about 1000° F., dependent largely upon the location of the point of introduction of hot gases into chamber 13, i. e. the higher the point of introduction of hot gases the lower the temperature of the discharged pebbles. It is advantageous that the point of introduction be somewhat above the bottom end of the oil cracking chamber to permit additional residence time of the feed-coated pebbles in chamber 13 subsequent to initial contact thereof with hot gases. In this manner, extended time is provided for cracking any remaining highly refractory oil feed components.

The combined cracking effluents are withdrawn from the oil cracking chamber and quenched to a temperature of 705° F. in heat exchange relation with a refractory quench oil, or water.

Products resulting from the combination of ethane and reduced crude cracking are summarized in the table herebelow. In the first column of the table are presented total production of cracking product in terms of pounds per day as obtained in accordance with the process of my invention; in the second column are presented total production when cracking ethane only.

	Total Production, pounds/day	Production from Ethane Cracking Only, pounds/day
Hydrogen.....	8,500	8,000
Methane.....	23,100	14,800
Acetylene.....	7,600	7,600
Ethylene.....	100,900	79,500
Ethane.....	10,000	7,800
Propylene.....	12,600	1,500
Propane.....	1,100	100
Butadiene.....	9,000	4,500
Butylenes.....	4,900	400
Butane.....	800	100
Light Oils ¹	68,600	8,700
Heavy Tar.....	89,300	
Coke.....	34,600	
	371,000	133,000

¹ Relatively rich in aromatics.

My process is flexible in a considerable degree. I find that by decreasing the heavy oil feed rate, larger amounts of olefinic hydrocarbons and smaller amounts of liquid products are produced.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of this disclosure and discussion, without departing from the spirit or scope of this disclosure or from the scope of the claims.

I claim:

1. A combination process for cracking normally gaseous hydrocarbon materials and higher boiling normally liquid hydrocarbon materials, comprising gravitationally passing a flowable contiguous mass of solid particulate material through a series of zones comprising a solids heating zone, a first cracking zone positioned below said solids heating zone, and a second crack-

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ing zone positioned below said first cracking zone; introducing a combustible fuel mixture containing sufficient oxygen for utilization described hereafter into said solids heating zone and therein burning said fuel; passing hot combustion gas formed by said burning in countercurrent flow and heat exchange relation with that portion of said solids mass in said heating zone to heat same to a predetermined temperature above a cracking temperature to be utilized in said first cracking zone; introducing a normally gaseous hydrocarbon into said first cracking zone and therein heating same to said cracking temperature to form cracking product in countercurrent flow and heat exchange relation with a portion of said solids mass heated as above described; introducing a hydrocarbon oil in the liquid phase into said second cracking zone in concurrent flow relation therein with a portion of said solids mass previously utilized in said first cracking zone; the temperature of the solids entering said second cracking zone being too low to effect substantial cracking of said oil; withdrawing hot gaseous effluent from said first cracking zone and introducing same into said second cracking zone in countercurrent flow and heat exchange relation with said oil and said solids mass therein, whereby oil and solids in said second cracking zone are heated, and oil is uniformly distributed therein on the surfaces of said solids, and gaseous cracking product in said effluent is quenched; the temperature of the resulting solids-gaseous effluent admixture in said second cracking zone being above that required for cracking said oil, whereby said oil on the solids surfaces is cracked and resulting carbonaceous by-product is uniformly deposited on said surfaces; withdrawing solids coated with said carbonaceous by-product from said second cracking zone, and passing same to said solids heating zone; in said solids heating zone burning said carbonaceous by-product with oxygen introduced with said combustible mixture as above described, whereby said carbonaceous by-product is efficiently utilized as fuel to produce hot heat exchange gas in said heating zone and solids are reconditioned for recirculation through said zones, and recovering effluents of cracking from said second cracking zone.

2. A combination process for cracking a normally gaseous hydrocarbon and a higher boiling normally liquid hydrocarbon, comprising passing a contiguous mass of pebbles through a series of zones comprising a pebble heating zone, a first cracking zone positioned below said pebble heating zone, and a second cracking zone positioned below said first cracking zone; passing a hot gas in countercurrent flow and heat exchange relation with that portion of said pebble mass in said heating zone to heat same to a temperature above that required for cracking a normally gaseous hydrocarbon; introducing a normally gaseous hydrocarbon into said first cracking zone and therein cracking same in countercurrent flow and heat exchange relation with pebbles heated as described above; introducing a hydrocarbon oil in the liquid phase into concurrent flow relation with pebbles in said second cracking zone; the temperature of the pebbles entering said second cracking zone being too low to effect substantial cracking of said oil; withdrawing hot gaseous effluent from said first cracking zone and introducing same into said second cracking zone in countercurrent flow and heat exchange relation with said oil and

pebbles therein; the temperature of the resulting pebbles-gaseous mixture in said second cracking zone being above that required for cracking said oil, whereby said oil is cracked; withdrawing pebbles from said second cracking zone; and recovering gaseous effluents of cracking from said second cracking zone.

3. The process of claim 2 wherein said oil is a petroleum residuum having a boiling range above 700° F.

4. The process of claim 2 wherein said oil is a gas oil.

5. The process of claim 2 wherein said normally gaseous hydrocarbon contains from 2 to 3 carbon atoms in the molecule.

6. The process of claim 2 wherein said oil is preheated prior to introduction of same into said second cracking zone.

7. A combination process for cracking a normally gaseous hydrocarbon and a hydrocarbon oil, comprising gravitationally passing a contiguous mass of pebbles through a series of zones comprising a pebble heating zone, a first cracking zone and a second cracking zone; introducing a combustible fuel mixture capable of burning to produce combustion gas at a temperature within the limits of 1400 to 3000° F. and containing sufficient oxygen for utilization described hereafter into said solids heating zone and therein burning said fuel; passing hot combustion gas formed by said burning in countercurrent heat exchange relation with that portion of said pebble mass in said heating zone to heat said mass therein to a temperature of from 100 to 300° F. above a cracking temperature within the limits of 1300 to 2200° F. to be utilized in said first cracking zone; introducing a normally gaseous hydrocarbon into said first cracking zone and therein cracking same in countercurrent flow and heat exchange relation with a portion of said pebble mass previously heated in said heating zone as described above; pebbles in said first cracking zone giving up heat to said cracking and being passed from said first cracking zone to said second cracking zone at the incipient cracking temperature of said oil; introducing a hydrocarbon oil in the liquid phase into said second cracking zone in concurrent flow relation therein with pebbles from said first cracking zone; withdrawing hot gaseous effluent from said first cracking zone at the maximum gas temperature therein; introducing said hot gaseous effluent into said second cracking zone in countercurrent flow and heat exchange relation with said oil and said pebbles therein to uniformly distribute liquid oil on said pebbles and to heat said oil and crack same at a temperature within the limits of 800 to 1600° F.; carbonaceous by-product from oil cracking in said second cracking zone being formed as a uniform coating on pebble surfaces therein; withdrawing pebbles from said second cracking zone containing adhered carbonaceous by-product of oil cracking, and passing same to said pebble heating zone; burning said carbonaceous by-product in said heating zone with oxygen introduced with said combustible mixture as above described; and recovering gaseous effluents from said second cracking zone.

8. A combination process for cracking a normally gaseous hydrocarbon and a hydrocarbon

oil, comprising cracking a normally gaseous hydrocarbon in countercurrent flow and heat exchange relation with hot pebbles in a first cracking zone, introducing a hydrocarbon oil in the liquid phase and pebbles from said first cracking zone in concurrent flow relation into a second cracking zone, said pebbles entering said second cracking zone at a temperature too low to effect substantial cracking of said oil, withdrawing hot gaseous effluent from said first cracking zone and introducing same into countercurrent flow relation with liquid oil and pebbles in said second cracking zone to heat said oil and crack same, and recovering product of cracking from said second cracking zone.

9. A combination process for cracking ethane and a petroleum residuum stock, comprising passing a contiguous mass of pebbles through a series of zones comprising a pebble heating zone, a first cracking zone positioned below said pebble heating zone, and a second cracking zone positioned below said first cracking zone; passing a hot gas in countercurrent flow and heat exchange relation with that portion of said pebble mass in said heating zone to heat same to a temperature from 100 to 300° F. above a cracking temperature to be employed in said first cracking zone and selected from within the limits of from 1300 to 2200° F.; introducing ethane into said first cracking zone and cracking same therein in countercurrent flow and heat exchange relation with pebbles heated in said heating zone as described; preheating a hydrocarbon residuum oil having a boiling range above 850° F. to a temperature within the limits of 800 to 1400° F. and introducing the preheated oil in the liquid phase into concurrent flow relation with pebbles in said second zone; said pebbles entering said second zone at the incipient cracking temperature of said oil; maintaining a ratio of pebbles to oil introduced into said second zone within the limits of 14:1 to 30:1; withdrawing hot gaseous effluent from said first cracking zone and introducing same into said second cracking zone in countercurrent flow and heat exchange relation with said oil and pebbles therein; the temperature of the resulting pebbles-gaseous effluent mixture in said second cracking zone being above that required to crack said oil at a temperature within the limits of 800 to 1400° F., whereby said oil is cracked; withdrawing pebbles from said second zone containing carbonaceous by-product of oil cracking on their surfaces and returning pebbles thus withdrawn to said pebble heating zone; in said heating zone burning said carbonaceous by-product free from said pebble surfaces; and recovering olefins and aromatic hydrocarbons from effluent of said second cracking zone as products of the process.

MYRON O. KILPATRICK.

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