

May 29, 1973

J. B. JONES, JR., ET AL

3,736,247

RETORTING OF SOLID CARBONACEOUS MATERIAL

Filed Nov. 1, 1971

3 Sheets-Sheet 1

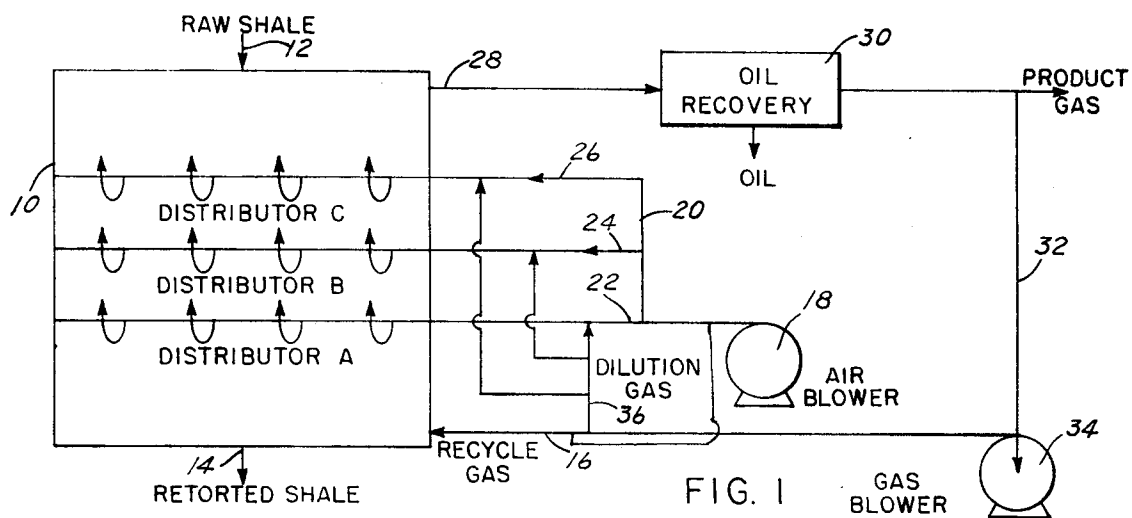


FIG. 1

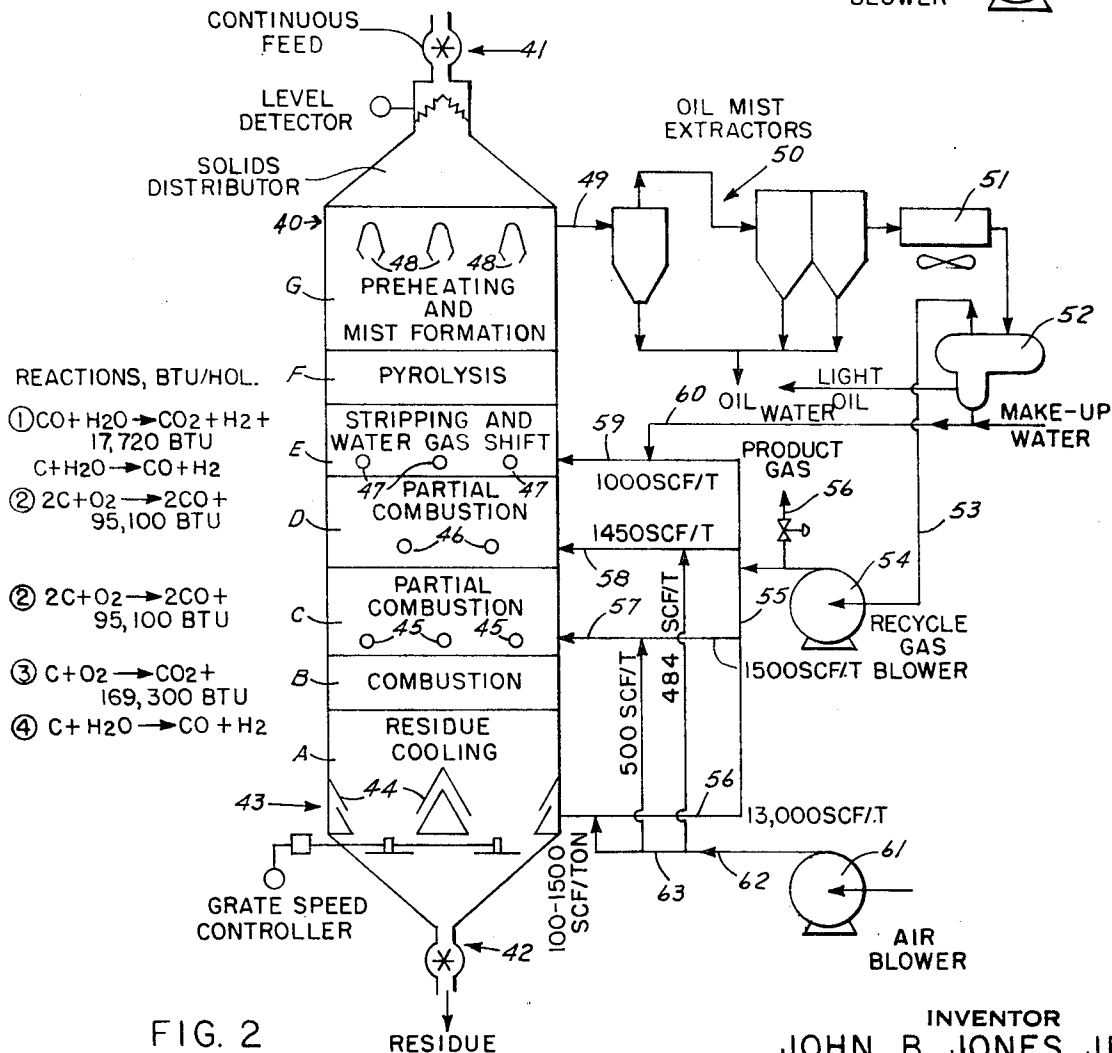


FIG. 2

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3 Sheets-Sheet 2

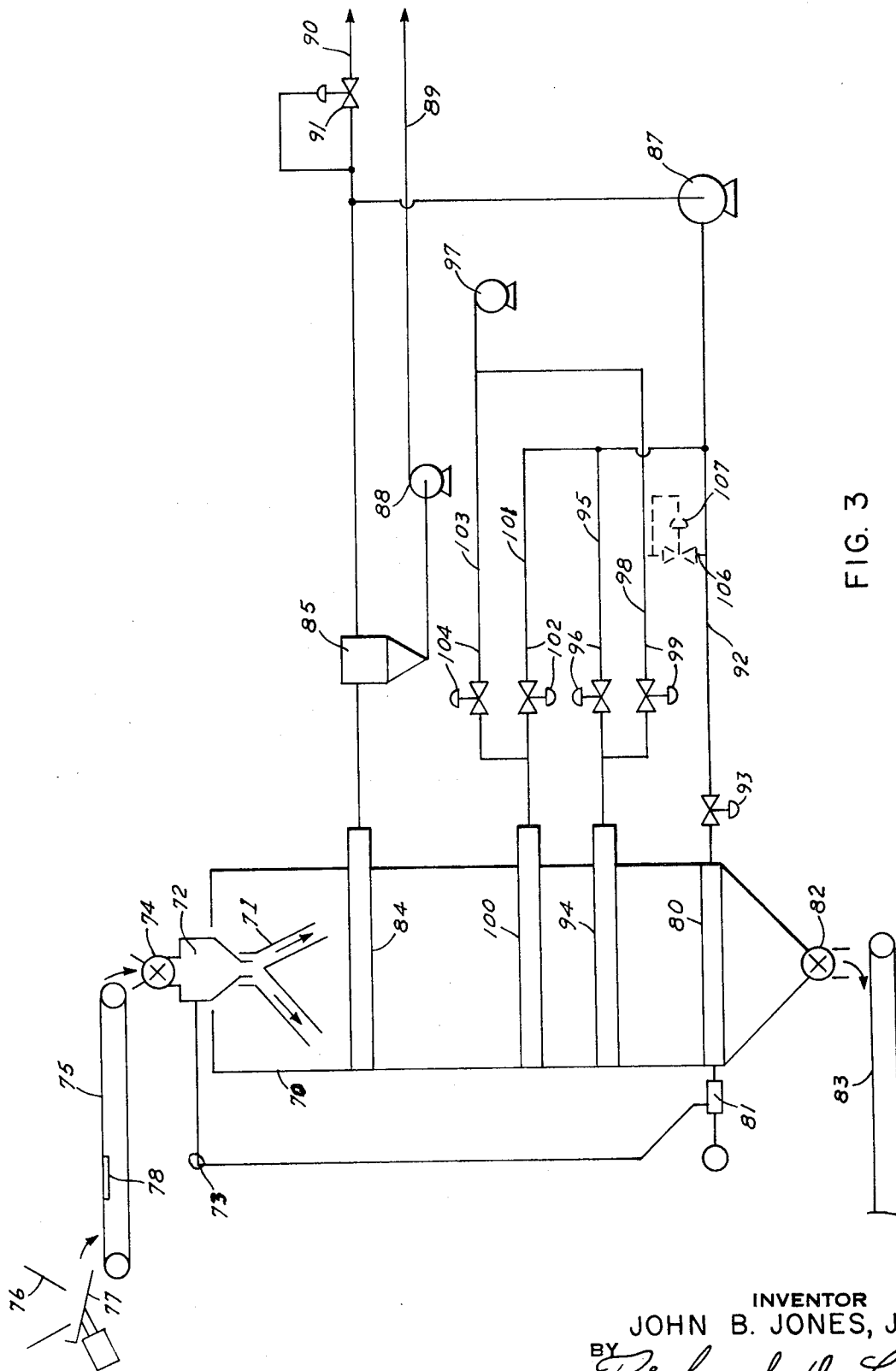


FIG. 3

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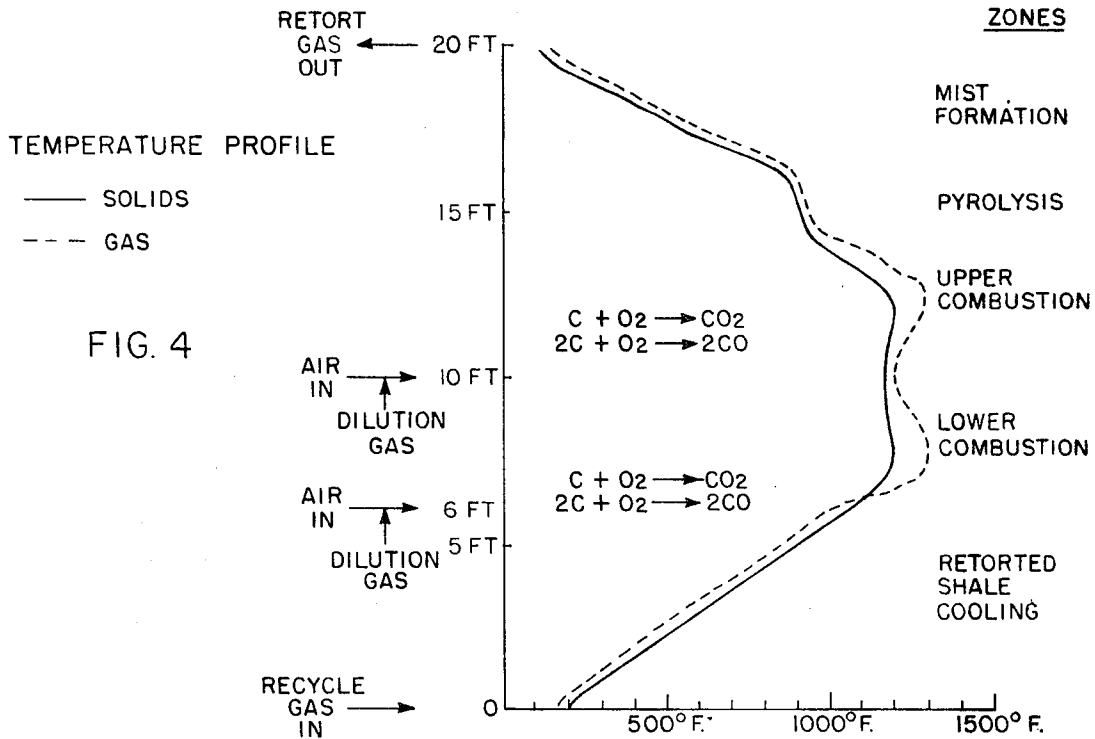
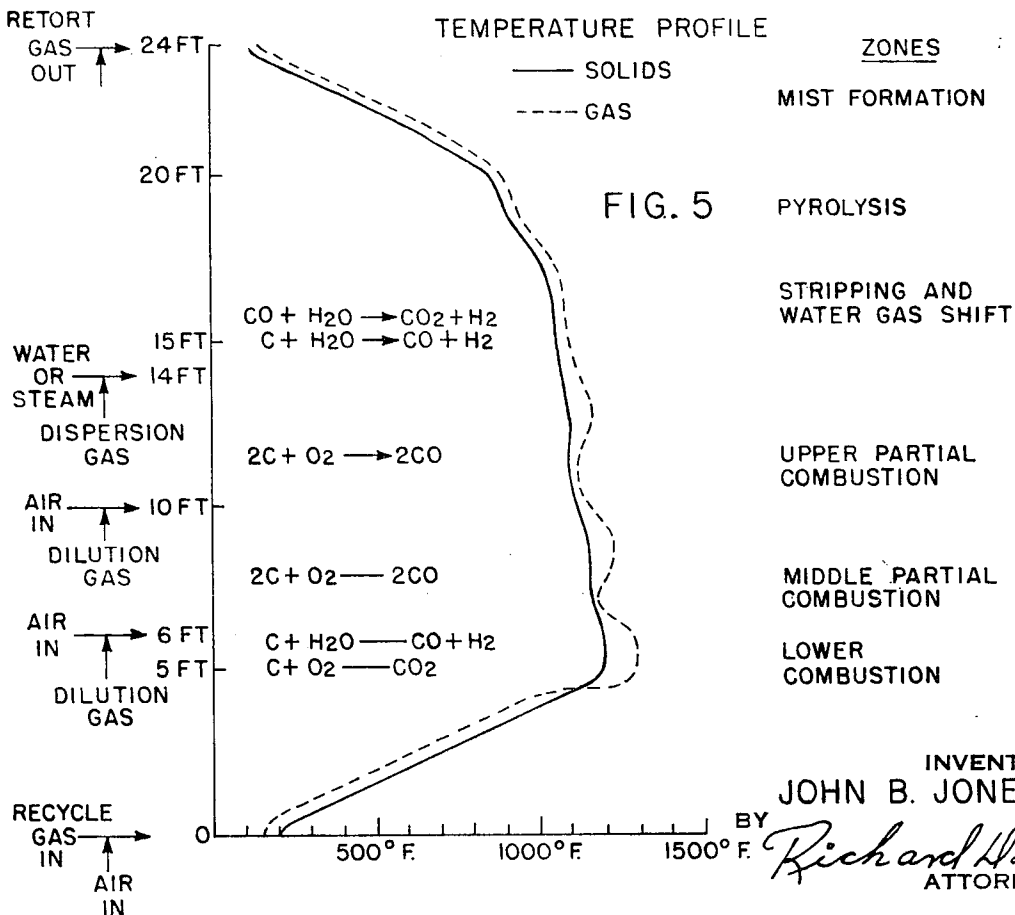
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RETORTING OF SOLID CARBONACEOUS MATERIAL

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3 Sheets-Sheet 3



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RETORTING OF SOLID CARBONACEOUS MATERIAL

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17 Claims

ABSTRACT OF THE DISCLOSURE

A process for the destructive distillation of the organic material in solid hydrocarbonaceous material in shaft vessels having a pulverulent solid moved downwardly in a continuous column through successive zones of pre-heat, destructive distillation, residue stripping, and water-gas shift, controlled combustion of carbonaceous residue at one or more levels of injection of an oxygeneous gas, and finally cooling and withdrawing the solid through a heat recovery zone. The gas stream leaving the top of the vessel is only slightly above the temperature of the entering hydrocarbonaceous material, generally providing a mist of oil droplets entrained in the gas stream.

Certain sedimentary rocks, commonly referred to as oil shale, on destructive distillation will yield a condensable liquid which is referred to as a crude oil and non-condensable gaseous hydrocarbons. The condensable liquid may be refined into products which resemble petroleum products. Extensive deposits of oil shale are found in the western part of the United States, particularly in Colorado, Utah, and Wyoming. However, oil shale deposits are found in many other parts of the world.

Other types of carbonaceous materials, both as an inclusion in rock, shale, sand, etc., or as a relatively low gangue content carbonaceous material, are treated in a heating process for the recovery of valuable products. Such materials as coal, tar, tar sands, asphalts, peat, and the like are amenable to heating processes, to produce gaseous as well as hydrocarbonaceous liquids.

In its fundamental aspects, the destructive distillation of oil shale, or other solid hydrocarbonaceous materials, appears to be a relatively simple operation. The process involves heating the solid material to a proper temperature and recovering the products which are emitted. In practical application, however, this apparently simple operation has not achieved a large scale commercial application, primarily due to economy and efficiency of the process. It is seen that two principal engineering problems are connected with the destructive distillation of oil shale on a large scale, and these include the material handling and the heat exchange to produce the proper distillation temperature in the oil shale. There is no economical way to extract the hydrocarbon material [usually called kerogen] and, therefore, the shale containing the kerogen must be heated to a temperature on the order of 800° to 1000° F. Since the kerogen constitutes a rather small percentage of the total amount of material, enormous quantities of shale must be heated to produce relatively small amounts of recoverable liquid and non-condensable gases. In various attempts at retorting to date, the most common approach is the heating of beds of relatively small particulate oil shale and providing a stream of hot gas flowing through the shale bed. Since a solid and a gas are the major components of the system, a countercurrent operation is the most conventional process encountered in the prior art. Because the destructive distillation takes place at a relatively high temperature, thermal efficiency dictates that the exhausting off gas and the exhausting spent shale leave the reaction vessel at a relatively low temperature.

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In prior art processes, particularly exemplified in U.S. Pat. No. 2,757,129, patented July 31, 1956, and U.S. Pat. No. 2,901,402, patented Aug. 25, 1959, the heating has been conducted in a single zone producing a single distillation zone immediately above the combustion zone. These two patents are but two of literally hundreds of retorting processes which have been proposed, each of which provides somewhat different choices and combinations of the many possible operation conditions in the retorting process.

From a practical consideration of the various processes, it has been found that the retorting should include a downward gravity feed of the solids through the retorting vessel and an upward rising gas and entrained liquid flow. This situation utilizes incoming cold solids to cool the rising stream of gases so that it leaves the bed at a relatively low temperature. In the same manner incoming gases are brought into the lower part of the solids bed to cool the retorted solids and to heat the gases to desired temperatures.

Among the objects and advantages of the present invention is to provide a process for retorting solid hydrocarbonaceous material in a generally oxygen-free pyrolysis to selectively maximize the formation of recovered liquid and to selectively form a gas, and minimize carbonaceous residue.

Yet another object of the invention is to provide a process for retorting solid hydrocarbonaceous material in a continuously moving vertical column and to release heat in said column by the preferential oxidation of the carbonaceous residue on the solid material, and to provide a heat release which is controlled to minimize the endothermic decomposition of carbonates in the solid matter.

A still further object of the invention is to provide a retorting process for solid hydrocarbonaceous material so as to provide pulverulent solid hydrocarbonaceous material at a controlled rate of feed on the top of a vertical column of such material and distributing such material as uniformly as possible with respect to size at a controlled total rate of feed and a controlled local rate of feed.

A further object of the invention is to provide a retorting process of solid hydrocarbonaceous material including a preheating zone established by countercurrent flow of solids and gas wherein processing parameters are regulated to recover efficiently the sensible heat in the gas and to establish oil vapor condensation in a manner to produce an oil mist in the exhaust gases at slightly above ambient temperature.

Another object of the invention is to provide a retorting process for solid hydrocarbonaceous material wherein oxydation reactions are controlled so that excess carbon residue from a destructive distillation is converted to a product gas utilizable internally and externally of the reaction vessel.

An additional object of the invention is to provide a retorting of solid hydrocarbonaceous material so as to recover sensible heat in the retorted solid material by a countercurrent exchange with produced gas from the process.

A still further object of the invention is to provide a retorting process for solid hydrocarbonaceous material providing a vertical column of pulverulent solid hydrocarbonaceous material wherein there are a series of contiguous zones including preheating, pyrolysis, residue stripping and water-gas shift, partial combustion, combustion and heat recovery in the vertical column.

An additional object of the invention is to provide a controlled distillation to effectively control the produced gas-liquid relationship.

Yet another object of the invention is to provide retorting process having a controlled rate of heat application to the material being treated.

Another object of the invention is to provide a retorting process in which the fluid atmosphere of the reactants is controlled as to composition throughout the bed of the solid reactants.

A further object of the invention is to provide a retorting process in which the inputs and outputs are accurately controlled to maintain selected fluid-solids ratios in the various zones of the process vessel.

These and other objects and advantages of the invention may be readily ascertained by referring to the following description and appended illustrations in which:

FIG. 1 is a schematic flow sheet of a process according to the invention;

FIG. 2 is a schematic materials flow and reaction sheet of the process of the invention applied to oil shale;

FIG. 3 is a schematic equipment flow sheet of the process of the invention;

FIG. 4 is a temperature profile chart of a reaction according to the invention; and

FIG. 5 is a modified temperature profile chart of the reaction zones in a particular vertical kiln applied to oil shale.

In a preferred embodiment of the invention, oil shale is treated in a vertical shaft vessel or kiln. Pulverulent oil shale is fed into the top of the kiln at a sufficient rate to maintain the vessel completely filled and to replace spent shale withdrawn from the bottom. A series of eight processing zones are established in the column including from top to bottom zones of solids preheat, oil mist formation, pyrolysis, residue stripping and water-gas shift, two zones for partial combustion, combustion, and heat recovery. These zones are contiguous in the column and are not physically separated. The pulverulent solids provide interstitial spaces between the solids where gas to gas reactions take place. The gas to solids reactions in the transfer of heat initiate at the solids-gas interfaces throughout the entire column.

To establish the desired conditions in each processing zone, it is necessary to inject fluids at different locations in the column, the fluids compositions and rates are preferably selected from the different processing zones. The principle of lateral injection and distribution of fluids into shaft vessels are described in U.S. Pat. No. 3,432,348, issued Mar. 11, 1969, entitled Fluid Distributor for Vertical Vessels. This patent describes the equipment necessary for the lateral distribution of fluids into a bed of pulverulent solids for uniform distribution across the lateral extent of the bed. According to the present invention there is defined a range of ratios of fluids to solids to be established by injection through the suitable fluid distribution devices into the various zones mentioned above.

Of particular importance in the present invention is to interpose a residue stripping and water-gas shift zone between the pyrolysis zone and a partial combustion zone for distributing water or water vapor into the bed of solids. The method also contemplates the injection of air, oxygen-enriched air, or other oxygen containing gas at more than one vertical location in the shaft vessel. The percentage of oxygen in the injected mixture is established for each level so that controlled reactions and controlled vertical temperature profiles may be established optimally.

An important aspect of the process of the invention is the control of the solids in the column which includes feeding the pulverulent solids at a constant and controlled weight rate into the fixed processing volume and to withdraw the residue after processing at a rate to maintain the volume in the kiln relatively constant. Suitable withdrawing devices are described in U.S. Pat. No. 3,401,992, issued Sept. 17, 1968, entitled Linear Grate for Shaft Kilns, and U.S. Pat. No. 3,373,892, issued Mar. 19, 1968, entitled Radial Grate for Shaft Kilns. Various sense de-

vices and controllers for controlling the level of the solids in the volume may be used since many are well known in the art.

In one embodiment of the invention control is provided by adjusting the withdrawal rate of one element to maintain a relatively constant temperature in one of the processing zones, and the off gas temperature or the solid exit temperature are relatively easy to measure. Thus, the temperature of these two elements may be used for the control in combination with the level control.

By establishing the above-mentioned zones, injected air combines preferentially with the carbonaceous residue from the pyrolysis of the oil shale. This differentiates from the prior art processes wherein internal combustion retorting is accomplished by the burning a major portion of recycled product gas resulting from the pyrolysis combined with injected air. To utilize the combustion of residue carbonaceous matter injected mixtures of air and gas are selected so that they are outside the limits of flammability for the temperature of the product gas in the various zones where the product gas is cycled or recycled. The retort gas should contain no oxygen but CO, CH₄, H₂. Allowing for variations in composition and effective temperature [higher temperature increases the range of flammability] injected mixtures should be less than about 25% gas or greater than about 75% gas.

Based on the flammability limits of the recycled gas, a large portion of the process air requirements are mixed with the recycled gas which is used as a coolant for the spent shale. For example, 2,000 s.c.f. air per ton mixed with 13,000 s.c.f. recycled gas per ton is an 86.6 percent gas mixture, too rich to burn, thus, this mixture, containing about 2.8% oxygen, is well mixed externally of the shaft vessel and is diffused throughout the cross-section of the column of pulverulent material and just above the grate where the spent shale is removed. This gaseous mixture cools the shale residue and the mixture becomes preheated as it rises through the shaft vessel. In a zone several feet above the grate, the oxygen combines preferentially with the carbon residue inside and outside of the retorted shale particles. The heat release takes place over a large cross-sectional area in the presence of a large amount of gas and shale residue. Therefore, the temperature level at this carbon combustion area remains relatively low [about 1100° F.] and inorganic carbonate decomposition is minimized. In the slow oxidation of this residual carbon, complete combustion to carbon dioxide is achieved, which is especially so in this zone which is relatively poor in carbon content.

The above process describes the lowest zone in the shaft kiln where preheating of recycled gas-air mixture is accomplished and the cooling of the spent shale is accomplished. The next zone described is the carbon combustion zone. Just above the lowest level of distributors 45 in zone C, FIG. 2, the desired combustion reaction is the partial combustion of carbon residue to produce carbon monoxide, leaving residual carbon on the spent shale for combustion in the next lower zone. With a portion of the total process air requirements injected in this level, 500 s.c.f. air per ton of raw shale, there is relative excess of carbon, thereby favoring the partial combustion reaction (Reaction 2 which is $2C + O_2 = 2CO$). A diluent may be added to the air injection at this point to assist in diffusing the oxygen into a broader zone. The injected mixture should be too rich to burn at the injection temperature. Recycled gas is used as the diluent (in one process) with the air and it should exceed 1500 s.c.f. per ton of the raw shale. Recovered CO₂ may be used as a portion of the diluent gas, maintaining it below about 25%.

The next higher level of distributors 46 are used in the same manner for partial combustion of carbon. The distributors of this level may be staggered laterally and are spaced above of the lower set, the distance between the two being at a greater distance than the horizontal

spacing of the distributors of the lower set. The staggered configuration of both sets gives maximum exposure of the gas-air mixtures to the shale residue and at the same time results in minimum resistance to the downward descent of the solids. The balance of the total air input shown in Table I below is injected with enough recycled gas diluent to produce a too rich mixture. The rates of air and gas shown in FIG. 2 are 484 s.c.f. air and at least 1450 s.c.f. of recycled gas respectively.

The temperature levels will remain relatively low in the two partial combustion zones since the heat release is throughout the large volume of solids and in the presence of relatively large volume of gases flowing upwardly. Carbonate decomposition in the shale should be quite low since both of these zones are at relatively low temperatures and there is a relatively high partial pressure effect from the carbon dioxide present in the fluids rising from below.

A stripping and water-gas shift zone is established above the top level of the distributors 47 by entraining a water fog in a portion of recycled gas. The reaction is mildly exothermic, but some heat will be absorbed in vaporizing the water. This zone E separates the highest temperature combustion zone from the pyrolysis zone and helps to prevent oxygen from entering the pyrolysis zone. The water vapor formed is a good stripping medium for the carbonaceous residue leaving the pyrolysis zone thereby increasing the liquid oil yield from the process. The hydrogen formed by the water-gas shift reaction; $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2 + 17,720 \text{ B.t.u.}$ will increase the partial pressure of hydrogen in the heated gas entering the pyrolysis zone. Another method of producing H_2 is the water gas reaction $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$, ($-70,000 \text{ B.t.u.}$). While the effect is relatively minor, pyrolysis will be more selective in increasing the liquid oil yield of the process.

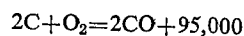
Another important feature of the present invention is a controlling of the temperature gradient in the mist formation zone which is controlled independently of the residue cooling and the combustion processes by injecting a controlled quantity of recycled gas above the combustion zones. This novel concept produces high efficiency in the distillation. It is noted that in the present process the amount of recycled gas required for cooling the shale residue has been decreased by adding a portion of the air necessary for the process to the shale residue cooling medium at the grate 43. Temperature levels in the combustion zones B, C and D have been decreased, resulting in less carbon dioxide production from carbonate (in the shale) decomposition, while on the other hand, carbon gasification to carbon monoxide in the partial combustion zones increases the gas quantity in the mist formation zone.

Another important feature of the present process is the ability to control the yield distribution from pyrolysis of hydrocarbonaceous materials. As the relative amounts of gas, oil, and carbonaceous residues are varied due to changes in the process parameters, the properties of the resultant gas and oil, also, change. The carbon to hydrogen ratio of the oil product is an important consideration in subsequent processing of the oil to finished products. The utilization of the product gas will depend on the unit heating value of that gas [B.t.u. per cubic foot] and the total heating value of the gas [B.t.u. per ton of raw shale]. The use of multiple level air injection sites at selected oxygen to combustible gas ratios at the different zones, along with the injection of diluent gas and entrained water [or steam] at a predetermined rate permits the control of selective yield distribution. The process of the invention is schematically shown in the flow sheet of FIG. 1, wherein a vertical shaft vessel 10 is provided with a feed of raw shale 12 and a discharge of spent shale 14 at the bottom. The process requires that the kiln be maintained completely filled of particulate shale, usually in the particle size range of $\frac{1}{2}$ inch to 4 inches.

Air and recycled gas enters the bottom of the vessel through line 16 which includes recycled gas and some air. An air blower 18 supplies air to a manifold 20, into a lower level distribution system 22 including distributor A, an intermediate distribution system 24 including distributor B, and an upper distribution system 26 including distributor C. Off-gas is removed from the kiln by an off-gas line 28 which passes through a recovery system 30 and a portion of the product gas is recycled along line 32 into a gas blower 34. Part of the recycled gas is transferred by line 36 into the distribution systems 22, 24, and 26. This provides the concept of at least three levels of fluid injection into the system, providing unique control of the combustion zones.

In the specific application of the invention, FIG. 2, a vertical kiln 40 is provided with a continuous feed mechanism for pulverulent oil shale, shown in general by numeral 41, and a spent shale discharge mechanism, shown in general 43, is similar to the grate mechanisms referred to above. A gas injection system 44 is provided above or in the grates for injecting recycled gas and air into the spent shale; this cools the shale and heats the incoming fluids. A lower distributor system 45 provides means for introducing recycled gas and air into a partial combustion zone immediately thereabove and above a combustion zone A for the gasification of carbon residue on the shale. Distributors 46, also, provide for the introduction of air and recycled gas for a second partial combustion zone immediately above the distributors 46. The combustion zone B and the partial combustion zones are established and are controlled by the quantity and composition of the fluids in the zone. Upper distributors 47 provide means for introducing recycled gas and water vapor into the kiln to produce a stripping and water-gas shift zone E immediately above that zone provides for the destructive distillation of the hydrocarbonaceous material in the kiln. The last zone G is a preheating and mist (liquid product) formation zone wherein the feed shale is heated and a mist of produced oil in the off-gas is produced. Off-gas collectors 48 permit withdrawn of the gas and oil mist from the shale bed. The gas and mist is withdrawn from the kiln by line 49 which passes through a series of oil mist extractors, shown in general by numeral 50, which may be cyclones, wire mesh pads, electrostatic precipitators, etc., followed by an air cooled (or other type) condenser 51. The stream from the air cooled condenser passes through a separator 52 for removing light oil from product gas which is removed from the separator and a line 53 which enters a recycled gas blower 54. A drier may be installed on line 56 or other line as desired. From the outlet of the gas blower the recycled gas goes into a manifold 55 or alternatively to product gas line 56. The manifold 55 feeds lower line 56 which enters the distribution system 44 just above the grate 43 in the kiln, manifold 57 which feeds the distributors 45, and manifold 58 which feeds the distributors 46, and another manifold 59 which feeds the distributors 47. A water makeup line 60 provides means for injecting water into the upper distributor system 47 for producing the stripping and water-gas shift. Air from a blower 61 provides air through an outlet line 62 into a manifold 63 which feeds the air to the manifolds 56, 57 and 58 for producing some combustion in the kiln.

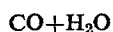
The various zones in the kiln are identified as Zone A where spent shale is cooled, a combustion zone B, a partial combustion zone C, a second partial combustion zone D, a stripping and water-gas shift zone E, a pyrolysis zone F, and a preheating and mist formation zone G which also includes the off gas collectors. The reactions which occur in the various zones, based on B.t.u. per mol include $\text{C} + \text{O}_2 = \text{CO}_2 + 169,300 \text{ B.t.u.}$ and



B.t.u. $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$ ($-70,000 \text{ B.t.u.}$) in a combustion zone B. The first partial combustion zone C provides

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a reaction of $2C + O_2 = 2CO + 95,100$ B.t.u. and $C + H_2O = CO + H_2$, while the second partial combustion zone D also includes the same reaction of $C + O_2 = CO_2$ with the same B.t.u. production. The first combustion zone B may include the $C + H_2O = CO + H_2$ due to residual moisture in the recycle gas and/or in the air. The stripping and water-gas shift, zone E, combines carbon monoxide and water according to the following formula:



goes to $CO_2 + H_2 + 17,720$ B.t.u. In the pyrolysis section the reaction is endothermic utilizing some of the heat produced by the combustion and partial combustions below the pyrolysis zone.

The amount of recycled gas per ton of shale is shown in FIG. 2, wherein 13,000 s.c.f. (standard cubic feet) per ton (shale) is injected into the bottom along with 100-1500 s.c.f. per tone of air. Into the first level of distributors 45, 500 s.c.f. air per ton is injected with recycled gas which is greater than about 1500 s.c.f. per ton. In the intermediate distributors 46, 484 s.c.f. of air is injected with recycled gas which is greater than about 1450 s.c.f. per ton. In the upper distributors 1,000 s.c.f. of recycled gas per ton of shale is injected with water and no air.

As has been discovered in the prior art, injection of air alone into the combustion zone produces high temperatures and burning a part of the gas product as well as part of the produced oil product. Therefore, it is important that all the oxygen be consumed below the pyrolysis or retorting zone so that little or no oil is burned, when the oil is the principle valuable product of the retorting process. It is, also, important that the gas burning in the combustion zone B be maintained at a minimum, particularly where the gas product is required to have some value. As explained above, combustible gas and air mixtures have upper and lower limits of flammability (in reference to the percentage of combustible gas in the air-gas mixture). The spread between the upper and lower limits decreases as a diluent (recycle gas and/or CO_2) is added, and the addition of CO_2 finally extinguishes the flame at a concentration of about 24% CO_2 in the mixture. Lower CO_2 concentrations will permit ignition to take place, but the limits of flammability are quite narrow. The present process provides means to prevent the burning of gas in the kiln or permits control combustion by controlling the amount of gas for the burning. In the lower levels of the kiln, oxygen in the injected air combines with the carbonaceous residue on the shale which amounts to 2 to 6% by weight of the retorted shale. This carbonaceous residue is of doubtful economic value since it is mixed with such large amounts of the spent shale. The residue will burn, however, at the temperature levels and the oxygen levels which may be maintained in the various zones in the retort. In addition to the reaction of the burning of carbon with oxygen as shown in the combustion zone above, the parameters in the combustion zone may be controlled so as to produce the following reaction: $CO_2C = CO$ (endothermic). By the law of mass action increasing the CO_2 concentration favors the formation of carbon monoxide, a gas having moderate heating value. Thus in the combustion zone the main reactions are the combining of carbon with oxygen to produce carbon dioxide and the combining of carbon and oxygen to produce carbon monoxide. The exothermic reactions to produce carbon dioxide and carbon monoxide is at a relatively low temperature level and is controlled to produce a combustible gas having some economic value. The heat liberated is used to supply the heat requirements for pyrolysis in the zone above the stripping and water-gas shift.

Carbon dioxide necessary to produce the carbon monoxide may be obtained by scrubbing the retort product gas with one of the ethanolamines using well known methods. In the operation of the shaft vessel, some carbon

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dioxide is produced from the combustion of organic matter in the shale, some will be produced by the decomposition of some of the magnesium carbonate in the shale, and some is produced by the actual burning of the carbon after pyrolysis. A side benefit of the use of ethanolamines scrubbing is to remove hydrogen sulfide and sulphur dioxide and thereby permit an economic recovery of sulphur from the product gas.

The introduction of carbon dioxide as a diluent in the product gas provides an additional control on the flammability of the injected cool gaseous mixture, which, also, incidentally suppresses combustion near the point of injection into the shale bed. As the gaseous mixture becomes heated by the hot shale it reaches a temperature where the mixture is flammable and the injected gas mixture rises above the distributors into the partial combustion zones where the controlled oxidation takes place. Thus, by controlling the carbon dioxide content and the recycled gas content of the injected gas-air mixture, the distance of the flame from the point of injection may be accurately controlled. By providing the two partial combustion zones above the combustion zone the residence time of the shale in the higher temperature level zones in the kiln may be greatly extended without increasing the shale temperature above the decomposition temperatures of the carbonates in the shale.

Specific controls of the process are shown in FIG. 3 where a kiln 70 is provided with a feed distributor 71 to provide uniform distribution of shale into the kiln 70, and the distributor is fed from a constant level hopper 72 controlled by means of a level controller 73. A star feeder 74 fed from a belt conveyor 75 maintains the hopper 72 full. A feed bin 76 feeds the belt conveyor 75 by means of a loader 77 controlled by a belt scale 78. This arrangement provides for a constant feed into the kiln through the feed distributor 71. The level controller 73 controls a discharge grate mechanism 80 at the lower part of the kiln, for example the linear grate explained in my patent above, through a control mechanism 81 to thereby provide for a constant level of shale in the kiln. A star feeder 82 feeds a spent shale discharge belt mechanism 83. Off gas is collected from the shale bed by means of an off gas collector 84 passing through a mist separator 85 and the product gas passing through a line 86 to a recycle gas pump 87. Liquid from the mist separator 85 passes through a pump 88 to a liquid product discharge line 89. Product gas is discharged through line 90 which is controlled by a control valve 91.

Recycled gas is injected into the grate mechanism through a line 92 controlled by a valve controller 93. The first level of distributors 94 is provided with recycled gas through line 95 from the recycle pump 87 controlled by a valve controller 96, and air from an air pump 97 is also injected into the distributor level 94 through a line 98 controlled by valve controller 99. The next level of distributor 100 is provided with recycled gas through line 101 controlled by line controller 102 and air is provided into the distributor through line 103 which is controlled by a valve controller 104. Where desired air can be introduced into the recycled gas into line 92 by means of line 106 controlled by line controller 107, in the manner explained above.

The two or more levels of distributors in the bed distributes an oxygen containing gas which may be accurately controlled by injecting a diluent gas with the air. As pointed out, the diluent gas may be recycled product gas, CO_2 or other gas in which to control the atmosphere within the combustion and/or partial combustion zones. The multiple level distributors increases the resident time of the shale at high temperatures in the kiln to produce a lower combustion zone temperature for the release of the heat required for the retorting of the oil shale, it, also, permits the introduction of oxygen containing gas below the pyrolysis zone in sufficient quantities to restore the stone temperature to desirable levels to compensate for

the endothermic heat of reaction in the pyrolysis zone, the lower combustion zone temperatures will cause fewer carbonates to be decomposed which will produce less carbon dioxide dilution in the product gas. The decrease in carbonate decomposition decreases the heat requirements which will, therefore, decrease the air requirements, and thereby decreasing the nitrogen dilution in the product gas. The net effect of the decrease in carbon dioxide and nitrogen dilution will improve the heating value of the product gas which may be recovered as a product of the pyrolysis. The deepening of the combustion zone, which, also, includes the partial combustion zones, will permit the use of higher solids throughput rates before contacting any oxygen in the carbonaceous distillation zone and the resulting burning of some of the oil values.

The temperature profile of FIG. 4, illustrates injection of fluids into two intermediate levels in the vertical vessel as well as some recycle gas in the bottom of the vessel. This is for countercurrent flow of solids from top to bottom, and fluids from bottom to top. Shale is introduced into the top of the vessel at the 20 ft. level at ambient temperature and rising gas raises the shale to pyrolysis temperature of about 900° F. in about 5 feet, or at the 15 foot level. Heat for the pyrolysis is provided by combustion in the upper combustion zone which results from the oxidation of the residual carbon into CO and CO₂. The lower combustion zone starts at about the 6 foot level and carbon is oxidized to CO and CO₂. The high temperatures (1000°-1200°) extends through both combustion zones over about 5-14 feet of the vessel, or just under half of the vessel. This provides a long residence time for the solids at the higher temperatures insuring efficient utilization of the residual carbon on the shale following pyrolysis. The incoming gas is heated by the spent shale, which in turn is cooled. The volume of gas induced into the vessel by forced draft is sufficient to entrain the mist which forms by condensation of vaporized liquid (from pyrolysis) contacting the relatively cooler shale. The entrained mist is then carried out for recovery by the off-gas.

The specific example shown by the flow sheet of FIG. 2 has a temperature profile as shown in FIG. 5. This includes three upper levels of fluid injection and three levels for oxygen containing gas injection. The ambient temperature shale enters the vessel, is heated in passing through the mixed formation and pyrolysis zones, which are maintained essentially non-oxygeneous. The heated shale from the pyrolysis zone, about 1000° F., is subjected to the stripping and water shift zone where both CO and C react with water to form CO₂ and hydrogen and CO and hydrogen, respectively. The shale then passes into a partial combustion zone where the oxygen content is maintained low to produce a partial oxidation of some of the residual carbon to carbon monoxide. The shale passed to middle partial combustion zone where a controlled oxygeneous atmosphere permits some additional residual carbon to partially oxidize to CO. The temperature of the shale rises somewhat through these two partial combustion zones. The shale then passes into the lower combustion zone where the remainder of residual carbon is utilized by oxidation and a water-gas shift (due to minor amounts of water entering via the air and recycle gas). The desired oxidation here is the complete oxidation of carbon to carbon dioxide. The spent shale heats the gas and is simultaneously cooled. The residence time of the shale above a 1000° F. is from 4 to 17 feet in a 24 foot vessel, or well over half the vessel.

We claim:

1. A process for heat treating particulate material in a vertical, hollow vessel wherein particulate material including combustible material is fed into the top of a bed of such material in the vessel and treated material is withdrawn from the bottom producing a gravity flow of material through said vessel and a treating gas is passed upwardly through said particulate material to provide treat-

ment of the combustible material in said vessel, the improvement of introducing a mixture of oxidizing gas and an inert gas under pressure into said bed in at least two spaced apart levels intermediate the top and bottom of the bed and below a level of heat treatment of said particulate material; the quantity of oxidizing gas in each said mixture at each said introducing level being maintained at substantially less than the total quantity needed for stoichiometric oxidation of combustible material in said level and the total quantity of oxidizing gas being sufficient to produce a predetermined amount of oxidation of the combustible material, but less than a quantity to produce oxidation in said heat treating level; maintaining the additive quantity of oxidizing gas at both said levels at a predetermined level so that essentially no oxidizing gas is passed upwardly from each said level; diluting said oxidizing gas with a sufficient quantity of non-combustible gas at each level to maintain the desired ratio of oxidizing gas and inert gas; and controlling the off-gas withdrawal to maintain a positive pressure internally of said vessel higher than ambient pressure and of a sufficient volume to entrain products of heat treatment in the gas leaving said vessel.

2. A process according to claim 1 wherein the oxidation in said two levels produces approximately the same temperature, thereby increasing residence time of said particulate material to said temperature.

3. A process according to claim 1 wherein said inert gas is recycled off-gas from said vessel.

4. A process according to claim 1 being further characterized by the introduction of oxidizing gas into the bottom of said bed to produce essentially complete oxidation of any combustible material moving downwardly from said lower of said two intermediate levels.

5. A process for retorting particulate oil shale in a vertical vessel wherein oil shale is fed into the top of a bed of shale maintained in the vessel and withdrawn from the bottom of the vessel providing a gravity flow of shale through the vessel and oxygen is introduced into the vessel in a counter-current flow for producing combustion in the shale bed, the improvement of introducing a low percentage oxygen containing gas under pressure into at least two levels intermediate the top and bottom of said shale bed and introducing a low percentage oxygen containing gas under pressure into the bottom of the shale bed to thereby establish at least four zones in said bed, namely a lower combustion zone, a first partial combustion zone thereabove, a second combustion zone immediately above said first partial combustion zone, and an upper pyrolysis zone, maintaining the oxygen level in the gas introduced into the bottom of the shale bed at a quantity to essentially burn residual carbon on the shale; maintaining the oxygen content of the gas introduced into said first partial combustion zone at less than about 1/4 necessary to burn the residual carbon on the shale; maintaining the oxygen content in said gas introduced into said second partial combustion zone at a level to produce combustion of substantially less than all the residual carbon in the shale in that zone whereby substantially non-oxygeneous gas passes into the pyrolysis zone thereabove; maintaining the total quantity of oxygen in each said zone at a level to produce a predetermined temperature, whereby the gaseous product of combustion are maintained at a temperature sufficient for retorting said oil shale; controlling the rate of flow of off-gas to maintain a positive pressure in said vessel above ambient pressure; and maintaining a sufficient volume of inert gas in said oxygen containing gases to entrain products of pyrolysis of the shale for exhausting with the off-gas.

6. A process according to claim 5 wherein sufficient oxygen is introduced into said combustion zone to cause only essentially complete combustion of residual carbon on said shale leaving said partial combustion zone.

7. A process according to claim 5 wherein the quantity of oxygen introduced into said first partial combustion

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zone is less than about 25% of the oxygen necessary to burn all the residual carbon in that zone.

8. A process according to claim 5 wherein the quantity of oxygen introduced into said first and second partial combustion zones is sufficient to maintain the temperatures in those zones substantially equal.

9. A process according to claim 5 wherein the bed is maintained to completely fill said vessel.

10. A process according to claim 5 being further characterized by introducing inert gas and water vapor in said bed above said second partial combustion zone to thereby establish a zone below said pyrolysis zone where water reacts with carbon to produce carbon monoxide and hydrogen in a water gas shift.

11. A process according to claim 10 wherein said inert gas is off-gas from said vessel.

12. A process according to claim 5 wherein a portion of said oxygen containing gas for each zone is carbon dioxide.

13. A process according to claim 12 wherein the quantity of carbon dioxide in said partial combustion and combustion zones is predetermined and is an amount of less than about 25% for each mixture.

14. A process according to claim 5 wherein the temper-

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ature of said combustion and partial combustion zones is maintained at less than about 1300° F.

15. A process according to claim 5 wherein at least the pyrolysis temperature of the shale in said vessel is maintained for more than half of the residence time of the shale in said vessel.

16. A process according to claim 5 wherein recycle gas is introduced into said bed above said first and second partial combustion zones to control the temperature of the gaseous products of combustion to about pyrolysis temperature.

17. A process according to claim 5 wherein the quantity of inert gas at each zone of introduction is controlled.

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