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COMPLETE SPECIFICATION

Improvements in or relating to the Process of Making Gas from Carbonaceous Solid Fuels

I, ERIC WILLOUGHBY ROLLINSON, a British Subject of the Firm of Stevens, Langner, Parry & Rollinson, Chartered Patent Agents, of 5/9, Quality Court, Chancery Lane, London, W.C.2, do hereby declare the invention (Communication from Pittsburgh Consolidation Coal Company, a corporation organised under the laws of the State of Pennsylvania, United States of America, of Koppers Building, Pittsburgh, Pennsylvania, United States of America), for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the gasification of carbonaceous solid fuels and, more particularly, to methods of reacting carbonaceous solid fuels with steam.

The primary object of this invention is to provide an improved process for converting carbonaceous solid fuels into a gaseous product by reaction with steam.

Another object of this invention is to provide a process in which steam reacts with solid carbonaceous fuels to yield a gaseous product under such conditions that no heat need be added to the system, i.e., under thermoneutral conditions.

A further object of this invention is to provide an improved process for making a high B.Th.U. fuel gas which is rich in methane.

Still another object of the present invention is to provide an improved method for converting carbonaceous solid fuels into a gas which is rich in hydrogen and which is substantially free of carbon dioxide.

According to the invention there is provided a process of making gas including passing steam into a mixture of carbonaceous solid fuel and calcium oxide or lime in a reaction zone and collecting the gaseous products, in which process the steam is introduced into the reaction zone at a temperature within the range of 1430° to 1800° F. and under a pressure which is at least

$$3.40-1.89\times10^{-2}(t-1430)+4.48\times10^{-4}(t-1430)^2$$

atmospheres where t is the temperature in °F., the amount of calcium oxide or lime present in the reaction zone being sufficient to convert substantially all the carbon dioxide produced to carbonate.

The invention also includes a process of making gas including mixing lime and a carbonaceous solid fuel, bringing steam into contact with the mixture, and recovering the gaseous products, wherein the relative proportions of lime and carbon are 120 to 300 parts by weight of lime for each 100 parts by weight of carbon contained in said carbonaceous fuel, and wherein the steam is circulated in reactive relationship with said carbonaceous fuel in a non-fluidized reaction zone, at a temperature within the range 1430° to 1800° F. and under a pressure which is at least

$$3.40-1.89\times10^{-2}(t-1430)+4.48\times10^{-4}(t-1430)^2$$

atmospheres where t is the temperature in °F., whereafter the circulation of steam is discontinued when the steam-carbon reaction is substantially completed and air is circulated at atmospheric pressure through the solid residue to regenerate the lime.

In order that the invention may be

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understood it will now be described with reference to the accompanying drawings in which:

Figure 1 is a graphical illustration of the critical relationship between pressure and temperature which governs the operation of the invention;

Figure 2 is a diagrammatic illustration of an apparatus comprising a one-vessel system adapted to carry out the preferred embodiment of the invention;

Figure 3 is a diagrammatic illustration of an apparatus comprising a multiple-vessel system adapted to carry out a modification of the preferred embodiment of the invention;

Figure 4 is a diagrammatic illustration of an apparatus adapted to carry out another modification of the preferred embodiment of the new process; and

Figure 5 is a diagrammatic illustration of an apparatus adapted to carry out a still further modification of the new process.

In the process according to the invention, the reaction between steam and carbon is utilized to convert solid carbonaceous fuels into a gaseous product in the presence of calcium oxide. Calcium oxide previously has been used in the water gas reaction in relatively small amounts as a catalyst or carbon dioxide acceptor. However, it has been discovered that when calcium oxide is mixed with carbonaceous solid fuels in the proper proportions and under certain critical conditions of temperature and pressure, the steam-carbon reaction is thermo-neutral; i.e. no heat need be added to the system to maintain the reaction. In fact, the reaction may even be exothermic and capable of generating the steam necessary for the process. Moreover, it was found that under these thermoneutral conditions, gases which contain unexpectedly high percentages of either methane or hydrogen can be selectively produced by operating under conditions lying within the critical range required to produce a thermo-neutral reaction.

More specifically, the new process comprises the use of calcium oxide and finely divided carbonaceous solid fuels in the proportions of at least 120 parts by weight of calcium oxide to 100 parts by weight of carbon contained in the fuels. This mixture is reacted with steam at a temperature between 1430° and 1800° F. It has been discovered, however, that there is a minimum pressure which must be attained in order that the overall reaction be thermally self-sufficient; i.e., at least thermoneutral and preferably exothermic. This minimum pressure is a function of the reaction temperature and, in the temperature range from 1430° to 1800° F., is expressed by the empirical relation

$$(1)\ p=3.40=1.89\times10^{-2}(t-1430)+4.48\times10^{-4}(t-1430)^2$$

where p is the pressure in atmospheres and t is the reaction temperature in °F.

The gas producing process of the invention may be operated thermoneutrally provided the minimum pressure is that defined by equation (1). However, it has been found that when the operating pressure is increased above the minimum value at a constant temperature, the proportion of methane in the gas produced increases while the proportion of hydrogen correspondingly decreases. Thus, at constant temperature, the composition of the product gas varies with the operating pressure.

If then a methane rich, high B.Th.U. gas product is desired, there is a second minimum operating pressure, arbitrarily chosen which must be exceeded in order that the heating value of the product gas (a measure of the methane content) will exceed 400 B.Th.U. per cubic foot. This minimum pressure can also be expressed as an empirical function of the reaction temperature by

$$(2)\ p=5.0+4.2\times10^{-2}(t-1430)+2.7\times10^{-4}(t-1430)^2$$

where p is the pressure in atmospheres and t is the temperature of the reaction zone in °F.

Equations (1) and (2) are shown graphically in Figure 1. The improved process of the invention will produce a hydrogen rich gas when the operating pressure lies between the curves representing equations (1) and (2) as determined by the reaction mixture.

A methane rich, high B.Th.U. gas can be produced when the operating pressure lies above the curve representing equation (2) as determined by the reaction temperature. The process of the invention will produce a methane rich gas within the temperature range from 1430° to 1800° F., but it is preferred to produce methane rich gas within the temperature range from 1520° to 1650° F., and at a corresponding pressure ranging from 10 to 40 atmospheres, the pressure being at least that determined by equation (2) depending upon the operating temperature.

A hydrogen rich gas can be produced in a thermoneutral reaction by the invention within the temperature range from 1430° to 1800° F., but it is preferred to produce hydrogen rich gas within the temperature range from 1520° to 1650° F., at a pressure corresponding to the temperature of the reaction, within the range from 5 to about 30 atmospheres provided, however, the pressure is at least that given by equation (1) and is less than that given by equation (2) according to the temperature employed.

It should be stressed at this point that the process of the invention will operate to produce a gas by a thermoneutral steam-carbon reaction so long as the pressure is at least that given by equation (1).

In the preferred embodiment of the invention, the reaction between steam and carbonaceous solids is carried out in a single vessel system utilizing an on-and-off cycle. Steam is passed through a bed of calcium oxide and the carbonaceous solids to yield a gas containing hydrogen, methane, carbon monoxide and carbon dioxide. Simultaneously calcium carbonate is formed in the vessel from the reaction between calcium oxide and the carbon dioxide in the gas produced. During the off cycle, air or any gas containing oxygen gas is circulated through the vessel to regenerate the calcium oxide from the calcium carbonate. Sufficient carbonaceous solids are oxidized during the regeneration cycle to raise the temperature of the carbonate above its dissociation temperature so that the carbonate decomposes into calcium oxide and carbon dioxide.

While it is preferred to use a non-fluidized system, nevertheless a fluidized system may be employed which comprises either a single vessel or a plurality of vessels as will be described in detail later. Whether the system is fluidized or non-fluidized, the yield of methane can be increased in the new process by deliberately establishing a temperature gradient through the steam-carbon reaction vessel in a manner which will be described in detail later. In this modification of the invention, the steam-carbon reaction is first carried out at a temperature preferably between 1670° and 1770° F. and the products therefrom are then passed in contact with carbonaceous solids at a lower temperature, preferably between 1430° and 1600° F. A large increase in methane production thereby results.

The yield of hydrogen, on the other hand, when the process is operated under the conditions set forth to produce hydrogen rich gas, can be further increased according to the conventional water gas shift reaction in which carbon monoxide and steam react to produce carbon dioxide and hydrogen. When the water gas shift reaction is conducted at temperatures in the range of 1200° to 1500° F. in the presence of lime, the carbon dioxide resulting from the shift is removed by the lime forming calcium carbonate. Since the main constituent (other than hydrogen) of the water gas produced by the process of the invention is carbon monoxide, the second reaction, in which substantially all the carbon monoxide is converted to hydrogen serves to produce a gas far richer in hydrogen than any previously made in a steam-carbon reaction.

In certain instances it may be desirable to accelerate the steam-carbon-calcium oxide reaction by the addition of catalytic materials. For example, the calcium oxide may be impregnated with small amounts of an oxide of the transition group metals, such as iron, nickel, cobalt or manganese. Alternatively, the calcium oxide may be impregnated with small amounts of an alkali or heavy alkaline earth carbonate, such as sodium carbonate, potassium carbonate, barium carbonate or strontium carbonate may be employed. Also certain other alkaline earth oxides may be incorporated with the lime to increase its physical strength, e.g., MgO as in dolomite.

In the following description of a specific embodiment of the invention, by way of example only, the new process is applied to the carbonaceous solid residue obtained by the low temperature distillation or carbonization of hydrocarbonaceous solid fuels such as the high volatile bituminous coal found in the Pittsburgh Seam. This residue, for the purpose of convenience, shall hereafter be referred to as "char." It is to be understood, however, that the process is generally applicable to any carbonaceous solid fuels which react with steam to produce water gas. Among such carbonaceous solids are included all ranks of coal, coke from coal, petroleum pitch coke, lignite, oil shale and tar sands. Highly reactive solid fuels such as char and lignite are preferred because of the moderate temperature at which the process is operated.

The apparatus shown in Figure 2 and its operation will now be described. A mixture of char and lime is introduced into a reaction vessel 10 of any suitable type adapted to retain a bed of solids at elevated temperatures and high pressures. The mixture of lime and char is obtained by charging lime and char in the proper proportions from their respective supply hoppers 12 and 14 to a mixing chamber 16 in which the two batches of solids are thoroughly mixed. From the mixer 16 the solids are transferred to the vessel 10 through a conduit 18 by a motor driven screw feeder 20. The relative amounts of char and lime in the mixture are regulated so that the resulting bed 22 in reaction vessel 10 contains at least 120 and preferably between 120 and 300 parts by weight of lime for every 100 parts by weight of carbon contained in the char. In order to raise the temperature of the bed to a point between 1430° and 1800° F., air is introduced through suitably valved conduits 24. A small amount of carbonaceous solids is burned by the air to supply the heat required to attain the temperature of the bed previously specified.

When the temperature of the bed 22 has reached the desired temperature in the range from 1430° to 1800° F., the flow of air through conduits 24 is discontinued and steam is introduced into vessel 10 through suitably valved conduits 26.

At the same time a valve 28 in the gaseous product line 30 is regulated so that the pressure within vessel 10 will be at least as high as the minimum pressure calculated from the following relation

$$(1)\quad p = 3.40 - 1.89 \times 10^{-2}\,(t - 1430) - 4.48 \times 10^{-4}\,(t - 1430)^2$$

where p is the pressure in atmosphere and t is the temperature in °F.

The pressure in vessel 10 should be at least as high as the minimum thermoneutral pressure calculated from equation (1) when a product is desired with maximum hydrogen content and should lie within the area bounded by curves (1) and (2) of Figure 1. The pressure is preferably within the range from 5 to 30 atmospheres from the production of a hydrogen rich gas. On the other hand, if a methane rich gas is desired, the pressure in vessel 10 should exceed that given by equation (2) and preferably should lie within the range from 10 to 40 atmospheres selected so that the pressure lies within the area above curve (2) as shown in Figure 1.

Steam passing up through bed 22 reacts with char to produce carbon monoxide, hydrogen, methane and carbon dioxide. The carbon dioxide contained in the product gas reacts with the lime in the bed 22 to produce calcium carbonate and to liberate heat. Under the conditions of temperature and pressure determined by the relation above, the heat developed by the reaction of the carbon dioxide with the lime is sufficient to maintain the temperature of the bed within the desired operating range and to provide the heat necessary for the endothermic reaction of the steam with the char. When most but not all of the carbonaceous fuel has been consumed by reaction with steam in the bed 22, the flow of steam into vessel 10 through conduit 26 is discontinued; the pressure in the vessel is reduced to atmospheric; and air is introduced through conduits 24. Sufficient residual carbon is deliberately left in the spent carbonate to provide heat for the regeneration step. The unconsumed carbon is then consumed by combustion with air introduced into vessel 10. The regenerated lime and ash are then withdrawn from vessel 10 through conduit 32 by means of a motor driven screw feeder 34. The lime, after its separation from the ash by any suitable manner, such as elutriation, is returned to hopper 12 for recirculation through the reaction zone. If desired, instead of an intermittent operation as described, the screws 20 and 34 may be operated continuously. In this case, bed solids containing carbonate, ash and some unconsumed carbon are treated in a separate vessel through which air is blown. Combustion of the unconsumed carbon supplies the heat necessary to convert the carbonate to lime. The regenerated lime then is separated from the ash as before and returned to the lime supply hopper 12.

The gas produced, substantially free of carbon dioxide, is conveyed through conduit 30 to any suitable point for further treatment or for immediate use or storage. It should also be pointed out that this product gas is relatively free from sulfur contamination because of the reaction of lime with sulfur containing components of the gas producing solid sulfides which remain in vessel 10. The resulting sulfides are moved along with the ash through draw-off conduit 32.

The following table lists the percentages of each of the components of the dry gas product as produced under different sets of temperature and pressure. Under heading (a) is shown the composition of the gas produced in the presence of lime under conditions of temperature and pressure favoring the production of hydrogen rich gas. It should be noted that when lime is used in accordance with the invention, the hydrogen content is greatly increased. Heading (B) shows the composition of the gas produced in the presence of lime under the critical conditions of the present invention. The increase in methane content achieved by the method of the invention will be observed.

TABLE I

Temperature °F.	Pressure Atm. Absolute	Per cent Steam Conversion	Gas Compositions				Gross Heating Value BThU/cu. ft. at 60° F.
			H_2	CH_4	CO	CO_2	
Without lime							
1520	5	50	55.5	3.5	19.8	21.2	279
1520	10	55	50.9	6.3	21.7	21.1	298
1610	37	50	41.5	10.9	34.9	12.7	358
1610	37	77	39.4	11.5	35.9	13.2	360
With lime (A) (At pressures selected to produce hydrogen rich gas)							
1520	10	55	74.1	11.0	7.4	7.5	377
1520	10	70	70.5	13.1	10.5	5.9	397
With lime (B) (At higher pressures selected to produce methane rich, high BThU gas)							
1610	37	50	70.6	22.0	4.3	3.1	466
1610	37	91	56.0	26.0	15.3	3.7	495

It will be noted that when water gas is produced using lime in accordance with the invention, there is a considerable improvement in the hydrogen content of the gas as compared with the production of water gas without lime when the operating pressure is only slightly higher than the minimum pressure as determined from the empirical relation above. It should be further noted that where the operating pressure is substantially greater than the minimum in the presence of lime, the methane content of the product gas is greatly increased over that of the gas produced without lime.

The per cent steam conversion is given in each of the above examples in Table I in order to permit a valid comparison to be made. The amount of this conversion is determined by the residence time as is well known. However, in the case where no lime is used the maximum obtainable conversion at 1610° F. and 37 atmospheres is 77 per cent while under the same conditions, where lime is employed, the maximum obtainable conversion is increased to 91 per cent. This marked increase in per cent steam conversion is also observed at other conditions of temperature and pressure within the critical range of the present invention.

It will thus be apparent that by proper selection of operating conditions within the above defined limits, it is possible to produce by a thermoneutral process a gas containing hydrogen, methane and carbon monoxide in a wide range of different relative proportions. Under certain selected conditions, a gaseous mixture may be produced in which the H_2/CO ratio is approximately 2/1. This mixture may be used as the synthesis gas for a Fischer-Tropsch conversion to liquid hydrocarbons.

In the operation of the apparatus shown in Figure 2 the regeneration of the lime was indicated as being carried out in a non-fluidized system. However, it is desirable whenever possible to regenerate the lime in a fluidized operation in order to obtain good heat control. While it is possible to effect the steam carbon reaction in a fluidized bed at relatively low pressures, it is not always possible to do so when operating at the high pressures preferred in the new process. The difficulty arises from the fact that, at the linear velocities required to maintain fluidized, deep beds are needed to obtain the necessary contact time at elevated pressures.

A system may accordingly be employed in which the steam carbon reaction is carried out in a non-fluidized bed while the regeneration of the lime is effected in a fluidized bed. The non-fluidized bed should rest upon a distribution plate to disperse the incoming steam uniformly over the base of the bed. The particle size range of the solids must be such as to permit fluidized operation in the regeneration cycle and non-fluidized operation in the steam-carbon reaction cycle; i.e., in the high pressure steam cycle the low linear gas velocities (e.g., 0.01 to 0.05 feet per second) should produce a quiescent non-fluidized bed of particles; however, in the lime regeneration cycle at atmospheric pressure the higher linear gas velocities (e.g., of the order of 1.0 feet per second) should produce a uniformly fluidized bed of particles. If the particles are too large the regeneration cycle will not be smoothly fluidized; if the particles are too small the maintenance of a fixed bed during the steam cycle may be difficult, because of the tendency of very fine particles to become fluidized even at the low linear velocities involved. In general, particles with a size range of −20 to +200 mesh should be satisfactory.

The fluidized lime regeneration process is carried out at substantially atmospheric pressure. The regeneration vessel has a much higher capacity than the steam-carbon reaction vessel and therefore one regeneration vessel may be employed in conjunction with anywhere from four to ten steam-carbon reaction vessels.

Such a system is shown in Figure 3, the operation of which will now be described. In the drawing like numbers designate corresponding parts. A lime-char mixture of the previously specified proportions is first prepared in the following manner. Char of −20 to +200 mesh particle size from a fuel hopper 50 is charged to a storage vessel 52. Similarly, regenerated lime or fresh lime of corresponding particle size distribution is transferred from a make-up lime hopper 54 to a storage vessel 56. However, to facilitate the subsequent separation of the lime particles from partially consumed char, it may be desirable to feed char whose particle size range differs from that of lime, where nevertheless, the particle size range of the bed is within the range of −20 to +200 mesh. For example, relatively coarse lime of −20 to +65 mesh is mixed with −65 mesh char; alternatively, −20 to +65 mesh char is fed along with fine lime particles, such as −100 mesh. From these two vessels 52 and 56 the char and the lime are conducted under the control of valves 58 and 60, respectively, to charging cylinders 62 and 64 which are sized according to the desired ratio of solids. Then the two batches of solids in the proper weight relation to each other are combined in a conduit 65 when they are picked up by a stream of flue gas or low pressure steam from conduit 66 and carried through conduit 67 to a cyclone separator 68. The latter separates the solids from the carrier gas and drops the solids into a solids feed manifold conduit 70. The carrier gas is exhausted through conduit 72. The solids feed manifold 70 is connected to a series of superimposed steam-carbon reaction zones 74 by valved interconnecting conduits 76. The series of reaction zones 74 may be confined in a single vessel, as shown, being separated from one another by imperforate plate members 78. Each of the reaction zones is adapted to contain a bed of solids 79 supported upon a perforated plate member 80. Steam is fed to the several zones below the perforated plate members 80 through valved conduits 82 which communicate with a higher pressure steam manifold conduit 84. Solids are discharged from the reaction zones 74 into a discharge manifold 86 through interconnecting valved conduits 88 which extend down into the beds 79.

In any given cycle some of the reaction zones 74 will not be in operation in order to permit discharge of their contents as will be described below. Those which are in operation to make gas are charged with an amount of lime-char mixture through conduits 76 to establish beds 79 of from one to ten feet in depth. Steam is then introduced below the perforated plate members 80 through conduits 82 and is caused to pass up through the beds 79 at a velocity insufficient to effect fluidization of the solids. The pressure within the reaction zones is maintained by means of valves 90 disposed in conduits 92 leading to a product gas manifold conduit 94. Steam is passed through the beds of solids in the vessel for from one to four hours or until the lime is substantially converted to carbonate. The composition and heating value of the high pressure product gas issuing through conduit 94 from the reaction vessel 74 correspond substantially to those listed in Table 1 and given in connection with the description of the operation of the apparatus of Figure 2 for the corresponding temperatures and pressures.

When the lime in reaction zone 74 has been substantially completely converted to carbonate, valve 90 in the product gas line 92 is closed and valve 100 is opened to permit the reaction zone to communicate with a low pressure low B.Th.U. fuel gas product line 96 which in turn communicates with a low pressure gas manifold 98. The product gas remaining in the reaction zone 74 enters the conduit 96 through valve 100. The introduction of steam through conduit 82 is continued and ordinary water gas is produced in reaction zone 74 until the temperature of the bed 79 falls below the water gas reaction temperature because of the endothermic character of the conventional water gas reaction. The gas issuing from manifold 98 can be used directly as a low B.Th.U. fuel gas or can be subjected to further processing as will be described later. In order to discharge the contents of the vessel 74, which after the gas producing cycle comprises largely carbonate mixed with a small amount of ash and unreacted carbonaceous fuel, the pressure is reduced and the velocity of the steam is increased to effect fluidization of the solids supported on distributor plate 80. The valved discharge conduit 88 is then opened and flue gas or steam or other inert gas circulating through conduit 102 draws the solids out of the reaction zone 79 through manifold conduit 86, then through conduit 102 and into a cyclone 104. The solids drop through cyclone leg 106 into a storage vessel 107 while the carrier gas escapes through a conduit 108. When it is desired to replace some of the lime with fresh lime it will be necessary to discharge carbonate from the system and this may be accomplished by a discharge or drawoff conduit 110. The mixture of carbonate and unreacted carbonaceous fuel drops through a valved conduit 112 into a conduit 114 and is carried by means of air into a regenerator 116 in which a fluidized state is maintained by proper control of the linear velocity of the air with respect to the particle size of the solids. Oxidation of the carbonaceous fuel with air in regenerator 116 provides the heat necessary to regenerate the lime. The flue gases leave generator 116 through a conduit 117 and enter a cyclone separator 118 from which they are discharged through effluent line 120. Separated fines return to regenerator 116 through a cyclone leg 121. Regenerated lime is conducted through a valved conduit 122 to the lime storage vessel 56 for recycling in the above process.

In the regeneration of the lime it is advisable to regulate the air current through the regenerator to prevent undue oxidation of the sulfides formed in the water gas reaction zones 79. When all the carbonaceous solids have been burned, these sulfides may react with excess oxygen to form sulfates unless sufficient opportunity is provided for their conversion into lime and sulfur dioxide.

Thus it will be seen that it is possible by the use of a single fluidized regeneration vessel to provide the requisite quantity of fresh lime to a plurality of fixed bed water gas reaction zones. Moreover the production of gas is made continuous by having a series of reaction vessels, some of which are discharging their reacted contents while the remainder are utilized in the manufacture of the desired product gas.

As indicated above, the use of a fluidized steam-carbon reaction zone is feasible provided the pressure is maintained at a relatively low level, i.e., in the neighbourhood of the permissible lower limits for this reaction, namely, five to about thirty atmospheres, and also if the beds are of substantial depths to afford adequate contact times. In Figure 4 of the drawings there is shown a completely fluidized system which, subject to the above limitations, is adapted to carry out the new process. This system and its operation will now be described.

Referring to Figure 4 of the drawings, pulverized char from a hopper 150 is fed continuously through a valved conduit 152 into a reaction vessel 154. Concurrently finely divided lime is continuously charged into reaction vessel 154 through a conduit 156 from a conduit 158. The relative proportions of lime and char are as previously stated. The bed of solids 160 confined in reactor 154 is maintained in a fluidized state by steam fed through conduit 156 from a conduit 162. To effect satisfactory fluidization, the particle size of the solids is preferably less than 20 mesh and the superficial linear velocity of the steam is of the order of 0.1 to 1 foot per second depending on the size distribution of the solids. In order to establish a temperature in the reactor 154 within the range of 1430° to 1800° F., air, instead of steam, is first introduced into reactor 154 through a conduit, not shown, to oxidize the char to develop the necessary required temperature. Once this temperature is established, steam replaces the air in order to carry out the steam-carbon reaction and under the conditions maintained in the reactor 154, no further heat need be added. The conversion of water to the steam required by the reaction is accomplished by heat exchangers hereinafter to be described which utilize only the heat developed during the reactions. The pressure in reactor 154 is maintained in accordance with the previously expressed equation relating minimum pressure with temperature but is preferably between ten and thirty atmospheres. Valve 164 in the product gas line 166 serves to control the pressure in reactor 154. Product gas is conveyed from reactor 154 through a conduit 165 to a cyclone 167 where it is separated from entrained solids which are returned to the reaction zone through a cyclone leg 168.

The reactions taking place in the reactor 154 during the gas manufacture are the same as those previously described in connection with the operation of the system illustrated in Figure 2. In this instance, however, instead of regenerating the lime in vessel 154, a mixture of calcium carbonate and char is withdrawn from a settling section 169 through a valved conduit 170 into a valved air line 172. The air carries this mixture of solids through the line 172 into the lime regenerator 174 wherein the lime is regenerated by the heat developed by the oxidation of the char with air. The flow of air through the bed of solids 176 confined in the lime regenerator 174 is regulated so as to maintain a fluidized bed in the same manner as in the reactor 154.

The regenerated lime and ash produced in regenerator 174 are conducted through a valved discharge conduit 176 to a separator 180 wherein the two solids are separated from each other and from any entrained gases. Ash particles are removed from the system through a valved discharge conduit 181. The separated lime is then returned through conduit 158 and conduit 156 to the reactor 154. Flue gases from the lime generator 174 are conducted through a conduit 182 to a cyclone 184. The precipitated solids are returned to the bed 176 through a cyclone leg 186 while the solid free gases are conducted by a conduit 188 to a conduit 190. Since the gases issuing from the lime regenerator are at an elevated temperature, the heat contained therein is utilized to raise the temperature of the incoming air to the generator by passing in heat exchange relation through an exchanger 192. The resulting flue gases are then conducted through conduit 191 to any suitable place of disposition.

Product gases from reactor 154 contains carbon monoxide, hydrogen, methane and some carbon dioxide, and as in the case described in connection with Figure 2, the product is suitable for use as a fuel gas having a composition corresponding to those listed in Table I when produced under similar reaction conditions.

As previously discussed, the reaction conditions in reactor 154 may be regulated to produce either a hydrogen rich gas product or methane rich, high B.Th.U. gas product.

Consider first the situation where a hydrogen rich product is desired. Reactor 154 is operated at a pressure only slightly above the pressure given by the empirical relation for minimum thermoneutral pressure. The gas product from reactor 154 contains carbon monoxide, hydrogen, methane and some carbon dioxide in a ratio adapted to produce additional hydrogen by the conventional water gas shift reaction. When a standard water gas shift catalyst, such as iron chromia, is employed at about 500° F. in the presence of excess steam, substantially all the carbon monoxide in the gas is converted into carbon dioxide and hydrogen. However, it is preferred to run the carbon monoxide conversion reaction in a third vessel containing lime in a fluidized condition. In this vessel, the carbon monoxide is converted into hydrogen and carbon dioxide. The carbon dioxide formed reacts with the lime, so that the gas product contains more hydrogen than the gas fed into the vessel, a small amount of hydrocarbonaceous gases, predominantly methane and substantially no carbon monoxide or carbon dioxide. Accordingly, the gas produced in vessel 154 is passed through a water gas shift reactor 194 which serves to convert some of the gas to additional hydrogen and to remove some of the carbon dioxide. The heat generated in reactor 194 may be utilized to generate steam required to carry out the reaction in vessel 154. If desired, a quantity of char may be added to the water gas shift reactor 194 as a catalyst, or a quantity of an active water gas shift catalyst such as iron-chromia may be added to the reactor to promote the shift reaction.

In the present instance, as shown in Figure 4, the product gas from reactor 154 is conducted through conduit 166 into the hydrogen generator 194. Some of the heat contained in the product gas from vessel 154 is utilized in heat exchanger 196 to raise the temperature of the water or steam being fed to the reactor 154 through conduit 162. The hydrogen synthesis in generator 194 can be carried out at about 1431° F. and at a pressure regulated by valve 198 in the effluent gas conduit 200, substantially the same as the pressure maintained in the steam-carbon reactor 154. Lime from separator 180 enters reactor 194 through conduits 158, 201 and 166, respectively. Calcium carbonate formed in reactor 194 is discharged from the reaction zone through conduit 203 and returned to the lime regeneration vessel 174 for reconversion to lime. The bed 202 is maintained in a fluidized state by proper sizing of the lime particles and by proper selection of linear velocities of the incoming gases. The resulting hydrogen enriched gas is conducted through a conduit 204 to a cyclone separator 206 from which solid fines are returned to the bed through cyclone leg 208. The substantially solid-free gas product is conducted through conduit 200 to a second cyclone 210 for removal of any extremely fine solid particles that may have passed through cyclone 206. These solids are removed through valved discharge conduit 212. The gaseous product is carried to storage through a valved conduit 216. The heat contained in the product gas issuing from the hydrogen generator is utilized in waste heat boiler 220 to raise the temperature of water or steam circulating through conduit 162. The steam or water from the waste heat boiler 220 is conducted in heat exchange relationship with the bed 202 in reaction vessel 194 and from there to heat exchanger 196.

As an example of the further improvement in hydrogen yield effected by the present invention, consider the case in which reactor 154 operates at 1750° F. and 40 atmospheres pressure at a steam conversion rate of 55 per cent. The gas leaving reactor 154 has the following composition:

	Dry Basis Volume per cent	Wet Basis Volume per cent
Hydrogen	61.7	36.2
Methane	12.3	7.2
Carbon Monoxide	14.9	8.7
Carbon Dioxide	11.1	6.5
Water	—	41.4
	100.0	100.0

When this wet product gas is passed through reactor 194 at 1431° F. without the addition of steam, the final product where water gas equilibrium is established in reactor 194, had the following composition on a dry basis:

	Volume per cent
H_2	84.7
CH_4	13.4
CO	1.2
CO_2	0.7

It may be desirable under certain circumstances to add more steam to the gas feed reactor 194 thereby increasing the concentration of hydrogen in the final product gas by shifting the equilibrium to favor greater conversion.

A comparison of the hydrogen composition of the final product gas produced by this new invention and that produced by conventional water gas reactions under similar conditions (see Table I) shows the vast improvement which can be realized when the method of the present invention is adopted and when a hydrogen rich gas is desired.

However, as previously discussed, the invention also can be utilized under other conditions to produce methane rich gas which can be upgraded by passing it over any standard methanization catalyst, such as nickel on aluminium oxide.

The increase in methane content attained by the practice of this process as described is sufficient for many industrial applications. However, it has been discovered that a greater increase may be effected if it should be found desirable or necessary, by establishing carefully controlled predetermined temperature differences in the reaction zone or zones in which the gas is made, the specific temperatures maintained being still within the range previously specified as critical to the successful operation of the process. In this modification of the process, most of the steam-carbon-lime reaction is carried out in a zone where the temperature lies between approximately 1670° and 1770° F. The product gases from this reaction are then caused to circulate through another zone, separate or contiguous, in which the carbonaceous solids are maintained at a temperature between 1430° and 1600° F. While this modified process may be practiced in either a fluidized or non-fluidized system, an apparatus is shown in Figure 5 for carrying out the process which involves a fluidized system by way of example only.

The operation of the modified system as shown in Figure 5 will now be described. Only the steam-carbon reaction vessel is illustrated since the method of regenerating the lime is the same as any of those previously described. Accordingly, the present description will be restricted to the operation of a reaction vessel 250. The latter is so designed as to provide a plurality of fluidized beds arranged one above the other with the flow of solids from one bed to the other being countercurrent to the flow of fluidizing gas, namely, steam in this instance. In addition, the temperatures of the three beds are maintained so that the temperatures decrease progressively from the bottom to the top. The pressure maintained throughout the system is at least as great as that given above by the empirical relation (2) as the minimum pressure necessary to produce a methane rich gas and is preferably from 30 to 50 atmospheres.

A mixture of char and lime in the previously specified proportions is introduced into the reaction vessel 250 through a conduit 258 into which char is fed from a char hopper 254 and lime is fed from a hopper, not shown, through conduits 266 and 252, respectively. This may be accomplished either by suitable screw feeding devices or by introducing carrier gases such as steam.

The incoming mixture of char and lime forms a bed 260 which is supported on a porous plate 262. Steam is introduced into the reactor 250 through a conduit 264, circulates up through the vessel and through porous plate 262 into bed 260. The superficial linear velocity of the steam is regulated to effect fluidization of the solid mixture which is composed of finely divided solids less than 20 mesh size. The mixture of char and lime is fed continuously to bed 260 with the result that the latter builds up until it overflows through a conduit 266 down onto a second porous plate 268. Here in turn a second bed 270 is established and is likewise maintained in a fluidized condition by the incoming steam. This bed over flows through a conduit 272 to the lower part of the vessel to form a bed 274.

As previously described, it is essential for the operation of this now process that the temperature within the beds lie within the range 1430° to 1800° F. but it has been found that a greater yield of methane is produced if most of the reaction between steam and the carbonaceous solids takes place at a temperature between 1670° and 1770° F. with the gaseous product of this reaction thereafter passing through a zone containing carbonaceous solids maintained at a temperature between 1430° and 1600° F., i.e., where the temperature gradient between the two zones is at least 100° F. Accordingly, in the reactor vessel 250, the flow of char and lime mixture through the bed 274 is regulated to maintain a temperature therein between 1670° and 1770° F. The hot product gases and unreacted steam pass up through porous plate 268 through bed 270 where further reaction with steam takes place. However, this bed is maintained at a lower temperature than bed 274 because of the reduction in temperature effected by the relatively cool solids which overflow from bed 260. Additional cooling may be required, i.e., the gases leaving bed 274 may be cooled by passing over a steam generating coil before entering bed 270. The gaseous products are carried up through porous plate 262 and bed 260 which is maintained at a temperature between 1430° and 1600° F.

Passage of the gaseous products containing carbon monoxide and hydrogen through bed 260 results in conversion of these gases to methane. The pressure maintained within the vessel is as previously described. A valve 276 in the product gas exit conduit 278 serves to maintain the pressure at the desired level. The product gases are conducted from vessel 250 through a conduit 280 to a cyclone 281 where solid fines are separated and returned to bed 260 through a cyclone leg 286. The solid free product gas leaves the cyclone through conduit 278.

Again as in the apparatus of Figures 2, 3, and 4, the process of Figure 5, carried out under these conditions, is essentially thermoneutral and may be even exothermic. Once the reaction has been started at the temperature and pressure stated, the requisite heat is supplied by the reaction between lime and the product carbon dioxide. The process is maintained continuous by removal of solids containing calcium carbonate and carbonaceous solids from the bottom of the vessel through a conduit 284. The calcium carbonate is regenerated to lime in any of the ways previously described. The product gases obtained from this reactor before being further subjected to methane synthesis have a composition depending upon the particular temperature gradient and the pressure established in the system, but are consistently higher in methane content than those obtained where the reaction zone is held at one temperature. As an example, it was found that where a temperature of 1700° F. was maintained in the lowermost bed, a pressure of 30 atmospheres in the reaction vessel and a temperature between 1430° and 1500° F. in the uppermost bed, a gas was obtained having a gross heating value of 625 B.Th.U. per cubic foot at 60° F. and containing 0.6% CO_2, 52.1% H_2 and 44.1% CH_4.

It is to be understood that wherever the word "char" is used in the foregoing description and in the accompanying claims, it is intended to signify the carbon-containing residue obtained from the low temperature distillation of a hydrocarbonaceous solid fuel.

What I claim is:—

1. The process of making gas including passing steam into a mixture of carbonaceous solid fuel and calcium oxide or lime in a reaction zone and collecting the gaseous products, in which process the steam is introduced into the reaction zone at a temperature within the range of 1430° to 1800° F. and under a pressure which is at least

$$3.40-1.89\times10^{-2}(t-1430)+4.48\times10^{-4}(t-1430)^2$$

atmospheres where t is the temperature in °F., the amount of calcium oxide or lime present in the reaction zone being sufficient to convert substantially all the carbon dioxide produced to carbonate.

2. The process according to claim 1, wherein the mixture contains at least 120 parts by weight of lime for each 100 parts by weight of carbon contained in the carbonaceous solids.

3. The process according to claim 1 or 2, wherein the mixture contains a maximum of 300 parts by weight of lime for each 100 parts by weight of carbon contained in said carbonaceous fuel.

4. The process according to any of the preceding claims, wherein after conversion of the carbon dioxide to carbonate, the steam is replaced by a gas containing oxygen gas such as air to reconvert the carbonate to lime.

5. The process of making gas including mixing lime and a carbonaceous solid fuel, bringing steam into contact with the mixture, and recovering the gaseous products, wherein the relative proportions of lime and carbon are 120 to 300 parts by weight of lime for each 100 parts by weight of carbon contained in said carbonaceous fuel, and wherein the steam is introduced in reactive relationship with said carbonaceous fuel in a non-fluidized reaction zone, at a temperature within the range 1430° to 1800° F. and under a pressure which is at least

$$3.40-1.89\times10^{-2}(t-1430)+4.48\times10^{-4}(t-1430)^2$$

atmospheres where t is the temperature in °F., whereafter the introduction of steam is discontinued when the steam-carbon reaction is substantially completed and air is introduced at atmospheric pressure through the solid residue to regenerate the lime.

6. The process according to claim 5, wherein the steam-carbon reaction with the regenerated lime and fresh carbonaceous fuel is repeated.

7. The process according to claim 5 or 6, wherein a plurality of independent non-fluidized reaction zones is provided and the air is introduced into the solid residues from the plurality of reaction zones in a single fluidized regeneration zone to effect regeneration of the lime.

8. The process according to any of the preceding claims, wherein the gas produced from the steam-lime-carbonaceous fuel reaction is introduced into a second reaction zone containing lime under proper conditions to effect a water gas shift reaction.

9. The process according to any of the preceding claims, wherein the flow of steam and solids through the reaction zone is regulated to produce a temperature difference of at least 100° F. between the inlet and outlet ends of said zone, with the higher temperature being at the inlet end.

10. The process according to claim 9, wherein the steam is passed through a plurality of successive reaction zones in reactive and countercurrent relationship to said carbonaceous solids, said temperature difference of at least 100° F. being maintained between the first and last reaction zone, with the higher temperature being in the first zone.

11. The process according to any of the preceding claims, wherein the pressure must not exceed

$$5.0+4.2\times10^{-2}(t-1430)+2.7\times10^{-4}(t-1430)^2$$

atmospheres where t is the temperature in °F.

12. The process according to any of claims 1 to 10, wherein the pressure of the reaction zone is at least

$$5.0+4.2\times10^{-2}(t-1430)+2.7\times10^{-4}(t-1430)^2$$

atmospheres where t is the temperatures in °F.

13. The process according to claim 11 or 12, wherein the temperature of the

reaction zone is maintained between 1520° and 1650° F.

14. The process of making gas from carbonaceous solid fuels substantially as described with reference to the accompanying drawings.

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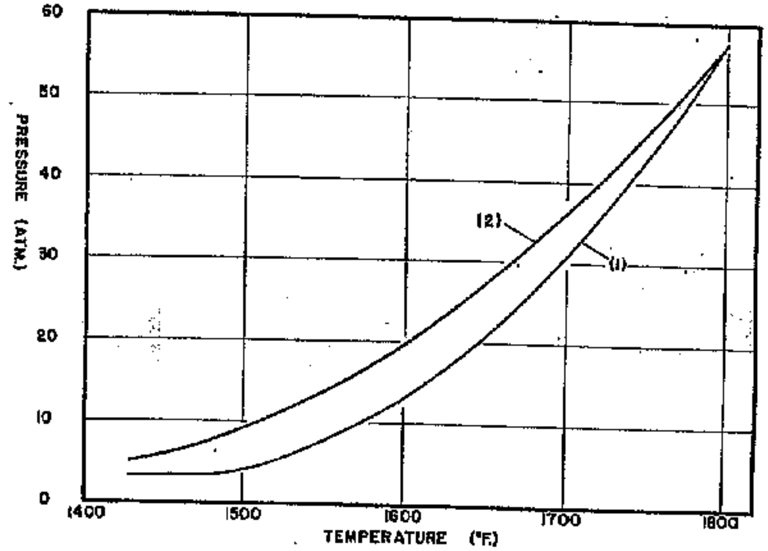
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50
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30
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1500
1600
1700
1800
TEMPERATURE (°F.)
(2)
(1)

FIG. 1

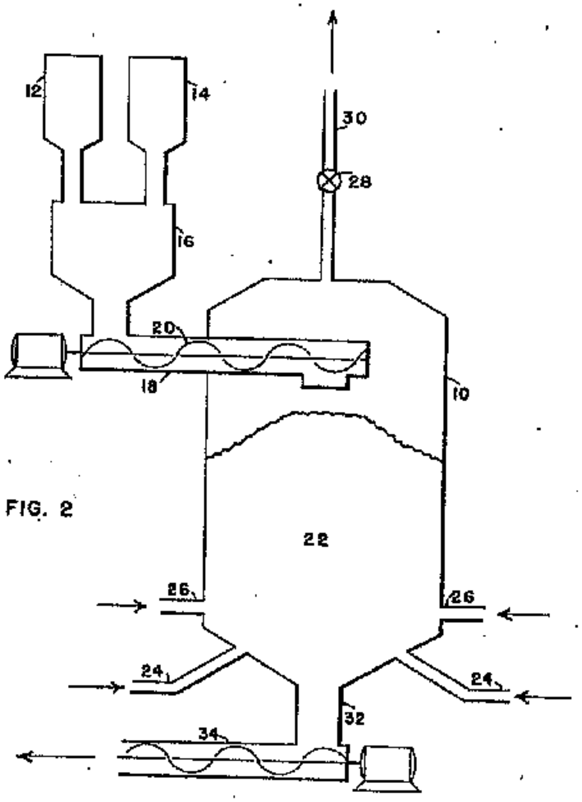
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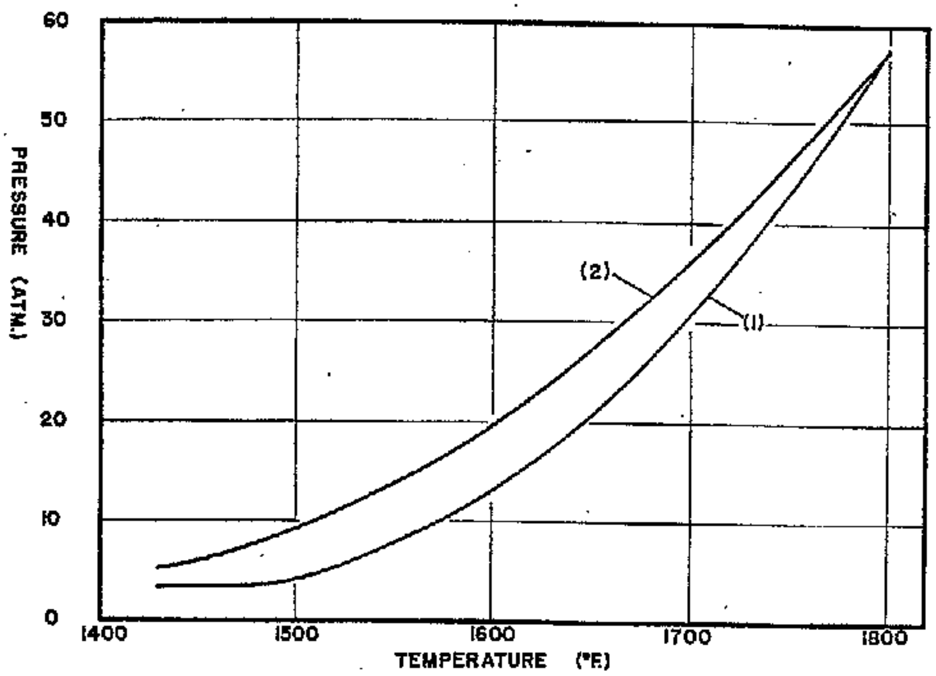
FIG. 2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1600
1700
1800
TEMPERATURE (°F)
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FIG. 1

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SHEETS 1 & 2

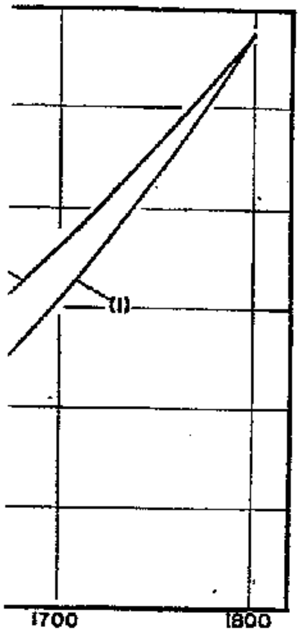

FIG. 1

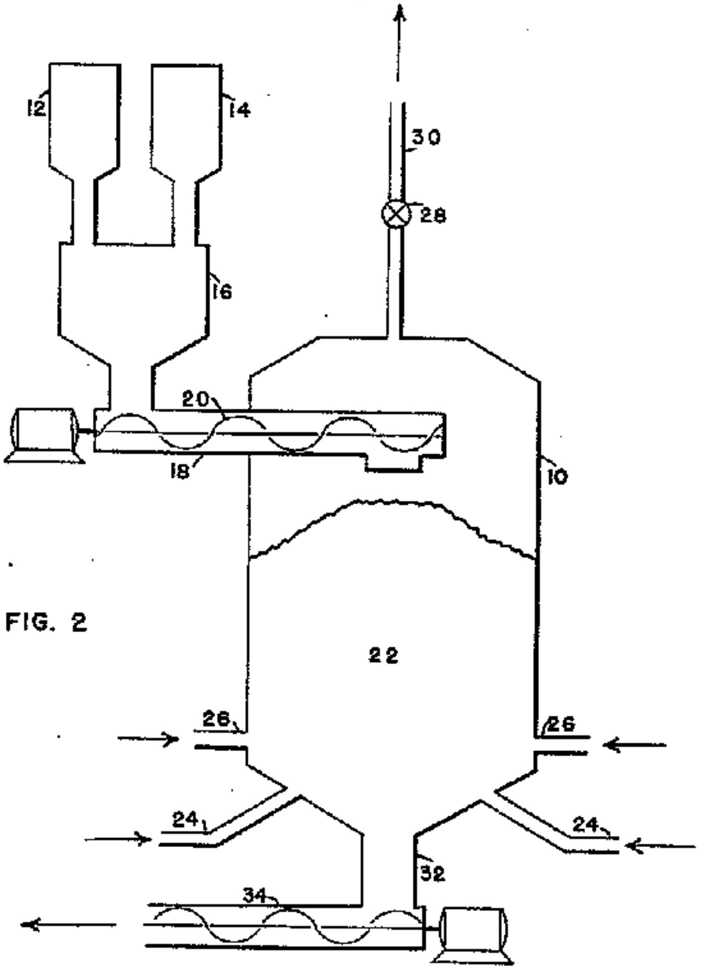

FIG. 2

673,170 COMPLETE SPECIFICATION

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SHEET 3

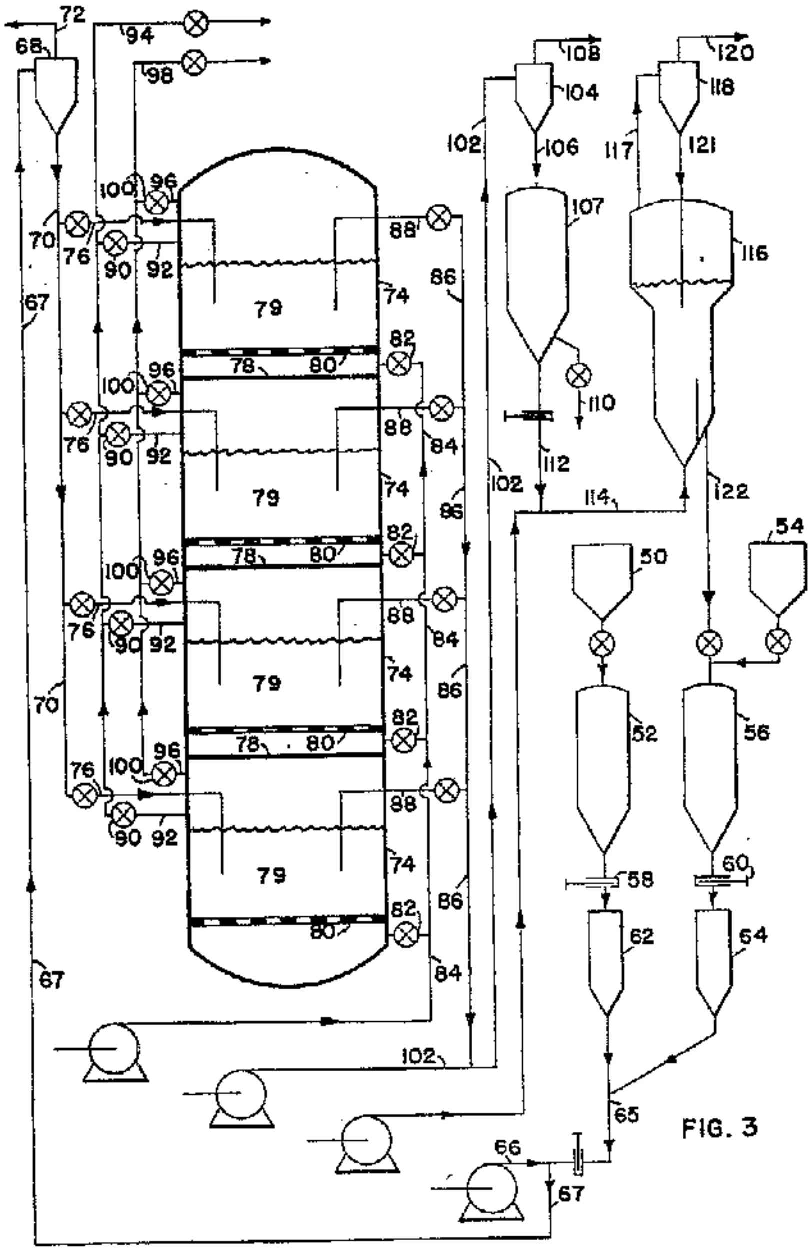

FIG. 3

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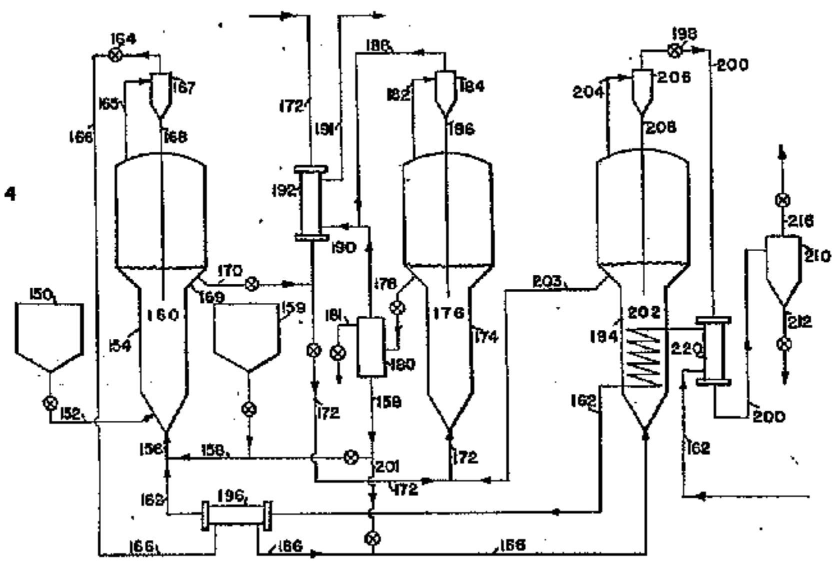


FIG. 4

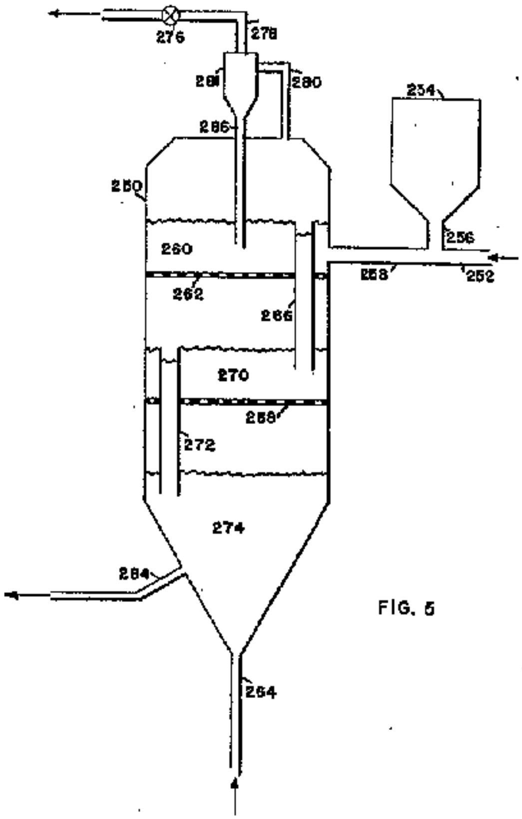
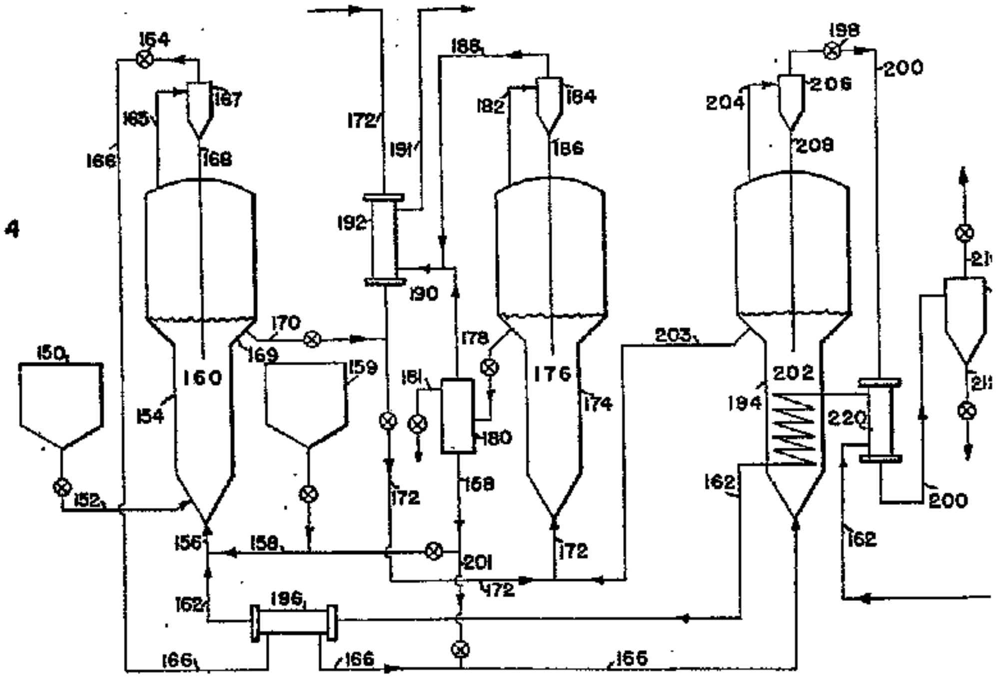


FIG. 5

FIG. 4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673,170 COMPLETE SPECIFICATION
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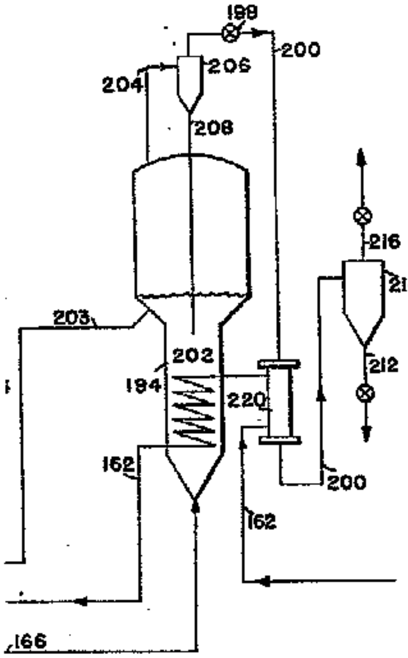
SHEETS 4 & 5



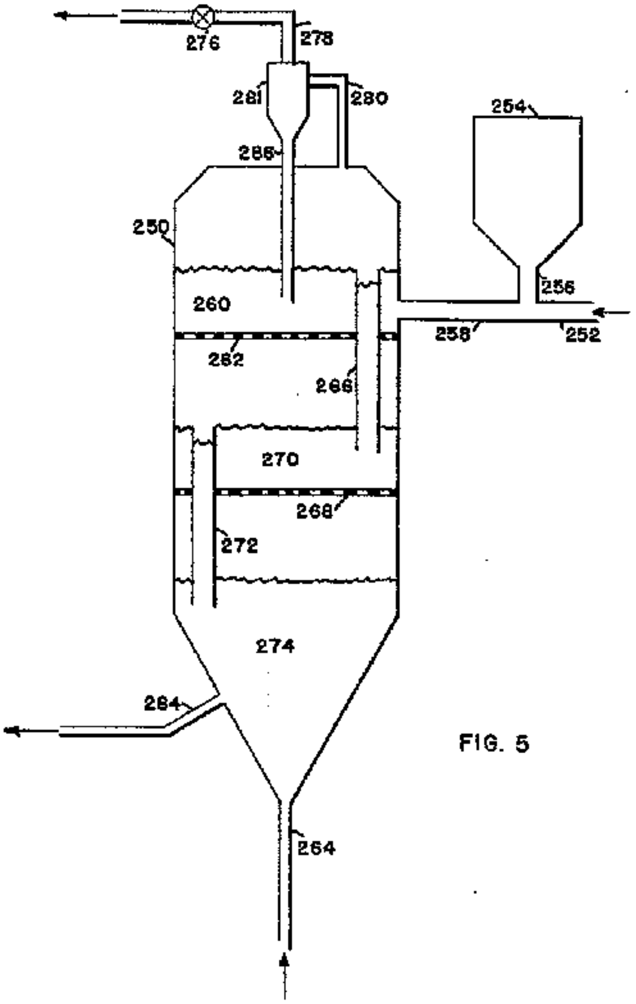


FIG. 5