

# RESERVE

## PATENT SPECIFICATION

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2705

### COMPLETE SPECIFICATION.

#### Improvements in or relating to the Method of Producing Hydrogen.

We, PITTSBURGH CONSOLIDATION COAL COMPANY, a Corporation organised under the laws of the State of Pennsylvania, United States of America, of Koppers Building, 5 Pittsburgh, Pennsylvania, United States of America (Assignees of EVERETT GOBIN), do hereby declare the invention, for which we pray that a patent may be granted to us, 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 manufacture of hydrogen and, more particularly, to a method of and apparatus for making hydrogen from a gaseous hydrocarbon by reacting the latter with steam.

The primary object of the invention is to provide an improved method and apparatus for making hydrogen by the reaction of steam and a hydrocarbon gas in the presence of lime.

Another object of the present invention is to react steam and a gaseous hydrocarbon in the presence of lime under certain critical conditions of pressure and temperature so that a high yield of hydrogen is obtained with little heat, other than that supplied by the reaction system, being required to maintain the reaction.

A still further object of the invention is to provide an improved method for making hydrogen at elevated pressures and temperatures.

In accordance with the invention, a method and apparatus have been provided for producing hydrogen in high yields in relatively pure form under nearly thermoneutral conditions, i.e., little heat other than that supplied in the reaction is required. The method comprises circulating steam and a hydrocarbon in gaseous phase in intimate contact with each other through a reaction zone containing sufficient calcium oxide in granular form to absorb substantially all the carbon dioxide produced by the steam-hydrocarbon reaction, the temperature of the reaction zone being between

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1400° and 1750°F. and the pressure being above about 2.7 atmospheres absolute. For each temperature within the range recited there is a corresponding minimum pressure above 2.7 atmospheres which must be maintained or exceeded. This critical relationship between the temperature and pressure is expressed by the following empirical equation:—

$$(1) p = 3.0 + 1.94 \times 10^{-2} (t-1431) + 3.41 \times 10^{-4} (t-1431)^2$$

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

The practice of the invention produces large yields of hydrogen gas of relatively high purity with very little heat being required to maintain the reaction. Optimum results are obtained if the temperature lies within the range 1500° to 1650°F. and the pressure is between 20 and 50 atmospheres, provided the relationship expressed in equation 1 is observed. Also, it is preferred that there be at least 250 parts by weight of calcium oxide present for each 100 parts by weight of carbon contained in the hydrocarbon gas passed through the bed of lime. Furthermore, when the hydrocarbon gas consists essentially of methane, it is desirable and preferred to employ a steam-hydrocarbon ratio of from 2 to 1 to 4 to 1.

Due to the relatively mild temperatures employed in the process, it is desirable to add catalytic agents. While the lime itself is a mild catalyst for the reaction, its catalytic activity can be supplemented by adding small amounts of more potent catalytic agents, particularly the metals of the Copper, Nickel, Cobalt and Iron disposed on suitable supports, i.e., copper on silicic gel, nickel, cobalt or iron on alumina, fused magnesia or silica gel. Alternatively, the catalyst may be incorporated directly on the lime by impregnation with aqueous solutions of the soluble salts, i.e., nitrates. Or nickel or stainless steel chips may be incorporated directly in the bed as a catalyst.

For a better understanding of the inven-

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tion, its objects and advantages, reference should be had to the following description and to the attached drawings, in which:—

Fig. 1 is a diagrammatic illustration of an apparatus for carrying out an embodiment of the invention; and

Fig. 2 is a diagrammatic illustration of a modification of the apparatus of Fig. 1 which is adapted to carry out another and preferred embodiment of the invention.

In the following description of a specific embodiment of the invention, by way of example only, the new process and apparatus are applied to the conversion of methane to hydrogen. It is to be understood, however, that the invention is generally applicable to any hydrocarbon gas which reacts with steam to produce hydrogen. Among such hydrocarbon gases are included the so-called permanent gases, such as methane, ethane, propane or butane. Also included are hydrocarbon gases produced by the vaporization of liquid hydrocarbons at the temperatures of the reaction, as well as hydrocarbon gases resulting from the thermal decomposition or cracking of liquid or solid hydrocarbonaceous materials, such as coal tar pitch.

The apparatus shown in Fig. 1 and its operation will now be described. Numeral 10 designates a reaction vessel which is adapted to hold a bed of calcium oxide supported upon a porous plate member 12 disposed near the bottom of the vessel. The bed of lime is first brought to a temperature between 1400° and 1750°F. by any suitable means such as external heating of the vessel or by burning producer gas or pulverized coal in the vessel itself. As soon as this temperature is attained, steam and methane are introduced through valved conduits 14 and 16, respectively, through the bottom of the vessel 10. The relative proportions of steam and methane preferably lie between 2 to 1 and 4 to 1 in order to obtain the optimum conversion of methane consistent with efficient utilization of the steam. The amount of lime contained in the bed is sufficient to absorb substantially all of the CO<sub>2</sub> produced as a result of the reaction between the steam and methane. Preferably, there are at least 250 parts by weight of the oxide for each 100 parts by weight of carbon contained in the methane passed through the bed. The particle size of the lime and the velocity of the steam and methane are regulated so that the bed of lime is maintained as a fixed or non-fluidized bed rather than as a fluidized bed. However, fluidized operation may be used if desired, particularly when operating at the upper end of the temperature range. The pressure within the vessel is maintained above 2.7 atmospheres in accordance with the relationship expressed by equation 1 by means of a valve located in

the product gas line 20.

The reaction between the steam and methane at a temperature between 1400° and 1750°F. under pressures as specified above produces a gas containing principally hydrogen with relatively small amounts of carbon dioxide, carbon monoxide and unreacted methane. Substantially all of the carbon dioxide produced is absorbed by the lime in situ with the resulting generation of heat which serves to supply most of the heat required for the endothermic reaction between the steam and the methane. The additional heat required may be supplied in any suitable manner as by external heating of the walls of the vessel (not shown) or by burning the necessary amount of carbonaceous material within the vessel itself, that is, by feeding in limited amounts of oxygen. The product gas is conveyed from the vessel 10 by a conduit 22 which leads to a cyclone separator 24 where the gas is separated from entrained solids, if any. The latter are then returned to the bed of lime by means of a dip leg 26. The product gas is conveyed to any suitable storage place or to a subsequent processing stage through the conduit 20.

The regeneration of calcium oxide from the calcium carbonate produced in the above reaction may be accomplished by heating the bed to the decomposition temperature preferably 1750° to 1800°F. and preferably under fluidized conditions by means of heat supplied by the combustion of producer gas or by the combustion of pulverized coal. In order to accomplish this, it is necessary to regulate the particle size of the lime so that under certain velocities of inlet gas a non-fluidized bed may be maintained, that is, during the hydrogen generation cycle; and under certain other velocities of inlet gas a fluidized bed may be maintained. The particle size range of the lime to permit fluidized operation in the regeneration cycle and non-fluidized operation in the steam-hydrocarbon reaction cycle may be, for example, —20 to +200 mesh on the Tyler scale. The linear velocities of the inlet gases during the steam-hydrocarbon cycle may be of the order of 0.01 to 0.10 feet per second under the pressures required for this particular cycle. On the other hand, a fluidized lime regeneration process which is carried out at substantially atmospheric pressure may be conducted at linear velocities of the order of 1.5 feet per second, i.e., 0.5 to 3.0 ft./sec. Since the vessel, when employed as a regenerator, has a higher capacity than during the steam-hydrocarbon cycle, one regeneration vessel may be employed in conjunction with anywhere from four to ten steam-hydrocarbon reaction vessels. In such a case it will be necessary to withdraw the lime in a fluidized state from a plurality of vessels 10 to a single

regeneration vessel (not shown).

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 relatively long residence time conditions to permit the reaction to reach equilibrium. The table also includes, for purpose of comparison, the composition of gas produced under the same

set of conditions where no lime is employed. It should be borne in mind that where no lime is employed, all the heat must be supplied for the endothermic reaction of steam with methane, while, in the cases where lime is employed, very little heat need be supplied in the system to maintain the reaction.

Temperature °F.	Pressure Atm. Absolute.	$H_2O/CH_4$ Ratio.	Gas Compositions				Per Cent Conversion of		
			$H_2$	CO	$CO_2$	$CH_4$	Steam.	Methane.	
20	Without Lime								
	1431	10	2	69.0	13.2	7.8	10.0	47.8	67.7
		30	2	61.6	8.9	8.1	21.4	31.7	44.3
	1521	30	2	66.0	12.2	7.4	14.4	41.1	57.6
25									
	1610	30	2	70.1	15.7	5.9	8.3	46.4	72.3
		40	2	68.5	14.6	6.2	10.7	42.9	66.0
		30	4	75.3	12.7	9.3	2.7	25.1	89.0
30	With Lime								
	1431	10	2	81.3	6.5	2.4	9.8	59.4	68.4
		30	2	81.5	1.7	0.5	16.3	55.4	56.3
	1521	30	2	80.5	4.7	1.7	13.1	54.5	61.8
	1610	30	2	75.2	12.2	3.9	8.7	51.5	76.1
		40	2	77.0	8.9	3.0	11.1	51.8	66.0
	30	4	84.6	7.8	5.3	2.3	36.6	91.0	

Referring now to Fig. 2 of the drawings, the preferred embodiment of the invention is disclosed. The apparatus disclosed therein comprises three similar reaction vessels 30, 32 and 34, respectively, in which a bed of calcium oxide is adapted to be supported on porous plates 36, 38 and 40, respectively, in the lower portions of the several vessels at the temperatures and pressures previously specified. Each of the vessels is provided with corresponding inlet and outlet valved conduits for carrying gases.

A main steam line 42 connects with a hydrocarbon gas feed line 44 to form a conduit 46 for conveying a mixture of steam and hydrocarbon gas. A valve 48 in conduit 42 and a valve 50 in conduit 44 serve to control the flow of steam and hydrocarbon gas, respectively, into the common conduit 46. The latter opens into the top portion of vessel 30 under the control of a valve 52, while a branch conduit 54 and a branch conduit 56 connect conduit 46 with the corresponding top portions of vessels 32 and 34 with control valves 58 and 60, respectively, disposed in the branch conduits 54 and 56 and corresponding to control valve 52.

The three vessels 30, 32 and 34 are interconnected at the bottom of each vessel by means of gas conduits 62, 64 and 66, having valves 68, 70 and 72, respectively, disposed therein. By means of these valved interconnecting conduits, gas may be conveyed from the bottom of one vessel to either of the other two vessels.

At the top of the three vessels 30, 32 and 34, gas conduits 74, 76 and 78, respectively, are provided for conducting exit or product

gases from the vessels to cyclone separators 80, 82 and 84, respectively. The latter serve to separate solids entrained in the discharged gases and return the solids to the beds in the vessels through dip legs 86, 88 and 90, respectively. The solid-free gases from the cyclone separators are carried by gas conduits, 92, 94 and 96, respectively, to the juncture of two main gaseous discharge systems. One system is adapted to carry off the hydrogen product when the vessel in question is functioning as a hydrogen generator, as will be described later, while the other system is adapted to carry off flue gas when the vessel in question is operating to regenerate the calcium oxide.

The hydrogen discharge system comprises a main gas conduit 98 leading from conduit 92 and communicating with conduits 94 and 96 by means of two branch conduits 100 and 102, respectively. Valves 104, 106 and 108 in conduits 98, 100 and 102 control the flow of hydrogen gas therethrough. The main line 98 is arranged in heat exchange relation with the main steam line 42 by means of a heat exchanger 110. A valve 112 in the hydrogen line 98 serves to regulate the pressure maintained in the vessels 30, 32 and 34 when they are functioning as hydrogen generators.

The flue gas discharge system comprises a main gas conduit 114 which connects directly with conduit 92 and with conduits 94 and 96 by means of branch conduits 116 and 118, respectively. Valves 120, 122 and 124 are provided in the conduits 114, 116 and 118, respectively, to control the flow of flue gas from the respective vessels when they are

functioning as lime re-generators. The main flue gas discharge conduit 114 is arranged to pass in heat exchange relation with the inlet gas-steam feed line 46.

5 Associated with the three vessels 30, 32 and 34 is a producer gas generation system for providing fuel to regenerate lime in each of the vessels. This system comprises a coal  
10 hopper 126 which discharges into a motor-driven screw 128 through a connecting conduit 130. A conduit 132 connects the screw 128 to a steam line 134 which is a branch from the main steam conduit 42. The  
15 passage of steam through line 134 is controlled by a valve 136. The branch steam line 134 communicates with the bottom of a producer gas generator vessel 138 which is provided with a valved ash discharge conduit 140, an air inlet conduit 142, and a  
20 valved producer gas discharge line 144 at the top. The latter communicates with a cyclone separator 146 from which entrained solids are returned to vessel 138 through a dip leg 148. ; A main conduit 150 for carrying solid free producer gas leads from the  
25 cyclone 146 to the bottom of vessel 30 and communicates with the bottom of vessels 32 and 34 by means of branch conduits 152 and 154, respectively. Valves 156, 158 and 160 are disposed in conduits 150, 152 and 154,  
30 respectively, to control the flow of producer gas to the vessels acting as lime regenerators. A branch air conduit 162 leading from the main air conduit 142 carries air to vessel 30 and to vessels 32 and 34 through branch conduits 164 and 166, respectively. Valves 168,  
35 170 and 172 are provided in these air conduits 162, 164 and 166, respectively, to control the flow of air to the respective vessels. Also, valves 174 and 176 are disposed in air conduits 142 and 162, respectively, to regulate the flow of air therethrough.

The apparatus shown in Fig. 2 and just described operates as follows. We have  
45 found that the yield of hydrogen is increased even above that obtained by operation of the system shown in Fig. 1 if the reaction between the steam and hydrocarbon gas is first conducted in the higher end of the  
50 range 1400° to 1750° F. and then completed at a temperature at least 100 degrees lower but still within the same range. This may be accomplished by establishing a temperature gradient of at least 100 degrees within  
55 the bed of calcium oxide in one of the vessels 30, 32 or 34.

The complete operation of the system takes place in three consecutive cycles. In a given cycle, each of the vessels 30, 32 and 34  
60 performs a different function from that of the other two vessels; and, in the three consecutive cycles, the same vessel performs a different function in each cycle. While one vessel is operating to regenerate lime from  
65 calcium carbonate formed in the preceding

cycle, one of the other two vessels is utilized as a preheating zone to bring the fresh reactants up to temperature by means of a hot bed of lime which was regenerated in the immediately preceding cycle. Since some  
70 reaction takes place between the steam and hydrocarbon gas in this preheating vessel, a temperature gradient is established between the inlet and outlet end of the bed and thus conditions the bed to act as the main hydro-  
75 gen generator in the next ensuing cycle. The third vessel is one in which a temperature gradient obtains in the bed by virtue of its having operated as a preheating zone in the preceding cycle. This vessel functions as the  
80 main hydrogen generator and, accordingly, at the conclusion of the cycle contains largely calcium carbonate which must then be regenerated in the next cycle.

Referring specifically to Fig. 2, let us  
85 assume the vessel 30 is operating as a lime regenerator, i.e., the calcium carbonate formed in the preceding cycle is being reconverted to calcium oxide; vessel 32 is functioning as a preheating zone for elevat-  
90 ing the temperature of the gaseous reactants to within the critical range; vessel 34 is operating as the main hydrogen generator.

The operation of vessel 30 as a lime regenerator is as follows. It should first be  
95 stated that, unless otherwise specifically provided, all numbered valves in the system are closed. Producer gas and air in the proper proportions are introduced into the vessel through conduits 150 and 162, respectively.  
100 Valves 156, 168 and 176 are open. The velocity of the gases so introduced is of the order of one foot per second. The particle size of the solids in the bed is between -20 and +200 mesh. Consequently, the bed of  
105 solids is maintained in a fluidized state upon the porous plate 36. The combustion of the producer gas is regulated to produce a temperature in the bed in the neighborhood of 1750° to 1800° F. which is above the decom-  
110 position point of calcium carbonate. The pressure in the vessel at the top of the bed is essentially atmospheric. The flue gases of combustion and the carbon dioxide evolved from the carbonate are carried to the cyclone  
115 separator 80 by conduit 74 and are there freed of entrained solids which are returned to the bed by the dip leg 86. The solid free gases are then discharged through conduits 92 and 114, valve 120 being open. The  
120 operation of the vessel is discontinued when the bed of solids consists essentially of calcium oxide at a temperature of about 1750° to 1800° F.

The producer gas utilized in the above  
125 operation is generated in vessel 138. Finely divided coal from hopper 126 is fed through conduit 130 to screw 128 which forces the coal through conduit 132 into steam line 134. The steam picks up the coal and conveys it 130

to vessel 138. Air is simultaneously introduced into the vessel through conduit 142, valve 174 being open. The coal particle size and inlet gas velocities are so regulated that a fluidized bed is maintained in the vessel. Ash is withdrawn as necessary through conduit 140, while producer gas is conducted through conduit 144 to cyclone separator 146. Entrained solids are returned to the bed through dip leg 148 and producer gas is discharged to conduit 150.

The operation of the preheating vessel 32 is as follows. Steam and methane are fed from conduits 42 and 44 into conduit 46 in relative proportions, regulated by valves 48 and 50, of preferably from 2 to 1 to 4 to 1.

The resulting mixture of steam and methane is circulated in heat exchange relation with the hot flue gas from vessel 30 and thereafter conducted by conduit 46 to branch conduit 54 in which valve 58 is open. Within the vessel 32, a bed of finely divided calcium oxide having a particle size between -20 and +200 mesh is supported upon the porous plate 38 in a fixed or non-fluidized state. The temperature of the bed is substantially uniform throughout and lies between about 1750° and 1800°F. by virtue of having been subjected to the above regeneration treatment in the preceding cycle. The pressure in the vessel is governed by the pressure established in vessel 34, as will be explained later, and lies above 2.7 atmospheres.

The mixture of steam and methane entering the vessel 32 from conduit 54 is forced to circulate downwardly through the hot bed of lime since all valves in the top discharge lines are closed. As the gaseous mixture progresses downwardly through the bed and becomes heated to reaction temperature, some reaction takes place. The carbon dioxide produced reacts with some of the lime with resultant evolution of heat. A temperature gradient is therefore established in the bed with the lower temperature being at the top where most of the heating of the incoming gas is effected and where initial endothermic reaction between steam and methane occurs. The lower end of the bed is maintained substantially at the original temperature by the heat evolved in the lime-CO<sub>2</sub> reaction. The amount of the temperature gradient can be regulated by the velocity and temperature of the inlet gases, and by the depth of the bed. We prefer that the gradient be at least 100°F. The down-flowing gases leave vessel 32 through conduit 64 in which valve 70 is open and are then conveyed by conduit 66 to the bottom of vessel 34, valve 72 being open. These gases are now at a temperature in the neighborhood of 1750°F. and contain some reaction products by virtue of the preliminary reaction in the preheating vessel 32.

The operation of vessel 34 as a hydrogen generator is as follows. A bed comprising largely finely divided calcium oxide of a particle size between -20 and +200 mesh is supported on the porous plate 40. A temperature gradient of at least 100°F. exists between the bottom and top of the bed by virtue of its having functioned as a preheating zone corresponding to vessel 32 in the immediately preceding cycle. The temperature of the bottom of the bed is the higher and lies in the neighborhood of 1750°F. The pre-heated reactant gases from vessel 32 enter the bottom of the vessel 34 from conduit 66 at a velocity of 0.01 to 0.10 foot per second, which is insufficient to effect fluidization of the solids in the bed. However, the porous plate 40 serves to disperse the gases uniformly throughout the bed. Most of the reaction between the steam and methane takes place at the higher temperature existing in the lower portion of the bed and is completed at the lower temperature obtained in the upper portion. The temperatures in the bed are maintained substantially at the same level by the heat of reaction between the lime and carbon dioxide. Should any additional heat be required, it may be supplied by transfer through the vessel walls or by combustion of a portion of the methane in the bed by the addition of small amounts of oxygen through conduit 166 (valves 176 and 172 being open). The product gases, comprising largely hydrogen, are discharged from the vessel through conduit 78 to a cyclone separator 84. The latter returns entrained solids to the bed through dip leg 90. The solid free product gas is then conveyed through conduits 96 and 102 (valve 108 being open) to the main hydrogen line 98. The latter carries the hot gas in heat exchange relation with the inlet steam line 42 to a suitable storage or subsequent purification stage. Valve 112 is regulated to maintain the pressure in vessel 34 and also in vessel 32 at the desired value which is determined by equation 1, the temperature employed for this purpose being the lowest existing in the hydrogen generator 34.

The composition of the gas produced in vessel 34 depends upon the temperatures and pressures employed but, in general, a larger percentage of hydrogen is obtained than in the case where no temperature gradient is employed. For example, reference to the above table shows that at 1610°F. and 30 atmospheres pressure with a H<sub>2</sub>O/CH<sub>4</sub> ratio of 2/1, a gas containing 75% hydrogen is obtained. Under the same conditions, except that the upper portion of the bed in vessel 34 is maintained at 1450°F. and the bottom portion at 1750°F., a gas containing 92% hydrogen is produced.

In the second cycle of operations of the three vessels 30, 32 and 34, vessel 30 operates

as a preheating zone and consequently functions in the same manner as vessel 32 in the first cycle just described. Vessel 32 becomes the hydrogen generator and is operated the same as vessel 34 in the above described cycle. Vessel 34 becomes the lime regenerator on reduction of pressure to atmospheric corresponding to vessel 30 in the first cycle. Similarly, in the third and last 10 cycle, vessel 30 becomes the hydrogen generator; vessel 32, the lime regenerator; and vessel 34, the preheating zone. Since each vessel is provided with the corresponding conduits, etc., the operation of each in 15 its respective rôle is the same as that of the corresponding rôle just described.

What we claim is:—

1. The method of producing hydrogen from gaseous hydrocarbons which comprises circulating a hydrocarbon in gaseous phase and steam in concurrent intimate contact with each other through a reaction zone containing calcium oxide in granular form, maintaining the reaction zone at a temperature between 1400° 20 and 1750° F. and at a pressure above 2.7 atmospheres absolute, the amount of oxide being sufficient to absorb substantially all the carbon dioxide produced, the pressure within said reaction zone exceeding that 25 given by the empirical relationship:—

$$p = 3.0 + 1.94 \times 10^{-2} (t - 1431) + 3.41 \times 10^{-4} (t - 1431)^2$$

where  $p$  is the reaction pressure in atmospheres and  $t$  is the temperature of the 35 reaction zone in °F. and recovering the gaseous product.

2. The method according to Claim 1 or 2, in which the amount of oxide is at least 250 parts by weight for each 100 parts by weight 40 of carbon contained in the gaseous hydrocarbon.

3. The method according to Claim 2, in which the temperature of the reaction zone is maintained between 1500° and 1650° F. 45 and the pressure between 20 and 50 atmospheres.

4. The method according to any of the preceding claims, in which the hydrocarbon gas is methane and the steam-methane ratio 50 is from 2 to 1 to 4 to 1.

5. The method according to Claim 1 or 2, in which there is a temperature gradient of at least 100° F. between the inlet and the outlet of the reaction zone with the higher 55 temperature being at the inlet end.

6. The method of producing hydrogen which comprises heating a bed of granular calcium oxide in a reaction zone to a substantially uniform temperature in the upper end of the range 1400° to 1750° F., circulating 60 steam and a hydrocarbon in gaseous phase downwardly through said bed until a

temperature gradient of at least 100° F. is established between the top and bottom thereof, circulating the gases issuing from 65 the bottom of said reaction zone upwardly through a bed of granular calcium oxide in a second reaction zone, the temperature of the bed in said second zone being between 1400° and 1750° F., maintaining the 70 pressure of both of said reaction zones above 2.7 atmospheres absolute, the amount of calcium oxide in said zones being sufficient to absorb all the carbon dioxide produced by the reaction of steam and hydrocarbon gas 75 circulating therethrough, recovering the gaseous product from the second zone, thereafter circulating steam and hydrocarbon gas upwardly through the first zone, and recovering the gaseous product. 80

7. The method according to any of the preceding claims, wherein the calcium oxide is regenerated from the calcium carbonate resulting from the method according to the preceding claims, the regeneration being 85 effected by heating the calcium carbonate to its decomposition temperature of preferably between 1750° and 1800° F., the heat being preferably supplied by the combustion of producer gas or of pulverized coal. 90

8. The method according to Claim 7, wherein the regeneration takes place under fluidized conditions.

9. The method according to Claim 8, wherein the particle size of the calcium 95 oxide is so regulated that under certain velocities of inlet gas a fluidized bed is maintained, while under certain other velocities a non-fluidized bed is maintained, the non-fluidized bed being maintained during the 100 hydrogen generation cycle.

10. The method according to Claim 9, wherein, to permit fluidized operation in the regeneration cycle and non-fluidized operation in the steam-hydrocarbon reaction cycle, 105 the particle size of the calcium oxide is between -20 and +200 mesh on the Tyler scale, the inlet gas velocity during the steam-hydrocarbon reaction cycle is between 0.01 and 0.10 ft. per second, and the inlet gas 110 velocity during the regeneration cycle is between 0.5 and 3.0 ft. per second.

11. The method of producing hydrogen substantially as described with reference to the accompanying drawings. 115

Dated the 7th day of September, 1950.  
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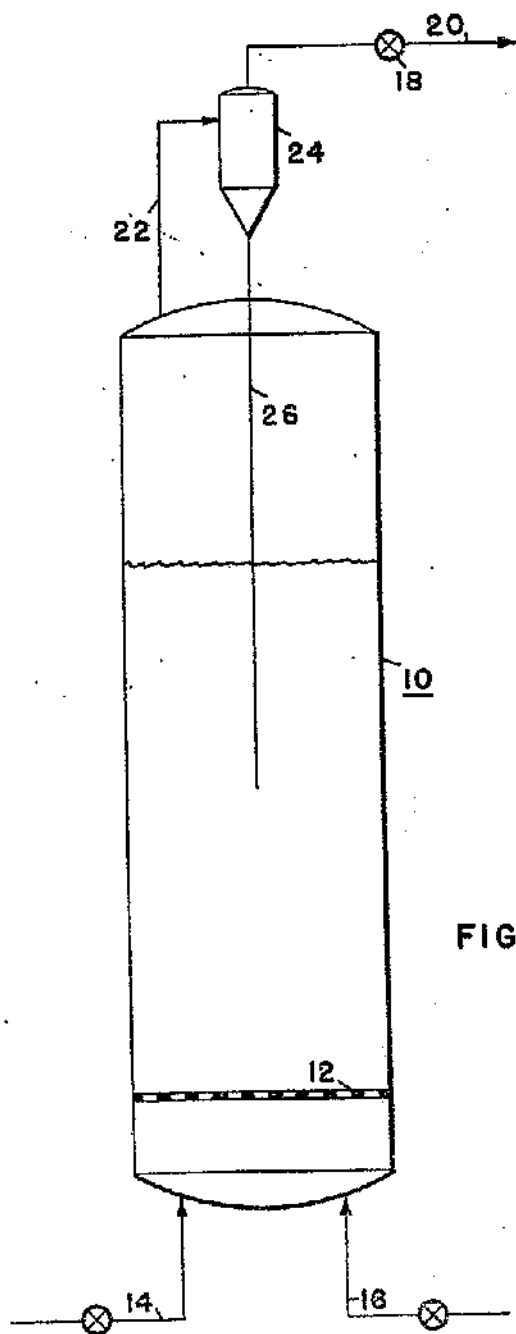


FIG. 1



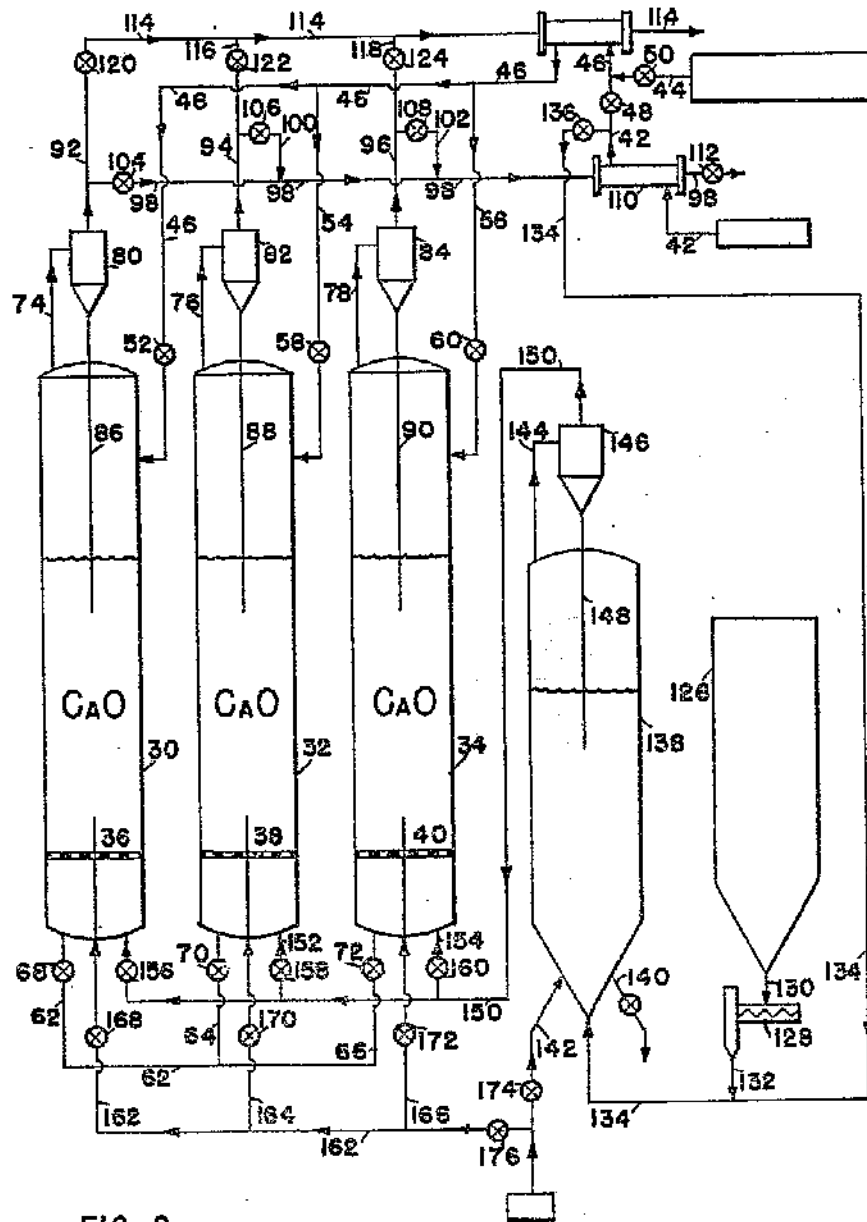


FIG. 2



673,333 COMPLETE SPECIFICATION  
 2 SHEETS  
 This drawing is a reproduction  
 of the original on a reduced scale.  
 SHEETS 1 & 2

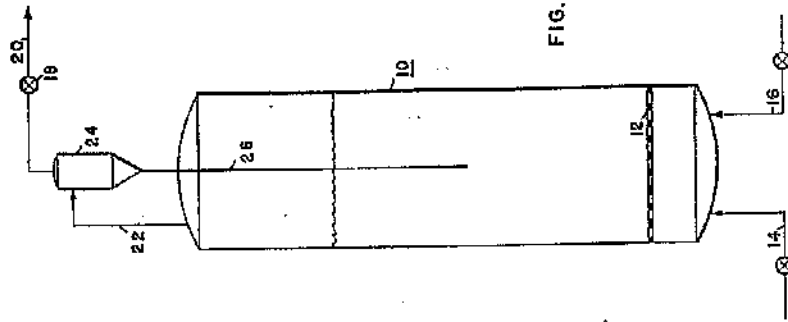


FIG. 1

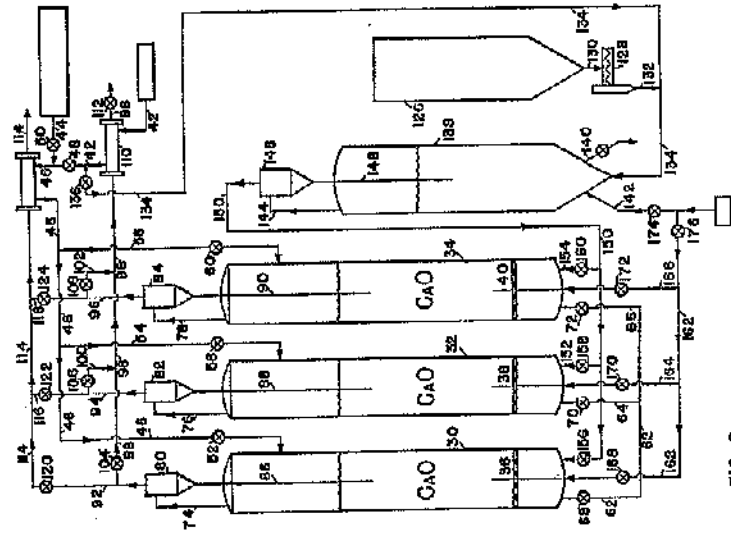


FIG. 2