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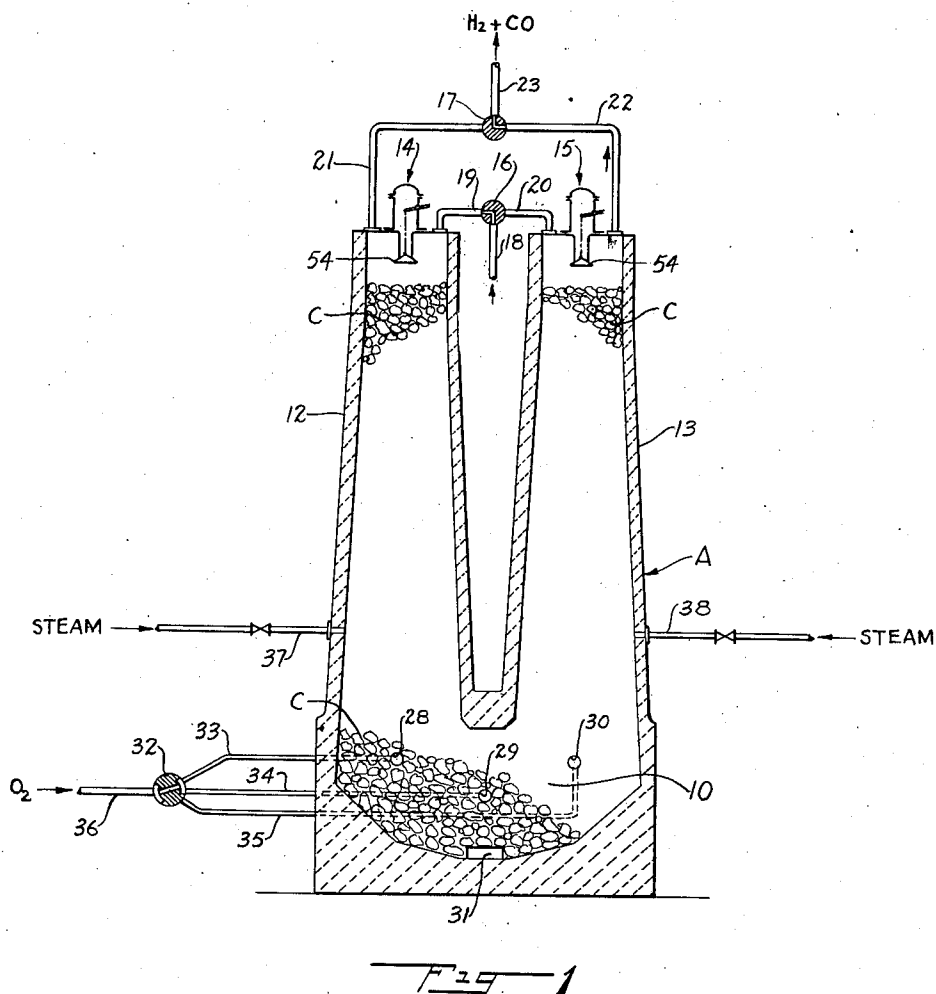
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2,170,265

PROCESS FOR PRODUCING HYDROGEN-ENRICHED GAS MIXTURES

Filed May 6, 1936

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

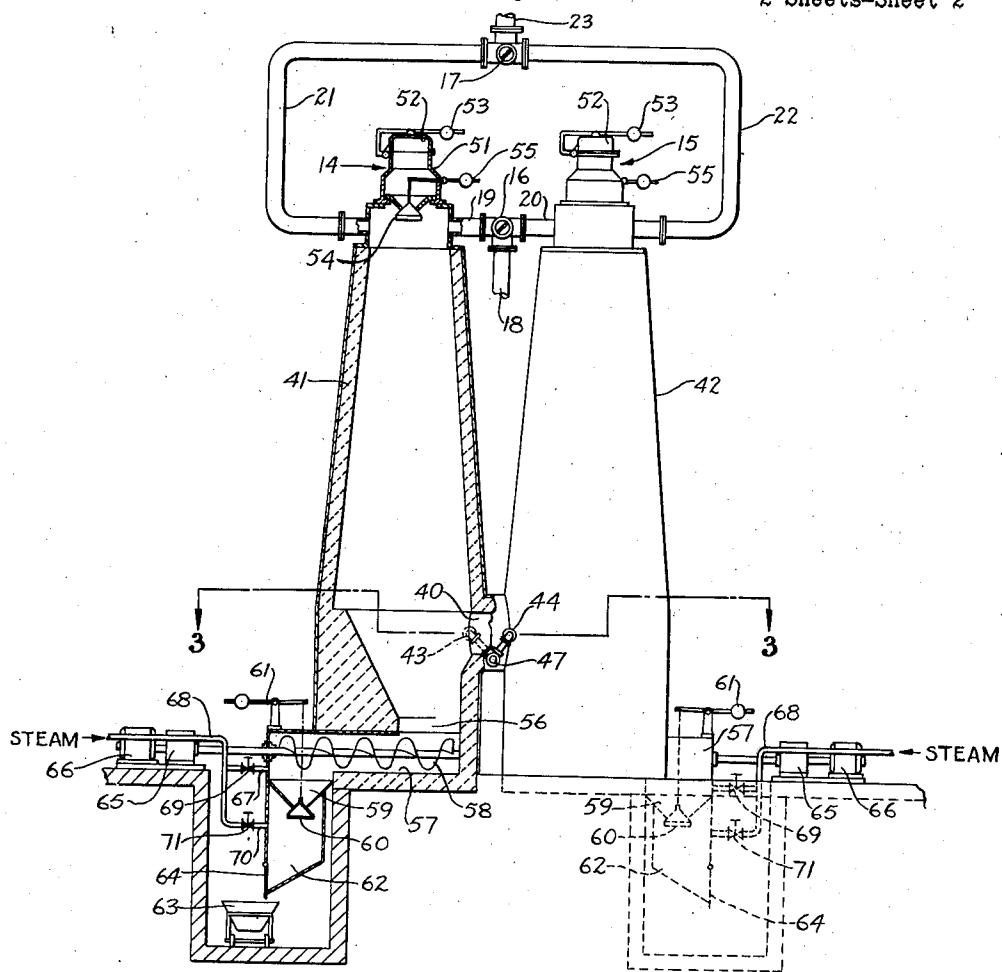


Fig. 2

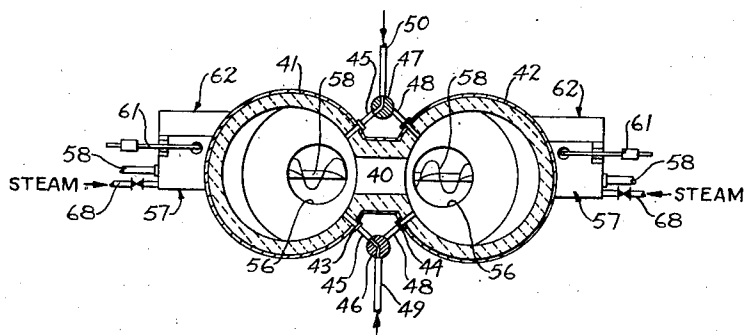


Fig. 3

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PROCESS FOR PRODUCING HYDROGEN-ENRICHED GAS MIXTURES

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The present invention relates to a process for producing hydrogen-enriched gas mixtures, and more particularly for the production of gas mixtures enriched in hydrogen by the controlled partial combustion of hydrocarbons and especially methane with oxygen. For the conversion of methane or methane-bearing gases by means of a reaction with oxygen to produce hydrogen-carbon monoxide mixtures, it has been proposed to preheat the methane and the oxygen by heat exchange with the gaseous products of the methane decomposition, to mix them for effecting a partial combustion of the methane, and to blow the products of the partial combustion through water cooled tuyères into an incandescent bed of coke.

During the preheating of the methane, soot is readily deposited in the heat exchanger, which soot obstructs the passage of the gas there-through and greatly interferes with the heat exchange between the heat exchanger surfaces and the gas, thus causing serious operating difficulties. A further disadvantage, particularly when treating gases which contain hydrogen in addition to methane such as, for example, coke oven gas, results from the tendency of the introduced oxygen to first react chiefly with hydrogen present in the gas mixture formed from a part of the methane, so that a further conversion of methane with the steam product of hydrogen-combustion is required for completely converting the methane into hydrogen and carbon monoxide. In such operations, an appreciable portion of heat is lost both in the combustion chamber and during the passage of the preheated and partly reacted gases through water-cooled tuyères into the chamber filled with highly heated coke. The heat lost is part of the heat carried by the gas and produced by the combustion at high temperature of hydrogen, and is required for breaking up methane. A portion of the methane therefore escapes the desired reaction, while the water resulting from the combustion of hydrogen is reduced by coke and not by methane as desired.

The principal object of the present invention is to provide a method for the production of hydrogen-enriched gas mixtures from hydrocarbon gases which will avoid the above-described difficulties. Another object is to provide a method for avoiding heat losses when carrying out such hydrogen producing reaction by the provision of means for passing the gases alternately in opposite directions through chambers filled with coke, which chambers are arranged to have

a highly heated intermediate zone of coke whereby the coke itself acts as the desired heat storing and exchanging medium. Another object is to provide a method for preventing the accumulation of excessive amounts of finely-divided carbon deposits upon coke used as a heat exchange medium by causing the continuous renewal of the coke filling by the addition of coke to the cold zones and the corresponding removal of coke from the heated zones. Still another object is to avoid heat and gas losses which may occur when removing coke from the heated zones by effecting a heat exchange between the coke removed with gas which is subsequently utilized in the process.

The above and other objects and novel features will be apparent from the following description taken together with the accompanying drawings, in which:

Fig. 1 is a diagrammatic elevational view of a furnace adapted for carrying out the process according to the invention;

Fig. 2 is an elevational view, partly in section, of another form of the apparatus according to the invention in which coke is removed from the heated zones mechanically; and

Fig. 3 is a horizontal plan view of a section of the furnace shown in Fig. 2 and taken on the line 3—3.

In accordance with the invention, the methane-bearing gas is conducted at regular periodical intervals through a layer or bed of coke previously highly heated or hot blown by contact with hot reaction product gases. At the hot zone of the coke bed, oxygen which is required for the methane oxidation is simultaneously introduced from the outside and during corresponding intervals the hot hydrogen carbon monoxide gas mixture produced by the reaction is led out through coke in an opposite sense to the fresh gas introduced, that is from the hot zone to the other cold end whereby the coke layer which was previously cooled by the fresh gas introduced during previous cycle is again hot blown. The methane-bearing gas is preferably introduced alternately into one of two shafts of a two-shaft furnace having a U-shaped chamber filled with coke, the gas being heated in the one shaft, converted into a hydrogen-carbon monoxide mixture in the heated reaction zone of the coke bed by reaction with the oxygen introduced at the lower portion of the shafts, and being again cooled by heat exchange with coke in the other shaft. In order to keep the shaft filling free from deposited soot which may result from the breakdown of

hydrocarbon gases, the combustion of a portion of the coke in the hot zone of the furnace with oxygen to produce carbon monoxide and ash is effected so that a slow renewal of the filling of the shafts is attained by the addition of coke at the top and removal of ash from the lower portion of the furnace. When, however, the gases to be converted contain heavy hydrocarbons of greater carbon content, the deposition of soot at zones where the introduced gases are being heated by coke in the shafts can attain such proportions that it becomes necessary, in order to keep the accumulator filling permeable to gases, to consume comparatively large quantities of coke. This is not always desirable in view of the purpose for which the gaseous product is to be used, due to the fact that larger quantities of carbon monoxide are then admixed with the final product.

Referring to Fig. 1 of the drawings, there is shown schematically a furnace A having a U-shaped chamber which is adaptable for carrying out the process. It has two shafts 12 and 13 above an interconnecting high-temperature zone 10. The high-temperature zone 10 and the shafts 12 and 13 are filled with coke indicated at C which is introduced through the charging devices 14 and 15 of the customary double valve variety used for charging furnaces and gas producers. The methane-bearing gas to be processed is introduced into the upper portion of a selected one of the two shafts 12 and 13, while the hydrogen-carbon monoxide mixture resulting from the reaction of the methane with the oxygen in the high-temperature zone 10 flows upwardly through the other shaft. Valves 16 and 17 are reversing valves provided to direct the gas flow. The gas to be processed is conducted to valve 16 by a conduit 18. Conduits 19 and 20 connect valve 16 to the upper portions of shafts 12 and 13 respectively. The flow reversing valve 16 is arranged to pass gas from conduit 18 to either conduit 19 or 20 during the desired periods of the operating cycle.

The gas produced is conducted from the upper portions of the shafts 12 and 13 through conduits 21 and 22 respectively leading to the valve 17 which connects either conduit to a discharge conduit 23 leading to a receiving device for the gaseous product. Commercially pure oxygen or a gas richer in oxygen than air is led into the bed of coke in the high-temperature zone 10 to react with methane passing there-through at several places, the inlets being indicated at 28, 29, and 30, the inlet 29 being midway between inlets 28 and 30 which are adjacent to the lower portions of shafts 12 and 13 respectively. The oxygen is preferably conducted into the shafts through inlets 28 and 29 during one period of the operating cycle only and then through inlets 30 and 29 during the period of flow in the opposite direction. The opening 31 in the lowest portion of the zone 10 is provided for the removal of ash which is preferably maintained in a molten state by the heat of the reactions so that it may be removed by tapping.

The oxygen is conducted to the openings 28, 29, and 30 from an oxygen control valve 32 by conduits 33, 34, and 35 respectively which connect to three outlets positioned at one side of the valve. The inlet to the valve located on the opposite side is connected to a conduit 36 which supplies oxygen or oxygen-containing gas from a source of supply. The rotor portion of the valve 32 is provided with a passage whose ends

are shaped so that in the position shown, oxygen is supplied to conduits 33 and 34 and by rotation of the rotor in a clockwise direction oxygen may be supplied to conduit 35 alone or to conduits 34 and 35 in the proportions desired. Assuming that the direction of flow of the gases is as illustrated in Fig. 1, the methane-bearing gas enters shaft 12 through conduits 18 and 19 where it is heated by the coke filling C with the result that the latter is correspondingly cooled. The coke filling of shaft 13 is simultaneously heated by the hot hydrogen-carbon monoxide mixture formed by the reaction in the high-temperature zone 10 and which flows upwards and out of shaft 13 through conduits 22 and 23. At certain intervals, the direction of flow of the gases through the two shafts is reversed by means of reversing valves 16 and 17 and the heat given up to the coke in shaft 13 by the previously outflowing gases is then transferred to gas introduced into the shaft 13 to be processed.

The temperatures in the high-temperature zone must be maintained at such a degree that, on the one hand, the decomposition of methane on the glowing coke proceeds with sufficient velocity and, on the other hand, the water vapor or carbon dioxide which may result as intermediate products of the reaction are substantially completely converted at the desired rate into hydrogen and carbon monoxide. It is therefore advisable to maintain temperatures of 1300° centigrade and higher.

The conversion of the preheated methane passing through the high-temperature zone into hydrogen and carbon monoxide produces an appreciable excess of heat even when the oxygen is added in a cold state. If the amount of excess heat produced exceeds the amount required for balancing the heat losses, the excess heat may be utilized by effecting additional endothermic or heat absorbing reactions such as, for example, a reaction between water vapor and carbon, that is, regulated amounts of steam are added to the methane, the reaction absorbing heat with a consequent reduction of temperature. If the heat losses from the high-temperature zone 10 should become greater than the amount of heat liberated during the methane operation, which may occur particularly when processing gases poor in methane, additional amounts of coke are burned with oxygen by increasing the oxygen supply until the necessary temperature in the combustion or high-temperature zone is maintained.

If it is desired to tap off the ash from the coke as a slag in the molten state from the opening 31, this may readily be accomplished by making suitable additions, such as lime or basic blast furnace slag to the coke which is charged into the furnace. The major portion of the sulphur contained in the coke and in the gas will thereby be absorbed by the slag.

If the greatest possible yield of hydrogen from the furnace is desired, water vapor is admixed with the upwardly flowing hydrogen-carbon monoxide mixture at a suitable point in its path and provision is made for the presence in the shafts of catalytic substances, such as calcium oxide, iron ore, or alkalized blast furnace coke. Low temperature carbonization coke and semi-coke produced from coal or lignite may also be used. The steam, preferably superheated to temperatures up to 500° centigrade, is blown into the shaft at an intermediate point where the temperature is such that the steam no longer re-

acts with the solid fuel. By this addition, a portion of the carbon monoxide is converted in the shaft to carbon dioxide and the subsequent conversion of that portion of carbon monoxide into carbon dioxide is eliminated.

Figs. 2 and 3 illustrate a modification of the furnace for effecting a more rapid cleaning and renewal of the coke used as a regenerative heat exchanging material, with means for mechanical removal of coke from the lower portions of the shafts.

The gas flow arrangements and method of operation are fundamentally the same as in the apparatus shown in Fig. 1. The two furnace shafts are indicated at 41 and 42 and may be constructed in the customary manner by providing an outer sheet steel casing and a lining of refractory brick. The shafts 41 and 42 are connected at the lower portion by a short horizontal passage 40. For the introduction of oxygen into the shafts 41 and 42, inlets or tuyères 43 and 44 respectively are provided, entering the shafts at approximately the same level as the passage 40 and preferably near its ends. The two tuyères 43 located on each side of the shaft 41 are connected to the outlets 45 of three-way valves 46 and 47 and the tuyères 44 are connected to the other outlets 48. Oxygen gas supply conduits 49 and 50 respectively conduct oxygen to the inlets of the valves 46 and 47. The rotors of valves 46 and 47 have passages so that, when in the position shown in Figure 3, conduits 49 and 50 communicate with tuyères 43 and when the valves are adjusted to the reverse position, the conduits 49 and 50 will communicate with tuyères 44.

The arrangements at the top of the shafts are substantially the same as shown in connection with the apparatus of Fig. 1. Gas to be processed is supplied through conduit 18 and passes through the reversible valve 16 alternately into the upper portions of the shafts. The processed gas, having been cooled in the shafts, leaves the furnace through conduits 21 or 22 in accordance with the position of valve 17. The coke charging means 14 and 15 at the tops of the shafts is here shown in greater detail, each comprising a chamber or hopper 51 having a gas-tight door or lid 52 which is held closed by a weighted lever 53 and a conical charging valve 54 for sealing the opening in the bottom of the hopper. The charging valve 54 is operated by a lever mechanism 55 having external and internal portions connected by a shaft portion that passes through the wall of the hopper in a gas-tight manner, the external portion of the lever 55 being weighted to hold valve 54 normally closed. To add coke to a shaft, the lid 52 is opened, the valve 54 being closed and preventing the escape of gas, and the hopper is charged. The lid is then closed and the lever 55 raised to open valve 54 which allows the charge to drop into the shaft.

The lower portion of each shaft, below the tuyères, tapers to a narrower portion 56 connecting to a horizontal passage 57 in which a screw conveyor 58 is disposed for discharging hot coke to a hot coke hopper 59 located at the outer end of passage 57. The lower portion of hopper 59 tapers to an opening sealed by conical valve 60 which is operated by lever mechanism 61 outside the hopper 59. Below hopper 59 is located a coke receiving chamber or bunker 62 for accumulating and storing the coke, ash and soot discharged until it is dropped into conveyor cars 63 for re-

moval, a door 64 at the lower portion of hopper 62 being located above the cars in the customary manner.

The conveyor 58 has a driving shaft extending outside the end wall of the passage 57, which shaft is connected to a speed reducing mechanism 65 which may be driven by a prime mover 66 that, for example, may comprise a steam turbine or electric motor.

A cooling gas, for example steam, is introduced into hopper 59 by branch conduit 67 of a steam supply conduit 68, the flow being controlled by valve 69. Thus gas flows against the coke in passage 57 and in the lower part 56 of the shaft, which coke is to be discharged by the conveyor 58 to the hopper. The steam is decomposed by reaction with a portion of the coke and cools the same. It is advisable to also wash the removal bunker 62 with steam introduced under a pressure slightly in excess of atmospheric pressure in order to prevent the entrance of air into the bunker and thus into the furnace shafts. To this end, another branch 70 of conduit 68 controlled by valve 71 is provided for conducting steam into the bunker 62.

In place of the screw conveyor depicted in the drawings other means may be employed for discharging the furnace filling material which will permit the removal of the coke without gas losses and without allowing air to enter the furnace, such means including, for example, a rotating table or conveying rollers rotating in opposite directions.

In order to assure safe operation, it is advantageous to renew the filling of the two shafts independently of one another and for this purpose the separate discharge means for each furnace shaft, as shown in Fig. 2, are provided. The communication between the two reaction zones is, therefore, provided by the short narrow cross channel 40 by which all the gas being processed is forced to pass through the hottest zone and thus be converted with the desired speed.

The process of the present invention has appreciable advantages over former methods of effecting partial oxidation of hydrocarbon gases with oxygen. These are attained by combining the heat exchanger, combustion chamber, and coke bed into a single apparatus and by the utilization of coke as a heat exchange medium or regenerative filler mass. Due to the fact that the chamber in which the hydrocarbon and oxygen come together is filled with incandescent coke, indirect ways taken by the reaction with the oxygen involving intermediate products are immaterial. The conditions are always maintained by which any intermediate products tending to form such as carbon dioxide, water, acetylene, or benzene are instantly converted into the end products carbon monoxide and hydrogen without the loss of high-temperature heat.

The present method provides substantially the highest possible hydrogen yield from the methane used, for the coke filling accelerates the decomposition of methane into carbon and hydrogen by a catalytic action. The coke is continuously renewed in two ways, firstly, by reaction with oxygen or steam so that a portion of the coke filling is consumed in the high-temperature zone with the result that any decomposed carbon deposited in the colder zones will disappear or will fall to the combustion zone; secondly, by the mechanical arrangement for the removal of coke from the bottom of the shafts, whereby it is possible to increase to any degree desired, the volume of

coke passed through the shaft as compared to the amount which can be put through the shafts when the coke to be removed must be burned to ash in accordance with the method of operation of the apparatus of Fig. 1, without causing an undesirable increase in the carbon monoxide content of the gas produced. Accumulations of soot and ash are thus prevented and the furnace filling remains continuously permeable to gas. If desired, it is possible to entirely eliminate a supplementary combustion of coke and to limit the supply of oxygen to that volume which is required for providing the heat requirements of the process by the formation of carbon monoxide.

The efficiency of coke as a heat accumulator and for the control of the reaction depends on the nature of its surface, that is, on the extent to which it is covered with soot or ash. With the apparatus of the present invention, it is possible by regulation of the rate of combustion and discharge, to maintain any desired nature of the coke surface. Additional advantages result in that the coke filling protects the furnace walls from the attacks of oxidizing gases, and furthermore coke is a relatively inexpensive material for use as a filling mass for the heat accumulator portions of the apparatus.

The production of large volumes of gas, which is becoming of increasing importance for effecting chemical synthesis, is greatly simplified by the present apparatus and method of operation because shaft furnaces of the type herein described, of any desired capacity, can be relatively inexpensively constructed and operated by those experienced in metallurgical technique. In addition to the conversion of methane, the present process and apparatus may be used for converting other hydrocarbons and mixtures of hydrocarbons into carbon monoxide and hydrogen.

While coke is described as the preferred material for filling the furnace shafts, other regenerative heat exchange materials may be used particularly, for example, in cases where the impurities contained in coke would be objectionable. When it is desired to convert hydrocarbons free from such impurities as sulphur, the shaft filler material used may be a granular refractory such, for example, as irregular pieces of silicon carbide or shaped lumps of carbofrax. Such filler material may then be withdrawn at a controlled rate from the bottom of the shafts, passed over dust-removing screens, conveyed out of contact with air to the charging hopper at the top of the shafts, and recharged into the furnace at the desired rate to replace that withdrawn. The refractory upon passing through the regenerative heat exchanging zones receives a deposit of carbon upon its surface. The carbon deposited is carried down into the reaction zones where it is effective for stabilizing the reactions in the manner described when coke is used. Steam or cooling gas passed through the refractory being discharged can be used for removing the residue of carbon from the surfaces of the refractory so that it may be reused in the shafts as well as for conserving the high-temperature heat.

The process, involving a constant renewal of the filling material for keeping towers containing a filler mass permeable during operation, also has general application in other systems for processing gases where the gases to be treated are laden with dust or where dust is formed by heating, cooling, or by chemical conversion. In such cases, likewise, the tower filling material is renewed during operation by the withdrawal of

portions of the filler bed at one end and the addition of new filler material at the other end. The present method of operation may also be used in connection with the operation of regenerators, heat accumulators or cold accumulators, or towers containing contact material in which gases of the above-described nature are to be treated. The dust removal is particularly efficient if the filler or contact material is moistened with a dust binding medium. The discharge means at the bottom of the shafts are adapted to the properties of the particular filler material to be used, that is, for example, materials which are mechanically fragile, would be resiliently held in the tower and discharged gently.

What is claimed is:

1. Process for converting hydrocarbon gas to carbon monoxide and hydrogen which comprises passing dry hydrocarbon gas in one direction through a confined and continuous heated body of coke, the intermediate zone of said body being maintained at a higher temperature than the end zones thereof; supplying sufficient oxygen to said intermediate zone to react with such hydrocarbon gas and produce hydrogen and carbon monoxide; and periodically reversing the direction of flow of hydrocarbon gas through said body, to preheat the incoming hydrocarbon before it reaches the intermediate zone and to abstract heat from the conversion products after they leave the intermediate zone.

2. Process for converting hydrocarbon gas to carbon monoxide and hydrogen which comprises passing dry hydrocarbon gas in one direction through a confined and continuous heated body of coke, the intermediate zone of said body being maintained at a higher temperature than the end zones thereof; supplying sufficient oxygen to said intermediate zone to react with such hydrocarbon gas and produce hydrogen and carbon monoxide; periodically reversing the direction of flow of hydrocarbon gas through said body, to preheat the incoming hydrocarbon before it reaches the intermediate zone and to abstract heat from the conversion products after they leave the intermediate zone; and effecting a continuous change of said body by removing portions thereof from the intermediate zone and adding corresponding portions to said end zones.

3. Process for the production of hydrogen-enriched gas mixtures by the partial combustion of methane with oxygen in contact with successive layers of coke forming a continuous bed, which comprises the steps of preheating the methane-bearing gas to the combustion temperature by passing said gas in intimate contact with a layer of heated coke; adding oxygen to said gas passing through the coke at an intermediate layer to effect a reaction converting the methane into a hot mixture of hydrogen and carbon monoxide and the conversion of coke to ash at a desired rate; regulating the addition of oxygen to maintain a temperature in said intermediate layer of coke sufficient to melt said ash and produce a molten slag; removing said slag while in the molten state from said intermediate layer; passing the hot gas mixture through another layer of coke for transferring heat thereto; and after a time interval reversing the flow of gas through said layers of coke so as to heat the methane-bearing gas by contact with said last-named layer of coke and to reheat said first-named layer of coke by contact with the result-

ing hot mixture; and adding fresh coke to said layers to replace the coke consumed.

4. Process for converting hydrocarbon gas to carbon monoxide and hydrogen which comprises passing hydrocarbon gas in one direction through a confined and continuous body of heated coke, an intermediate zone of said body being maintained at a higher temperature than the end zones; supplying oxygen to said intermediate zone at a rate sufficient to react with said gas and with a portion of the coke in said intermediate zone; maintaining a temperature in said intermediate zone sufficient to melt the slag resulting from the reaction; removing said slag while in the molten state from said intermediate zone; periodically reversing the direction of flow of hydrocarbon gas through said body, whereby the incoming hydrocarbon gas is preheated in an end zone of said body before it reaches the intermediate zone and the conversion products give off heat in an end zone of said body after leaving the intermediate zone; and adding coke to said end zones to replace the coke consumed in the intermediate zone.

5. Process for the production of hydrogen-enriched gas mixtures by the partial combustion of hydrocarbon gas with oxygen while in contact with carbon, which comprises the steps of introducing the hydrocarbon gas into one of two ends of a continuous bed of heated coke, said bed having a hot center portion and relatively cold end portions; adding oxygen to the hot center portion of said bed to effect an exothermic reaction converting the hydrocarbon gas to hydrogen and carbon monoxide and producing a molten slag; passing the converted gas mixture through the end portion of said bed opposite to the gas inlet for transferring heat thereto; withdrawing the molten slag from the hot center portion; and periodically reversing the gas flow through said bed.

6. Process for the production of hydrogen-enriched gas mixtures by the partial combustion of hydrocarbon gas with oxygen in accordance with claim 5, including the additional step of supplying steam to the converted gas mixture immediately adjacent to the hot center portion of the coke bed to increase the yield of hydrogen in said mixture.

7. Process for the production of hydrogen-enriched gas mixtures by the partial combustion of hydrocarbon gas with oxygen in accordance with claim 5, including the additional step of supplying steam to the hydrocarbon gas immediately adjacent to the hot center portion of the coke bed to effect an endothermic reaction maintaining the temperature of said hot center portion within desired limits.

8. Process of converting hydrocarbon gas as claimed in claim 1, in which steam is supplied to said body of coke immediately adjacent to the intermediate zone to increase the yield of hydrogen in the converted gas mixture.

9. Process for converting hydrocarbon gas to carbon monoxide and hydrogen which comprises passing dry hydrocarbon gas through a confined body comprising layers of coke, the intermediate layers of said coke being continuous with and maintained at substantially higher temperatures than the end layers thereof, said hydrocarbon gas being introduced at one of the cold end layers and gaseous products of conversion being withdrawn at the opposite end layer; supplying sufficient oxygen at said heated intermediate layers to react with such hydrocarbon gas and produce hydrogen and carbon monoxide; and periodically reversing the direction of flow of the hydrocarbon gas through said layers of coke to preheat the incoming hydrocarbon gas before it is reacted and to abstract heat from the conversion products after the reaction.

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