PATENT SPECIFICATION

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1124

COMPLETE SPECIFICATION.

Improvements relating to the Production of Hydrogen and Carbon Monoxide.

We, HYDRO NITRO SOCIÉTÉ ANONYME, a Company organised under the laws of Switzerland, of 8, Quai du Cheval Blanc, Geneva, Switzerland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for the production of hydrogen and carbon monoxide, or hydrogen, carbon monoxide and nitrogen.

It is well known that methane and other hydrocarbons can be caused to interact at high temperatures with water vapour to give hydrogen and carbon monoxide according to the endothermic reaction.

$CH_4 + H_2O \longrightarrow CO + 3H_2 - 50800$ calories.

According to the present invention a mixture of carbon monoxide and hydrogen is produced as a result of the interaction of hydrocarbon gases and water vapour at high temperatures in the presence of a refractory mass, the gases being first preheated and partially reacting by being passed vertically upwards through a zone of increasing temperature and further reacting while passing vertically downwards through a zone of decreasing temperature, the heating of the zones being accomplished by burning gases in a region in the gas circuit between the tops of the zones.

Air, or air enriched with oxygen, may be added to the reacting gases in definite amounts in order to produce a hydrogen-nitrogen mixture suitable for use in the manufacture of ammonia.

The apparatus employed in carrying out the invention comprises two similar vertical chambers placed adjacent to one another and connected by a passage at their tops, each chamber being filled in its lower part with checker brickwork or the like adapted to form a preheating or regenerative zone, broken material as distinguished from refractory bricks or shapes being placed on top of the brickwork to form a refractory mass adapted to form a reaction zone. Provision may be made in this apparatus for admitting air or gas above the reaction zone. During the decomposition, oxygen, air or air enriched in oxygen may be added to the mixture of hydrocarbons either prior to the admission of that mixture into the apparatus or at any desired point during its passage through the apparatus so as to maintain the desired temperature in the refractory mass or reaction zone. By proceeding in the manner set forth, the high temperatures in excess of 1300° C. which are required for decomposition can easily be obtained in large apparatus and the losses of heat from the apparatus may be reduced to a minimum.

It will be appreciated that in the process according to the invention the temperatures at the lower part of the apparatus are lower than at the top and that therefore the problem of supporting the refractory mass is much simpler in that the greater weight of bricks is always supported by the colder bricks at the lower part of the apparatus.

The highly heated reaction zone is, as stated, formed of broken refractory pieces lying on the top of a checker brickwork. Special refractory shapes in which highly refractory material is bonded with material of lower fusing point are not required. Therefore the refractory mass is cheaper and able to stand higher temperatures than when such shaped bricks are used. Pure Al_2O_3 as prepared by fusing bauxite in an electric furnace has a melting point of 2050° C., whereas the best refractory bricks made by mixing the Al_2O_3 with a binding material fuse at only 1800° C. and soften at about 1450° C. Similarly MgO prepared by burning best quality magnesite melts at 2500° C., whereas the highest quality magnesite bricks melt at 2100° C. and soften at 1600° C.

In order that the invention may be clearly understood and readily carried into effect, one apparatus for use in accordance therewith will now be described by way of example with reference to the accompanying drawing which shows this diagrammatically.

This apparatus is especially suitable for the production of a mixture of nitrogen, carbon monoxide and hydrogen which

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after suitable subsequent treatment may be used for the synthesis of ammonia, the nitrogen, carbon monoxide and hydrogen being formed from methane, steam and air. The apparatus consists essentially of two vertical chambers 1 and 2 connected by a passage 3 at the top which may be of smaller cross-sectional area than that of the chambers 1 and 2. Each chamber is heavily insulated to prevent heat losses and is filled up to about two-thirds of its height with broken fire bricks or checker brickwork 4 and 4^1. On the top of this brickwork there is placed a mass 5 and 5^1 of broken high temperature refractory material as distinguished from refractory bricks or shapes. At the bottom of the chambers there are openings 6 and 6^1 which serve for the introduction of the hydrocarbon gas and steam to be decomposed and for the withdrawal of the decomposed gases during the cracking period and for the introduction of the air, and withdrawal of the products of combustion during the heating period. A series of small openings 7 is provided near the top of each chamber to serve for the introduction of air during the cracking period and gas during the heating period.

First of all the refractory material 5 and 5^1 is heated to from 1200 to 1500° C. by burning gas and air in the region between the tops of the two masses of refractory material. The air is introduced through the pipe 6, the gas through the pipes 7 and the products of combustion leave through the pipe 6^1. In order to equalise the temperatures in the two sides of the apparatus, the admission of air and the withdrawal of the products of combustion may be reversed from time to time, the air being admitted through 6^1 and the products of combustion leaving through 6. Heating in this way gives a zone in which the temperature increases from the bottom to the top in each of the chambers 1 and 2.

When the refractory material 5 and 5^1 has been heated to 1500° C. methane mixed with steam in the ratio of one volume of methane to three volumes of steam is admitted through the opening 6. This gas mixture passes upwards, being gradually heated by its contact with the hot brickwork 4. The gas then passes through the refractory material 5 and 5^1 where it is decomposed to carbon monoxide and hydrogen. The decomposed gases pass downwards from the refractory material 5^1 through the brickwork 4^1, giving up their sensible heat to that brickwork which acts as a regenerative zone and they pass out through the opening 6^1. The flow of the gases may be reversed from time to time to obtain any desired temperature conditions on the two sides of the apparatus, that is the methane and steam may be introduced through the opening 6^1 and the cracked gases may leave at 6.

During the cracking operation air may be admitted through the pipes 7 in such a proportion that after subsequent treatment and purification including removal of carbon monoxide the gas produced will contain one part of nitrogen to three parts of hydrogen. If oxygen is available in sufficient amounts to enrich the air, it is possible to operate continuously with a temperature in the hot zone of 1200 to 1500° C.

When the reaction zone cools to 1200° C., or when the reaction is not sufficiently hot to give the desired degree of decomposition, the cracking period is discontinued and heating of the refractory mass is begun again. Such control of the operation may be more easily effected by automatic equipment which changes the flows automatically on any pre-determined cycle.

We are aware of Specifications Nos. 196,496 and 269,711 and make no claim to anything described or claimed therein.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of hydrogen and carbon monoxide as a result of the interaction of hydrocarbon gases with water vapour at high temperatures in which the gases and water vapour are first preheated and partially react while passing vertically upward through a zone of increasing temperature and further react while passing vertically downward through a zone of decreasing temperature, the zones being of refractory material, and in which the supply of heat necessary for the reaction is accomplished by burning gases in a region in the gas circuit between the tops of the zones.

2. A process according to Claim 1, in which a hydrogen-nitrogen mixture suitable for use in the manufacture of ammonia is produced by adding air, or air enriched with oxygen in definite amounts to the gases between the points of entry and exit of the gases.

3. A process according to Claim 1, in which air, oxygen, or air enriched in oxygen, is supplied to the gases either continuously or intermittently in sufficient amounts to maintain the desired temperature in the refractory mass.

4. A process according to Claim 1, in which air, oxygen, or air enriched in oxygen, is added continuously in the heat-

ing region to the reacting gases in such amounts that the heat of combustion of the oxygen with the gases between the points of entry and exit of the gases is sufficient to maintain practically constant temperatures in the reaction zone.

5. An apparatus for the carrying out of the process according to Claim 1, consisting of two similar vertical chambers placed adjacent to one another and connected by a passage at their tops, each chamber being filled in its lower part with checker brickwork or the like adapted to form a pre-heating or regenerative zone, broken material as distinguished from refractory bricks or shapes being placed on top of the brickwork to form a refractory mass adapted to form a reaction zone.

6. An apparatus according to Claim 5, in which means are provided for admitting air or gas above the reaction zone.

7. An apparatus for use in producing a mixture of hydrogen and carbon monoxide, or hydrogen, carbon monoxide and nitrogen, constructed and arranged substantially as described with reference to the accompanying drawing.

Dated this 5th day of October, 1931.

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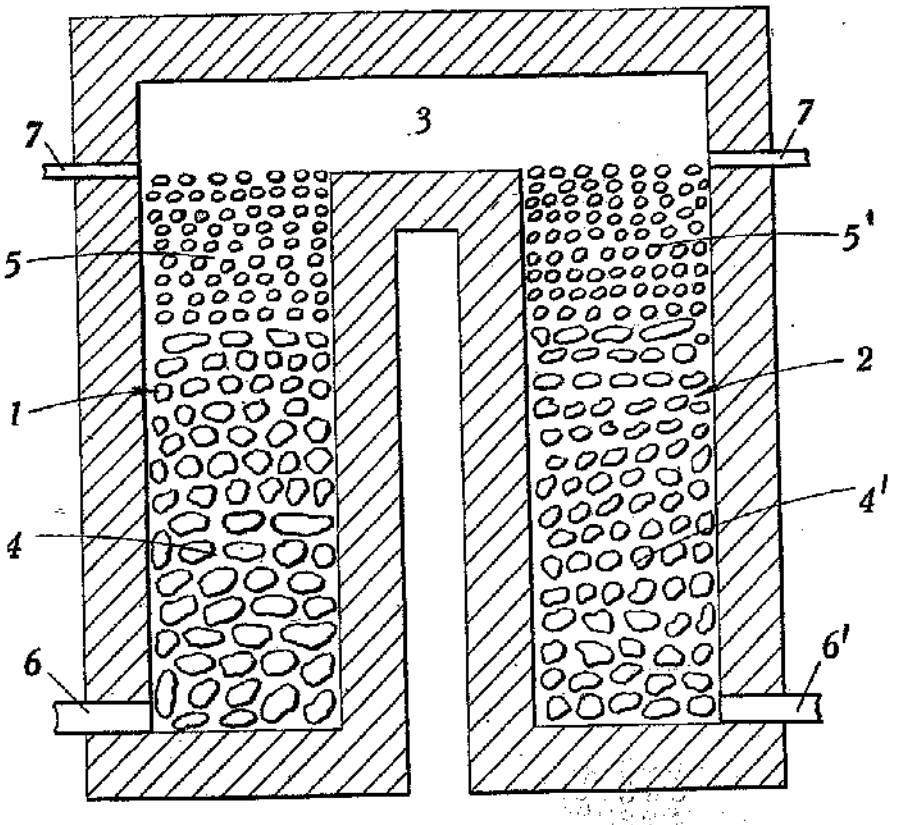

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