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PATENT SPECIFICATION

Inventor: LOUIS BOUDINEAU

655,869

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COMPLETE SPECIFICATION

A Method and a Plant for the Production of Mixtures of Hydrogen and Carbon Monoxide

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CORRECTION OF CLERICAL ERROR

SPECIFICATION NO. 655869

The following correction is in accordance with the Decision of the Assistant Comptroller, acting for the Comptroller-General, dated the twentyfirst day of February, 1952:-

Page 1, lines 3 - 4, *delete* "35, Rue Emile Barriere," *insert* "143, route d'Espagne."

THE PATENT OFFICE,
6th May, 1952.

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In a great many industrial operations the catalytic conversion is effected with the aid of steam, which reaction has a decided endothermic character. In order to avoid the necessity of working by alternating periods of heating and conversion one is led to arrange the catalyst in an externally heated bundle of alloy steel tubes. Such plants consequently are always quite costly. Besides, the thermal efficiency is always rather poor and considerable amounts of gas fuel have to be expended for heating purposes.

The use of oxygen or of air enriched in oxygen makes an internal heating possible and is thus seemingly advantageous; however, it actually involves a number of inconveniences such as the formation of carbon black, the early wear of the ovens and exhaustion of the cata- and explosion hazards.

controlled

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the formation of carbon black.

In this manner, gaseous hydrocarbons or gases containing the same, notably methane or natural gas, are converted with oxygen in such conditions that the hydrogen-carbon monoxide mixture obtained will contain less than 1% of methane.

In order to obtain a low methane content in the converted gas it is necessary to keep the catalyst at a high temperature. According to the invention, a temperature higher than 850° C. is to be maintained at the outlet from the catalyst chamber. Since the temperature in the catalyst oven decreases from the inlet towards the outlet it is advantageous for the obtainment of a long life of the refractory lining of the oven that such excessive local temperature should be avoided as would unavoidably occur at the inlet of the oven if the gases were insufficiently mixed together or as a result of the formation of flame jets. A further feature of the invention consists

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COMPLETE SPECIFICATION

A Method and a Plant for the Production of Mixtures of Hydrogen and Carbon Monoxide

We, Office National Industriel de L'Azote, a Society duly organized and existing under the French laws, of 35, Rue Emile Barriere, Toulouse (Haute-Garonne Department), France, 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:—

It has often been proposed to convert gaseous hydrocarbons and more particularly methane into a gas which is rich in hydrogen and carbon monoxide by means of steam, carbon dioxide or oxygen with or without the presence of catalysts. The gas obtained in this manner is suitable for various industrial applications. For the particular purpose of ammonia synthesis the converted gas must contain a particularly low percentage of methane. This makes it necessary, not withstanding the use of a catalyst, not withstand-conversion at comparatively high temperatures, e.g. of the order of 900° C.

In a great many industrial operations the catalytic conversion is effected with the aid of steam, which reaction has a decided endothermic character. In order to avoid the necessity of working by alternating periods of heating and conversion one is led to arrange the catalyst in an externally heated bundle of alloy steel tubes. Such plants consequently are always quite costly. Besides, the thermal efficiency is always rather poor and considerable amounts of gas fuel have to be expended for heating purposes.

The use of oxygen or of air enriched in oxygen makes an internal heating possible and is thus seemingly advantageous; however, it actually involves a number of inconveniences such as the formation of carbon black, the early wear of the ovens and exhaustion of the catalysts, and explosion hazards.

According to the invention, a controlled combustion without flame is arranged to take place in contact with a conversion catalyst which preferably is of the nickel-base type. This catalytic combustion substantially prevents the formation of carbon black which regularly occurs in combustion with flame. In order to ensure that the reaction will in fact take place without the formation of carbon black, particles of the catalyst according to the invention, have a diameter of not more than approximately 1 cm., thus causing the interstices between the particles to be too small for the combustion with flame, which could take place in these interstices, to be able to lead to the formation of carbon black.

In this manner, gaseous hydrocarbons or gases containing the same, notably methane or natural gas, are converted with oxygen in such conditions that the hydrogen-carbon monoxide mixture obtained will contain less than 1% of methane.

In order to obtain a low methane content in the converted gas it is necessary to keep the catalyst at a high temperature. According to the invention, a temperature higher than 850° C. is to be maintained at the outlet from the catalyst chamber. Since the temperature in the catalyst oven decreases from the inlet towards the outlet it is advantageous for the obtainment of a long life of the refractory lining of the oven that such excessive local temperature should be avoided as would unavoidably occur at the inlet of the oven if the gases were insufficiently mixed together or as a result of the formation of flame jets. A further feature of the invention consists

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in that the oxygen-methane mixture is introduced through a porous diffuser. Also the addition of steam to the mixture is recommended since steam is useful both as an inhibitor that will prevent the formation of carbon black and for homogenising the temperature in the oven.

Thus, according to the present method, the oxygen-methane mixture or gases containing such a mixture, which may or may not be preheated, are led through a porous diffuser into a very compact catalytic mass. The reaction then occurs in two stages, of which the first one consists in the complete combustion of a portion of the methane present leading to the formation of carbon dioxide and steam (reaction No. 1); while the second step (reaction No. 2) consists in the conversion proper (of endothermic character) of the remainder of the methane with the oxidising gases, the carbon dioxide and the steam that result from the reaction No. 1. In fact, reactions Nos. 1 and 2 are always more or less simultaneous, which makes it possible, by the use in the conversion reaction (reaction No. 2) of a nickel-base catalyst, that is to say of a catalyst which is highly effective as regards this reaction, to work below such excessive temperatures as would lead to straight combustion.

The nickel catalysts accelerate the conversion reaction which takes place according to the formulæ

$$CH_4 \div H_2O = CO \div 3H_2$$
$$CH_4 \div CO_2 = 2CO \div 2H_2$$

As a consequence, these reactions take place very rapidly after the formation of water and carbon-dioxide by the combustion of the methane.

The precautions recommended hereinbefore, i.e. the use of a porous diffuser for the introduction of the gases and the use of a nickel-base conversion catalyst, make it possible to work in substantially isothermal conditions. At all events, the temperature drop from the inlet to the outlet of the oven will not exceed a few hundred degrees centigrade.

A plant suitable for the performance of the method thus defined is illustrated diagrammatically in the appended drawing.

The plant is composed primarily of a vertical metal oven 1 lined inside with refractory blocks and heat-insulating materials 2 and closed at the bottom thereof with a porous refractory plate 3 that performs the function of a diffuser. The pre-mixed reaction gases are first passed through a heat-insulating block 4 through which extend narrow channels the purpose of which is to preclude backfire, after which they bow through the diffuser and become ignited at the surface of the latter which supports a pile of catalyst 5 consisting of nickel deposited on a refractory carrier containing silicon and aluminium, for example a carrier consisting of kaolin.

With the apparatus thus described gases are obtained which flow out at 6 and which contain no more than 1% of methane, the consumption of either pure or mixed oxygen fed through the catalyst being 550 cbm. per 1000 cbm. of methane.

Where it is desired to obtain a still lower residual methane percentage it may be advisable, instead of increasing the temperature within the oven by increasing the percentage of oxygen, to complement the cracking oven proper with a post-combustion chamber similar to those which are arranged below the tube bundles in the classical plants for effecting the conversion of methane with the aid of steam, and more particularly in the Bamag process.

The post-combustion chamber 8 is connected in series with the oven with which it communicates at its upper portion, and is provided at its top with an air inlet 7, thus permitting partial combustion of the gas coming from the oven whereby its temperature is increased before the gas reaches a charge 9 of a nickel-base catalyst provided on a refractory carrier in the post-combustion chamber. This catalyst may be the same as the catalyst employed in the oven 1. After passing this charge the resulting gas is discharged at the bottom of the said post-combustion chamber.

In a particular embodiment of the invention preheated or non-preheated air may be used instead of oxygen or enriched air. It is then possible in the same plant and in conditions similar to those described hereinbefore to produce at particularly low cost a gas which can be used for domestic purposes in town gas supply systems. In fact, the said gas may be admixed with natural gas for the purpose of increasing its heating power.

EXAMPLE 1.

A mixture of oxygen with methane and steam in the proportion of 550 cbm. of oxygen to 1000 cbm. of methane and 100 or more cbm. of steam is fed through a porous diffuser into a mass of catalyst consisting of nickel deposited on particles of a kaolin-type refractory material of approximately 6 mm. diameter arranged in a conversion oven.

As normal working conditions become established in the oven, the combustion localizes on the porous diffuser itself. The temperature within the oven ranges from

1100° C. at the inlet to 850° C. at the outlet of the oven. For every 1000 cbm. of methane supplied there is thus obtained a gas which when freed from the water vapour present therein contains 2900 cbm. of hydrogen + carbon monoxide together with some carbon dioxide and small amounts of residual methane as impurities. The percentage of the latter ranges from .5 to 1.0%.

EXAMPLE 2.

To the conversion oven used in Example 1 there is annexed a post-combustion chamber into the top of which air is forced. A methane-oxygen-air-steam mixture in the volumetric proportion 1000—500—250—100 is supplied to the intake of the conversion oven. Fed into the top of the post-combustion chamber are 750 parts by volume of air. When the steam in the mixture is condensed to water, 3400 parts by volume of a hydrogen-carbon monoxide-nitrogen mixture are obtained which contain 800 parts by volume of nitrogen. The residual methane content is not in excess of .2%. The gas temperature at the outlet of the post-combustion chamber exceeds 1000° C.

EXAMPLE 3.

In the conversion oven used in Example 1 a methane-air-steam mixture containing 3000 cbm. of air and 100 cbm. of steam to 1000 cbm. of methane is similarly forced through a porous diffuser into a catalyst mass likewise consisting of nickel deposited on 6 mm. diameter grains of a kaolin-type carrier. In normal working conditions there is obtained a regenerated gas the composition of which is approximately as folows:

CO_2	5%
CO	13%
H_2	34%
CH_4	4%
N_2	44%

in the approximative yield of 4350 cbm. per 1000 cbm. of methane subjected to the reaction. The heating power of the said regenerated gas is only 1800 calories per cbm. This heating power can be brought to a desired higher value by the addition of methane. For instance, in order to obtain a gas having a heating value of 5500 calories per cbm., it is only necessary to admix methane to the said regenerated gas in the proportion of 48 cbm. of the former to 52 cbm. of the latter.

In all the examples, the nickel deposit is produced on the silicon and aluminium base refractory bodies by soaking the said bodies with a solution of nickel nitrate, which is then evaporated and finally calcined to obtain thermic decomposition of the nickel nitrate. This well-known method results in the formation of a nickel deposit in the form of very fine granules.

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

1. A method of catalytically converting gaseous hydrocarbons, more particularly methane, or gases containing such hydrocarbons, into hydrogen and carbon-monoxide by controlled combustion with oxygen or with air which may be enriched with oxygen, characterised in that controlled flameless combustion is arranged to take place in contact with a conversion catalyst, preferably a nickel-base catalyst, in the form of particles which have a diameter not exceeding 1 cm., whereby the formation of carbon black by combustion with flame in the interstices between adjacent particles is substantially prevented.

2. A method according to claim 1, wherein the intimately pre-mixed gases for the reaction are introduced into the conversion oven through a porous diffuser.

3. A method according to claim 1 wherein aqueous vapour in a quantity of at least 10% of the methane is admixed to the reaction gases prior to their admission into the conversion chamber.

4. A method of producing a mixture of hydrogen and carbon-monoxide according to claim 1, in which a mixture of oxygen, methane and aqueous vapour in a proportion of 550 cbm. of oxygen to 1,000 cbm. of methane and at least 100 cbm. of aqueous vapour is forced through a porous diffuser into contact with very finely granulated nickel deposited on fragments of a refractory mass containing silicon and aluminium, for example, kaolin.

5. A method as claimed in claim 1 in which the gas mixture obtained in the conversion chamber is introduced into a catalyst-charged post-combustion chamber in which it is mixed with an addition of air so as to raise its temperature and obtain the conversion of the residual methane.

6. A method of producing a gas mixture according to claim 1, consisting in forcing a mixture of methane, air and aqueous vapour in a proportion of approximately thirty parts of air to ten parts of methane and not less than one part of aqueous vapour through a porous diffuser into contact with a catalyst constituted by nickel in very fine granular form deposited on a carrier mass containing silicon and aluminium, for example on kaolin or like refractory material.

7. Apparatus for carrying out the method as claimed in claim 1, comprising a cylindrical vertical metal oven lined inside with refractory blocks and heat-insulating materials, a refractory porous plate arranged at the bottom of the oven and through which the gas mixture is forced in, a charge of a nickel-base catalyst resting on said plate, a flue for the discharge of the gases, a post-combustion chamber connected in series with the said oven and communicating therewith at its upper end, said post-combustion chamber containing a charge of a nickel-base catalyst supported by a refractory carrier, for example a catalyst charge similar to that of the oven and having an air inlet near its highest point, and a gas discharge orifice at the bottom whereby the gases coming from the oven are subjected to a partial combustion to raise their temperature before reaching the catalyst in the post-combustion chamber.

Dated this 3rd day of December, 1948.

BARRON & WARREN,
16, Kensington Square, London, W.8,
Chartered Patent Agents.

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