[Second Edition.]

PATENT SPECIFICATION

Application Date: June 2, 1926. No. 13,935/26.

274,610

Complete Accepted: July 26, 1927.

COMPLETE SPECIFICATION.

A Process for the Preparation of Mixtures of Carbon Monoxide and Hydrogen from Hydrocarbons.

I, Dr. LUIGI CASALE, Chemist, of 9, Via del Parlamento, Rome, Italy, an Italian subject, do hereby declare the nature of this invention and in what

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SPECIFICATION No. 274,610. (2nd Edition.)

In the heading on Page 1, *for* "July 26, 1927." *read* "July 28, 1927."
Page 2, line 62, *for* "and" *read* "or"

THE PATENT OFFICE,
11*th April*, 1928.

(R2326) Wt 920/568 125 4/28 H & Sp Gp 112

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In the thermic decomposition of hydrocarbons, as above mentioned, carbon, hydrogen and methane form the intermediate products; the methane is the last to disappear.

Thus, in the decomposition in presence

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a) is maintained at low pressures, always below atmospheric pressure;

b) attains a temperature above 1000° C., even when the reaction occurs in the presence of catalysts;

c) contains a large excess of steam over and above that entering into reaction.

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I, Dr. LUIGI CASALE, Chemist, of 9, Via del Parlamento, Rome, Italy, an Italian subject, 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:—

Almost all the hydrocarbons, when brought to temperatures above 1000° C., are more or less rapidly decomposed into carbon, hydrogen and methane. The latter also decomposes, but with more difficulty, so that finally almost exclusively carbon and hydrogen are obtained. When a mixture of hydrocarbons and water is brought to the said temperature, it decomposes analogously, but with the difference that, instead of carbon and hydrogen, the end-product consists of carbon monoxide and hydrogen, the amount of the latter being of course increased because of water decomposition. The two said reactions are endothermic, particularly the second. On the basis of these reactions various methods for preparing hydrogen have been proposed; but the difficulty of economically performing endothermic reactions at such high temperatures has hitherto prevented the industrial success of such methods.

In spite of the great practical importance of the problem, especially for the production of hydrogen from coke-oven gases, these methods, as well as other analogous ones, have so far as I am aware not yet been industrially applied.

In the thermic decomposition of hydrocarbons, as above mentioned, carbon, hydrogen and methane form the intermediate products; the methane is the last to disappear.

Thus, in the decomposition in presence of water the most important reaction to render rapid and complete is:

$$CH_4 + H_2O = CO + 3H_2$$

For the equilibrium-constant

$$Kp = \frac{pCO \times p(H_2)^3}{pCH_4 \times pH_2O}$$

the calculation gives the following values (H. S. Taylor—Industrial Hydrogen, page 151)

T° abs.	=500°	800°	1000°	1500°
Kp	$=4 \times 10^{-11}$	0.03	35	6×10^5

Now the industrial success of this process depends on the purity of the hydrogen produced and on the facility of a large production. This renders necessary the complete decomposition of the methane and an enormous velocity in the reaction chamber. In other words, industrial success will be attained only when in the reaction chamber conditions are realised under which the value of concentration of the methane is practically nil, even when this value has reached only a fraction, for example $^1/_3$—$^1/_4$ of the value corresponding to the equilibrium.

According to this invention these conditions are realised when in the reaction chamber the system of the reacting gases consisting of gaseous hydrocarbons and steam or gaseous hydrocarbons, oxygen or air or air enriched with oxygen and steam.

a) is maintained at low pressures, always below atmospheric pressure;

b) attains a temperature above 1000° C., even when the reaction occurs in the presence of catalysts;

c) contains a large excess of steam over and above that entering into reaction.

An explanation of the first condition is

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unnecessary because of the great increase in the volume caused by the reaction, while the second and third conditions can be easily derived from the equilibrium-constant referred to above.

The process of the invention is illustrated by the accompanying example:

A mixture of methane and oxygen is drawn rapidly by means of a blower through a reaction apparatus constructed so that the reaction mixture is heated at the expense of the heat possessed by the gases which have already reacted so that almost all the heat possessed by the latter is recovered, thus reducing also to a minimum the quantity of heat which is to be expended for producing the necessary steam from water introduced into the apparatus.

The temperature of the reaction effecting the decomposition of the methane is maintained between 1100° C. and 1300° C. and is easy to regulate, it being sufficient to vary the amount of oxygen sent into the apparatus. The blower maintains the pressure of the reacting gases below that of the atmosphere. Working under these conditions and without the necessity of furnishing any external heat to the apparatus 1.5 cubic metres of hydrogen and carbon monoxide can be obtained from a cubic metre of coke oven gas, or 1.5 cubic metres of hydrogen when the carbon monoxide is catalysed with steam and the carbon dioxide thereby obtained eliminated.

In the case of methane the following reactions occur:

(1) $CH_4 + H_2O \text{ (vap)} = CO + 3H_2 - 50 \text{ cal}$
(2) $CH_4 + O = CO + 2H_2 + 9 \text{ cal}$

so that if it is desired that the two reactions should occur simultaneously without introducing external heat it is necessary to operate so that while a volume of methane reacts according to reaction (1) approximately 5.6 volumes of methane react according to reaction (2), so that the negative thermal effects of reaction (1) will be compensated by the positive effect of reaction (2).

If water in liquid state is introduced into the reaction chamber the following reaction takes place:

(3) $CH_4 + H_2O \text{ (liq)} = CO + 3H_2 - 60 \text{ cal}$

and thence reactions (2) and (3) occurring simultaneously so that in this case while a volume of methane reacts according to reaction (3) approximately 6.7 volumes of methane react according to the reaction (2) in order to compensate the corresponding thermal effects.

If only reactions (1) and (3) are utilised, the requisite heat is supplied internally or externally of the apparatus.

The final gas obtained in accordance with the process of this invention is practically free from methane and is composed of a mixture of hydrogen and carbon monoxide.

After suitable corrections, the mixture can be employed in the synthesis of alcohols.

If, immediately after the reaction, the mixture is cooled to about 500° C. by addition of water or steam, it is ready for the catalytic conversion:

$$CO + H_2O = CO_2 + H_2.$$

In this case the end-product freed from carbon dioxide can be used in ammonia synthesis or in other hydrogenations.

When, instead of pure oxygen, air or air enriched with oxygen is used, it is possible to obtain an end-product consisting of the hydrogen-nitrogen mixture such as it is required in the synthesis of ammoni.a

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

1. A process for the production of mixtures of hydrogen and carbon monoxide free from methane from gaseous hydrocarbons and steam or from mixtures containing gaseous hydrocarbons, oxygen and steam, in which the reaction between the said substances is carried out at a temperature above 1000° C. in the presence of an excess of steam and at a pressure below that of the atmosphere.

2. A modification of the process as claimed in Claim 1, in which hydrocarbons in gaseous form, steam and air or air enriched with oxygen are used as the originating materials and the resulting gaseous mixture is treated in order to yield a gaseous mixture of nitrogen-hydrogen substantially as described.

3. A process for the production of gaseous hydrogen or a mixture of hydrogen and carbon monoxide or a mixture of hydrogen and nitrogen, substantially as described.

Dated this 2nd day of June, 1926.

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Agents for the Applicant.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 67A—125/1/1928.]

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