



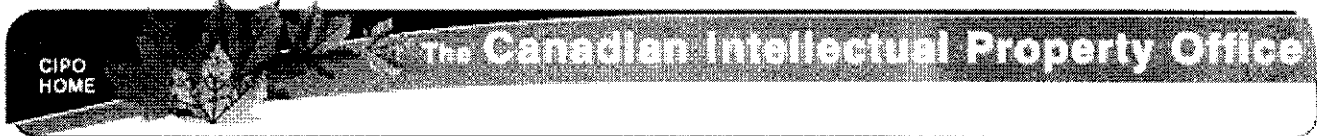
Industry
Canada Industrie
Canada

Canada

strategis.gc.ca

Strategis Index:

CIPO  OPIC



Canadian Patents Database

12/19/2001 - 08:27:56

(11) CA 360194

(12) Patent:

(54) CARBON MONOXIDE CONVERSION

(54) CONVERSION DU MONOXYDE DE CARBONE

(72) Inventor (Country): **FRITZ HANSGIRG** (Not Available)
 (73) Applicant (Country): **THE AMERICAN MAGNESIUM METALS CORPORATION**
 (71) Assignee (Country):
 (74) Agent:
 (45) Date of issue: **Sep. 1, 1936**
 (22) Date of filing:
 (43) Date of publication:
 (52) International Class: **23/355**
 (51) International Class: **N/A**

(70) Inventor's name as shown: **No**

(30) Application number: **None**

(71) Applicant's name: **N/A**

(72) Inventor's name: **Unknown**

(73) Applicant:

(74) Agent:

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
- Disclosures Image
- Drawings Image

4

4

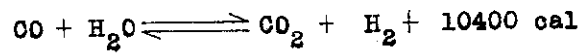
250194

This invention relates to the catalytic decomposition of carbon monoxide with steam.

It is an object of the present invention to provide a simple and economical process for producing hydrogen and more particularly hydrogen low in carbon monoxide.

Another object is to devise a process for eliminating carbon monoxide from water gas or from gaseous mixtures of similar composition.

The conversion of carbon monoxide (or gases containing same) by steam is intended, according to the equation:



of the so-called watergas equilibrium, to yield carbon dioxide and hydrogen as the end products. The values of the equilibrium constants for the temperature range of 300 to 1000°C. are known. These values show that, at lower temperatures, carbon dioxide and hydrogen, and at higher temperatures carbon monoxide and steam, form the most stable constituents of the watergas equilibrium. In practice, it has always been the aim to effect the conversion at the lowest possible temperature when the production of hydrogen was desired. However, inasmuch as the attainment of the equilibrium conditions is progressively protracted as the temperature falls, until such attainment fails to eventuate, it is necessary to accelerate the reaction catalytically. Even under these conditions however, it has not been found practicable, in large scale operation, to reduce the temperature below about 400°C., at which limit an amount of about 10% of carbon monoxide is still stable in the equilibrium.

5 This is the reason for modifying the procedure
so that - in addition to using catalysts by which only the
attainment of the equilibrium conditions can be assisted -
the position of the equilibrium itself is displaced, that
10 is to say, the percentage ratio of the reaction components
in equilibrium is changed. This object can be attained by
operating with a large excess of steam. Nevertheless, if
it were desired to reduce the carbon monoxide content, in
this manner, to such an extent that only small quantities
15 are stable in the equilibrium, this would necessitate such
a considerable excess of steam, even at relatively low tem-
peratures, as to put such a process out of consideration,
for economical reasons. The position of the equilibrium
can be displaced, in a different manner, by lowering the
20 tension of the carbon dioxide. In known processes of this
kind, the carbon dioxide is continuously removed from the
equilibrium by combining it with lime. This method of
operation also makes use, in general, of the catalytic
acceleration of the reaction. Catalysts of the iron group
25 were employed at first, but it was afterwards proposed to
employ magnesium oxide as catalyst, furnaces charged with
dolomite being used in carrying out the process in practice.
In this way the same carbon monoxide content can be obtained,
with a little more than the theoretical quantity of water,
30 as in operating with a large excess of steam but without
absorption of carbon dioxide. However, in processes of this
kind, the lime, or the lime content of the dolomite, takes
part in the reaction in stoichiometrical quantities, for which
reason it is necessary to regenerate the resulting calcium
carbonate to calcium oxide, by burning between each two

gasification stages, and to re-cool the furnace to reaction temperature afterwards.

According to the present invention, the conversion of the carbon monoxide by steam is effected under a pressure increased over that of the atmosphere by employing a mixture of magnesium oxide and carbon or alkali carbonate, or of magnesium oxide, carbon and alkali carbonate, (more particularly potassium carbonate) as catalyst.

Since the total number of molecules on each side of the equilibrium equation is the same, the water gas equilibrium is independent of pressure. However, the practice has already been adopted (U.S.A. Patent No. 1,157,669) of catalytically converting carbon monoxide by steam under pressure (4 to 40 atmospheres and over), in order to economise reaction space and steam.

However, in operating with the catalysts usually employed, the advantages of employing elevated pressure are offset by very considerable drawbacks.

In the first place, the deposition of carbon according to the reversible reaction $2CO \rightleftharpoons C + CO_2$, is increased by positive pressure. Since two molecules of starting gas are reduced to one volume of resulting gas, this reaction is dependent on pressure in the sense that the formation of carbon increases with the pressure. As a matter of fact, when causing carbon monoxide and steam to react at low temperatures under pressure above atmospheric in the presence of catalysts of the iron group, the deposition of carbon is so extensive that the gas passages soon become clogged and the catalyst useless. In contradistinction thereto, when catalysts with the composition (MgO + C) or (MgO + alkali carbonate) or (MgO + alkali carbonate + C) are employed, the deposition of carbon does not occur.

in operation under positive pressure, even at the temperature most suitable for the conversion of the CO to CO₂ and H₂.

In like manner also the formation of methane is facilitated by increased pressure. The formation of methane proceeds, with reduction in volume, both in the synthesis from hydrogen and carbon monoxide, and in the synthesis from hydrogen and carbon dioxide. Consequently a displacement of the equilibrium in favour of the formation of methane is theoretically to be expected. As a matter of fact, in the catalytic watergas process employing metallic catalysts, the formation of methane, in the temperature ranges most suitable for the conversion of carbon monoxide with steam, becomes excessive when the operation is performed under pressure. This inconvenience also is unexpectedly prevented, up to almost practical completeness, when the said mixed catalysts are employed. Thus, for example, with a pressure of 4 to 6 atmospheres above the atmospheric pressure, no formation of methane occurs, even at temperatures below 400°C., so long as the temperature in the catalyst remains constant.

Consequently, as the result of the combination of the special catalysts with the condition of carrying out the reaction under a pressure higher than atmospheric, in the conversion of carbon monoxide by steam a hitherto unattainable technical result of considerable importance ensues. This combination makes it possible to utilize to the full the special property of the said catalysts in respect of the complete establishment of the equilibrium in the temperature range from 400°C. down to 320°C., by counteracting, by means of increased pressure, the inevitable de-

A

200194

crease in the velocity of reaction due to the low temperature of working. In this manner, optimal results are obtained, even if the conversion should proceed for the greater part within the temperature range most favorable for the watergas equilibrium, and consequently with maximum economy in respect of steam consumption.

For this purpose, it is advisable to perform the conversion in two, or more, working stages, the first in a temperature range of 400 to 500°C. and the second (or last) in a range of 400-320°C. In larger plants it is of advantage to effect this two- (or more) stage conversion in separate contact furnaces for each stage, with interposed heat exchangers. By this means, the higher temperature of the catalyzed gaseous mixture issuing from the first contact furnace (or furnaces) can be utilized for preheating the starting gases, instead of allowing it to be dissipated, in the form of radiant heat, by progressively cooling the furnace zones down to the lowest reaction temperature.

A type of plant that is well adapted for carrying out the hereindescribed process is diagrammatically illustrated in the accompanying drawing.

1 is a stock vessel, from which the starting gas, such as watergas, is passed, by means of a compressor 2 into an irrigation tower 3, charged with Raschig-rings, after which the gas, charged with steam from the pipe 10, flows through the two heat exchangers 4 and 5. When preheated to the desired temperature, the mixture of watergas and steam enters the contact furnace 6, where the first stage of conversion is carried out at temperatures between 400°C to 500°C. This mixture, which should contain 1.5 to 2 volumes of steam per volume of carbon monoxide

4

191

in the starting gas, is passed into the top of the contact furnace 6 at such a temperature that, as a result of the exothermic reaction, the temperature of the contact mass is raised to about 500°C.

A typical catalyst is composed of caustic calcined magnesia and finely ground calcined potassium carbonate, in the proportion of 3:1 to 5:1 and with 3 to 5 units of wood charcoal to each unit of this mixture. The mixture, in a finely ground condition, is granulated by the aid of an aqueous emulsion of asphalt, and is heated to 600 to 800°C. out of contact with air.

The catalysed gaseous mixture issuing from the bottom of the contact furnace 6 passes into the heat exchanger 5 where it flows in the opposite direction to that of the starting gas introduced at the top of the heat exchanger, and is cooled, to the desired intake temperature of the second contact furnace 7, so that the contact mass can attain a final temperature of about 320°C.

The catalysed gaseous mixture passes from the furnace 7, in a condition free from all but a very small remainder of carbon monoxide, through the heat exchanger 4 in counterflow to the starting gas, into the cooling tower 8 (charged with Raschig-rings), in which the surplus steam is condensed by injecting cooling water, thus furnishing water with a temperature of 120° to 180°C. according to the working pressure. This hot water is delivered by the pump 9 into the irrigation tower 3, in which a preliminary saturation of the starting gas with steam is effected, so that only a portion of the steam required for the conversion has to be introduced through the pipe 10. The hot water under pressure issuing from the condenser 8 may, however,

10

4

200191

be relieved from pressure, the resulting steam being utilised for the watergas producers or as boiler feed water for the steam generator.

The entire plant is maintained under a pressure of 1 to 20 atmospheres, preferably 6 to 7 atmospheres.

I use the term magnesium oxide in the following claims to include not only preformed magnesium oxide, but also magnesium compounds yielding magnesium oxide under the temperature conditions of the present process (such as for instance magnesium carbonate), and mixtures of magnesium oxide with such substances. The term carbon is used to include carbonaceous material.

11
A
191
WHAT I CLAIM IS:

1. A process for converting carbon monoxide by steam by causing the carbon monoxide and steam to react under a pressure higher than atmospheric in the presence of a mixed catalyst of the group consisting ^{of} ~~of~~ (a) magnesium oxide and carbon, (b) magnesium oxide and alkali carbonate, (c) magnesium oxide, carbon and alkali carbonate.

2. A process for converting carbon monoxide by steam by causing the carbon monoxide and steam to react under a pressure higher than atmospheric in the presence of a mixed catalyst of the group consisting of magnesium oxide and carbon, and of magnesium oxide, carbon and potassium carbonate.

3. A process as defined in claim 1 in which the conversion is effected at reacting temperature within the range of from 500^oC to 320^oC.

4.- A process for converting carbon monoxide by steam which comprises causing the carbon monoxide and steam to react under a pressure higher than atmospheric in the presence of a mixed catalyst of the group consisting of (a) magnesium oxide and carbon, (b) magnesium oxide and alkali carbonate, (c) magnesium oxide, carbon and alkali carbonate, the conversion being effected in several working stages the first of which proceeds within a temperature range of 400^o to 500^oC, and the last in a temperature range of 400 to 320^oC.

5. The process of removing carbon monoxide from a gaseous mixture containing the same, which comprises contacting said gaseous mixture, together with steam, at reacting temperature within the range of 500 to 320^oC and at a pressure higher than atmospheric, with a mixed catalyst of the group consisting of (a) magnesium oxide and carbon, (b) magnesium oxide and alkali carbonate, (c) magnesium oxide, carbon and alkali carbonate.

12

4

662194

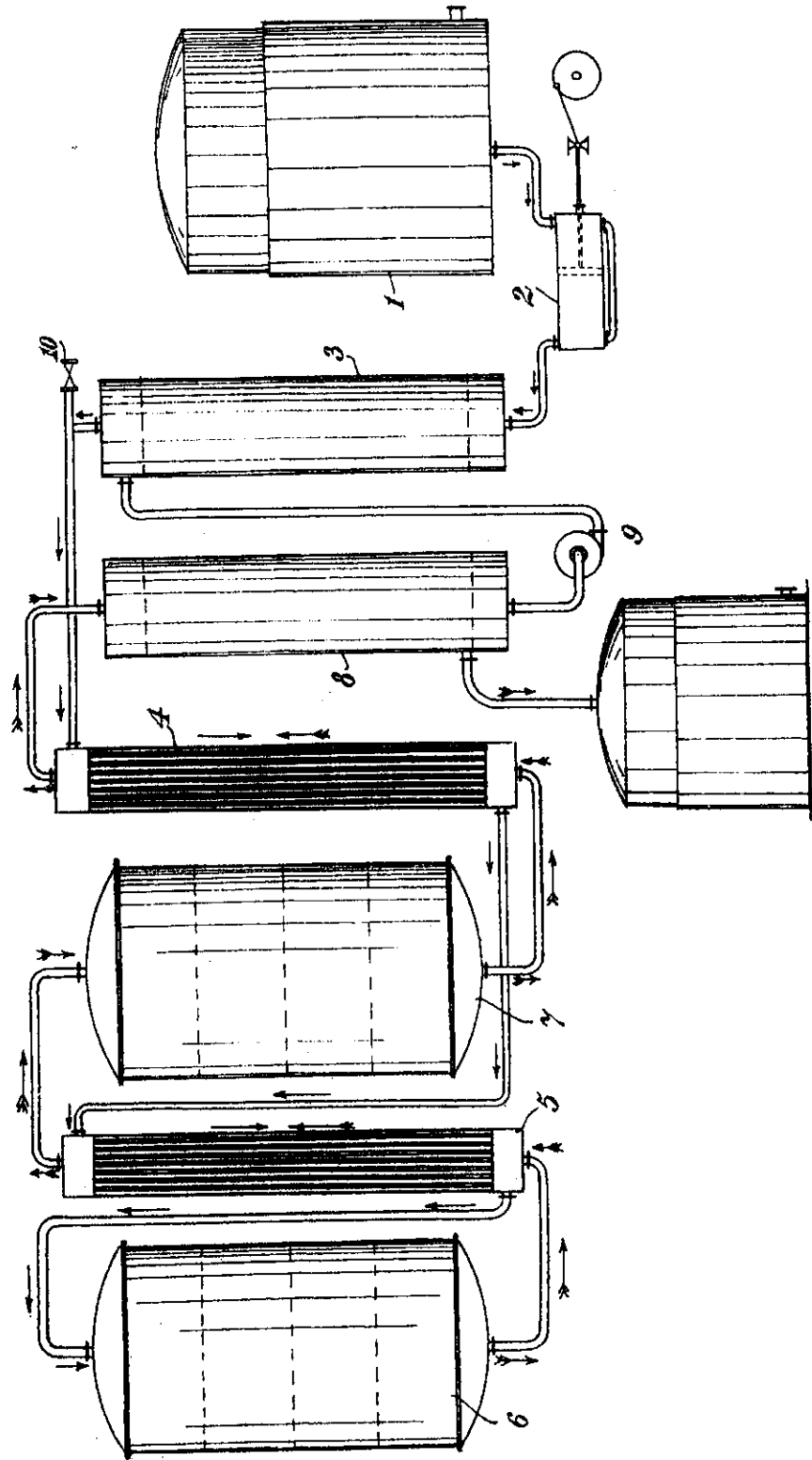
6. The process of removing carbon monoxide from a gaseous mixture containing the same, which comprises contacting said gaseous mixture, together with steam, at reacting temperature within the range of 400 to 320°C., and a pressure higher than atmospheric, with a catalyst of the group consisting of a mixture of magnesium oxide and carbon, and of a mixture of magnesium oxide, carbon and potassium carbonate.

7. The process of removing carbon monoxide from a gaseous mixture containing carbon monoxide and hydrogen, which comprises contacting said gaseous mixture, together with steam, at reacting temperature within the range of 500 to 320°C. with a catalyst of the group consisting of a mixture of magnesium oxide and carbon, and a mixture of magnesium oxide, carbon and potassium carbonate, the decrease in the velocity of reaction due to the low temperature of working being counteracted by applying a pressure increased over that of the atmosphere.

Process of Converting Carbon
Monoxide with Steam.

360194

360194



CERTIFIED TO BE THE DRAWINGS
REFERRED TO IN THE SPECIFICATION
HEREUNTO ANNEXED.

OTTAWA *March 17, 1934* BY

INVENTOR

J. Banerjee
Merle Clerk
ATTORNEYS