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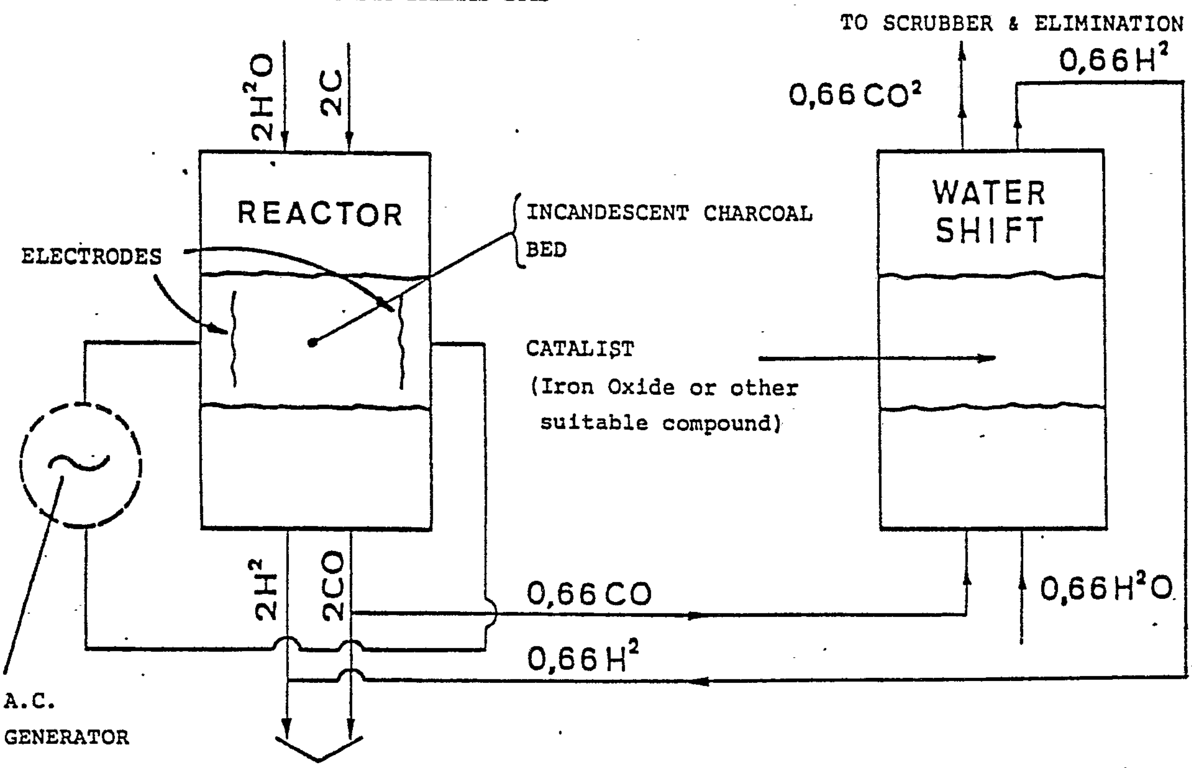
(54) Title: PROCESS FOR MAKING SYNTHESIS GAS



(57) Abstract

Water, instead of carbon dioxide, is reacted with red hot charcoal which leads to use of less electric power when making methanol from the syngas. The reaction heat is supplied by passing an electric current through the charcoal, by combustion of auxiliary fuel, or by waste heat recovery.

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TITLE OF INVENTION.

Specification on Patent of Invention concerning "PROCESS FOR MAKING SYNTHESIS GAS.

This patent derives from a previous process by the author whose brazilian patent has been applied December 29, 1978, under serial nº 7808650.

In the previous process, carbon monoxide was generated by the dissociation of a stream of carbon dioxide (CO^2) gas flowing through glowing charcoal bed.

The current patent constitute an improvement into above described process, and said improvement consists in using water steam in lieu of carbon dioxide. It is to be understood that the current patent as well as the previous one, were meant to produce synthesis gas using charcoal as feedstock suitable to the manufacture of methanol and other chemicals, such as gasoline & oil (F-P process), amonia, SNG, reducing gas for steel making, etc.

This improvement leads to a considerable economy of electric power per ton of methanol. Also considerable less carbon monoxide needs to be converted in hydrogen through the shift converter.

The new process can be thus described :

1. A reactor preferably a metalic vessel whose shape should preferably be that of a hollow cylinder. In-

side said cylinder a charcoal bed is kept white hot by means later to be described.

Said reactor should better be lined with fire and insulating bricks. Such lining makes that reactor suitable for standing high interior temperatures and avoid loss of heat as much as possible.

2. The reactor will be built in such way that a flow of water steam in forced through the charcoal bed which is kept white hot by means later described.

In contact with white hot carbon , the water steam undergoes the following reaction,

(1) $C + H^2O = H^2 + CO - 28$ Kcal.

The reaction is than an endothermic one. Therefore to keep the charcoal bed at steady temperature, heat must be continously supplied at a rate which can be exactly calculated for any given flow of steam.

According to the operating temperature it is possible that alternative reactions might take place e.g.

$$C + 2H^2O = 2H^2 + CO^2 - 18 \text{ Kcal.}$$

This reaction to be followed by Boudouard reaction

$$CO^2 + C = 2CO - 38 \text{ Kcal.}$$

At any rate, if the exit gas passes through a suficiently hot charcoal bed, the result will always be a mixture of $CO + H^2$ in even molal percentage no matter which intermediate path the reacting substances follow.

3. Therefore, for every mole of H^2O fed to the reactor, we will find one mole of CO plus one mole of H^2 coming out.

As a matter of precaution, the tickness of the charcoal bed must be figured so, that the residence time is long enough to assure the completition of the Boudouard reaction should such reaction take place, once Boudouard reaction can be somewhat slow.

The available data indicates that one second residence time through a charcoal bed 900° Cent a hot, is enough to secure substantialy complete dissociation of CO^2.

As far as reaction (1) is concerned, the kinetics of it are so great as to avoid any concern about residence time, provide the charcoal is kept in the neighborhood of 1000° Cent.

4. As seen above one mole of H^2O undergoing equation (1) absorbed 28 Kcal while generating one mole of CO plus one mole of H^2.

To further convert a gas containing even molal percentage of CO and H^2 into syntheses gas for methanol production we have to take 1/3 of the CO content and have it undergo the shift convertion.

This is done in a special department called "water shift department".

It consists normaly of a steel cylinder containing catalyst, usualy iron oxide. Inside that vessel a stream of CO plus steam flows through hot iron oxide catalyst. The CO plus H^2O react as per equation

$$(2) \quad CO + H^2O = H^2 + CO^2$$

5. Therefore for every mole of CO, one mole of H^2 plus one mole of CO^2 comes out of the shift converter.

To balance the proportion of H^2 to CO to the desirable figure we can take one out of every 3 of the outgoing moles of CO through the shift department and convert this mole in one extra mole of hydrogen.

The shift convertion, rather undersirably, produces also one mole of CO^2 for every mole of H^2 produced. The unwanted CO^2 can be discarded by several well known processes. If all the CO^2 produced during the shift reactions is eliminated the resulting gas will be :

$$3 - 1 = 2 \text{ moles of } CO$$
$$\text{plus } \; 3 + 1 = 4 \text{ moles of } H^2$$

The ration $H2 / CO = 2$

Such ration makes the gas quite suitable for the synthesis reaction in a methanol plant.

Incidentaly, a shift department always exists in any methanol unit.

The methanol can be synthetized simply by compressing, in the presence of suitable catalyst, the resultant gas in which as explained the ratio $H2 / CO$ has been adjusted to the desired ratio two to one.

Therefore the following reaction takes place

$$(3) \quad 2CO + 4H^2 = 2\ (CH_3 - OH)$$

methanol

In other words : the gas resulting from the reaction of 3 moles of steam over red not charcoal synthetises 2 moles of methanol after original proportion of H^2 to CO have been adjusted.

6. Any impurity that might be present, e.g. sulfur compounds, can be disposed of by usual procedures before synthesis loop is reached.

7. As far as the CO^2 molecules (produced in

the shift reaction) are concerned, some of them, up to a discret proportion, might not be washed away because, usualy they rather improve the activity of the catalyst. If CO^2 is present the correct proportion of the three gases must be such as to satisfy the following rule in which H^2, CO^2 and CO are molal percentages of these gases in the synthesis gas

$$\frac{H^2 - CO^2}{CO + CO^2} = 2$$

From the above we see that the present process for methanol production uses only two feedstocks: charcoal and water.

The easiest and cleanest means of keeping constant the temperature of the charcoal bed is to pass an electric current through it. It is a well known property that hot charcoal have a very low electric resistivity.

Therefore couple hundred volts applied over a rather long column of glowing charcoal is capable of generating several thousand amperes current that , by Joule effect, generate huge volumes of heat right inside the reacting mass of charcoal.

We have seen in paragraph 4 that for every mole of steam reacting with coal we have to supply 28 Kcal absorbed by the endothermic reaction if we are to keep constant the temperature of the charcoal. For 3 moles we need supply 84 Kcal.

According to equation (1) three moles of steam react with 3 moles of carbon to form a gas composed of 3 moles of CO and 3 moles of H^2. After converting one mole of out of every 3 into an extra mole of hidrogen we end up with a syngas that can be converted into 2 moles (64 gr) of methanol, as per equation (3). As we have seen above, these 2 moles (64 gr) of methanol had required 84 Kcal in the reactor.

Converting Kcal to kWh we came to the conclusion that we need in the gasifying operation 1526 kWh to produce one ton of methanol.

It must be understood that this power is spent in the gaseification of charcoal alone, and such figure does not include the needs for further operations in the process of converting a mixture of CO + H^2 into syngas whatever composition it is choosen.

The attached figure describes the process.

CLAIMS

1. Process for making synthesis gas suitable to the manufacture of methanol and other chemicals to be defined by the fact that the CO and H^2 content of the synthesis gas are originaly generated by the reaction of water steam over a bed of hot charcoal, whose temperature would preferably be above 500^o Cent and said temperature has been sustained without involving the combustion of any fraction of said charcoal bed.

2. Process for making synthesis gas suitable to the manufacture of methanol and other chemicals as claim 1 to be defined by the fact the heat absorbed by the chemical reactions of steam over hot charcoal

$$2H^2O + C = 2H^2 + CO^2 - 18 \text{ Kcal}$$

$$CO^2 + C = 2CO - 38 \text{ Kcal}$$

or if in one step :

$$C + H^2 = CO + H^2 - 18 \text{ Kcal}$$

is supplied by Joule effect of electric current flowing through the reacting charcoal mass.

3. Process for making synthesis gas suitable to the manufacture of methanol and other chemicals as claim 1 to be defined by the fact that the heat absorbed by the reaction of steam over hot charcoal

$$2H^2O + C = 2H^2 + CO^2 - 18 \text{ Kcal}$$

$$CO^2 + C = 2CO - 38 \text{ Kcal}$$

or if in one step :

$$C + H^2 = CO + H^2 - 18 \text{ Kcal}$$

is supplied by the combustion of an external fuel, whatever the process chosen to transmite said externally generated heat, to the reacting charcoal, so to sustain its temperature to adequate levels required by high efficient Boudouard reaction.

4. Process for making synthesis gas suitable to the manufacture of methanol and other chemicals as claim 1 through claim 3 in which the heat absorbed by the chemical reactions involved,

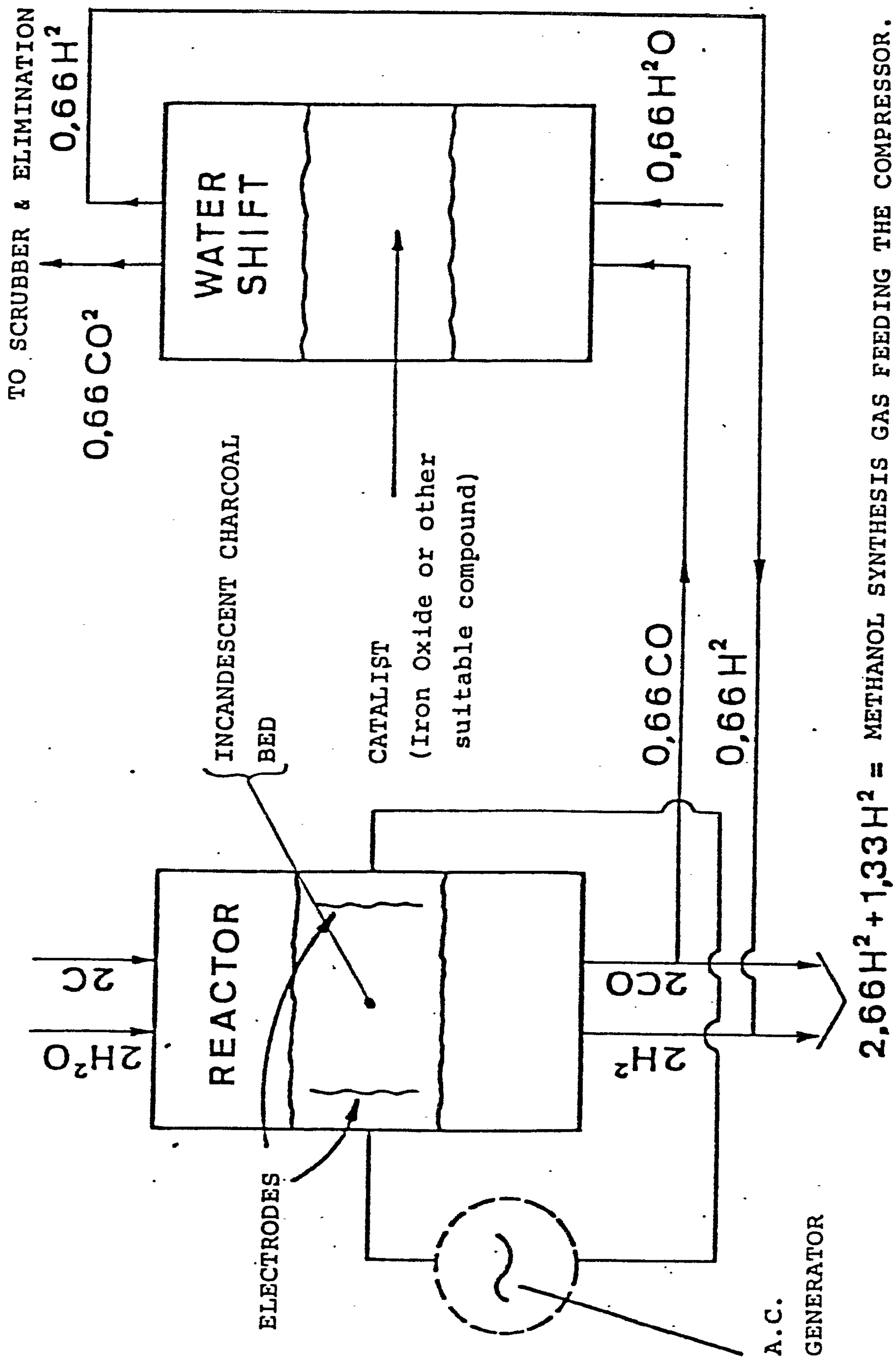
$$2H^2O + C = 2H^2 + CO^2 - 18 \text{ Kcal}$$

$$CO^2 + C = 2CO - 38 \text{ Kcal}$$

or if in one step :

$$C + H^2 = CO + H^2 - 18 \text{ Kcal}$$

is supplied total or partialy by recovered waste heat, otherwise lost in some other place along the process or in other nearby processes.


TO SCRUBBER & ELIMINATION
$0{,}66CO^2$
$0{,}66H^2$
WATER SHIFT
$0{,}66H^2O$
INCANDESCENT CHARCOAL BED
CATALIST (Iron Oxide or other suitable compound)
$0{,}66CO$
$0{,}66H^2$
REACTOR
2C
$2H^2O$
2CO
$2H^2$
ELECTRODES
A.C. GENERATOR
$2{,}66H^2 + 1{,}33H^2$ = METHANOL SYNTHESIS GAS FEEDING THE COMPRESSOR.

INTERNATIONAL SEARCH REPORT

International Application No PCT/BR80/00004

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.[3] C10J 3/06,10,18
U.S. CL. 252/373; 48/202

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	252/373; 48/65, 197R, 202

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US,A, 2,093,493, PUBLISHED 21 SEPTEMBER 1937, STITZER.	1,2,4
X	US,A, 3,252,773, PUBLISHED 24 MAY 1966, SEE COLUMN 3, LINES 63-70, SOLOMAN ET AL.	1-4
X	US,A, 3,847,566, PUBLISHED 12 NOVEMBER 1974, WILSON.	1,3,4
X	US,A, 3,850,839, PUBLISHED 26 NOVEMBER 1974, SEGLIN ET AL.	1,3,4
X	US,A, 4,069,304, PUBLISHED 17 JANUARY 1978, STARKOVICH ET AL.	1,3,4
X	DE,C, 298,149, PUBLISHED 31 MAY 1917, HOLMGREN ET AL.	1,2,4

* Special categories of cited documents: [15]

"A" document defining the general state of the art

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"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
08 JULY 1980	15 JUL 1980
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	Peter J. Kratz PETER F. KRATZ