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(21) International Application Number: PCT/BR80/00004 (22) International Filing Date: 7 April 1980 (07.04.80) (31) Priority Application Number: PI 7902079 (32) Priority Date: 4 April 1979 (04.04.79) (33) Priority Country: BR (71) Applicant; and (72) Inventor: DE OLIVEIRA, Eduardo, Sabino [BR/BR]; Rua Carlos Milan, 132 7o andar, CEP 01455 - São Paulo - SP (BR). (74) Agent: GNOCCHI, Fernando, Garcia; Avenida Ipiranga 313 7o andar CEP 01046 - São Paulo - SP (BR).		(81) Designated States: CF (OAPI patent), CG (OAPI patent), FR (European patent), GA (OAPI patent), MG, MW, NO, SE, SN (OAPI patent), TG (OAPI patent), US. Published <i>With international search report</i>
(54) Title: PROCESS FOR MAKING SYNTHESIS GAS <pre> graph TD A[2H2O, 2C] --> B[REACTOR] B --> C[2H2, 2CO] C --> D[WATER SHIFT] E[0,66 CO, 0,66 H2] --> D D --> F[0,66 CO2, 0,66 H2] F --> G[2,66 H2 + 1,33 H2 = METHANOL SYNTHESIS GAS FEEDING THE COMPRESSOR.] </pre>		
(57) Abstract $2,66\text{H}^2 + 1,33\text{H}^2 = \text{METHANOL SYNTHESIS GAS FEEDING THE COMPRESSOR.}$ 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.

5 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 (CO²) 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 metallic vessel whose shape should preferably be that of a hollow cylinder. In-

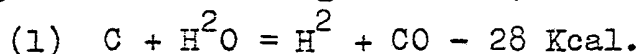


side said cylinder a charcoal bed is kept white hot by means later to be described.

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.

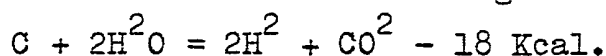
2. The reactor will be built in such way that a flow of water steam is forced through the charcoal bed which is kept white hot by means later described.

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

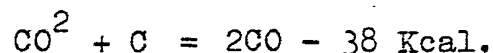


The reaction is then an endothermic one. Therefore to keep the charcoal bed at steady temperature, heat must be continuously supplied at a rate which can be exactly calculated for any given flow of steam.

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



20 This reaction to be followed by Boudouard reaction



At any rate, if the exit gas passes through a sufficiently hot charcoal bed, the result will always be a mixture of CO + H² in even molal percentage no matter which intermediate path the reacting substances follow.

3. Therefore, for every mole of H²O fed to the reactor, we will find one mole of CO plus one mole of H² coming out.

30 As a matter of precaution, the thickness of the



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

5 The available data indicates that one second residence time through a charcoal bed 900° Cent a hot, is enough to secure substantially complete dissociation of CO².

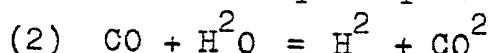
10 As far as reaction (1) is concerned, the kinetics of it are so great as to avoid any concern about residence time, provide the charcoal is kept in the neighborhood of 1000° Cent.

15 4. As seen above one mole of H²O undergoing equation (1) absorbed 28 Kcal while generating one mole of CO plus one mole of H².

To further convert a gas containing even molal percentage of CO and H² into syntheses gas for methanol production we have to take 1/3 of the CO content and have it undergo the shift conversion.

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

It consists normally of a steel cylinder containing catalyst, usually iron oxide. Inside that vessel a stream of CO plus steam flows through hot iron oxide catalyst. The CO plus H²O react as per equation



5. Therefore for every mole of CO, one mole of H² plus one mole of CO² comes out of the shift converter.

30 To balance the proportion of H² to CO to the



desirable figure we can take one out of every 3 of the out going moles of CO through the shift department and convert this mole in one extra mole of hydrogen.

The shift conversion, 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:

$$\begin{array}{l} 3 - 1 = 2 \text{ moles of CO} \\ \text{plus } 3 + 1 = 4 \text{ moles of H}^2 \end{array}$$

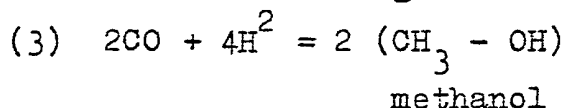
The ration $\text{H}_2 / \text{CO} = 2$

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

Incidentally, 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 H_2 / CO has been adjusted to the desired ratio two to one.

Therefore the following reaction takes place



In other words: the gas resulting from the reaction of 3 moles of steam over red hot charcoal synthesizes 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, usually 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

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

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.

5 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
10 does not include the needs for further operations in the process of converting a mixture of $\text{CO} + \text{H}^2$ into syngas whatever composition it is choosen.

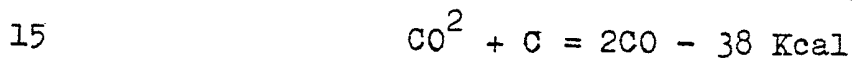
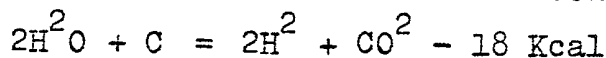
 The attached figure describes the process.



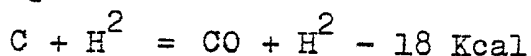
CLAIMS

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 H² content of the synthesis gas are originally generated by the reaction of water steam over a bed of hot charcoal, whose temperature would preferably be above 500° 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

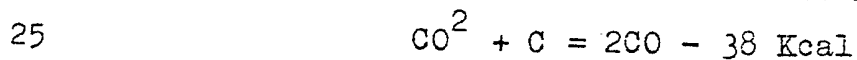
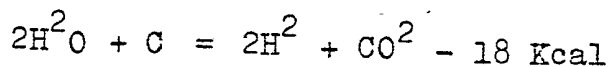


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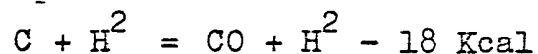


is supplied by Joule effect of electric current flowing through the reacting charcoal mass.

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

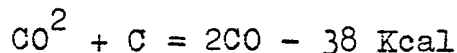
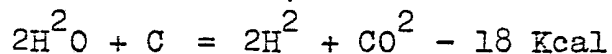


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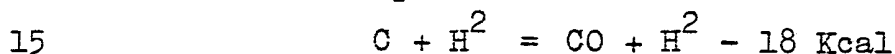


is supplied by the combustion of an external fuel, whatever the process chosen to transmute said externally generated heat, to the reacting charcoal, so to sustain its temperature to adequate levels required by high efficient Boudouard reaction.

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,

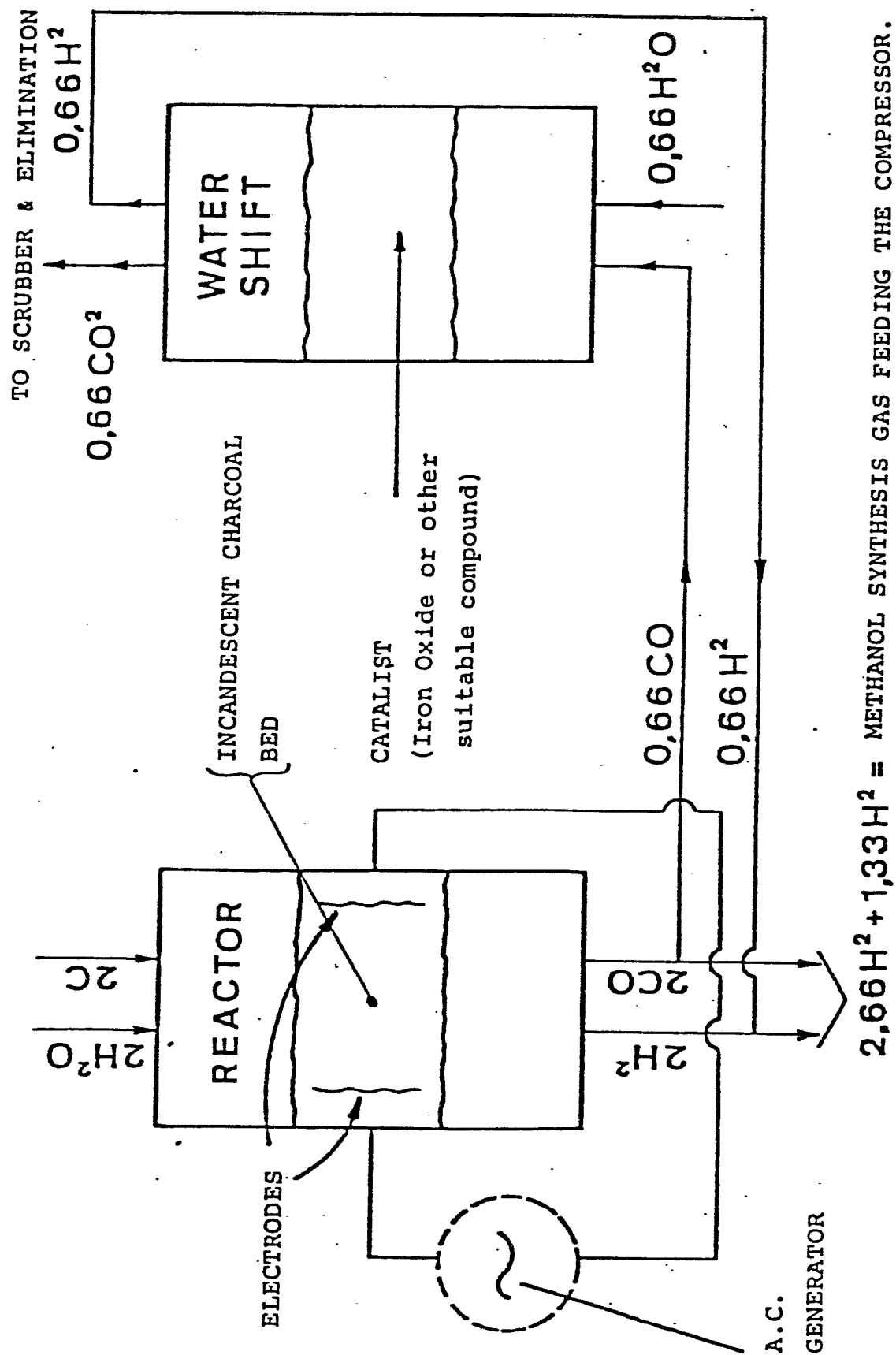


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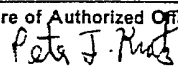
is supplied total or partially by recovered waste heat, otherwise lost in some other place along the process or in other nearby processes.

- 1 -



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. 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 ⁶		
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 "E" earlier document but published on or after the international filing date "L" document cited for special reason other than those referred to in the other categories "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but on or after the priority date claimed "T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention "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	
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