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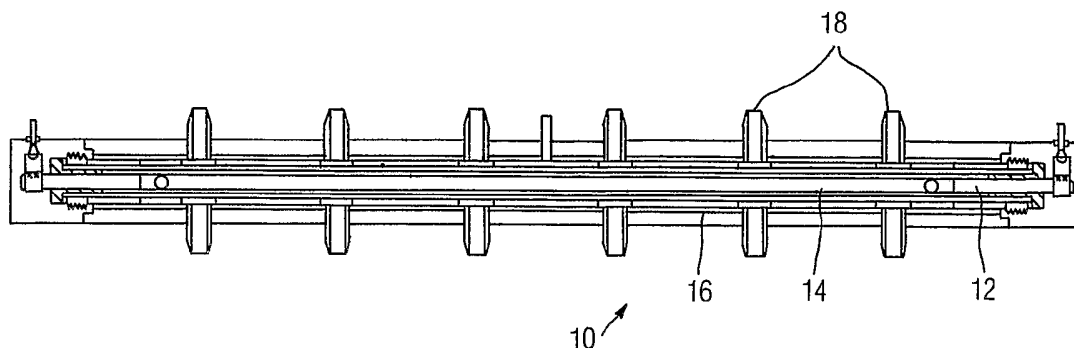
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(54) Title: PROCESS AND APPARATUS FOR HIGH PRODUCTIVITY CARBURIZING



(57) Abstract: This invention is directed to a process and apparatus for producing high productivity carburizing. A process is introduced that uses a gas mixture made up of CO, H₂, CO₂, H₂O, CH₄ and N₂, such that the product of the %CO and %H₂ is greater than about 1600; the ratio of CO/CO₂ is greater than 10; and the ratio of H₂/H₂O is greater than about 10. The gas mixture is controlled for a short time. A reactor [10] for generating a gas mixture for carburizing steel is also introduced. This reactor [10] is composed of a cylindrically symmetric body; a first central tube [12] containing electrical heating elements [14] for gas flow; a second central tube [16] concentrically disposed around the first central tube [12]; and a plurality of catalyst beds [18] disposed in an annular space in a segmented fashion around the second central tube [16].



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PROCESS AND APPARATUS FOR HIGH
PRODUCTIVITY CARBURIZING

[0001] This application is a continuation-in-part of prior U.S. application Serial No. 10/162,754 filed June 5, 2002.

Field of the Invention

[0002] This invention relates to a process and apparatus for producing atmospheres for high productivity carburizing. More particularly, this invention is directed to a process and apparatus for producing an atmosphere suitable for accelerated carburizing process using noble metal catalyst.

Background of the Invention

[0003] Carburizing is a widely used process for hardening the surface of steel parts by diffusion of carbon into the steel surface at high temperature. The carbon is supplied to the steel surfaces by a carrier gas having a high carbon potential. The most commonly used carburizing gas mixture is an endothermic gas which consists of 20% carbon monoxide (CO), 40% hydrogen (H₂) and 40% nitrogen (N₂). It is believed that the dominant reaction at the surface of the steel during the carburizing process is:



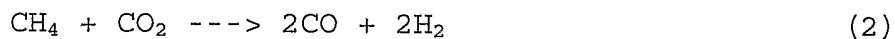
[0004] The rate at which carbon is put into the steel is therefore proportional to the product of the CO and H₂ concentration in the carrier gas. It is believed that the most productive reactive makeup for the reactant is a 50% CO and 50% H₂ mixture. This

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mixture may decrease the carburizing times by as much as 50%, thereby doubling the furnace productivity. However, there is presently no practical and economical generator available to produce carburizing gas with high percentage of CO and H₂. It would therefore be a benefit in the art to provide a process and apparatus for producing carburizing gas with a high percentage of CO and H₂.

[0005] There have been various attempts in the art to increase the CO and H₂ levels during the carburizing process. For example, one method includes direct injection of methanol into the furnace to generate an atmosphere with 33% CO and 67% H₂. However, additional thermal load relating to methanol dissociation exists. Furthermore, this method is comparatively very expensive as the atmospheric costs associated with this method is calculated to be about 4.5 times the costs for the endothermic gas.

[0006] Another method involves direct injection of methane (CH₄) and carbon dioxide (CO₂) into the furnace, as in U.S. Patent No. 5,676,769. Theoretically, this method can generate a 50% CO and 50% H₂ mix in the furnace using the reaction:



[0007] This reaction is highly endothermic and requires a catalyst to proceed at the typical carburizing temperature of between about 900°C to about 960°C. As a result, this makes the process difficult to control, requiring long residence times of the gas in the furnace. Long residence times have the disadvantage of generating H₂O in the furnace while the steel picks up carbon. Therefore, a large amount of

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methane injection is required to reform the H_2O and keep the carbon potential of the gas phase high. A major drawback to this method is that the high methane concentration often leads to excessive soot buildup in the furnace.

[0008] It is desirable to have a method that cures the deficiencies in the prior art. One such method is found in the present application having a high CO/H_2 mixture that is prepared in a separate reactor by reforming a CH_4/CO_2 mixture over a noble metal catalyst. This avoids the problems associated with direct injection of CH_4/CO_2 into the furnace and is significantly less costly than the direct injection of methanol.

Summary of the Invention

[0009] This invention is directed to a process for carburizing steel parts in a furnace comprising introducing into the furnace a gas mixture comprising CO , H_2 , CO_2 , H_2O , CH_4 and N_2 such that the product of the % CO and % H_2 is greater than about 1600, preferably greater than 2000; the ratio of CO/CO_2 is greater than 10; and the ratio of H_2/H_2O is greater than about 10; and controlling the gas mixture in the furnace for less than about 5 minutes, preferably less than 3 minutes, and most preferably less than 1 minute.

[0010] In another embodiment, this invention is directed to a process for carburizing steel parts in a furnace comprising introducing into the furnace a gas mixture comprising CO , H_2 , CO_2 , H_2O , CH_4 and N_2 such that the product of the % CO and % H_2 is greater than about 1600, preferably greater than about 2000; the

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ratio of CO/CO_2 is greater than 10; and the ratio of $\text{H}_2/\text{H}_2\text{O}$ is greater than about 10, the gas mixture being generated by a mixture of CH_4 and CO_2 over a noble gas catalyst, preferably platinum or rhodium, on a metallic carrier, preferably alumina carrier, at the temperature range of between about 850°C and 950°C ; and controlling the gas mixture in the furnace for less than about 5 minutes.

[0011] In yet another embodiment, this invention is directed to a reactor for generating a gas mixture for carburizing steel which comprises a cylindrically symmetric body; a first central tube containing electrical heating elements for gas flow; a second central tube concentrically disposed around the first central tube; and a plurality of catalyst beds disposed in an annular space in a segmented fashion around the second central tube. There may be six catalyst beds disposed in an annular space in a segmented fashion around the second central tube. The electrical heating elements maintain the gas mixture about 850°C to about 950°C .

Brief Description of the Drawings

[0012] Other objects, features and advantages will occur to those skilled in the art from the following description of preferred embodiments and the accompanying drawings, in which:

[0013] Fig. 1 is a drawing of the reactor for use in this invention; and

[0014] Fig. 2 is a schematic flow diagram of the mass and heat flow for Method 3 (see below) in this invention, where $x=0.5$ (no intermediate water removal).

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Detailed Description of the Preferred Embodiment

[0015] This invention involves a process for carburizing steel parts in the temperature range of 900°C to 960°C in which the rate of carburization is enhanced by:

[0016] 1. introducing into the furnace a gas mixture having CO, H₂, CO₂, H₂O, CH₄ and N₂, such that the product (%CO)*(%H₂) is greater than 1600, preferably greater than 2000, and the ratio of CO/CO₂ and H₂/H₂O in the gas mix is greater than 10. This combination provides a gas with a high carbon potential and thereby minimizes the need for extensive reforming of CO₂ and H₂O in the furnace by injection of enriching gas (CH₄ or Propane). This process is believed to avoid furnace sooting.

[0017] 2. The residence time of the gas mixture in the furnace is kept short, preferably less than 5 minutes, more preferably less than 3 minutes, and most preferably about 1 minute. This process effectively purges the furnace of the H₂O generated by combining CO and H₂, and again minimizes the need for large amounts of enriching gas.

[0018] 3. The gas mixture is economically produced in a novel generator. In this generator, mixtures of CH₄ and CO₂, with possible additions of O₂, air and/or electrical heat, are introduced over a noble metal catalyst, preferably platinum or rhodium, on an alumina carrier in the temperature range of between 850°C to 950°C. Palladium and iridium are alternative noble metal catalyst. Silica, zeolite and zirconia are alternative supports.

[0019] For (%CO)*(%H₂) = 1600, the carbon transfer rate is about 70% higher than for conventional endothermic gases, where (%CO)*(%H₂) = 800. CO/CO₂ and H₂/H₂O ratios > 10 are believed to limit the amount of

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reforming to be done in the furnace via direct injection of additional methane. This non-catalytic reforming inside the furnace is a slow reaction thereby requiring longer gas residence time. This leads to difficulties in maintaining high carbon potentials and also increases the likelihood of sooting.

Example

[0020] 250 kg. of 16MnCr5 steel was carburized in an Ipsen T-7 batch furnace at 930°C. A carburizing gas mixture containing about 44% CO and 52% H₂ (balance CO₂, H₂O and residual CH₄) was produced in a catalytic reactor according to invention Method 1 below with x being about 0.4 (24%O₂, 34% CO₂, balance CH₄). The (%CO)*(%H₂) is about 2300. In the furnace, the %CO was 44%, CO₂ was 0.5%, and the initial carbon potential of about 1.4.

[0021] The carbon potential was easily controlled without sooting on an O₂ probe and via injection of propane or air. Carburizing was for 3 hours at 930°C followed by 10 minutes at 870°C (diffusion step). The observed case depth was 1 mm.

[0022] A comparison test was done using direct injection of methanol + N₂ with %CO in the furnace being 25%, therefore (%CO)*(%H₂) is about 1250, as in the prior art. The observed case depth was 0.7mm, which indicates that the case depth in the inventive process could reduce the carburizing time by about 50%.

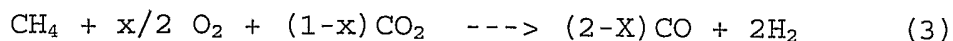
[0023] High CO/H₂ mixtures are prepared in a separate reactor by reforming a CH₄/CO₂ mixture over a noble metal catalyst. This avoids control problems associated with direct injection of CH₄/CO₂ into the furnace.

[0024] Three methods have been identified for preparing the gas mixture:

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Method 1: CH₄ + CO₂ with O₂ addition

[0025] When mixtures of CH₄, CO₂ and O₂ are introduced over the catalyst, the overall reaction can be described by



[0026] Carburizing gas compositions achievable with reaction (3) are given in the following Table 1.

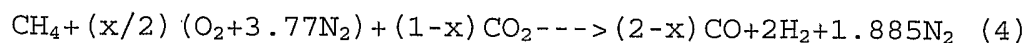
Table 1

x	%CO	%H ₂	%N ₂	(%CO)x(%H ₂)	Req. Heat Input (kWh.CCF endo)	Ad. Temp. Rise (°C)
0.0	50.0	50.0	0.0	2500	2.021	endothermic
0.2	47.4	52.6	0.0	2493	1.640	endothermic
0.4	44.4	55.6	0.0	2469	1.217	endothermic
0.6	41.2	58.8	0.0	2422	0.745	endothermic
0.8	37.5	62.5	0.0	2344	0.214	endothermic
0.9	35.5	64.5	0.0	2289	-0.078	107.0
1.0	33.3	66.7	0.0	2222	-0.388	431.1

[0027] The most desirable composition for a rapid carburizing process is when x=0 (50% CO, 50% H₂). Because reaction (1) is highly endothermic ($\Delta H = -59\text{kcal/mol CH}_4$), addition of O₂ to the reaction mix can significantly reduce the required heat input. The disadvantage in this method is that two oxidants are required (O₂ and CO₂).

Method 2: CH₄ + CO₂ with air addition

[0028] Alternatively, air can also be added to the CO₂/CH₄ mix. The overall reaction on the catalyst is then described by:



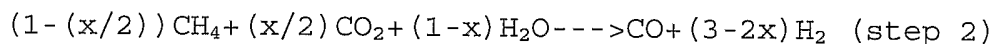
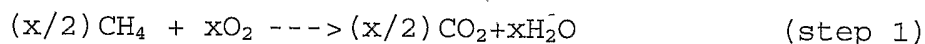
[0029] The achievable carburizing gas compositions with reaction (4) are given in the following Table 2.

Table 2

x	%CO	%H ₂	%N ₂	(%CO)x(%H ₂)	Req. Heat Input (kWh.CCF endo)	Ad. Temp. Rise (°C)
0.0	50.0	50.0	0.0	2500	2.021	endothermic
0.2	43.1	47.9	9.0	2063	1.492	endothermic
0.4	36.7	45.9	17.3	1688	1.006	endothermic
0.6	30.9	44.1	25.0	1364	0.559	endothermic
0.8	25.5	42.5	32.0	1083	0.145	endothermic
0.9	22.9	41.7	35.4	956	-0.050	78.1
1.0	20.5	40.9	38.6	838	-0.238	275.1

Method 3: In-situ CO₂ Generation

[0030] A convenient method of producing gas mixtures with high (%CO)*(%H₂) product values is to first combust natural gas with O₂ as in step 1 below. Part or all of the water is removed and the remainder CH₄/CO₂/H₂O mixture is reformed over a noble metal catalyst as in step 2.



[0031] The achievable gas compositions with this method are listed in Table 3 below.

Table 3

x	%CO	%H ₂	%N ₂	(%CO)x(%H ₂)	Req. Heat Input (kWh/CCF endo)	Adiabatic Temp. Rise (°C)
0.50	33.3	66.7	0.0	2222	-0.388	431
0.55	34.5	65.5	0.0	2259	-0.724	687
0.60	35.7	64.3	0.0	2296	-1.084	873
0.65	37.0	63.0	0.0	2332	-1.470	1006
0.70	38.5	61.5	0.0	2367	-1.885	1101
0.75	40.0	60.0	0.0	2400	-2.334	1171
0.80	41.7	58.3	0.0	2431	-2.821	1225
0.85	43.5	56.5	0.0	2457	-3.350	1266
0.90	45.5	54.5	0.0	2479	-3.927	1300
0.95	47.6	52.4	0.0	2494	-4.558	1327
1.00	50.0	50.0	0.0	2500	-5.253	1350

[0032] Note that the combustion in O_2 always supplies sufficient heat to drive the reforming reactions. The amount of water to be removed after complete combustion of the natural gas is $(2x-1)$ moles per mole of total methane used. This is illustrated in Table 4 below.

Table 4

x	mols H_2O /mol CH_4 (to be removed)	% H_2O in oxidant to reformer	dewpoint in oxidant to reformer ($^{\circ}F$)
0.50	0.00	66.67	192
0.55	0.10	62.07	189
0.60	0.20	57.14	185
0.65	0.30	51.85	181
0.70	0.40	46.15	175
0.75	0.50	40.00	169
0.80	0.60	33.33	161
0.85	0.70	26.09	151
0.90	0.80	18.18	136
0.95	0.90	9.52	113
1.00	1.00	0.00	-460

[0033] The apparatus required to implement this method is described below.

[0034] Generally, to obtain the compositions in this invention, and to avoid soot deposition on the catalyst, the catalyst temperature should not drop below about $800^{\circ}C$. Since the reaction is endothermic, this requires a reactor of a special type. Fig. 1 provides an example of such a reactor. The reactor 10 is preferably cylindrically symmetric. A central tube 12 is provided which contains electrical heating elements 14 or in which combustion gases flow in countercurrent with the $CH_4/CO_2/O_2$ or air mix. This mix is introduced into the reactor in the annular space defined by a second tube 16 concentrically disposed

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around the central tube. Six catalyst beds 18 are disposed in this annular space in a segmented fashion. The catalyst beds are in the shape of doughnuts and the spacing between them is such that the central tube 12 reheats the reacting gases to about 900°C before they contact the next catalyst bed. The gas mixture introduced to the reactor is preheated to about 900°C using a conventional gas to gas heat exchanger using the exit gas from the reactor and/or combustion gases from the reactor. Electrical heat can also be used for preheating the gas mix. Six catalyst beds 18 and electrical heating in the central tube 12 is suitable, although any number of catalyst beds are believed to be operational. Another preferred embodiment is the use of ten catalyst beds. Preferably, the electrical heating elements maintain the temperature of the gas mixture between about 750°C to about 1050°C, more preferably between about 800°C to about 1000°C, and most preferably between about 850°C to about 950°C.

[0035] A schematic example of mass and heat flows for Method 3 with $x=0.5$ (no intermediate water removal) is shown in Fig. 2. For $x>0.5$, some or all of the water at the exit of the burner must be removed, preferably by cooling the gas stream to the temperatures indicted in the last column of Table 4. The gas stream is then reheated using an additional heat exchanger.

[0036] The control of the accelerated carburizing process can be done by conventional means. For example, such means may include oxygen probes, CO/CO₂ measurements or H₂O measurements. In all three methods, the CO level must be measured in the furnace since the percent of CO in the furnaces is typically in excess of 30% and may vary. During the initial phase of the carburizing process, the carbon potential is set

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to equal or exceed the solubility of carbon in austenitic phase of the alloy being treated. Typically, this can be up to about 1.4%. This results in rapid saturation of the surface with carbon. During the diffusion phase of the carburizing process, the carbon potential in the gas phase can be lowered to match the desired surface carbon level (e.g., 0.8% C) in the part being treated. This lower carbon level can be conveniently achieved in the accelerated carburizing gas by dilution with N₂.

[0037] Those skilled in the art will recognize that numerous changes may be made to the process described in detail herein, without departing in scope or spirit from the present invention as more particularly defined in the claims below.

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What is claimed is:

1. A process for carburizing steel parts in a furnace comprising
 - a. introducing into said furnace a gas mixture comprising CO, H₂, CO₂, H₂O, CH₄ and N₂ such that the product of the %CO and %H₂ is greater than about 1600; the ratio of CO/CO₂ is greater than 10; and the ratio of H₂/H₂O is greater than about 10; and
 - b. controlling the gas mixture in said furnace for less than about 5 minutes.
2. The process of claim 1 wherein said product of %CO and %H₂ is greater than about 2000.
3. The process of claim 1 wherein said gas mixture is controlled in the furnace for less than about 3 minutes.
4. The process of claim 3 wherein said gas mixture is controlled in the furnace for less than about 1 minute.
5. A process for carburizing steel parts in a furnace comprising
 - a. introducing into said furnace a gas mixture comprising CO, H₂, CO₂, H₂O, CH₄ and N₂ such that the product of the %CO and %H₂ is greater than about 1600, the ratio of CO/CO₂ is greater than 10, and the ratio of H₂/H₂O is greater than about 10; said gas mixture being generated by a mixture of CH₄ and CO₂ over a noble gas catalyst on a ceramic carrier at the temperature range of between about 850°C and 950°C; and

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b. controlling the gas mixture in said furnace for less than about 5 minutes.

6. The process of claim 5 wherein said product of %CO and %H₂ is greater than about 2000.

7. The process of claim 5 wherein said noble gas catalyst is platinum.

8. The process of claim 5 wherein said noble gas catalyst is rhodium.

9. The process of claim 5 wherein said ceramic carrier is an alumina carrier.

10. The process of claim 5 wherein said gas mixture is generated by a reactor that comprises a cylindrically symmetric body; a first central tube containing electrical heating elements for gas flow; a second central tube concentrically disposed around said first central tube; and a plurality of catalyst beds disposed in an annular space in a segmented fashion around said second central tube.

11. The reactor of claim 10 comprising six catalyst beds disposed in an annular space in a segmented fashion around said second central tube.

12. A reactor for generating a gas mixture for carburizing steel which comprises

a. a cylindrically symmetric body;

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- b. a first central tube containing electrical heating elements for gas flow;
- c. a second central tube concentrically disposed around said first central tube; and
- d. a plurality of catalyst beds disposed in an annular space in a segmented fashion around said second central tube.

13. The reactor of claim 12 comprising six catalyst beds disposed in an annular space in a segmented fashion around said second central tube.

14. The reactor of claim 12 wherein said electrical heating elements maintains the gas mixture about 850°C to about 950°C.

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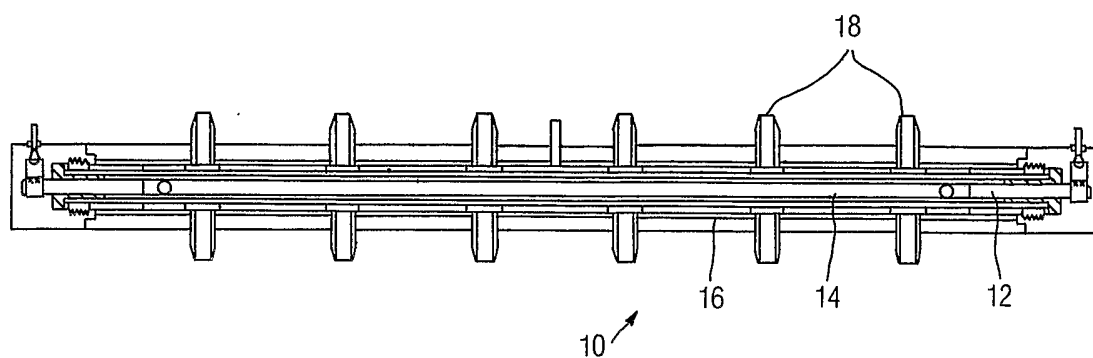


FIG. 1

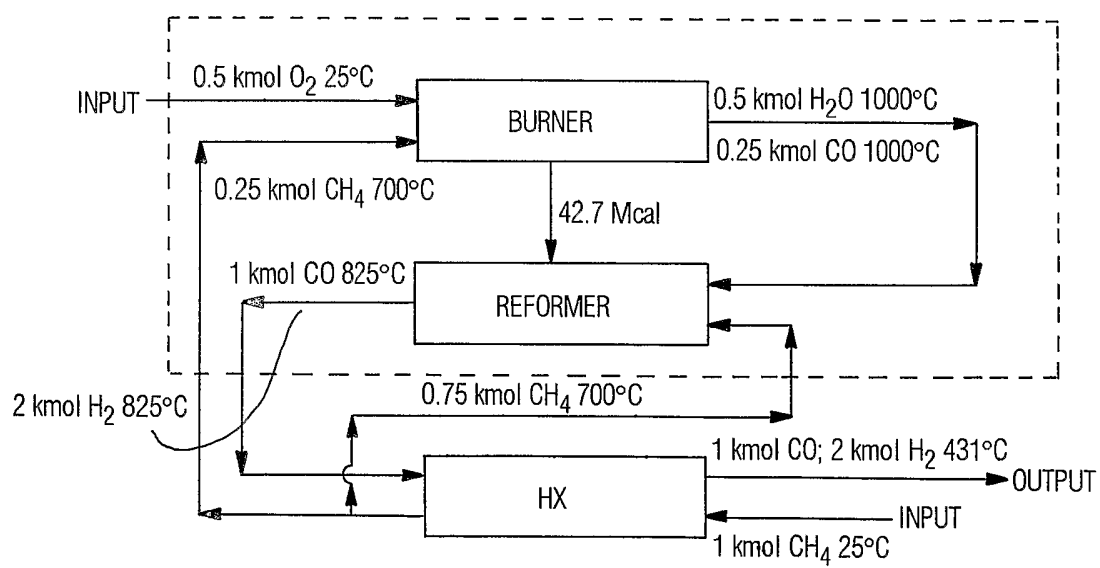


FIG. 2