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PARTIAL OXIDATION OF HYDROCARBONS

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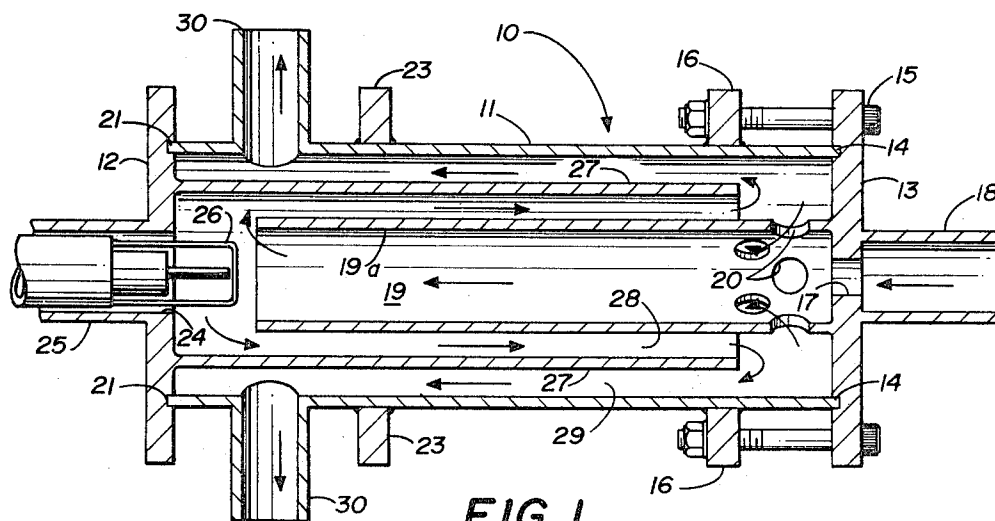


FIG. 1

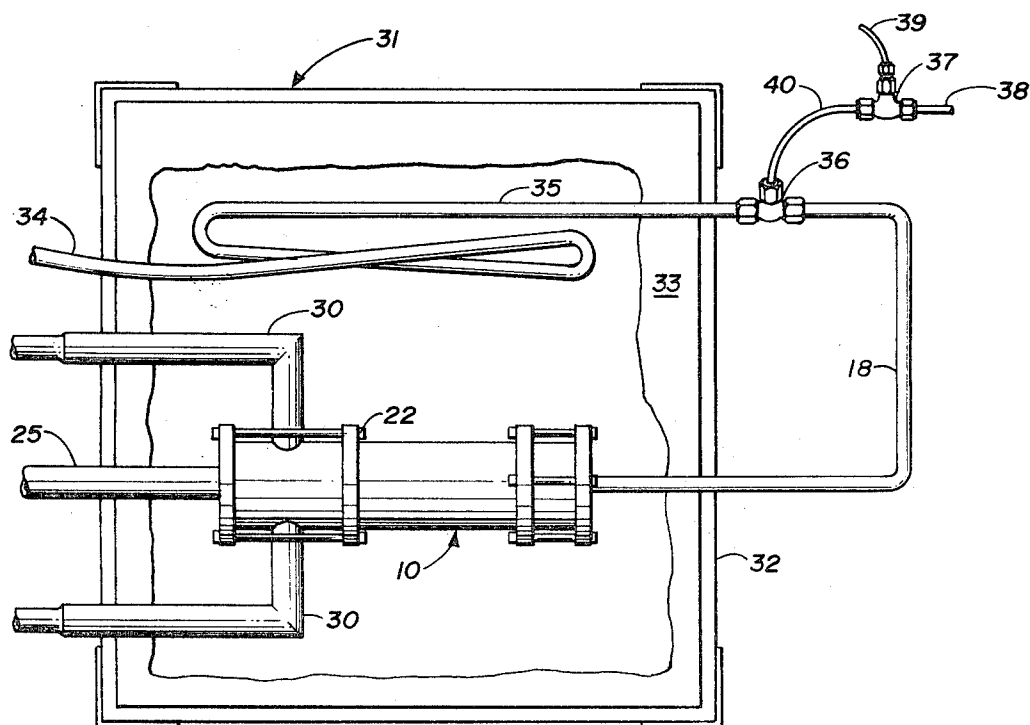


FIG. 2

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PARTIAL OXIDATION OF HYDROCARBONS

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8 Claims

ABSTRACT OF THE DISCLOSURE

A partial oxidation reactor for oxidizing a hydrocarbon stream to a carbon monoxide-hydrogen product stream containing substantially no free carbon. The reactor is equipped with an orifice leading into a combustion zone which includes conduits for recycling combustion products into the combustion zone adjacent the orifice, and a high temperature stabilization zone following the combustion zone.

This invention relates to the partial oxidation of hydrocarbons. In another aspect, this invention relates to an improved method and reactor for partially oxidizing a hydrocarbon stream to yield a carbon monoxide stream containing substantially no free carbon.

Various chemical reactors and processes are known in the art which provide product streams comprising carbon monoxide and/or hydrogen. One particular application for such a stream is a feed stream for a conventional molten carbonate fuel cell. In such an operation, a feed stream comprising hydrogen is fed to the fuel cell anodes which are spaced from the cathodes by a suitable molten carbonate electrolyte such as an alkali metal carbonate. Oxygen is supplied to the cathode. Half cell reactions between the reactants and electrolyte occur causing a flow of current through the cell.

Hydrogen feed streams for these fuel cells are conventionally formed by oxidizing hydrocarbons at less than stoichiometric oxygen requirements within a combustion chamber. However, these conventional oxidation reactions usually result in the formation of free carbon which is deposited in the combustion chamber, or remains entrained in the product gases as soot. This free carbon not only contaminates the product stream but can build up to such a degree in the combustion chamber and exhaust ports from the combustion chamber that the reactor must be periodically shut down and cleaned out in order that an efficient oxidation process can be carried out.

Therefore, one object of this invention is to provide an improved method and apparatus for producing carbon monoxide and hydrogen.

Another object of this invention is to provide an improved method and apparatus for the partial oxidation of hydrocarbons which yields substantially no free carbon in the product stream.

According to the invention, a product stream comprising carbon monoxide and hydrogen with substantially no free carbon contained therein is produced by passing a vaporous hydrocarbon admixed with less than a stoichiometric amount of oxygen into a heated reaction zone, igniting the mixture to form a combustion stream, and passing a first portion of the combustion stream into the hydrocarbon stream entering the reaction zone and a second portion of the combustion stream through a heated stabilization zone, and then to a cooled outlet.

According to another embodiment of this invention an apparatus is provided for carrying out the above described process.

This invention can be more fully understood from a study of the drawings in which:

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FIG. 1 is a cross sectional view of a preferred partial oxidation apparatus of this invention; and

FIG. 2 is a schematic view illustrating the partial oxidation apparatus of FIG. 1 connected to feed inlet and outlet conduits and disposed within a suitable heating device.

Now referring to FIG. 1, a cross sectional view of the partial oxidation reactor of this invention is illustrated in detail. Reactor 10 generally comprises a tubular member 11 enclosed by end plates 12 and 13, respectively.

End plate 13 carries seating areas 14 which receive the end portions of tubular member 11 in operative relationship. End plate 13 is held in place by nut and bolt assemblies 15 and connect to annular member 16 which in turn is operatively fastened to tubular member 11. End plate 13 carries orifice 17 therethrough which communicates between inlet conduit 18 and cylindrical reaction zone 19. As illustrated, cylinder 19a, which defines cylindrical reaction zone 19, extends from orifice 17 to a point adjacent end plate 12. Recirculation passages 20 communicate through cylinder 19a adjacent orifice 17.

End plate 12 carries seating areas 21 which receive the end portions of tubular member 11. End plate 12 is held in operative position by nut and bolt assemblies 22 (FIG. 2) which fasten between enclosure 12 and annular ring 23 which in turn is fastened to tubular member 11. End plate 12 carries aperture 24 concentrically positioned therethrough which is in communication with conduit means 25. Conduit means 25 contains an elongated spark plug means 26 which is adapted to extend to any desired point within cylindrical reaction zone 19 and initiate the combustion reaction. The preferred combustion initiation position of spark plug means 26 is a position between end plate 12 and the end of cylinder 19a, for example, the position illustrated in FIG. 1.

Cylindrical baffle means 27 is operatively connected to end plate 12 and extends therefrom to a point adjacent recirculation passages 20 to thereby form an annular reaction zone 28 between cylindrical reaction zone 19 and baffle 27, and annular stabilization zone 29 between baffle 27 and tubular member 11. Exhaust conduits 30 communicate through tubular member 11 to annular stabilization zone 29 adjacent end plate 12.

The connection of partial oxidizer reactor 10 to feed inlet and outlet conduits within a suitable heating zone is illustrated in FIG. 2. Furnace box 31 comprises an enclosed structural frame 32 which contains a suitable heating element such as a gas heater (not shown) for heating the contents thereof, a suitable insulation material 33 such as a ceramic molded around the inside of frame 32, and a top closure means (not shown). To initiate the partial oxidation reaction, furnace box 31 is preheated to a desired initiation temperature (depending on the particular fuel being utilized and spark plug 26 is extended within reactor 10 to a point adjacent the end of cylinder 19a as illustrated in FIG. 1. Air is passed into conduit 34 and through heating coil 35. The air from heating coil 35 will pass into T junction 36 wherein it is mixed with an air-fuel stream. The air-fuel stream originates at junction 37. Air is passed to junction 37 via conduit 38 and a hydrocarbon fluid enters junction 37 via conduit 39. The hydrocarbon fluid can be either liquid or vaporous; however, the particular arrangement illustrated in FIG. 2 is ideally suitable for use with a liquid fuel. By this arrangement, a hydrocarbon-air mixture will pass to junction 36 via conduit 40 and admix with the heated air stream in the junction 36. The resulting heated air-fuel mixture is passed to orifice 17 within end plates 13 via conduit 18. The mixture is then ignited within cylindrical reaction zone 19 by spark plug means 26.

The actual combustion temperature within cylindrical reaction zone 19 and annular reaction zone 28 will be a temperature within the range of about 900° C. to about 1200° C. Generally from about 60 to 90 percent of the total oxygen will be supplied through conduit 34 and the rest supplied through conduit 38. Therefore, the amount of air supplied through conduit 34 and preheated coil 35 versus the amount of air supplied through conduit 38 can be manipulated to control the inlet temperature of the preheated air-hydrocarbon stream entering the reactor so that the ultimate internal reaction temperature can be thereby controlled.

In order to provide the incomplete combustion of the hydrocarbon material, the oxygen-carbon atom ratio of the feed material flowing to orifice 17 and conduit 18 should be below the value which will result in complete combustion of the hydrocarbon, and above 1.0 which will result in free carbon formation. Preferably the oxygen-carbon atom ratio of the feed material flowing to orifice 17 is in the range of about 1.1 to 1.6. Generally, any suitable hydrocarbon material can be utilized, for example, vaporous hydrocarbons including methane, ethane, propane, butane and pentane, and liquid hydrocarbons up through the diesel oil fractions including naphtha, gasoline, kerosine and gas oil. Likewise, any oxygen-containing gas stream which contains no components deleterious to the reaction can be used in the process of this invention. For example, suitable feed streams comprise oxygen, carbon dioxide, water vapor, and mixtures thereof. The oxygen atom-carbon atom ratio can be easily controlled by one skilled in the art by adjusting the air flow through conduits 34 and 38 and the flow of the particular hydrocarbon material through conduit 39.

In operation, the furnace box 31 is heated to a suitable temperature, generally no greater than about 700° C. This temperature will not only maintain the partially combusted products within exhaust conduits 30 above the equilibrium carbon deposition temperature of carbon monoxide, but will maintain annular zone 29 at an elevated temperature of no less than about 200° C. below the reactor temperature as will be explained in detail below. Additionally, the elevated temperature will heat coil 35 to effectively heat the air entering junction 36 so that a preheated hydrocarbon vapor-air feed stream will enter orifice 17 via conduit 18. Combustion is then initiated by spark plug means 26 as the air-hydrocarbon stream passes through orifice 17 to form a combustion mixture throughout cylindrical reaction zone 19. After the combustion is initiated, spark plug means 26 can be withdrawn from the high temperature environment to prevent thermal damage thereto. Orifice 17 is sized so that a jet stream is formed by the action of the fluid flowing therethrough. In essence, an aspirator action is effected which will create a vacuum adjacent the periphery of the jet stream flowing from orifice 17 and thereby cause combustion products which are passing from annular zone 28 to pass in conduits 20 and admix with the feed stream entering cylindrical reaction zone 19.

The partial combustion of the hydrocarbon is initiated and conducted in cylindrical reaction zone 19, and substantially completed in annular reaction zone 28. In a conventional type partial oxidizer, baffle 27 is not present, and outlet conduits 30 are positioned through tubular member 11 adjacent recirculation passages 20. In this type reactor, it was found that substantial formation of free carbon was present as was evident by clogged exhaust lines and entrained smoke within the product stream. By adding baffle 27, it was discovered that the formation of free carbon was substantially stopped. It is not completely understood why the addition of the annular stabilization zone reduces the formation of free carbon. It is theorized that many active radicals which are potential free carbon forming agents are stabilized in the form of

the carbon monoxide-hydrogen product while being passed through the heated stabilization zone prior to being quenched or cooled when passing through the air-cooled outlet conduits. It is preferred that annular stabilization zone 29 be heated to a temperature of no less than about 200° C. below the mean temperature within cylindrical reaction zone 19 and annular reaction zone 28. Generally, the temperature within annular stabilization zone 29 will be substantially the same as the mean temperature within these reaction zones.

The combustion stream from annular reaction zone 28 is divided into two basic portions. The first basic portion is recycled via recirculation passages 20 to the combustion stream within cylindrical reaction zone 19. Generally from 10 to 50 percent of the stream from annular zone 28 is recycled into the cylindrical reaction zone in this manner. This recycling enhances a completion of the combustion between available oxygen and carbon within the reactor, while suppressing the formation of unwanted by-products such as free carbon and free carbon forming species. The second basic portion of the product stream from annular reaction zone 28 is passed to annular stabilization zone 29. It is believed that even though the combustion is substantially complete for the stream entering the annular stabilization zone, various activated species are present in the stream, and the passage through the heated zone before cooling will stabilize the product stream in the form of the carbon monoxide and hydrogen components.

The following example is given to further facilitate the understanding of this invention.

EXAMPLE

Several runs were made by using the partial oxidation apparatus illustrated in FIGS. 1 and 2. Referring to FIG. 1, the reactor was made of high temperature alloy steel and had the following dimensions: tubular member 11 was eleven inches long and made from a two inch diameter schedule 40 pipe; baffle 27 was nine inches long and was made from a one and one-half inch diameter schedule 80 pipe with its outside diameter turned to 1.7 inches; cylindrical reactor 19a was eight inches long and was made from a ¾ inch diameter schedule 40 pipe; eight ¾ inch recirculation conduits 20 were present, orifice 17 was 0.25 inch in diameter, and conduits 18 and 30 were made from ¾ inch diameter schedule 40 pipes.

Several runs were made using Texaco regular grade gasoline as the hydrocarbon admixed with sufficient air to yield an oxygen to carbon atom ratio in the range of from 1.25-1.3. The oxidizer was operated at the rate of about 1.25 lbs. per hour of gasoline. The reactor was positioned within the 700° C. furnace and operated at an internal reactor temperature of from 1,000 to 1,200 degrees C. No evidence of free carbon formation was found. A chemical analysis of a product stream (dry basis) which occurred when the internal reaction temperature was stable at about 1125° C. was as follows:

Product:	Mole percent
H ₂ -----	16.4
N ₂ -----	56.4
CO -----	22.2
CH ₄ -----	3.5
CO ₂ -----	2.5

While this invention has been described in reference to its preferred embodiments, it is to be understood that various changes and modifications may be suggested to one skilled in the art upon reading this specification, and it is intended to cover such changes and modifications that fall within the scope of the invention as defined in the appended claims.

What is claimed is:

1. A partial oxidation reactor comprising:

(a) an elongated tubular reactor enclosure with a

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first end and a second end and having feed injection means operatively connected to said first end;

(b) a first tubular reactor means disposed within said enclosure defining a central reactor zone in communication with the said feed injection means and extending therefrom to a point adjacent said second end, said first tubular means having recirculation passages therethrough adjacent said first end;

(c) a second tubular reactor means operatively connected to said second end, positioned around said first tubular reactor means and extending to a point adjacent said recirculating passages to thereby form a first annulus between said first and second tubular reactor means, in direct communication with said central reactor zone by means of said recirculation passages, and a second annulus between said enclosure and said second tubular reactor means; and

(d) product withdrawal conduit means communicating with said second annulus at a point adjacent said second end of said enclosure.

2. The partial oxidation reactor of claim 1 further comprising means communicating through the second end of said enclosure for inserting a spark plug means within said first tubular reaction means.

3. The partial oxidation reactor of claim 1 disposed within an oven means.

4. The partial oxidation reactor of claim 3 wherein said feed injection means comprises an orifice means.

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5. The partial oxidation reactor of claim 4 further comprising an air conduit means operatively connected to said feed injection means.

6. The partial oxidation reactor of claim 5 further comprising a preheater means to heat said air conduit means.

7. The partial oxidation reactor of claim 6 wherein said preheater means comprises a length of said air conduit coiled within said oven means.

8. The partial oxidation reactor of claim 7 further comprising means to inject a fuel in said air conduit between said preheater means and said orifice means.

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