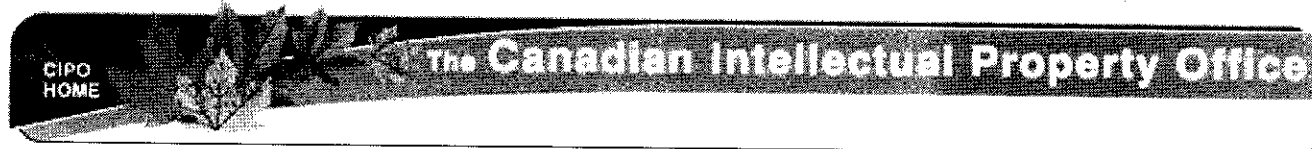




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(12) Patent:

(54) PRODUCTION OF HYDROGEN AND CARBON MONOXIDE MIXTURES

(54)

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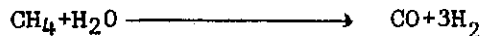
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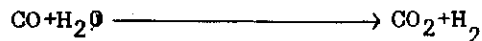
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This invention relates to the production of an H₂+CO mixture from a light hydrocarbon such as natural or refinery gas. More particularly, this advance gives rise to an improvement in reformer operation.

Considering reformation in gross and taking methane as a typical light hydrocarbon fee, the reaction may be illustrated as follows:



When used for the production of H₂, reformation can be followed by a conversion of CO with steam according to the equation:



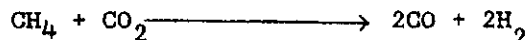
and subsequent CO₂ removal.

Reformation is often used to produce H₂ and CO mixtures having definite ratios of H₂ to CO by introducing CO₂ with steam as the reformer oxidant.

The following equation illustrates the production of gas containing H₂ and CO in the ratio of 2 to 1.



For the preparation of a gas mixture with an H₂ to CO ratio of 1 to 1, methane may be reformed with CO₂ after the following equation:



The foregoing equations merely characterize principal gross reactions. In this regard, complete conversion of methane is not actually attained, nor is the selectivity toward CO reformation 100 percent. Even with feed adjustments, unconverted methane, and water appear in the product gas.

It is well known that reformation yield increases with energy input. Yet, reformers employed in this task have generally been limited to reactant outlet temperatures in the range of 1400 to 1600°F. Pressures have also been restricted because of strength characteristics of the tube metals. Industry was satisfied to get along with relatively incomplete reformation or employ excessive quantities of oxidant. Emphasis has been devoted to the addition of more steps downstream of the reformer to compensate for inadequate conversion.

10

The present advance focuses on relationships within the reformer, itself. It was reasoned that since the reaction rate at any point in one of the parallel catalyst tubes is a function of concentration of hydrocarbon and oxidant, temperature, and catalyst activity at that point; the reaction could not progress at a constant rate throughout the length of the tube. Where reaction rates are highest, energy demand is greatest. The reaction initially proceeds more rapidly at the entrance portion of the catalyst tubes than at the other portions of the tubes causing a relatively rapid catalyst deactivation at the entrance portions, requiring a shift in energy input along the tubes to optimize the reaction. Therefore, a plurality of zones are here provided with each zone having a relatively closed convective system and each zone provided with an independent radiant energy source.

20

Basically zonal heat flux control accommodates heat input to the reaction rate attainable in each zone thereby improving yield and minimizing or obviating downstream corrective measures. This feature also achieves fuel economy and prevents local hot spots and catalyst deactivation.

716505

Nickel oxide catalysts are generally accepted for this application. In reformation as here practiced, it has been found that an oxidant to hydrocarbon ratio of from 1.8:1 to 9.0:1 moles of oxidant per moles of hydrocarbon is acceptable. Gas is preheated to a 700-1000°F. range. Outlet pressures from slightly above atmospheric to 400 psig are employed. Tube outlet temperatures from 1100 to 2300°F may be employed but the 1450 to 2300°F range is preferred. Space velocities of from 500 to 5000 standard cubic feet of theoretical H₂ yield per hour per cubic foot of catalyst may be employed with the 2500 to 5000 range preferred. A three zone downpass reformer is preferred with from 50 to 65 per cent of the total heat admitted to each tube in its upper zone, 25 to 40 per cent in its middle zone and 10 to 25 per cent in its lower zone.

These and other features will appear more fully when considered with the accompanying drawing of a system embodying the invention.

In the drawing natural gas, CO₂, and steam are introduced through lines 1, 2 and 3, respectively. Instead of using natural gas, methane or any normally gaseous or gasified hydrocarbon containing one to four or more carbon atoms in its molecule and which is of satisfactorily low sulphur content could be employed. In some cases it may be economical to use a narrow boiling gasoline fraction. Then special catalysts might be necessary and high steam to carbon ratios would be used to resist coke deposition from higher boiling hydrocarbons.

It is usually necessary to desulphurize the hydrocarbon by contact with activated carbon as shown in flow through reactors 4. In analogous manner CO₂ may be desulphurized by bubbling it through a potassium permanganate solution

(K Mn O₄) in reactor 4a.

Confluence of the hydrocarbon, CO₂ and steam is effected in line 5 and the mixture is passed through preheater 6 where it is heated to a temperature of from 500 to 1100°F. Thereafter, the feed gas is transmitted via conduit 7 to a preferred type of reformer generally designated 8 containing catalyst filled tubes 9. The tubes are positioned mid-way between oppositely disposed side walls 11. The side walls have inclined planes 12 faced with refractory material and have burners 13 which are associated with upper 14, middle 16 and lower 17 radiant energy sources. Employing opposed radiant energy emitters 14, 16 and 17 achieves improved heat flux distribution about the periphery of the tubes. Ledges 18 prevent upper 19, middle 21 and lower 22 zones from seeing radiation emitted by the radiant energy source of the other zones. Restricted passages 23 defined by opposed ledges 18 induce gas turbulence and tend toward circulation in relatively closed convective systems between successive passages 23. Of course, burners 13 individually regulate the intensity of heat flux in the relatively closed convection systems as well as the intensity of radiation emitted from inclined planes 12.

By way of example, a methane conversion of 98.8 percent was attained using a nickel oxide catalyst, in a three zone reformer, on natural gas feed, with a steam and CO₂ oxidant, at an outlet pressure of 50 psig, an inlet temperature of 800°F, an outlet temperature of 1530°F, and a space velocity of 2500 standard cubic feet of theoretical H₂ per hour per cubic foot of catalyst. In this conversion, 57 percent of

the total heat input is introduced into the upper zone, 33 percent in the middle zone and 10 percent in the lower zone.

As a second example, a methane conversion of 99.5 percent was attained, using nickel oxide catalyst, in a three zone reformer, on natural gas feed, with a steam and CO₂ oxidant, at a pressure of 350 psig, an inlet temperature of 1000°F, an outlet temperature of 1930°F, and a space velocity of 4700 standard cubic feet of theoretical H₂ per hour per cubic foot of catalyst. In this conversion, 52 percent of the total heat input is introduced into the upper zone, and 15 percent in the lower zone.

It will be understood by those skilled in hydrocarbon engineering that changes may be made in this process and the apparatus for carrying it out without departing from the scope of the invention defined in the claims.

716505

WHAT IS CLAIMED IS:

1. A process for manufacturing carbon monoxide and hydrogen from a normally gaseous light hydrocarbon feed containing from 1 to 4 carbon atoms in its molecule by catalytically reforming the hydrocarbon, the process comprising the steps of forming a mixture of the hydrocarbon feed with an oxidant selected from a group consisting of steam and carbon dioxide in the ratio of 1.8 to 9.0 moles of oxidant per mole of hydrocarbon, passing the mixture through at least one tube at atmospheric pressure, disposing a suitable catalyst in said tube having zones therein, the rate of reaction being dependent upon the amount of hydrocarbon, oxidant, temperature, and catalyst activity, introducing the mixture as it passes through said tube, uniformly along predetermined lengthwise zones of the tube, said zones large in comparison with the diameter of the tube, varying the rate of heat input to the mixture as said mixture passes through the zones to correspond to changing process heat requirements occurring in the zones towards increasing in each zone the carbon monoxide and hydrogen yield and towards maintaining in each zone the temperature of the reactants above 1200°F.

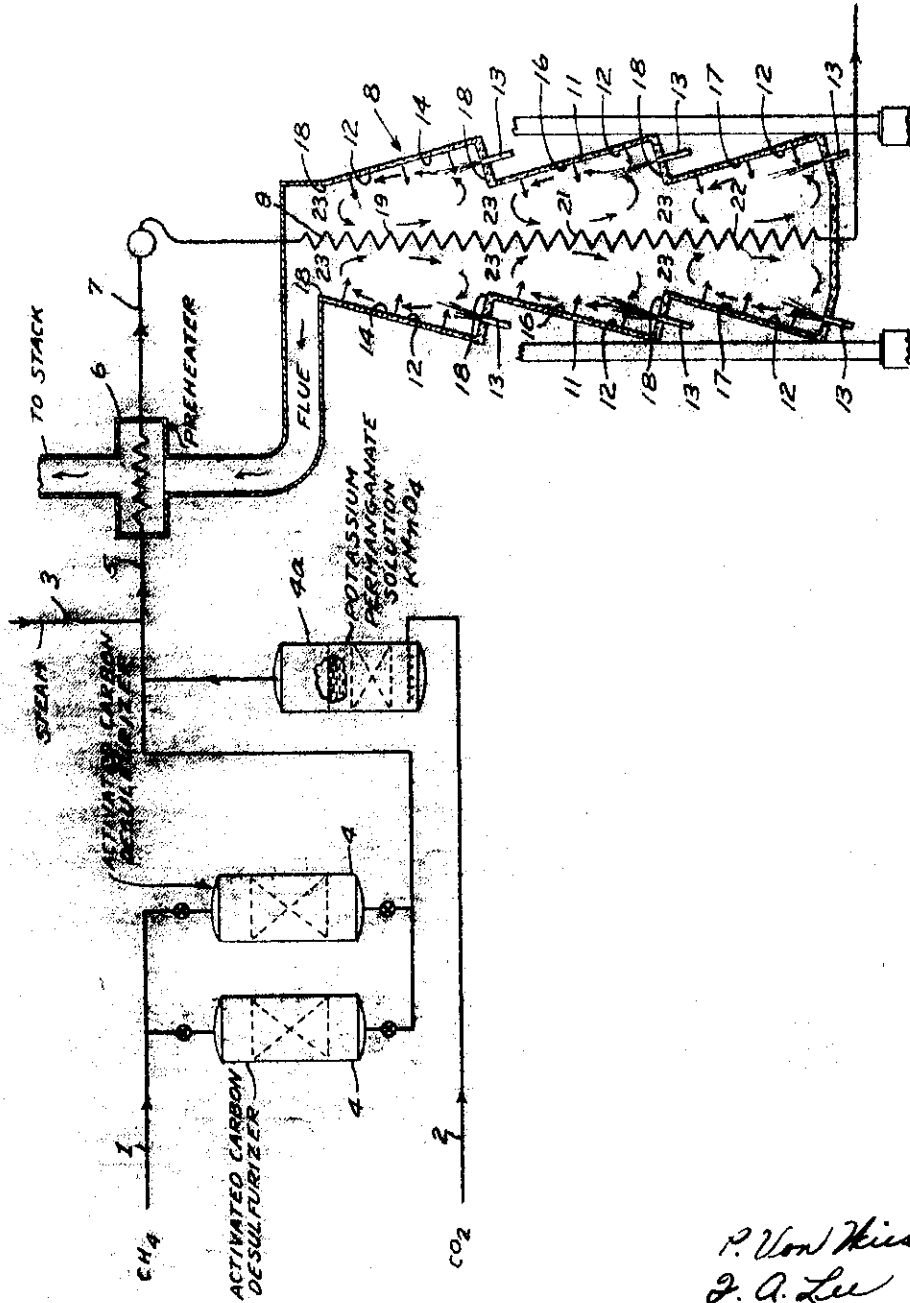
2. A process for manufacturing carbon monoxide and hydrogen from a normally gaseous light hydrocarbon feed containing from 1 to 4 carbon atoms in its molecule by catalytically reforming the hydrocarbon, the process comprising the steps of forming a mixture of the hydrocarbon feed with an oxidant selected from a group consisting of steam and carbon dioxide in the ratio of 1.8 to 9.0 moles of oxidant per mole of hydrocarbon, passing the mixture through at least one tube,

providing said tube with a plurality of zones each large in comparison with the diameter of the tube, oriented lengthwise along the axis of said tube, passing the mixture through said zones, disposing a suitable catalyst in said tube, the rate of reaction being dependent upon the amount of hydrocarbon, oxidant, temperature and catalyst activity, introducing heat into each zone uniformly by convection and radiation thereby heating the mixture passing therethrough, heating each zone independently of the other zones, varying the rate of heat input to the mixture of said mixture passes through the zones to correspond to changing process heat requirements occurring in the zones towards increasing in each zone the carbon monoxide and hydrogen yield and towards maintaining in each zone the temperature of the reactants above 1200°F, providing a super-atmospheric pressure of from 150 - 400 psig. within the said tube.

3. A process for manufacturing carbon monoxide and hydrogen from a clearly gaseous light hydrocarbon feed containing from 1 to 4 carbon atoms in its molecule by catalytically reforming the hydrocarbon, the process comprising the steps of forming a mixture of the hydrocarbon feed with from 1.8 to 9.0 moles of an oxidant per mole of hydrocarbon wherein the oxidant is selected from a group consisting of steam and carbon dioxide, passing the mixture downward through at least one vertical tube, providing said tube with an upper, a middle, and lower zone along the tube, said zones large in comparison with the diameter of the tube, disposing a nickel-oxide catalyst in said tube, passing the mixture through said

716505

tube at a space velocity of from 2500 to 5000 standard cubic feet of theoretical hydrogen gas molecules yield per hour per cubic foot of catalyst, providing a pressure of from 150 to 400 psig. within said tube, the rate of reaction being dependent upon the amount of hydrocarbon, oxidant, temperature and catalyst activity, introducing heat into each zone uniformly by convection and radiation thereby heating the mixture passing therethrough, introducing heat into each zone independently of the other zones, each zone shielded from the source of radiation of the other zones, providing the upper zone with 50 to 65 per cent of the total heating input to said tube, the middle zone with 25 to 40 per cent of the total heating input to said tubes and the lower zone with from 10 to 25 per cent of the total heat input to said tube, varying the rate of heat input to the mixture as said mixture passes through the zones to correspond to changing process heat requirements occurring in the zones towards increasing in each zone the carbon monoxide and hydrogen yield and towards maintaining in each zone temperature of the reactants between 1200 and 2500°F.



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