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(54) PRODUCTION OF HYDROGEN AND CARBON MONOXIDE MIXTURES

(54)

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(57) Abstract:

(57) Summary of the Invention:

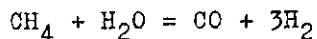
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This invention relates to the production of hydrogen and carbon monoxide mixtures from a light hydrocarbon. It is a process which permits the use of heavier feed gases.

5 Methane reformation may be illustrated as follows:



10 The equation merely characterizes the main endothermal reaction. As is well known by industry, CO_2 might be added to the steam oxidant to adjust the hydrogen-carbon monoxide ratio. In performing this reaction, a mixture of feed hydrocarbon and oxidant is passed through catalyst filled tubes of a furnace. Along the catalyst filled tubes a plurality of zones with different heat flux intensities may be provided.

15 Methane feeds have generally contained various portions of heavier hydrocarbons of the alkane series such as ethane, propane and so forth which are characterized by the formula $\text{C}_n \text{H}_{2n+2}$. It has been found that
20 unconverted hydrocarbon downstream of the tube furnace is practically pure methane. Accordingly, it is reasoned that when these heavier molecules are reformed, they are first broken down into hydrogen and carbon monoxide plus methane which is the basic and most stable compound of the
25 series. Alkyl radicals are successively reformed and finally the basic methane itself is converted. Preferential oxidation of carbon is believed to take place because oxidation of hydrogen is inhibited by the presence of its oxide (steam which is a source of oxygen in the
30 feed mixture). By way of illustration, steam selectively



oxidizes the carbon in ethane, C_2H_6 , to yield methane, carbon monoxide and hydrogen, while preventing the deposition of elemental carbon. The methane so formed is in turn reformed in the usual manner as flow of the reactants progresses through the tube furnace.

Protracting the preferential oxidation phenomenon, it has been feasible to reform alkanes heavier than methane. But propane and butane have represented the upper limit suitable for reformation. This restriction has been imposed by carbon precipitation which defeats the designed reaction and deactivates the catalyst. The hydrocarbon can be heated quickly up through the critical carbon deposition range in the vicinity of $1200^\circ F$. Then the control problem with these heavy unstable alkanes is that reformation may progress so rapidly that the heat supplied by the furnace is inadequate to sustain the endothermal reaction and heat is extracted from the reactants thereby causing a drop in the temperature and instability of the reaction with consequent carbon deposition.

The heater control for the higher homologues of methane is further complicated by their lack of stability, their increased proportion of carbon and increased susceptibility to pyrolytic dehydrogenation yielding olefins and hydrogen.

To prevent carbon deposition it is necessary to maintain operating parameters so that temperature in the vicinity of $1200^\circ F$ are avoided. Toward this end, the present invention adds a new dimension to tube furnace design and operation for use in the production of CO and

H₂ mixtures. This advance is accomplished by disposing a plurality of catalyst activity levels along the catalyst tubes.

5 This teaching offers greater versatility. By it, tube furnaces can satisfactorily convert heavier alkane hydrocarbons ranging through the pentanes to octanes and heavier. Catalyst activity in the upstream zone of the tube is selected sufficiently low so that alkyl radicals can be reformed under stable conditions without the
10 reaction outracing the heat supplying capability of the furnace. Thus, cooling of the reactants and consequent carbon deposition are obviated.

The foregoing and other features of the process will appear more fully from the accompanying drawing which
15 depicts a system embodying this invention.

As shown in the drawing, a hydrocarbon with less than ten carbon atoms in its molecule is introduced through line 1. Carbon dioxide and steam are admitted through lines 2 and 3, respectively.

20 If necessary, the hydrocarbon may be desulfurized by contact with activated carbon in flow through reactors 4. Analogously, CO₂, if employed, may be desulfurized by bubbling it through a potassium permanganate solution (K M_n O₄) in reactor 6.

25 Tube furnace designated 7 is preferably operated with from less than 1.0 to 9.0 moles of oxidant per mole of product H₂. Inlet pressures from atmospheric to 400 psig or higher, preheat temperatures from 500°F to 1000°F tube outlet temperatures from 1300°F to 2300°F and
30 space velocities from 500 to 5000 standard cubic feet of

theoretical H₂ yield per hour per cubic foot of catalyst are employed.

5 Confluence of the hydrocarbon, CO₂ and steam is effected in line 8 and the mixture is passed in flow series through preheater tubes 9 wherein it is preheated by flue gases. Thereafter the feed gas is transmitted via line 11, inlet manifold 12 and flexible inlet conduits 13 to reformer tubes 14 which are positioned by support means shown as counterweight 16 and pulleys 17.

10 Tube furnace 7 includes setting 18 which has roof 19 and floor 21 penetrated by tubes 14. In the preferred type of furnace here depicted, the setting defines combustion chamber 22 embraced by a pair of stepped oppositely disposed side walls 23. Above steps 24, 26 and 15 27 each side wall 23 slopes inwardly so that the side walls define a number of coplanar surfaces 28 faced with refractory material 29. Each refractory surface 28 has a bottom 31 and an upper extremity 32. The cross section of 20 combustion chamber 22, although being generally rectangular is substantially that produced by the outline of a number of regular trapezoids stacked small base on large base with a common axis of symmetry.

25 Along steps 24, 26 and 27 are arranged sets of linear burners which project their flame streams through longitudinal troughs 34 upward each to sweep an associated coplanar surface 28. Thus, each of these surfaces 28 can be uniformly heated to evenly emit re-radiation therefrom. Inner rims 36 divert the streams of flame away from direct impingement onto tubes 14.

30 Control means (not shown) are associated with

each burner to regulate the intensity of heat flux input. By altering the firing rate of any set of paired burners disposed at the same elevation in steps 24, 26 and 27, respectively, different zones 37, 38 and 39 of reformer tubes 14 can be subjected uniformly to heat flux intensities suitable for the reaction rate attainable or desirable therein. It is generally feasible to add from 50 to 65 percent of the total heat influx to the tubes in upper zones 39, 25 to 40 percent in middle zone 38 and the balance in lower zone 37.

Upper extremities 32 of paired coplanar surfaces 28 project toward each other to form restricted throats 41 therebetween so that combustion gases will tend toward being confined to circulate in relatively closed convection systems.

The catalysts contemplated for services in tubes 14 may be of any commercially available variety selected from the class consisting of nickel oxide, nickel-thoria-magnesia, nickel-alumina-magnesia, nickel-magnesia, nickel on carbon, or nickel on alumina; other suitable catalysts may include cobalt molybdate supported on alumina, a group VIII metal on metal oxide on a suitable support, nickel and iron on a support or carrier, and the like.

As is well known in catalyst manufacture, different activity levels can be provided by either using different catalysts or by choosing among the different catalyst activity levels attainable in the preparation of a single catalyst. Reformer catalyst activity is customarily measured in terms of standard permissible

space velocities of theoretical H₂ yield per hour cubic foot of catalyst. As here considered, a space velocity of less than 1800 standard cubic feet per hour per cubic foot of catalyst is regarded as one of low activity. From 5 1800 to 3000 would be intermediate and greater than 3000 standard cubic feet per hour per cubic foot of catalyst is regarded as high activity.

In the preferred embodiment here depicted, it is contemplated to use low activity catalyst in upper zone 10 39 of tube 14, an intermediate activity catalyst in lower zone 37, although these selections may be reduced to two activity level zones or increased above three as particular feed or process conditions might require. It is not necessary that the number of catalyst activity zones 15 correspond with the number of heat flux intensity zones. By the arrangement here set forth, conditions may be maintained in upper zone 39 so that heavier hydrocarbon molecules can be reformed to methane without depositing elemental carbon. When the reaction has proceeded 20 sufficiently, reformation of basic methane is accomplished in succeeding zones 38 and 37.

Reformed gas exits from tube 14 via conduit 43 and outlet manifold 44.

It will be understood by those skilled in 25 hydrocarbon reforming and catalyst preparation that wide changes may be made in the details of this process without departing from the theme of invention defined in the claims.

WHAT IS CLAIMED IS:

1. A process for manufacturing a mixture of CO and H₂ from a hydrocarbon feed containing more than one carbon atom in its molecule and having a low sulfur content, the process comprising the steps of mixing the hydrocarbon feed with an oxidant selected from a class consisting of steam and CO₂ and mixtures thereof, passing the mixture through a heated tube under superatmospheric pressure, providing at least two catalyst filled zones in flow series along the length of the tube with at least one of the zones having a different catalyst activity level from the other.

2. The process of Claim 1 with two of said catalyst filled zones including an upper zone and a lower zone, the catalyst activity level in the lower zone greater than that in the upper zone.

3. A process for manufacturing a mixture of CO and H₂ from a hydrocarbon feed containing more than one and less than ten carbon atoms in its molecule and having a low sulfur content, the process comprising the steps of mixing the hydrocarbon feed with an oxidant selected from a class consisting of steam and CO₂ and mixtures thereof, passing the mixture through a heated tube under super-atmospheric pressure, providing three catalyst filled zones in flow series along the length of the tube including an upper zone and a middle zone and a lower zone, the catalyst activity level in the upper zone less than 1800 standard cubic feet per hour of theoretical H₂ yield per cubic foot of catalyst, the catalyst activity level in

the middle zone between 1800 and 3000 standard cubic feet per hour of theoretical H_2 yield per cubic foot of catalyst, and the catalyst activity level in the lower zone greater than 3000 standard cubic feet per hour of theoretical H_2 yield per cubic foot of catalyst.

4. The process of Claim 3 with each of the zones subjected to indirect heat exchange relationship with heat flux of a different intensity.

5. The process of Claim 4 with from 1.0 to 9.0 moles of oxidant mixed with each mole of hydrocarbon.

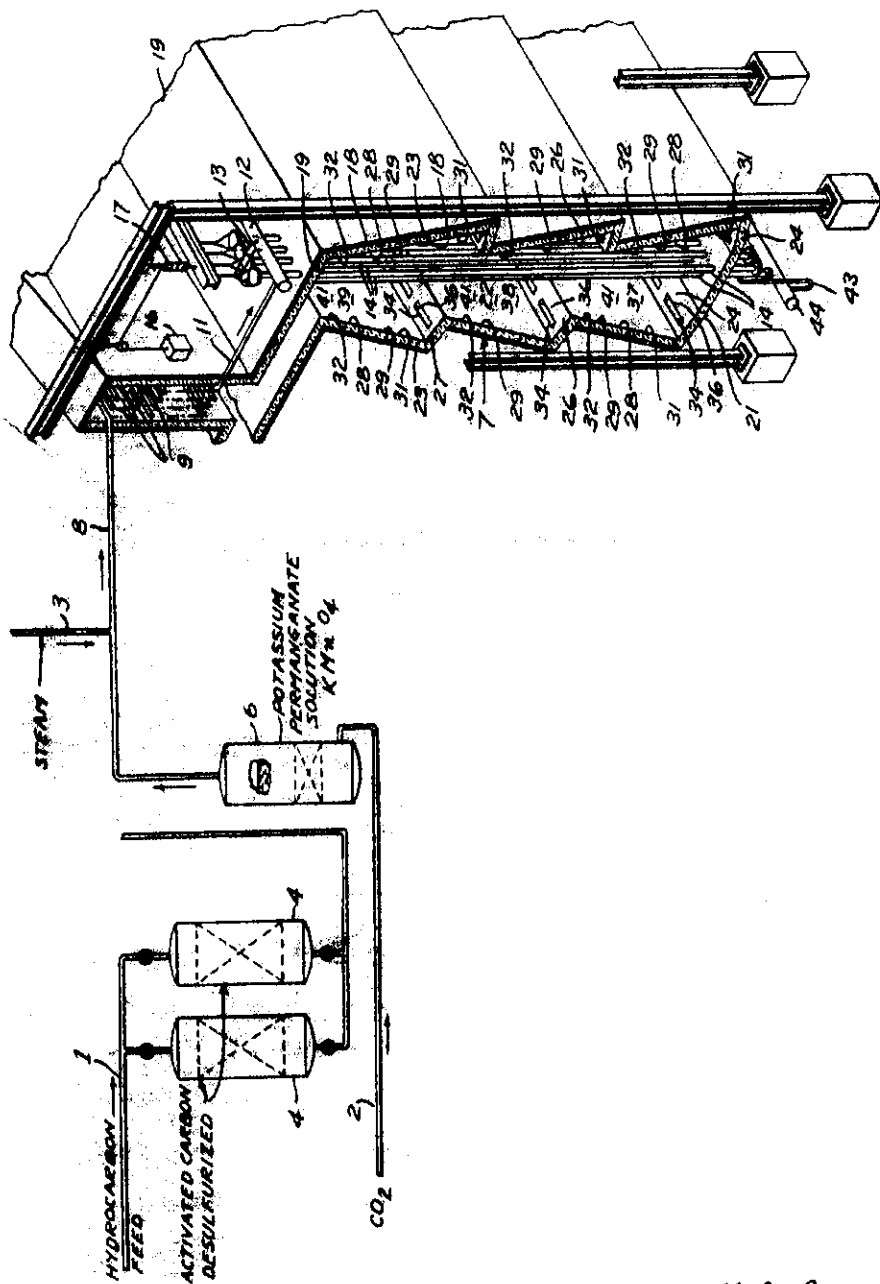
6. The process of Claim 5 with the mixture passing through the tubes under an outlet pressure from 50 to 400 psig.

7. The process of Claim 6 with the mixture passing through the tube with a tube outlet temperature of from 1300°F to 2300°F.

8. The process of Claim 7 with the mixture passing through the tube at a space velocity from 500 to 5000 standard cubic feet of theoretical H_2 yield per hour per cubic foot of catalyst.

9. The process of Claim 8 with the mixture passing through the tube with a tube outlet temperature from 1700 to 2300°F.

10. The process of Claim 9 with the mixture passing through the tube at a space velocity of from 2500 to 5000 standard cubic feet of theoretical H_2 yield per hour per cubic foot of catalyst.



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