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(54) PROCESS FOR MANUFACTURE OF SYNTHESIS GASES FROM HYDROCARBONS

(54) PROCÉDÉ POUR LA FABRICATION DE GAZ DE SYNTHÈSES D'HYDROCARBURES

(72) Inventor(s) (Country):WARREN K. LEWIS (Not Available)
EDWIN R. GILLILAND (Not Available)(73) Owners (Country):

STANDARD OIL DEVELOPMENT COMPANY

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CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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The present invention relates to a hydrocarbon synthesis process. It is more particularly concerned with an improved process for the preparation of the feed synthesis gases. In accordance with the present invention substantial improvements are secured by controlling the character of the catalyst employed with respect to the feed gases. Furthermore, in accordance with this invention substantial economies are secured by utilizing a novel operating technique wherein the heat evolved in one reaction zone is economically utilized in the other. These novel operating techniques, coordinated with the control of the catalysts, result in substantial improvements in a process for the production of feed gases suitable for a hydrocarbon synthesis reaction.

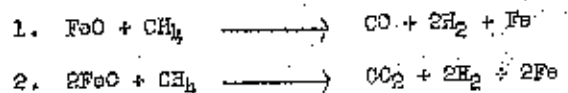
It is well known in the art to conduct hydrocarbon synthesis reactions by contacting hydrogen and oxides of carbon with catalysts under various temperature and pressure conditions. The catalyst employed is usually selected from the iron group metals, as, for example, iron, cobalt, and nickel. The catalysts are utilized either alone or on suitable carriers, such as kieselguhr, diatomaceous earth, synthetic gels, silica, and alumina. Promoters such as oxides of chromium, zinc, aluminum, magnesium, and the rare earth metals are used with the iron group metals. These catalysts are employed either in fixed bed or in fluid catalyst operations.

The temperatures employed in the synthesis reaction vary widely as, for example, in the range from about 300°F. to about 800°F. and are generally in the range from about 350°F. to about 700°F. The pressures likewise vary considerably and are a function of other operating conditions, such as catalyst employed, activity of the catalyst, character of the feed gases, and the temperatures utilized. Pressures in the range from about 1 to 100 and higher atmospheres have been suggested. The character

of the feed gases, introduced into the synthesis reaction zone depends somewhat on the particular temperatures and pressures and upon the catalyst employed. For example, when employing iron type catalysts, it is preferred to use about 1 mol of carbon monoxide to about 2 mols of hydrogen, while when a cobalt catalyst is utilized equal mols of hydrogen and carbon monoxide in the feed synthesis gases are desirable.

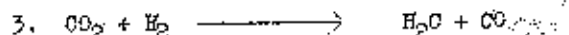
This invention is particularly concerned with the production of a mixture of hydrogen and carbon monoxide from hydrocarbons, particularly methane or from natural gas, and consists in oxidizing the hydrocarbons with a metal oxide. This procedure per se is old in the art. For example, U.S. Patent 1,899,184, issued to Martin and Artin de Sino, discloses the use of reducible metal oxides, such as oxides of iron, chromium, copper, nickel, manganese, and zinc for the oxidation of hydrocarbons comprising methane to produce hydrogen and oxides of carbon, particularly carbon monoxide. These reactions are generally conducted at temperatures in the range from about 950° to about 1,900°C.

It has now been discovered that providing the character of the catalyst is controlled within the reaction zone, that is the zone where the synthesis gases are produced from hydrocarbons comprising methane, unexpected desirable results are secured. The important thing about the chemistry of this process is the fact that when a hydrocarbon gas or vapor, such as methane, reacts with a reducible metal oxide, such as FeO, both of two reactions occur. These reactions are as follows:



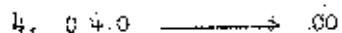
The first reaction is where one iron oxide reacts with one methane to form CO and two hydrogens and the second reaction is where two iron oxides react with one methane to form CO₂ and two hydrogens. These are relatively slow but the CO₂ reacts with some of the hydrogen

very rapidly to form water and more CO as follows:



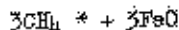
We do not desire either water or CO₂ left in the resultant product gas. Iron will not reduce either of these two gases beyond a certain fraction, very approximately, 50%. Consequently, some other means must be employed to eliminate the CO₂ and water vapor.

These gases can be eliminated by taking advantage of the fact that carbon at elevated temperatures in the following reactions:

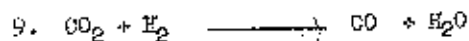
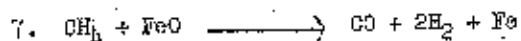


has a far greater affinity for a single atom of oxygen to form CO than the affinity of either iron or of hydrogen for oxygen. Consequently, in any system in which we do not have an excess of one atom of total oxygen for one atom of total carbon we will secure these two elements combined as CO (plus excess carbon, if it be present), provided the reaction of formation of CO can be speeded up so that substantial equilibrium is achieved. In this process it is proposed to furnish at least one atom of carbon for each atom of oxygen combined with metal as reducible oxide entering the reaction zone. Assuming that the hydrocarbon is methane and that the metal oxide is FeO, we will have one or more mols of methane for each mol of FeO entering the reaction zone. The initial reaction between this methane and iron oxide will produce some CO₂ and water vapor and result, in consequence, in unreacted methane being left in the gaseous mixture. To eliminate the CO₂ and water vapor, we react them with this unreacted methane. These reactions are illustrated as follows:

Feed

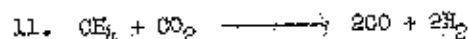
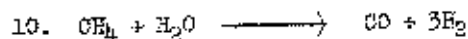


*At least three mols.



Unreacted (1) CH_4 of feed.

Reforming Reactions:



These so-called reforming reactions, unfortunately, are very slow unless catalyzed with an effective catalyst. Iron, cobalt, nickel, et seq. are such catalysts. It is, therefore, proposed to admit to the reaction zone at least one mole of methane for each FeO added and provide in the reaction zone a large amount of active iron or nickel or equivalent for the completion of the desired reaction by catalysis of the reforming reaction. If excess methane relative to the FeO is used, practically all of it will be cracked to carbon and hydrogen. Obviously, the desirable thing is to use stoichiometrical proportions.

In the broad scope of this invention we admit substantially one atom of carbon for each atom of oxygen combined as reducible metal oxide in the reaction zone and provide in the reaction zone effective contact of the reacting gases with an amount of metal very large relative to the amount entering with the hydrocarbon as reducible oxide.

The amount of reducible metal oxide present in the reduction zone is negligible. This is possible because of the extraordinarily rapid rate of reaction between the reducible metal oxide and the hydrocarbon at the temperatures employed relative to the rate of the reforming reaction. In this process we secure as complete reaction between the metal oxide and the hydrocarbon in the line going to the reforming mass so as to leave as little reduction of metal oxide to be carried out in the reformer itself as possible.

The process of this invention may be readily understood by reference to the attached drawing illustrating one modification of the same. Hydrocarbon feed gases comprising methane are introduced into reaction zone (1) by means of line (2). These gases flow downwardly through reaction zone (1) and contact a solid fluid catalyst, the upper level of which is maintained at point (A). Temperature and pressure conditions in reaction zone (1) are maintained in the range to secure this desired reaction. The reactant gases comprising hydrogen and carbon monoxide are removed overhead from reaction zone (1) by means of line (3) and handled in any manner desirable. Generally these gases are fed directly to a hydrocarbon synthesis zone under conditions to produce hydrocarbon constituents.

In accordance with the process of this invention a relatively large volume of catalyst in reaction zone (1) is maintained. For the purpose of illustration it is assumed that the catalyst in reaction zone (1) comprises an iron type catalyst. In accordance with this invention the iron type catalyst or at least the greatest proportion of said catalyst is maintained in the reaction zone in the form of metallic iron. This is accomplished by withdrawing from reaction zone (1) a relatively small proportion of the catalyst by means of line (4) and passing the same to oxidation zone (5). In zone (5) the relatively small proportion of the iron catalyst which was withdrawn is oxidized by means of an oxygen containing gas or pure oxygen which is introduced into zone (5) by means of line (6). For the purpose of illustration it is assumed that the oxygen containing gas introduced by means of line (6) comprises air. The combustion gases are withdrawn from zone (5) by means of line (7) and disposed of in any manner desirable. The oxidized catalyst is removed from zone (5) by means of line (8) and mixed with additional feed hydrocarbons which are introduced by means of line (9). The catalyst, together with the additional feed hydrocarbons comprising methane are

returned to reaction zone (1) by means of line (10).

In accordance with the preferred modification of this invention, the heat evolved in reaction zone (5) is absorbed in a transfer medium and is transferred by the medium to the gas producing zone (1). For the purpose of illustration it is assumed that the transfer medium comprises a fused salt circulating system. The heat evolved in reaction zone (5) is utilized to heat the salt in zone (11). The fused salt is removed from zone (5) by means of line (12) and passed through zone (13) in zone (1). The salt is cooled and the heat is utilized in the endothermic reaction occurring in reaction zone (1). The relatively cool fused salt is passed to surge tank (14) and then returned to zone (11) by means of line (15) and pump (16).

This invention generally comprises controlling the character of the catalyst in the reaction zone in a manner that the greatest proportion of the catalyst in the reaction zone is in the form of a metal. A relatively small proportion of the catalyst is circulated to the oxidation zone. The amount of catalyst circulated to the oxidation zone is controlled in a manner so that one atom of oxygen, combined as reducible metal oxide, is introduced into the reaction zone per atom of carbon in the hydrocarbon gases. In accordance with a preferred modification of this invention the heat evolved in the oxidation zone is transferred to the reaction zone by means of a fused salt transfer medium.

The amount of catalyst maintained in the form of a metal in the reaction zone may vary appreciably. In general, it is preferred to have at least 70%, and preferably 90 to 95%, of the catalyst in the form of a metal.

A particularly desirable modification of the invention comprises the use of mixed metals as, for example, nickel and iron. When operating in this manner it is preferred that approximately 90 to 95% of the catalyst by weight be nickel and that approximately 5 to 10% by weight of

the catalyst comprise iron. Thus in an operation of this character the iron functions substantially as the oxygen carrier, while the nickel functions in the reaction zone as the reforming catalyst. A combination catalyst such as iron and cobalt may also be employed. A very desirable catalyst to be used as described in the present process is to use a mixture of iron and zinc in the proportions of about 90 to 95% zinc and from 5 to 10% iron.

The temperatures maintained in the reaction zone may be in the range from about 1200°F. to about 2200°F. and the pressures in the range from 200 to 300 lbs./sq. in. In general, it is preferred that the temperature be in the range from about 1700°F. to about 1900°F. and that the pressure be about 100 lbs./sq. in. The temperatures maintained in the oxidation zone are generally in the range from 1300°F. to 2300°F. and the pressure about atmospheric. Preferred temperature in the oxidation zone is about 1800°F. to 2000°F.

The fused salt or metal circulated may be any salt or metal which is liquid at operational temperatures and pressures. Satisfactory salts are, for example, sodium and potassium nitrates and nitrites. Suitable metals are, for example, molten sodium, bismuth, lead or tin.

The process of this invention is not to be limited by any theory as to mode of operation but only in and by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Improved process for the production of carbon monoxide and hydrogen from hydrocarbon gases which comprises contacting hydrocarbon feed with a fluidized iron group metal catalyst selected from the class consisting of iron, cobalt and nickel, maintained in the form of a turbulent fluid bed within a reaction zone at an intermediate level by passing said hydrocarbon gas upwardly therethrough at such a velocity that said bed assumes a definite upper surface, maintaining the major portion of the catalyst in said reaction zone in the form of free metal particles with at most a minor amount of metal oxide, continuously circulating a relatively small percentage of said catalyst to an oxidation zone and back to said reaction zone at such a rate that substantially one atom of oxygen combined as reducible metal oxide is introduced into said reaction zone per atom of carbon in the total hydrocarbon feed, forming a suspension of said metal oxide at reaction temperature in at least part of said hydrocarbon feed and causing the rapid oxidation of the hydrocarbon in this suspension to a gas containing carbon dioxide and water vapor while reducing the reactant metal oxide therein to the form of solid particles of the free metal, thereafter introducing said suspension upwardly through the turbulent fluid bed of metal catalyst in said reaction zone and reforming the carbon dioxide and water vapor therein together with the remaining portion of said total hydrocarbon feed to produce a product gas consisting essentially of carbon monoxide and hydrogen.

2. Improved process for the production of gases comprising carbon monoxide and hydrogen from hydrocarbon gases comprising methane which comprises contacting feed gases comprising methane with a fluidized iron-group metal catalyst maintained in the form of a turbulent fluid bed within a reaction zone by passing said gas upwardly therethrough at such a velocity that said bed assumes a definite upper surface, maintaining the major portion of the catalyst in said reaction zone in the form of particles of the free metal containing a minor amount of metal oxide, continuously circulating a relatively small percentage of said catalyst to an oxidation zone and back to said reaction zone at such a rate that substantially one atom of oxygen combined as reducible metal oxide is introduced into said reaction per atom of carbon in the hydrocarbon feed gases introduced thereto, bringing said oxide into contact with at least part of said methane feed gas to form a suspension, causing the complete reaction of methane in said suspension with at least part of said metal oxide to form carbon dioxide, steam and solid particles of reduced free metal, thereafter passing said suspension into the reaction zone and bringing it into effective contact therein with the relatively large amount of free metal catalyst in said turbulent fluid bed.

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3. A process in accordance with claim 2 in which said reduced metal catalyst is a composition comprising nickel and iron.

4. An improved process for the manufacture of gases comprising carbon monoxide and hydrogen from feed gases comprising methane which comprising mixing hot finely divided iron oxide and a methane-containing feed gas at a temperature such that the mixture undergoes a rapid oxidation reaction resulting in the reduction of iron oxide to iron and the oxidation of methane to carbon dioxide and water vapor, passing the hot mixture thus produced to an externally unheated reaction zone, maintaining said reaction zone at a desired temperature under conditions to oxidize additional and unreacted methane to carbon monoxide and hydrogen by reaction with said carbon dioxide and water vapor while maintaining effective contact between the reacting gases and reduced iron oxide catalyst, withdrawing solid catalyst particles comprising free metallic iron from said reaction zone and oxidizing the same in an oxidizing zone, absorbing the heat evolved in said oxidizing zone by a transfer medium maintained in a confined stream within a highly turbulent fluid bed of oxidized iron partly filling said oxidizing zone, simultaneously withdrawing hot iron oxide from said oxidizing zone for use in said methane oxidation reaction and passing said transfer medium to a heat transferring path maintained within a highly turbulent bed of iron catalyst partly filling said reaction zone, whereby the temperature of said reaction zone is maintained at the desired level.

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5. The process of producing a gas consisting essentially of carbon monoxide and hydrogen which comprises combining in a reactant feed line a stream of hydrocarbon gases and finely divided solid particles of hot reducible metal oxide, the metal of which is capable of catalyzing the reforming reaction between hydrocarbon, carbon dioxide and steam to produce carbon monoxide and hydrogen, rapidly reacting said hydrocarbon with hot metal oxide in said line and producing by said reaction a mixture of carbon dioxide, steam and free particles of solid metal, feeding said reactants and mixed reaction products continuously through said line and introducing said mixture and additional hydrocarbon gases into a subsequent reaction zone which provides effective contact of the reacting gases with a turbulent fluid bed of catalyst containing large quantities of solid metal particles relative to a minor amount of metal oxide, said metal oxide representing less than 30% of the total solid present, reacting said hydrocarbon with said carbon dioxide and steam in the presence of said catalyst, and recovering a product gas consisting essentially of carbon monoxide and hydrogen.

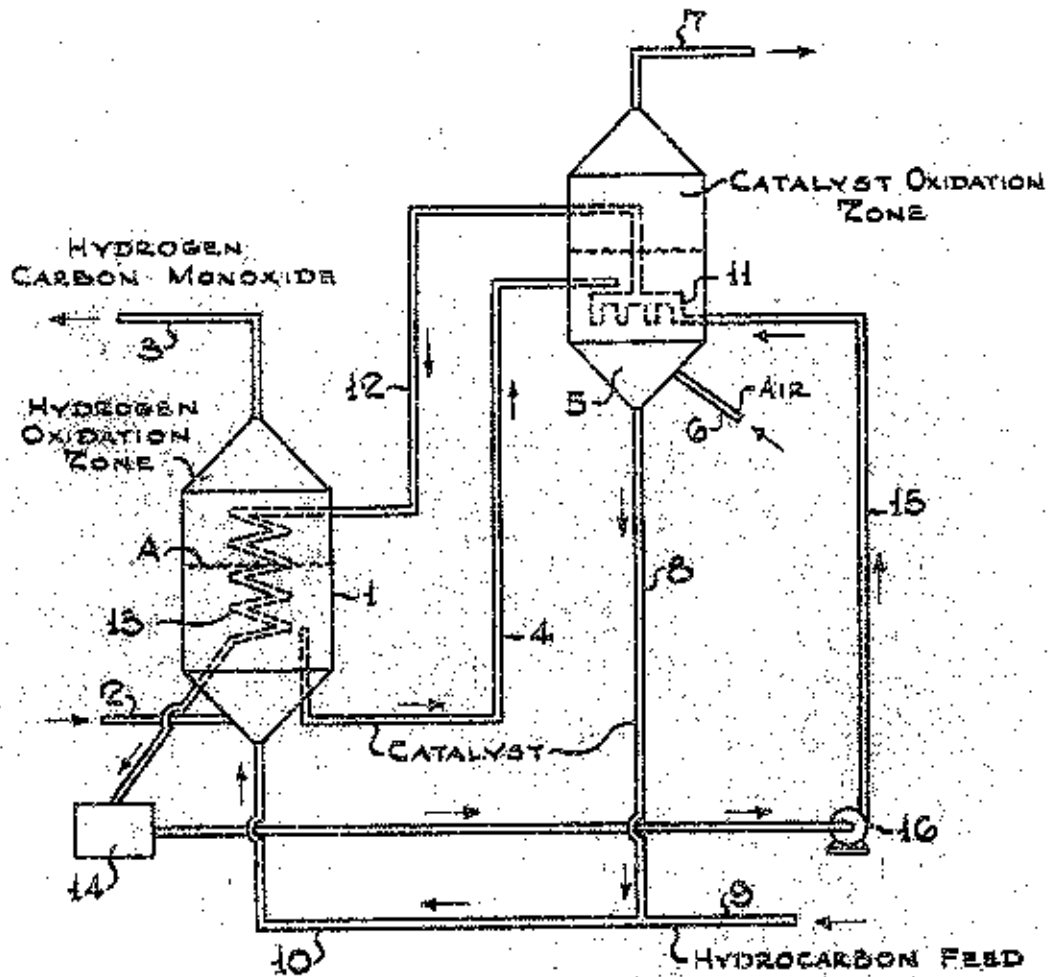
6. Process in accordance with claim 1 in which heat evolved from said catalyst circulated to said oxidation zone is transferred to the endothermic reaction zone by means of a heat transferring medium independent of said circulating metal oxide.

7. Process in accordance with claim 2 in which the catalyst is iron and the amount of iron maintained in the metallic state is in the range of about 90 to about 95% of metallic iron as compared to about 5 to about 10% of iron oxide.

8. Process in accordance with claim 3 in which the amount of nickel in the catalyst comprises about 90 to 95% of nickel and about 5 to 10% of metallic iron by weight.

9. The process of claim 1 wherein said reaction zone is maintained at a superatmospheric pressure.

10. The method according to claim 5 in which heat is supplied to the fluid bed of catalyst within an externally unheated reaction space by continually withdrawing a portion of said metal-containing solid particles from the reaction space and introducing said particles together with a stream of oxidizing gas into a turbulent fluid bed maintained in a separate oxidation zone, absorbing the heat evolved in said oxidation zone in a heat transfer medium maintained in a confined stream within said turbulent fluid bed, continuously withdrawing hot metal oxide from said oxidation zone for said hydrocarbon gas reaction and simultaneously passing said transfer medium to a heat transferring path confined within the turbulent solid in said reaction space, whereby the temperature of the solid within said reaction space is maintained at the desired level.



Standard Oil Development Company

Certified to be the drawings referred to in the specification herewith annexed.

Ottawa, Apr. 23 1927.

Mason & Clark
ATTORNEYS