PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Feed Gases for the Synthesis of Hydrocarbons

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the production of Fischer-Tropsch synthesis gas mixtures containing carbon monoxide and hydrogen by the oxidation of hydrocarbons, such as methane. In accordance with the present invention substantial improvements are secured by controlling the character of the catalyst employed with respect to the hydrocarbon feed to the process. 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.

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, 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 has previously been disclosed. These reactions are generally conducted at temperatures in the range from about 950° to about 1000° C. and the preferred metal oxide is zinc oxide which is used in a quantity of one mol of oxide per atom of carbon to be oxidized.

The present invention employs a catalyst comprising iron, cobalt or nickel, or mixtures thereof with or without zinc and it has been found that providing the character of such catalyst is controlled within the reaction zone, i.e. the zone wherein the synthesis gases are produced from the hydrocarbon fuel, unexpectedly desirably results are obtained. According to the invention the character of the catalyst in the reacion zone is controlled in such a manner that the greater proportion thereof is in the form of metal. Further a relatively small percentage of the catalyst in the reaction zone is passed to an oxidation zone and oxidized catalyst is withdrawn therefrom and recycled to the reaction zone in an amount substantially stoichiometrically equivalent to the hydrocarbon feed to the reaction zone, so as to provide in the reaction zone one atom of oxygen combined as reducible metal oxide per atom of carbon. The important thing about the chemistry of the process with which the invention is concerned 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:—

1. $FeO + CH_4 \longrightarrow CO + 2H_2 + Fe$
2. $2FeO + CH_4 \longrightarrow CO_2 + 2H_2 + 2Fe$

The first reaction is where one mol of iron oxide reacts with one mol of methane to form CO and two mols of hydrogen and the second reaction is where two mols of iron oxides react with one mol of methane to form CO_2 and two mols of hydrogen. These are relatively slow but the CO_2 reacts very rapidly with some of the hydrogen to form water and more CO as follows:—

3. $CO_2 + H_2 \longrightarrow H_2O + CO$

It is not desirable that either water or CO_2 should be left in the resultant pro-

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duct 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 CO_2 and water vapor.

These gases can be eliminated by taking advantage of the fact that in the following reactions:—

4. $C + O \longrightarrow CO$
5. $Fe + O \longrightarrow FeO$
6. $H_2 + O \longrightarrow H_2O$

carbon at elevated temperatures 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 there is not an excess of one atom of total oxygen for one atom of total carbon these two elements will be obtained combined as CO (plus excess carbon, if it be present), provided the reaction of formation of CO is speeded up by the employment of a catalyst so that substantial equilibrium is achieved. In the process of the present invention it is proposed to furnish substantially 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 and that there are 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 CO_2 and water vapor and will result, therefore, in unreacted methane being left in the gaseous mixture. To eliminate the CO_2 and water vapor, they are reacted with this unreacted methane. These reactions are illustrated as follows:—

Feed $3CH_4$ (at least 3 mols) $+ 3FeO$
7. $CH_4 + FeO \longrightarrow CO + 2H_2 + Fe$
8. $CH_4 + 2FeO \longrightarrow CO_2 + 2H_2 + 2Fe$
9. $CO_2 + H_2 \longrightarrow CO + H_2O$
Unreacted (1) CH_4 of feed.
Reforming reactions:—
10. $CH_4 + H_2O \longrightarrow CO + 3H_2$
11. $CH_4 + CO_2 \longrightarrow CO + 2H_2$

These so-called reforming reactions however are very slow unless catalysed with an effective catalyst. Iron, zinc, cobalt and nickel, are such catalysts. It is, therefore, proposed to admit to the reaction zone substantially one mol 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. It is clearly desirable then to use stoichiometrical proportions.

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

In carrying the invention into practice, it is preferred to utilize the so-called "fluidized solids" technique and in this case the amount of reducible metal oxide present in the reaction zone is negligible. This is possible because of the extraordinarily rapid rate of reaction between the fluidized reducible metal oxide and the hydrocarbon at the temperatures employed relative to the rate of the reforming reaction.

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 upwardly through reaction zone (1) and contact a fluidized bed of catalyst having a well defined upper level (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 fluidized catalyst is maintained in reaction zone (1). 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 oxidation 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 oxidation 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 fluidized 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) in sufficient amounts to maintain the catalyst in a fluidized state. The fluidized 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).

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 100 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.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. An improved process for the production of gases containing carbon monoxide and hydrogen which comprises contacting in a reaction zone a gaseous hydrocarbon feed with a catalyst comprising iron, cobalt or nickel or mixtures thereof with or without zinc, maintaining the greater percentage of said catalyst in the reaction zone in the form of a metal, passing a relatively small percentage of said catalyst to an oxidation zone, withdrawing oxidized catalyst therefrom and recycling it to the reaction zone in an amount substantially stoichiometrically equivalent to the hydrocarbon feed so as to provide in the reaction zone one atom of oxygen combined as reducible metal oxide per atom of carbon.

2. A process in accordance with Claim 1, wherein the percentage of catalyst maintained in the metallic state in the reaction zone is in the range from 90 to 95%.

3. A process in accordance with Claim 2, wherein the catalyst is iron and the amount of iron maintained in the metallic state is in the range of 90 to 95% of metallic iron as compared with 5 to 10% of iron oxide.

4. A process according to Claim 1, wherein said catalyst is an iron-nickel catalyst, preferably containing from 90 to 95% of nickel and from 5 to 10% of iron by weight.

5. A process in accordance with Claim 1, wherein the heat evolved from said catalyst in the oxidation zone, is utilized in the reaction zone by means of a heat transfer medium.

Dated this 17th day of March, 1947.

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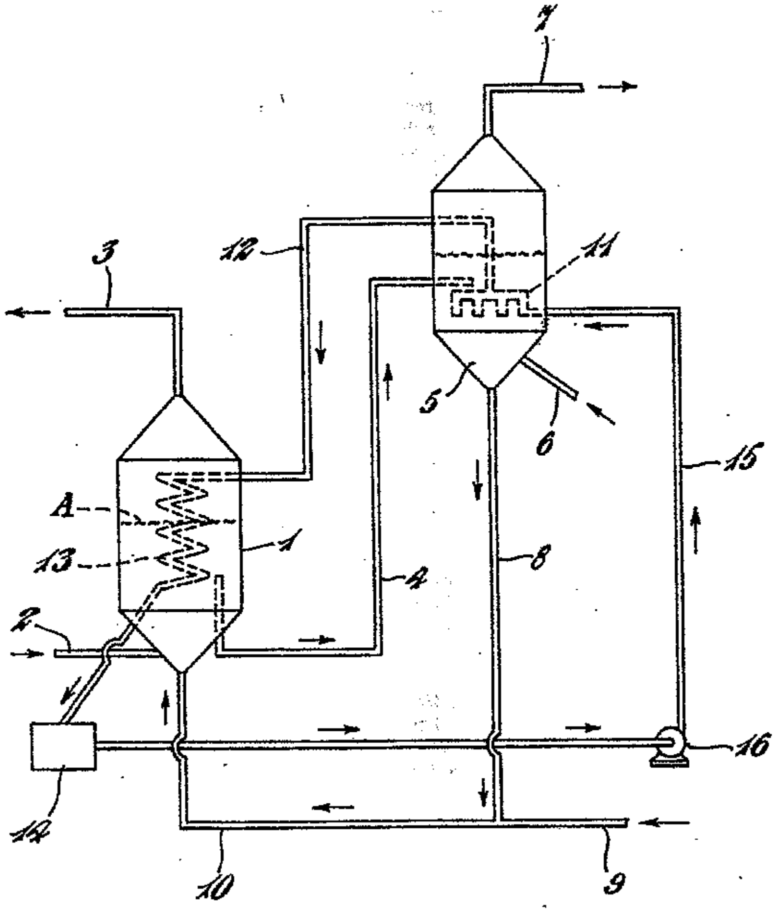
641,945 COMPLETE SPECIFICATION 1 SHEET

[*This Drawing is a reproduction of the Original on a reduced scale.*]



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