RESERVE COPY

THE PATENT OFFICE LONDON

PATENT SPECIFICATION

634,933

Date of Application and filing Complete Specification: April 21, 1947.
No. 10650/47.
Application made in United States of America on Nov. 15, 1946.
Complete Specification Published: March 29, 1950.

3523

Index at acceptance:—**Class 90,** D.

COMPLETE SPECIFICATION

A Method for the Production of Industrial Mixtures of Carbon Monoxide and Hydrogen

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 Elizabeth, 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 is directed to a method for producing industrial mixtures of carbon monoxide and hydrogen. More specifically, the invention contemplates the production of such a mixture in suitable proportions for use in the production of liquid hydrocarbons by what is known as the Fischer-Tropsch Synthesis.

In the production of industrial mixtures of carbon monoxide and hydrogen, one of the most serious problems is to produce such a mixture free from substantial amounts of contaminants, such as carbon dioxide, nitrogen, methane, and the like. It has been proposed to produce such mixtures by burning a hydrocarbon, such as methane, with pure oxygen. This, of course, creates immediately the problem of producing the pure oxygen in an economical manner.

It has also been proposed to react hydrocarbons, such as methane, with metal oxides under conditions under which the metal oxide will give up some of its oxygen. Ordinarily this procedure involves difficult control problems because of the tendency of the reaction to go toward the production of carbon dioxide. A metal oxide which produces a product gas of desirable composition is zinc oxide, but working with this oxide is rendered difficult by the volatility of the metallic zinc.

The oxide which most readily suggests itself for use in a process of this type is iron oxide, both because of its cheapness and availability and the readiness with which it is regenerated after undergoing reduction. It is to a process of the type described in which iron oxide is employed that the present invention is directed.

The greatest drawback to the use of iron oxide to supply the oxygen for oxidation of hydrocarbons such as methane is that the reaction follows a course which does not lead to the desired product gas. Considerable experience with various types of iron oxides indicates that the course followed by the reaction, for example, of methane with the oxide, is, first, practically complete conversion of the methane to carbon dioxide followed shortly thereafter by a rapidly increasing conversion of methane to carbon and hydrogen with carbon monoxide appearing in an intermediate stage, usually in an amount which increases with time to a maximum which, however, is far below the desired level and then falls off. It is assumed that this course of reaction arises from the production of free iron in the catalyst bed at an early stage and that this free iron acts as a cracking catalyst, the amount of free iron increasing as the operation progresses and, therefore, the production of carbon increasing with time. This theory of the mechanism of the reaction naturally points to the desirability of so conducting the reaction as to avoid the presence of free iron.

The present invention is based on the discovery that, contrary to expectation, if free iron is included in the reaction mixture at the outset in an amount bearing a predetermined relation to the amount of iron oxide present, the reaction progresses much more smoothly with a high selectivity for the production of carbon monoxide and hydrogen and with practically no formation of carbon. The amount of free iron to be incorporated in the reaction mixture varies within limits which may be generally expressed as being such that the atomic ratio of oxygen to

[P

free and combined iron in the mixture is between 1.25 and .5 to 1, at least 1/6 of a gram atom of free iron being present per gram atom of oxygen. This ratio of iron to combined oxygen may readily be achieved by a suitable combination of free iron with iron oxides. A very effective combination is one in which one gram atom of free iron is combined with one gram mol of Fe_2O_3. Various other combinations will suggest themselves, the important point being that a substantial part of the iron present in the mixture from the start is present as free iron and that the reaction be not continued to the point where the free iron in the mixture substantially exceeds the upper limit heretofore given.

The employment of a contact mass containing free iron in admixture with iron oxide according to the present invention does not fundamentally change the other operating conditions customary with a reaction of this type. In general, variations of these other reaction conditions vary the extent of the conversion of the hydrocarbon in a known manner without substantially changing the composition of the product gas. The reaction temperature, for example, may vary between 1600° and 2000° F. The pressure maintained in the reactor can be varied over a fairly wide range, up to about 600 lbs./sq.in. The rate at which the feed gas is passed over the contact mixture may also be varied within substantial limits as from at least 5.0 V/V/Hr. to as high as 500 V/V/Hr. and will, in general, be higher the higher the temperature employed. The period for which the hydrocarbon gas can be passed over the contact mass is limited, as before indicated, by the extent to which free iron is formed in the mixture, and this period will depend on various other factors involved to such an extent that no definite limits for it can be stated. By periodically analyzing the contact mixture, however, it can be determined when this period is terminated. This, of course, can also be ascertained from an analysis of the product gas.

The foregoing discussion has dealt with an operation in which the contact mass is employed as a fixed bed. The preferred operation, according to the present invention, is one in which the contact mixture is employed in finely divided form in suspension in the feed gas in accordance with the technique commonly referred as as the fluidized solids technique. In this type of operation the solids employed will preferably have a degree of fineness less than 10 mesh, predominantly smaller than about 100 mesh, and will be present in a plurality of sizes suitably combined to impart to the mixture good fluidizing properties. This means that there should be particles as fine as, or finer than, 20 microns in a substantial amount, as well as particles of larger size, the smaller sizes, say from 20 to 80 microns, constituting not more than 30% of the mixture. With the solids present in various sizes, of the order of magnitude heretofore mentioned, the feed gas is passed through the contacting zone at a velocity selected to insure proper fluidization and the maintenance of a dense phase of solid particles in the reactor. Generally this velocity will be between about .3 and 5 ft./second, depending on the particle size distribution. Usually a velocity between .5 and 2 ft. per sec. will give satisfactory fluidization.

In operating according to the fluidized solid technique, it is customary to employ at least two reactors, in one of which the hydrocarbon contacts the mixture of free metal and metal oxide and in the other of which the spent solid mixture from the first reactor is oxidized by being blown with air. It is important to observe that the flow of solids in such an operation will be so regulated that at no time will the free metal content in the solid mixture in the hydrocarbon reactor exceed the limit heretofore specified. This means that at all times the flowing stream of solids will consist of a mixture of free metal and metal oxide.

The nature of the present invention will be more clearly understood from the following detailed description of the accompanying drawing in which the single figure is a front elevation in diagrammatic form of one type of unit suitable for the practice of said invention.

Referring to the drawing in detail, numeral (1) designates a reactor provided at its upper end with a cyclone or other separator (2) from which gas leaves through line (3) and solid falls back into the reactor through line (4). Near the bottom of the reactor is an inlet line (5) terminating within the reactor in a funnel (6) covered with a grid or grate (7).

The bottom of the reactor is provided with a draw-off line (8) emptying into a conduit (9) and provided with a slide valve or other suitable control element (10). The line (9) has an open end for the introduction of gas for carrying the finely divided solid through the conduit. Line (9) terminates in a funnel (11) in chamber (12) which is similar to reactor (1). Funnel (11) is also provided with a grid or grate (13). In the upper part of chamber (12) is a cyclone or other separator (14) from the top of which gas leaves through line (15) and from the bottom of which solid is returned to chamber (12) through pipe (16). Depending from the bottom of chamber (12) is a standpipe (17) provided with aerating jets (18) and a slide valve or other control element (19) and emptying into conduit (5).

Reactor (1) is provided with a side wall receptacle (20) having a draw-off line (21) at its bottom provided with a slide valve or other control element (22) and emptying into a conduit (23). Conduit (23) terminates in a funnel (24) arranged in a chamber (25) similar to chamber (12). Funnel (24) is covered with a grid or grate (26). Chamber (25) is provided at its upper end with a cyclone or other separator (27) having an upper gas outlet (28) and a lower solids draw-off (29). Depending from the bottom of chamber (25) is a standpipe (30) provided with aerating jets (31) and a slide valve or other control element (32) and emptying into line (5).

Conduits (9), (17), (23) and (30) are shown broken to indicate that chambers (12) and (25) are located at a much higher level than reactor (1). The purpose of this arrangement is to build up a pressure head at the bottoms of standpipes (17) and (30) so that reactor (1) may be operated at an elevated pressure while the operations in chambers (12) and (25) may be conducted at lower or atmospheric pressure.

In carrying out the process of the present invention, a suspension of finely divided iron and iron oxide containing at least 5% by volume of solid is maintained in reactor (1). The level of the dense suspension is maintained where desired by adjusting the velocity of the gas through the reactor and the rate of feed or solid into line (5). The gas feed to the reactor is ordinarily a hydrocarbon, such as methane.

Reduced iron oxide-iron mixture is withdrawn from the reactor (1) through line (8) and conducted through conduit (9) into chamber (12). The carrying gas may be an oxidizing gas, such as air, oxygen, steam, carbon dioxide, or mixtures of two or more of these such as steam and oxygen. Ordinarily, the oxidation in chamber (12) can be controlled so as to maintain in the mixture in reactor (1) the desired percentage of free iron. Whether or not this control is being maintained may be readily ascertained by sampling the mixture in reactor (1) and analyzing it for free iron content.

For easier control of the composition of the mixture of solids fed to reactor (1), a portion of the mixture in (1) is continuously withdrawn through line (21) and fed to chamber (25) suspended in a reducing gas. By continuously operating chamber (12) under oxidizing conditions and chamber (25) under reducing conditions, the desired composition of solids in reactor (1) may be readily maintained.

The solids in chambers (12) and (25) are maintained in the same fluidized state of dense suspension as the solids in reactor (1). The oxidizing gas is fed into conduit (9) through line (33). The hydrocarbon is fed into line (5) through line (34). When steam is used as the oxidizing gas, with or without free oxygen, the exit gas from chamber (12) will ordinarily be of a reducing nature. This gas may be fed to conduit (23) or a separate reducing gas may be introduced through line (35). Also, if desired, where the exit gas from chamber (12) is composed mainly of steam and hydrogen, it may be fed to line (5) with the hydrocarbon. Alternatively, in this case, the gas from chamber (12) may be combined directly with the product gas in line (3) to increase the hydrogen content of the latter.

The following comparison indicates the nature of the improvement resulting from the present invention. Two runs were made in which methane was passed at 1700° F. into contact with oxygen-yielding, ferrous solid. In the one run the ferrous solid was FeO while in the other run it was a mixture of Fe_2O_3 and Fe having an atomic ratio of oxygen to iron of one. In the first run, using FeO, after the reactor had been on-stream 60 minutes with a feed rate of 70—100 V/V/Hr., the operating data indicated a methane conversion of 99.4%. Of the converted methane 31% appeared in the product as CO, 16% appeared as CO_2 and 53% appeared as carbon. In the second run, after the reactor had been on-stream for 70 minutes with a feed rate of 140 V/V/Hr., the operating data showed a conversion of 48.8% of methane. Of the converted methane 69% appeared as CO, 31% appeared as CO_2 and none appeared as carbon. It will be seen, therefore, that, while in the two cases the atomic ratio of oxygen to iron was the same, when the free iron was present there was no carbon formation and a much higher selectivity to CO at a much higher feed rate.

In practicing the present invention in the specific embodiment described, it is desirable to admix with the ferrous material a refractory light carrier, such as MgO, Al_2O_3, or the like. This light material in finely divided form may be mixed with the powdered ferrous material or the latter may be deposited on the refractory material by any of the commonly known techniques. This light material improves the fluidizing properties of the ferrous material and serves to prevent agglomeration at the elevated temperatures employed.

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

1. A method for converting a gaseous hydrocarbon into a gas containing CO which comprises contacting said hydrocarbon at an elevated temperature above or about 1600° F. with an oxygen-containing solid ferrous material containing at least 1/6 gram atom of free iron per gram atom of oxygen and having an atomic ratio of oxygen to free and combined iron between the approximate limits of 0.5 and 1.25 to 1.

2. A method for converting a gaseous hydrocarbon into a gas containing CO which comprises establishing a pair of zones, the first being a reaction zone and the second being a regenerating zone, circulating between said zones a suspension of finely divided oxygen-containing solid ferrous material containing free iron, maintaining in said reaction zone a dense fluidized suspension of said solid ferrous material by flowing hydrocarbon gas upwardly through said zone at a velocity between about 0.3 and 5 ft./second, maintaining in the solid in said reaction zone an atomic ratio of oxygen to free and combined iron between the approximate limits of 0.5 and 1.25 to 1, and at least 1/6 gram atom of free iron per gram atom of oxygen, maintaining in said reaction zone a temperature suitable for reaction between the gaseous hydrocarbon and said solid ferrous material, and maintaining a dense suspension of said solid ferrous material in said regeneration zone by passing an oxidizing gas upwardly through said zone at a velocity between about 0.3 and 5 ft./second at a temperature suitable for the oxidation of metallic iron.

3. A method for converting a gaseous hydrocarbon into a gas containing CO which comprises passing said hydrocarbon upwardly through a reaction zone at a velocity between about 0.3 and 5 ft./second, continuously feeding to said reaction zone an oxygen-containing solid ferrous material in finely divided form at a rate sufficient to maintain in said reaction zone a fluidized suspension containing at least about 5% by volume of said solid, maintaining in said reaction zone a temperature suitable for reaction between the gaseous hydrocarbon and the oxygen-containing ferrous material, continuously withdrawing product gas from said reaction zone, continuously withdrawing solid from said reaction zone at a rate so correlated with the feed of said solid to said zone as to maintain in said zone a solid having an atomic ratio of oxygen to free and combined iron between the approximate limits of 0.5 and 1.25 to 1 and having at least 1/6 gram atom of free iron per atom of oxygen, continuously feeding said withdrawn solid to an oxidizing zone and returning oxidized solid from said oxidizing zone to said reaction zone.

4. A method according to Claim 3, wherein the solid withdrawn from the reaction zone is continuously fed together with an oxidizing gas containing a large proportion of steam through said oxidizing zone, the exit gas from said oxidizing zone being combined with the aforesaid product gas.

5. A method for converting a gaseous hydrocarbon into a gas containing CO which comprises passing said hydrocarbon upwardly through a reaction zone at a velocity between about 0.3 and 5 ft./second, continuously feeding to said zone a finely divided oxygen-containing solid ferrous material at a rate sufficient to maintain in said zone a fluidized suspension containing at least 5% by volume of said solid, maintaining in said zone a temperature suitable for reaction between the hydrocarbon and the ferrous solid, continuously removing product gas from said reaction zone, continuously removing a major stream of finely divided solid from said reaction zone, reacting said stream with an oxidizing gas in an oxidizing zone, returning oxidized solid from said oxidizing zone to said reaction zone, continuously removing a minor stream of solid from said reaction zone, continuously reacting said solid in said minor stream with a reducing gas in a reducing zone, continuously returning finely divided solid from said reducing zone to said reaction zone, and correlating the rate of feed of said solids to said reaction zone with the rate at which solids are withdrawn therefrom so as to maintain in said reaction zone solids having an atomic ratio of oxygen to free and combined iron between the approximate limits of 0.5 and 1.25 to 1 and having at least 1/6 gram atom of free iron per atom of oxygen.

6. A method according to Claim 5, wherein the oxidizing gas referred to contains a large proportion of steam and the exit gas from the oxidizing zone is utilised as the reducing gas in the reducing zone.

7. A method according to any one of the preceding claims, wherein the atomic ratio of oxygen to free and combined iron is 1:1.

Dated this 21st day of April, 1947.

D. YOUNG & CO.,
29, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agents for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1949.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s 0d. each (inland) 2s. 1d. (abroad) may be obtained.

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