PATENT SPECIFICATION

635,909

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COMPLETE SPECIFICATION

Improvements in the Production of Industrial Mixtures of Monoxide and Hydrogen

SPECIFICATION NO. 635,909

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Standard Oil Development Company, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, and 100 West 10th Street, Wilmington, Delaware, both in the United States of America.

THE PATENT OFFICE,
26th May, 1950

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particularly described and by the following statement:—

The present invention is directed to a method for producing industrial mixtures of carbon monoxide and hydrogen.

In many industrial processes, the raw material is composed of a mixture of carbon monoxide and hydrogen. Chief among these processes are the so-called Methanol Synthesis, in which carbon monoxide and hydrogen are reacted in the presence of a suitable catalyst to produce oxygenated organic compounds, and the Fischer-Tropsch Synthesis, in which carbon monoxide and hydrogen, in suitable proportions, are reacted in the presence of a suitable catalyst and under selected conditions to produce a product primarily composed of liquid hydrocarbons. In processes of this type, it is highly desirable that the feed gas be free from contamination with inert gaseous substances.

The obvious way to obtain a mixture of carbon monoxide and hydrogen is to subject a mixture of a hydrocarbon, such as methane, and air to controlled combustion. This procedure, however, results in a gas containing a large quantity of nitrogen. This detrimental dilution has led to much study and experimentation, directed toward the development of a method for producing the desired "make gas" free from contaminants and diluents.

One procedure which has been suggested is to use a metal as an oxygen

gases of which hydrogen constitute only a minor part. For example, using iron as an illustration, there are several reactions involved when the oxide is reacted with a hydrocarbon, such as methane. The oxide can react with methane to produce carbon monoxide and hydrogen. These can also react to produce carbon dioxide and hydrogen. Both of these reactions are fairly slow. The hydrogen produced, on the other hand, reacts rapidly with the iron oxide to produce iron and water. Likewise, the carbon monoxide can react with iron oxide to produce iron and carbon dioxide. Again, the hydrogen produced reacts fairly rapidly with the carbon dioxide to produce water and carbon monoxide. The reduced iron at the temperature of operation is a very active cracking catalyst for the hydrocarbon, converting it to carbon and hydrogen. The carbon produced reacts fairly rapidly with water to produce carbon monoxide or carbon dioxide and hydrogen. The overall tendency, therefore, is to produce a gas containing substantial amounts of carbon dioxide and water as well as some unreacted hydrocarbon.

According to the present invention, the composition of the product gas in a process of the aforesaid type is adjusted in the direction of increased production of carbon monoxide and hydrogen by subjecting the product of this reaction to a re-

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COMPLETE SPECIFICATION

Improvements in the Production of Industrial Mixtures of Carbon Monoxide and Hydrogen

I, JOHN CONRAD ARNOLD, a British subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention (a communication from Standard Oil Development Company, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, Linden, New Jersey, United States of America), 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.

In many industrial processes, the raw material is composed of a mixture of carbon monoxide and hydrogen. Chief among these processes are the so-called Methanol Synthesis, in which carbon monoxide and hydrogen are reacted in the presence of a suitable catalyst to produce oxygenated organic compounds, and the Fischer-Tropsch Synthesis, in which carbon monoxide and hydrogen, in suitable proportions, are reacted in the presence of a suitable catalyst and under selected conditions to produce a product primarily composed of liquid hydrocarbons. In processes of this type, it is highly desirable that the feed gas be free from contamination with inert gaseous substances.

The obvious way to obtain a mixture of carbon monoxide and hydrogen is to subject a mixture of a hydrocarbon, such as methane, and air to controlled combustion. This procedure, however, results in a gas containing a large quantity of nitrogen. This detrimental dilution has led to much study and experimentation, directed toward the development of a method for producing the desired "make gas" free from contaminants and diluents.

One procedure which has been suggested is to use a metal as an oxygen carrier, said metal being first reacted with air to produce an oxide, which then is reacted with the hydrocarbon to produce a mixture of carbon monoxide and hydrogen. Most of the metals useful for this purpose which do not introduce physical difficulties, of which iron is a typical example, are subject to the defect that reaction of their oxides with a hydrocarbon does not produce the desired mixture of carbon monoxide and hydrogen, but produces a conglomeration of gases of which carbon monoxide and hydrogen constitute only a minor part. For example, using iron as an illustration, there are several reactions involved when the oxide is reacted with a hydrocarbon, such as methane. The oxide can react with methane to produce carbon monoxide and hydrogen. These can also react to produce carbon dioxide and hydrogen. Both of these reactions are fairly slow. The hydrogen produced, on the other hand, reacts rapidly with the iron oxide to produce iron and water. Likewise, the carbon monoxide can react with iron oxide to produce iron and carbon dioxide. Again, the hydrogen produced reacts fairly rapidly with the carbon dioxide to produce water and carbon monoxide. The reduced iron at the temperature of operation is a very active cracking catalyst for the hydrocarbon, converting it to carbon and hydrogen. The carbon produced reacts fairly rapidly with water to produce carbon monoxide or carbon dioxide and hydrogen. The overall tendency, therefore, is to produce a gas containing substantial amounts of carbon dioxide and water as well as some unreacted hydrocarbon.

According to the present invention, the composition of the product gas in a process of the aforesaid type is adjusted in the direction of increased production of carbon monoxide and hydrogen by subjecting the product of this reaction to a reforming operation in which the gas resulting from the reaction between the metal oxide and the hydrocarbon, preferably after adjustment of its hydrocarbon content, is contacted with a suitable catalyst at elevated temperature and pressure to effect a combination of reactions, including the reaction of carbon dioxide with hydrocarbon to produce carbon monoxide and hydrogen, and the reaction of water with hydrocarbon to produce carbon monoxide and hydrogen.

The present invention contemplates a process in which a suitable metal, such as iron, is subjected to oxidation by air, its oxide is reacted with a hydrocarbon, such as methane, and the gaseous product of this reaction is passed over a reforming catalyst, such as iron or nickel, as such or in combination with suitable carriers such as alumina, magnesia or the like. The present invention also contemplates such operations in which the oxidation of the metal is conducted at substantially atmospheric pressure, while the reaction between the metal oxide and the hydrocarbon and the reforming step are conducted at elevated pressures. More specifically, the present invention contemplates the employment of finely divided metal oxide, the maintenance of this material in the process in a fluidized state, and the utilization of the fluidized metal oxide to produce a pressurehead for the portions of the process to be conducted under pressure, by locating the vessel in which the oxidation of the metal is performed at a considerably higher level than the other vessels and connecting of the former with the latter by a standpipe in which the metal oxide is maintained in a fluidized state, in which it exhibits the hydraulic and hydrodynamic properties of a liquid.

The present invention also contemplates a process in which the exothermic heat of reaction in the oxidation stage is carried directly into the reduction and reforming stages by a heat carrier travelling through such stages, which heat carrier may comprise the metal used in the process in its free state and in its various stages of oxidation. Also contemplated is the provision in such a process of a relatively long period of contact between the hydrocarbon and the metal oxide before this mixture enters the reforming stage. This is particularly important where the reforming catalyst is an active cracking catalyst as in the case of iron and nickel, because it minimizes the production of carbon in the process. Because the contact material passes through all the stages, any deposition of carbon on the material represents a loss of carbon in the process because it will be burned off in the oxidation stage.

The nature of the present invention may be more clearly understood from the following detailed description of the accompanying drawing, in which:

Fig. 1 is a front elevation in diagrammatic form of one type of plant suitable for the practice of the present invention;

Fig. 2 is a similar view of a simplified form of apparatus for the practice of one embodiment of the present invention; and

Fig. 3 is a similar view of apparatus for the practice of another embodiment of said invention.

Referring to the drawing in detail, numeral (1) designates a reaction vessel which may be termed the oxidation chamber, numeral (2) represents a second vessel which may be termed a reduction chamber, and numeral (3) designates a third chamber which may be termed a reforming chamber. Solid material in finely divided form travels from chamber (1) through standpipe (4) in conduit (5) to chamber (2), thence through pipe (6) to chamber (3), back through bottom drawoff (7) from chamber (3) to chamber (2) and from there through bottom drawoff (8) back to chamber (1). Standpipe (4) and bottom drawoff (8) are broken to indicate a considerable difference in elevation between chamber (1) and chambers (2) and (3), respectively. This difference in elevation remains sufficiently great so that the finely divided solid in fluidized condition in standpipe (4) will constitute a column of sufficent height to create a hydrostatic pressure adequate for the maintenance of the desired pressure in chambers (2) and (3), it being desired to operate chamber (1) substantially at atmospheric pressure.

The finely divided solid material in chamber (1), at any given instant, is predominantly a metal oxide which, in the case of a metal having a plurality of oxides, may be a mixture of these oxides. In the ordinary case, some free metal will also be present in this chamber. The solid leaving this chamber, however, is predominantly metal oxide, it being understood, of course, that the presence of inert solids, such as sand and other substances stable under the operating conditions and having a high heat capacity, is also contemplated. In chamber (2) the finely divided solid, in addition to any inert heat carrier, will be mainly metal with some residual metal oxide. In chamber (3) the finely divided solid, apart from any inert heat carrier, will normally be free metal.

In carrying out the process of the present invention, finely divided solid in the system is maintained in a fluidized state. For this purpose, the solid is employed in the form of fine particles, substantially none of which is larger than 10 mesh and the major portion of which is smaller than 100 mesh, this latter portion including particles as small as 20 microns in diameter or less. Good fluidization is promoted by providing particles of sizes covering a wide range. For example, if about 30% of the particles are smaller than 80 microns in diameter, larger particles up to 10 mesh may be tolerated. If difficulty is encountered in the fluidization of free metal, this may be mitigated by employing a light, finely divided powder, such as magnesia or clay in conjunction with the metal, either as a mechanical mixture therewith or in the form of a support upon which the metal is deposited.

When it is desired to maintain the finely divided solid in a fluidized state in such a manner as to establish a suspension of the solid having a high density, say, of at least 20 lbs./cu. ft., the velocity of the fluidizing gas must be adjusted with reference to the particle size and particle size distribution of the finely divided solid. For most materials, a suitable gas velocity for this purpose is within the range of .5 to about 7 ft./second. With heavier materials, the velocity is in the upper end of this range. Generally, a velocity within the range of 1 ft. to 5 ft./sec. is satisfactory with materials of the type referred to herein. This is with particular reference to the velocity of the gas in chambers (1) and (3). In chamber (2) a higher velocity will normally obtain because it is desired to take the bulk of the solid material passing through chamber (2) up into chamber (3). By suitably proportioning chambers (2) and (3), the velocity in the latter may be maintained within the range specified while the velocity in the former may be as high as 20 ft./sec. or higher.

As previously indicated, a mass of solid particles comprising predominantly free metal, although lower oxides may also be present, is conveyed from chambers (2) and (3) to chamber (1) through line (8). Air is introduced into line (8) through line (9) to facilitate the travel of solid material therein into chamber (1) in which it is discharged out of a funnel-like member (10). With a suitably adjusted air velocity in line (8), the solid spouting out of the funnel (10) forms a dense suspension above the funnel having a definite upper level. The maintenance of this suspension is aided by the introduction of additional gas into the bottom of chamber (1) through inlets (11). This gas will usually be air but it may contain adjusted amounts of a cheap combustible material, such as torch oil or finely divided coke, or the like. The purpose of this is to develop as much heat as possible in chamber (1) compatible with the maintenance of the desired temperatures in the other chambers. Ordinarily, the temperature in chamber (1) will be maintained between 1700° and 2300° F., preferably in the upper end of this range.

The combustion gases leave the upper end of chamber (1) through line (12) and pass through a cyclone separator (13) from the bottom of which solid is drawn off through pipe (14) and from the top of which hot gas is led away through line (15) which passes through a heat exchanger (16) in which it gives up heat to the incoming air in line (9).

Finely divided metal oxide, either as such or mixed with an inert heat carrier of the type heretofore mentioned or deposited on a carrier such as pure Al_2O_3 in granular form or magnesia, depending upon what solid is employed in the process, continuously falls out of the dense phase above the funnel (10) into bottom drawoff or standpipe (4). This pipe is provided with suitably spaced jets or nozzles (17) for bleeding into the standpipe suitable quantities of gas to maintain the solid therein in a fluidized condition. The lower end of the standpipe is provided with a conventional slide valve or star wheel or other device (18) for controlling the flow of solid from the standpipe into the conduit (5). Pipe (14) is provided with a branch (19) controlled by valve (20) for the return of recovered solid from the off gases from chamber (1) to the standpipe. Line (14) is also provided with a control element (21) for permitting the withdrawal of solid from the system.

Just ahead of its junction with standpipe (4) conduit (5) is connected with a feed line (22) for hydrocarbon which, for illustrative purposes, may be considered to be methane. This feed line passes through the heat exchanger (23) where it picks up heat from the combustion gas in line (15), the latter normally having sufficient heat after passing through heat exchanger (16) to raise the temperature of the feed hydrocarbon to 500° F. or higher. The hydrocarbon and the metal oxide pass concurrently through conduit (5) which, of course, will be suitably lagged as will all other conduits to prevent loss of heat. This conduit is made sufficiently long so that at the velocity of flow employed there will have been formed ample quantities of carbon oxides and water by the time the mixture reaches the free metal or reforming catalyst in the reforming chamber (3).

By suitably adjusting the feed rates of solids and hydrocarbon to conduit (5) with relation to its length and with relation to the volume of zone (2), it is possible, by reason of the concurrent flow of these materials, to secure adequate production of CO_2 and water vapor for prevention of carbon deposition. The excess CO_2 and water vapor are subsequently reformed in zone (3).

Under the temperature and pressure conditions existing in conduit (5) and zone (2) the iron oxide, as for instance FeO, reacts with the hydrocarbons, as, for example, methane, to produce CO, CO_2, hydrogen, water and free metal. The free metal in turn functions as a cracking catalyst with respect to the unreacted hydrocarbons, which may result in an intermediate production of free carbon.

However, under the conditions of this process this free nascent fine carbon reacts with CO_2 and water, resulting in insignificant net production of free carbon. Thus, the solids remain substantially free of deposited carbon.

By operating in accordance with this process the production of non-nascent carbon, which will not react or which will react with difficulty under the conditions of the process, is avoided. It is well recognized that it is practically not possible to secure absolutely thorough and immediate mixing of a body of solids and a gas stream.

Thus, if the body of solids from zone (1) were mixed with the full feed stream of hydrocarbons, carbonization would occur as discussed heretofore. However, due to the difficulty of securing absolutely thorough mixing, localization of the carbonization reaction would occur in instances in zones containing inadequate CO_2 and water. With inadequate CO_2 and steam, the carbon would build up on the solids and assume a condition where it would not react or would react only with difficulty under the conditions of operation.

By operating in accordance with this process, wherein part of the hydrocarbons are introduced through line (22) and the remainder preferably by means of lines (25) and (27), the ratio of iron oxide to hydrocarbons is relatively large, for example a ratio obtained by using an amount of iron oxide substantially in excess of that stoichiometrically required to convert all the carbon in the hydrocarbon feed to carbon monoxide and the presence of a necessary oxidizing zone assumed in zones (5) and (2).

The conduit (5) terminates in chamber (2) in a cup-shaped receptacle (24) in which there is some increase in density in the suspension. The suspension passes from the cup-shaped member into the larger chamber (2) in which there is a further increase in density and a decrease of velocity with a consequent dropping out of some solid material to the bottom of chamber (2). As the mixture passes upwardly through pipe (6), additional hydrocarbon is injected through feed line (25).

The pipe (6) terminates in chamber (3) in a funnel-shaped member (26) from which the suspension emerges in the form of a fountain forming a dense phase having a definite upper level above the funnel-shaped member. To aid in the maintenance of this dense phase, additional quantities of hydrocarbon are injected into the bottom of chamber (3) through inlets (27). Solid particles continually fall out of the dense phase into drawoff (7) at the bottom of chamber (3). The reformed gas leaves the top of chamber (3) through line (28) and passes with its entrained solid to a cyclone separator (29) from the top of which product gas is recovered through line (30). The separated solid is drawn off the bottom of separator (29) by pipe (31) which empties into the lower part of chamber (2) after receiving the solids carried by bottom drawoff (7).

It is important that the solid in chamber (3) be predominantly free from metal or reforming catalyst. A very suitable solid material for use in the process is alumina or magnesia carrying nickel and iron, the nickel constituting from 5 to 20% by weight of the combination and the iron constituting from about 5 to 10%. The iron component serves as the oxygen carrier while the nickel and magnesia or alumina, as the case may be, serve as the primary reforming catalyst. In any case, however, and considering iron itself for illustrative purposes, a supply of free iron is maintained in a hopper (32) which feeds into a standpipe (33) which discharges through a suitable control element (34) into the dense phase in chamber (3). The composition of the solid in chamber (3) should be frequently analyzed, and when it shows any appreciable build up of iron oxide, or other metal oxide used as the oxygen carrier, solids should be withdrawn from the system through line (14) and continuously replaced by free metal from hopper (32) until the composition of the solids in chamber (3) is satisfactory. Alternatively, the rate of feed of solid from standpipe (4) into conduit (5) may be decreased and iron added to the system, when necessary, as iron oxide supplied to chamber (1).

As has previously been indicated, it is desirable to operate chambers (2) and (3) at an elevated pressure because the product gas is used in a process operated at elevated pressure. A suitable operating pressure lies in the range of 200 lbs. to 600 lbs./sq. in. and this pressure is realized at least in part by providing a standpipe (4) of adequate height. Chamber (2) will ordinarily be maintained at a temperature between 1600 and 2000° F. while chamber (3) will usually be maintained at a temperature between 1500 and 1900° F.

In order to realize satisfactory heat transfer from the oxidation chamber to the reduction and reforming chambers, it is advantageous to use an inert heat carrier. When such as sand is employed, it will constitute between about 30 and 60% of the stream of circulating solid and will be present in the form of particles covering a wide range within the limits heretofore specified. Even when such an inert heat carrier is employed, it is advantageous to include in the stream of circulating solids a small percentage, up to approximately 5%, of powdered magnesia to assist in fluidization.

In order to impart greater flexibility to the process and to preclude packing in the bottom of chamber (2), it is advantageous to inject into the bottom of this chamber through inlets (35) steam or carbon dioxide or both. It will be understood that the product gas will be customarily analyzed and from this analysis the adjustment of the various feeds will be determined. The feed rate of hydrocarbon through line (22) will be dictated by the velocity required for smooth operation in chambers (2) and (3), and adjustments of the composition of the product gas will be made by varying the hydrocarbon and steam and/or carbon dioxide feeds in inlets (25), (27) and (35).

Referring to Fig. 2, elements corresponding to elements in Fig. 1 bear the same numerals. That portion of the system in which the metal is oxidized is the same as in Fig. 1, including the elevated oxidation chamber (1) with the upright standpipe (4). In this case the conduit (5) is provided with a jacket (36) to which the hot residue gas from oxidizing zone (1) is fed through line (15). This hot gas is introduced into the jacket near the end of conduit (5) and leaves the jacket near the beginning of conduit (5) through line (37) which passes through heat exchanger (16) to give up heat to the hydrocarbon feed in line (22). Line (5) is provided with a plurality of valved branch lines (38) through which may be introduced reactants, such as hydrocarbon, steam, and/or carbon dioxide. Which of these reactants are to be added and in what quantities is indicated by the composition of the product gas. If this gas contains excess CO_2, water and/or hydrocarbon should be added. If it contains substantial quantities of hydrocarbon, water and/or CO_2 should be added. To supplement the heat supplied by the residue gas from the oxidizing chamber flue gas or other hot combustion gas may be introduced into the jacket at various points through valved lines (39). If desired, the gas fed into these lines may be a combustible mixture and combustion may be carried out inside the jacket. In some cases it is desirable to utilize part of the tail gas from the synthesis operation in which the product gas of the present process is utilized as the combustion gas fed in through lines (39).

The conduit (5) is made sufficiently long to provide suitable reaction time, taking into account the rate of feed of solid and hydrocarbon through this conduit for the reaction between the hydrocarbon and the metal oxide and for the reforming reaction between hydrocarbon, carbon dioxide and water, or any two thereof, in the presence of the reduced metal oxide. For this purposes it will be desirable to maintain the temperature along the conduit in the range of 1500° to 2000° F.

The conduit (5) discharges into a separator (40) provided with suitable baffles (41) to induce a number of reversals of direction of flow of the gas therethrough to thereby facilitate separation of the solid. The solid drops out of the bottom of this separator through a valve (42) into line (8) in which it is returned to the reactor (1). The product gas leaves the separator through line (43) and passes through heat exchanger (44) in which it gives up heat to incoming air in line (9). If required, one or more cyclone separators may be included in line (43) to complete separation of solid from gas and the solids so recovered are likewise introduced into line (8).

It will be understood that the specific procedure heretofore described can be altered substantially without departing from the scope of the present invention. While iron has been mentioned as the oxygen carrier for illustrative purposes, it will be clear that other metals capable of being oxidized by air and giving up their oxygen under the conditions obtaining in chamber (2) may be employed.

Referring to Fig. 3 of the drawing in detail, numeral 101 designates a vessel in which the metal is converted to its oxide, while numeral 102 designates a similar vessel in which the metal oxide is reacted with a hydrocarbon. The metal is introduced as its oxide in finely divided form into vessel 101 by way of a feed pipe 103, which may be provided with a hopper 104, connected to pipe 103, through a suitable valve 105, such as a slide valve or a star wheel, for controlling the flow of finely divided solids to provide for the introduction of metal oxide into the system. The feed pipe 103 terminates in vessel 101 in a funnel-shaped member 106, spaced from the bottom thereof.

The oxide together with finely divided metal from 102 mixed with gas enters the vessel in the form of a suspension which spouts upwardly from the funnel 106, much in the same manner as water in a fountain. At the same time, preheated air is introduced into the bottom of the vessel through line 107 at a velocity such as to maintain the finely divided metal in suspension in the vessel for a predetermined period of time, depending on the particle size distribution of the metal and the velocity of the gases.

The reaction which is conducted in vessel 101 is exothermic. This reaction proceeds rapidly at temperatures between 1700 and 2100° F. If the temperature tends to become excessive, it can be maintained at the desired level by feeding in less highly preheated air or even steam.

When the reaction in vessel 101 is in progress, the finely divided metal and metal oxide are in the form of a dense suspension in the upflowing air above the funnel 106. The upper level of this dense suspension may be regulated by suitably adjusting the velocity of the air and the rate of feed of the solid. The finely divided solid continuously falls out of said dense suspension and leaves the bottom of vessel 101 through standpipe 108, which is provided with suitably arranged injection nozzles 109, through which may be injected puffs of air or steam to keep the solid in the standpipe in a fluidized condition. Some solid will be carried off overhead from vessel 101 through line 110, this is knocked out of the exit gas in a suitable separator 111, such as a cyclone separator. The recovered solid is conveyed from the separator to standpipe 108 by line 112. The combustion gases leave the top of the separator through line 113 and pass through a heat exchanger 114, in which they impart heat to the incoming air in line 107.

Methane or other hydrocarbon, preferably preheated, is injected at the bottom of standpipe 108 at a point below a suitable valve 115 in standpipe 108, which controls the rate of discharge of solid from the standpipe. The mixture of hydrocarbon and solid oxide passes through line 116, which terminates in a funnel-shaped member 117 at an intermediate point in vessel 102. Additional hydrocarbon may be injected at spaced points 118 along the line 116 to facilitate movement of the solid. Some reaction between the hydrocarbon and the oxide occurs in line 116, and this reaction is desirable.

Again, the rates of feed of the hydrocarbon and the oxide are adjusted so as to maintain in vessel 102 above funnel 117 a dense suspension of the solid particles in the upflowing gases. Additional hydrocarbon may be fed into the bottom of vessel 102 through line 119. The temperature in this vessel is maintained within the range of 1600 to 2000° F. The heat required for the reaction is carried in by the finely divided solid which absorbs heat in vessel 101. For this purpose, it is particularly desirable to have a large amount of inert solid having a fairly high heat capacity in the circulation of solid particles. The materials heretofore mentioned as fluidizing aids may serve this purpose to some extent, and they may be supplemented by other finely divided solids of high heat capacity, such as sand. Pure Al_2O_3 in granular form, employed as a carrier for the metal, functions well, both as a fluidizing aid and a heat carrier.

Reduced metal oxide, preferably in the form of a lower oxide, drops out of the dense phase in vessel 102 into line 103, which is connected to vessel 102 as a bottom draw-off. This line is provided with suitably spaced nozzles 120, through which a suitable gas, such as air or steam, may be injected to facilitate movement of the solid through line 103.

The gases leaving the vessel 102 overhead through line 121 discharge into a cyclone separator or other suitable separator for solids and gases 122, from which the separated solid leaves the bottom through draw-off 123. This recovered solid may be fed into line 103 by way of branch line 124 provided with a suitable control valve 125. Draw-off 123 is also provided with a suitable valve 126, through which any desired quantity of the solid may be removed from the system. Removal of this solid in small quantities from time to time may be desirable in the event that the solid becomes contaminated in such a way as to interfere with its efficiency as an oxygen carrier.

The gases leaving the upper end of separator 122 through line 127 will contain hydrogen, carbon monoxide, carbon dioxide, steam and some unconverted hydrocarbon. The amount of supplemental hydrocarbon to be added should be that required for reaction with the carbon dioxide and steam in the gas mixture in line 127. Periodic analysis of this latter gas mixture will serve as a guide to the amount of supplemental hydrocarbon required. This gas is preferably mixed with a further quantity of hydrocarbon which may be preheated and introduced by way of line 128. The resulting mixture passes through a reaction coil 129, arranged in a furnace 130 and packed with a suitable reforming catalyst 131, which may be iron or nickel or a combination of these, preferably supported on a carrier such as pure Al_2O_3 in granular form or magnesia. The burners 132 of the furnace are operated so as to maintain a temperature in the reforming zone in the range of 1500 to 1900° F. The reformed gas, consisting predominantly of carbon monoxide and hydrogen leaves the reforming zone through line 133 and passes through a heat exchanger 134, in which it gives up heat to the hydrocarbon feed to zone 102. Sufficient heat is recovered from this product gas to raise the temperature of the hydrocarbon feed to about 500° F., leaving the product gas at a temperature suitable for immediate use in a synthesis of the type heretofore mentioned. It may be pointed out here that by suitably adjusting the height of the standpipe 108, a pressure upwards of about 200 pounds may be provided in the reactions in vessel 102 and reformer 129, whereby the product gas is recovered at a pressure which may amount to the whole or a large part of that suitable for direct use in a Fischer-Tropsch synthesis. In the event that the allowable hydrocarbon feed to reactor 102 is inadequate properly to fluidize the solid therein, a suitable amount of product gas may be recycled to line 116 or reactor 102 through line 136.

Having now particularly described and ascertained the nature of the said invention, and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for the production of a mixture of carbon monoxide and hydrogen from a hydrocarbon, which comprises reacting the hydrocarbon with a finely divided fluidized reducible metal oxide whereby reduced metal oxide and a gas mixture containing carbon monoxide, hydrogen, carbon dioxide and water are produced, thereafter contacting said gas mixture together with sufficient hydrocarbon to react with the carbon dioxide and water with a reforming catalyst under conditions suitable for the reaction of carbon dioxide and water with hydrocarbon to produce additional carbon monoxide and hydrogen, and separating product gas.

2. A process according to Claim 1, wherein said metal oxide yields on reduction free metal which is capable of acting as a reforming catalyst.

3. A process according to Claim 1 or 2, wherein at least part of said reforming catalyst comprises free metal formed in the metal oxide reduction stage and withdrawn therefrom.

4. A process according to any one of Claims 1 to 3, wherein free metal is withdrawn from the metal oxide reduction stage and/or the reforming stage, reoxidized and recycled to said reduction stage.

5. A process according to any one of the preceding claims, wherein the amount of metal oxide used is substantially in excess of that stoichiometrically required to convert all the carbon in the hydrocarbon feed to carbon monoxide.

6. A process according to any one of the preceding claims, wherein the metal oxide reduction stage is subjected to the hydrostatic pressure exerted by the maintenance of an elongated vertical column of fluidized finely divided reducible metal oxide, fluidized metal oxide being continuously withdrawn from the bottom of said column and passed to said reduction stage.

7. A process according to Claim 6, wherein said column is maintained in a finished state by feeding small quantities of gas at spaced points therealong.

8. A process according to Claim 6 or 7, wherein the metal withdrawn from the metal oxide reduction stage and/or reforming stage is re-oxidized in a fluidized condition in an elevated zone by the passage upwardly therethrough of an oxidizing gas, finely divided metal oxide being continuously withdrawn from said zone into the top of said column.

9. A process according to any one of Claims 6—8, wherein said elevated zone also contains fluidized inert solids of high heat capacity, whereby the total solids withdrawn from said zone contain a substantial portion of the heat required for the subsequent treatment thereof with the hydrocarbon.

10. A process according to Claim 9, wherein the temperature of said elevated zone is maintained between 1700° and 2300° F.

11. A process according to any one of the preceding claims, wherein the temperatures of said metal oxide reduction

stage and reforming stage are maintained between the ranges of 1600° to 2000° F. and 1500° to 1900° F. respectively.

12. A process according to any one of Claims 1—10, wherein the metal oxide reduction stage and the reforming stage are carried out consecutively in an elongated conduit, a fluidized mixture of metal oxide and hydrocarbon being passed concurrently along said conduit and sufficient contact time being provided for the substantial completion of the desired reduction and reforming reactions.

13. A process according to Claim 12, wherein at least one constituent selected from the group consisting of hydrocarbon, water and carbon dioxide is added to the concurrently flowing hydrocarbon and metal oxide at a selected point therealong when the composition of the product gas indicates a need for such additional component.

14. A process according to Claim 12 or 13, wherein said conduit is maintained at a temperature between 1500 and 2000° F.

15. A process for the production of a mixture of carbon monoxide and hydrogen which comprises providing a closed cycle for the circulation of a finely divided solid material, including an oxidation zone, a reduction zone, and a reforming zone, circulating through said cycle a fluidized mass of finely divided solid having a substantial heat capacity and including a metal having a reducible oxide reactive with a hydrocarbon at temperatures between about 1600 and 2000° F. and capable, when in its free state, of catalyzing the reaction between a hydrocarbon and steam and carbon dioxide at a temperature between about 1500° F. and 1900° F., subjecting said stream to oxidizing conditions in the oxidation zone, adding to said stream leaving said oxidation zone a hydrocarbon and causing the mixture to pass concurrently through said reduction zone, adding further hydrocarbon to said mixture leaving said reduction zone and entering said reforming zone, maintaining the reduction and reforming zones at temperatures within the ranges heretofore specified and recovering a product gas from said reforming zone.

16. A process for the production of a mixture of carbon monoxide and hydrogen under pressure which comprises establishing an elevated oxidizing zone, maintaining in said zone a body of finely divided solid, including a metal undergoing oxidation to an oxide capable of reacting with a hydrocarbon at temperatures between 1600° and 2000° F., the said metal being capable of catalyzing the reaction between a hydrocarbon and steam and carbon dioxide at a temperature between about 1500° and 1900° F., passing an oxidizing gas upwardly through said zone at a rate sufficient to maintain said finely divided solid in a fluidized turbulent condition, withdrawing hot finely divided solid containing oxidized metal from said zone into an elongated upright column, maintaining the solid in said column in a fluidized condition whereby it provides a hydrostatic pressure head, continuously feeding hot finely divided solid from the bottom of said column into a stream of hydrocarbon, passing the mixture through an elongated conduit, discharging said mixture into an enlarged zone in which a partial separation of solid from said mixture occurs, passing the resulting mixture together with additional hydrocarbon into a second enlarged zone wherein residual solid is maintained in a fluidized condition, recovering product gas from said latter zone and returning solid from said latter zone to said oxidizing zone.

17. A process according to any one of the preceding claims, wherein said reducible metal oxide is deposited on light carrier.

18. A process according to Claim 17, wherein said light carrier comprises magnesia or alumina.

19. A process according to any one of the preceding claims, wherein said hydrocarbon is a gaseous hydrocarbon, such as methane.

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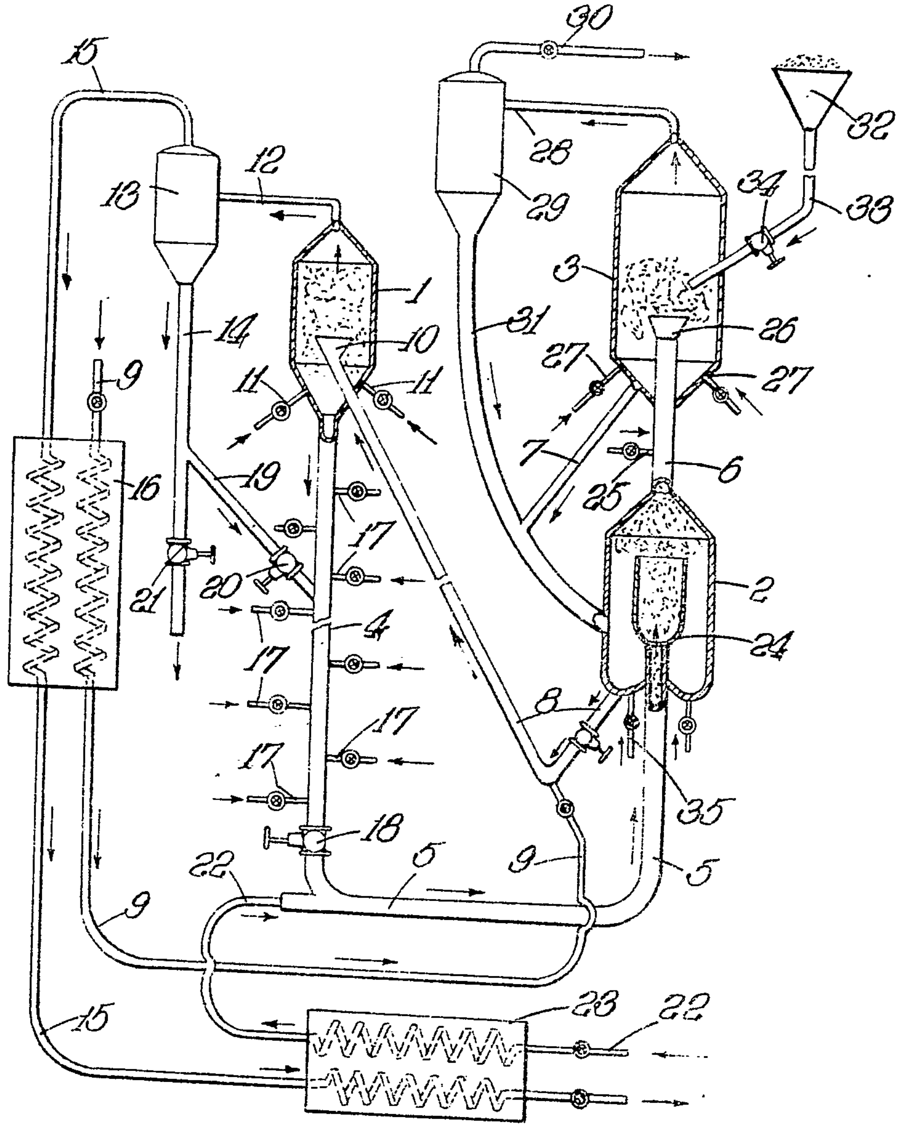
Fig. 1.



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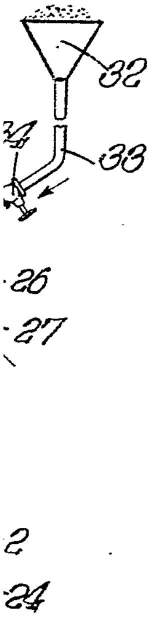

3 SHEETS
SHEET 3

Fig. 3.

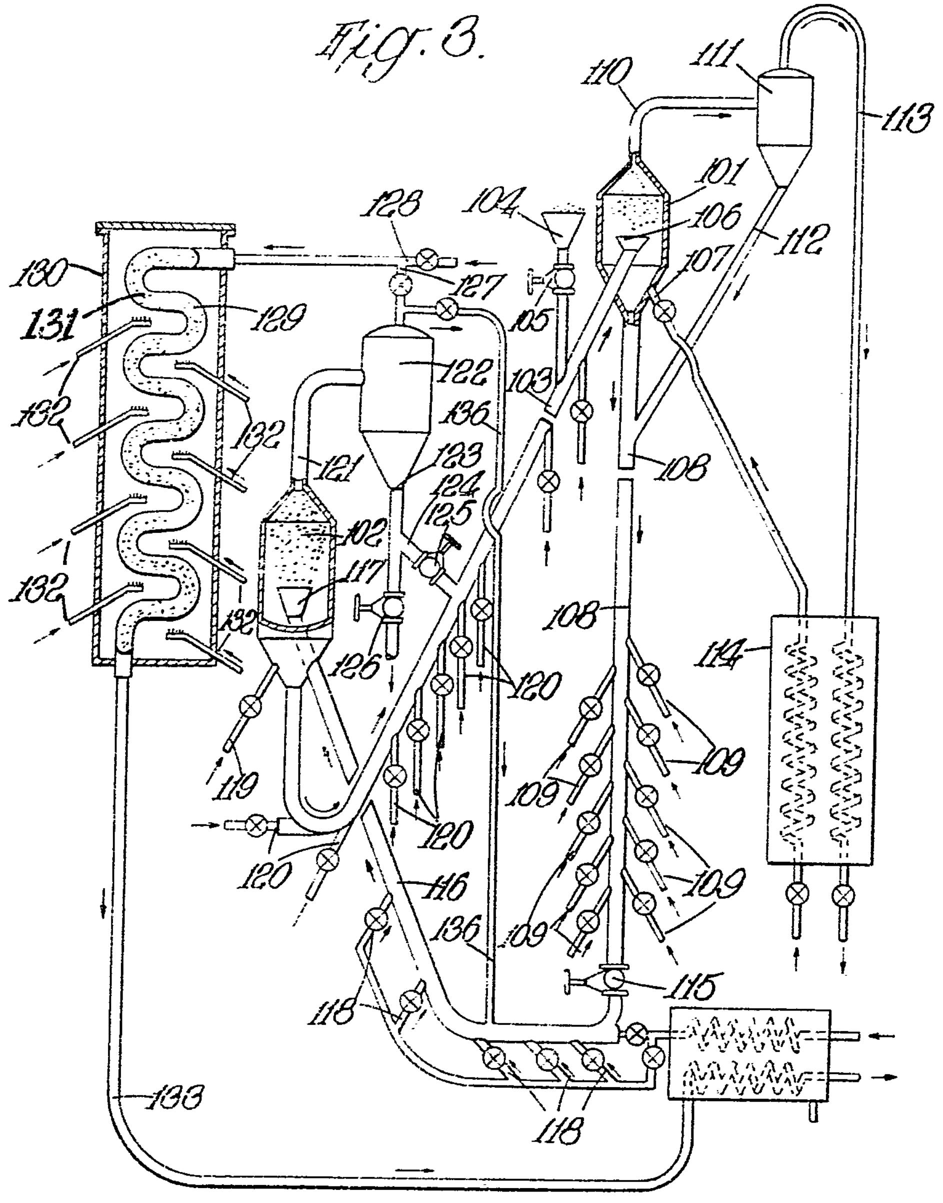

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Fig. 1.

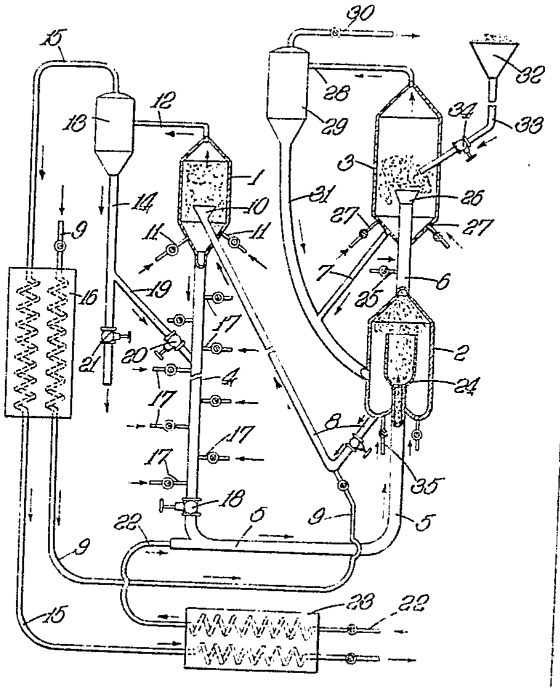

Fig. 3.

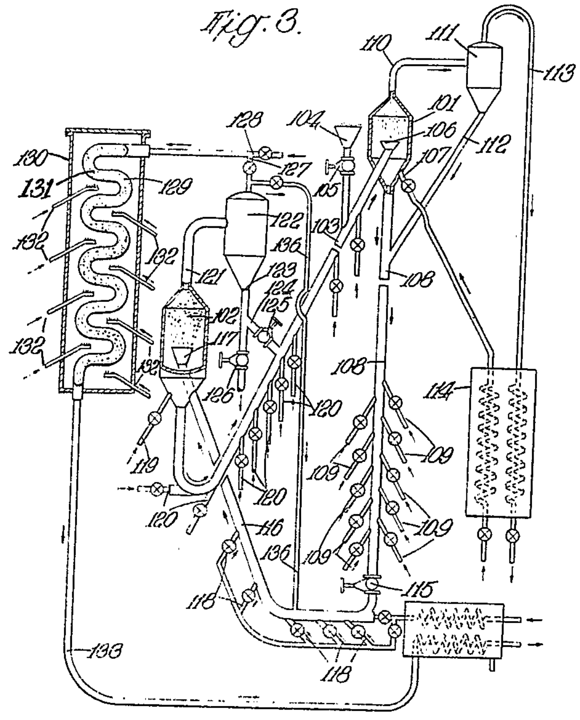

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Fig. 2.