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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Gases Containing Carbon Monoxide and Hydrogen from Hydrocarbons

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of 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 gases containing carbon monoxide and hydrogen from gaseous hydrocarbons. More specifically, it relates to the production of a gaseous mixture substantially entirely consisting of carbon monoxide and hydrogen from methane.

In many processes, the raw material is composed of or essentially contains, 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 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 from 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 lead to much study and experimentation directed toward the development of a method for producing the desired "make gas" free from contaminants and diluents.

Among the procedures which have been proposed for producing from hydrocarbons a suitable gas mixture containing carbon monoxide and hydrogen free from large volumes of diluent gas is that in which a metal is used as an oxygen carrier. The general procedure proposed is to react the hydrocarbon, such as methane, with a metal oxide until the latter is depleted in oxygen content, then to reoxidize the depleted oxide with air, venting off the residue gases, and again react the regenerated oxide with the hydrocarbon. By this procedure the gas resulting from reaction of the hydrocarbon with the metal oxide is obtained separately from the gaseous residues from the oxidation of the metal with air.

It has been proposed to employ in a multistage process of this type the so-called fluidized solids technique which is characterized by the fact that contact or reaction between a gasiform material and a solid is effected by suspending the solid in finely divided form in an upflowing stream of the gasiform material, the solid for this purpose being employed in the form of particles of mixed sizes ranging upwards from about 5 microns to about 100 mesh, and containing substantial quantities of sizes between 200 mesh and 400 mesh, and the velocity of the upflowing gasiform material being maintained between about .3 and 5 feet per second; these values representing superficial velocity of gas through an empty contacting zone. By suitably adjusting the velocity of the upflowing gasiform material within the range given and by feeding to the contacting zone finely divided material as rapidly as such material leaves the zone, it is possible to maintain in the contacting zone a high concentration, between 10 and 25% by volume of the finely divided material in

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a highly turbulent state. The finely divided material leaves the contacting zone either by being carried off overhead by the gas or by being withdrawn directly from the dense suspension in the contacting zone, in which case the dense suspension may be drawn off the bottom of the contacting zone or overflow from the top of the contacting zone or drawn off at any intermediate point. In the dense suspension in the contacting zone, by reason of its high degree of turbulence, there is a thorough mixing of the finely divided material and the gasiform material resulting in a substantial uniformity of temperature throughout the zone and a homogeneity of the mixture throughout the zone; thus, if there is added to the suspension finely divided material of a character somewhat different from that already contained within there is rapidly formed throughout a zone a homogeneous mixture of the different solid materials.

In applying this technique to the process under discussion, finely divided metal oxide is fed to a contacting zone together with a gasiform hydrocarbon, such as methane. Finely divided material is continuously withdrawn from the zone and is fed to a second contacting zone together with air. In the first contacting zone the reaction involves the oxidation of the hydrocarbon and the reduction of the metal oxide. If the oxidation of the hydrocarbon is controlled to produce carbon monoxide and hydrogen, it is only slightly exothermic. The reduction of the metal oxide, on the other hand, is endothermic to an extent corresponding to the heat of formation of the metal oxide. The overall result is that heat must normally be supplied to this contacting zone. It has been proposed to supply this heat in the form of heat contained in the metal oxide fed from the oxidization zone, in which the reaction is exothermic, to the hydrocarbon conversion zone. The amount of heat that can be so supplied, however, is limited by the amount of solid feed which the hydrocarbon conversion zone will tolerate.

In applying this technique it has been proposed to maintain in the hydrocarbon conversion zone an excess of metal oxide so that some of the hydrocarbon is converted to carbon dioxide, thereby supplying a large quantity of heat. This carbon dioxide, however, must be removed from the "make gas" and this involves a reforming operation which again creates a problem of heat supply.

It has been proposed to use iron oxide as the oxygen carrier in a procedure of this type because of its cheapness and ready availability. Iron oxide has a high heat of formation and, therefore, absorbs large quantities of heat during its reduction. This places an extreme heat load on the hydrocarbon conversion zone.

From the foregoing discussion, it becomes apparent that in an operation of this type for overall heat balance it is preferable to use as the oxygen carrier a metal the oxide of which has a substantially lower heat of formation than iron oxide. A readily available cheap material answering this requirement is copper. Previous attempts to employ copper in this process have resulted in a substantially complete conversion of the hydrocarbon to carbon dioxide and water, rather than to carbon monoxide and hydrogen. Furthermore, copper oxide and copper itself do not fluidize readily but tend to agglomerate at the temperature of operation in finely divided form.

It has now been found that copper may be used as an oxygen carrier in this process if it is employed on a carrier and if there is maintained in the hydrocarbon conversion zone a fluidized bed consisting substantially entirely of copper supported on a finely divided carrier to which is added, continuously, copper oxide supported on a finely divided carrier in an amount stoichiometrically equivalent to the hydrocarbon fed to the contractor. In other words, the rates of feed of the hydrocarbon and the copper oxide to the contacting zone are so controlled that for each atom of carbon fed to the contacting zone there is fed an atom of oxygen.

In the process of the present invention the methane reacts quite rapidly with the copper oxide at a fairly low temperature. If carbon monoxide and hydrogen are first produced, they react much more rapidly with the copper oxide than with the methane. On the other hand, the methane may be converted directly to CO_2 and H_2O. In either case the copper oxide is fully utilized before the methane is consumed, and such methane as is converted goes primarily to carbon dioxide and water. One virtue of the process, however, is that the copper is an effective reforming catalyst whereby the carbon dioxide and water produced react with the unconverted methane to produce carbon monoxide and hydrogen. As previously pointed out, this reaction is quite endothermic. On the other hand the reaction between the methane and the copper oxide to produce carbon dioxide and water is highly exothermic. Moreover the heat of reduction of the copper oxide is relatively low. Because of the thorough mixing which is realized in the contacting zone, the heat generated by the methane-copper oxide reaction, together with the sensible heat brought into the contacting zone both as preheat of the methane and heat carried in by the copper oxide, supported on the carrier is sufficient to support the hydroforming reaction. It may be noted here that the copper oxide forms only a minor amount of the total solid fed to the contacting zone, the remainder being in the form of a heat carrier having relatively high heat capacity which carries considerable heat from the oxidization zone to the hydrocarbon conversion zone.

The copper, in order to function satisfactorily in the fluidized solids technique employed in the process of the present invention must be supported on a carrier. Any one of a number of materials may be used to impart the desired fluidizable character to the copper. Among these materials are magnesia, alumina, zirconia, thoria, silica and other highly refractory oxides. For the best effectiveness of the supported copper as a reforming catalyst, however, it is preferred to employ silica as the carrier. Copper on silica at a given temperature is a much more effective reforming catalyst than copper on magnesia. Copper on alumina is intermediate these two in effectiveness. It is to be understood that any of these carriers may be employed to catalyze effectively the reforming reaction, but when silica is employed as a carrier, it is possible to complete the reforming reaction at a lower temperature. For example with copper on silica it is possible to operate the hydrocarbon conversion zone at a temperature as low as about 1450° although for best results the operaton is conducted in the neighbourhood of 1600—1850° F. With copper on magnesia, on the other hand, the minimum temperature at which substantial reforming occurs is about 1650° F., and in general for a given degree of reformation it is necessary to use a temperature of from 100—200° higher with copper on magnesia than with copper on silica. In this connection it must be borne in mind that the temperature maintained in the hydrocarbon conversion zone is dictated primarily by the temperature requirement of the reforming reaction since the reaction between the methane and the copper oxide proceeds at substantially lower temperatures, even below 1000° F.

It is not sufficient for the purpose of the present invention to use copper in the form of a mechanical mixture with silica. Rather it is required that the copper and silica have that degree of intimacy of admixture attainable by impregnating the silica with a solution of a copper salt or, preferably, that greater degree of intimacy of admixture attainable by coprecipitating the copper and the silica. A very useful catalyst for the purpose of the present invention is prepared by soaking silica gel in an aqueous solution of a copper salt of such concentration as to deposit on the gel between about 3 and about 30% by weight of copper. The soaked gel is then dried and roasted to convert the copper salt to the oxide which then may be readily reduced by a treatment with hydrogen or a hydrocarbon gas or other reducing gas.

This catalyst has the desirable characteristic that when it is employed in finely divided form of particle size less than 100 mesh, and with a suitable particle size distribution, it is readily fluidizable, as distinguished from powdered copper which is difficult, if at all possible, to fluidize because of the tendency of finely divided copper to agglomerate at elevated temperature. Consequently the catalyst of the present invention is ideally suited to reforming operations conducted while employing the so-called fluidized solids technique in which the catalyst in finely divided form is suspended in an upflowing stream of the gasiform reaction material travelling at a velocity such as to maintain the finely divided catalyst in the form of a dense highly turbulent suspension having the flow characteristics of a liquid. For use in this type of operation the catalyst is preferably in the form of fine particles of mixed sizes the largest of which is not substantially greater than 100 mesh and a large portion of which pass 200 mesh. With a catalyst in this state of subdivision the suspending gasiform material should be a velocity between about .3 and 5 ft./sec., preferably in the lower end of this range, the velocity figures being given superficial velocity or velocity of the gasiform material through an empty contacting zone.

The process of the present invention makes possible the production from a hydrocarbon of a gas mixture predominantly composed of carbon monoxide and hydrogen. In this process substantially complete conversion of the hydrocarbon to the desired gas mixture may be effected. In a typical operation, for example, methane may be converted to the extent of 97% with at least 90% of the converted methane going to carbon monoxide and hydrogen. These results may be achieved by the use of copper oxide as an oxygen carrier only when care is taken to control the feed rates of the hydrocarbon and the copper oxide to the hydrocarbon conversion zone. If a large excess of the copper oxide is employed, the hydrocarbon will be substantially completely converted, but the resulting gas will be practically entirely composed of carbon dioxide and water. It is not necessary to maintain a precise stoichiometric balance between the copper oxide and the hydrocarbon. A slight excess of the former will benefit the operation by converting more of the hydrocarbon to carbon dioxide with a resultant increase in the heat supply in the conversion zone. This, however, is at the expense of selectivity of the conversion to carbon monoxide and hydrogen, and is feasible only where an increased content of carbon dioxide can be tolerated in the make gas.

Another feature of the process of the present invention is that carbon formation during the hydrocarbon conversion is substantially eliminated. One of the difficulties encountered in previous attempts to oxidize hydrocarbons by a reducible metal oxide has been the loss of considerable quantities of the hydrocarbon in the form of carbon deposits on the finely divided metal or metal oxide. In extended periods of operations in accordance with the present invention no carbon was observed on the finely divided solid leaving the hydrocarbon conversion zone, and carbon balances on the operations indicated that substantially all of the carbon in the hydrocarbon was converted to useful gases.

There is evidence that in order to produce continuously a "make gas" of fairly uniform composition, according to the procedure outlined above, continuous control must be exercised on the feed rates of the hydrocarbon and metal oxide to the hydrocarbon conversion zone. The operator must be able to tell quickly when his "make gas" deviates from the desired composition so as to be able to quickly make the necessary adjustments to maintain the composition of the "make gas" uniform. More specifically, he must be able to ascertain if he is feeding to the hydrocarbon conversion one atom of oxygen for each atom of carbon, and he must always be able to ascertain if the reforming reaction is going to completion; that is to say, he may be feeding the proper proportions of carbon and oxygen, but the reforming activity of the contact mixture in the hydrocarbon conversion zone may decrease so that the composition of his "make gas" suffers.

According to a modification of the present invention, control of the operation of the aforesaid type may be readily effected by making a few simple determinations on the "make gas." For complete control, the operator must first determine the carbon dioxide content of the "make gas." Then, according to the present invention, the operator subjects a small quantity of the "make gas" to a reformation operation in which is utilized a highly active catalyst at a temperature sufficiently high to secure completion of the reforming reaction. The operator then determines the carbon dioxide content of the product of this reforming reaction. In order to make possible control of this type it is necessary to feed to the reactor an amount of copper oxide slightly in excess of the stoichiometrical equivalent of the carbon to produce carbon monoxide. In other words, it is necessary to ensure that the "make gas" will always contain some carbon dioxide. Thus the control method does not provide for maintenance of precise stoichiometrical quantities of copper oxide and carbon in the feed to the hydrocarbon conversion zone but for the maintenance of the slight excess of copper oxide over these proportions which may be tolerated.

If, in the practice of the control method of the present invention, the carbon dioxide content of the "make gas" exceeds a predetermined quantity the operator knows that he is feeding an excess of oxygen over the predetermined amount to the hydrocarbon conversion zone, or that the reforming reaction in the conversion zone is not going to completion. Then, if the off gas from the pilot reforming operation contains an amount of carbon dioxide in excess of that predetermined for satisfactory operation, he knows that he is feeding too much oxygen to the hydrocarbon conversion zone and can either reduce the oxygen feed or increase the carbon feed correspondingly. On the other hand, if the product gas from the pilot reforming operation contains an amount of carbon dioxide predetermined for satisfactory operation he knows that, the carbon dioxide content of the "make gas" being excessive, the reforming operation in the hydrocarbon conversion zone is not going to completion. This can be compensated for in the ordinary case by increasing the temperature in the hydrocarbon conversion zone or increasing the residence time of the reactants by slowing down the gas velocity in the hydrocarbon conversion zone.

Several types of devices for quickly determining the carbon dioxide content of a gas are known and any of these may be employed in the practice of the present invention. For example, the infra-red ray spectrometer quickly and accurately gives a measure of very minute amounts of carbon dioxide in gas; also, a conventional pH meter may be employed for this purpose, utilizing water as the medium in which the hydrogen electrode is immersed and passing the gas to be examined through the water. These and other types of indicators indicate the carbon dioxide content of the gas as an electrical quantity. This electrical quantity may be utilized to actuate valves controlling the feed of metal oxide or hydrocarbon or both to the hydrocarbon conversion zone. These specific control arrangements constitute no part of the present invention since, for the purpose of the present invention, the operator, having made the determinations which constitute the real control method of the present invention, can manipulate the feeds of the hydrocarbon and the metal oxide manually.

In the pilot reforming operation of this modification of the present invention there is employed a highly active catalyst such as nickel alumina catalysts prepared by coprecipitation of the nickel oxide and the alumina, or a copper silica gel catalyst which may likewise be prepared by a coprecipitation method or by impregnation of silica gel with a copper salt solution, followed by the usual drying, roasting and reducing steps. These catalysts are highly effective catalysts in this reforming operation, even at temperatures as low as 1600° F. In order, however, to ensure completion of this reaction, this pilot reforming unit is operated at a temperature between 2000 and 2400° F.

By way of explanation, it may be pointed out that if the feeds of copper oxide and hydrocarbon to the main process were in exactly stoichiometrical amounts for the production of carbon monoxide and hydrogen the gas produced in the pilot reforming step would contain only traces of carbon dioxide, regardless of what happened in the main process. If the copper oxide fed to the main process were supplied in excess of the amount to convert the hydrocarbon fed to carbon monoxide the products of the pilot reforming operation would contain a small amount of carbon dioxide which can be determined by calculation, regardless of what happened in the main process. Therefore, in accordance with the present invention control of the process is predicated on maintaining a content of carbon dioxide in the product gas of the pilot reforming operation between fixed relatively narrow limits, as, for example, between ½ and 2% or perhaps between 1 and 3%. If the carbon dioxide content of this gas falls below the fixed minimum, the operator knows that his feed of copper oxide to the hydrocarbon conversion step is deficient. On the other hand, if the carbon dioxide content of this gas exceeds the fixed maximum, the operator knows that his copper oxide feed to the hydrocarbon conversion step is excessive. It is to be emphasized, however, that knowledge of this one fact is not adquate to ensure proper control of the main process for the production of the desired "make gas." In addition the operator has to know the carbon dioxide content of the "make gas" itself.

The nature of the present invention may be more fully understood from the following detailed description of the accompanying drawings in which

Figure 1 is a front elevation in diagrammatic form of one type of apparatus in which the process of the present invention may be practiced and

Figure 2 is a similar illustration of the same apparatus including novel process control means.

Referring to Figure 1, numeral (1) designates a hydrocarbon conversion reactor, and numeral (2) designates a similar reactor in which metal is oxidized. These reactors may assume many shapes. In the form illustrated each reactor is cylindrical for most of its length, having a constricted entry portion (3) at its lower and surmounted by a grid (4) and having at its upper end an expanded section (5).

Depending from the expanded section (5) of reactor (1) is a drawoff leg or overflow pipe (6). The lower end of this pipe is connected with the bottom of reactor (2). In like manner a drawoff leg or overflow pipe (7) connects the expanded portion (5) of reactor (2) with the lower end of reactor (1). Pipes (6) and (7) may be provided at spaced points along their length with jets (8) through which aerating gas may be introduced into the pipes. In the case of pipe (6) a suitable aerating gas is the make gas from the reactor (1). For pipe (7) a suitable aerating gas is air, steam or any other non-reducing gas.

The make gas leaves the reactor (1) through line (9) which discharges into a cyclone separator (10) from the bottom of which separated solids are returned through leg (11) to drawoff pipe (6) and from the top of which make gas leaves the system through line (12). In like manner residual air leaves the upper end of the reactor (2) through line (13) which discharges into a cyclone separator (14) from the bottom of which separated solids are returned to overflow pipe (7) through leg (15) and from the upper end of which residual air leaves the system through line (16).

Near the lower end of overflow pipe (7) there is provided a flow control member (17) which may be a slide valve or other suitable device for controlling the flow of solid from pipe (7) into the bottom of reactor (1). Connected to the bottom of reactor (1) is an inlet line (18) for gasiform hydrocarbon controlled by valve (19). This line is preferably so connected as to pick up solids discharged from the lower end of pipe (7) and lift them upwardly through the reactor (1). Similarly connected to the lower end of reactor (2) is an inlet line (20) for air. It will be understood that these inlet lines for gasiform hydrocarbon and air may include suitable preheaters in which the fed gas is passed in the heat exchange relation with off-gases from the system, such as the gas in line (12) and the gas in line (16).

In practicing the present invention in a system such as that described, vessel (1) is charged with copper carried on a finely divided support while vessel (2) is charged with copper oxide carried on a finely divided support. The size of the charge in each vessel is preferably such that when gas is passed through the vessel, exerting a lifting effect on the finely divided solids, the charge will expand to fill the vessel and overflow through the lines (6) and (7) respectively. The respective vessels may readily be brought to operating temperature by burning hydrocarbon gas in them. With the vessels at a suitable operating temperature, usually between about 1600 and 1850° F., gasiform hydrocarbon material is fed in in controlled amounts through line (18) and supported on a finely divided carrier copper oxide in controlled amounts is fed simultaneously into the bottom of reactor (1). It is repeated that the rates of feed of these materials are such as to provide one atom of oxygen for each atom of carbon introduced as hydrocarbon feed into reactor (1). It may transpire that the amount of hydrocarbon permitted according to this formula will not be sufficient to provide adequate fluidization in the reactor (1). This deficiency may be supplied by recycling to the bottom of the reactor make gas from line (12) in adequate quantity to provide in the reactor (1) a rising gas stream having a velocity within the range heretofore specified adequate effectively to fluidize the finely divided solids in this vessel. With the operation on stream, reduced copper oxide supported on finely divided carrier continuously overflows from reactor (1) into overflow line (6) and is conducted to reactor (2) through which it is passed upwardly in a rising stream of air at a temperature suitable for the oxidation of copper.

Referring to Figure 2 in detail, numeral (101) designates a hydrocarbon conversion reactor, and (102) designates a metal oxygen reactor. Each of these reactors is provided at its lower end with a constricted portion (103), surmounted by a grid (104) and at its upper end with an expanded portion (105). Depending from the expanded portion (105) of reactor (101) is an overflow pipe (106) which is connected to the constricted portion of reactor (102). In like manner, an overflow pipe (107) connects the expanded portion (105) of reactor (102) with the restricted portion to the reactor (101). This pipe is provided with a slide valve or with another feed control element (108).

A feed line (109) for hydrocarbon gas is provided below the constricted portion (103) of reactor (101). This feed line is preferably arranged so as to pick up finely divided solid leaving the lower end of pipe (107) and carry it up into reactor (101). In like manner there is provided below the constricted portion (103) of reactor (102) a feed line (111) for air, arranged to pick up finely divided solid leaving the lower end of overflow pipe (106) and carry it up through reactor (102). A sufficient quantity of solids is maintained in the system so that when it is in operation finely divided solids are continuously overflowing from each reactor into the other.

Residual air leaves the top of (102) through line (112) which discharges into a cyclone (113) from the bottom of which separated solid is returned to pipe (107) through leg (114) and from the top of which residual air leaves the system through line (115).

"Make gas" leaves the top of reactor (101) through line (116) which discharges into a separator (117) from the bottom of which separated solid is returned to pipe (106) through leg (118) and from the top of which "make gas" leaves the system through line (119).

Attached to line (119) is a branch line (120) controlled by a valve (121). This line conducts a small portion of the "make gas" to an analytical unit (122) which is a suitable device of the type heretofore specified for indicating the carbon dioxide content of the "make gas." Also attached to line (119) is a branch line (123) controlled by a valve (123a) by manipulation of which a measured amount of "make gas" can be fed continuously to a reformation unit (124). This unit is illustrated merely as a reactor (124) which is loaded with reforming catalysts and is suitably heated by an electrical coil. It will be apparent, of course, that this reforming unit may assume many forms. It may, for example, be a unit operated according to the fluidized solid technique. The gas leaving this unit is piped by line (125) to an analytical unit (126) which will, in the ordinary case, be the same as unit (122).

The foregoing operation is conducted at substantially atmospheric pressure. The operation may be conducted at elevated pressure but as the operating pressure is increased, the temperature in the hydrocarbon conversion zone must be increased. It has heretofore been mentioned that the temperature in this zone will ordinarily be above 1500° F. and preferably between 1600° and 1850° F. Actually there is no upper limit on this temperature except that imposed by the ability of the apparatus to tolerate high temperatures. With increased pressures of the order of 400 lbs. per sq. inch, this temperature may be as high as 2400° F. and with higher pressures may be still higher.

As has already been indicated, the flow of materials through the reactor is only concurrent in the sense that both the gas and the solids enter the bottom of the reactor and leave at the top. Actually the finely divided solids are in a state of violent motion in which each individual particle may traverse the length of the reactor several times in the course of its passage therethrough. In other words the finely divided solid is present in the reactor in the form of a dense fluidized highly turbulent mixture which overflows into the drawoff lines in the same way as a liquid. It is to be borne in mind that this same dense bed may be maintained with a definite upper level in the reactor with drawoff from any part of the dense suspension, the upper level of the bed being determined by the rate of drawoff. It is a pecularity of this physical state of suspension that a distinct upper level may be maintained in a fixed position over a wide range of solid feed rate to the suspension.

Referring again to the supported copper, it may be mentioned that the amount of copper carried on the support may vary between about 3% and 30%. A very effective carrier is one containing about 15% of copper oxide supported on silica gel.

In operations according to the present invention the feed rate of the hydrocarbon gas may vary widely depending on other operating conditions. In general permissible feed rates will be higher the higher the operating pressure and temperature. Feed rates as low as 10 standard cubic feet of gas per hour per pound of copper in the reactor are contemplated, and this feed rate may be as high as 300—500 standard cubic feet of methane per hour per pound of copper in the reactor. The residence time of the oxygen carrier in the hydrocarbon conversion zone will vary according to the temperature of operation which in turn determines reaction rates between the metal oxide and the hydrocarbon. Actually the copper oxide appears to exist for a very brief period in the convertor. The item of importance is to provide in the convertor sufficient contact time between the upflowing gases and the copper to permit completion of the reforming reaction in this vessel.

The following table of data shows runs made in accordance with the fluidized solids technique with the catalyst according to the present invention, as well as with silica alone. In these runs the catalyst employed was prepared by dissolving a weighted amount of copper nitrate in water to which was added silica gel and additional water until a pasty mixture resulted. The mixture was then stirred and heated until the water was evaporated and the copper nitrate was largely decomposed to the oxide, after which the powder was placed in a muffle furnace at 1400° F. for about six hours to decompose any remaining oxide. The powder was then ground until the particle size was 50% between 100—200 mesh and 50% 200 mesh and smaller. The catalyst so prepared contains about 10% by weight of copper, the remaining being silica gel.

The finely ground catalyst was introduced into a reaction zone and the copper oxide reduced to copper with methane at a temperature of about 1600° F. and then a series of runs were made by passing a mixture of carbon dioxide and methane in substantially equal quantities upwardly through the reaction zone at a velocity such as to fluidize the finely divided catalyst in the reactor. Similar runs were made utilizing finely divided silica gel as the contact mass. The relevant data on these runs were as follows:

Run Number	1	2	4	5 SiO_2	6 SiO_2
Inlet gas rate, L/min., 1 atm, 70°F.	.772	.772	.985	.776	.776
Inlet gas composition, % CH_4	48.0	48.0	48.3	48.0	48.0
CO_2	50.0	50.0	49.7	50.0	50.0
N_2	2.0	2.0	2.0	2.0	2.0
Wt. cat. fluid, g.	200	200	200	160	160
Temp. of reactor, °F.	1630	1588	1600	1708	1590
Dry outlet gas rate L/min, 1 atm, 70° F.	1.44	1.42	1.54	.816	.786
Fract. CH_4 reacting	.93	.90	.68	.13	.04
Fract. CO_2 reacting	.97	.96	.83	.22	.13
Gas vel. entering bed, feet/sec.	.33	.32	.41	.34	.32
Composition of exit gas, dry basis % CO_2	.7	1.2	5.4	36.9	43.0
O_2	.2	.2	.4	—	—
H_2	48.0	46.3	36.5	8.2	3.0
CO	48.0	48.1	45.9	13.6	6.8
CH_4	1.8	2.7	9.8	39.8	45.1
N_2	1.3	1.5	2.0	1.4	1.8
Carbon deposition, % total carbon	4.0	2.4	2.6	3.2	1.7

The following table of data represents three runs at different temperatures and with slightly different ratios of copper oxide to methane and illustrates the variation in the result with temperature. The essential operating data are given in the table.

Run No.	9	10	11
Solid Used	15% Cu O deposited on silica gel from previous run in each case		
T°F.	1450	1600	1690
CH_4 in L/min. 40°F., 1 atm.	0.695	0.665	0.695
Dry exit gas in L/min. 40°F., 1 atm.	1.26	1.64	1.82
Solids rate grams/min.	1.52	1.56	1.54
Gas velocity in top of reactor ft./sec.	0.45	0.58	0.65
Exit Gas Composition			
CO_2	11.0	5.4	3.2
C_2H_4	—	—	—
O_2	0.3	0.1	0.3
H_2	45.8	61.5	64.3
CO	19.0	28.1	29.8
CH_4	20.0	2.7	0.9
N_2	3.9	2.2	1.5
	100.0	100.0	100.0
O/C ratio	1.11	1.23	1.07
fraction CH_4 decom.	.60	.94	.97
Sel. to CO, %	63	84	90.3

As is apparent from the above data the hydrocarbon conversion and the selectivity to carbon monoxide increased with temperature. It is noteworthy that in run 11 with an oxygen to carbon ratio of 1.07, the selectivity to carbon monoxide was 90.3 as compared with the selectivity of 84 in run 10 where this ratio was 1.23. The effect of this ratio is also reflected in the carbon dioxide content of the make gas in the respective runs.

By way of contrast a run was made in which the contact mass was a physical mixture of 15% CuO and 85% silica gel. The conversion temperature was 1600° F., and other operating factors were comparable to those of run 10. In this run only 27% of the methane was converted and the selectivity to carbon monoxide was only 6%.

In the runs tabulated above and in the run with the physical mixture of copper oxide and silica gel the finely divided solids were composed of a mixture of about 50% of solids, between 100 and 200 mesh, and about 50% below 200 mesh. In each of the tabulated runs fluidization was highly satisfactory and no carbon was perceptible in the solids removed from the hydrocarbon convertors.

From these data it can be seen that the copper on silica catalyst is a highly effective reforming catalyst giving practically complete conversion of methane and carbon dioxide to carbon monoxide and hydrogen at about 1600° F. Silica gel alone on the other hand at the same temperature effects practically no reaction between the carbon dioxide and the methane.

In order to test the relative effectiveness of copper on silica and copper on magnesia, two runs were made in which methane and copper oxide were fed to a fluidized bed of copper, the copper and the copper oxide both being supported on silica gel in one run and on magnesia in the other. In these runs part of the methane reacted with the copper oxide to produce a mixture of unreacted methane carbon dioxide and water, and this mixture was reformed by contact with the supported copper. The results obtained in these runs were as follows:

Run No.	2—2	5—8
	Mgo. (Periclase)	SiO_2 Silica Gel
	1540° 600 gms 10% CuO	1530° 200 gms 15% CuO
CO_2	20.3	5.0
O_2	0.6	0.2
H_2	6.5	43.1
CO	2.7	20.0
CH_4	58.1	12.8
N_2	11.8	18.9
	100.0	100.0
$\frac{H_2 \text{ formed}}{CH_4 \text{ reacted}}$	0.283	1.72
$\frac{CO \text{ formed}}{CH_4 \text{ reacted}}$	0.117	0.80
$\frac{CH_4 \text{ reacted}}{CH_4 \text{ in}}$	0.284	0.662
Gas Velocity Entering Bed ft./sec.	0.22	0.60
Bed Depth, Ft.	4	4

It will be seen that in the run using magnesia there was considerably more copper available, about twice as much, than in the silica gel run. Likewise the temperature was somewhat higher in the magnesia run. Nevertheless in the silica run the selectivity for carbon monoxide was about 90% as compared with 11.7% in the magnesia run, and the silica run about 66.2% of the methane was converted whereas in the magnesia run only 28.4% was converted. Furthermore in the silica run the through-put of gas was almost three times as great as in the magnesia run.

It is to be borne in mind that neither of these runs was conducted under the preferred conditions for the contact mass employed. Both performed considerably better at higher temperatures. The runs, however, are selected for illustrations, because they are so nearly comparable. They do demonstrate a very striking superiority of the silica gel supported copper over magnesia supported copper. Corresponding runs made with copper supported on alumina indicate that this material is intermediate the two compared above in effectiveness.

Throughout the specification and claims, the mesh screen sizes referred to are those defined by the United States Bureau of Standards, standard screen series, 1919.

Our Specification No. 635,909, which was not published at the date of application of the present case, claims 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.

It particularly claims such processes wherein the metal oxide yields on reduction free metal which is capable of acting as a reforming catalyst.

The present invention is, however, directed to the use of metallic copper supported on a finely divided support as the contact material.

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 process for converting a hydrocarbon into a gas containing carbon monoxide and hydrogen which comprises passing the hydrocarbon in gaseous form upward through a reaction zone at an elevated temperature containing a bed of finely divided contact material comprising metallic copper carried on a finely divided support at such a velocity to maintain the said finely divided contact material in the form of a dense highly turbulent mass of solid suspended in the gas, and continuously feeding to the said reaction zone an amount of copper oxide supported on a finely divided supporting material stoichiometrically equivalent to the amount of hydrocarbon fed to the said reaction zone, continuously removing the product gas from said reaction zone and continuously removing metallic copper carried on a finely divided supporting material from said reaction zone.

2. A process as claimed in claim 1 wherein the metallic copper carried on the finely divided supporting material withdrawn from the reaction zone is transferred to a regeneration zone where it is contacted with an upflowing stream of air or oxidizing gas at such a velocity to maintain the material in the form of a dense turbulent fluidized mass and under such conditions of temperature and pressure to convert the copper to copper oxide and withdrawing copper oxide carried on a finely divided supporting material from said regeneration zone and transferring it to the reaction zone.

3. A process as claimed in claims 1 or 2 in which two interconnecting beds of metallic copper carried on a finely divided supporting material are maintained, a gaseous hydrocarbon is passed at an elevated temperature upwardly through the first of said beds at a velocity sufficient to maintain said bed in a fluidized state, an oxidizing gas is passed upwardly through the second bed at a velocity sufficient to maintain the said bed in a fluidized state and at a temperature to convert the metallic copper to copper oxide, a product gas is continuously removed from first of said beds, a quantity of copper in the finely divided support is continuously removed from said first bed and passed to said second bed and a quantity of copper oxide on finely divided supporting material is continuously removed from said second bed and transferred to said first bed.

4. A process as claimed in claims 1—3 wherein the hydrocarbon conversion reaction is carried out at a temperature above 1500° F. and preferably between 1600° F. and 1850° F.

5. A process as claimed in any of claims 1 to 4 wherein the contact material comprises copper carried on alumina, magnesia or silica and preferably silica gel.

6. A process as claimed in claim 1 to 5 wherein the contact material is prepared by impregnating the support with a solution of a copper salt, drying, calcining and reducing the impregnated carrier.

7. A method as claimed in any of claims 1—5 wherein the contact material is prepared by coprecipitating copper oxide and the supporting material from solutions of salts of the respective metals, drying the precipitates and reducing it to convert the copper oxide to copper.

8. A process as claimed in claims 1—7 wherein the contact material contains from 3 to 30% by weight of copper.

9. A process as claimed in any of claims 1—8 wherein the contact material is employed in the form of particles ranging in size from 5 microns to 100 mesh and contains a substantial proportion of particles between 200 and 400 mesh.

10. A process as claimed in claim 9 wherein the contact material contains 50% of particles having a size between 100 mesh and 200 mesh and the remainder smaller than 200 mesh.

11. A modification of process as claimed in any of the preceding claims wherein slightly more than the stoichiometric quantity of copper oxide is fed to the reaction zone and the amount of such excess copper oxide added is determined by determining the carbon dioxide content of the make gas, by subjecting a portion of the said gas to an additional reforming operation controlled to ensure complete reaction between any hydrocarbon carbon dioxide and water contained therein and determining the amount of carbon dioxide

from this reforming operation.

12. A process as claimed in claim 11 wherein the make gas is reformed by being contacted with copper supported on a finely divided support at a temperature between 2000 and 2400° F.

13. A process as claimed in claims 11 and 12 wherein the feeds of metal oxide and hydrocarbon to the reaction zone are controlled to maintain the carbon dioxide content of the product gas from the reformation of the make gas between ½ and 3%.

14. A process as claimed in any of claims 11—13 where the amount of copper oxide fed to the reaction zone is controlled to be between ½% and 2%, in excess of the stoichiometrical quantity required to convert the carbon in the hydrocarbon feed to carbon monoxide.

15. The process for the conversion of hydrocarbons to a gaseous mixture of carbon monoxide and hydrogen as hereinbefore described.

Dated this 8th day of March, 1949.

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FIG.1.

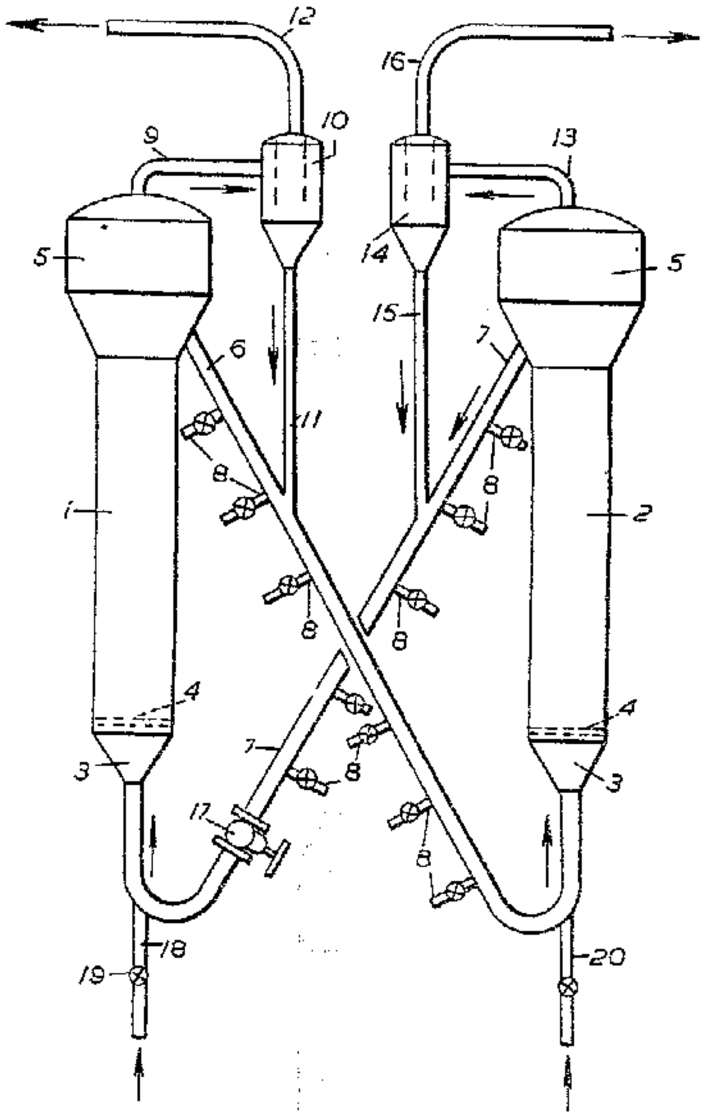

FIG.2.

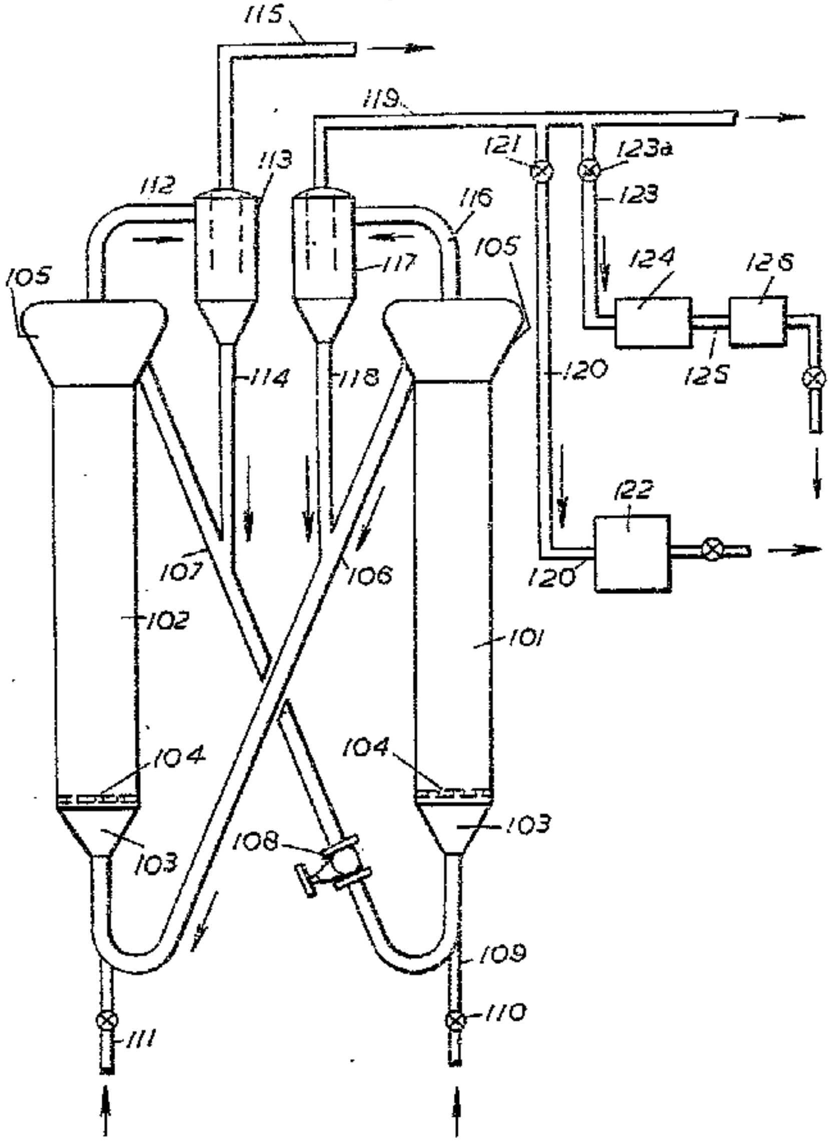

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FIG 1.

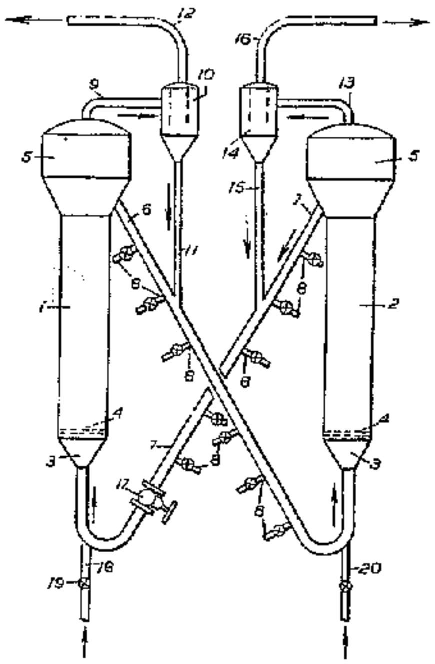

FIG 2