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SYNTHESIS OF METHANE

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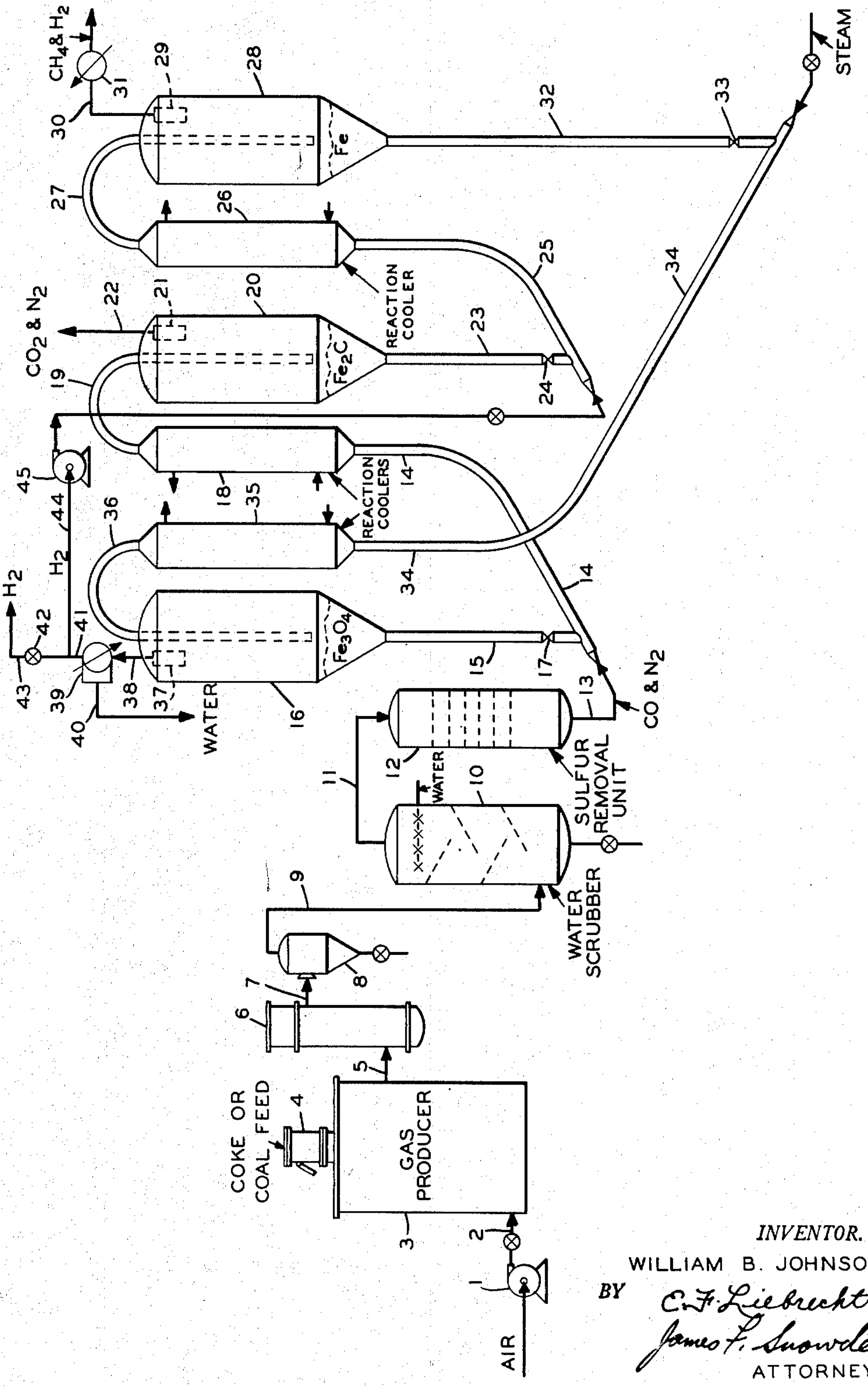

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UNITED STATES PATENT OFFICE

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SYNTHESIS OF METHANE

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16 Claims. (Cl. 260—676)

This invention relates to a synthesis of methane from carbon monoxide and steam; more particularly it is concerned with a synthesis in which producer gas is the source of the carbon monoxide. In this manner a gas of low heating value is converted into one of high B. t. u. content.

Producer gas, although easily made from any available type of coal or coke, is of comparatively limited utility because of its extremely low gross heating value of approximately 136 B. t. u. per cubic foot. While this gas is widely used in industry, it is not distributed without enrichment to the public. In addition, larger distribution lines are required as the use of a greater volume of gas is necessary to furnish any given quantity of heat. Consequently, there is a need for an economical process for obtaining a gas of high heating value from the product of a simple and inexpensive producer gas system. This richer gas should desirably be suitable for mixing with any heating gas in order that it may serve as an enriching agent for manufactured gases and as an extender for limited supplies of natural gas. Methane is ideal for the purpose in view of its high heating value, low toxicity and the close similarity of its combustion characteristics to those of common natural gases. Moreover, the proper utilization of methane is already well understood by public utility companies, servicemen and gas appliance manufacturers.

Other processes for the synthesis of hydrocarbons from carbon monoxide have involved the preliminary removal of inert nitrogen from air and the burning of coal or coke in relatively pure oxygen. However, elimination of nitrogen by liquefaction and fractional distillation of air is a very costly process. Further, the extremely high temperatures produced by the combustion of coal or coke in oxygen introduced major design problems. The process of the present invention avoids the disadvantages and difficulties inherent in these steps.

An object of the invention is to provide a synthesis for methane in which the only reactants consumed are inexpensive and readily available.

A second object of the invention is to provide an improved method for manufacturing a gas of high heating value.

A third object of the invention is to provide a method for synthesizing methane from producer gas which does not require a preliminary removal of nitrogen.

A fourth object of the invention is to provide a synthesis of methane which does not involve burning coal or coke in substantially pure oxygen.

A fifth object of the invention is to provide a new process for making methane in which substantially pure hydrogen is also produced.

A sixth object of the invention is to provide an economical, continuous, cyclic process for producing methane and hydrogen from inexpensive and readily available raw materials.

Other objects of the invention will in part be obvious and will in part appear in the detailed description hereinafter.

The present invention concerns a cyclic process for synthesizing methane from carbon monoxide, preferably furnished by producer gas, and steam in which a carbide-forming metal is reacted with steam at a sufficiently high temperature to produce hydrogen and an oxide of the metal. The metal oxide is then carbided with carbon monoxide at a suitably elevated temperature and the metal carbide is reduced with the aforementioned hydrogen at a temperature high enough to produce methane and regenerate the metal. The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified in the method hereinafter disclosed, and the scope of the invention will be indicated in the claims.

The process of the present invention consumes only air, water and either coal or coke in producing methane and hydrogen, for the metal in powdered form is regenerated and recycled, while the hydrogen required in one step is produced in excess in another reaction. Moreover, no extreme temperatures are encountered, since the coal or coke may be burned in air rather than substantially pure oxygen. Nitrogen and other inerts, as well as carbon dioxide, are eliminated inexpensively and without difficulty by merely venting all gaseous products of the carbiding reaction to the atmosphere; alternatively, some or all of the nitrogen may be recovered in relatively pure form. All of the chemical changes described hereinafter are exothermic and the water employed as a coolant in a variety of heat exchangers provides a more than ample supply of steam for the oxidation step. In the preferred process the oxidation, carbiding and reduction reactions are carried out simultaneously and continuously in different reaction zones by circulating the fluidized solids through the system.

The base metal employed in the process is a reactant and not a catalyst in the true sense of the term. Nevertheless, catalysts may be advantageously used along with the carbide-forming

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metal in practicing the present invention, for they permit the carbiding operation to be conducted at lower temperatures. Examples of such catalysts include manganous oxide, manganese dioxide and copper, among others; and they are used in small quantities, as for instance 1% or 2% by weight of the metal reactant.

Promoters in small amounts ranging up to 1.5% of the weight of the base metal may also be added to the carbide-forming metal or to the mixture of metal and catalyst. These substances increase the carbon content of the metal carbide, thereby permitting a reduction in the quantity of primary metal employed in the process. Non-volatile alkali and alkaline earth oxides, as for instance the oxides, hydroxides and carbonates of potassium, sodium, calcium, strontium and barium are suitable promoters. In general, it may be said that any catalyst or promoter which has been successfully used in the Fischer-Tropsch synthesis will produce equivalent effects in the present process.

Any metal capable of forming a carbide may be utilized in this synthesis. Iron, cobalt, nickel, zinc, manganese, chromium, tin, and molybdenum constitute only a few of the metals available for the purpose. The first three named, which make up the fourth period of group VIII of the periodic table of elements, appear superior to the others, and iron is the preferred metal by reason of low cost and high activity. Best results are secured when the metal is in fluidized form in order to obtain the advantages inherent in a continuous, cyclic, fluidized process in which the solid reactants are rapidly circulated while suspended in streams of gaseous reactants, and flow under the influence of gravity like pseudo-liquids developing pseudo-hydrostatic fluistatic pressures after separation from the gas streams. Fluidized operations not only provide superior control of reaction temperatures but also afford maximum surface contact between the reacting gases and solids. Moreover, due to the increased surface area of the fluidized solids, their chemical activity is enhanced and all of the reactions involving them are carried out at lower temperatures than is the case with larger particles.

For the application of the fluid technique described herein, the powder should all pass through a 40-mesh screen. But to reduce the minimum transport velocity in the reaction coolers and to minimize bridging or blocking during gravity flow down the hoppers and standpipes, it is desirable to have a range of particle sizes averaging about 200-mesh or finer.

The temperatures of each of the three reactions involving a metal or compound thereof vary with the different carbide-forming metals; those required for iron, cobalt and nickel are set forth below. Pressures ranging from atmospheric to 50 pounds per square inch gage (p. s. i. g.) are recommended for all three reactions, but higher pressures, up to say 500 p. s. i. g., may be justified in order to increase reaction rates or permit the use of smaller and less expensive equipment.

As the source of carbon monoxide, producer gas is preferably employed in the instant process; its production is exemplified in the following equation:

I. $$\text{Air }(7O_2+26N_2)+14C\rightarrow 14CO+26N_2$$

Water gas may be substituted but is less satisfactory inasmuch as the relatively large quantity of hydrogen present reduces the carbon efficiency in the carbiding reaction. For the same reason, coke is a better fuel for the producer than coal inasmuch as coal producer gas contains a minor amount of hydrogen.

Carbon monoxide from any other source may be used provided there are no excessive quantities of impurities which will inhibit or interfere with the carbiding reaction described below unless such impurities can be removed in a commercially feasible manner.

In another step a carbide-forming metal at an elevated temperature is oxidized with steam to produce a metal oxide and hydrogen.

II. $$6Fe+8H_2O\rightarrow 2Fe_3O_4+8H_2$$

An excess of steam, amounting to say 50%, is recommended to obtain substantial completion of the reaction. The broad range of operative reaction temperatures runs from 700 to 1200 degrees Fahrenheit for iron and from 800 to 1200 degrees Fahrenheit in the case of either cobalt or nickel. Within these ranges higher temperatures increase the reaction rate but reduce the yield slightly in the case of finely divided iron; accordingly, it is recommended that, with iron, the temperature be maintained between 950 and 1050 degrees Fahrenheit.

The oxide, such as fluidized ferrosic oxide, is then reacted with the producer gas to form a metal carbide.

III. $$2Fe_3O_4+14CO+26N_2\rightarrow 3Fe_2C+11CO_2+26N_2$$

This reaction proceeds very rapidly and a more active carbide results when pressures ranging from atmospheric up to 30 p. s. i. g. are employed. It is thought that a variety of carbides of the selected metal are actually produced, especially when ferrosic oxide is involved. However, the carbon content of the mixture of iron carbides appears to approximate that of ferrous carbide and the product may be regarded as ferrous carbide for all practical purposes. The nitrogen in the producer gas is inactive in this reaction and the only effects due to its presence arise from its reduction of the carbon monoxide partial pressure. In this instance only the solid resultant is essential in the present process, so the gaseous products as well as inert gases are usually vented to the atmosphere. However, a portion of the exhaust gases may be scrubbed free of carbon dioxide in any suitable manner to provide substantially pure nitrogen which may be added to the excess of almost pure hydrogen produced in reaction II to form a satisfactory feed for an ammonia synthesis plant. In addition, the carbon dioxide may be recovered from the absorption liquid and recycled back to the gas producer where it will be reduced by the incandescent coke to carbon monoxide thereby increasing the carbon efficiency of the process.

The yield of metal carbide is substantially that of theory when an excess of ferrosic oxide is employed. Where the carbon monoxide is in excess, an undesirable deposition of carbon on the ferrous carbide occurs. Not only does this reduce the carbon efficiency of the process, but it also retards the subsequent reduction of the metal carbide to methane and iron. An excess of ferrosic oxide on the other hand increases the carbiding rate and this excess of solids permits better control of heat transfer throughout the system without interfering with the other reactions of the process cycle. Thus, a deficiency of the oxide is disadvantageous and it should be present in at least stoichiometric proportions or an ex-

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cess ranging up to say 1000% or more. Preferably the excess of ferrosic oxide amounts to 50 to 150% over theory.

A particular advantage is realized here by using a concurrent flow fluidized process in that the very fast reaction rate is not slowed down as it is in the case of a dense phase fixed or circulating bed of ferrosic oxide where the rate is reduced by the introduction of carbon monoxide into solids of sub-normal activity due to their substantial ferrous carbide content and also by the increasing concentration of carbon dioxide as the gases rise through the bed.

Suitable temperature ranges for the carbiding operation are 450 to 800 degrees Fahrenheit in the case of iron, 550 to 650 degrees Fahrenheit being preferred, and 300 to 500 degrees Fahrenheit for either cobalt or nickel. Lowering the temperature favors the reaction equilibrium while raising it increases the reaction rate.

Next the metal carbide is reacted with all or a portion of the hydrogen produced in reaction II. The hydrogen reduces the carbide to the metal and combines with the carbon liberated to form methane.

IV. $3Fe_2C+6H_2 \rightarrow 6Fe+3CH_4$

Moderately elevated pressures of a few atmospheres favor the reaction, while higher pressures tend to yield higher hydrocarbons than methane. With stoichiometric proportions of reactants this fairly rapid reaction proceeds to over 95% of completion, and where hydrogen in a desirable excess of about 10% is used, the yields are very close to that of theory. It will be noted that the hydrogen produced in reaction II amounts to one-third more than is required for reaction IV, and all of this excess may be employed in the latter reaction where a product gas of somewhat lower heating value is acceptable. The operative temperature range for iron extends from 650 to 950 degrees Fahrenheit and the latter figure should not be exceeded inasmuch as iron begins to soften and become somewhat tacky at 950 degrees. For iron the recommended temperature range is from 750 to 800 degrees Fahrenheit. Considerably less heat is required for cobalt or nickel as the temperature may range from 400 to 600 degrees Fahrenheit.

The invention is best understood by reference to the accompanying drawing which is a flow sheet of the novel process in its preferred form. This figure is purely schematic in nature and is not intended to illustrate the optimum locations or dimensions of any of the apparatus depicted.

Air from the blower **1** is supplied through valved line **2** to gas producer **3** which is preferably of the slagging type. The coke or coal feed for the producer enters through hopper **4** and the producer gas passes through line **5** to a waste heat boiler **6** where it gives up most of its heat. Leaving through line **7**, the gas passes to a cyclone separator **8** in which fly ash is removed from the gas stream. Pipe **9** carries the gas to a scrubber **10** where it is scrubbed with water to further cool it and remove any dust, carbon or remaining ash. It is then transferred through line **11** to a conventional sulfur removal unit **12**. This device need only be employed where the sulfur content of the coke or coal is sufficient to inhibit the carbiding reaction, and any equipment suitable for removing sulfur from city gas will serve the purpose here. At this point the moisture content of the producer gas is insufficient to interfere with the subsequent reaction with ferrosic oxide.

Next the gaseous mixture, consisting chiefly of nitrogen and carbon monoxide, proceeds through pipe **13** into transport line **14** where the hot fluidized ferrosic oxide, usually in stoichiometric excess, is injected from standpipe **15** attached to a sealed vessel **16** and controlled by a slide valve **17**. If necessary a small quantity of a suitable aerating agent, such as steam, may be introduced into pipe **15** and also at the bottom of hopper **16** at one or more points to maintain the finely divided oxide in fluidized condition. As the powdered oxide sweeps up through line **14** as a dilute turbulent suspension in the carrier stream of gases an exothermic reaction commences in which the carbide of the metal is formed. The density of the suspension in this carrier line is a function of the static pressure and the preferred range is from 0.3 to 5.0 lbs./cu. ft. The optimum velocity of the mixture is about 20 to 30 ft./sec. Such conditions are readily obtained by known design principles in selecting the proper pressure drop through pipe **14** and choosing an internal diameter for this line adequate for the flow rates of reactants. The heat necessary to initiate the reaction is furnished by the ferrosic oxide which enters pipe **14** at a temperature in the neighborhood of 1000 degrees Fahrenheit for the producer gas is not far above atmospheric temperature. A water-cooled reaction cooler **18** is provided to maintain a reaction temperature of 550 to 650 degrees Fahrenheit. In this vessel, the reaction zone is of greater cross-sectional area than line **14**, thereby reducing the velocity of the suspension to about 3 to 10 ft./sec. and increasing its density to approximately 20 to 40 lbs./cu. ft. The length of this reaction zone is of course determined by the requirements of adequate time for the reaction and sufficient heat transfer area to maintain the reaction temperature within the limits indicated. Line **19** which carries the mixture into the closed vessel **20** extends well down into the interior but not below the surface of the dense bed (approximately 70 to 100 lbs./cu. ft.) of iron carbide and excess ferrosic oxide stored therein. At this point the gases in the mixture, chiefly carbon dioxide and nitrogen under a pressure of 20 to 30 p. s. i. g., separate from the finely divided solids, and the settling or separation efficiency is enhanced greatly by the downward discharge of the suspension into settler **20**. The diameter of this vessel is selected to provide an upward velocity of gases therein of from 1 to 2 ft./sec. and its length is designed to furnish storage space for an ample supply of the metal compounds plus sufficient disengaging space thereabove to attain the optimum gravity separation of powder from the gases. The gases are exhausted to the atmosphere through a filtering device **21** and exhaust pipe **22**. Any entrained fine particles are removed by the filter, which is preferably of porous metal or ceramic construction, and consists of several sections. A valve arrangement operated by an automatic time cycle controller (not shown) is provided to clear the filter of adhering powder by blowing back the exit gases through each section of the filter in succession. This mechanism is so adjusted as to always be clearing one section of the filter while the other sections are filtering the exhaust gases. If a cyclone separator is used in place of the filter, the exit gases from the cyclone should

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be passed through a water scrubber to avoid the loss of fines.

In the event that either the nitrogen or carbon dioxide in the exhaust gases are to be recovered, line 22 is connected to an absorber or scrubber (not shown) where the carbon dioxide is dissolved by passing the gases through any suitable absorption liquid from which the carbon dioxide may later be recovered. The absorber effluent consists of relatively pure nitrogen contaminated with the rare gases of the atmosphere in small amounts along with lesser quantities of unreacted carbon monoxide and perhaps hydrogen.

The hot metal carbide and oxide, at a temperature only a few degrees below that in reactor 18, descend from tank 20 through standpipe 23 controlled by slide valve 24 into a rapid current of hydrogen in line 25. Any aeration necessary for tank 20 or pipe 23 can be supplied by flue gases or by compressing and recycling the effluent from line 22. The hydrogen employed in this step is produced in excess in the oxidation of the metal as described hereinafter. Since this gas is comparatively cool, the hot solids furnish all or most of the heat required to start the rapid exothermic reaction. In pipe 25 and enlarged reaction cooler 26, which maintains the reaction temperature between 750 and 800 degrees Fahrenheit, the metal carbide in the suspension is reduced while in concurrent flow to iron and methane by the hydrogen which is preferably present in 10% stoichiometric excess. This powdered iron and ferrosic oxide suspension is then discharged by line 27 just above the bed of solids in hopper 28 where the pressure is in the 20 to 30 p. s. i. g. range. The methane and any unreacted hydrogen separate from the powder and leave through filtering device 29, similar to filter 21. Thereafter the product gas is passed through pipe 30, cooler 31 and then to suitable storage facilities.

From the bottom of vessel 28, where the density is of the order of 70 to 100 lbs./cu. ft. and its temperature only slightly below that of reaction cooler 26, the hot fluidized metal and excess oxide flow down standpipe 32 controlled by slide valve 33 to carrier line 34 and are there picked up by a swift, valve-controlled stream of steam from the boiler 6 or reaction coolers. The turbulent suspension of reactants passes through enlarged reaction cooler 35 maintained at 950 to 1050 degrees Fahrenheit and the powder is deposited by pipe 36 in tank 16 on top of the layer of metal oxide which has a density of about 50 to 80 lbs./cu. ft. The steam enters transport line 34 at a pressure equal to the 20 to 30 p. s. i. g. maintained in hopper 16 plus the designed pressure drop between the bottom of standpipe 32 and hopper 16. Its temperature is adjusted to the minimum required to initiate reaction with the iron in the powdered mixture to form hydrogen and ferrosic oxide while in transport to the receiving hopper.

The hydrogen and excess steam leave tank 16 through the cyclone or filter 37 which separates the fines. Since the steam constituent of the effluent in pipe 38 will inhibit the reduction of iron carbide by hydrogen in the following step of the cycle, as much moisture as possible is condensed out of the mixture in a water-cooled condenser from which the condensate leaves by trap line 40 while the hydrogen passes up pipe 41. By suitable adjustment of valve 42 some or all of the excess hydrogen may be drawn off, if desired, through line 43 as a substantially pure product while the remainder is recycled through pipe 44 and compressor 45 to transport line 25 for the reduction stage of the process. Any excess hydrogen recycled through the reduction step is not lost and will be recovered along with the methane from cooler 31.

Where it is necessary, to aerate the bottom of tank 28 and/or line 32, this may be accomplished with either some of the excess hydrogen from pipe 43 or 44 or product gas from cooler 31.

In maintaining the desired concurrent flow in all three reactions involving fluidized solids, the maintenance of approximately equal velocities in carrier lines 14, 19, 25, 27, 34 and 36 of from 20 to 30 ft./sec. is recommended and the densities in these lines are from 0.3 to 5 lbs./cu. ft. depending on reaction pressure. The velocities in reaction coolers 18, 26 and 35 are preferably 3 to 10 ft./sec. and the suspensions there have densities of 20 to 40 lbs./cu. ft. In settlers or hoppers 16, 20 and 28, upward gas velocities of from 1 to 2 ft./sec. are preferred. These velocities are obtained by designing this equipment along the lines indicated previously.

The proper lengths of standpipes 15, 23 and 32 are determined in conventional manner to produce sufficient fluistatic pressure to inject the solid reactant into the carrier lines at suitable rates. Since none of the hoppers may collect fluidized solids at a greater rate than the other settlers over an extended period without throwing the system out of operating balance, it is apparent that the flow rates of solids, calculated as Fe, down each of the three standpipes must be equal in the long run. Therefore, the operating adjustments on the plant to attain the desired velocities and stoichiometry will be made on the fluid reactants by means of the valves in lines 2, 44 and the steam line.

In the event that it proves desirable to achieve better control of reactant temperatures, this may be readily accomplished by the installation of heat exchangers in one or more of the reactant supply lines (the standpipes and pipes 13 and 44) to heat or cool the reactant to the desired figure.

The process described above is cyclic and involves the rapid circulation of fluidized solids with the various reactions occurring simultaneously and continuously in different reaction zones. This represents the greatly preferred form. Nevertheless, it is readily apparent that the process can be performed in an intermittent manner with all reactions occurring in sequence in a single reaction zone, or alternatively in fixed beds of solids in three reactors using known cycle control devices. In such cases, the particle size of the solid reactant may range from the fine powders discussed hereinbefore up to granules of approximately 3/8" diameter. However, it is to be understood that the efficiency of the intermittent cyclic process is considerably below that of the continuous circulatory one because the reactor or reactors would necessarily be kept at a single average temperature rather than in the optimum range for each of the reactions and the temperature control in a wide fixed bed is inferior to that obtainable in a turbulent circulating suspension of the solids in a relatively narrow stream of gas. Where the fixed bed consists of granular rather than fluidized solids, the variations in temperature in various parts of the bed are far greater and higher reaction temperatures are required. In addition the operating costs of the intermittent process would obviously be much greater than the circulating continuous process.

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Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described, and all statements of the scope of the invention, which as a matter of language might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent, is:

I claim:

1. A cyclic process for the synthesis of methane from carbon monoxide and steam which comprises reacting a carbide-forming metal obtained from the reduction step mentioned hereinafter with steam at a temperature sufficiently elevated to produce principally hydrogen and an oxide of the metal, reacting carbon monoxide with said metal oxide at a temperature sufficiently elevated to produce a carbide of the metal, and reducing said metal carbide with a least a portion of said hydrogen at a temperature sufficiently elevated to produce the metal and a gasiform mixture comprising chiefly methane.

2. A process according to claim 1 in which the metal and said metal compounds are in fluidized form.

3. A cyclic process for the synthesis of methane from carbon monoxide and steam which comprises reacting a metal of the fourth period of Group VIII of the Periodic Table of Elements obtained from the reduction step mentioned hereinafter with steam at a temperature sufficiently elevated to produce principally hydrogen and an oxide of the metal, reacting carbon monoxide with said metal oxide at a temperature sufficiently elevated to produce a carbide of the metal, and reducing said metal carbide with at least a portion of said hydrogen at a temperature sufficiently elevated to produce the metal and a gasiform mixture comprising chiefly methane.

4. A cyclic process for the synthesis of methane from carbon monoxide and steam which comprises reacting iron obtained from the reduction step mentioned hereinafter with steam at a temperature sufficiently elevated to produce principally hydrogen and ferrosic oxide, reacting carbon monoxide with the ferrosic oxide at a temperature sufficiently elevated to produce a carbide of iron, and reducing said carbide of iron with at least a portion of said hydrogen at a temperature sufficiently elevated to produce iron and a gasiform mixture comprising chiefly methane.

5. A cyclic process for the synthesis of methane from carbon monoxide and steam which comprises reacting cobalt obtained from the reduction step mentioned hereinafter with steam at a temperature sufficiently elevated to produce principally hydrogen and an oxide of cobalt, reacting carbon monoxide with said oxide of cobalt at a temperature sufficiently elevated to produce a carbide of cobalt, and reducing said carbide of cobalt with at least a portion of said hydrogen at a temperature sufficiently elevated to produce cobalt and a gasiform mixture comprising chiefly methane.

6. A cyclic process for the synthesis of methane from carbon monoxide and steam which comprises reacting nickel obtained from the reduction step mentioned hereinafter with steam at a temperature sufficiently elevated to produce principally hydrogen and an oxide of nickel, reacting carbon monoxide with said oxide of nickel at a temperature sufficiently elevated to produce a carbide of nickel, and reducing said carbide of nickel with at least a portion of said hydrogen at a temperature sufficiently elevated to produce nickel and a gasiform mixture comprising chiefly methane.

7. A cyclic process for the synthesis of methane from carbon monoxide and steam which comprises reacting iron obtained from the reduction step mentioned hereinafter with steam at a temperature of from 700 to 1200 degrees Fahrenheit to produce principally hydrogen and ferrosic oxide, reacting carbon monoxide with the ferrosic oxide at a temperature of from 450 to 800 degrees Fahrenheit to produce a carbide of iron, and reducing said carbide of iron with at least a portion of said hydrogen at a temperature of from 650 to 950 degrees Fahrenheit to produce iron and a gasiform mixture comprising chiefly methane.

8. A process according to claim 7 in which the iron and said iron compounds are in fluidized form.

9. A cyclic process for the synthesis of methane from carbon monoxide and steam which comprises oxidizing iron obtained from the reduction step mentioned hereinafter with steam at a temperature of from 950 to 1050 degrees Fahrenheit to produce principally hydrogen and ferrosic oxide, reacting carbon monoxide with the ferrosic oxide at a temperature of from 550 to 650 degrees Fahrenheit to produce a carbide of iron, and reducing said carbide of iron with at least a portion of said hydrogen at a temperature of from 750 to 800 degrees Fahrenheit to produce iron and a gasiform mixture comprising chiefly methane.

10. A process according to claim 9 in which all reactions take place at less than 50 pounds per square inch gauge pressure.

11. A cyclic process for the synthesis of a gas of high heating value which comprises burning carbonaceous matter in a restricted quantity of air to form producer gas, reacting a carbide-forming metal obtained from the reduction step mentioned hereinafter with steam at a temperature sufficiently elevated to produce principally hydrogen and an oxide of the metal, reacting the producer gas with said metal oxide at a temperature sufficiently elevated to produce a carbide of the metal, and reducing said metal carbide with at least a portion of said hydrogen at a temperature sufficiently elevated to produce the metal and a gasiform mixture comprising chiefly methane.

12. A process according to claim 11 in which the metal and said metal compounds are in fluidized form.

13. A cyclic process for the synthesis of a gas of high heating value which comprises burning carbonaceous matter with a restricted quantity of air to form producer gas, oxidizing iron obtained from the reduction step mentioned hereinafter with steam at a temperature of from 700 to 1200 degrees Fahrenheit to produce principally hydrogen and ferrosic oxide, reacting the producer gas with the ferrosic oxide at a temperature of from 450 to 800 degrees Fahrenheit to produce a carbide of iron, and reducing said carbide of iron with at least a portion of said hydrogen at a temperature of from 650 to 950 degrees Fahrenheit to produce iron and a gasiform mixture comprising chiefly methane.

14. A continuous cyclic process for the syn-

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thesis of methane from carbon monoxide and steam which comprises oxidizing a suspension of a carbide-forming fluidized metal obtained from the reduction step mentioned hereinafter with a carrier stream of steam at a temperature sufficiently elevated to produce principally hydrogen and an oxide of the metal, separating the hydrogen and said metal oxide, reacting a suspension of said fluidized metal oxide with a carrier stream of carbon monoxide at a temperature sufficiently elevated to produce a carbide of the metal, separating said metal carbide from the gases in the reaction products, reducing a suspension of said fluidized metal carbide with a carrier stream comprising at least a portion of said hydrogen at a temperature sufficiently elevated to produce the metal and a gasiform mixture comprising chiefly methane, and separating the fluidized metal and the methane.

15. A continuous cyclic process for the synthesis of methane from carbon monoxide and steam which comprises oxidizing a suspension of fluidized iron obtained from the reduction step mentioned hereinafter with a carrier stream of steam at a temperature of from 700 to 1200 degrees Fahrenheit to produce principally hydrogen and ferrosic oxide, separating the hydrogen and ferrosic oxide, reacting a suspension of the fluidized ferrosic oxide with a carrier stream of carbon monoxide at a temperature of from 450 to 800 degrees Fahrenheit to produce a carbide of iron, separating said carbide of iron from the gases in the reaction products, reducing a suspension of said fluidized carbide of iron with a carrier stream comprising at least a portion of said hydrogen at a temperature of from 650 to 950 degrees Fahrenheit to produce iron and a gasiform mixture comprising chiefly methane, and separating the fluidized iron and the methane.

16. A continuous cyclic process for the synthesis of a gas of high heating value which comprises burning carbonaceous matter in a restricted quantity of air to form producer gas, oxidizing a suspension of fluidized iron obtained from the reduction step mentioned hereinafter with a carrier stream of steam at a temperature of from 700 to 1200 degrees Fahrenheit to produce principally hydrogen and ferrosic oxide, separating the ferrosic oxide and the hydrogen, reacting a suspension of the fluidized ferrosic oxide with a carrier stream of producer gas at a temperature of from 450 to 800 degrees Fahrenheit to produce a carbide of iron, separating said carbide of iron from the gases in the reaction products, reducing a suspension of said fluidized carbide of iron with a carrier stream comprising at least a portion of said hydrogen at a temperature of from 650 to 950 degrees Fahrenheit to produce iron and a gasiform mixture comprising chiefly methane, and separating the fluidized iron and the methane.

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