United States Patent

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[54] **AGGREGATE PROCESS FOR PETROLEUM PRODUCTION**
10 Claims, 6 Drawing Figs.

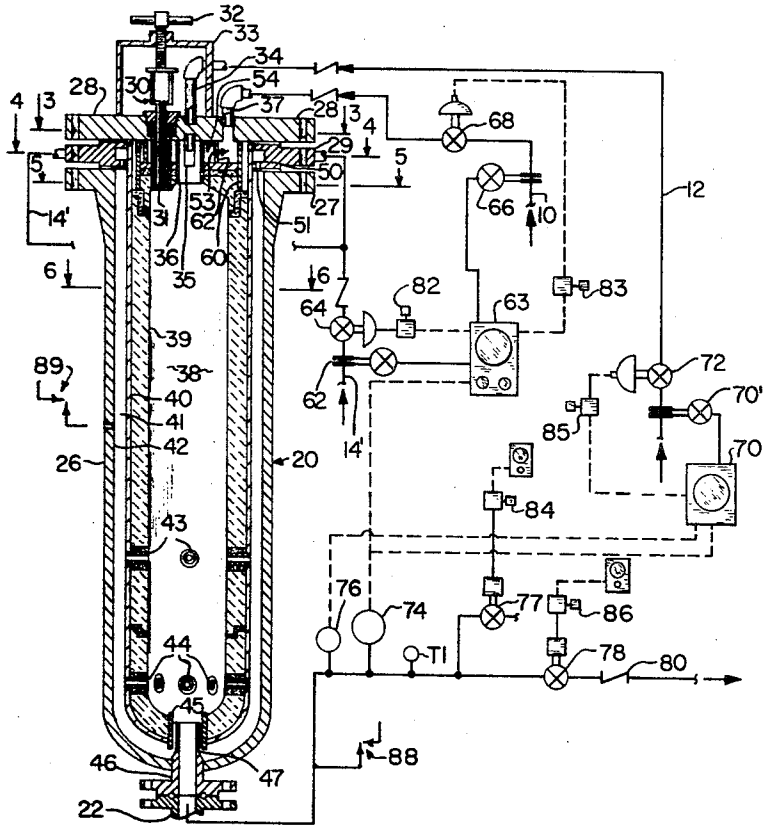
[52] **U.S. Cl.** **166/303,** 166/250, 166/64
[51] **Int. Cl.** **E21b 43/24**
[50] **Field of Search** 166/272, 260, 251, 256, 261, 302, 303, 57

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ABSTRACT: Water, hydrocarbons, and air are reacted together within a catalytic chamber to provide high temperatures, high-pressure products of reaction having increased percentage composition of hydrogen and carbon dioxide therein. A catalyst in the form of an alkali metal oxide or an alkaline earth metal oxide is carried to the reaction zone in the water stream, thereby providing the additional function of treating the water. The high temperature oxygen free gases are injected into a reservoir and contact the oil bearing formation thereof to increase the production of crude therefrom.



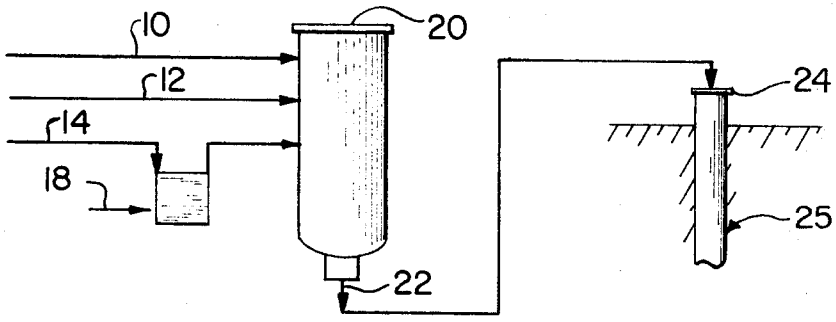
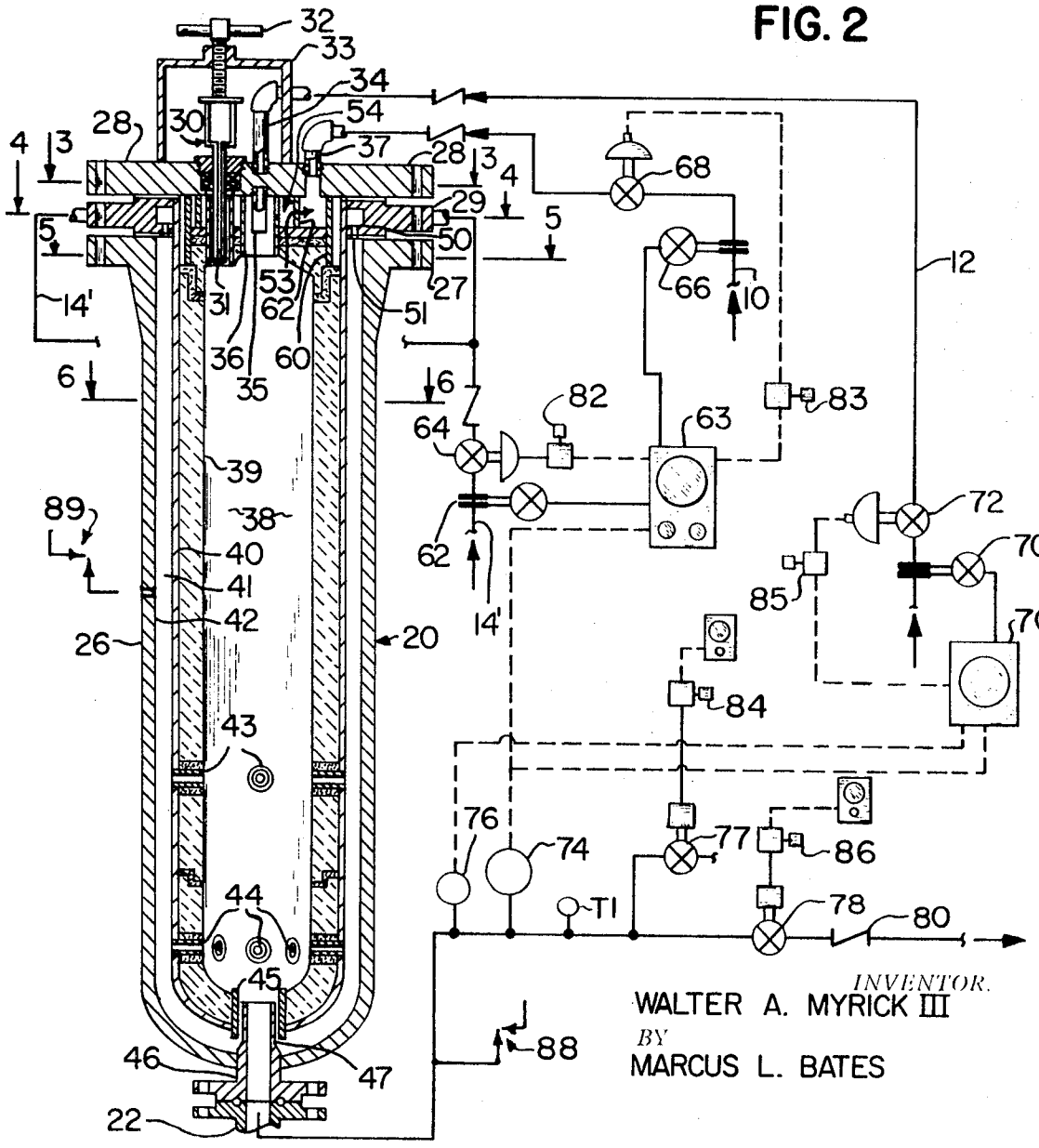


FIG. 1

FIG. 2



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FIG. 3

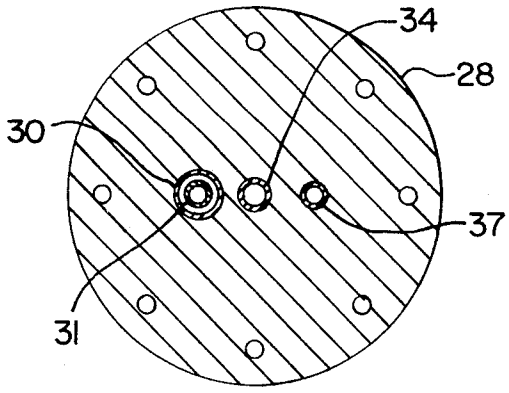


FIG. 4

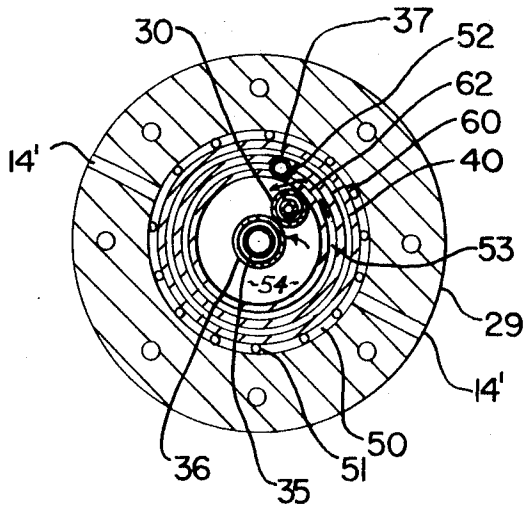


FIG. 6

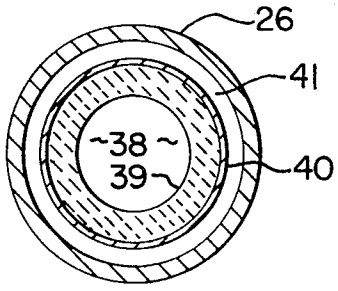
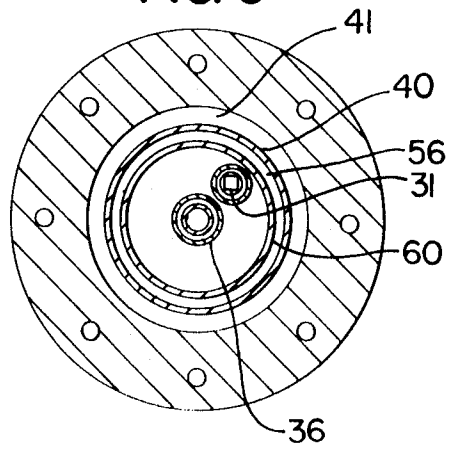


FIG. 5



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AGGREGATE PROCESS FOR PETROLEUM PRODUCTION

BACKGROUND OF THE INVENTION

The normal percentage recovery of liquid products from most petroleum reservoirs is between 30 percent and 40 percent, however, some distillate fields yield as high as 50 percent and some low gravity fields less than 10 percent. Hence, the majority of reservoirs contain more than 60 percent of the original oil after they have been subjected to normal production methods. It is for this reason that secondary recovery operations are being vigorously pursued by the petroleum industry. Some forms of secondary recovery systems include the use of steam flood, water flood, fire flood, stripping or gas purge, inert gas, and dilution wash. Many low A.P.I. gravity oil fields exhibit low yields regardless of the methods of production employed and most field still contain at least 50 percent of the original liquid petroleum after application of secondary recovery methods thereto. The many theoretical advantages of the various secondary recovery processes have not been fully realized in most installations because of the high cost of the original installation as well as the many mechanical and process problems encountered.

It is therefore desirable to incorporate the more successful features of the older secondary recovery processes into a simple unified system while circumventing many of the imperfections and drawbacks inherent in the older methods, along with improved selection of temperature and pressure ranges so as to control the combustion process in a manner to provide a mixture of gases having chemical and physical properties which are highly desirable for adding displacement energy to the natural underground reservoirs, and in producing changes in the physical properties of the petroleum oils as well as the production formation to thereby facilitate increased recovery of the contained oils in a manner which has heretofore been unknown.

SUMMARY OF THE INVENTION

This invention embraces a method of secondary recovery of petroleum oils from formations by the provision of a controlled combustion process which entails the production of mixed gases by the reaction of a hydrocarbon, including natural gas, along with air, and water. The reaction occurs within a reactor at relatively high pressure and temperature and in the presence of an alkali metal oxide or an alkaline earth metal oxide catalyst to thereby provide combustion products having chemical and physical properties which are highly desirable for adding displacement energy to underground reservoirs as well as changing the physical properties of both the petroleum oils and the production formation in a manner which facilitates increased recovery of the contained oils. The catalyst also serves as a water treating chemical, and has advantages when carried downhole into the oil bearing formation.

It is therefore a primary object of the present invention to provide a new catalytic reaction process for producing products of combustion for use downhole in an oil well.

Another object of the present invention is the provision of a method of increasing the H_2 and CO_2 content of products of combustion.

Still another object of the present invention is the provision of an improved method of secondary recovery of petroleum oils from oil bearing formations.

A further object of the present invention is the provision of a catalyst which is carried into a combustion reaction by means of a water stream.

Another object is the provision of products of combustion which treat an oil reservoir in a new and different manner.

A further object of the present invention is the provision of a reactor for converting fuel, air, and water into products of combustion.

The above objects are attained in accordance with the present invention by the provision of a new process which is carried out essentially as set forth in the above abstract and summary.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a flow sheet n the form of a schematical drawing or diagram which sets forth a generalization of the method of the present invention;

FIG. **2** is a cross-sectional detail of a hydrocarbon reactor which can be used in conjunction with the method taught in FIG. **1**; and with additional flow control means and conduits being schematically represented therein;

FIG. **5** is a cross-sectional view taken along line **3–3** of FIG. **2**;

FIG. **4** is a cross-sectional view taken along line **4–4** of FIG. **2**;

FIG. **5** is a cross-sectional view taken along lie **5–5** of FIG. **2**; and

FIG. **6** is a cross-sectional view taken along line **6–6** of FIG. **2**.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In carrying out the method of the present invention, air, a hydrocarbon such as natural gas, and water, respectively, are flow conducted through conduits **10**, **12**, and **14**, respectively, and into a hydrocarbon reactor. An alkali metal or an alkaline earth metal oxide, including potassium, and magnesium, and specifically potassium sulfite and potassium carbonate, is transferred at **18** into a water treatment tank **16** prior to the treated water being flow conducted into the hydrocarbon reactor **20**. The air, gas, and water react together within the combustion zone of the reactor and emerge as off-gases at **22** where they are subsequently flow conducted through a wellhead **24** and downhole as seen at **25** to the production zone.

The air, fuel, and water enter into chemical reaction in the presence of one or more of the before-mentioned catalyst at elevated temperatures and pressures, for example, 700 p.s.i.g. and 750° F. The catalyst serves the dual purpose of increasing the oxidation of the reactants to H_2 and CO_2 as well as reducing the corrosion and collection of scale which would otherwise occur throughout the system, as well as consuming and reacting with the dissolved oxygen which is present in the injection water, as will be described in greater detail later on.

Looking now to the details of FIG. **2**, in conjunction with the remaining figures, the hydrocarbon reactor **20** is seen to have an external high-pressure shell **26** which terminates in an inner flange **27**, with the flange being bolted to outer blind flange **28**, and with central flange member **29** being sandwiched therebetween.

An igniter **30** has an ignition means **31** associated therewith and is operably disposed within the reactor where it is controllably extended into close proximity of the combustion area by means of adjustment handle **32**. Housing **33** forms a support for the igniter control means.

Gas conduit **34** flow connects a regulated or controlled gas supply **12** with a gas nozzle **35**. Burner **36** is spaced apart from and circumferentially encloses the gas nozzle therein, thereby leaving the illustrated annulus therebetween.

Air conduit **37** interconnects controlled air supply **10** with a toroidallike air passageway which serves as a preheater, as will be better appreciated when discussed in greater detail later on.

Reaction zone **38** is defined by the high temperature insulation **39** which is bonded to inner shell **40** with the inner shell being connected to the before-mentioned central flange **29**. The inner shell together with the inside peripheral wall **42** of the outer shell cooperates together to form an annulus **41** therebetween. A series of nozzles, **43** and **44**, are spaced apart from one another and flow communicate with annulus **41**. Sleeve **45** is affixed to the lowermost portion of the inner shell

of the reactor where it slidably receives reduced portion 47 of outlet tubing 46 in a telescoping manner to thereby provide an expansion joint.

Looking again now to the details of FIGS. 2 through 5, it will be noted that the center flange supports the inner shell and also serves as a means of controlling the flow of water and catalyst into the reactor. Water inlet passageways 14' are flow connected to the before-mentioned source of water 14, and each of the passageways inwardly terminates in a circumferentially extending concavity or grooved passageway 50, with the lower wall surface of the concavity receiving a multiplicity of apertures in the form of spaced apart drilled passageways 51, each of which flow communicate the water supply with the annulus 41.

Looking now to the details of the toroidal air passageway, and in particular FIG. 2 in conjunction with FIG. 4, the air inlet 37 is seen to be connected to annulus 53 at a point adjacent to the illustrated baffle 52 which provides a circular flow path to the illustrated inlet located on the opposite side of the baffle so as to provide a continuous flow path for the air into chamber 54. Chamber 54 conducts the airflow through port 54' and into the annulus formed between burner 36 and gas nozzle 35 to thereby enable air and gas to be admixed at the free depending terminal end of the burner. The cylindrical housing 60 is spaced apart from cylindrical housing 40 so as to provide a dead air space therebetween.

Looking now to the flow control details as set forth in the schematical portion of FIG. 2, there is disclosed the before-mentioned water and catalyst flow passageway 14, having flow measuring orifice assembly 62 controllably connected to the recording ratio flow controller 63 which in turn is controllably connected to and actuates a motor control valve 64, thereby enabling the flow rates to be carefully maintained within a predetermined range of values. The ratio flow controller is connected to flow measuring orifice 66 and actuates the motor control valve 68 of the air supply. Pressure controller 74 resets ratio flow controller 63 so as to control the flow rate of water and air to thereby maintain a preset pressure.

There is schematically shown a recording temperature controller 70 which is pneumatically connected to the control valve 72, and which actuates the valve in accordance with a signal received from temperature transmitter 76. Additionally, the recording temperature controller records the pressure and flow rate sensed at 74 and 70', respectively.

Pneumatically manually operated vent valve 77 provides a safety bypass for venting the gases to the atmosphere. Pneumatically manually operated flow line valve 78 provides a means for interrupting flow to the wellhead. Check valve 80 prevents return flow of products and gases from the wellhead.

Electrically actuated solenoid valves 82, 83, 84, 85, and 86 are actuated by switches (not shown) associated with recording temperature controller 70, so as to enable emergency shutdown of the system, and to vent the effluent to the atmosphere.

Relief valves 88 and 89 are automatically actuated at elevated pressures which exceed the designed operating pressure of the system.

OPERATION

In operation, natural gas is preferred as the reactor feed stock because of its low cost and ease of handling, however, other hydrocarbon gases including propane, butane, as well as any suitable liquid hydrocarbon can be used to advantage in the present invention. The quantity of gas consumed by the reactor varies in accordance with the operating conditions, and assuming a 10/1 air to fuel ratio with a flow rate of 100 mcf. of natural gas being consumed, 135 barrels of treated water will be required. The water must be clarified and preferably contains less than 1600 p.p.m. dissolved solids. The sodium chloride content as well as the dissolved silica should not be excessively high. The injection pressure, that is, the pressure within the reactor or at the wellhead is generally determined by the type and thickness of the reservoir formation and is limited in accordance with the thickness of the overburden. However, it is desired to maintain the temperature between 500°—750° F. with the pressure being controlled at 700 p.s.i.g. where permissible. The following examples of flow rates are typical of most installations of the process:

Air flow, m.c.f.	Natural gas m.c.f.	A/F ratio	Bbl. water feed per day	H_2, mole percent	CO_2, mole percent	Temp., ° F.	Pressure, p.s.i.g
200	16.6	12/1	27.0	0	4.0	731	165
200	19.2	10.02/1	27.0	1	4.6	740	170
200	20.7	9.85/1	27.5	2	4.8	725	178
200	26.3	7.65/1	29.0	6	5.7	678	208
200	28.5	7.0/1	29.0	5.6	5.4	650	196
1,000	84.5	12/1	136.8	0	4.0	735	596
1,000	96.0	10.02/1	136.8	1	4.6	750	608
1,000	101.9	9.85/1	138	2	4.8	738	628
1,000	131.0	7.65/1	144	6	5.7	690	700
1,000	143.0	7.0/1	144	5.6	5.4	660	691

As seen in the above examples which set forth two different airflow rates, when the A/F ratio is maintained within the desired perimeters the hydrogen content and CO_2 content increase as the A/F ratio decreases. The formation of H_2 is increased while the formation of CO_2 also increases but at a relatively slower rate for the reason that the production of CO is largely avoided due to the water reaction. When the hydrocarbon feed rate is increased to a value which exceeds the above desired perimeters, the hydrogen and CO_2 content decrease due to the formation of excessive carbon monoxide and free carbon. When the A/F ratio is increased within the desired perimeters the hydrogen and CO_2 content is decreased.

An increase in the flow rate of injection water lowers the temperature of the off-gases and tends to more readily quench the reaction, which increases the formation of H_2 and decreases the formation of CO.

The optimum conditions for natural gas (1,000 B.t.u./ft.^{3}) are set forth under column three of the above table. The actual mass flow rate of effluent gases can be adjusted in accordance with the number of wells undergoing treatment. Generally the gas consumption will be 46,000—140,000 scf./D for one reactor which is flow connected to several injection wells.

The treatment chemicals which are added to the injection water for corrosion control serve as a catalyst to increase the oxidation of the carbon monoxide to carbon dioxide and to enhance the formation of hydrogen. The catalyst is an alkali metal oxide or an alkaline earth metal oxide, or a combination of the two, and preferably is added to the raw water as potassium carbonate and potassium sulfite, although magnesium carbonates and sulfites are also acceptable catalysts. The catalyst is an agent which is selected from the following group of materials: potassium, lithium, rubidium, cesium, magnesium, calcium, strontium, and barium, wherein the agent is in the form of a bisulfate bicarbonate, sulfite, carbonate, or a nitrite, Any combination of these substances can be used, however, it is preferred to use a mixture comprised of potassium carbonate and potassium sulfite so as to realize the maximum advantage of the catalyst since this form of the catalyst offers some form of treatment throughout the system.

The catalysts are added to the feed water, as for example,

potassium bisulfite, and as potassium carbonate for pH control. Potassium sulfite and potassium bicarbonate can also be used where deemed desirable. Where removal of dissolved oxygen from the feed water is required, the catalyst can be introduced as potassium nitrite as well as the sulfite as an oxygen scavenger.

As a more specific example of catalyst introduction into the feed water, and assuming the metal potassium to be available for use, sufficient sulfite or nitrite is added to remove the free oxygen from the feed water. Potassium bicarbonate and potassium carbonate is then added in order to balance the pH. The total weight percent of potassium must provide sufficient potassium ions to promote the desired reaction within the combustion chamber. This requirement will vary between 10 and 100 p.p.m. potassium ions in the feed water, with 30 p.p.m. being considered optimum.

Assuming that the feed water has been chemically treated by the catalysts, and flowing through conduit **14**, its rate of flow will be maintained constant by the ratio flow controller as the water enters passageway **14'**. The water flows through the grooved passageway, through the apertures **51**, and through the annulus **41** where it enters the reactor at **43**, **44**, and through the slip joint between sleeve **54** and **47**, thus maintaining the shell **40** within its structural limitations so far as regards the temperature and pressure existing within combustion chamber **38**. As the water, along with the catalyst, enters the combustion chamber, it is a least partially in the form of steam and accordingly the potassium carbonate, for example, will now be converted to potassium oxide, which is the required form of the catalyst in order to promote or influence the combustion reaction to be driven in a direction which enhances the formation of CO_2 and H_2, and minimizes the presence of O_2 and CO.

Motor valve **68** controls the rate of flow of air as it enters inlet **37**, flows about the path formed by annulus **53**, through the illustrated port adjacent the baffle, into the chamber **54**, where it continues to flow about the igniter and burner and then enters the port **54'** and flows into the burner annulus where the air then mixes with the natural gas or other suitable hydrocarbon from nozzle **35**. The igniter **31**, when it is not in use, is maintained in the retracted position clear of the area of intense heat within the combustion chamber.

Generally, the system is controlled as follows: the temperature transmitter **76** forms the primary control means for controlling the combustion process. The transmitter provides a signal which is sensed by the recording temperature controller **7**, which is pneumatically connected to the control valve **72** in order to actuate the valve in accordance with the signal. This enables the temperature at **70** to be selected, whereupon the temperature will thereafter be maintained within a predetermined limit.

The pressure controller **74** resets the ratio flow controller **63** in accordance with the pressure sensed at **74**, and maintains the flow ratio of water and air within a predetermined range of values. The pressure controller is connected back to the recording temperature controller for recording purposes, as well as enabling actuation of the before-mentioned pressure limit switches. Also associated with the recording temperature controller are temperature limit switches connected to sense the temperature at transmitter **76**. The pressure and temperature limit switches are connected to valves **82** through **86** to provide automatic shutdown in the event the temperature or pressure of the system should diverge from a predetermined range or limit of values.

As the water, hydrocarbons, and air are burned or reacted together within the reaction chamber of the reactor, a multitude of complex reactions occur, the details of which are unnecessary for a clear understanding of the invention, but which may be summarized as follows:

$$C_nH_{2n+2} + H_2O + O_2 + N_2 \rightarrow H_2O + CO_2 + H_2 + N_2 + CO + \text{trace of NO and } NO_2$$

The catalyst, together with the reactants exit at outlet tubing **22** along with a significant quantity of potassium sulfite, which becomes available as an oxygen scavenging agent as the gases flow through the remainder of the equipment.

The catalyst, in addition to removing free oxygen from the feed water, enhances the combustion of CO to Co_2 by causing the dissociated oxygen from the water molecule to combine with the CO molecule, which in turn leaves the dissociated hydrogen from the water molecule free to recombine with itself, thereby increasing the molecular hydrogen content of the effluent gases to a value between the limits of 1 percent to 6 percent, depending upon the flow rates of the air, gas, and water. The water of combustion together with the excess feed water remains in the gaseous phase, and is referred to herein as superheated steam.

The superheated steam is available to increase the temperature of the formation downhole in the well to thereby reduce the viscosity and specific gravity of the petroleum contained within the reservoir which in turn reduces the oils resistance to flow. The increased temperature coupled with the carbon dioxide which is adsorbed in the condensate enables the water to preferentially wet or to be adsorbed on the surface of the sand or production formation, thereby displacing oil therefrom. In paraffinic oil the increased temperature increases the solubility of the paraffin in the formation oils thus reducing the tendency of the paraffin to plug the well bores. The Co_2 also dissolves in the oil to reduce its viscosity as well as its specific gravity, while some of the CO_2 combines with water to form carbonic acid which reacts with lime, dolomites, and other calcareous formations to produce water soluble salts, thereby increasing the porosity of the formation. The carbonated water droplets are more easily pushed through the formation by the nitrogen and accordingly tends to wash the oil from the formation. The carbonic acid lowers the ph of the formation fluids thereby lowering the surface tension of the oil which enables the oil to be washed or displaced from the surface of the sand.

The nitrogen increases the reservoir pressure and drives the condensed steam through the formation so as to produce a washing action. The small amount of nitrogen oxides which are produced in the reactor is converted to nitrous and nitric acids in the production formation and reacts with calcareous formations to produce soluble salts. The acids also produce free hydrogen ions which are available to displace alkaline earth elements from the lattice structure of the clays, thus effectively increasing the porosity of the formation.

The potassium oxide is converted back to potassium carbonate due to the presence of CO_2 downhole, which enables reaction with various alkaline earths to occur; calcareous deposits for example, to give a potassium-magnesium carbonate, which is soluble in water, thus enabling the calcareous rock deposits to be solubilized, to thereby effectively increase the porosity of the formation.

Hydrogen produced by the reactor serves in a manner similar to nitrogen but more importantly it produces a reducing atmosphere which tends to reduce corrosion of the metal equipment. Dissolved hydrogen tends to reduce oil viscosity and specific gravity. The hydrogen is readily dispersed through the formation because of its small molecular size.

As will now be evident to those skilled in the art, the water injection within the reactor is utilized to produce superheated steam which is the primary carrier of heat into the formation; to react with carbon monoxide and hydrocarbons to produce hydrogen and CO_2 which improves the overall efficiency of the operation by producing a larger volume of gas per unit of fuel consumed; to control the reaction temperature as well as to cool the reactor and the reaction products; and as the solution medium for carrying the catalyst into the reactor where the catalyst can promote production of hydrogen and CO_2 from hydrocarbons and CO.

The increased pressure in the formation caused by the injection gases tends to reduce the flashing of the light ends from the petroleum which would otherwise be caused by the increased temperature within the formation. The light ends (C_1, C_2, C_3, and C_4) are maintained in solution and contribute to

reduction of viscosity and specific gravity.

The wells are placed on 3- to 10-day cycles, depending upon the formation depth and characteristics. At the end of each injection period, upon initial production, dissolved salts will be returned to the wellhead where they can be accumulated for subsequent disposal.

It is necessary to insulate the upper portion of the production tubing to prevent damage to the well head, cement, and casing.

The cost of operation and installation is low, the apparatus lends itself to automatic control, and many wells heretofore considered depleted by secondary recovery methods can actually be revitalized by the instant invention, and hence in many cases the present invention constitutes a tertiary recovery system rather than a secondary recovery system.

I claim:

1. An improved method of recovering hydrocarbons from a well bore which is connected to a subterranean natural reservoir by treating the reservoir according to the following steps:
   1. treating water with an agent selected from the group consisting of potassium, lithium, rubidium, cesium, magnesium, calcium, strontium, and barium, wherein the agent is in the form of either a bisulfite, bicarbonate, sulfite, carbonate, or a nitrite;
   2. reacting the treated water of step (1) by combusting the water with a hydrocarbon in the presence of air to produce a gaseous product comprised of superheated steam, the agent, and flue gases;
   3. maintaining the product obtained in step (2) at a temperature which avoids condensation of the superheated steam within the injection tubing of the well bore;
   4. flowing the product into the subterranean reservoir.

2. The method of claim 1 wherein the gaseous products are maintained above 500° F. and 170 p.s.i. at the reactor outlet.

3. The method of claim 1 wherein the agent is comprised of a mixture of potassium carbonate and potassium sulfite.

4. The method of claim 1 wherein the agent is comprised of potassium nitrite, and the air/fuel ratio is maintained between the limits of 8/1 and 12/1.

5. The method of claim 1 wherein the agent is comprised of potassium bicarbonate, and the air/fuel ratio is between the limits of 8/1 and 12/1.

6. The method of claim 1 wherein the agent is magnesium and is in the form of a nitrite or a carbonate.

7. The method of claim 1 wherein the agent is magnesium nitrite and the air/fuel is 8/1 to 12/1.

8. An improved method of recovering hydrocarbons from a well bore which is connected to a subterranean natural reservoir by treating the reservoir according to the following steps:
   1. treating water with an agent selected from the group consisting of potassium and magnesium wherein the agent is in the form of a carbonate, sulfite, or nitrite;
   2. reacting the treated water of step (1) by combusting the water with a hydrocarbon in the presence of air to produce a gaseous product comprised of superheated steam, the agent, and flue gases;
   3. flowing the product obtained in step (2) into the subterranean reservoir by using an injection tubing within a well bore connected to the reservoir;
   4. maintaining the product obtained in step (2) at a temperature which avoids condensation of the superheated steam within the injection tubing of the well bore.

9. The method of claim 8 wherein the agent is comprised of a mixture of potassium carbonate and potassium sulfite.

10. The method of claim 8 wherein the agent is magnesium and is in the form of a nitrite or a carbonate.