

[54] OIL SHALE HYDROGASIFICATION
PROCESS

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[*] Notice: The portion of the term of this patent subsequent to June 24, 1992, has been disclaimed.

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[52] U.S. Cl. 48/197 R
[51] Int. Cl. C10j 3/06
[58] Field of Search 48/197 R, 211, 213, 210,
48/199 R, 201

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UNITED STATES PATENTS

3,118,746 1/1964 Stratford 48/197 R
3,708,269 1/1973 Linden 48/197 R

FOREIGN PATENTS OR APPLICATIONS

654,289 12/1962 Canada 48/197 R
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thetic pipeline gas from oil shale. The process includes providing a hydrogasification reaction chamber having a hydrogen partial pressure of at least 100 psig and a temperature of about 1000°–1400°F. The shale is introduced at the top of the reaction chamber which includes an upper, oil shale preheat zone having a temperature up to 1000°F., a hydrogasification reaction zone at a temperature of about 1000°–1400°F. and a lower hydrogen preheat zone, also having a temperature of about 1000°–1400°F. Solids from the shale are passed downwardly through the chamber so that the shale, and particularly the oil therein, is gradually heated to the reaction temperature over a relatively extended period of at least ten minutes so as to inhibit the formation of a carbon residue. A hydrogen rich gas, containing hydrogen in excess of stoichiometric amounts needed for the hydrogasification of the oil in the shale, is passed upwardly in the reaction chamber and countercurrent to the shale solids passing downwardly therethrough. A hydrogenation reaction is promoted in the reaction chamber between the oil or organic material in the shale and the hydrogen so as to produce a gaseous mixture which includes volatilized liquids, methane and hydrogen. The mixture is thereafter separated into hydrogasifiable and non-hydrogasifiable liquid fractions, hydrogen, and the desired high methane content synthetic pipeline gas. The hydrogen and the hydrogasifiable liquid fraction are circulated back to the reaction chamber, the hydrogen being used as at least a portion of the hydrogen rich gas reacting in the chamber and the hydrogasifiable liquid enters the hydrogasification or the hydrogenation reaction.

[57] ABSTRACT

A process for producing a high methane content, syn-

10 Claims, 3 Drawing Figures

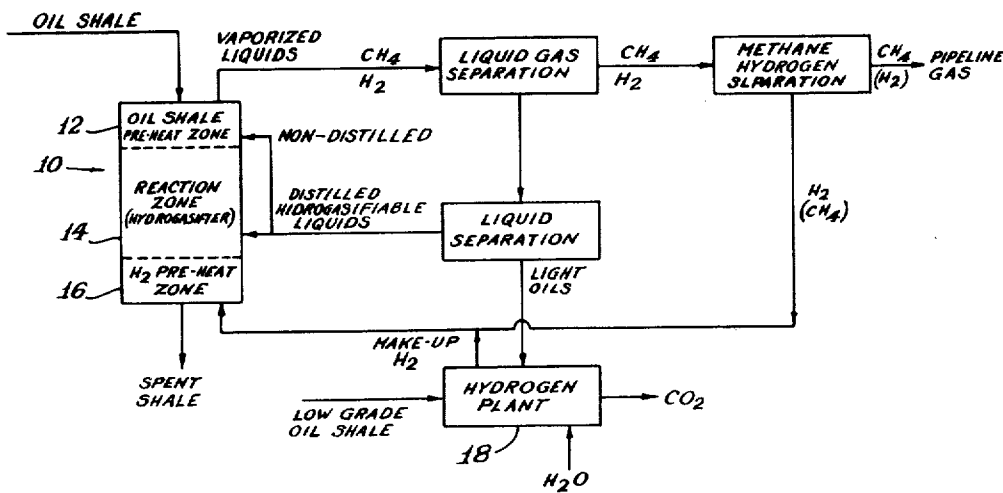


FIG. 1.

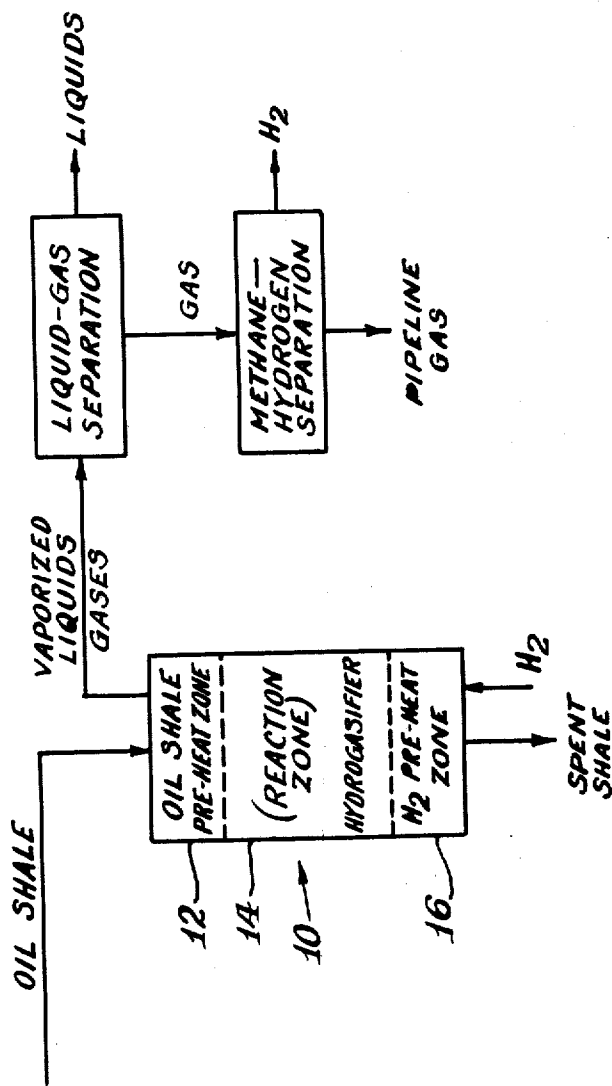


FIG. 2.

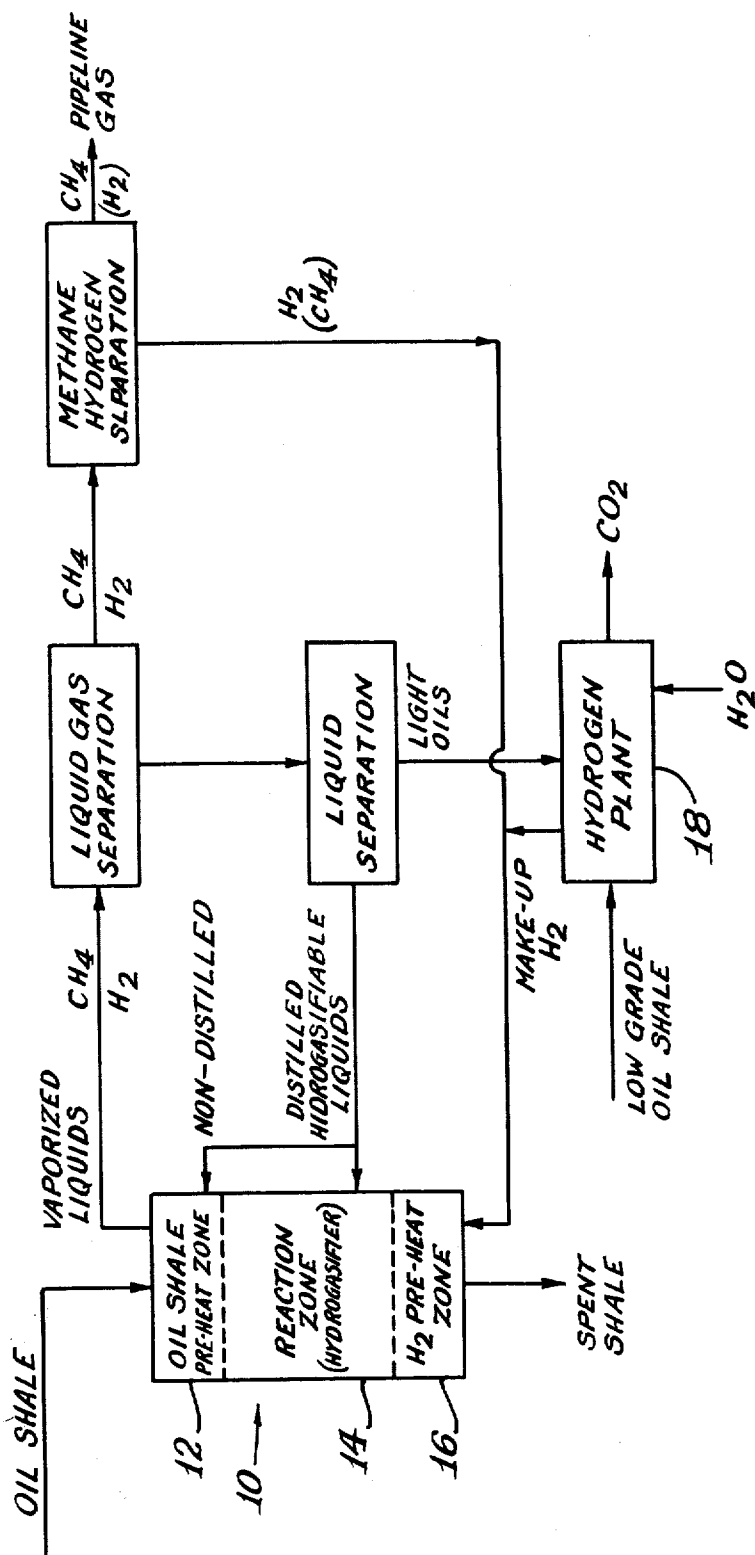
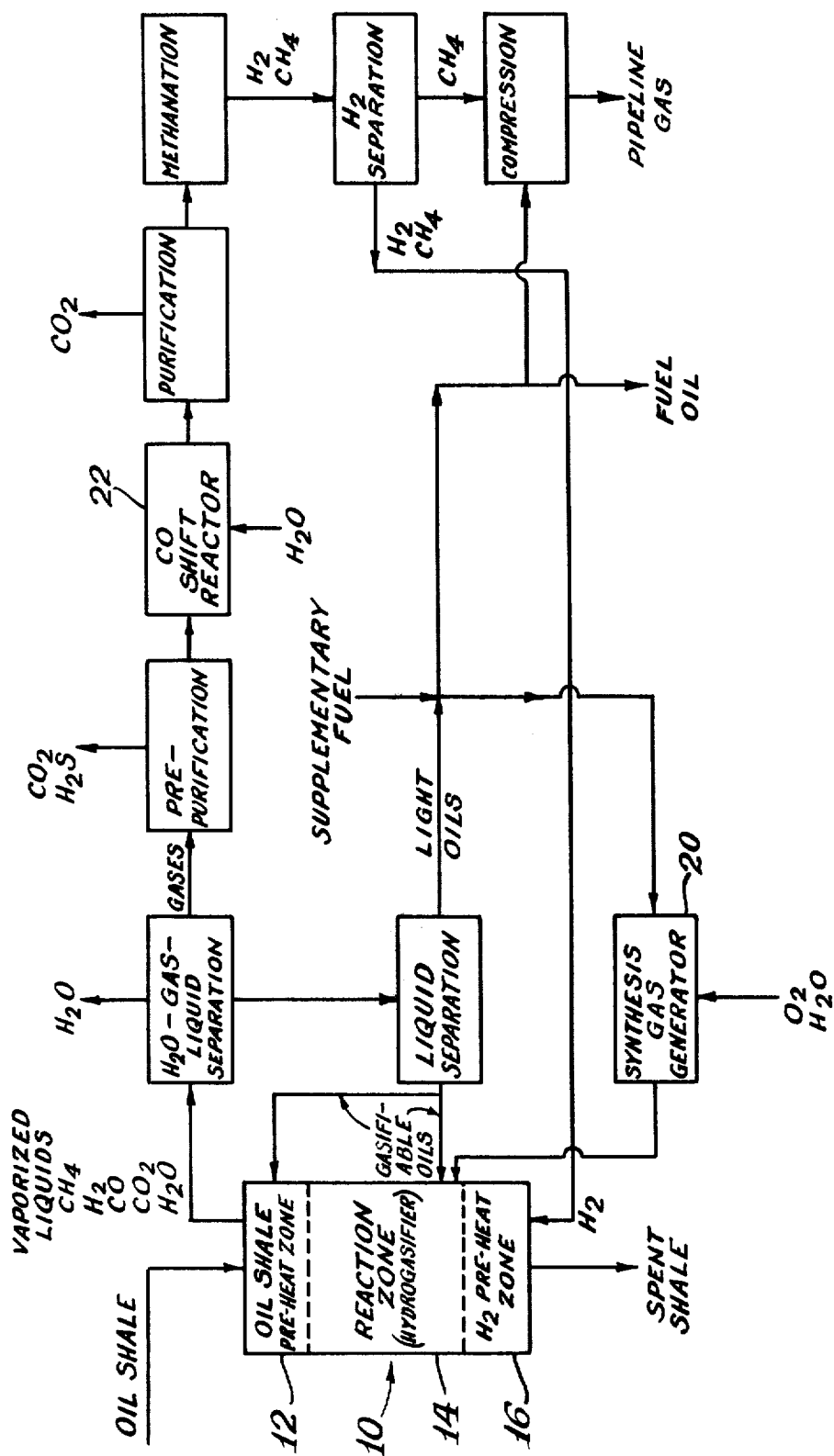


FIG. 3.



OIL SHALE HYDROGASIFICATION PROCESS

BACKGROUND OF THE INVENTION FIELD OF THE INVENTION and DESCRIPTION OF THE PRIOR ART

This invention relates to a process for the production of a high methane content, synthetic pipeline gas suitable for use as a substitute for or as a supplement to natural gas, and the invention particularly relates to a process wherein oil shale is used in the production of the synthetic gas.

It is well recognized that there is an increasing shortage of natural gas supplies in the United States, and there is a generally limited supply of natural gas throughout the world, as compared to more abundant reserves of liquid petroleum oils, coal, oil shale, etc. Natural gas suitable for distribution to residential, commercial and industrial consumers is characterized by heating values ranging from about 900 to 1100 Btu/SCF and by a high methane content, normally 80 percent by volume or greater. Such natural gas often includes ethane and sometimes nitrogen. If the nitrogen content is high in natural gas, propane and butane may be added and ethane may be left in the gas to compensate for the diluting effect of the nitrogen. Various sulfur compounds, carbon dioxide, and higher hydrocarbons are normally removed from natural gas before distribution to consumers because such components have an undesirable effect on transmission, distribution and usage of the natural gas. Therefore, in order to provide a suitable substitute for or supplement to natural gas, such a substitute or supplement should consist largely of methane, some ethane, but should have only a minimum of other constituents.

The elementary composition of suitable natural gas supplements or substitutes is about 25 percent by weight of hydrogen and 75 percent by weight of carbon. Substantial difficulties are encountered in producing natural gas substitutes or supplements from oil shale because oil shale contains organic carbon and hydrogen in a much higher weight ratio than 3:1, as about 7 - 8:1 and the organic material (kerogen) in the oil shale is intimately bound up with inorganic shale components. Thus, in order to produce a suitable synthetic pipeline gas from oil shale, hydrogen must be added during the manufacturing process and the kerogen or organic material must be separated from the shale. The presently known conventional methods of usefully removing the organic material from oil shale still leaves 20 to 30 percent of the organic material or kerogen with the spent shale in a form of carbon which, as presently known, cannot be reacted by any method other than by burning the organic material as a low grade fuel. The potential shortages of natural gas and of energy, in general, place emphasis on more efficient use of the kerogen in the shale, that is, a greater useful recovery of the kerogen or organic material is highly desirable.

It is therefore, clearly highly desirable to provide a hydrogasification process for oil shale, wherein the amount of unreacted carbon residue is minimized so as to lead to an overall improvement in the economics of the process and in the conservation of energy resources.

The classical or conventional method for recovering kerogen from oil shale is by retorting by heating the shale to about 900°-1000°F. at atmospheric pressure to

produce a crude shale oil which can then be gasified by several known techniques including direct hydrogenation with an external source of hydrogen and/or indirect hydrogenation by reaction of the oil shale with steam to form hydrogen and carbon monoxide which are then recombined to form methane by a catalytic process.

The Fischer Assay Test is a laboratory evaluation test for oil shales based on the retort procedure. In studies by the Bureau of Mines (RI 4825), such retorting leaves behind about 20 percent of the organic carbon in the spent shale. When the retorting is carried out in a hydrogen atmosphere, the process has been referred to as "hydrotorting". In typical processes exemplified in U.S. Pat. Nos. 3,565,784; 3,617,469 and 3,617,470, the hydrotorting is carried out at several hundred pounds pressure of hydrogen and the shale is brought to and maintained at temperature (700°-1100°F) for a total of less than 3 minutes. The resultant shale oil is greater in the hydrotorting process. However, as reported in U.S. Pat. No. 3,565,784, the organic carbon residue is 3.5 percent of the spent shale which corresponds to 20 percent of the original organic carbon according to Bureau of Mines Report, RI 4825.

In another process wherein hydrogen was reacted with oil shale at temperatures suitable for formation of methane (1150°-1360°F.), the shale and hydrogen are rapidly heated to the reaction temperature in a co-current manner and the shale is maintained at such a temperature for about ten minutes. In this process, it is preferable to use large hydrogen to shale ratios to achieve low carbon residues. Even then, however, the minimum carbon residue achieved was 13 percent of the original organic carbon in the shale.

Another recent process for the production of pipeline quality gas from oil shale is set forth in U.S. Pat. No. 3,703,052 wherein both a gasifier and a hydrogasifier are used and circulating solids are used as a heat transfer medium. This process involves rapid retorting of the shale, followed by hydrogasification of the shale oil thereby leaving about 20 percent of the kerogen in the retorted state to be used as a low grade fuel.

SUMMARY OF THE INVENTION

It is therefore an important object of this invention to provide a process for producing a synthetic pipeline quality gas from oil shale wherein the process is characterized by a greatly reduced amount of unreacted carbon residue remaining with the spent shale.

It is also an object of this invention to provide a highly economical and thermally efficient process for producing a synthetic pipeline quality gas from oil shale wherein the product gas has a heating value in substantially the same range as natural gas, such as 900-1100 BTU/SCF.

It is a further object of this invention to provide a process for producing a high methane content, synthetic pipeline gas from oil shale wherein the shale, by proper heating, in a stream of hydrogen, has the organic material removed therefrom to a greater extent than in known prior art processes.

It is yet another object of this invention to provide a continuous process for producing synthetic pipeline quality gas from oil shale.

Further purposes and objects of this invention will appear as the specification proceeds.

It is known that high hydrogen/oil ratios, that is, at least above the stoichiometric ratio, are necessary to avoid severe carbon formation at temperatures in the range of about 1200°–1500°F., which temperatures are generally considered necessary for hydrogasification. It is also known that, even at high hydrogen/oil ratios, rapid heat up, as of the order of a minute, to hydrogasification temperatures, can result in severe carbon deposition. Our experiments have shown that if the shale is properly heated in a stream of hydrogen, it is possible to remove and recover the organic material from the shale to a greater extent than previously developed processes. Particularly, it was found that very rapid heat up of an oil shale in hydrogen to temperatures required for hydrogasification, leaves a characteristic minimum amount of carbonaceous residue, in some instances, as much as 12 percent. However, if the same shale is, in excess hydrogen, brought to temperature slowly, of the order of 20 minutes or longer to go from 600° to 1300°F., the residual carbon will be much less than half that value. Even a 10 minute heat up period shows significant improvement. Furthermore, if the same principle of slow heatup is applied to any non-volatile component of the products of primary shale treatment, it is possible to get maximum net conversion of kerogen to substitute natural gas.

We have discovered that the foregoing objects are accomplished by providing a process for producing a high methane content, synthetic pipeline quality gas from oil shale wherein the process includes passing the oil shale through a hydrogasification reaction chamber. The shale is passed through the reaction chamber at a flow rate which provides at least ten minutes for heating the shale, preferably 10 to 120 minutes and the carbonaceous material therein, gradually, to a reaction temperature of about 1200°–1500°F. The hydrogen rich gas, which is supplied in a quantity to provide a high hydrogen/oil ratio, is passed upwardly through the reaction chamber in countercurrent flow to the downwardly moving oil shale in the reaction chamber. In the hydrogasification chamber, a hydrogenation reaction is promoted between the organic material in the shale and the hydrogen rich gas in order to produce a gaseous mixture which includes volatilized liquids, methane and hydrogen. Preferably, the shale, in the presence of excess hydrogen, is heated for at least ten minutes, or even more preferably, for twenty minutes, to increase the temperature of the shale from 600° to 1300°F. The hydrogen in the product gas is desirably separated from the methane and is recirculated back to the hydrogasifier for reaction while the methane rich gas is fed to the pipeline.

BRIEF DESCRIPTION OF THE DRAWINGS

Particular embodiments of the present invention are illustrated in the accompanying drawings wherein:

FIG. 1 is a block diagram illustrating a simplified embodiment of our inventive process;

FIG. 2 is another block diagram illustrating one preferred and more efficient form of our inventive process; and

FIG. 3 is a further block diagram illustrating another preferred and more efficient form of our invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, our hydrogasification process for

oil shale is illustrated in an extremely simplified diagrammatic form. A hydrogasifier or reactor 10 includes three major heating zones. The top portion of the reactor or hydrogasification reaction chamber 10 is an oil shale preheat zone 12. The second major zone of the hydrogasification reaction chamber 10 is the central portion or reaction zone 14. The third major zone in the bottom portion of the chamber 10 is the hydrogen preheat zone 16.

The oil shale useful in our process, is generally of the type which is found in the deposits in the northwestern area of Colorado, and in the adjoining areas of Utah and Wyoming. The oil shale which is introduced to the reactor 10 has been previously subjected, in a conventional manner, to an oil shale crusher (not shown) for reducing the mined oil shale to the size of pebbles having a diameter in the range of about ¼ – 1 inches. The shale is moved downwardly in the reactor 10, in the pebble form, in a packed moving bed, or alternatively, in a series of fluidized beds which are heated by the upwardly moving or countercurrent flowing hydrogen rich gas. The shale moving downwardly in the reactor 10 generally has a velocity range of about 0.2 to 2 feet per minute, and preferably has a velocity of about 1 foot per minute.

The flow rate of the oil shale causes the shale, including the organic material or kerogen therein, to be preheated to the reaction temperature, gradually for at least 10 minutes. More specifically, the shale is preferably heated from a temperature of 600° to 1000°F., in a period of at least 10 minutes, and then to 1200°–1300°F. in at least an additional 5 minutes.

The oil shale then moves into the reaction zone 14 where the temperature is at about 1200°–1500°F. in order to achieve proper hydrogasification conditions. The residence time of the shale in this zone is not considered critical since the organic material or kerogen in the shale has been removed from the shale in the previous or oil shale preheat zone 12. Therefore, in the reaction zone 14, the shale is in a free fall condition or a moving bed condition, whichever is convenient. The length of time at which the shale is at the reaction temperature need not be more than about 10 seconds although longer times, as up to several minutes, is not considered detrimental. The residence time of the hydrogen rich gas in the reaction zone is more significant, as will be discussed hereinafter in more detail.

The hydrogen preheat zone 16 is used to preheat the hydrogen rich gas by heat exchange with the hot shale which is moving downwardly from the reaction zone 14. The shale solids leaving the hydrogen preheat zone 16 may be as low as 300° – 700°F. The spent shale is discharged from the system after passage from the lower end of the reactor 10.

The hydrogen rich gas stream is introduced at the bottom of the reactor 10 and flows upwardly or countercurrent to the shale passing downwardly in the reactor 10. The hydrogen gas enters the reaction zone 14 in order to react with the various organic materials which are introduced directly into the reaction zone or which are introduced with the oil shale. The gas or hydrogen flow rate and size of the reaction zone 14 is designed for a hydrogen residence time of about 20 – 50 seconds within the reaction zone 14, although somewhat longer periods of time are not considered detrimental to the process. The upwardly moving product gas stream, at this position, consists of hydrogen, gase-

ous hydrogasification products, and volatilized liquid products, which then pass up to the shale preheat zone. Reaction between the shale and hydrogen also occurs in the preheat zone for generating additional gaseous and volatilized liquid products. This gaseous mixture is carried upwardly and out of the reactor 10 by the gas stream to a series of processing steps, to be hereinafter described, utilized for the separation of the substitute and supplementary natural gas, primarily methane, from the other gases or volatilized liquids in the gaseous mixture.

The pressure in the reaction chamber 10 has a hydrogen partial pressure of at least 100 psig. Preferably, the partial pressure of the hydrogen in the chamber 10 is about 500 psig. Although the upper limit of the total pressure in the reactor 10 is not considered critical to the process, a typical practical total pressure limit in the chamber 10 is about 1500 psig. The pressure conditions are similar in all three zones, 12, 14 and 16 of the hydrogasification reaction 10.

As seen in the simplified flow diagram of our process illustrated in FIG. 1, vaporized liquids and gases are produced in the hydrogasification reaction 10. These gases generally include methane, hydrogen, and carbon dioxide, while the vaporized liquids include aromatic compounds formed in the high temperature regions and lighter oils formed in the low temperature regions.

The first step in the process, following the formation of this mixture of vaporized liquids and gases, is the separation of the mixture into a liquid phase and a gaseous phase. The liquid-gas separation step can be accomplished by any suitable cooling technique, such as a quenching operation by a direct water spray quench or a heat recovery system. The quenching or cooling of the mixture coming from the reactor 10 may reach a rather low temperature, as 100°F., so as to separate the original gaseous mixture into a normally liquid phase and a normally gaseous phase. The separated gaseous phase is then separated into a high methane content, as at least 80 percent by volume, of a pipeline quality gas, having a heating value in the range of 900-1100 BTU/SCF, and a hydrogen rich fraction. In the methane-hydrogen separation step, the separation is preferably accomplished by subjecting the gaseous mixture of methane and hydrogen to cryogenic temperatures, at least about -260°F., the approximate boiling point of methane. The methane condenses and the hydrogen fraction remains in the gaseous state. Any suitable separation method can be used such as chemical processes wherein the hydrogen is extracted by reaction and is subsequently regenerated.

In the simplified diagrammatic embodiment shown in FIG. 1, there is no indication of further use of the separated hydrogen or separated liquids. In the practical and preferred application of our process, however, the hydrogen and separated liquids are used as integral parts of the process in order to provide a highly thermally efficient process. FIG. 2 illustrates one preferred embodiment of our invention, wherein the hydrogen is separated from the methane and is recycled back to the reactor 10 and the liquid phase is separated into a heavy liquid fraction, which is subsequently gasified and a light liquid fraction, consisting primarily of benzene and other light aromatics, which are difficult to hydrogenate. This embodiment provides one type of highly thermally efficient manner of using our process.

As seen in FIG. 2, the light oils are introduced to a hydrogen plant and are reacted with steam in order to produce hydrogen useful as make-up hydrogen for passage to the reactor 10. Alternately, if desired, these light aromatic liquids can be sold and hydrogen produced from less expensive carbonaceous materials. The gaseous mixture of methane and hydrogen is also separated into a hydrogen rich fraction, which is recirculated back to the reactor 10, and a methane rich fraction which is useful as the pipeline quality gas. As can be seen from the embodiment of FIG. 2, a highly thermally efficient process is provided for hydrogasifying a high proportion of the organic material in the shale for the production of a methane content pipeline quality gas.

In the embodiment of FIG. 2, the hydrogasifier reactor 10 is constructed in the same manner as the hydrogasification reactor 10 of the embodiment of FIG. 1. Again, there is an oil shale preheat zone 12, a reaction zone 14, and a hydrogen preheat zone 16. The temperature and pressure conditions are also the same as for the process discussed in connection with the simplified process embodied in FIG. 1. As in the embodiment of FIG. 1, the flow rate of the shale passing through the reactor 10 and the flow rate of the hydrogen passing upwardly, in the embodiment of FIG. 2, is such as to provide the desired heating of the shale to the reaction temperatures, as discussed in the process embodiment of FIG. 1. The spent shale is discharged and disposed at the bottom of the reactor 10.

In the process embodiment of FIG. 2, for simplification of discussion, the oil shale being fed to the hydrogasifier 10 will be considered as a 25 gal./ton Fischer Assay oil shale which contains 11.5 percent organic carbon by weight and a carbon-hydrogen weight ratio of 7.2. Upon hydrogasification of the shale, the product gas passing from the top of the hydrogasifier 10 includes methane, hydrogen, carbon dioxide, water vapor, aromatic products of hydrogasification, such as benzene, naphthalene, and higher aromatic and vaporized liquids from the shale having an empirical formula of $\text{CH}_{1.7}$. The gaseous stream passing from the reactor 10 may also carry, as a mist, condensed liquids derived from the shale. The mixture of gases and liquids are separated into a liquid phase and a gaseous phase, as by the quenching operation described in connection with FIG. 1.

The liquid phase separated during the liquid-gas separation step includes both readily and difficultly hydrogasifiable oils. The most difficult hydrogasifiable oil is benzene which is also the component with the lowest boiling point in the liquid phase and is most easily separated by a simple distillation procedure. The remaining liquid fraction is further separated, as by distillation, into a distillate fraction, preferably at a temperature below about 650°F., and an undistilled fraction. The distillate fraction is returned or recycled directly to the reaction zone 14 of the reaction chamber 10, as it is not necessary to subject these distilled liquids to the important gradual heat up. However, the undistilled fraction is directed to the oil shale preheat zone 12, as this fraction must undergo the gradual heat up. Specifically, the non-distilled fraction is added to the shale preheat zone 12 at a position where the temperature is in a range of 600°-700°F., whereby the downwardly moving shale in the reactor 10 raises these nonvolatile or nondistilled

components gradually to reaction temperature in the reaction zone 14.

As to the light oils, primarily benzene, these oils are directed to the hydrogen plant 18 of a commercially available type to produce make-up hydrogen used as part of the reactant hydrogen in the hydrogasifier 10. The hydrogen plant 18 may be of any suitable commercial available design, such as a hydrogen plant using the well known steam-iron process or a hydrogen plant using the well known partial oxidation method.

As indicated in FIG. 2, a raw or retort oil, as shale oil, derived from the shale fed to the hydrogasifier 10, or from shale fines or other less desirable shale components, may, if needed, be added to the hydrogen plant 18 in order to make an adequate amount of hydrogen for use in the hydrogasifier 10. As indicated, the make-up hydrogen passing from the make-up hydrogen plant 18 is mixed with the hydrogen rich mixture passing from the methane-hydrogen separation. Instead of the low grade shale oil, other cheaper fossil fuels, if available, may be used to produce hydrogen in the hydrogen plant 18.

Intermediate the liquid gas separation step and the methane-hydrogen separation, the gas stream preferably undergoes purification steps not indicated in FIG. 2, for removal of carbon dioxide, hydrogen sulfide, and water vapor as discussed below. The methane-hydrogen separation step is accomplished by any suitable technique, as cryogenically, and produces the hydrogen rich fraction and the high methane content synthetic pipeline gas fraction or substitute natural gas. Generally, the pipeline quality gas resulting from the methane-hydrogen separating step contains at least about 80 percent by volume of methane. Also, at least 80 percent by volume of the hydrogen rich fraction is hydrogen. Also, as shown in the flow diagram of FIG. 2, for the thermally efficient operation of our process, the hydrogen rich fraction resulting from the methane-hydrogen separation step is combined with make-up hydrogen coming from the hydrogen plant 18 in order to provide a sufficient amount of hydrogen for use in the reaction zone 14 of the hydrogasifier 10.

Referring to FIG. 3, there is shown another embodiment of our invention, also providing a practical, thermally efficient hydrogasification system for oil shale. As in the embodiments of FIGS. 1 and 2, the hydrogasifier 10 of the embodiment of the process shown in FIG. 1 includes the shale preheat zone 12, the hydrogenation reaction zone 14, and the hydrogen preheat zone 16. Also, the same reaction pressures and zone temperatures are provided in the hydrogasifier 10 of the embodiment of FIG. 3, as is done in the process embodiments of FIGS. 1 and 2. Again, the flow rate of the shale passing through the reactor 10 provides the important gradual heat up of the shale to the reaction temperature. The spent shale is discharged from the bottom of the reactor 10. As in the embodiment of FIG. 2, the embodiment of the process described in FIG. 3 relates to the use of a shale having a 25 gallon per ton Fischer Assay which contains 11.5 percent organic carbon by weight and a carbon-hydrogen weight ratio of 7.2 as an example.

The embodiment of FIG. 3 is preferably used when it is desirable to add heat to the reactor 10. More specifically, the embodiment of FIG. 3 uses a hot synthesis gas, to supply the make-up hydrogen for hydrogasification. Other gases and steam entering the hy-

drogasifier 10 are included in the synthesis gas, whereby the product gas passing from the hydrogasifier 10 of FIG. 3 includes carbon monoxide, carbon dioxide and steam, in addition to methane, hydrogen and heavy and light liquids found in the product gas in the hydrogasification reactors of the process embodiments of FIGS. 1 and 2.

The first step following the formation of the product gas in the process of FIG. 3 is the separation of the mixture into three fractions. The first fraction is water, which is simply separated. The second fraction is the gaseous fraction, and the third fraction is the liquid or oil fraction. The preferred technique for the water-oil-gas separation step is quenching the whole mixture in a quenching tower (not shown), for example, which separates the normal gases and normal liquids from each other. The liquids, containing oil and water, are allowed to settle in a settling tank separator (not shown) wherein water is removed from the bottom and oil from the upper layers.

The oils resulting from the water-oil separation step are further separated into heavy or hydrogasifiable oils and light liquids or oils. The gasifiable oils are fed directly to the hydrogasification zone, in the case of distillates and to the oil shale preheat zone 12, in the case of undistilled liquids, as in the case of the embodiment of FIG. 2. As described in the embodiment of FIG. 2, the undistilled fraction is gradually heated to reaction temperatures from a range of 600°-700°F. while the distillates may be fed directly to the reaction zone 14. The recycle hydrogen from the hydrogen-methane separation step is fed to the hydrogen preheat zone 16, as will be described hereinafter.

The embodiment of FIG. 3 is preferably used when it is desirable to add heat to the reactor 10. The synthesis gas generated in the synthesis gas generator has a temperature as high as 2200°F., whereas in the embodiment of FIGS. 1 and 2, the hydrogen may be at room temperature. The synthesis gas generator 20 desirably uses the well known partial oxidation process for making synthesis gas which includes hydrogen, carbon monoxide, carbon dioxide, and gaseous water, resulting from the reaction of steam, oxygen and a suitable hydrocarbon such as from a supplementary fuel.

The synthesis gas generator may also react the light oils passing from the liquid separation step either alone or in combination with the supplementary fuel. The light oils from the liquid separation step may, alternatively, be used in the overall process, as for example, by use as an energy source in the compression of the high methane content pipeline quality gas resulting from the described process.

As to the gaseous phase, resulting from the water-liquid-gas separation step, the gases are pre-purified to remove carbon dioxide and hydrogen sulfide. Suitable pre-purification techniques include the well known hot carbonate and monoethanolamine scrubbing systems. Following the pre-purification step, the gaseous mixture is passed to a shift reactor 22, wherein the gases are subjected to the well known water gas shift reaction. In this reaction, carbon dioxide is formed to be subsequently removed by a technique similar to that used for purification. The gas, with the carbon dioxide removed, is then methanated using any conventional methanation technique to result in the gaseous mixture of hydrogen and methane.

The mixture of hydrogen and methane then undergoes a methane-hydrogen separation step, as by use of a cryogenic technique wherein the methane is condensed and the hydrogen remains in the gaseous state. The methane or methane rich pipeline quality gas is then compressed. The high methane content, as at least 80 percent methane, synthetic pipeline quality gas has a heating value of 900-1100 BTU/SCF. The hydrogen fraction, as at least 80 percent hydrogen, resulting from the hydrogenmethane separation, is used as the principal source of hydrogen for the hydrogasifier 10. As with the embodiment of FIG. 2, the process embodiment of FIG. 3 is a highly thermally efficient process for the hydrogasification of oil shale.

While in the foregoing, there has been provided a detailed description of particular embodiments of the present invention, it is to be understood that all equivalents obvious to those having skill in the art are to be included within the scope of the invention as claimed.

What we claim and desire to secure by Letters Patent is:

1. A process for producing a high methane content, synthetic pipeline quality gas from kerogen containing oil shale, wherein there is a minimal carbon residue formation resulting from the conversion of the kerogen to the pipeline quality gas which comprises the steps of:
 - a. continuously flowing the kerogen containing oil shale through a preheat zone at a flow rate sufficient to provide at least ten minutes to gradually heat the oil shale from a temperature of 600° to a temperature of 1000°F.;
 - b. continuously contacting the oil shale in the preheat zone during the gradual heating with a countercurrently flowing hydrogasification product gas stream as removed from a hereinafter defined hydrogasification zone;
 - c. said hydrogasification gas stream containing at least stoichiometric amounts of hydrogen to achieve a high hydrogen to oil ratio in the preheat zone;
 - d. withdrawing a preheated kerogen containing oil shale from the preheat zone and passing the preheated shale to a hydrogasification zone;
 - e. hydrogasifying, in the hydrogasification zone, the preheated kerogen containing oil shale at a temperature of 1200°-1500°F. in the presence of a countercurrently flowing hydrogen rich gas stream containing at least stoichiometric amounts of hydrogen to achieve a high hydrogen to oil ratio and, to produce hot spent shale and a hydrogasification product gas stream;
 - f. passing said hydrogasification product gas stream to said preheat zone of step (b) as said hydrogasifi-

- g. maintaining the hydrogen partial pressure in the preheat and hydrogasification zone at a pressure of at least 100 psig.;
- h. withdrawing a final product gas stream from said preheat zone comprising hydrogen, volatilized liquid products and gaseous hydrogasification products;
- i. separating said final product gas stream into a hydrogen rich gas stream, said high methane content synthetic pipeline gas, a hydrogasifiable liquid distillate fraction and a hydrogasifiable non-distillate fraction;
- j. recycling the hydrogen rich gas to said hydrogasification zone;
- k. passing the hydrogasifiable distillate fraction to the hydrogasification zone; and
- l. passing the non-distillate fraction to the preheat zone at a point where the shale is at a temperature of 600°-700°F. whereby a maximum net conversion of kerogen to substitute natural gas is obtained.
2. A process according to claim 1 where the hydrogen rich gas stream passed to the hydrogasification zone is first contacted with the hot spent shale.
3. A process according to claim 1 wherein said shale is additionally gradually heated from 1000° to 1200°F. for at least 5 minutes in said preheat zone.
4. A process as in claim 1 wherein said hydrogen partial pressure is about 500 psig..
5. A process as in claim 1 wherein the oil shale has a residence time in the preheat zone of 10 - 120 minutes.
6. A process as in claim 1 wherein said hydrogen rich gas stream has a residence time in the hydrogasification reaction zone of 20 - 50 seconds.
7. A process as in claim 1 wherein said hydrogasifiable liquid distillate includes a light liquid fraction, said light liquid fraction being converted to make up hydrogen for use in said process.
8. The process of claim 1 including the step of producing said hydrogen rich gas in a synthesis gas generator, said hydrogen rich gas having a temperature up to 2200°F., said synthesis gas also including carbon monoxide, carbon dioxide and steam.
9. The process of claim 1 wherein said oil shale is first crushed to provide shale pellets having a size of about ¼-1 inches in diameter.
10. A process as in claim 1 wherein said non-distillate fraction is provided by distillation and boils above 650°F..

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