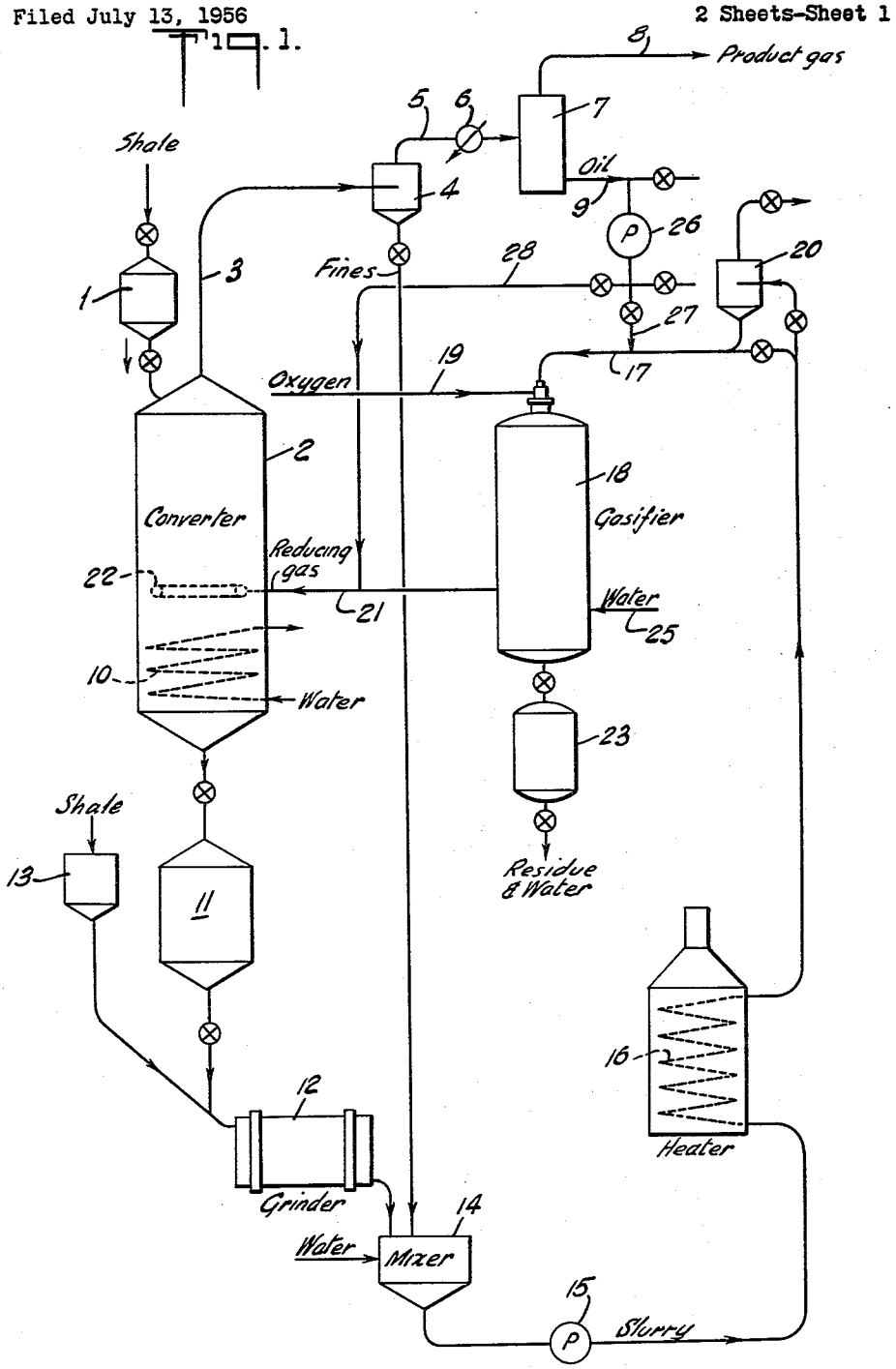
Jan. 21, 1964 W. M. STRATFORD 3,118,746

GENERATION OF FUEL GAS FROM OIL SHALE

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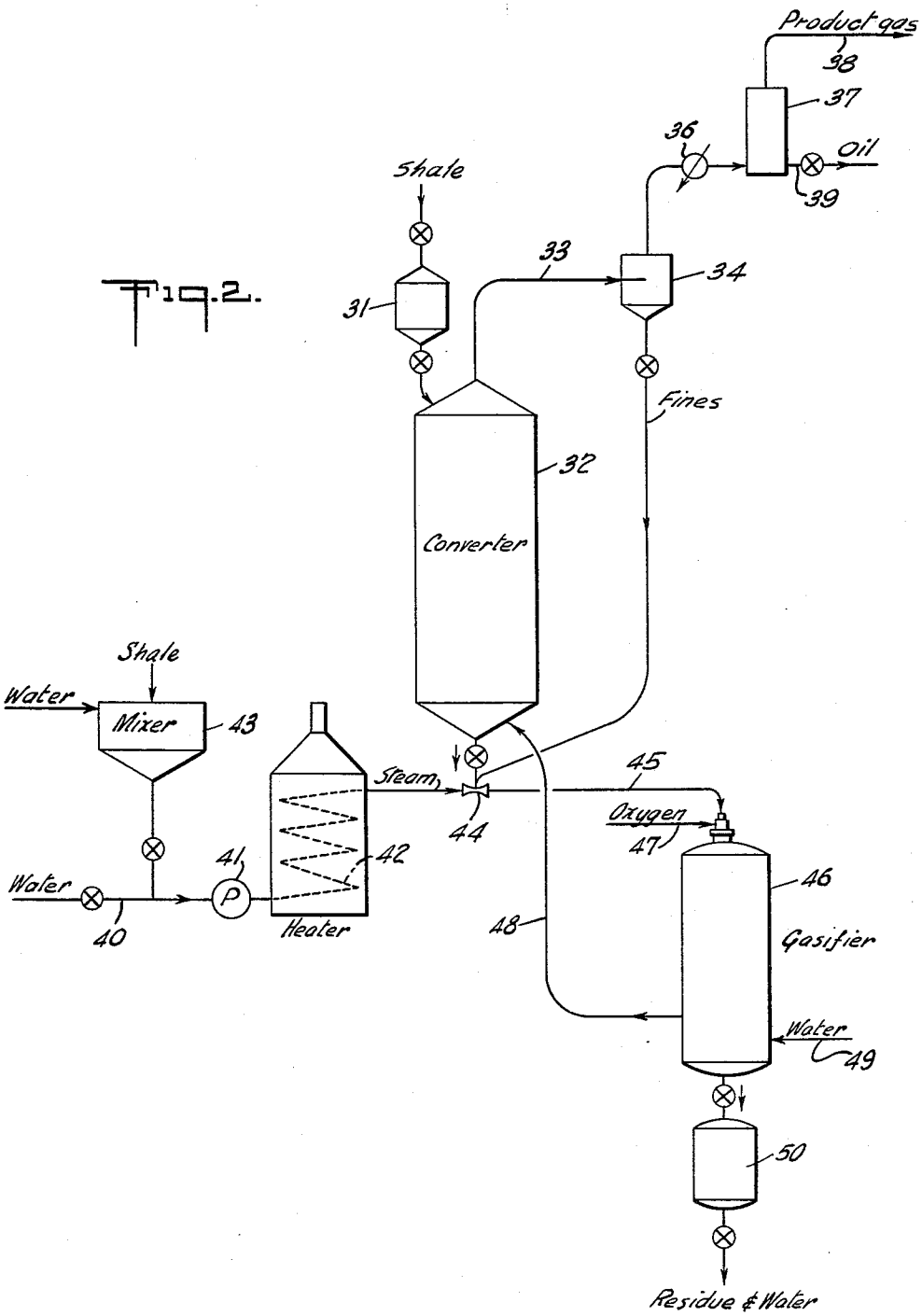


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Fig. 2.



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GENERATION OF FUEL GAS FROM OIL SHALE

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This invention relates to a process for the production of fuel gas from oil shale. In one of its more specific aspects, this invention relates to a improved process for the production of the fuel gas from oil shale.

Oil shale contains a carbonaceous substance, known as kerogen, which may be converted on heating into shale oil a hydrocarbon liquid resembling low grade heavy crude oil. A portion of the shale oil may be recovered from the shale by roasting. Once the shale oil is recovered from the shale, it must be subjected to extensive refining operations to produce marketable fuel products.

The process of the present invention produces fuel gas directly from oil shale. The process involves conversion of kerogen in oil shale to volatilizable hydrocarbons, including gaseous hydrocarbons, by subjecting the shale to heat treatment in the presence of a reducing gas, e.g., carbon monoxide, hydrogen, or a mixture thereof to produce a fuel gas of relatively high heating value. Residual fuel values of the shale, i.e., unvaporized carbonaceous residue, may be utilized in the generation of the reducing gas.

The oil shale may be fed to the process in the form of relatively large lumps, for example, lumps having an average diameter as large as 4 to 6 inches. Preferably, moderately crushed shale ranging from about 2 inches in average diameter to about ¼ inch in average diameter, is used. The shale is fed into a conversion zone or heat treating zone wherein it is contacted with hot synthesis gas, rich in hydrogen and containing carbon monoxide, at a temperature sufficient to convert kerogen in the shale to shale oil; temperatures in the range of 1200° F. to 1600° F. are preferred. At temperatures above 1200° F., mainly gaseous hydrocarbons are produced.

Disintegration of the shale takes place on heating. Most shales, on heating, are decrepitated to fine powder; others are rendered more friable. The treated shale drawn from the retort may be pulverized, if necessary, preferably while hot, as described in more detail hereinafter. The treated shale is preferably reacted with free oxygen and steam at a temperature above about 2000° F. effecting partial oxidation of the carbonaceous residue in the shale and producing a hot gas stream comprising hydrogen and carbon monoxide, together with steam and some carbon dioxide.

Gas or oil derived from the shale, or a suitable carbonaceous fuel from some other source, e.g., petroleum, may be used, if desired, for the production of the carbon monoxide and hydrogen, either in lieu of the treated shale, or as a supplement thereto.

The hot gas stream from the partial oxidation reaction zone is supplied to the treating zone effecting conversion of kerogen in the oil shale to volatilizable hydrocarbons and converting a considerable portion of the hydrocarbon so produced to gaseous hydrocarbons. The hydrogen present in the gas is important in this step as shale oil is notably deficient in hydrogen. The hydrocarbon from the shale enriches the gas stream from the oxidation reaction and produces a high B.t.u. fuel gas. In general, the product gas will have a lower heating value within the range of 500 to 800 B.t.u.'s per cubic foot. The heat content of the gas from the partial oxidation reaction zone is sufficient, not only to convert the kerogen in the shale to oil, but also to crack the shale oil and effect reaction between

hydrocarbons of the shale oil with hydrogen, steam and carbon dioxide to produce a heating gas containing carbon monoxide, hydrogen and gaseous hydrocarbons.

Shale oil is generally characterized by nitrogen compounds which impart an unpleasant odor to the shale oil and products derived therefrom. Malodorous compounds resulting from the treatment of shale by the process of this invention preferably are retained in the fuel gas, although they may be removed, if so desired. In some cases in which natural gas is transported in a pipeline from a source convenient to a source of shale the natural gas may be blended with gas produced by the present process to produce a composite of high heating value. In the latter case the gas from the oil shale may serve as an odorant for the entire gas stream and eliminate the necessity for further addition of an odorant to the natural gas.

Spent shale from the process may be useful for the production of Portland cement. Oil shales from a number of sources are suitable raw materials, when combined with limestone, for cement production.

Although the operation may be carried out at atmospheric pressure, a pressure in the range of 150 to 750 p.s.i.g. is preferred for the conversion zone. If desired, higher pressures up to 2000 p.s.i.g. may be employed; these higher pressures, however, are generally not economical.

The invention will be more readily understood from the following detailed description and accompanying drawing. The detailed description, which is illustrative of operation in accordance with the present invention, is to be taken as a specific example and not as limiting the invention.

FIGURE 1 is a diagrammatic elevational view illustrating a preferred method of operation in accordance with the process of the present invention.

FIGURE 2 is a diagrammatic elevational view illustrating another method of operation in accordance with the present invention.

With reference to FIGURE 1, crushed shale is introduced through a lock hopper 1 into conversion zone 2. The lock hopper permits introduction of shale into the conversion zone at an elevated pressure. Conversion zone 2 comprises a pressure vessel wherein hot gases comprising carbon oxides and hydrogen from a source described hereinafter are contacted with the shale in a relatively deep bed. Preferably the shale is maintained in a downwardly moving settled bed. Alternatively, a fluid bed may be employed, preferably a dense phase fluidized bed having the appearance of a boiling liquid.

In conversion zone 2, the shale is subjected to heat treatment with the hot gases at a temperature sufficient to convert the kerogen contained therein to hydrocarbons and to effect distillation and cracking of the hydrocarbons. Steam, hydrogen and carbon oxides contained in the gas stream react with the hydrocarbons, and with one another, to produce fuel gas of high heating value.

There are numerous possible reactions which may occur in the conversion zone. The more important reactions are hydrogenation of the shale oil and reactions between carbon contained in the shale oil and oxidizing components of the hot gas stream, particularly steam.

The product gas from the conversion zone comprises hydrogen, carbon monoxide, gaseous products of distillation and reaction from the oil shale and shale oil, together with unreacted steam and liquid hydrocarbon components distilled from the shale and shale oil.

The resulting gaseous product from the conversion zone passes through line 3 to separator 4, suitably a cyclone separator, in which solid particles, for example powdered shale or ash, are separated from the gas stream.

The gases from separator 4 pass through line 5 and cooler 6 to a separator 7 in which the oil or condensible hydrocarbons are removed from the gas stream. Separator 7 preferably comprises a gas-liquid scrubber in which the gases are scrubbed with oil effecting condensation of normally liquid constituents of the gas stream and the removal of any solids remaining in the gas stream leaving separator 4. The product gas, suitable as fuel gas, per se, or for blending with gas from another source, for example, natural gas, is discharged from the separator 7 through line 8. Oil separated from the gas stream is discharged through the separator through line 9. This oil may be returned to the conversion zone, preferably at or near the point of introduction of the hot gas stream, or it may be fed to the subsequent gasification zone, described hereinafter, as fuel therefor, preferably to supplement the fuel contained in the treated shale, or recovered as a product of the process. The product gas may be subjected to further purification steps for removal of water and other undesirable constituents.

Shale from the conversion zone 2 may be cooled by a cooling coil 10 to reduce its temperature prior to discharge therefrom. Cooling coil 10 may take the form of a waste heat boiler.

Shale is discharged through a lock hopper 11 into a grinder 12 in which it is pulverized while at an elevated temperature. It has been found that pulverization of shale is much more readily accomplished at elevated temperature than at atmospheric temperature. Preferably the temperature in the grinder is within the range of about 400° F. to about 1200° F. If desired, fresh shale from hopper 13 may be added to treated shale supplied to the grinder to supplement the fuel supply to the subsequent gasification zone, described hereinafter. In this case, the hot treated shale heats the raw fresh shale and improves its grindability.

In the grinder all of the shale is reduced to a particle size of less than ¼ inch in average diameter, and preferably, finer than about 100 mesh. The ground shale, which may contain lime if cement is also a desired product, is discharged into mixer 14.

A vaporizable liquid, generally preferably water, is introduced into the mixer in an amount sufficient to form a flowable mixture or slurry. Solids separated from the gas stream in separator 4 also may be introduced into the mixer. In the mixer, a slurry of the solids in a suitable vaporizable liquid is prepared. As mentioned, in general, water is preferred as the vaporizable liquid although the water may be supplemented by the addition of oil or oil may be substituted for the water. Oil from line 9 may be added to the shale at this point, not illustrated in the drawing.

The slurry is withdrawn from mixer 14 to a pump 15 and forced under pressure through heating coil 16 wherein the liquid is vaporized forming a dispersion of shale particles in vapor. The dispersion is passed through line 17 to a gasifier or gas generator 18 where it is admixed with oxygen from line 19. The dispersion may be subjected to very high turbulence if desired, e.g., by discharge from opposed nozzles, to effect pulverization of the shale particles. If desired, part of the steam may be separated from the solid by means of a suitable separator 20, e.g., a cyclone separator, operated at the desired pressure.

In the gasifier 18, the residual shale is reacted with oxygen and steam to produce a stream of hot gases comprising hydrogen and carbon monoxide. The gas stream also contains some carbon dioxide and steam. The hot gas stream is discharged from the gasifier through line 21 into conversion zone 2. A distributor ring 22 assures even distribution of the gas in the shale bed. The gasifier 18 is operated as a flow generator with the reactants in dilute phase, i.e. with the solid suspended in gaseous reactants and reaction products. A suitable gasifier is disclosed in the copending application of Du Bois Eastman, Serial No. 525,240, filed July 29, 1955. Residual solids from the gasifier are collected in water introduced into the gasified vessel through line 25. Solid residue comprising spent shale in water is discharged through lock hopper 23 for disposal.

As previously mentioned, oil from line 9 may be supplied to the gasifier by addition to the shale in mixer 14. Alternatively, and generally preferably, the oil is supplied to the generator, if desired, by injection into the steam-solid dispersion in line 17. This may be withdrawing oil from line 9 to pump 26 and injecting the oil through line 27 into line 17. Alternatively, or simultaneously, oil from separator 7 may be passed by pump 26 through line 28 into converter 2 for further treatment with the shale. Oil from line 28 may, if desired, be injected directly into line 21 into admixture with the hot gases from the gasifier 18 or it may be separately introduced into converter 2.

The heat contents of various streams in the process, e.g., in gas in lines 6 and 8 may be recovered by suitable heat exchange and the heat utilized to preheat the oxygen, steam, or slurry supplied to gasifier 22 and the crushed shale supplied to conversion zone 2. Since heat exchange, per se, is not a part of the present invention, the heat exchangers are not illustrated in the figure.

If desired, carbon monoxide in the gas stream from gasifier 18 may be reacted with steam in a shift conversion step to produce carbon dioxide and hydrogen, carbon dioxide may be removed from the gas stream, and substantially pure hydrogen supplied to the conversion zone.

Oil shale compositions vary considerably. For example, the recoverable shale oil content may vary from 20 to 120 gallons per ton of shale. About 20 to 30 gallons of shale oil, or its equivalent in fuel value, is required to generate the reducing gas for the present process. Accordingly, those oil shales having the higher oil contents, e.g., those containing at least 40 gallons of reconverable shale oil per ton, are preferred. Obviously the more recoverable shale oil contained in the raw shale the better, since the richer shales produce relatively more high B.t.u. gas per ton than the poorer shales, handling costs and plant investment are generally lower, and, if desired, shale oil may also be recovered as a product of the process. In addition, the oil may be upgraded by additional hydrogenation with hydrogen available from the gasifier.

With reference to FIGURE 2 of the drawings, apparatus is illustrated which is particularly adapted to the conversion of oil shales which disintegrate to powder on heating. In this embodiment, the crushed shale is charged through lock hopper 31 into converter 32, similar to convert 2 of FIGURE 1, in which a downwardly moving bed of shale is maintained. Hot reducing gas from a gas generator, described hereinafter, is passed upwardly through the converter to convert the kerogen in the shale to shale oil and gases as described in connection with FIGURE 1.

Gaseous effluent from converter 32 is passed through line 33 to a separator 34, suitably a cyclone separator, in which solid particles are removed from the gaseous effluent stream. Gaseous effluent leaving separator 34 is passed through cooler 36 to a separator 37 in which oil is removed from the gas stream. Product gas is discharged from separator 37 through line 38, while the oil, together with solid particles removed from the gas with the oil, is withdrawn through line 39. As in the case of the embodiment illustrated in FIGURE 1, oil from separator 37 may be returned to conversion zone 32 for further conversion to gases, or withdrawn as product, or supplied to the gasification zone, described hereinafter, as fuel therefor, preferably to supplement the fuel contained in the treated shale from the converter.

Oil recovered in separator 7 or 37 may be subjected to fractionation, e.g., fractional distillation, to recover de-

sirable liquid products; less desirable fractions may be used as recycle to the converter or as fuel for the gas generator. In general, the highest boiling fraction is best utilized in the gas generator, motor fuel boiling range fractions are desirable as products, and intermediate fractions are desirable for recycle to the converter.

Water from a suitable source is introduced through line 40 and is forced by pump 41 under pressure through a heating coil 42 wherein it is converted to steam. If desired, additional fresh shale, for example, fine particles of shale from crushing operations, may be mixed with water in mixer 43 to form a flowable mixture which is pumped through heating coil 42, either in lieu of or in addition to water from line 40, forming a dispersion of the shale particles in steam which serve to supplement the fuel supply to the gasifier.

In converter 32, as the crushed shale moves downwardly through the converter and is heated by hydrogen-rich reducing gas, the shale disintegrates to a fine powder. Hot, treated, powdered shale is withdrawn from converter 32 into a mixer 44 in which the powdered shale is dispersed in steam from heating coil 42. A steam jet type aspirator is suitable as the mixer 44.

The resulting powdered shale dispersed in steam, is passed at relatively high velocity, above about 20 feet per second, and relatively high temperature, generally above 1000° F., through line 45 into gasifier 46 where it is admixed with oxygen-containing gas, preferably relatively pure oxygen, introduced through line 47. The dispersion of powdered shale in steam is discharged into gasifier 46 through a suitable burner, not illustrated in the drawing, wherein the solids and reactant gases, i.e., steam and oxygen, are intimately admixed, preferably within the gasifier. Sufficient oxygen is admitted into the gasifier, or reducing gas generator, to maintain the temperature in the gasifier within the range of 2000 to 3500° F., preferably in the range of 2200 to 2800° F. The gasifiers 18 and 46 are preferably compact, unpacked reaction zones well insulated and designed to operate at an elevated temperature.

Product gas is discharged from the gasifier substantially at operating temperature through line 48 into the lower part of converter 32.

Solid residue from the gasifier is separated from the gas stream and collected in water introduced through line 49 into the gasifier vessel at a point below the gas outlet line 48. Water and cooled residual solids are drawn from the gasifier through lock hopper 50 for disposal.

Fines separated from the gaseous effluent in converter 32 by means of separator 34 may be admixed with the powdered treated shale from converter 32 as feed to mixer 44, as illustrated, or supplied to mixer 43, not illustrated in the drawing, or may be discarded.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope of the invention, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the generation of fuel gas from oil shale which comprises contacting oil shale in lump form having an average particle diameter within the range of ¼ to 6 inches in a conversion zone at a temperature within the range of about 1200 to 1600° F. with a treating gas consisting essentially of carbon monoxide and hydrogen at a temperature above about 2000° F. effecting

conversion of kerogen in said shale to mainly gaseous hydrocarbons, shale oil vapor and unvaporized hydrocarbons; withdrawing a stream of said normally gaseous hydrocarbons together with said shale oil vapor and excess carbon monoxide and hydrogen from said conversion zone; cooling said stream and effecting condensation of said shale oil vapor to shale oil; separating condensed shale oil from accompanying gases; recovering said gases as fuel gas product; withdrawing treated shale containing said unvaporized hydrocarbons from said conversion zone; subjecting said treated shale at elevated temperature to pulverization; passing both said treated shale and said shale oil concurrently to a gas generation zone; subjecting said treated shale together with said shale oil to reaction with an oxygen-containing gas comprising free oxygen and with steam in said gas generation zone at a reaction temperature above about 2000° F. under conditions effecting the production of gas consisting essentially of hot carbon monoxide and hydrogen gases; and passing resulting hot carbon monoxide and hydrogen gases at substantially said reaction temperature into contact with said lump shale in said conversion zone as said treating gas.

2. A process as defined in claim 1 wherein fresh raw shale is admixed with said treated shale and the resulting mixture subjected to said pulverization.

3. A process in accordance with claim 1 wherein said treated shale is subjected to pulverization by forming a flowable mixture thereof with a vaporizable liquid, passing said flowable mixture through a long tubular zone while heating said flowable mixture to vaporize liquid content thereof and form a flowing dispersion of said shale in vapor, and passing said flowing dispersion to said gas generation zone; and wherein said separated condensed shale oil is introduced into said flowing dispersion prior to introduction thereof into said gas generation zone.

4. A process in accordance with claim 1 wherein said treated shale is subjected to pulverization and said shale oil is introduced into said gas generation zone by forming a flowable mixture of said treated shale with a vaporizable liquid at least in part comprising said separated condensed shale oil, passing said flowable mixture into a long tubular zone while heating said flowable mixture and forming a flowing dispersion of said shale in vapor, and passing said flowing dispersion into said gas generation zone.

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