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[54] **PROCESS FOR PRODUCTION OF HYDROCARBON LIQUIDS AND GASES FROM OIL SHALE**

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[52] **U.S. Cl.** ..... **208/11**; 48/197 R

[51] **Int. Cl.²** **C10B 53/06**

[58] **Field of Search** ..... 208/11; 48/197 R

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[57] **ABSTRACT**

A process for the production of hydrocarbon liquids and gases from oil shale comprising the steps of gradually preheating oil shale in a preheat and prehydrogenation zone to a temperature of about 700° to about 950°F. in the presence of hydrogen-rich gas without substantial production of liquid and gas in the preheat and prehydrogenation zone, then destructively distilling the preheated and prehydrogenated oil shale in a hydroretort zone at a temperature of about 850° to about 1,250°F. in the presence of hydrogen-rich gas to form aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic hydrocarbon gases from the preheated and prehydrogenated organic hydrocarbon portion of the oil shale. The hydrogen-rich gas may be passed countercurrent in thermal exchange relation to the spent shale to recover heat from the spent shale heating the hydrogen-rich gas for passage countercurrent and in thermal exchange relation to fresh oil shale in the preheat and prehydrogenation zone. The improvement of this process lies in the exceptionally high conversion of the organic component of oil shale to products of high value including high yields of readily distillable liquids comprising a high proportion of aliphatic and alicyclic hydrocarbon liquids and to low molecular weight paraffinic hydrocarbon gases. The process can be controlled, if desired, to maximize production of aliphatic and alicyclic hydrocarbon liquids. The liquids produced by this invention may be utilized for a wide variety of purposes including gasification for the production of synthetic pipeline-quality gas from oil shale.

18 Claims, 2 Drawing Figures

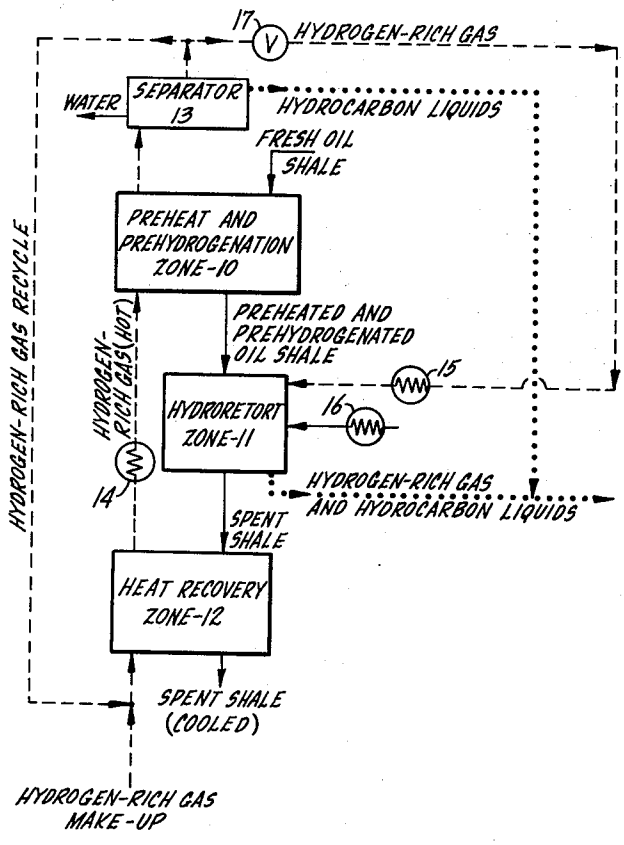
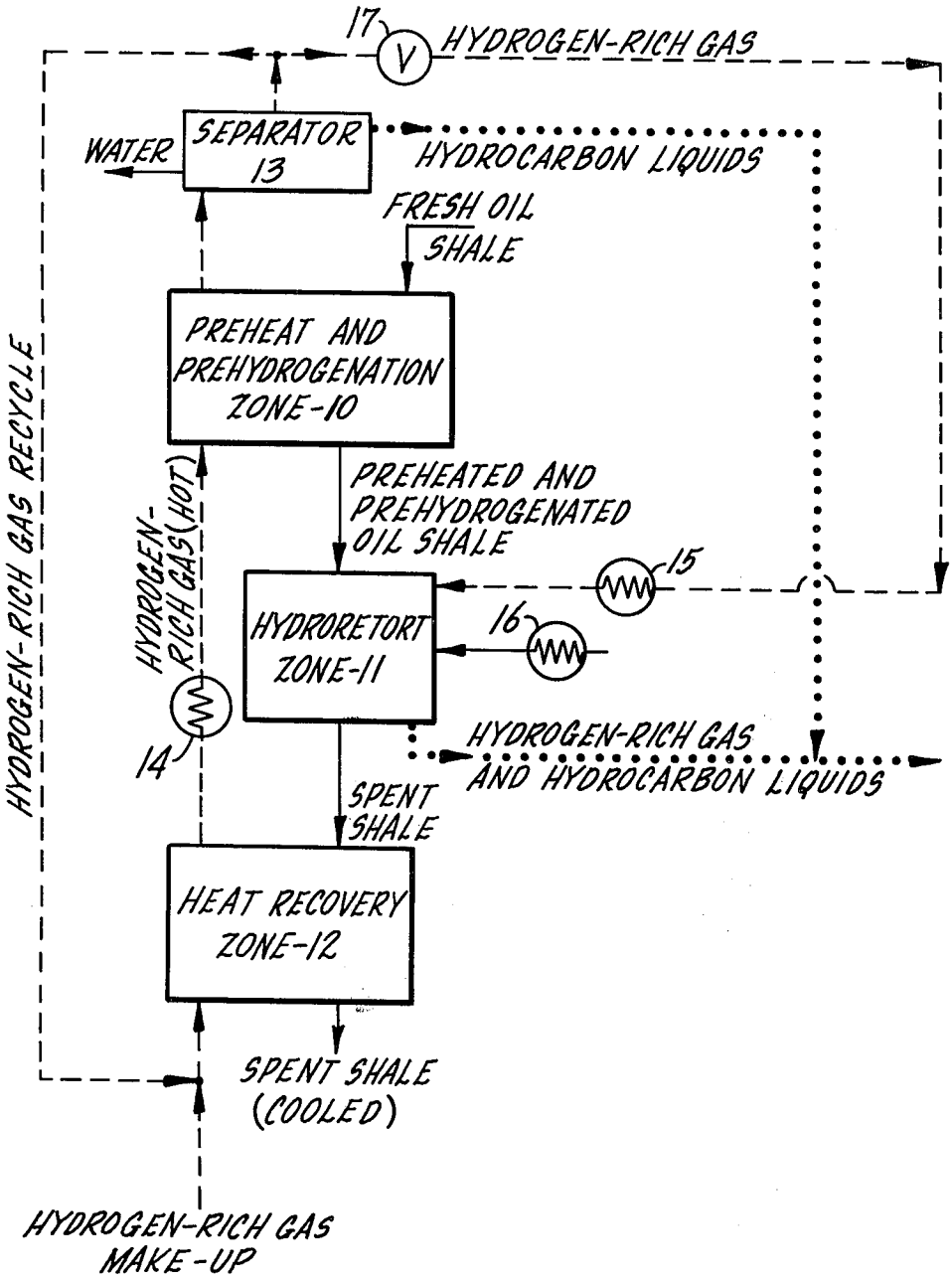


fig. 1.


17
V
HYDROGEN-RICH GAS
SEPARATOR 13
WATER
HYDROCARBON LIQUIDS
FRESH OIL SHALE
PREHEAT AND PREHYDROGENATION ZONE-10
HYDROGEN-RICH GAS RECYCLE
PREHEATED AND PREHYDROGENATED OIL SHALE
HYDROGEN-RICH GAS(HOT)
15
HYDRORETORT ZONE-11
16
14
HYDROGEN-RICH GAS AND HYDROCARBON LIQUIDS
SPENT SHALE
HEAT RECOVERY ZONE-12
SPENT SHALE (COOLED)
HYDROGEN-RICH GAS MAKE-UP

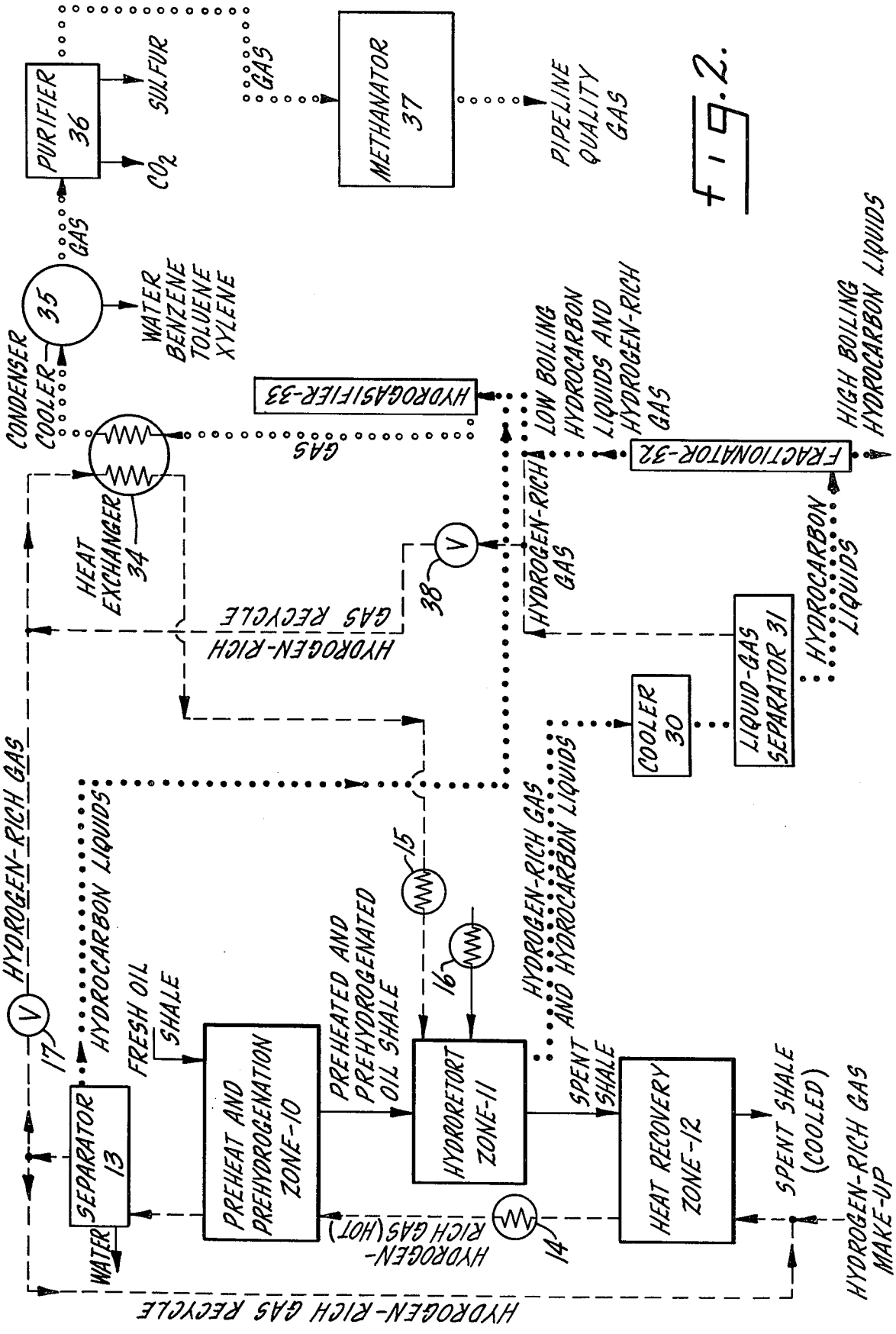

HYDROGEN-RICH GAS
HYDROCARBON LIQUIDS
FRESH OIL SHALE
PREHEAT AND PREHYDROGENATION ZONE-10
PREHEATED AND PREHYDROGENATED OIL SHALE
HYDRORETORT ZONE-11
SPENT SHALE
HEAT RECOVERY ZONE-12
SPENT SHALE (COOLED)
HYDROGEN-RICH GAS MAKE-UP
SEPARATOR 13
WATER
HYDROGEN-RICH GAS (HOT)
14
15
16
17
HYDROGEN-RICH GAS AND HYDROCARBON LIQUIDS
COOLER 30
LIQUID-GAS SEPARATOR 31
HYDROCARBON LIQUIDS
FRACTIONATOR-32
HIGH BOILING HYDROCARBON LIQUIDS
LOW BOILING HYDROCARBON LIQUIDS AND HYDROGEN-RICH GAS
HYDROGASIFIER-33
HYDROGEN-RICH GAS
38
HEAT EXCHANGER 34
HYDROGEN-RICH GAS RECYCLE
CONDENSER COOLER 35
GAS
WATER
BENZENE
TOLUENE
XYLENE
PURIFIER 36
SULFUR
CO_2
GAS
METHANATOR 37
PIPELINE QUALITY GAS

FIG. 2.

PROCESS FOR PRODUCTION OF HYDROCARBON LIQUIDS AND GASES FROM OIL SHALE

This invention relates to an improved process for the production of aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic gases from oil shales. Aliphatic hydrocarbons include open, straight or branched chain molecules which may be saturated or unsaturated. Alicyclic hydrocarbons are cyclic molecules substantially free from aromatic double bonds. Low molecular weight paraffinic hydrocarbon gases include molecules of 4 and less carbon atoms, namely methane, ethane, propane, butane and isobutane. The aliphatic and alicyclic hydrocarbon liquids produced by the process of this invention are especially suited for various further processing. One important use of such liquids is preparing a high methane content pipeline-quality gas suitable as a substitute for or as a supplement to natural gas. Other important uses of such hydrocarbon liquids include production of naphtha, gasoline, kerosine, jet fuel, diesel oil and light fuel oils, and other low boiling distillate oils.

Oil shales are sedimentary rocks which are thought to have been formed from finely divided mineral matter and organic debris from aquatic organisms and some plant matter which were deposited on the bottoms of shallow lakes and seas and later solidified. The resulting oil shales are fine-grained impermeable rocks in which it is almost impossible to separate the organic component and the inorganic mineral matter without changing the structure of the organic component. The largest inorganic constituent of oil shales are carbonates. Oil shales vary in the amount and in the constitution of the organic component which is called kerogen. Typical oil shales contain about 10 to 30 weight percent kerogen. Kerogen is a high molecular weight hydrocarbon having a molecular weight of over 3000 and a carbon to hydrogen weight ratio (C/H) typically of about 7/1 to 8/1.

Due to the high demands upon natural gas supplies and their limited reserves, synthetic pipeline gas will be needed to supplement such natural gas in the United States and other countries of the world. The interest in an economical process for producing synthetic pipeline gas from oil shales is high. There are abundant reserves of commercial grades of oil shales in the United States, particularly in the northwestern areas of Colorado and adjoining areas of Utah and Wyoming.

To be suitable as use for pipeline gas, the heating value must be about 900 to 1100 BTU/SCF which results from high methane content, normally 80 percent by volume or greater. Such specifications require that for pipeline-quality gas the carbon to hydrogen weight ratio be low, approaching as low as 3/1.

To produce a high yield of valuable hydrocarbons from oil shales, it is desirable to limit the coking and aromatization of the oil shales' organic component and to maximize the production of low-boiling aliphatic and alicyclic hydrocarbon liquids from the oil shales. In further processing such hydrocarbons, in turn, give the highest yields of valuable liquid products or fuel gases and cause the least formation of high-boiling aromatic oils and carbon or coke during gasification. It is also desired in the production of desired quality hydrocarbons from oil shales, to limit decomposition of mineral carbonates present in the oil shale and resultant carbon dioxide formation which increases process heat requirements, consumption of hydrogen, and greatly increases the difficulty of further processing.

Previous processes for the production of hydrocarbon fuels from oil shale have the disadvantages of lower thermal efficiency and/or lower conversion of the organic component oil shale to suitable gas or readily gasifiable liquids.

It is an object of this invention to optimize the production of aliphatic and alicyclic hydrocarbon liquids and paraffinic hydrocarbon gases from oil shale suitable for further processing.

It is another object of this invention to provide a process for the production of aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic hydrocarbon gases from oil shale wherein the oil shale is preheated and prehydrogenated by countercurrent flow of hydrogen-rich gas and may be hydroretorted by countercurrent or cocurrent flow of hydrogen-rich gas.

It is still another object of this invention to provide a process for high yield production of pipeline-quality gas from oil shale by a process characterized by its high thermal efficiency.

Further objects of this invention will appear to one skilled in the art as this description proceeds and by reference to the figures.

Preferred embodiments of this invention are illustrated in the drawings wherein:

FIG. **1** is a block flow diagram illustrating the production of hydrocarbon liquids from oil shale using one embodiment of the process of this invention; and

FIG. **2** is a block diagram showing the production of pipeline-quality gas from oil shale by one embodiment of this invention.

The process of this invention is applicable to a wide variety of oil shales. For high efficiency it is desired that the Fischer Assay, which indicates the oil yield obtained by conventional retorting of the oil shale, be **25** gallons per ton or more. However, the process of this invention is also applicable to oil shales having lower Fischer Assays, down to about **10** gallons per ton.

The size of the shale particles used in the process of this invention is not important, but particles generally of the size 1/16 inch to 1 inch diameter are utilized. Use of very fine particle shales may give difficulty in clogging during processing and large particle shales have a lower surface area and may result in longer processing times.

The fresh oil shale is fed into a preheat and prehydrogenation zone and gradually preheated to a temperature of about 700° about 950°F. in the presence of hydrogen-rich gas. It is preferred that the temperature to which the oil shale is heated in the preheat and prehydrogenation zone is about 750° to about 850°F. At 700°F. the rate of adequate prehydrogenation is slow, but may be achieved by a residence time of several hours. At the higher temperatures of about 950°F. prehdyrogenation occurs in a few minutes. The criteria of adequate prehydrogenation is the ultimate increased recovery of organic matter from the shale which is expressed most conveniently in terms of organic carbon recovery. By the process of this invention, as much as about 95 percent of the organic carbon can be removed from oil shale in the form of valuable liquid and gaseous hydrocarbons. Longer residence times at the higher temperatures lead to undesired production of oil and gas by hydroretorting in the preheat and prehydrogenation zone. It is desired to limit oil production in the preheat and prehydrogenation zone to avoid plugging of

the shale in this zone. It is desired not to produce substantial quantities of hydrocarbons in the preheat and prehydrogenation zone, preferably less than about 15 to 20 weight percent of the organic component of the shale is converted to normally liquid or gaseous hydrocarbons. It is especially preferred to convert less than about 10 weight percent of the organic component of the shale to liquid or gas in this zone.

The terminology "hydrogen-rich gas" throughout this description and claims, means gases with sufficient hydrogen partial pressure to effect high organic carbon recovery from the organic material in the oil shales. Such hydrogen- rich gases may be obtained by a number of processes well known in the chemical process industry. Table I shows the effect of the hydrogen partial pressure and the heatup rate upon organic carbon recovery from prehydrogenated oil shales which had an original organic carbon content of 21.1 weight percent. The maximum temperature to which the shale was heated was 1150°F.

TABLE I

Hydrogen Partial Pressure (psia)	Total Pressure (psia) at Indicated Hydrogen Content			Percent Organic Carbon Recovery at Indicated Heating Rate (°F/min)		
	25%	50%	90%	10	30	50
0	Inert gas (500psig Helium)			77	77	77
35	140	70	39	87	87	87
115	460	230	128	89	87	87
215	860	430	239	92	88	87
515	2060	1030	572	94	92	88

Table I shows that hydrogen-rich gases of 35 psia hydrogen partial pressure are suitable for use in this invention. It is preferred to use hydrogen-rich gas having a partial pressure of hydrogen greater than about 100 psia. The upper operating pressures are limited only by equipment and economic considerations. One benefit of the higher hydrogen partial pressure is that it allows higher rates hence, less residence time and smaller reactors. Total operating pressures throughout the system are usually substantially the same. Normally the process of this invention may be carried out at total pressures of about 40 to about 1500 psia, preferably about 500 to 1000 psia.

It is preferred that the oil shale not be thermally shocked by abrupt temperature changes, but that it be gradually heated at a rate in the order of less than about 100°F. per minute. It is preferred that the heating rate be less than about 50°F. per minute.

The oil shale and hydrogen-rich gas may be heated by external heating means or internal heating means in the preheat and prehydrogenation zone by a wide variety of methods which are readily apparent to one skilled in the art. Such variety of heating means allow both cocurrent and countercurrent operation of the preheat and prehydrogenation zone with respect to the shale and hydrogen-rich gas. One method which is preferred is the introduction of oil shale at ambient temperatures at one end of the preheat and prehydrogenation zone and the introduction of the hydrogen-rich gas at the other end of the preheat and prehydrogenation zone at a temperature in quantities sufficient to heat the oil shale to about 700° to about 950°F. by countercurrent flow of the hydrogen-rich gas in thermal exchange relation to the oil shales. To maximize the production of aliphatic and alicyclic hydrocarbon liquids from the oil shales, it can be seen from Table I that the preferred partial pressure of hydrogen at its introduction to the preheat and prehydrogenation zone should be about 100 psia, or greater.

The preheated and prehydrogenated oil shale is destructively distilled in a hydroretort zone at a temperature of about 850° to about 1250°F. in the presence of hydrogen-rich gas to form aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic hydrocarbon gases from the preheated and prehydrogenated organic portion of the oil shales. It is necessary to reach a temperature of about 850°F. in order ot obtain the desired hydroretorting in a reasonable period of time. It is desired, in order to obtain the maximum yield of aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic hydrocarbon gases, to maintain the temperature in the hydroretort zone at lower than about 1250°F. The maintenance of the temperature in the hydroretort zone at lower than about 1250°F. limits the inorganic carbonate decomposition to acceptable levels and also limits the destructive hydrogenation of organic matter to gaseous paraffinic hydrocarbons called hydrogasification, in the hydroretort zone. Formation of carbon dioxide by inorganic carbonate decomposition in the hydroretort zone is undesirable due to its direct dilution of the hydrogen-rich gas, its consumption of hydrogen in conversion to carbon monoxide and steam, and its use of heat for decomposition. Therefore, if pipeline-quality gas is desired, additional purification is required to remove the carbon dioxide and carbon monoxide so formed.

Table II shows the effect of temperature in the hydroretort zone upon the decomposition of mineral carbonate under conditions wherein the oil shale was heated at a rate of 33°F. per minute and the original mineral carbonate content of the oil shale was 12.54 weight percent.

TABLe II

Temperature °F	Percent Mineral Carbonate Decomposition
1000	0
1100	7.1
1200	13.3

Hydrogasification in the hydroretort zone is not necessarily detrimental if the desired product is only fuel gas. At higher temperatures than about 1250°F., increasing proportions of paraffinic hydrocarbon gases are formed which are the most valuable constituents of fuel gases and are the only acceptable major constituents of pipeline-quality gas. However, at temperatures above about 1250°F. the yield of liquid hydrocarbons begins to decrease substantially and the liquids which are produced become increasingly aromatic in composition. The data showing product distribution and organic carbon recovery are illustrated in Table III for a typical heat-up rate and hydrogen partial pressure in laboratory work simulating the combined results of the preheating, prehydrogenation and hydroretorting steps. Eventually, as temperatures are increased further, the total organic carbon recovery drops to unacceptable levels because of coke and carbon formation of the organic component of the oil shale.

TABLE III

Maximum Temperature °F.	Average Hydrogen Partial Pressure (psia)	Percent Organic Carbon Recovery Total	As Gases	As Liquids	Liquid Product Properties I.B.P.—400°F. Distillate (percent)	I.B.P.—400°F. Distillate Fraction (percent) Aliphatic and Alicyclic Saturated	Olefinic	Aromatic
1203	247	90.8	10.7	80.1	31	28	65	7
1298	252	95.0	50.7	44.3	36	5	39	56
1414	236	92.8	63.3	29.5	40	5	35	60

NOTE: *I.B.P.—400°F. shows the fraction boiling between the initial boiling point and 400°F.

As can be seen from Tables II and III, the maximum hydroretorting temperature to obtain a combination of low mineral carbonate decomposition, high total organic carbon recovery and a high proportion of low boiling aliphatic and alicyclic hydrocarbons in the hydrocarbon liquid products, is about 1250°F. The preferred temperature range is about 950° to about 1150°F. These temperatures vary somewhat over the specified ranges of hydrogen partial pressure and heat-up rate or retention time.

One further consideration which favors hydroretorting at temperatures not exceeding about 1250°F., is that the increase in hydrogasification reached at the higher temperatures may cause temperature control problems since hydrogasification is exothermic.

The hydrogen-rich gas supplied to the hydroretort zone should contain sufficient hydrogen to meet the chemical requirements sufficient to convert the organic portion of the oil shale to aliphatic and alicyclic hydrocarbon liquids and paraffinic hydrocarbon gases. It may also be desirable to add a controlled excess of hydrogen to the hydroretort zone. For example, sufficient excess hydrogen may be added to the hydroretort zone to ultimately convert all of the hydrocarbons recovered, and the carbon monoxide remaining after final purification, to methane. The use of such an excess of hydrogen in the hydroretort zone is also a means for providing a portion of the heat necessary to achieve the desired temperatures in the hydroretort zone. However, other heating means may be used and such excess hydrogen may be added at a later stage. More than such excess of hydrogen, if not separated prior to subsequent gasification, will only dilute the gaseous products and may require further separation if pipeline-quality gas is desired. Less than such excess may lead to undesired carbon deposition if the aliphatic and alicyclic hydrocarbon liquids are subsequently hydrogasified in another processing step. Lesser than the amounts of hydrogen required chemically for conversion of the prehydrogenated component of oil shale to aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic hydrocarbon gases results in lower organic carbon recovery.

The hydrogen-rich gas may be passed cocurrent or countercurrent to the oil shale in the hydroretort zone. It is preferred to pass the hydrogen-rich gas in cocurrent thermal exchange relation with the preheated and prehydrogenated shale in the hydroretort zone to avoid condensation of hydroretorted liquids. The retention time in the hydro-retort zone is sufficient, dependent upon the particular temperature, pressure and hydrogen concentration in the hydrogen-rich gas, to produce by hydroretorting a quantity of aliphatic and alicyclic hydrocarbon liquids and low molecular weight gases from the preheated and prehydrogenated organic components of the oil shale equivalent to a total organic carbon recovery of above 85 percent, and preferably above 90 percent. If the desired end product is pipeline-quality gas, the amount of low molecular weight gases produced in the hydroretort zone is not important. However, when the aliphatic and alicyclic hydrocarbon liquids are going to be further processed to a liquid product, it may be desirable to limit gas formation in this zone by operation in the lower ranges of temperature.

The hydroretort zone may be heated by any suitable method as will be obvious to one skilled in the art. One method is to supply hydrogen-rich gas of sufficiently high temperature to raise the temperature of the shale to the desired temperature by direct thermal exchange. The hydroretort zone may be optionally internally heated by any suitable means such as fuel oil/oxygen burner.

Referring to FIG. **1**, the fresh oil shale is supplied to preheat and prehydrogenation zone **10** wherein hot hydrogen-rich gas passes countercurrent and in thermal exchange relation to the oil shale at a temperature sufficient to gradually preheat the oil shale to a temperature of about 700° to about 950°F. The preheated and prehydrogenated oil shale is then passed to hydroretort zone **11** wherein it is passed cocurrently and in thermal exchange relation with hydrogen-rich gas of sufficient temperature to heat the oil shale to a temperature of about 850° to about 1250°F. In hydroretort zone **11**, the organic component of the oil shale is destructively distilled to form aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic hydrocarbon gases. The aliphatic and alicyclic hydrocarbon liquids, remaining hydrogen-rich gas and any newly formed gaseous hydrocarbons are removed from the hydroretort zone. The aliphatic and alicyclic hydrocarbon liquids may be subjected to further treatment to form other desired products, such as pipeline-quality gas. The spent shale is removed from hydroretort zone **11** and passed through heat recovery zone **12** in countercurrent and thermal exchange relation to hydrogen-rich gas which cools the spent shale to less than about 300°F., preferably to about 150°F. The hydrogen-rich gas is heated in heat recovery zone **12** for recycle to preheat and prehydrogenation zone **10.**

One advantage of the process of this invention is the high thermal efficiency wherein the hydrogen-rich gas may remove a large portion of the thermal energy of the spent shale for reutilization in preheating of the fresh oil shale. FIG. **1** shows a preferred embodiment of this invention wherein hydrogen-rich gas from preheat and prehydrogenation zone **10** passes through separator **13** for removal of liquids, namely water and hydrocarbon liquids which may be formed in preheat and prehydrogenation zone **10.** The organic hydrocarbon liquids from separator **13** may be fed into the hydrocarbon liquid output from hydroretort zone **11.**

The hydrogen-rich gas leaving separator **13** follows a split stream, one portion recycling to heat recovery zone **12** and another portion supplying hydroretort zone **11.** Valve **17** adjusts the split in the hydrogen-rich gas flow dependent upon the chemical hydrogen requirement in hydroretort zone **11.** The hydrogen-rich gas passing from separator **13** to hydroretort zone **11** may be heated by any suitable heating means shown as **15,** prior to introduction to hydroretort zone **11.** Alternatively, the hydrogen-rich gas may be supplied directly to the hydroretort zone **11** without preheating and hydroretort zone **11** may be heated by any suitable means shown in FIG. **1** as heat input means **16.** Heat input means **16** may be combustion of fuel with oxygen.

The other portion of the stream of hydrogen-rich gas from separator **13** is recycled to heat recovery zone **12.** The amount of hydrogen-rich gas makeup is determined by the amount of hydrogen consumed in the prehydrogenation and hydroretort zones and discharged from hydroretort zone **11.** The hydrogen-rich gas is heated in heat recovery zone **12** and upon passing from heat recovery zone **12** may be further heated by any suitable heater means **14** prior to introduction to preheat and prehydrogenation zone **10** to obtain the desired temperature for entry to preheat and prehydrogenation zone **10.** It is seen from FIG. **1** that a larger volume of hydrogen-rich gas passes through preheat and prehydrogenation zone **10** then passes through hydroretort zone **11.**

The advantages of the process of this invention appear to be achieved by the controlled gradual preheating and prehydrogenation in zone **10** followed by higher temperature hydroretorting of the preheated and prehydrogenated oil shale in zone **11.** While prior processes of retorting oil shale without gradual preheating and prehydrogenation of the organic component have resulted in less than 80 percent recovery of the organic carbon from the shale, we have found that with our two-zone hydroretorting process, it is possible to recover as much as about 95 percent of the organic carbon from the oil shale.

One important use for the aliphatic and alicyclic hydrocarbon liquids obtained from the hydroretort zone by the process of this invention, is for further processing to produce pipeline-quality gas. Pipeline-quality gas may be obtained from such readily gasifiable liquids by any suitable method of producing a methane-rich gas. The aliphatic and alicyclic hydrocarbon liquids may be further treated to produce pipeline-quality gas by many known processes including hydrogasification by gas recycle hydrogenation or fluidized bed hydrogenation, naphtha reforming, catalytic-rich gas, methane-rich gas or Lurgi Gasynthan processes.

FIG. **2** illustrates a preferred embodiment of this invention in the production of pipeline-quality gas. Aliphatic and alicyclic hydrocarbon liquids are produced in generally the same manner as previously described with further increases in thermal efficiency of the process being obtained by recovery of some hydrogen-rich gas recycle from the product of hydroretort zone **11** and by utilization of heat from a heat exchanger cooling the gas output of a hydrogasifier to heat hydrogen-rich gas input to hydroretort zone **11.**

In the embodiment shown in FIG. **2,** the effluent stream of hydroretort zone **11** is passed through cooler **30** and liquid-gas separator **31** to separate the hydrocarbon liquids from hydrogen-rich gas. A portion of the hydrogen-rich gas so separated may then be recycled to hydroretort zone **11** through control valve **38.** Any hydrogen-rich gas not necessary in hydrogasifier **33** may be recycled in this manner. The hydrocarbon liquid output from liquid-gas separator **31** is passed to fractionator **32** which separates high boiling hydrocarbon liquids from the low boiling hydrocarbon liquids, thereby obtaining the preferred C/H ratio of about 7/1 prior to hydrogasification. The high boiling liquids may be used as fuel to supply heat to the process or as feed to produce hydrogen make-up gas. The low boiling hydrocarbon liquids from fractionator **32** are then fed through a convention hydrogasifier shown as **33** which is usually maintained at a temperature of about 1200° to about 1500°F. and suitable pressure to effect gasification. The effluent gas from hydrogasifier **33** is passed through heat exchanger **34** wherein the hydrogen-rich gas passing to hydroretort zone **11** may be heated by thermal exchange with the hydrogasified gas. The cooled by hydrogasified gas is then passed through a condenser-cooler removing water, benzene, toluene, xylene followed by purification to remove any remaining quantities of undesired steam, carbon monoxide carbon dioxide, hydrogen sulfide, and nitrogen. Following such purification, the hydrogasified product is methanated in a conventional manner to increase the amount of methane in the resulting pipeline-quality gas.

The combination of the hydrogasifier process with the process for production of hydrocarbon liquids and gases from oil shale results in high overall thermal efficiency.

Suitable apparatus for use in the process of this invention will be readily apparent to one skilled in the art. It is apparent that the process of this invention may be operated in a physically separated preheat and prehydrogenation zone and hydroretort zone or the preheat and prehydrogenation zone and the hydroretort zone may be physically contained in one vessel appropriately separated. When operated on a batch basis, the preheat and prehydrogenation conditions may first be subjected to a single zone to which same zone the hydroretort conditions are later applied. It is readily apparent the process of this invention may be carried out on either a batch or continuous flow basis. A continuous flow process is preferred.

While no specific means of distribution of the hydrogen-rich gas throughout the zones containing oil shale is shown, it is readily apparent that it is desirable to have a suitable gas distribution means such as a gas manifold distribution system at the introduction area of the gas to the particular zone. The desirable factor is that the hydrogen-rich gas be effectively distributed to the cross-sectional area of the zone upon its introduction or shortly thereafter.

Suitable materials for construction of an apparatus suitable for the process of this invention are well known to persons skilled in the art and need only be sufficient to contain the pressures obtained in the process and to effect suitable heat retentions in the different thermal zones of the process of this invention.

EXAMPLE I

Oil shale having a Fischer Assay of 24 gallons per ton was crushed into particles of about one-half inch in size. The crushed shale, at ambient temperature of about 77°F., was introduced into a vessel having an upper preheat and prehydrogenation zone, a hydroretort zone in the middle and a heat recovery zone

in the lower portion. These zones are separated by two decks, one between the bottom of the preheat and prehydrogenation zone and the top of the hydroretort zone and the other between the bottom of the hydroretort zone and the top of the heat recovery zone. Solid flow by gravity through these zones was controlled by a solids flow controller at the spent shale exit in the bottom of the heat recovery zone. The entire system operated at a total pressure of 1000 psia and lock hoppers were used to introduce the crushed shale to the upper end of the preheat and prehydrogenation zone and moved through this zone countercurrent to hydrogen-rich gas. Hydrogen-rich gas containing 93.9 mol percent hydrogen was introduced at a rate of 4.3 mols/hr. at a temperature of 950° F. to the bottom of the preheat and prehydrogenation zone through a gas distributor. The shale was introduced at the rate of 100 pounds per hour for a residence time of about 15 minutes flowing countercurrent to the hydrogen-rich gas. The shale left the preheat and prehydrogenation zone at a temperature of 850°F. and entered directly to the top of the hydroretort zone. About 0.6 pounds per hour of hydrocarbon oils having a carbon/hydrogen ratio of 6.95/1 and about 0.34 pounds per hour of water were formed in the preheat and prehydrogenation zone. The oil and water were removed from the hydrogen-rich gas leaving the top of the preheat and prehydrogenation zone and the oil was fed directly to a gas phase hydrogasifier.

The shale was further heated in the hydroretort zone to 1100°F. by a combination of cocurrent flow with hydrogen-rich gas introduced to the top of the hydroretort zone at 1350°F. and by direct firing of fuel and oxygen within the zone. 0.12 pound per hour of the aromatic liquids produced in the gas phase hydrogasifier were used as fuel for this purpose. 0.5 mols/hr. of gas containing hydrogen were supplied to more than satisfy the chemical requirements for complete hydroretorting. This gas was removed from the top of the preheat and prehydrogenation zone and after liquids removed, was heated to 1350°F. and introduced to the top of the hydroretort zone. The residence time of the shale in the hydroretort zone was about 5 minutes. The output of the hydroretort zone showed that 90.8 percent of the organic carbon in the shale had been converted, 82.7 percent to hydrocarbon liquids having a C/H ratio of 7.4/1 and 8.1 percent to low molecular weight paraffinic hydrocarbon gases.

The spent shale was removed from the bottom of the hydroretort zone to the top of the heat recovery zone wherein it was cooled to 150°F. by countercurrent flow with hydrogen-rich gas recycled from the preheat and prehydrogenation zone. 3.8 mols per hour of gas containing 93.8 mol percent hydrogen were recycled from the preheat and prehydrogenation zone at 100°F., heated to 792°F. in the heat recovery zone and further heated to 950°F. by a furnace in the recycle line bypassing the hydroretort zone and fed to the bottom of the preheat and prehydrogenation zone. 0.51 mols/hr. of 94.4 percent hydrogen-rich make-up gas was added to the hydrogen-rich gas fed to the bottom of the heat recovery zone. 10.3 pounds per hour of hydrocarbon liquids from the hydroretort zone and 1.2 pounds per hour of water were separated from the product gases by cooling. The hydrocarbon liquids were then fractionated and the low boiling hydrocarbon fraction produced at the rate of 4.2 pounds per hour and having a C/H ratio of 7.0/1 were fed, together with the product gases from the separator, to a recycle type gas phase hydrogasifier operated at 1400°F. Hydrocarbons having a C/H ratio of 7.0/1 or less limit the carbon deposition in the hydrogasifier. The high boiling hydrocarbon fraction produced at the rate of 6.0 pounds per hour and having a C/H ratio of 7.7/1 were fed to a partial oxidation plant for producing hydrogen-rich gas make-up for use in the process. The product of the hydrogasifier at 1400°F. was passed in thermal exchange relation with the hydrogen-rich gas removed from the top of the preheat and prehydrogenation zone prior to its introduction to the top of the hydroretort zone, heating such hydrogen-rich gas from 100°F. to 1350°F. and cooling the product of the hydrogasifier to 720°F. After passing through this heat exchanger, the gaseous product was further cooled and 0.034 pounds per hour of water and 0.73 pounds per hour of aromatic liquids were removed. Then 0.012 mols per hour of carbon dioxide and 0.010 mols per hour of hydrogen sulfide were removed and the gas methanated resulting in dried pipeline-quality gas having a gross heating value of 951 BTU/SCF and containing less than 0.1 percent carbon monoxide. 1.58 SCF of pipeline-quality gas containing 92.8 mol percent methane was produced per pound of dry shale.

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

We claim:

1. A process for the production of aliphatic and alicyclic hydrocarbon liquids from oil shale wherein above about 77 percent of the organic carbon in said oil shale is converted to said liquids and gases comprising the steps:

introducing fresh oil shale into a preheat and prehydrogenation zone;

gradually preheating, at a rate of less than about 100°F. per minute, oil shale in the preheat and prehydrogenation zone to a temperature of about 700° to about 950°F. in the presence of hydrogen-rich gas with less than about 20 weight percent of the organic component of oil shale converted to liquid and gas in said preheat and prehydrogenation zone, said hydrogen-rich gas and shale passing countercurrently in said zone;

destructively distilling the preheated and prehydrogenated oil shale in a hydroretort zone at a temperature of about 850° to about 1250°F. in the presence of at least a stoichiometric amount of hydrogen-rich gas to form aliphatic and alicyclic hydrocarbon liquids and low molecular weight paraffinic hydrocarbon gases from the preheated and prehydrogenated organic portion of said oil shale; and

said hydrogen-rich gas being supplied to said preheat and prehydrogenation zone in larger volumes than the hydrogen-rich gas supplied to said hydroretort zone.

2. The process of claim **1** wherein spent shale is passed from said hydroretort zone to a heat recovery zone wherein hydrogen-rich gas recycled from said preheat and prehydrogenation zone passes countercurrent and in thermal exchange relation to said spent shale

cooling the spent shale and heating the hydrogen-rich gas for introduction to said preheat and prehydrogenation zone.

3. The process of claim **2** wherein hydrogen-rich gas make-up is added to said hydrogen-rich gas recycle prior to introduction to said heat recovery zone.

4. The process of claim **2** wherein hydrogen-rich gas make-up is added to said heat recovery zone.

5. The process of claim **2** wherein said heated hydrogen-rich gas is further heated during passage from said heat recovery zone to said preheat and prehydrogenation zone.

6. The process of claim **2** wherein the hydrogen-rich gas recycle is passed through a liquid separator after leaving the preheat and prehydrogenation zone and prior to the addition of hydrogen-rich gas make-up.

7. The process of claim **2** wherein the hydrogen-rich gas stream leaving said preheat and prehydrogenation zone is split with one portion, containing sufficient gas to provide at least the chemical hydrogen requirements in the hydroretort zone, is passed to said hydroretort zone and the other portion is recycled to said heat recovery zone.

8. The process of claim **7** wherein said one portion of hydrogen-gas stream is further heated during passage to said hydroretort zone.

9. The process of claim **1** wherein the oil shale is preheated to about 750° to about 850°F. in said preheat and prehydrogenation zone.

10. The process of claim **1** wherein said preheated and prehydrogenated oil shale is passed through said hydroretort zone in cocurrent thermal exchange relation with said hydrogen-rich gas.

11. The process of claim **1** wherein the preheated and prehydrogenated oil shale is heated to about 950° to about 1150°F. in said hydroretort zone.

12. The process of claim **11** wherein the preheated and prehydrogenated shale in the retort zone is heated by an internal heating means.

13. The process of claim **1** wherein the preheat and prehydrogenation zone and the hydroretort zone is at a total gas pressure of about 40 to about 1500 psiz.

14. The process of claim **13** wherein the hydrogen partial pressure is greater than about 100 psia.

15. The process of claim **1** wherein hydrogen-rich gas is separated from the aliphatic and alicyclic hydrocarbon liquids formed in said hydroretort zone and recycled to said hydroretort zone.

16. The process of claim **11** wherein more than about 80 percent of the organic portion of oil shale is converted to liquid.

17. The process of claim **1** wherein above about 85 percent of the organic carbon in said oil shale is converted to said liquids and gases.

18. The process of claim **1** wherein said aliphatic and alicyclic liquids are gasified in a hydrogasifier and wherein the hydrogen-rich gas provided to said hydroretort zone is heated by thermal exchange with the output stream of said hydrogasifier.

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