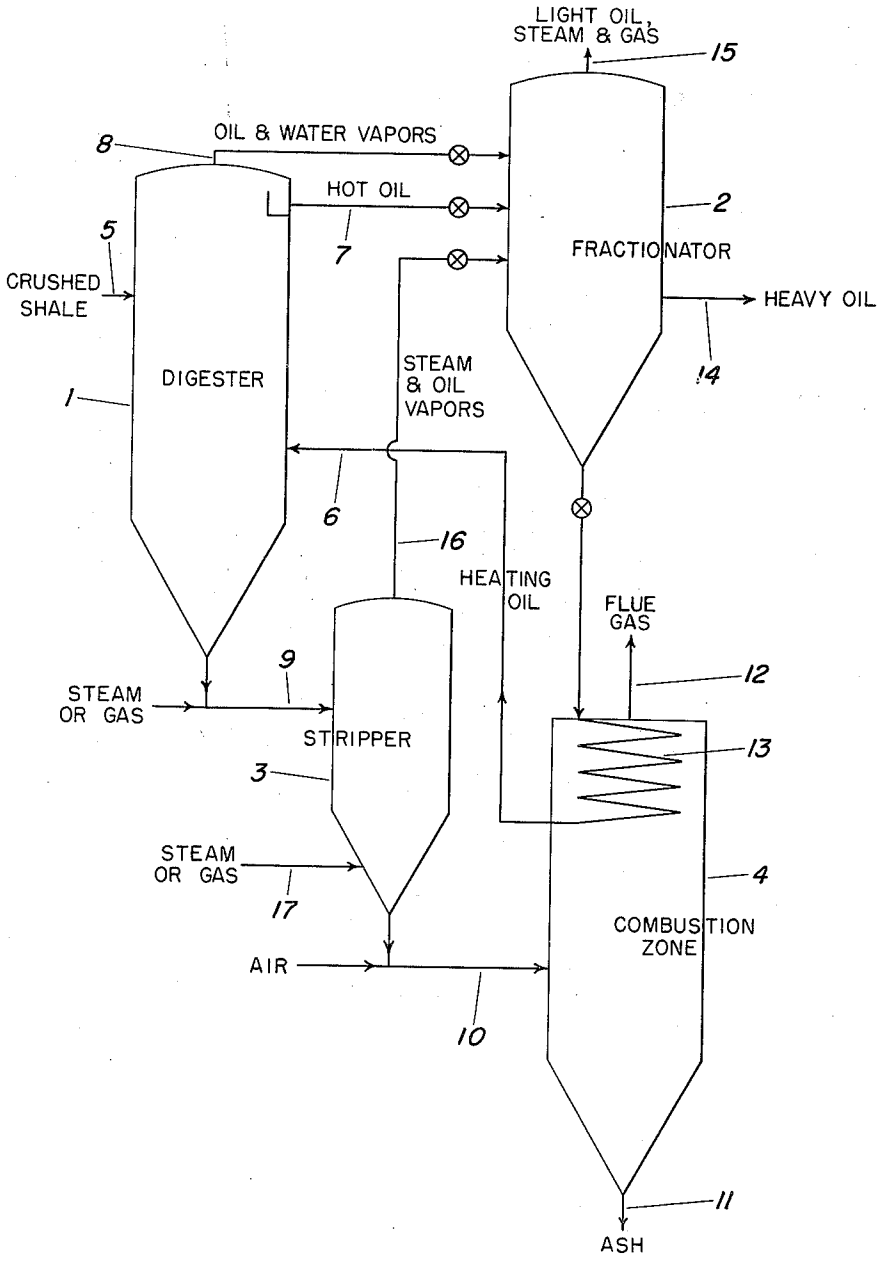
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CONTINUOUS PROCESS FOR THERMAL EXTRACTION OF OIL SHALE

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INVENTOR FREDERICK E. BUCHAN

BY Donald G. Welch

ATTORNEY

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CONTINUOUS PROCESS FOR THERMAL EXTRACTION OF OIL SHALE

Frederick E. Buchan, Falls Church, Va., assignor to the United States of America as represented by the Secretary of the Interior

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The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor. This application is a continuation-in-part of my copending application S. N. 614,588 for Processing Oil Shale, filed September 5, 1945, now Patent No. 2,487,788.

It is an object of this invention to provide a continuous process for conversion of the organic matter of kerogen rocks, especially oil shale and similar minerals, to liquid fuel fractions.

Another object of this invention is to effect a more efficient separation of liquid fuel fractions from the mineral residue after conversion of the kerogen.

Another object of this invention is to improve the conversion of kerogen by closer control of heat during digestion of the shale.

A further object of this invention is to improve the efficiency of recovery of solvent and liquid fuel fractions in the conversion of kerogen.

It is a further object of this invention to secure the maximum recovery of the heating value of the kerogen of the raw shale. These and other objects of my invention will be apparent from the following description and claims.

It is generally recognized that kerogen rocks are sedimentary rocks containing organic matter which yield an oil equivalent to approximately 50 percent of the organic content when subjected to destructive distillation ("Classification of Oil Shales and Cannel Coals," by Downs and Himus, 1940). Such rocks occur in continuous seams in many localities throughout the world. Kerogen as such has been defined as the material in Scottish shales which yields oil upon destructive distillation ("Shale Oil," by R. N. McKee, 1925). In the United States, these rocks are commonly designated as "oil shale" without regard to more exact mineralogical terminology. The oil shales of the western United States have been extensively studied and are particularly suitable for commercial development. Extensive deposits of lean oil shale occur in the eastern United States, chiefly in the Kentucky-Indiana area. A typical sample of Green River shale from Colorado has the following composition:

	Per cent
Kerogen	21.6
Dolomite and calcite	38.4
Analcite	17.1
Quartz	12.1

For convenience, therefore, whenever the term "oil shale" is used herein, in the specification or

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claims, it is understood that the term is intended to include all kerogen containing rocks, regardless of their common or scientific designations.

The kerogen of oil shales is neither an oil, such as petroleum, nor is it a semisolid, such as bitumen or asphalt. It does, however, yield a mixture of hydrocarbons and certain nitrogen and phenolic compounds, usually called "shale oil," upon pyrolytic conversion.

Shale oil has been produced for many years in Scotland, Sweden, and Estonia by the destructive distillation of local kerogen rocks. The industry, however, is not large, as the methods in use are relatively inefficient. In general, the kerogen rock is heated in batches in comparatively small retorts or ovens, thereby decomposing the kerogen, part of which is ultimately recovered as an oil resembling crude petroleum, the remainder appearing as fixed gases and carbon. The percentage recovery, as oil, of the organic matter originally present in the oil is low by these methods. Many types of retorts for handling oil shale have been developed, but even the best operations result in relatively high conversion of kerogen to carbon and permanent gases, which are of low economic value as compared with liquid fuels. Temperatures in these retorting operations are approximately 1,000° F. or even higher. Obviously, unless the products can be removed almost instantaneously, there is considerable secondary cracking of the oil vapors in contact with the shale spent, or partially spent. Shale apparently is an excellent cracking catalyst. Consequently, under even the best retorting conditions, the yield of liquid products cannot be materially increased, and there will always be large losses in the form of carbon (in the spent shale) and as gases.

The conversion of the kerogen by heating in contact with so-called "solvents" has been proposed as a solution to the problem of gas and carbon formation. Numerous patents have issued on some of these proposals, but prior to my invention as described in my copending application S. N. 614,588, no extractive process had proven satisfactory or even competitive with the established retorting methods.

In my copending application S. N. 614,588, there is described a process wherein the kerogen rock is treated with a heavy hydrocarbon oil at temperatures above about 700° F. and not exceeding about 800° F., with yields of liquid products substantially higher than otherwise obtainable.

This invention is based upon the discovery, as determined from actual experiments with oil shale, of the following facts:

1. Kerogen itself is not soluble in the usual liquid solvents and various fractions of shale oil and similar liquids, previously proposed for its extraction.

2. On heating at various temperatures for varying periods of time, kerogen is converted to bitumen, the percentage conversion increasing with the temperature and time of heating.

3. The resulting bitumen is soluble in certain fractions of shale oil, including the heavier fractions.

4. Prolonged contact of the extracted bitumen with the remaining shale results in cracking of the bitumen to yield various lower boiling fractions of liquid hydrocarbons, such as gas, gasoline, fuel oil, etc., the extent of the cracking depending on the time of contact and temperature.

There is an optimum relation of time and temperature whereby it is possible to effect a maximum conversion of the kerogen to the desired primary liquid products. These conditions may vary in minor respects for different shales, depending upon the kerogen content.

My process may be considered as involving the following stages:

1. Initial heating of shale to a predetermined range to drive off free moisture in the shale.

2. Conversion of the kerogen of the shale to bitumen and some lighter products.

3. Cracking of the bitumen and heavy oil to lighter products.

This theory, it should be understood, is offered by way of explanation, and is not intended to limit my invention to any particular theory of mechanism of chemical changes.

Since these reactions occur at varying rates, close control of products and yields is difficult in batch or semibatch operations, and it is the object of this invention to adapt the principles of my earlier case to continuous operations.

To clarify and explain my invention more fully reference is made to the accompanying drawing of an embodiment of my invention, in which the flow of materials and products is shown by legends and arrows. In this system, the several treating zones are represented by digester 1, for treating the raw shale, a fractionator 2, for separating desired liquid products from the kerogen of the shale, a stripper 3, for removing oily residues from spent shale discharged from the digester 1, and a furnace 4, for heating the oil supplied to the digester by combustion of carbonaceous material remaining in the spent shale from the stripper 3.

Crushed shale is supplied to the digester 1 through line 5, either by essentially mechanical means, such as a screw conveyor or in admixture with a suitable liquid. The shale will be crushed to pass a one-inch screen or smaller. With Colorado shales, the necessary fineness is roughly inversely proportional to the richness of the shale. The shale is fed to the digester 1 near the top thereof and passes downwardly, countercurrent to heated oil which enters the lower portion of the digester 1 through line 6. Liquid effluent from the digester 1 is removed through line 7 and passes to fractionator 2, and vapors accumulating at top of the digester 1 are transferred to the fractionator 2 through line 8.

The treated solids accumulating in the bottom of digester 1 are transferred through line 9 to stripper 3, where volatile products are removed, and the resulting spent shale is substantially dry but contains solid or semisolid carbonaceous residues of kerogen conversion. The amount and character of these residues vary with the richness of the original shale and the treatment to which it has been subjected. The heating value of these residues is recovered by combustion with the air in the furnace 4, into which the spent shale is injected through line 10. Ash is discharged from furnace 4 at 11, and flue gas is discharged at 12.

In furnace 4, heavy oil from fractionator 2 is heated to a temperature below the cracking temperature, preferably about 825° F. in coil 13 and injected through line 6 in the digester 1.

Any desired number of product cuts may be made in fractionator 2, but ordinarily at least two streams will be withdrawn, a heavy oil fraction in the lower zone through line 14 and a light overhead fraction through line 15. Steam and oil vapors from stripper 3 are passed to the fractionator through line 16. If desired, additional steam or gas for stripping the spent shale may be injected into stripper 3, through the separate line 17.

The ash discharged from combustion zone 4 carries considerable sensible heat. This heat may be recovered, if desired, by suitable heat exchangers, not shown, for air, steam, or other fluids.

In the batch or semibatch treatment of oil shale by thermal solution methods, it has heretofore been considered necessary that the shale must be highly comminuted in order to insure extraction of the organic matter. This in turn has involved serious difficulties in effecting a separation of the solvent and liquid products from the solid residue. Various expedients, such as gravity settling, filtration, and centrifugation, separately or in combination, have been suggested.

In the patent to Ryan, 1,327,572, the shale is reduced to a finely divided form and charged to a rotating cylindrical screen, the lower portion of which is immersed in a bath of heavy oil. However, even though the mesh of the screen is finer than the particle size of the oil shale charge, a considerable amount of solids pass therethrough and are withdrawn with oil accumulating in the retort. The oil and suspended solids are discharged into a settling tank. Such solids as are separated in the settling tank are withdrawn as a thick slurry containing considerable quantities of oil and must be further heated in an effort to remove the oil.

Another process, described in the more recent patent to Hampton, 1,778,515, reduces the shale to a fine powder in a ball mill, which is circulated in the form of a slurry with oil boiling above about 700° F., such as cylinder stock, through a series of heated tubes. This hot mixture is thereafter subjected to centrifugation, with or without dilution. Even after centrifuging, the discharged solids carry considerable oil and must be washed with a suitable solvent and further distilled in order to recover the maximum amount of oil.

Aside from inefficiencies inherent in these steps of fine grinding, settling, filtration, centrifugation and the like, these prior art methods also involve serious practical operating difficulties when carried out on an industrial scale. For example, with shales averaging a recovery of 21 gallons per ton of raw shale charged, a commercial unit producing 5,000 barrels of shale oil per

day would have to have fine grinding equipment capable of handling 10,000 tons per day of raw shale, with corresponding capacity in settling tanks, centrifuges, or filtration equipment.

My method, on the contrary, does not involve fine grinding, and there is no need for handling a large tonnage of more or less colloidal residual material. In treating oil shale according to my invention, separation of residual solids may be readily effected in relatively simple equipment having a very high daily throughput capacity.

As mentioned above, oil shale for solvent extraction in accordance with the principles of my invention, may be as coarse as one inch, particularly when treating the richer shales, but preferably would average about one-half inch size. At 775° F., for example, with shale averaging 53 gal./ton (Fischer assay), recovery from one-half inch size material is approximately 83% of the kerogen content in a batch treatment of approximately thirty minutes. Under the same conditions, about 81 percent of the kerogen will be converted in shales averaging about 27 gal./ton. For shale as lean as 11 gal./ton, extractions as high as about 85 percent have been made under these conditions.

It is interesting to note that the disintegration of these shales, in my process, is roughly proportional to the assay value. Thus the richer shales tend to disintegrate in the course of the solvent extraction, whereas the lean shales retain more of their original physical form.

Accordingly, the size of the shale fed to digester 1 will be determined by the richness of the shale and by the conditions of treatment. For most conditions and grades of shale, preferably this will be about one-half inch, as this permits a satisfactory conversion of kerogen at high throughput rates, with high liquid product yields and without excessive formation of colloidal suspensions due to disintegration of the shale.

In reactor 1, temperatures preferably will be within the range of about 700°–800° F. Below about 700° F., there is little or no conversion of kerogen to useful liquid products, whereas above about 800° F., it is difficult to avoid degradation of liquid products due to cracking of the primary oil. Under some conditions, however, it is possible to inject the heavy oil solvent at a temperature as high as 875° F. At rapid flow rates and high throughput of shale, heat from the oil, even though initially at 875° F., is rapidly transferred to the shale, without appreciable cracking of the oil.

In general, the ratio of oil to shale in the digester will be about 1:1 by weight. Higher, or even lower, ratios even may be used, however, without departing from the spirit of my invention.

Pressures within digester 1 may range from substantially atmospheric to as high as 400 p.s.i.g. Preferably, the pressure will be no more than necessary to prevent excessive volatilization of solvent and products, thereby facilitating the feed of raw shale to the digester.

The oil shale is fed to the upper portion of digester 1, initially contacting effluent vapors and oil, which are discharged through lines 8 and 7, respectively. This serves to preheat the shale and to remove moisture therefrom. The preheated and dried oil shale descends in the digester 1 against a rising stream of solvent and liquid products. Treated shale is continuously withdrawn from the bottom of digester 1 through

line 9 and discharged into the stripper 3. The rates of charging and withdrawal are so adjusted as to secure the desired residence time of the shale in digester 1. The shale is subjected to contact with hot oil above 700° F. for from thirty to ninety minutes, depending upon the temperature of the solvent oil and the richness of the shale. In some cases, residence time may be as short as twenty, or even ten, minutes with satisfactory conversion of kerogen. Excessive residence time, however, is to be avoided since the throughput of shale is thereby reduced and, at higher temperatures, there may be more cracking of oil, with little or no compensating advantages by way of kerogen conversion to useful liquid products.

The treated shale is subjected to the action of steam or suitable non oxidizing gas, in stripper 3, to remove the oil associated therewith. If desired, additional stripping fluid may be injected through line 17, in the lower portion of stripper 3. Where the digester is operated under substantial pressure, removal of oil from the treated shale will be materially assisted by a sharp reduction of pressure within stripper 3. Much of the oil will thereby flash into vapor and be swept out by the current of gases.

The vapors from stripper 3, together with the vapors and liquid streams from the digester, are mixed and fractionated in fractionator 2.

Steam and gas will be withdrawn from the system through line 15, in admixture with the more volatile shale oil fractions. This stream will be subjected to further refining as desired to recover the several products in required purity. The heavier, liquid products accumulating in fractionator 2 are withdrawn through line 14. This stream represents the bulk of the shale oil and will be treated by the usual refining operations, such as distillation, cracking, hydrogenation, and chemical treatment to secure the desired products.

Sufficient heavy oil to keep the system full is continuously withdrawn from the fractionator 2 through the line including the heating coil 13. This stream is heated to the desired temperature in furnace 4 and passed through line 6 into the digester 1. Here it contacts the oil shale as described above, and in admixture with the thereby produced shale oil, is returned to fractionator 2.

From the stripper 3, spent shale is passed directly to combustion zone, or furnace 4, where the residual carbon in the spent shale is burned with air or other oxidizing gas. The amount of carbon in the spent shale will vary with the initial kerogen content of the shale and the character and extent of the conversion of the kerogen. Except for some of the leaner shales, there will usually be sufficient fuel value in the spent shale to provide the heat required for the process. If necessary, any additional heat required in combustion zone 4 may be secured by burning a portion of the gas separated from the overhead fraction leaving fractionator 2.

It is apparent from the foregoing description that other modifications of my process may be made by those skilled in the art without departing from the spirit of my invention. Accordingly, it is understood that my invention is not limited to the exact embodiments shown and described herein, and that various other modes of practicing the invention may be employed within the scope of the appended claims.

I claim:

1. A continuous process for the production of shale oil by thermal extraction of oil shale with a liquid hydrocarbon comprising the steps of passing fresh, relatively coarse oil shale to an extraction zone, and therein passing said shale countercurrently in contact with a liquid solvent consisting of a heavy shale oil fraction previously derived from the process, maintaining the temperature of the shale in said extraction zone from about 700° to 800° F. whereby the kerogen content of said shale is converted into products soluble in said oil, while maintaining the pressure in said extraction zone substantially above atmospheric to prevent excessive volatilization of said oil and extraction products in said extraction zone, continuously removing an effluent from said extraction zone comprising a volatile overhead stream and a liquid stream consisting of extraction products dissolved in said solvent oil, separating said effluent into a plurality of fractions, including a heavy fraction, in a fractionating zone, continuously withdrawing extracted spent shale containing substantial quantities of adhering liquid hydrocarbons from said extraction zone, passing said extracted shale to a stripping zone maintained at a pressure substantially less than that in said extraction zone whereby a large portion of said adhering oil flashes into vapor, passing hot inert gas in contact with said extracted shale in said stripping zone to complete the removal of said adhering oil therefrom, passing said stripped spent shale to a combustion zone and therein burning the carbonaceous residue on said shale, passing at least a portion of the heavy oil fraction from said fractionating zone into said combustion zone in indirect heat exchange contact with hot combustion products, thereby heating said oil to a temperature greater than 700° F., but not exceeding 875° F., and then recycling said heated oil to said extraction zone in countercurrent contact with said shale.

2. A process in accordance with claim 1 in which said heavy oil fraction is heated in said combustion zone to a temperature of about 825° F. before recycle to said extraction zone.

FREDERICK E. BUCHAN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,406,810	Day	Sept. 3, 1946
2,487,788	Buchan	Nov. 15, 1949