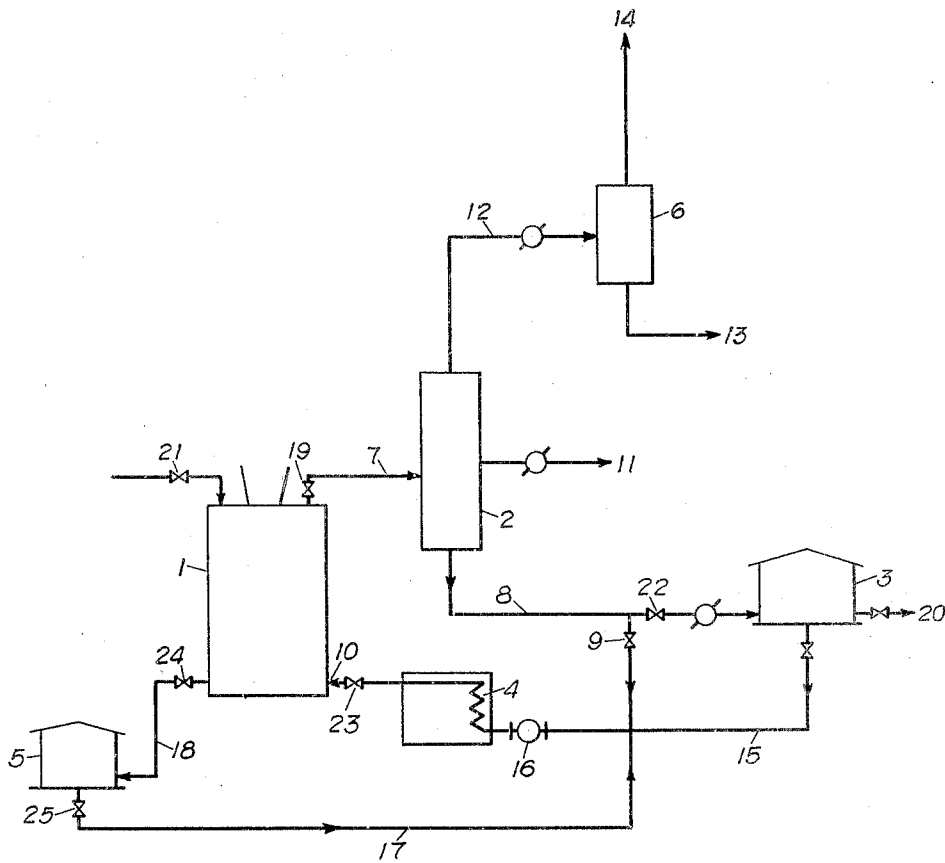


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PROCESSING OIL SHALE
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PROCESSING OIL SHALE

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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 invention relates to the recovery of hydrocarbon liquids and/or gases from carbonaceous mineral materials, more particularly to the production of high quality liquid fuel fractions from kerogen rocks.

It is an object of the invention to increase the yield of useful products from kerogen rocks, especially oil shales such as occur in the United States. Another object of the invention is the recovery of crude liquid hydrocarbons that may be further processed satisfactorily either by conventional refining operations or, at the most, with only minor modification thereof. A further object is the provision of an improved heating method whereby the percentage recovery as a liquid of the organic matter initially present in the rock is materially increased over prior methods, without excessive decomposition and consequent formation of carbon in the residual material. Other objects will be apparent or will appear herein-after.

Kerogen rocks are defined by Down and Himus (Classification of Oil Shales and Cannel Coals (1940)) as sedimentary rocks containing organic matter which, on destructive distillation, yield an oil equivalent to approximately 50 percent of the organic content. They occur in continuous seams scattered all over the world, and the western deposits in the United States are particularly suitable for development, although large quantities of lean oil shale occur in the Kentucky-Indiana area. A typical sample of Green River shale from Colorado according to Bradley (Geol. Survey Prof. Paper 168 (1931)) consists of kerogen 46 percent, clay 21 percent, excess silica 10 percent, and magnesium carbonate 9 percent. Kerogen itself, according to Brown (Shale Oil—R. N. McKee (1925)) is the material in Scottish shales, which, on destructive distillation, yields oil. It is neither petroleum nor bitumen, but an organic substance yielding petroleum and nitrogenous compounds upon pyrolytic conversion.

It has been the common practice for many years to distill destructively kerogen rocks, such as Scottish shale in large vertical retorts thereby decomposing the kerogen and recovering part of it in the form of oils resembling crude petroleum while a part of it is lost as fixed gases and residual carbon. However, the percentage recovery, as oil, of the organic matter present in the shale is low and this fact has led to the development of many types of retorts to improve the process. In spite of all these efforts, to date the total recovery of the kerogen in the shale remains relatively low, as some of it is always reduced to carbon and permanent gases, which have some usefulness but are not as desirable products as the crude oils.

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In order to overcome this difficulty, it has been proposed to extract the kerogen from the shale with liquid solvents, and thereby increase the recovery of crude oils and avoid the formation of excess carbon and permanent gases. Numerous patents have been granted covering the broad aspects of this idea, but so far a successful process to compete with the established retort methods, has not been developed.

In my investigations of the broad problem of extractive recovery of organic matter in oil shales and other kerogen rocks, I have discovered the following pertinent 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.

The correlation of temperature and time of digestion with respect to items 2 and 4 above in the batch treatment of a Colorado oil shale are summarized in the tables below:

Heating Time (Hours)				
	0.5	1.0	1.5	2.0

I. T=707° F. (375° C.)

Kerogen converted.....	6.9	13.4	19.4	25.0
Gas.....	2.4	4.9	7.2	8.7
Light Oils.....	0.6	1.2	1.7	2.2
Heavy Oils.....	3.9	7.3	10.5	14.1
Carbon.....				

II. T=752° F. (400° C.)

Kerogen converted.....	22.1	39.4	52.8	63.2
Gas.....	3.0	5.9	8.5	10.9
Light Oils.....	2.6	4.6	6.2	7.9
Heavy Oils.....	16.5	28.9	38.1	44.5
Carbon.....	Nil	Nil	(?)	(?)

III. T=797° F. (425° C.)

Kerogen converted.....	51.8	76.8	88.8	96.0
Gas.....	4.7	9.0	13.0	18.9
Light Oils.....	6.2	11.0	14.9	19.0
Heavy Oils.....	34.9	44.3	42.9	33.1
Carbon.....	(6.0)	(12.0)	(18.0)	(25.0)

NOTE: Figures represent percentage by weight based on the kerogen initially present in shale.

These data indicate that under the conditions

of these tests there is an optimum relation of time and temperature for the maximum conversion of kerogen to liquid fuels, such as gasoline and heavier oils, and a minimum conversion to gases and residual carbon. Obviously with other shales, the yields and products distribution may vary from those given above for like conditions, and the optimum conversion conditions for yields of liquid products may differ with shales of varying kerogen content.

Based on experimental evidence available at this time, my treating process may be considered as involving the following stages:

1. Initial heating of shale to a predetermined temperature and to drive off free moisture in the shale.
2. Conversion of kerogen of the shale to bitumen and some lighter products.
3. Cracking of bitumen and heavy oil to lighter products.

This theory is advanced merely by way of explanation and it will be understood that the description of my invention is not intended to be limited to any particular theory as to the mechanism of the reaction whereby kerogen of the shale is recovered as useful liquid products.

In a batch treatment, as described herein, by reason of lack of uniformity in the chemical composition and physical character of the charge, the heating rate and other factors, obviously these stages will not appear to be separate and distinct. Some conversion of kerogen to bitumen and cracking of bitumen and heavy oil may occur during the initial heating stage. Likewise there may be appreciable cracking of heavier products concurrently with the conversion of kerogen to bitumen in the second stage of the process. In general, however, each stage will be characterized by the predominant physical or chemical changes occurring at the time.

In my combined heating and extracting method for the recovery of shale oil, I have found that it is unnecessary to resort to fine grinding of the raw shale and that the process is effective if the shale is coarsely crushed to about one-half inch size.

A suitable procedure for realizing the desired optimum conditions for conversion of the kerogen of oil shale to useful liquid products is described in connection with the accompanying drawing.

A Colorado oil shale, crushed to approximately one-half inch size, is fed into a vertical reactor 1, which is preferably lagged to minimize heat loss. When the desired quantity of material has been placed in the reactor, a high boiling fraction of shale oil is withdrawn from tank 3 passing through valve controlled line 15 and pump 16 to heater 4. In heater 4, the heavy oil is heated to about 425° C. and passes to reactor 1 through line 10. The overflow from reactor 1 passes through line 7 to separator 2 where water vapor and lighter oils are separated and oils heavier than furnace oils are withdrawn through line 8 to heater 4 and back to reactor 1. Heavy oil over and above that required for the extractive treatment of the shale is accumulated in tank 3 and may be withdrawn from the system by line 20. The flow of heavy oil to tank 3 is controlled by closing valve 9 and opening valve 22.

Lighter products, including gases and water, removed from the circulating stream in separator 2, flow through line 12 to stripper 6. Gases are taken off overhead from stripper 6 through line

14, while the light liquid products flow out through line 13 for further treatment.

The gases taken off at 14 may be used as fuel in heater 4 or may be separated into various fractions as is well known in the refining art.

Fractions of intermediate boiling range, such as furnace oil, gas oil, and the like may be withdrawn in one or more side streams, as at 11, from separator 2.

For a maximum recovery of liquid fuels from Colorado oil shale, circulation of the heavy oil at about 425° C. is maintained for not in excess of one and one-half hours after the oil shale charge is brought to this temperature. Under these conditions, as shown in the above tables, approximately 90 percent of the kerogen is converted to extractable material, and at least 18 percent light oil and 42 percent heavy oils will be recovered. This is equivalent to a conversion of 60 percent of the total kerogen to liquid products, of which the major portion represents desirable liquid fuel fractions.

By operating at a lower temperature for a longer period of time, a higher proportion of the extracted bitumen may be recovered as useful liquid fuels, although there will be a corresponding decrease in kerogen conversion and the total amount of these liquid products recovered may be lower than when the conditions are as described in the foregoing example. From a two and one-half hour treatment at 400° C., the recovery of liquid products on the basis of kerogen converted $(57/71) = 80$ percent as compared with $(60/90) = 67$ percent under the higher temperature and shorter time conditions. Where an increased recovery of heavier oils is desirable such conditions obviously are indicated.

At the end of the treating period, circulation of the heavy oil through heater 4 is discontinued and valve 23 is closed. Liquid materials in reactor 1 are allowed to drain into surge tank 5 through line 18 by opening valve 24 and closing valve 19. Any oil remaining in or on the treated shale in reactor 1 may be recovered by displacement with steam or gases admitted through valve controlled line 21. The spent shale in reactor 1 is then discharged and the reactor is refilled with fresh oil shale. The contents of tank 5 are pumped through line 17 and heater 4 into reactor 1 by closing valve 24 opening valves 23 and 25 and starting pump 16. Additional oil to fill the reactor is drawn from tank 3 and the treating cycle is repeated.

For reasons of economy of operation, a plurality of reactors 1 may be employed with suitable connections to heater 4, surge tank 5 and separator 2, so that at the close of the treating cycle in one reactor, treatment of fresh shale may be continued in a second reactor. In this manner heavy oil and any material dissolved therein may be continuously circulated through heater 4, the shale charge in one of the reactors 1 and separator 2 back to the heater 4, without a substantial loss of process time in charging and discharging the reactors 1.

It is understood, of course, that my invention is not limited to the exact conditions and embodiments shown and described herein and that various other means and conditions may be employed within the scope of the appended claims.

I claim:

1. A process for the recovery of valuable liquid products from kerogen containing rock which comprises treating kerogen containing rock in coarsely crushed form with a hydrocarbon oil

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maintained at a temperature within the range of about 375°-425° C. and for a period of time not in excess of two and one-half hours thereby converting a substantial portion of the kerogen of said rock to predominantly liquid products, miscible with said oil, removing fluids from contact with the treated rock and fractionating the thus separated fluids into fractions of desired boiling ranges.

2. A process as in claim 1 in which the hydrocarbon treating oil comprises a fraction of the heavy oils produced from kerogen containing rock, said fraction having an initial boiling point above 200° C.

3. A process as in claim 1 in which the treating period is between one and two hours.

4. A process as in claim 1 in which the yield of liquid products is equivalent to at least fifty percent of the kerogen initially present in the rock.

5. A process for increasing the percentage recovery of normally liquid hydrocarbons from the pyrolytic conversion of kerogenous materials which comprises subjecting kerogen containing solids in the form of coarsely crushed lumps to the action of a heavy hydrocarbon oil at a temperature within the range of from 375° C. to 425° C. for at least one hour and not substantially in excess of two hours, separating the thus treated solids from the said oil and liquid conversion products, distilling the separated effluent and recovering fractions of desired boiling ranges.

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6. A process for the production of hydrocarbon oils from oil shales which comprises passing a shale oil fraction heavier than furnace oil in contact with shale in a conversion zone maintained within the range 375°-425° C., fractionating effluent from said reaction zone to separate lighter products and to recover a fraction heavier than furnace oil, heating said heavier fraction to the temperature of said conversion zone and returning said heated fraction to said conversion zone, circulation of said heavier fraction being continued for from one to two hours, whereby substantial conversion of kerogen to hydrocarbon oils is effected, separating the thus treated shale from further contact with said oil and conversion products and recovering fractions of desired boiling ranges from said oil and conversion products.

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