

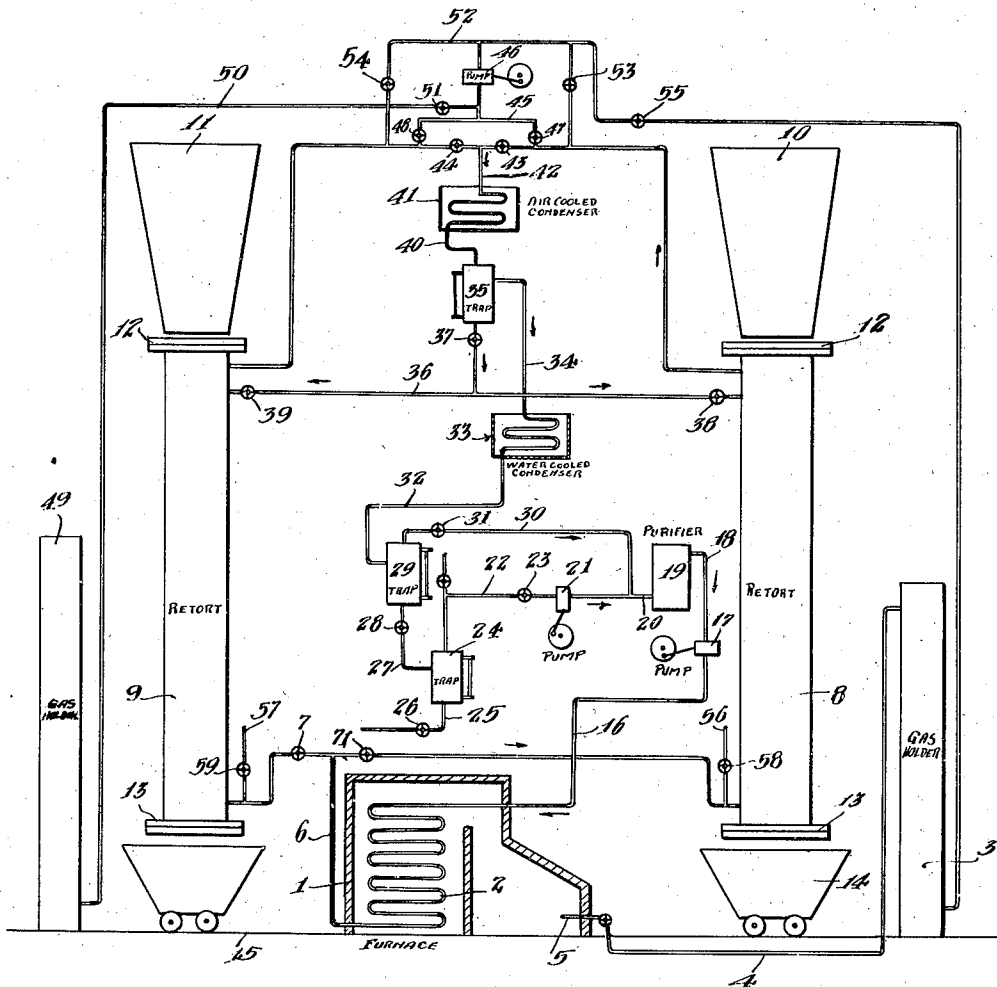
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PROCESS OF INCREASING THE YIELD OF LIGHT HYDROCARBONS FROM OIL SHALES

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PROCESS OF INCREASING THE YIELD OF LIGHT HYDROCARBONS FROM OIL SHALES

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This invention relates to processes of treating oil shales to obtain various products therefrom, and an object of the invention is to secure a more complete recovery of the carbon, present in the shale, as light hydrocarbons of a superior quality.

When oil shales are heated, the kerogen or pyrobitumen contained therein is transformed to soluble bitumen at a fairly definite temperature. The thermal conductivity of the shale being relatively low, the temperature of transformation proceeds slowly inward from the surface of the shale particles. At temperatures slightly above this temperature of transformation the soluble bitumen begins to distil from the mineral matter, which constitutes the body of the shale, and at the same time to crack to lighter hydrocarbon products.

A large amount of carbon is deposited in the ash during the cracking of the soluble bitumen and the crude shale hydrocarbons have a low degree of saturation. Hydrogen containing gas, if introduced at atmospheric pressure, diffuses but slowly through the layer of ash left on the surface of the particles of shale as the cracked products are vaporized and carried away, and consequently it is always relatively far removed from the zone of reaction as said zone proceeds toward the center of the shale particles. Accordingly, it will be seen that there can be little, if any, benefit derived from the presence of the hydrogen-containing gas introduced at atmospheric pressure to the retort excepting, possibly, for a slight buffer action in protecting the hydrocarbon molecules from the superheated walls of the retort.

We have discovered that, by circulating hydrogen-containing gas under high pressure and temperature through the retort, such hydrogen gas serves to convey the requisite amount of heat to the zone where the reactions should be completed in order to utilize the carbon content of the shale, and the hydrogen-containing gas also serves to remove the products of the reaction. When hydrogen-containing gas, under relatively high pressure and temperature is in-

troduced to the retort, the highly compressed gas diffuses readily through the porous ash to the region of reaction and because of such gases possessing a relatively great capacity for heat, the temperature of the shale mass is raised without difficulty to a degree sufficiently high for rearrangement of the molecules and also the temperature may be raised sufficiently for cracking with sufficient uniformity and rapidity so that the several reactions may proceed as a substantially single rearrangement instead of in separate steps as results when the hydrogen is not circulated under high pressure. The presence of highly reactive hydrogen because of the porosity of the shale at the immediate point at which these extensive molecular rearrangements are taking place permits of the nearly complete saturation of the chemical affinity of the carbon atoms, and thus prevents the separation of free carbon atoms and insures a high degree of saturation of the products formed. This may result in increasing the yield of light hydrocarbon materials by as much as from fifty to one hundred per cent.

The hydrogen-containing gas may be employed under pressures of about 50 up to 250 atmospheres and under temperatures of about 400° C. to 500° C. In the present process the shale may be employed as mined and crushed to from one to two inch mesh. The oil shale subjected to the operations of this process may have associated with it coal or a material occupying the region between shales and lignites, but such coal or other associated material does not have the porosity that is an important factor in this process and, therefore, the shale should be in predominating volume.

It is well known that many reactions, involving one or more gases, are very materially hastened by the presence of certain highly porous materials such as the many forms of active charcoal and silica-gel. An exactly analogous action is obtained in this process by the presence of the highly porous shale ash which markedly increases the activity of the hydrogen. The beneficial effect, obviously, will vary somewhat with the

chemical nature of the ash from different shales but to a far greater degree the effect will vary with the physical structure of the ash and, accordingly, the pressure of the hydrogen used in the process for securing a given amount of hydrogenation may vary between wide limits. The partial pressures of hydrogen employed may vary from about 800 lbs., per square inch to well above 2000 lbs., per square inch. Pressures of about 1000 lbs., are preferred.

The yield of ammonia is highly sensitive to the amount of water vapor present in the gases of the retort. For this reason it will be usually desirable to circulate a small per cent of steam along with the hydrogen in the retort. The addition of steam may not be necessary during the early stages of the retorting as sufficient moisture will usually be found in the shale to generate the necessary steam, but after this moisture has disappeared the supply will need to be augmented from without.

As the reaction progresses hydrogen is used up and light hydrocarbons are produced, thus making it necessary to eventually remove the fixed hydrocarbon vapors and replenish the supply of hydrogen. These ends may be accomplished by the catalytic decomposition of the light hydrocarbons, such, for example, as propane, butane, methane and the like, without their removal from the circulating gases, thus materially reducing the amount of hydrogen that must be supplied. It is to be understood that pure hydrogen gas is not required, and any gas containing hydrogen in sufficient quantities to be effectively used, such as gas from the catalytic decomposition of light hydrocarbon mentioned above, may be employed. Pure hydrogen gas is, of course, preferred but its use may not be economically possible under some conditions.

The process may be performed in any suitable apparatus and one such apparatus is illustrated in the accompanying drawing which is a more or less diagrammatic view thereof.

The apparatus illustrated is constructed as follows:

There is provided a heater or furnace 1 and inside thereof is a hydrogen-containing gas heating coil 2. The furnace may be heated by any suitable means, as by gas flowing from a gas holder 3 through a pipe 4 to a burner 5 positioned in the combustion chamber of the furnace.

The lower end of the coil 2 is connected by a branched pipe 6, provided with valves 7, 71, with the lower portions of retorts 8, 9. One retort is sufficient for carrying out the process, but when a plurality is employed the process is semi-continuous. The retorts 8, 9 are fed with shale from hoppers 10, 11, respectively, and removable covers 12 are pro-

vided to close the upper ends of the retorts during the retorting operation. Also the lower ends of the retorts 8, 9 are likewise closed by removable covers 13. Below the retorts 8, 9 are ash conveying means 14 which, in this instance, are in the form of cars running on tracks 15.

The upper end of the coil 2 is connected by a hydrogen-containing gas carrying pipe 16 to a circulating pump 17 which in turn is connected by a pipe 18 to a purifier 19. The purifier 19 is connected by a pipe 20 with a pump 21 which is connected by a pipe 22, having a valve 23, with a trap 24. Leading from the trap 24 is a pipe 25 provided with a valve 26, and said pipe may extend to any desired place of discharge. Leading into the trap 24 is a pipe 27 having a valve 28 and leading from the lower portion of a trap 29. Leading from the upper portion of the trap 29 is a by-pass pipe 30 having a valve 31 and connected with the pipe 20 between the pump 21 and purifier 19.

Leading into the upper portion of the trap 29 is a condensate pipe 32 connecting with a water cooled condenser 33, and leading to said condenser is a vapor pipe 34 that is connected with the upper end of a trap 35. Leading from the lower portion of the trap 35 is a condensate pipe 36 which is branched and which connects with the upper portions of the retorts 8, 9. The pipe 36 is provided with a valve 37 and with valves 38, 39 on its branches.

Leading into the trap 35 is a condensate pipe 40 that connects with an air cooled condenser 41 which in turn is connected by a branched vapor pipe 42 with the upper portions of the retorts 8, 9, the branches of said pipe being provided with valves 43, 44. The branches of the pipe 42 are connected by a branched pipe 45 with a pump 46, and the branches of the pipe 45 are provided with valves 47, 48, respectively. Connecting the pipe 45 with a gas holder 49 is a pipe 50 provided with a valve 51 and the pump 46 is connected by a branched pipe 52 to the branches of the pipe 42. The branches, of which there are three, of the pipe 52 are provided with valves 53, 54, 55, respectively. The branch of the pipe 52 on which is positioned the valve 55 connects with the lower end of the gas holder 3. Connected with the branches of the pipe 6 are pipe 56, 57 provided, respectively, with valves 58, 59.

The process is performed in the apparatus above described as follows:

The shale is charged from one of the hoppers 10, 11 into the associated retort. For example, it may be assumed at the beginning that the shale is discharged from the hopper 10 into the retort 8. Before charging, the cover 12 is removed and after the charging is completed the cover 12 will be secured in place. Hydrogen-containing gas from a

suitable source, for example from the gas holder 49, will then be pumped into the retort 8 by operation of the pump 46, all valves being closed excepting 51, 53, 43, 31, 71 and 28. When the system, including the retort 8, the condensers 33, 41, the traps 24, 29, 35, the purifier 19, the pump 17, and the heating coil 2 is pumped to the proper pressure by operation of the pump 46, the valves 51 and 53 will be closed and the pump 46 stopped. The pressure is comparatively high, for example, around 250 atmospheres.

Then the circulating pump 17 is started into operation and the furnace is heated so as to heat the coil 2. The hydrogen containing gases will be heated in the coil 2 and will pass therefrom into the retort 8 and through the mass of shale in said retort, thence into the condensers 41, 33. Because of the porosity of the shale, the hydrogen gas thoroughly and quickly penetrates the shale, and this results in the hydrogen being present at the immediate point at which the molecular rearrangements are taking place, permitting of the nearly complete saturation of the carbon atoms, thus preventing the production of free carbon atoms and insuring a high degree of saturation of the desired products. The increase in the yield of light hydrocarbon materials within the gasoline range may amount to from 50 to 100%. The reaction of the hydrogen gas with the hydrocarbon is materially hastened by reason of the reaction occurring in the presence of the highly porous shale, similar to the increased chemical reaction that occurs in the presence of active charcoal and silica-gel.

As the circulation of the hydrogen-containing gas continues, the pyrobitumen in the shale is decomposed and the bitumen hydrogenated, cracked and distilled in the retort. The heavy vapor products, carried out of the retort with the gases through the pipe 42, are condensed in the condenser 41. The heavy liquid products are caught in the trap 35 and the gases and lighter vapors pass on to the condenser 33. These heavy liquid products may be returned, if desired, to the retort 8 for further cracking by opening the valves 37, 38.

The lighter vapors are removed in the condenser 33 and caught in the trap 29 and they may be drained, from time to time, into the trap 24 in which the pressure is relieved and from which the liquid products are drawn off by opening the valve 26.

The gases which remain when the pressure is relieved in the trap 24, are pumped back into the system by operating the pump 21 which forces the gases through the purifier 19. The purifier 19 may be charged with such reagents as will remove detrimental impurities. From the purifier the gases are again circulated by operation of the pump 17, and

their temperature is raised to the desired degree in the coil 2.

After the process has been operated for a time sufficient to use up the moisture contained in the shale, steam will be admitted through the pipe 56 by opening the valve 58 and when, during the operation of the process, it becomes necessary to admit a new supply of hydrogen-containing gas, the valves 51 and 53 will be opened and the pump 46 operated.

The circulation of the hot hydrogen-containing gases is maintained until such time as it is found that substantially all of the pyrobitumen in the shale has been converted into the desired products.

In order to remove the gases from the retort 8 and carry them to the retort 9, the pump 46 is operated and the valves 47 and 54 will be opened and the valves 43, 53, 71 and 38 will be closed. For still more completely removing the gases from the retort 8 it may be necessary to open the valve 58 and inject steam into said retort. When all the gases are exhausted from the retort 8, the valves 47, 54 will be closed, valves 44 and 7 opened, and the treating of the shale in the retort 9 will be effected the same as previously described for the shale in the retort 8. While the shale in the retort 9 is being treated, the covers 12, 13 of the retort 8 will be removed and the residue dumped from the retort 8 into the associated car 14.

The form of construction of the furnace 1 will depend on the disposition it is desired to make of the fixed gases produced during the reaction in the retorts, or, in other words, whether or not it is desired to burn the excess fixed gases in the furnace. Such gases will accumulate and, if not removed produce undesirable dilution of the hydrogen. The introduction of the necessary catalyst and the operation of an apparatus for cracking these gases to produce hydrogen and carbon black or to effect polymerization to liquid hydrocarbons need not affect the operation of the process above described.

Under certain conditions it may be found necessary to remove a part or all of the fixed gases from the system rather than to pump them to another retort. This can be done by opening the valve 55 and operating the pump 46 to force the gases to the gas holder 3. These gases can then be conveyed to the furnace through the pipe 4 and burned, if that be desired.

It will be readily understood that in the process the materials to be treated are placed in a circuit of hydrogen-containing gas under pressure, and that the gas is heated while circulating.

We claim:

1. The process of increasing the yield of light hydrocarbons from oil shales which

- consists in charging the oil shale into an enclosed space, compressing a hydrogen-containing gas to a pressure of about 250 atmospheres, heating the compressed gas to a temperature of about 500 degrees C., circulating the hot compressed hydrogen-containing gas through the enclosed space to decompose and hydrogenate and crack and distil the pyrobitumen in the shale and to carry off the resulting heavy and light vapor products and the fixed gases, condensing the heavy vapors, separating the resulting condensate from the fixed gases and lighter vapors, and condensing said lighter vapors.
2. The process of increasing the yield of light hydrocarbons from pyrobituminous oil shales, which comprises subjecting a bed of pyrobituminous oil shales in a pressure reaction zone to the action of a current of hydrogen-containing gas heated to a temperature of between 400° C., and 500° C., and at a pressure of above about 800 lbs., per square inch, whereby hydrocarbons are hydrogenated at the time of their formation from kerogen in such pyrobituminous oil shale, permitting the current of gas to carry the resulting heavy and light hydrocarbon vapors out of said reaction zone, condensing and separating heavy hydrocarbons from said current of gas, and condensing and separating the light hydrocarbon vapors from the uncondensable gases.
3. The process of increasing the yield of light hydrocarbons from pyrobituminous oil shales, which comprises forming a bed of a pyrobituminous oil shale in a pressure reaction zone, compressing hydrogen gas to a pressure above 800 lbs., per square inch, heating the compressed gas to above 400° C., passing the hot compressed gas through the reaction zone to remove moisture from said pyrobituminous oil shale, continuing to pass the hot compressed gas therethrough so as to hydrogenate hydrocarbons at the time of their formation from said pyrobituminous oil shale, removing the resulting mixture of light and heavy hydrocarbon vapors and hydrogen and fixed gases from said pressure zone, condensing and separating heavy hydrocarbon vapors from said mixture of vapors and gases, and finally condensing and separating light hydrocarbons from the uncondensed hydrogen-containing gas.
4. The process of increasing the yield of light hydrocarbons from pyrobituminous oil shales which comprises forming a bed of pyrobituminous oil shale in a pressure reaction zone, compressing hydrogen gas to a pressure above 800 pounds per square inch, heating the compressed gas to above 400° C., and passing the hot compressed hydrogen gas through the reaction zone to remove moisture from said pyrobituminous oil shale, continuing to pass the hot compressed gas therethrough so as to hydrogenate hydrocarbons at the time of their formation from said pyrobituminous oil shale, removing the resulting mixture of light and heavy hydrocarbon vapors and hydrogen and fixed gases from said pressure reaction zone, condensing and separating heavy hydrocarbon vapors from said mixture of vapors and gases, condensing and withdrawing light hydrocarbons from the uncondensed hydrogen-containing gas, and reusing uncondensed hydrogen-containing gases in cyclic operation of the process.
- Signed at Richmond, California this 12th day of September 1925.
- PHILIP S. DANNER.
ERNEST E. LYDER.