

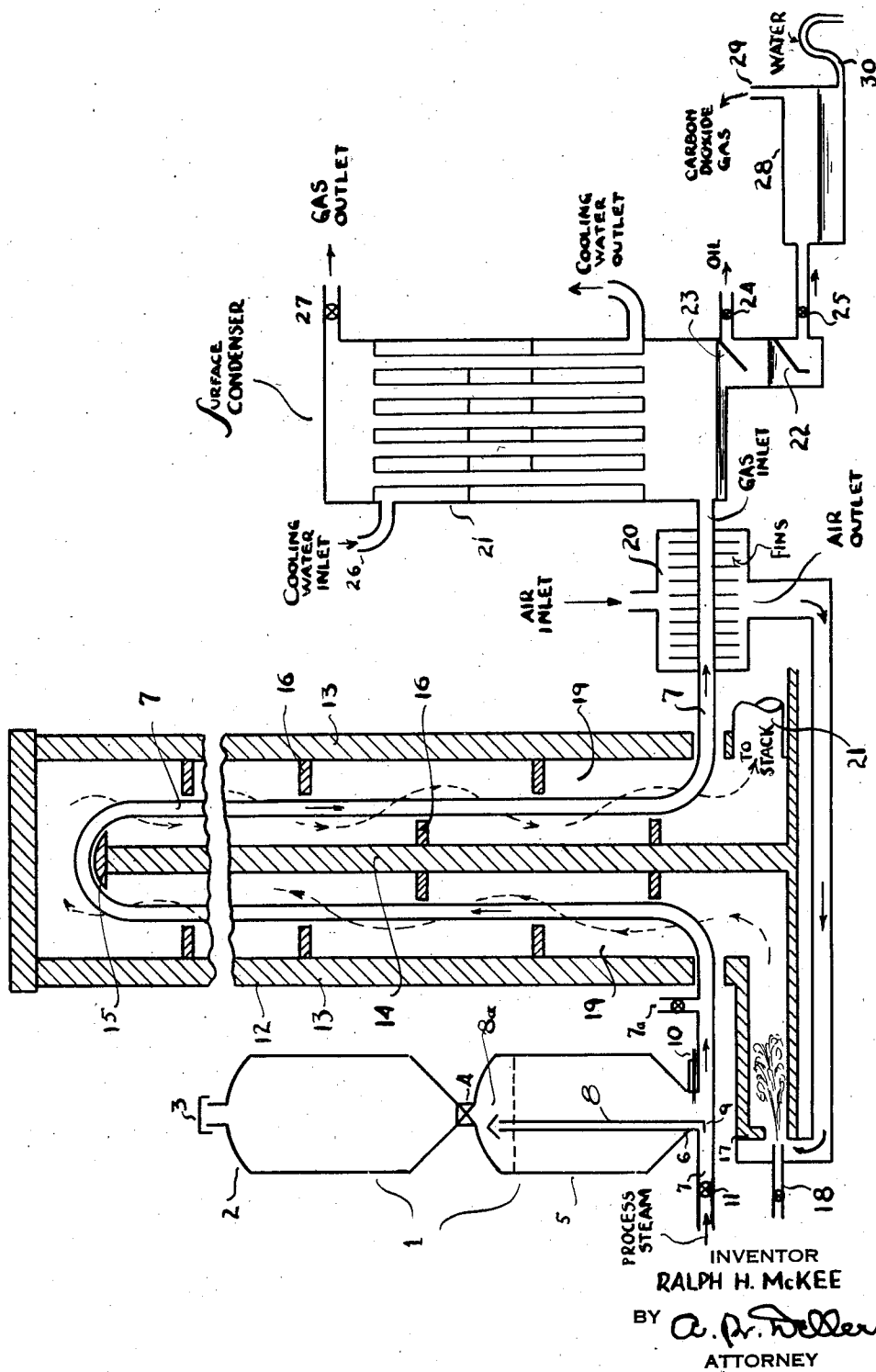
Jan. 2, 1934.

R. H. McKEE

1,941,809

ART OF HYDROGENATING AND DISTILLING OIL SHALE

Filed Oct. 12, 1929



UNITED STATES PATENT OFFICE

1,941,809

ART OF HYDROGENATING AND DISTILLING
OIL SHALE

Ralph H. McKee, Jersey City, N. J.

Application October 12, 1929. Serial No. 399,390

2 Claims. (Cl. 202—23)

The present invention relates to the art of treating oil shale, and more particularly to a process of treating oil shale in a fluid medium under the combined application of heat and pressure.

5 An object of my invention is to provide a process of treating oil shale in a practical and economic manner to obtain, among other useful products, a crude motor fuel and a combustible gas having relatively high calorific value.

10 Another object of my invention is to provide a process of heating finely-divided particles of oil shale suspended in a fluid medium to accentuatedly high temperatures and under relatively high pressures to effect a release of valuable material including bitumens from the oil shale and to cause chemical reactions to occur in said released material whereby more valuable materials and a greater yield of hydrocarbons, containing motor fuel, are produced.

15 A further object of my invention is the provision of a procedure which can be carried on practically and satisfactorily on an industrial scale wherein oil shale is subjected to heat treatment in the presence of a catalytic agent tending to increase the yield of valuable products.

20 It is also within the contemplation of my invention to provide a process in which vapors obtained from the heat treatment of oil shale are subjected to the influence of intense degrees of heat and pressure in the presence of steam or other gaseous media.

25 Furthermore, the invention contemplates providing a process for heat treating oil shale in the presence of steam to cause the formation of water gas which, due to its hydrogen content, tends to facilitate the hydrogenation of oils.

30 Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the drawing which illustrates diagrammatically a preferred apparatus for carrying the present invention into practice.

35 Broadly stated, my invention comprises comminuting oil shale to finely divided particles and then treating said particles while suspended in or carried by a fluid medium to accentuatedly high temperatures and pressures, preferably in the presence of a catalyst, to produce a wide range of volatile products. The reaction products produced by the aforesaid process are thereafter separated from each other by suitable and appropriate apparatus, such as dust extractors, condensers, separators, stills and other devices well known to those skilled in the art.

40 For a better understanding of my invention the following typical example will be given for purposes of illustration. It is to be understood, of course, that the purview of the invention is not to be confined to any illustrative statement here-

in made and that the scope of the invention is to be confined to the appended claims.

Oil shale, for instance, is crushed and ground to pass a 20 mesh screen or finer. The oil shale particles are preheated to say about 300° C. and then, in the preheated condition, are fed into tubes of relatively narrow inside diameter, say approximately 1 to 2 inches, by any suitable feeding device, such as a barrel valve, a screw feed, a piston feed or other devices known to those skilled in the art. The tubes are of relatively great length say 100 to 300 feet or they may be much longer and the shale particles are passed therethrough. Instead of having the tube of great length the latter part which is heated to a lower temperature may be replaced by a shorter tube of larger diameter and the desired time for the reaction thereby obtained. Steam preheated to about 650° C. is passed into the tubes with the oil shale particles. In the preferred embodiment, steam is utilized for carrying the particles through the tubes. Steam and shale are preferably mixed in the proportion of 1 pound of the former to about 1 pound of the latter. If the shale is particularly rich in carbonaceous material, the proportion of steam may be increased with advantage.

Heat is applied in any convenient way to the tubes to raise them to a temperature of upwards of 650° C. The tube walls are preferably maintained at a temperature in the region of 900° C. throughout a portion of their length, say one-half, and then reduced to from 250° C. to 450° C. in the latter part of their length. When the thermal conditions are maintained for the hot part of the tube at a temperature of about 900° C. a heating period for the hot part of the tube of approximately a fraction of a second, say one-fourth of a second, is sufficient to cause the desired reaction to take place. With a higher temperature less time is needed.

For the purpose of giving those skilled in the art an understanding of carrying the present invention into practice, the following description is given of a preferred form of apparatus in which my process may be conducted.

Oil shale, for instance, is crushed and ground to pass a 20 mesh screen or finer. The oil shale particles are charged into the pressure feed device 1, which comprises an upper steel magazine 2 with top and bottom closures 3 and 4, respectively. The lower closure 4 also communicates with a lower steel chamber 5 into which the oil shale is free to run when the common closure 4 is open. The lower chamber 5 connects at its bottom 6 with a wide opening into the tube 7 through which superheated steam flows in the direction shown by the arrow. The chamber also contains a vertical pipe 8 (with a hood 8a) which serves to equalize the pressure in the top of the chamber

with that in the tube 7, and also to preheat the contents of chamber 5. The bottom of the pipe 8 has an elbow 9 which may be turned up or down stream so as to make use of the velocity head of the flowing steam to raise or reduce the pressure in the chamber 5 above or below that in the tube 7. A regulating gate 10 is used to control the opening at the bottom of the chamber 5 and, consequently, the rate at which the oil shale is fed into tube 7. High pressure steam, preheated to about 650° C., from a source not shown, is passed through valve 11 into the tube 7 with the oil shale particles. In the preferred embodiment, steam is utilized for carrying the particles through the tubes. Steam and shale are preferably mixed in the proportion of 1 pound of the former to about 1 pound of the latter. If the shale is particularly rich in carbonaceous material, the proportion of steam may be increased with advantage. Hydrogen gas may be passed into the reaction mixture through pipe 7a.

The tube 7 containing the high pressure steam and suspended oil shale passes into the bottom of tower 12 and up between outer wall 13 and inner wall 14, thence over the return support 15 and down the opposite side of the inner wall 14. In case greater length is desired the tube may turn and pass again up and down the tower 12 before passing out of tower 12. Baffles 16 serve to make the heating gases pass back and forth across tube 7.

Heating is applied in any convenient way to the tubes to raise them to a temperature of upwards of 650° C. In the drawing means are shown for heating the tube 7 by gases obtained from the furnace 17 in which pulverized coal, shale, oil, or gas, for example, are burned by means of burner 18. The hot gases pass into the tower 12 and through the hot gas space 19 as indicated by the dotted arrows. The tube walls are preferably maintained at a temperature in the region of 900° C. throughout a portion of their length, say one-half, and then reduced to from 250° C. to 450° C. in the latter part of their length. When the thermal conditions are maintained for the hot part of the tube a heating period of approximately a fraction of a second, say one-fourth of a second, is sufficient to cause the desired reaction to take place. With a higher temperature less time is needed.

The steam and reaction products pass out of the tower at its bottom by tube 7 and then are cooled from a temperature of about 900° C. to between 250° and 450° C. by means of heat exchanger 20 shown as an air heater. The waste gases from the space 19 pass out of the tower 12 at connection 21 and so to the chimney, not shown.

The tube 7 carrying reaction products and coming from the tower 12 is preferably passed through a surface condenser, indicated diagrammatically by 21, whence the reaction products enter a dust extractor (not shown) to remove dust and solid particles from the hot vapors and gases. The condensed water and oil on reaching the bottom of the condenser pass under the shields 22 and 23, respectively, whereupon the oil rises to the surface and is withdrawn by valve 24, which is set so as to cause a slight trickle of water to issue, thus insuring the complete withdrawal of all the oil formed from the oil shale. In the drawing another opening with valve 25 is located at the very bottom of the condenser and this serves to remove the water and remaining

dust. The condenser is also supplied with cold water inlet 26 and gas outlet 27 as indicated.

The liquid products issuing from the condenser are collected in suitable receptacles (not shown) and can be refined by methods well known in the art.

The valve 25 connects with the expansion chamber and separator 28 wherein the carbon dioxide and water are separated from each other. When the valve 25 is cracked the release of pressure causes the carbon dioxide absorbed in the water to boil out thus permitting a fairly pure gas to be obtained. The carbon dioxide is withdrawn from the separator 28 by pipe 29 and the water, with any suspended dust, now at substantially atmospheric pressure, by pipe 30.

I do not limit myself to vertical tubes and towers, but may accomplish the same treatments by using horizontal tubes in long tunnels.

In the apparatus, the tubes are preferably constituted of chromium nickel steel, such as 18% chromium, 8% nickel, a low percentage of carbon and about 1% silicon. In arranging the tubes, sharp bends should be avoided. With moderate curves, say of the order of 90° and a radius of above ten inches, used, substantially no adherence between the heated particles and the heated walls of the tubes occurs. With increase of radius of curvature, there is a decrease of wear of walls of the tube due to abrasion and a decrease of adherence of carbonaceous material. This becomes particularly important in treating fusible types of carbonaceous materials.

When the tubes contain nickel and chromium they serve at least in part as a catalyst for certain desired reactions. Additional catalysts such as cobalt oxide or nickel oxide or iron oxide carrying an alkali may be used to produce gaseous reaction products low in carbon dioxide and high in both gaseous and liquid saturated compounds and alcohols. Under the conditions of the process the metallic oxides are largely reduced to the metals and these are the effective catalysts. If it is desired to produce a gas high in carbon dioxide, say above 12%, a catalyst, such as iron dust formed by reduction of iron oxide or chromium oxide, may be used. These solid catalysts can be fed into the apparatus in the form of dust with the particles of oil shale or can be introduced at a later point and can be recovered by filtration from the condensate and re-used in the process. The chemical reactions occurring in the vapor phase are facilitated by the numerous solid surfaces disposed within the gaseous reaction fluid such as steam.

The reaction products coming from the terminal end of the tubes are preferably first passed through a heat interchanger and then through a dust extractor to remove dust and solid particles from the hot vapors and gases. These vapors and gases are then flowed through a vertical surface condenser. I prefer to introduce the hot vapors and gases at the bottom of the condenser and the cooling water at the top. This procedure is just the reverse of the ordinary practice where the hot vapors are introduced at the top of the condenser and the cooling water at the bottom. The removal of dust prior to condensation decreases the emulsification tendencies of the aqueous condensate.

In most instances, it may be desirable to effect condensation under pressure. In this case, carbon dioxide from the gases is dissolved in the water and can be recovered therefrom. In some instances a jet condenser using cold water may

be used instead of a surface condenser for condensing the hot vapors.

The liquid product issuing from the condenser can be collected in some suitable receptacle and can be refined by methods well known in the art. The principal liquid products produced are light oils of the order of lubricating oil, mineral spirits like kerosene, gasoline and the like and light spirits. Combustible gases are also withdrawn from the condenser and normally have a heating power upwards of 500 B. t. u. per cubic foot.

In carrying out my process, the particles of oil shale first decompose to form a semi-solid organic material which, for convenience, I term a "primary bitumen", and which in part vaporizes. The primary bitumen and accompanying by-products under the influence of the accentuatedly high pressure and temperature and in the presence of steam and water gas formed from the steam and carbonaceous residue of the shale are subjected to processes of decomposition and synthesis wherein the heavy molecules are broken up to yield alcohols and saturated and unsaturated hydrocarbons, a portion of which are hydrogenated by the hydrogen of the water gas. By my process, it is possible to obtain a higher yield of motor fuel than by the usual methods of shale oil production and refining in which the motor fuel produced is a cracked distillation product of the primary bitumen or of the crude oil formed from it, and much of the bitumen is lost as oil-coke left in the shale. Furthermore, it is found that the new method produces a motor fuel having a higher carbon to hydrogen ratio than is present in the gasoline normally produced by cracking well petroleum. Also there is produced a large yield of combustible gas of high calorific value.

In practice the pressure may be varied from atmospheric pressure to exceedingly high pressure. Of course, pressure facilitates the thermo-chemical reactions of decomposition and synthesis of light liquid products containing a large percentage of combined carbon and it also aids in the hydrogenation of the unsaturated hydrocarbons. Pressures as high as 2500 pounds per square inch are suited to this process. Pressures of about 1000 pounds per square inch will also serve.

By the use of high pressure the apparatus required is smaller and a high relative throughput is obtained as well as more complete hydrogenation of the primary products. The process will give some water gas by the reaction of the steam with any residual carbon formed from the bitumens and thus this reaction will aid in keeping carbon from accumulating on the walls of the reaction tube.

To summarize, the principal products obtained by treating oil shale in accordance with my process are as follows:

1. Residue from the shale.

2. A motor fuel produced by the thermal decomposition of the original bitumen of the shale or coal by synthesis and hydrogenation of the decomposition products, the said motor fuel being capable of refining by methods well known in the art.

3. A high pressure gas of high heating power per cubic foot and suited to long distance transmission by its own energy.

4. And, if condensation takes place under pressure, an aqueous layer carrying large amounts of carbon dioxide and also an oil layer carrying dissolved low boiling hydrocarbons.

The two gaseous products, fuel gas and carbon dioxide, of course, have a ready market, the first for use by public utility companies and the second for the making of solid carbon dioxide which is used extensively as a dry refrigerant. It will be necessary, however, to purify this carbon dioxide, after releasing it from its solution in the water, by passing it through adsorbent carbon, or other purification process, in order to obtain carbon dioxide of the right quality for the manufacture of salable carbon dioxide. As the illuminating gas to be delivered to the gas companies is already under high pressure, it will be the more welcome to them as it will permit them, after cleansing, to use it at once in their high pressure gas mains.

While I have described a specific embodiment of my invention and one system for carrying it into practice merely by way of illustration, it is to be understood that I am not to be confined to the exact steps, pressures, temperatures, velocities, reaction intervals, catalysts, proportions, particular devices or specific statements mentioned hereinabove as they are to be regarded only as illustrative and typical. For instance, various carbonaceous materials such as lignite, bituminous coal and related products can be utilized in place of oil shale and when I mention oil shale in the claims, these various materials are to be considered as equivalents. Then again instead of using steam other fluids may be employed as the carrying agent such as high pressure water gas, its component gases or other hydrogenous gaseous fluids—these are to be considered as equivalents.

Various embodiments of my invention may obviously be readily made by those skilled in the art without departing from the spirit and scope of my invention as defined in the appended claims.

I claim:

1. The process of hydrogenating and distilling oil shale, which comprises grinding the oil shale to a fineness of at least 20 mesh, preheating said ground oil shale to a temperature of about 300° C., suspending said ground oil shale in its preheated condition in a rapidly moving stream of steam to give a mixture having about equal parts of oil shale and steam present therein by weight, passing said mixture through a highly heated metallic tube while under a pressure of at least 1,000 pounds per square inch and less than about 2,500 pounds per square inch, maintaining a temperature of about 900° C. throughout the first half of said metallic tube and a temperature of about 250° C. to about 450° C. throughout the second half of said tube, controlling the movement of the stream containing the mixture of oil shale and steam in said tube so that the oil shale is only subjected to said heat for a relatively short period of time of the order of seconds to insure the evolution of vapors from said oil shale without deleteriously affecting said vapors and said shale, withdrawing the hot vapors and gases produced by the preceding step, subjecting said products to heat exchange, condensing the vapors, and separating the products.

2. The process set forth in claim 1 in which the metallic tube contains substances comprising nickel and chromium, which catalyze the reactions occurring in said tube.

RALPH H. MCKEE.