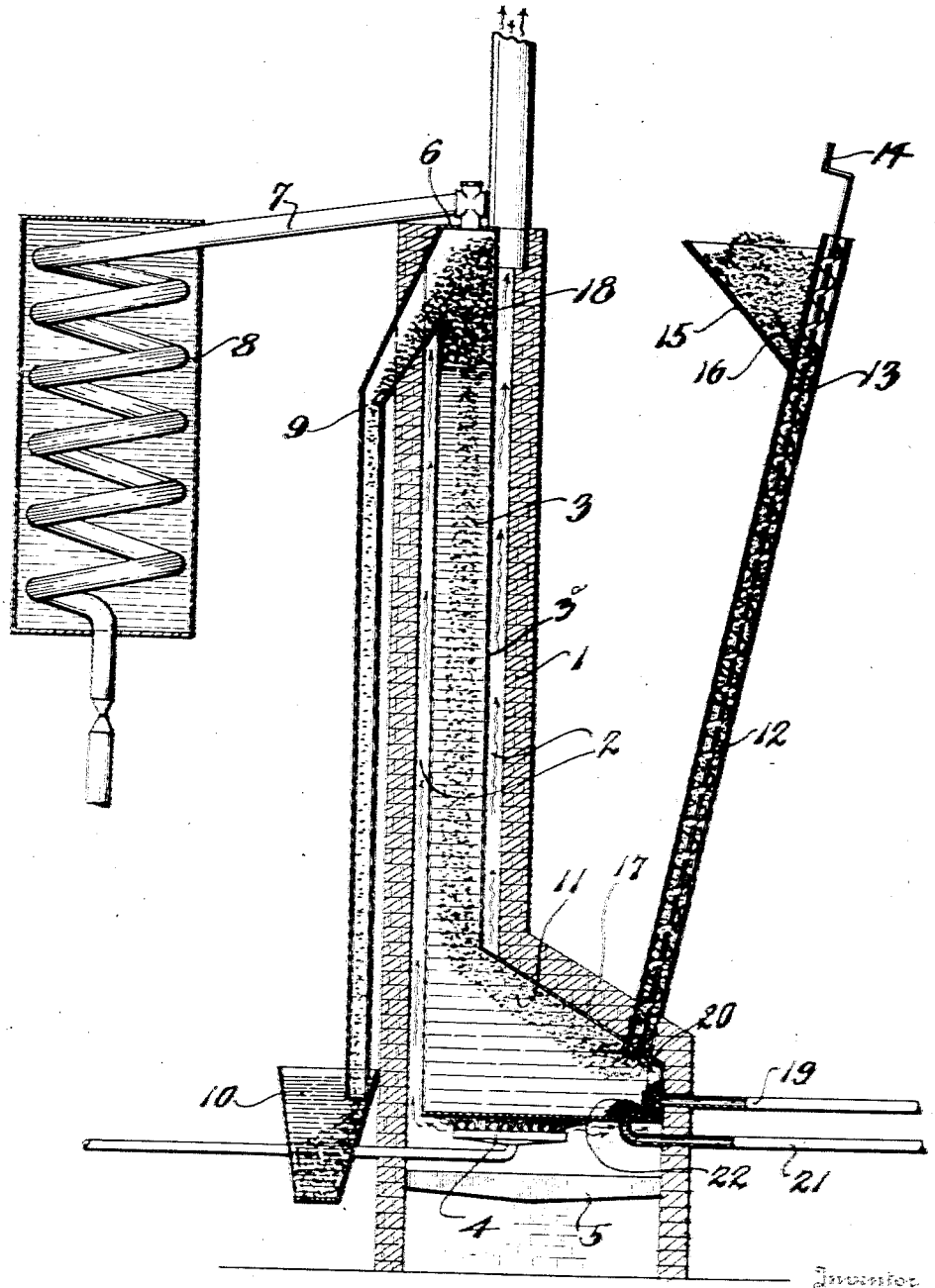
Nov. 12, 1929. J. B. JENSON 1,734,970

PROCESS AND APPARATUS FOR TREATING PETROGEN CONTAINING SUBSTANCES

Filed July 22, 1921



Witness:
Ott. Wagner.

Inventor
J. B. Jenson

By Robt. Pollock Hill

Attorneys.

Patented Nov. 12, 1929

1,734,970

UNITED STATES PATENT OFFICE

JAMES B. JENSON, OF SALT LAKE CITY, UTAH

PROCESS AND APPARATUS FOR TREATING PETROGEN-CONTAINING SUBSTANCES

Application filed July 22, 1921. Serial No. 486,729.

The present invention relates in general to a novel method of process for the treatment of hydrogen and carbon containing materials, whether solid, liquid or gaseous, for the purpose of distilling or cracking the same to obtain hydrocarbon products, and to an apparatus for carrying out the same. At the same time any metal values which may be contained in the materials undergoing treatment can be extracted, and this is an important feature of my invention.

While one of the main objects of the invention is to provide a novel process for the retorting or production of oil from oil-yielding shales, it will be understood that the process can be used to advantage in many cases where liquid oil is to be cracked and distilled under pressure, as well as where gaseous products are to be treated to bring about the decomposition and rearrangement of the atoms and molecules into desired products.

In a number of foreign countries, notably Scotland and France, the retorting of shale deposits to obtain hydrocarbon and ammonia products has been carried on quite extensively for a number of years on a commercial basis. There are extensive shale fields in this country, including the shales of Colorado, Utah, Wyoming, New Brunswick and the Devonian shales of Kentucky, and these shales are largely capable of being treated to obtain petroleum and hydrocarbon compounds, although they have characteristics which are different from the shales of Scotland and France and require somewhat different treatment and handling to obtain satisfactory results. In fact, it has been found by experiment that the type of retorts used successfully in Scotland are failures when used with most of our shales, especially the high grade massive shales which it is more especially desired to treat from a profit standpoint. Of course, certain of our fields produce a character of shale which may be treated in a more or less satisfactory manner by Scotch methods, although the massive shales which are the most productive of petroleum compounds cannot be treated satisfactorily in retorts of the Scottish type, owing to the fact that the shale will flux in such retorts. Further difficulties encountered are the secondary decomposition of the gases produced at the lower temperature by bringing them into contact with a higher temperature, and also the formation of a large proportion of unsaturated hydrocarbons. It may be explained that the Scotch retorts do not subject the shale or gases of distillation to pressure, but the crushed shale is permitted to descend gradually through the retort where it is subjected to a progressively increasing heat, the gases of distillation rising to the top of the retort and being conveyed from thence to a condenser while the spent shale is discharged from the bottom of the retort. In other words, the shale is crushed and submitted to destructive distillation by heat in a closed chamber, although the distillation does not take place under pressure.

In order that the process may be more fully understood, some explanation of the nature of shales is necessary. Our Colorado-Utah shales are not oil-shales and contain no oil, but rather are shales which contain the materials from which petroleum can be produced, not extracted, but produced. These are different from the true oil-shales which contain petroleum, very much as our saturated oil sands do, and oil may be extracted from such shales. While the Colorado-Utah shales do not contain petroleum, they may and do contain the basic elements of petroleum, namely, hydrogen and carbon, in their primary unretorted conditions, and by properly treating these shales the molecules are decomposed and broken up and caused to combine in different arrangements so that petroleum is produced. From the fact that the hydrogen and carbon as contained in the shales is the source of the petroleum, the word petroliferous has been adopted to indicate the material which through destructive distillation produces or yields petroleum. To those shales, such as the Colorado-Utah shales previously mentioned which are still in their primary unaltered condition, containing petroliferous substances but not petroleum, and which are therefore as yet only a source of petroleum, the term oil shales has been applied. This term applies in general to the shales of

Colorado, Utah, Wyoming, New Brunswick and the Devonian shales of Kentucky.

The so called oil shales are commonly spoken of as two kinds—"massive" and "paper" shale. There is primarily no difference between the two, except that the paper shale consists of much thinner beddings or measures than the massive. Between each bedding is a thin layer of argillaceous material containing no petroliferous substance. As a rule, though not always, the massive variety is of slightly higher grade than the paper shale.

In order to convert the petroliferous material into petroleum, it is necessary to effect a chemical change of the hydrocarbons and this is done by destructive distillation, by the application of heat. The shale oil is then volatilized or converted into a gas which is conveyed into a suitable cooling system where the greater portion of it condenses and forms crude petroleum. There are certain portions, however, which cannot be condensed. These constitute what are termed the fixed or permanent gases, and after having been scrubbed to remove the remaining naphtha and ammonia contained in them, these permanent gases may be used for fuel under the retort or for power purposes. Shales yielding 45 gallons or better to the ton are usually capable of producing sufficient fuel for their own retorting.

Owing to the fact that these petroliferous substances contain a much larger proportion of carbon than of hydrogen, and that our petroleum products require possibly from two to three times as many hydrogen atoms as carbon atoms, it is evident that the resultant products and spent shale will ordinarily have a tendency to contain a considerable amount of carbon which has not been able to secure the required amount of hydrogen for the production of a staple petroleum product. These are the unsaturated hydrocarbons which should be kept as low as possible, since the loss in distillation is heavy where the percentage of these unsaturated hydrocarbons is large.

The crude oil obtained, ranges in color from a dark brown to olive green and in specific gravity from .841 to .925. It consists largely of oils of the paraffin and olefine series comparable with paraffin well oil of the highest grade.

These shales also generally contain some metal values which range from traces of silver and gold, frequently accompanied by platinum, up to values reaching several dollars per ton, of the combined metals. I have discovered that the metallic particles contained within the shale are so thoroughly macerated and finely ground in character that they are carried away by the fumes in the ordinary furnace, and one of the objects of this invention is to provide a process which provides for the recovery of these metal values.

One form of apparatus which is adapted for use in carrying out the process is illustrated by the figure of the accompanying drawing which shows a vertical sectional view through the apparatus.

Referring to drawing, the numeral 1 designates a tower which may be constructed of masonry or other suitable material, said tower being formed with the flues 2 and containing a column 3 of molten metal. This column 3 of molten metal is contained in a receptacle 3^a which is arranged within the tower 1, having portions thereof spaced from the walls of the tower to provide the flues 2. A gas or oil burner 4 is arranged at the base of the tower and under the column of molten metal for the purpose of heating the metal and maintaining it at the proper temperature. A grate 5 is also shown and this may be used if coal or solid fuel is employed. The top of the tower is suitably closed by a cap member 6 which excludes air from the space above the molten metal. A gas pipe 7 leads from the top of the cap 6 to a suitable condenser 8. A spent shale discharge pipe 9 extends downwardly on the outside of the tower from the cap 6 to a vessel or receptacle 10 containing water to provide a water seal for the discharge pipe 9 and prevent the entrance of air into the retorting tower through the said pipe.

The base of the masonry tower and colum of molten metal are enlarged laterally, as indicated at 11, and a feed pipe 12 for the crushed shale leads into this enlarged lower portion of the column of molten metal. A suitable conveyer such as the screw conveyer 13 extends through the feed pipe 12 and provides a means for positively feeding the crushed shale into the molten metal. Any suitable means may be provided for driving the conveyer, a crank handle 14 being indicated in the present instance at the upper end thereof. A hopper 15 at the upper end of the feed pipe 12 receives the crushed shale or coal and delivers it into the feed pipe through an opening 16. Any suitable apparatus may be employed to crush the shales, and good results are obtainable with about one-half inch particles and a minimum of fines. The particles should be sufficiently small so that they can be properly acted upon by the heat and the spaces between the particles should remain open so that the gases can circulate freely through the column of crushed material.

Any suitable metal may be used, although I have found that a lead bath alone gives splendid results for the usual distillation or cracking of hydrocarbons, and that if a portion of zinc is added, forming a lead-zinc alloy ranging from 1% of zinc upwards, the precious metals may be recovered. The greater the amount of precious metals the

higher the zinc percentage that is necessary to get the best results. The affinity of the precious metals is greater for the zinc than for the lead, and the zinc being of lower specific gravity, has a tendency to rise to the surface of the lead, taking with it the precious metals which it has collected. The zinc is then removed, either after partially solidifying or while still molten, and undergoes the usual method of refining or separation from the silver-gold values, after which the zinc may again be charged into the lead bath.

It will be obvious that the molten metal at the base of the retort tower is under a heavy pressure, depending upon the height of the column of molten metal, and this may be varied as is found necessary to produce the best results. The degree of pressure is limited only by the strength of materials used in the construction of the plant, and by increasing the height of the column of molten metal which is utilized for transmitting heat units to the material being treated, any degree of pressure may be obtained. The pressure desired will, of course, depend upon the character of the material being treated and will range between a few ounces to several hundred pounds per square inch. For special purposes when extreme "cracking" is required, it may go much higher. When a simple distillation only is required, it is necessary to submerge the material to be treated only an inch or two beneath the surface, whereas when it is desired to produce excessive decomposition, such as is necessary in the high cracking of heavy petroleum products, or when it is desired to decompose non-condensable gases with a view to utilizing certain of the products thereof in the subsequent making condensable gases, such as is possible through the treatment of the natural gases from wells and gases from other sources, or when it is desired to produce a highly saturated product direct from the destructive distillation of shale, coal, peat or other solid hydrocarbon materials, then high pressure and high temperature become necessary and the material is submerged at a sufficient depth to procure the required degree of pressure.

The crushed shale, coal or other material to be treated is fed into the retort at the lower end of the column of molten metal, and this crushed material is immediately heated to a high temperature by the molten metal with the result that destructive distillation takes place and gases of distillation are given off. The shale particles and bubbles of gas are completely surrounded by the molten metal and tend, of course, to rise to the top of the molten metal, although this is delayed by the shape of the retorting chamber, it being preferred that the material shall remain near the bottom of the molten metal so as to be subjected to the maximum pressure until the desired chemical changes have been substantially completed. In the present instance, the enlarged base of the retorting chamber has an inclined wall 17 which gradually deflects the particles toward the upper portion of the column of molten metal, although it delays their rise and keeps them at the bottom of the retorting chamber for the desired period of time. As the crushed shale is forced into the bottom of the retort through the feed pipe 12 it gradually forces the crushed shale already in the retort along the inclined top wall 17 of the enlarged base of the retorting chamber, and the feeding of the shale into the retort determines the length of time that is required for the shale within the enlarged base of the retorting chamber to get beyond the inclined wall 17 and reach the vertical portion of the retort chamber so that it will rise to the top of the retort. The shale can thus be kept in contact with this inclined wall 17 and maintained at the bottom of the retort chamber under the maximum pressure for the full length of time that may be necessary for the decomposition thereof. The inclination of the inclined wall 17 enables the gases to escape readily as they are formed and facilitates the shoving forward of the shales as fresh charges of shale enter the retort.

The spent shale accumulates on the top of the column of molten metal, as indicated at 18, and the gases filter through this mass of spent shale until they reach the entrance to the pipe 7 which conveys them to the condenser 8. Additional spent shale rising from below gradually lifts the mass of spent shale resting on the metal until it assumes such a depth that the upper portion thereof is discharged through the discharge pipe 9. This hot spent shale is of importance as a filter medium, and it may be augmented by the use of hot fuller's earth, clay or other filtering mediums, these being maintained at a high temperature and in sufficient quantities to thoroughly filter the gases before condensation.

The bottom of the retorting chamber is also provided with a gas inlet 19 through which a portion of the non-condensable gases may enter. A screen 20 is arranged over the mouth of the gas inlet 19 and serves to break up the larger bubbles of gas into fine bubbles which mingle intimately with the shale particles and gases of distillation. The intense heat acts upon the gas entering through the inlet 19 to partially decompose the same and provide a supply of hydrogen which is available for combination with those of the carbon atoms in the shale which did not otherwise get all the hydrogen they could absorb or combine with. The hydrogen thus produced from the gas or already contained therein is maintained in intimate contact with these carbon atoms under a high pressure and at a high temperature. Under these conditions it

has been found that the carbon and hydrogen will combine and the additional hydrogen supplied by the admission of gas reduces the percentage of the unsaturated and unstable portions of the final product.

A steam inlet 21 may also be provided at the bottom of the retort chamber, and a similar screen 22 extends across the mouth of this inlet pipe. The steam is preferably superheated before being introduced into the retorting chamber, and the high temperature of the molten metal acts upon the steam to partially decompose, and break it up into hydrogen and oxygen. The hydrogen, as in the previous instance is maintained in intimate contact with the unsaturated carbon molecules of the shale under a high pressure and at a high temperature, with the result that a chemical combination takes place and the unsaturated hydrocarbon molecule is converted into a saturated hydrocarbon molecule. By passing the gases through a molten metal, preferably lead, I find that a higher combination of the hydrogen and carbon atoms can be effected and the ultimate oil yield greatly increased, in some instances as much as 50% over that obtained by the ordinary retorting methods. At the same time there is a higher degree of saturation and a lower refinery loss. Owing to the fact that every particle from the minutest to the coarsest of the hydrocarbon material is completely submerged, surrounded and contacted by the molten metal and a uniform temperature thereby imparted to each particle, retorting is effected with a very much lower fuel consumption than is possible by any other method. A uniform pressure is also brought to bear on every bubble of gas as it forms from the decomposing petrogen of the shale, thereby compelling an intimate contact between the hydrogen and carbon atoms before they are released from the bath, and thereby effecting a more complete saturation. It has, of course, long been known that unsaturated hydrocarbons are condensed to saturated hydrocarbons by the action of heat and pressure, and that if free atoms of hydrogen within the retort can be brought into intimate contact with unsaturated hydrocarbon molecules, saturated and stable molecules are produced, and while this has been partially accomplished in the cracking of petroleum products through the pressure effected by the gases within the still, such for instance as is disclosed by the Burton Patent #1,049,667, it has not been possible thus far to utilize this knowledge in the commercial destructive distillation of shale and similar products.

The lead bath alone has been found to be very satisfactory for the distillation or cracking of hydrocarbons, although if a higher temperature should be desired than can be obtained by the lead or lead-zinc combination, it is obvious that copper or other metals may be added to raise the melting point of the alloy to the required temperature.

It is well known that sulphur is an objectionable element in oil and that it is almost always present in oil-shales and coals. With the ordinary retort a complex sulphur-bearing oil which is difficult and expensive to refine is obtained. This disadvantage of operating with an ordinary retort is entirely eliminated by the present process wherein the sulphur, when released, is immediately taken up and held by the metal bath, from which it is periodically removed by the usual methods of "softening" lead. The oil gases produced by the present process thus pass to the condensers practically sulphur-free.

A plant for carrying on the present process may be built in a number of units, each of which is a substantial duplicate of the other. For instance, the first unit may treat the raw shale and, after condensation, the heavy crude oil or such portions thereof as it is desired to crack or treat further may be passed through a second unit, and the heavy products from the second unit may pass through a third unit, and so on. It thus becomes possible to construct a plant of great capacity at minimum cost and to permit the continuous and constant operation of all units.

In shale, coal, peat and other analogous substances which may be retorted to obtain hydrocarbon products, there is always an insufficient number of hydrogen atoms to satisfy the carbon present, with the result that there is necessarily a large amount of carbon which can form no combination whatever with hydrogen and has a tendency to attach itself either to the metal wall portions of the usual retort or to the unvolatilized or solid portions of the shale. In addition to this free carbon or coke, there are also many other carbon particles which only combine with a portion of the hydrogen necessary to form a saturated molecule. As previously indicated, these hydrocarbon molecules which are deficient in hydrogen are termed "unsaturated" molecules, and both heat and pressure are necessary to cause these unsaturated molecules to combine with the additional hydrogen atoms necessary to convert them into saturated molecules. It is not practical to produce pressure within the ordinary shale retort which has been previously used, and therefore a very large percentage of the ordinary shale oils hitherto produced, both in this country and in Scotland, consist of unsaturated products. Owing to the fact that the unsaturated oils are unstable and do not have good keeping qualities, it is desirable to remove a very large proportion of these unsaturated products in the subsequent refining process. This causes a heavy refinery loss and additional refinery cost.

The free carbon which adheres to the walls of the ordinary retort also tends to clog the

retort and to interfere with the transmission of heat through the walls of the retort to the shale. This difficulty is completely avoided by the present process in which any free carbon is carried to the top of the molten metal with the spent shale and discharged with the spent shale. It cannot interfere in any manner with the continuous retorting action and the apparatus can be kept in continuous operation. Not only is the continuous and uninterrupted operation of the plant made possible, but all danger of explosion due to carbon accumulations within the retort is eliminated.

The ordinary form of retort has the further disadvantage that the heating of the shale is neither uniform nor under perfect control. The shale at the middle of the retort is not heated as quickly as the shale adjacent the retort walls, and there is danger that portions of the shale will be over-heated with the result that a large percentage of non-condensable gas is produced. The gases within the retort are formed at different temperatures, and unless those formed at lower temperatures are immediately removed from the retort they undergo secondary decomposition which converts them into non-condensable gas producing a lower yield of oil. These objectionable features of the ordinary retort are completely avoided in carrying on the present process, since every minute bubble of gas and particle of shale is completely surrounded and contacted by the molten metal with the result that the heat is uniformly applied to the substance being treated. The entire mass of the shale or material is subjected to a uniform heat and the temperature is under far more perfect control than is possible with the old form of retort.

A most important feature of this process is the utilization of pressure for the conversion of the unsaturated molecules into saturated molecules. With the old form of retort it is not possible to utilize pressure and, in fact, a slight vacuum is created to withdraw the gases as formed and to drive them through the condenser system. In the absence of pressure the unsaturated molecules do not seem to combine readily with additional hydrogen to produce saturated molecules, even where the hydrogen is present, and the resulting product accordingly contains a large percentage of the unsaturated molecules which are unstable and objectionable as previously explained. The present process simultaneously subjects the material to high pressure and high temperature, with the result that where additional free hydrogen is rendered available the carbon particles and unsaturated hydrocarbon molecules tend to combine with the hydrogen to produce a large percentage of saturated hydrocarbon molecules.

While this process is more especially adapted for the treatment of shales for the production of petroleum products, it is also adapted to be used for the treatment of liquid oil or other hydrogen and carbon containing materials, whether solid, liquid or gaseous, where it is desired to bring about a decomposition and rearrangement of the atoms and molecules into new products.

When the process is used for the treatment of shales, in many instances there will be only two or three feet, and possibly less, of the molten lead, and distillation takes place at about a temperature of 621° F., which is the melting point of lead. The temperature ranges between 621° F. and 1000° F., increasing as the pressure becomes greater. A great deal of the work upon our average shales can be done with a shallow depth of the molten metal and a correspondingly low pressure and temperature. The molten metal provides a perfect treating medium and enables the temperature to be kept under perfect control. The terms "high pressure" and "high temperature" as used herein are to be understood in this manner, and do not necessarily mean a tremendous pressure or an excessively high temperature, but such a pressure and such a temperature as will give the best results upon the material being treated, both the pressure and temperature being variable within wide limits. For instance, when excessive cracking is desired a considerable depth of the molten metal would be used to give a high pressure and the required high temperature would be used, while for ordinary distillation a shallow depth of molten lead and a temperature of about 621° would be satisfactory.

The various steps incident to carrying on the process and obtaining the specified results have been accurately set forth and those chemical reactions which are thought to take place have been stated, although these chemical reactions are based upon theory and may not set forth exactly what happens in the treatment of the shale to obtain hydrocarbon products.

Having thus described my invention what I claim as new and desire by Letters Patent is:

1. The method of treating shale to obtain petroleum products therefrom, which consists in subjecting the shale to a hot bath of molten metal in the presence of an auxiliary supply of hydrogen whereby carbon atoms and unsaturated hydrocarbon molecules can combine with the necessary hydrogen to produce saturated hydrocarbon molecules, the depth of the bath being sufficient to subject the shale and gases to pressure and the shale being retarded at the bottom of the bath where it is subjected to the maximum pressure of the bath until it is substantially decomposed, after which the spent materials are released and permitted to rise quickly to the

top of the bath, and collecting the resultant gases and condensing the condensable portions thereof.

2. The method of treating shale to obtain petroleum products therefrom, which consists in subjecting the shale to a hot bath of molten metal whereby portions of the shale are volatilized, introducing steam into the molten metal which partially decomposes the steam and provides hydrogen atoms which are held in intimate contact with the shale and gases driven therefrom so that carbon atoms and unsaturated hydrocarbon molecules can combine with the auxiliary hydrogen to produce saturated hydrocarbon molecules, and collecting the gases and condensing such portions thereof as are condensable.

3. The method of treating shale to obtain petroleum products, which consists in crushing the shale and subjecting it to a hot bath of molten metal, which is of a sufficient depth to subject the metal to a high pressure, the heat of the molten metal acting upon the shale to volatilize portions thereof, introducing hydrogen into the bath and maintaining the hydrogen in intimate contact with the shale and hydrocarbon gases produced therefrom so that carbon atoms and unsaturated hydrocarbon molecules can combine with the auxiliary hydrogen to produce saturated hydrocarbon molecules, and collecting and condensing the gases.

4. The method of treating shale to obtain petroleum products, which consists in crushing the shale and subjecting it to a hot bath of molten metal at a sufficient depth to be under considerable pressure, the high temperature of the molten metal acting upon the shale to volatilize portions thereof and the shale and volatilized portions thereof being detained at the bottom of the bath so as to be simultaneously subjected to pressure and high temperature for a sufficient length of time to enable the volatilized portions to decompose and the atoms to rearrange themselves to provide hydrocarbon gases after which the spent shale is released and permitted to rise quickly to the surface of the molten metal, introducing an auxiliary supply of hydrogen containing substance into the molten metal to provide additional hydrogen which is maintained in intimate contact with the shale and gases driven therefrom so that carbon atoms and unsaturated hydrocarbon molecules can combine with the auxiliary hydrogen to produce saturated hydrocarbon molecules, and collecting the gases and subjecting them to the action of a condenser.

5. An apparatus for the treatment of oil bearing materials comprising a receptacle for containing a column of a hot molten metal, means for heating the column, means for introducing the material to be treated into the lower portion of the column of molten metal to subject the same to the pressure and heat of the molten metal, means for retarding the material at the lower portion of the column where it is subjected to a maximum pressure for the desired period of time and then releasing it so that it can rise quickly to the surface of the molten metal, and means for collecting the gaseous products.

6. An apparatus for the treatment of oil-bearing materials comprising a vertically arranged tower, a receptacle within said tower and spaced from the inner faces of the walls thereof, a column of molten substance in the receptacle, a heater beneath the base of the receptacle, and means for introducing into the base portion of the receptacle the materials to be treated, said receptacle being formed with an enlargement at its base portion whereby to effect retardation of movement of the material through the column of molten substance.

7. An apparatus for the treatment of oil bearing materials comprising a receptacle for containing a column of hot molten substance, means for heating the column, said receptacle having an offset at the base thereof with a wall overhanging said offset, means for introducing the material to be treated into the offset portion at the base of the column whereby the material is subjected to the pressure and heat of the molten substance, the material being retarded at the bottom of the receptacle by the before mentioned overhanging wall and rising quickly to the surface of the molten material as soon as it has become disengaged from the overhanging wall.

8. An apparatus for the treatment of oil-bearing materials comprising a vertically arranged receptacle for holding the column of molten material, said receptacle having an offset at its base portion constituting a retarding means for the material introduced thereinto, means for introducing into said column materials to be treated in comminuted condition, separate means for introducing into said column liquid or gaseous materials at will, and means for heating the column of molten substance.

In testimony whereof I affix my signature.

JAMES B. JENSON.