Aug. 25, 1959 M. W. PUTMAN 2,901,402

PROCESS FOR DESTRUCTIVE DISTILLATION OF HYDROCARBONACEOUS MATERIALS

Filed July 19, 1957 3 Sheets-Sheet 1

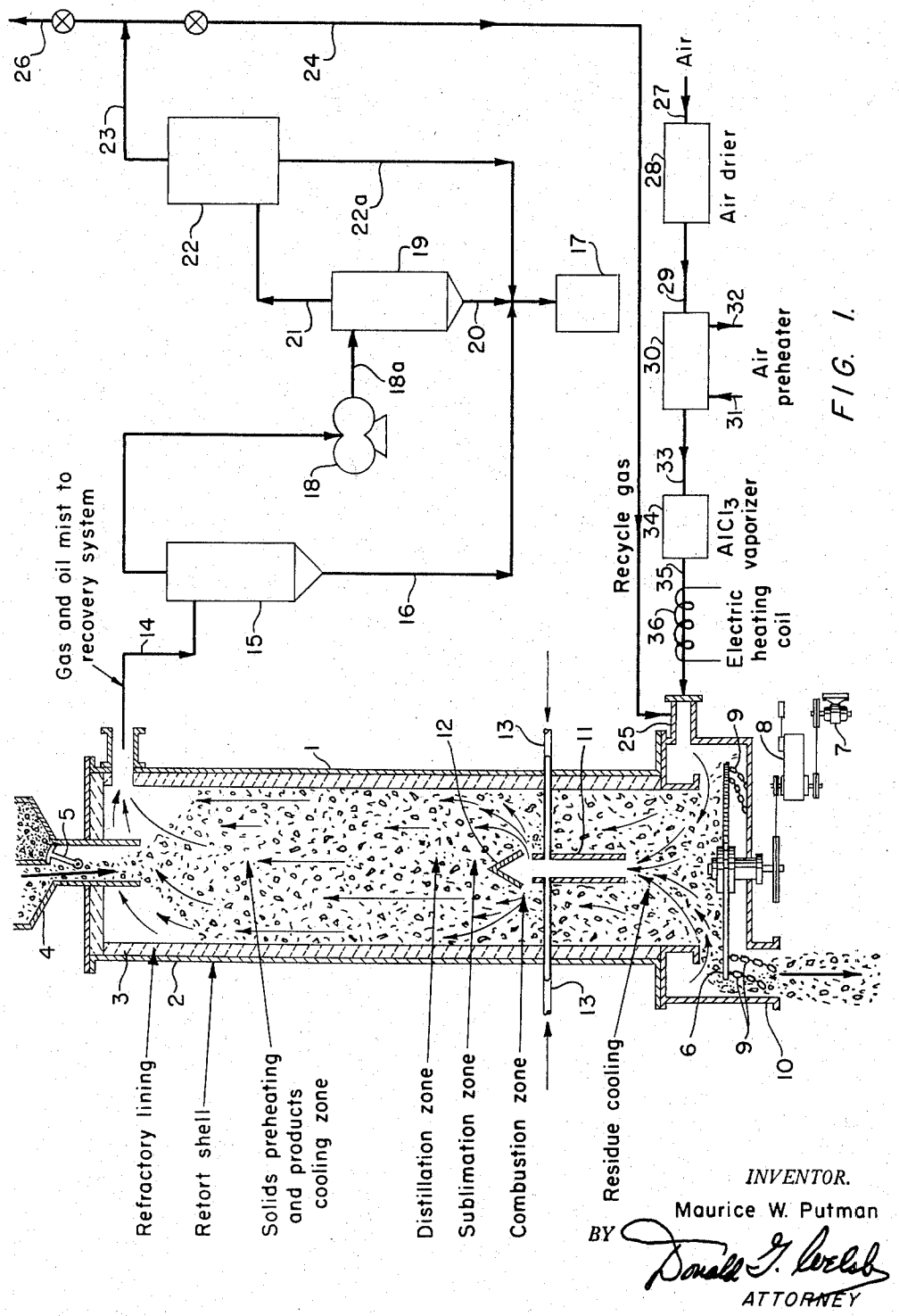


FIG. 1.

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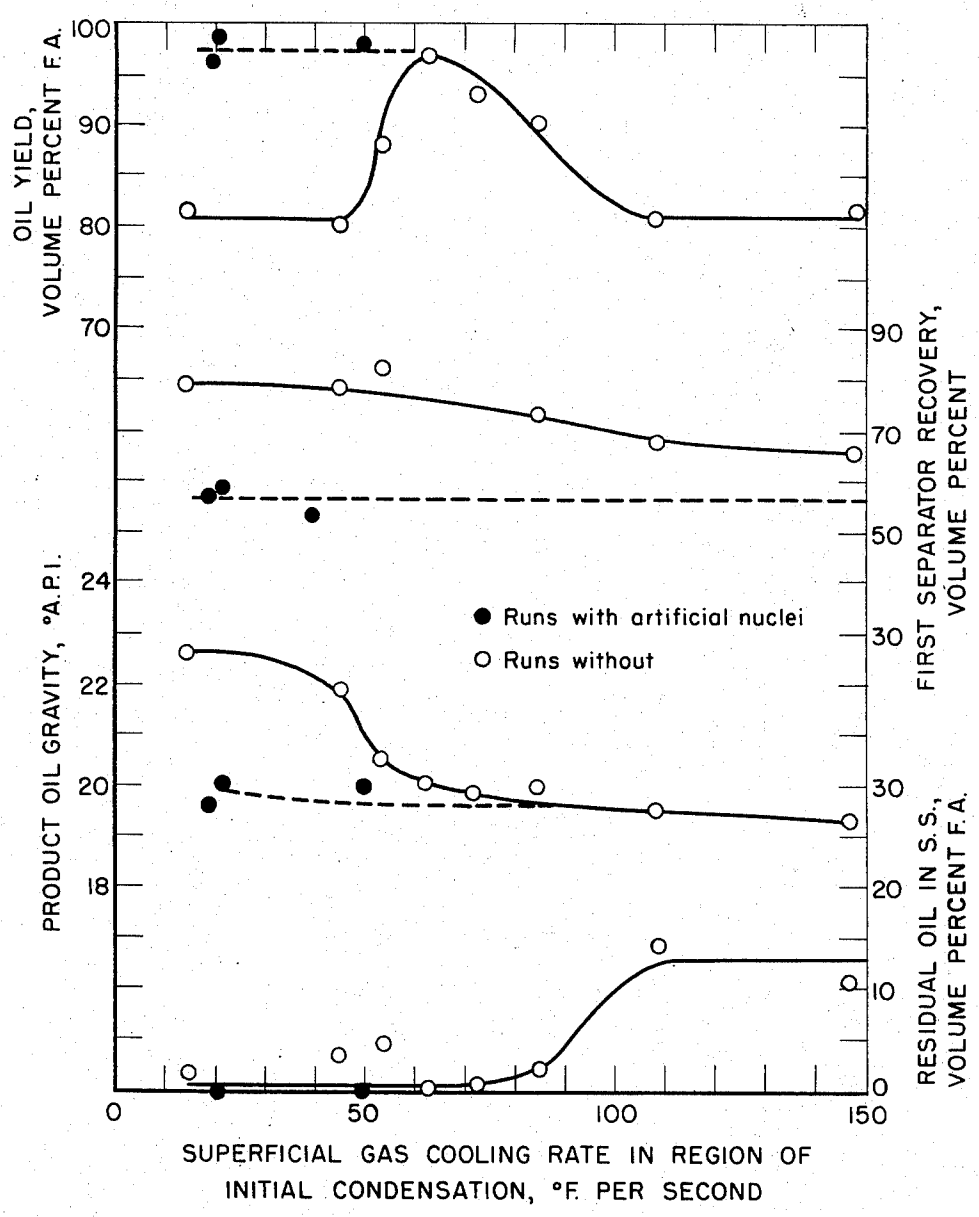


FIG. 2.

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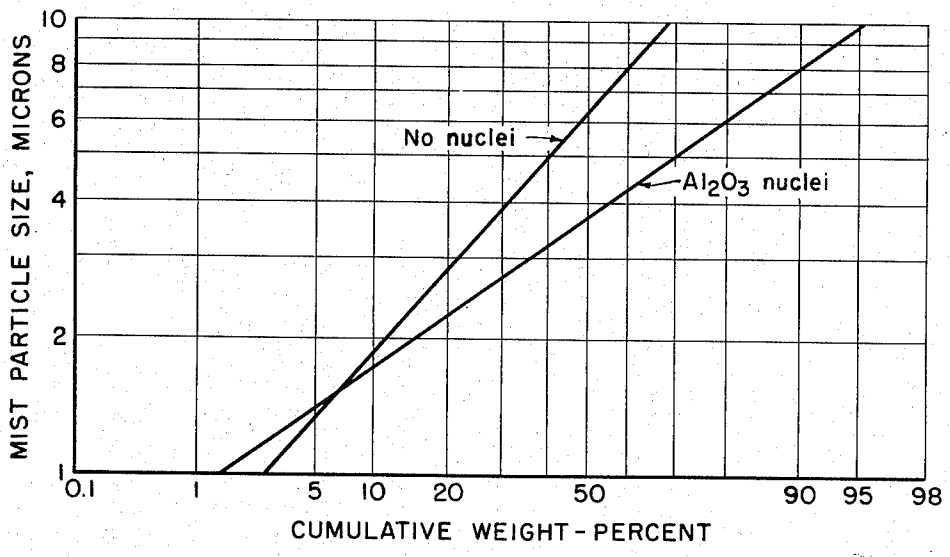


Fig. 3.

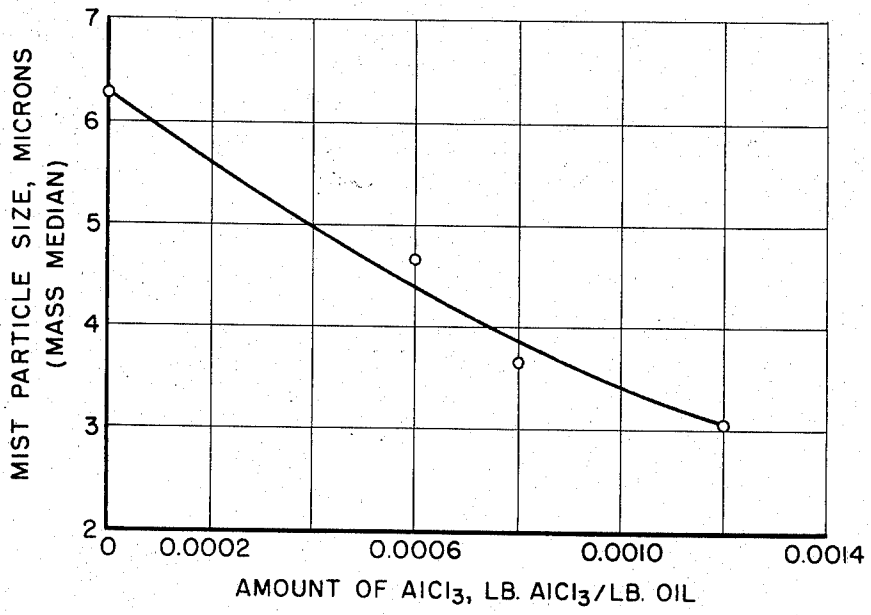


Fig. 4.

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United States Patent Office 2,901,402
Patented Aug. 25, 1959

2,901,402

PROCESS FOR DESTRUCTIVE DISTILLATION OF HYDROCARBONACEOUS MATERIALS

Maurice William Putman, Midland, Mich., assignor to the United States of America as represented by the Secretary of the Interior

Application July 19, 1957, Serial No. 673,099

9 Claims. (Cl. 202—6)

(Granted under Title 35, U.S. Code (1952), sec. 266)

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 royalties thereon or therefor.

This invention is generally related to the destructive distillation of solid hydrocarbonaceous materials and is particularly concerned with a method for the destructive distillation of oil shale to produce useful liquid products.

It is, of course, well known that certain sedimentary rocks, commonly referred to as oil shale, upon heating, yield appreciable quantities of relatively crude oil as well as gaseous hydrocarbons. This oil may be refined into valuable products such as gasoline, diesel oil, jet fuel, and fuel oil. Likewise, valuable by-products such as tar acids and waxes are recoverable from the crude shale oil. Extensive deposits of oil shale are found in this country, particularly in the so-called Green River shale formation located in the States of Colorado, Utah, and Wyoming. Important oil shale deposits are likewise found in other parts of the world. With diminishing world petroleum reserves, there has been considerable interest in developing a commercially feasible process, suitable for application on a large scale, for retorting (i.e., destructive distilling) oil shale to recover its potential yield of crude oil.

The two principal engineering problems connected with oil-shale retorting on a large scale are those of materials handling and of heat exchange. In such an operation literally thousands of tons of shale must be moved through the retorting vessel and auxiliary heat exchange vessel, if any. This shale must be heated in some manner to retorting temperatures, of the order of 800° to 1000° F. This involves the exchange of enormous quantities of heat since not only the organic matter (usually termed kerogen) must be heated, but also the inert, inorganic portion of the shale, which usually comprises from 80 to 90 percent by weight of the total shale.

With respect to the materials handling problem, obviously the simplest and most inexpensive manner of operation would be to feed the shale downwardly by gravity through the retorting vessel.

Thus far, the most attractive manner of heating the shale to retorting temperature appears to be direct heat exchange between the shale as a bed of broken solids, and a hot gas stream flowing through the shale bed. In a continuous process, the shale bed and gas stream preferably flow counter-currently to one another. In such a process it is highly desirable, from the standpoint of thermal efficiency, and from the standpoint of certain operational difficulties, otherwise encountered, that the outgoing bed of shale and the outgoing gas stream, containing the product oil, both leave the processing vessel at low temperatures.

It is particularly desirable that the product gas stream, carrying the oil, give up most of its heat to the incoming shale before leaving the retort. First of all, at high gas exit temperature, e.g., 400° to 500° F., there is a strong tendency for the oil vapors to deposit coke upon

the walls of the outlet ducts, eventually plugging the outlets completely, thus causing periodic shutdowns. In addition to the coking problem, a high exit temperature for the oil-bearing gas stream requires the use of expensive cooling equipment to condense out the oil vapors from the relatively large volume of retorting gases. Furthermore, large quantities of cooling water would also be required. In this country, where substantially all the commercially interesting oil-shale deposits are located in arid regions, this type of operation would be practically out of the question in a large-scale operation.

From the considerations discussed above, it is apparent that a practical retorting process should include both downward gravity feed of the shale through the retorting vessel and the use of the incoming cold shale to cool the ascending stream of retorting gases containing the product oil vapors, so that this gas stream leaves the shale bed at a temperature such that no further cooling is necessary. However, to avoid cooling the gas stream after its exit from the retort, it is apparent that it must be cooled below the condensation temperature of the oil vapors which it contains before it leaves the shale bed; and since the shale itself is cooling the gas stream, it is obvious that some of the product oil vapors will tend to condense upon the cold shale. Any oil condensing upon the shale will tend to flow by gravity downwardly in the retort toward the hot zone of distillation, and eventually is revaporized and carried once again toward the top of the shale bed where it may again condense upon the cold incoming shale and trickle downward through the shale bed. Since the crude oil is for the most part a high boiling material, and quite unstable thermally, constant revaporization of the oil in the shale bed is invariably accompanied by uncontrolled thermal cracking reactions which destroy a large fraction of the potential oil yield. Equally undesirable as the loss in oil yield, is the fact that refluxing of large quantities of oil in the upper part of the retort leads to operational difficulties, particularly those connected with "channeling" of the gas stream in the shale bed. Channeling, that is, the failure of the gas stream to flow through the entire cross-section of the shale bed, is brought about when the oil refluxes at such a rate as to render sections of the shale bed impervious to the passage of the gas stream.

Therefore, condensation of the oil vapors upon the surface of the shale to any substantial extent must be avoided in this type of process, where the shale flows downwardly, and the gas stream flows upwardly, and is cooled to a low temperature by the incoming cold shale before it leaves the top of the retort, and instead the oil vapors must be caused to condense preferentially in the gas stream as mist droplets as the gas stream is cooled by the bed of shale, it is equally imperative that the droplets formed be small enough that they may be carried upwardly through the shale bed and out of the top of the shale bed in the gas stream without substantial disengagement from the gas stream by impingement on the shale particles, but large enough that they may be recovered by the relatively cool gas stream with little difficulty by passing the gas stream through a centrifugal separator or other collector for example.

Because of the physical properties of Colorado shale oil, such a preferential condensation of the major portion of the oil vapors as a fog or mist in the gas stream may be achieved readily. The size of the mist droplets is determined ordinarily by the gas cooling rate in that portion of the shale bed where vapor condensation is initiated (high gas cooling rates produce smaller sized mist droplets than low gas cooling rates). However, satisfactory operation of such a process can be achieved over only a very narrow range of operating conditions because of the gas cooling rate limitation which must be satisfied.

Therefore, it is obvious that if the gas cooling rate limitation could be eliminated, the performance and operability of such a process would be greatly enhanced and its adoption assured because of the apparent advantages of such a process.

In accordance with this invention, it has been found that by providing artificially induced condensation nuclei in the condensing zone, that the size of the fog or mist droplets may be controlled so that none of the droplets are so large that they are disengaged from the gas stream by impingement in passing through the shale bed, nor none so small that they are difficult to recover from the relatively cool gas stream by conventional methods, irrespective of the gas cooling rate in that portion of the shale bed where vapor condensation is initiated. (The formation of a fog or mist is accomplished at low degrees of supersaturation only in the presence of a large number of nuclei on which the saturated vapors may condense.)

In my copending application Serial No. 610,849, filed September 19, 1956, now U.S. Patent 2,813,823, I have disclosed employing various salts, especially sodium chloride, as nucleating agents. The instant case is directed to the oxides of aluminum, tin, and titanium, which I have found to be very effective condensation nuclei. The invention will be described with particular reference to aluminum oxide, but it is to be distinctly understood that the tin and titanium oxides may be substituted therefore in the nucleation process.

The aluminum oxide nuclei may be prepared by vaporizing aluminum chloride, and then introducing the vapors into the recycle gas stream where the aluminum chloride reacts with a portion of the water vapor present to form aluminum oxide nuclei.

In its broader aspects, the process envisioned by the present invention involves continuously passing the oil shale downwardly as a bed of broken solids in a substantially vertical column. The solid residue is removed in a cool condition at the bottom of the column while the distillation and combustion products, including a noncondensable gas, are removed from the top of the column. At least a portion of this noncondensable gas, in a cool condition, is recycled to the bottom of the column and passes upwardly through the downwardly moving residue, thus cooling the hot residue and itself becoming heated. At this point in the retort the gas stream is raised to a still higher temperature, preferably by passing through a combustion zone in the retort itself. As the gas stream passes on up through the column of shale, it delivers its heat to the cold incoming shale, thus gradually heating it to progressively higher temperatures. The descending shale, consequently, passes successively through a preheating zone, where it meets the still hot vapor-gas mixture rising from the distillation zone, and through a distillation zone where it reaches retorting temperature.

In the distillation zone the organic content of the shale undergoes thermal decomposition producing condensable product vapors which are carried upwardly in the gas stream. The gas-vapor mixture rising from the distillation zone encounters progressively cooler shale as it passes upwardly through the shale preheating zone, and, of course, in this way, itself becomes progressively cooled. Eventually the gas-vapor mixture encounters shale below the initial dew point temperature of the mixture and condensation of the vapor begins.

Aluminum chloride is vaporized in a separate vessel outside the retort, and the vapors, carried along by a dried air stream, are introduced into the stream of recycle gas entering the bottom of the retort. Hydrated aluminum oxide particles are formed by the reaction of the aluminum chloride with water vapor present in the recycle gas stream. These particles are carried up through the retort and are dehydrated by the time they reach the products cooling zone at the upper portion. By withdrawing the gas stream from the top of the shale bed at a sufficiently low temperature, viz, between 100° and 200° F., and preferably between 115° and 175° F., substantially the entire vapor content of the gas stream undergoes condensation in the shale bed on the aluminum oxide nuclei in the gas stream.

The principles of the invention are applicable to any sort of retorting process where the shale is fed downwardly by gravity, countercurrent to a stream of retorting gases in which artificially induced condensation nuclei are present, and where the gas stream is withdrawn from the shale bed at a temperature sufficiently low so that substantially all, or the major portion, of the vapor content of the gas stream undergoes condensation before leaving the shale bed.

Preferably, however, a retorting process is employed such as that described in U.S. Patent 2,757,129 entitled "Method for the Destructive Distillation of Hydrocarbonaceous Materials" by Reeves, Putman, Jones, and Tripp. This and other preferred embodiments of the invention will be set out in detail in the subsequent description.

For a better understanding of the invention, reference now is made to the accompanying drawings wherein:

Fig. 1 is a semi-diagrammatic illustration of a retort suitable for carrying out a preferred embodiment of the process of the invention, together with a schematic illustration of the product recovery and gas circulation systems serving the retorting vessel;

Fig. 2 is a graphical correlation of the data from a number of runs performed in the retort illustrated in Figure 1;

Fig. 3 is a graphical comparison of the mist particle size distribution of shale-oil mists, produced with and without the addition of aluminum oxide nuclei;

Fig. 4 is a graph showing the variation of mass nuclei particle size of mist droplets vs. the amount of aluminum chloride added.

Referring now particularly to Figure 1, reference number **1** refers generally to a cylindrical, upright retorting vessel comprising a metal shell **2**, suitably insulated with a refractory lining **3**. A charge hopper **4** is disposed at the top of the retort. The charge hopper may be of any suitable construction, but should be adapted to maintain a continuous feed of solid material into the top of the retort and at the same time maintain a gas-tight seal to prevent the escape of gases and vapors from the retort through the charging mechanism. A sliding valve **5**, is provided to open simultaneously one compartment to the retort and to close off the other for recharging.

At the bottom of the retort, a discharging mechanism is provided consisting of a turntable **6**, driven by a variable speed motor **7**, through a gear box **8**. The rate of shale discharge is controlled by regulating the speed of the rotating turntable **6**. With the help of the drag chain **9**, the turntable **6** discharges residual solids into an ash-leg **10**, for disposal in any desired fashion. Ash-leg **10**, is equipped with a suitable gas seal (not shown).

At the vertical axis of the retorting vessel, at an intermediate level therein, an open ended cylindrical tube **11**, is provided, directly above the upper end of the tube **11**, is positioned a hollow, cone-shaped deflector **12**. As can be seen, the base of the cone-shaped deflector **12**, is spaced from the upper end of the tube **11**, and is somewhat larger in diameter so as to effectively prevent solid material flowing downwardly through the retort from entering the tube. A plurality of gas conduits **13**, are provided for admitting an oxygen-containing gas, such as air, into the upper portion of the tube **11**, as shown in the drawing.

Serving this retorting vessel, a product recovery and gas circulation system is provided. This system, which is shown schematically, comprises centrifugal separators **15** and **19**, a positive displacement blower **18**, an oil receiver **17**, and an electrostatic mist precipitator **22**, together with connecting conduits.

The operation of this retort now will be described. Oil

shale crushed to a suitable particle size is continuously introduced into the top of the retort by means of hopper 4, at substantially atmospheric temperature. The shale particles size can vary within relatively wide limits both as to maximum and minimum particle size and particle size distribution, depending upon the size of the retort and the operating conditions.

The shale moves downwardly through the retort by gravity as a bed of freely moving particles and passes successively through a shale-preheating and product-gas-stream-cooling zone, a distillation zone, a sublimation zone, a combustion zone, and a residue cooling zone. The stream of retorting gases, carrying the product oil is removed from the top of the retort through duct 14, at a temperature sufficiently low so that substantially all, or the major portion of, the oil vapors already have undergone condensation. For substantially all grades of oil shale, the gas stream outlet temperatures should be below 200° F., and preferably between about 115° and 175° F. At these outlet temperatures, the product oil comes out of the retort in the gas stream as an oil mist.

The cool gas stream, carrying the mist, is conducted first to a centrifugal separator 15, where the major portion of the mist particles are agglomerated and removed from the gas stream by centrifugal action. Liquid oil from separator 15, is removed to oil receiver 17, by line 16. The gas stream carrying a relatively small amount of fine oil particles is then conducted to a positive displacement blower 18 where the gas stream is repressured. Some further agglomeration of the mist occurs in the blower 18, and further separation of the mist from the gas stream is effected by a second centrifugal separator 19, located in the blower discharge line 18*a*. The oil recovered here is led to storage by line 20, while the gas stream, still containing a small amount of fine oil mist, is conducted by line 21, to an electrostatic precipitator 22, to recover any residual oil which is led to storage by line 22*a*.

A portion of the clean gas stream flowing by line 23, from the electrostatic precipitator 22, is withdrawn to be recycled to the retort by line 24, while a portion is vented from the system by line 26. The gas stream recycled to the retort by line 24, consists essentially of the flue gases resulting from combustion within the retort enriched by noncondensable hydrocarbon gases produced by thermal decomposition of the kerogenous material in the shale. As used in the specification and in the claims, the term "non-condensable gas" refers to gases which fail to condense to liquids at atmospheric temperatures and under pressures, including the light hydrocarbon gases (such as methane, ethane, propane, ethylene, propylene, etc.) produced during the destructive distillation of the hydrocarbonaceous material, and the flue gases resulting from combustion including carbon dioxide, carbon monoxide, and nitrogen. The recycle gas stream ordinarily will be lean in combustibles since it will be rather highly diluted with combustion products, with carbon dioxide resulting from decomposition of the mineral carbonates in the shale, and with nitrogen when air is employed to support combustion within the retort. Typically, in the case of oil shale, the product gas stream will contain from 6 percent to 25 percent combustibles and have a heating value of 40 to 160 B.t.u./std. c.f. depending upon the richness of the shale and the operating conditions.

A stream of air is pumped (pump not shown) via line 27 through an air drier 28. The latter is packed with desiccants, such as silica gel for example, in a manner known to the art, to render the air stream substantially anhydrous. Dry air is removed from 28 via line 29 and is led into a preheater 30 which is indirectly heated by steam admitted into a heat exchanger by line 32, condensate being removed via line 32. Preheated dried air is led via line 33 into a vessel 34 containing aluminum chloride. There the aluminum chloride is vaporized and the mixture of air and aluminum chloride vapors is conducted via pipe 35, heated by electric coil 36, into section 25 of the retort vessel. The aluminum chloride vapors there contact water vapor in the relatively cool (120° F. to 160° F.) recycle gas from line 24, forming hydrated aluminum oxide.

The lean recycle gas, containing a suspension of hydrated aluminum oxide particles and added air flows upwardly through the downwardly flowing residue from the combustion zone. In the portion of the retort, herein termed the residue cooling zone, direct heat exchange is effected between the relatively cool recycle gas mixture and the hot residue; the cool recycle gas mixture is preheated by recovering sensible heat from the hot shale which in turn is cooled and leaves the retort at a temperature approximately that of the cool incoming recycle gas mixture.

As the preheated recycle gas reaches the upper portion of the residue cooling zone a substantial portion of this gas following the path of lesser resistance provided by the tube 11, becomes disengaged from the column of shale and passes into the lower portion of the tube, as indicated by the arrows in the drawing. The remainder of the recycle gas flows upwardly through the column of shale in the annulus between the tube 11, and the walls of the retort.

An oxygen-containing gas, preferably air, preheated if desired, is injected into the upper portion of the tube 11, by line 13. The oxygen-containing gas is mixed with the preheated recycle gases rising through the tube and this mixture then passes out of the upper portion of the tube, is deflected downwardly and outwardly by the hollow, cone-shaped deflector 12, and is distributed into a uniform manner throughout the cross-section of the retort.

Combustion of the recycle gas-air mixture takes place in the vicinity of the upper extremity of the tube 11, and may take place partly in the upper portion of the tube and partly in the shale bed, or more desirably, chiefly within the shale bed.

The hot gases rising from the combustion zone raise the temperature of the descending shale to temperatures between 1000° and 1700° F., and thermal decomposition of the oil shale occurs, producing condensible oil vapors as well as noncondensable hydrocarbon gases. Dehydration of the aluminum oxide takes place at this elevated temperature. The gas-vapor mixture rising upwardly from the distillation zone encounters progressively cooler shale and thus itself becomes progressively cooled. Eventually, the gas-vapor mixture encounters shale at a temperature below its initial dew point temperature, and condensation of the oil vapor on the aluminum oxide nuclei begins. By properly adjusting the height of the shale bed and the rate of flow of shale, and the rate of flow of the gas stream, the exit temperature of the gas stream from the shale bed may be regulated to any value above the inlet temperature of the shale. As previously mentioned, this exit temperature is regulated so that substantially the entire oil content of the gas stream condenses upon the aluminum oxide nuclei while the gas stream is still within the shale bed.

By substituting titanium tetrachloride and stannic chloride in vaporizer 34, the corresponding oxide nuclei are produced in a manner similar to that described above for the production of aluminum oxide nuclei.

For this process to operate successfully, suitable and an adequate number of condensation nuclei must be present in the gas stream for the vapors to condense upon as a mist. The number of nuclei present determines the diameter of the mist droplets, and if an insufficient number are present, the droplets are so large that they deposit on the shale by impingement.

The number of aluminum oxide nuclei present is determined by the rate of aluminum chloride vaporization, which in turn is controlled by the temperature and quan-

tity of air. Sufficient nuclei also may be produced by a self-nucleation mechanism characteristic of the shale-oil-vapors themselves providing the gas-vapor mixture is cooled very rapidly in the region of initial vapor condensation. A relative value for the gas-cooling rate in the critical region can be determined with reasonable accuracy as the product of the superficial gas velocity times the average bed temperature gradient for the same region. As used herein, the term "bed temperature gradient" is intended to mean the rate of change of temperature with bed height, expressed in °F. per inch of bed height. The value of the bed temperature gradient may be most conveniently observed experimentally, and with fair accuracy, by recording the temperature in the shale bed at various levels therein. This can be done, for example, by inserting thermo-couples into the shale bed at various levels and recording these temperatures simultaneously.

Attention is now directed to Figure 2. In this figure values for the oil yield, the amount of oil collected in the first separator, the gravity of the oil collected, and equivalent amount of residual oil in the spent shale has been plotted as a function of the gas cooling rate in the region of initial vapor condensation for a series of runs. Oil yield is the principal criterion for judging whether a run is satisfactory or not. The amount of oil collected in the first separator is a reliable indication of the diameter of the oil mist particles. This is so because the separator is of the centrifugal type whose efficiency is a function of the particle size, that is, it is more efficient on large size particles than small. The gravity of the oil collected is a measure of the amount of oil trapped in the shale bed by impingement and carried down by the shale into the hotter zones and revaporized. This is so because shale oil is a relatively unstable mixture of compounds and successive revaporization causes thermal cracking to occur. Oils subjected to this type of thermal cracking are characterized by relatively high ° API gravity, low viscosities, and low Conradson carbon values. However, this type of uncontrolled cracking reaction does not upgrade the oil recovered enough to compensate for the decrease in yield associated with this phenomenon. Any hydrocarbons remaining in the spent shale is another potential source of loss in oil yield and these data are also shown to explain the oil yield curve.

Examination of the curves shown in Figure 2 reveals the effect of the gas cooling rate on the variables listed above. When artificial nuclei were not added to the shale, the amount of oil collected in the first separator decreases as the gas cooling rate increases. The abrupt decrease in the gravity of the oil collected as the gas cooling rate increases from 50° to 60° F./sec. indicates that at cooling rates below 60° F./sec. the mist droplets are so coarse that they are readily separated from the gas stream by impingement on the shale particles and are subjected to successive revaporizations. A similar abrupt increase in oil yield coincides with the change in gravity of the oil collected. At still higher gas cooling rates the oil yield again declines. However, the decrease in yield is attributable to the potential oil remaining in the spent shale. At these higher gas cooling rates, the size of the mist particles is favorable, but the conditions required to achieve these high gas cooling rates are unfavorable for attaining complete retorting of the shale. The process variables which determine the gas cooling rate are the gas-shale flow rate ratio in the vapor condensation zone, volume of air per ton of shale, bed height, shale particle size and grade, and shale rate. Of these, the first has the greater influence; that is, at high gas-shale flow rate ratios the gas cooling rate is very low. The normal supply of condensation nuclei in the retort gas stream should be supplemented by artificially induced condensation nuclei, in order that the fog or mist droplets will be sufficiently small so that they will not be filtered out of the gas stream by impingement on the shale particles. A sufficient number of artificially induced condensation nuclei should be provided by proper selection of the aluminum chloride vaporization rate.

While the invention does not depend upon any particular theory, it is believed that the following is an explanation of the results discussed above. In order to produce condensation of the vapors as a mist rather than on the surface of the shale, two conditions must be satisfied: (1) a condition of supersaturation must be produced in the gas stream; (2) nuclei must be present for the supersaturated vapors to condense on.

The effect of aluminum oxide injected into the retort as a source of nuclei for condensation of shale-oil mist is shown clearly in Figure 3. In this illustration the cumulative weight percent of mist is plotted against the mist particle size. Two curves are shown. The first shows the distribution of mist particle size when no nuclei are added and the second shows the distribution of mist particle size, when aluminum oxide particles were injected into the recycle gas stream. It is apparent from the curve that the size distribution of the aluminum oxide nuclei-oil mist droplets is relatively uniform. This is desirable because few particles are produced which are difficult to separate by inertial separators but yet the largest are small enough to pass through the shale bed with a minimum amount of impingement. A comparison of the mist particle size of 50% of the particles indicates that when aluminum oxide nuclei were introduced into the retort mist particle size was about 3.6 microns as against about 6.2 microns when no aluminum oxide was used. This is important, since the smaller mist droplet size enables more of the mist to traverse the retort, and consequently more shale-oil mist is recovered in the collection system.

The amount of aluminum chloride added to the recycle gas stream determines the size of the mist droplets, as shown in Figure 4, whereas the curve of mist particle size is plotted against the amount of aluminum chloride added.

In the countercurrent system such as exists in the vapor condensation region of the retort, where the vapor-gas stream encounters progressively cooler shale, two important physical actions occur:

(1) There is a transfer of heat from the vapor-gas stream to the shale.
(2) There is a mass transfer of oil from the vapor-gas stream to the shale.

It is obvious that a condition of supersaturation in the gas stream may be arrived at if, in cooling the gas-vapor mixture, the rate of decrease of the partial pressure of the vapors by condensation is low relative to the rate at which the temperature of the gas-vapor mixture decreases. This will tend to occur when the vapors have a low diffusivity since, in such a system, the rate of diffusion of the vapors to the cooling surface controls the rate of mass transfer. Oil-shale vapors, like other heavy hydrocarbon vapors, have a characteristically low diffusivity, and accordingly, it is relatively easy to produce a condition of supersaturation when cooling a gas stream containing these vapors.

The second condition which must be satisfied is that nuclei must be present for the supersaturated vapors to condense upon. It is well known that a solid aerosol in a gas-vapor mixture greatly reduces the degree of supersaturation required for mist formation. Normally the air supplied to the retort contains a few solid aerosol particles and more are produced by combustion within the retort but the total supplied from these sources is insignificant compared to the total number required. The primary source of nuclei when artificially induced nuclei are not present in the gas stream is by a self-nucleation mechanism favored by high vapor-gas cooling rates. Thus when the gas-cooling rate is relatively high, sufficient nuclei are formed by this self-nucleation mechanism

to insure the formation of small enough mist particles to escape being trapped in the shale bed by impingement.

However, it is difficult to achieve a high gas-cooling rate and complete retorting of the shale simultaneously. This inflicts a very narrow range of operating conditions in which satisfactory oil yields and operability can be attained. Providing sufficient artificially induced condensation nuclei in the gas-vapor stream completely eliminates the gas-cooling rate in the zone of initial condensation as an important process variable. This is particularly advantageous in applying such a process to a large-scale retorting plant. As the cross-section of the retort is expanded, it becomes increasingly difficult to maintain the same operating conditions in all areas of the cross-section.

It is to be understood that other retorting methods than those specifically described may be employed within the scope of the invention. Thus, while it is preferred to employ a retorting process such as is illustrated in Figure 1, which includes a combustion zone in the retort itself, and where the oxygen containing gas is introduced into an intermediate portion of the retort, thereby fixing the combustion zone in a definite location, other types of retort methods may be employed. For example, it may be desirable to heat the retorting gas stream or a portion thereof in a vessel separate from the retorting vessel, such that no combustion takes place in the retorting vessel proper.

Although the process has been described particularly with reference to oil shale, it is also generally applicable to other types of processes for the destructive distillation of hydrocarbonaceous materials where the oil vapors produced have a low diffusivity such that they may be caused to condense preferentially as a mist in the retorting gas stream.

It is to be understood that the above description, together with the specific examples and embodiments described, is intended merely to illustrate the invention, and that the invention is not limited thereto, nor in any way except by the scope of the appended claims.

I claim:

1. A method for the destructive distillation of oil shale for the production of useful liquid products which involves the steps of continuously passing the shale as a bed of broken solids downwardly in a substantially vertical column successively through a preheating zone and a distillation zone, continuously passing a stream of noncondensable gases containing artificially induced condensation nuclei selected from the class consisting of aluminum oxide, titanium oxide and tin oxide upwardly through said distillation zone at a temperature sufficient to effect thermal decomposition of said oil shale, thereby producing condensable product vapors which are carried upwardly in said gas stream containing artificially induced condensation nuclei, permitting said vapor-containing gas stream to pass upwardly through said preheating zone, whereby the descending shale becomes progressively heated, withdrawing said gas stream from said column at a temperature sufficiently low so that substantially the entire vapor content of said gas stream containing artificially induced condensation nuclei undergoes condensation within said column, whereby the major portion of the vapors condense on the artificially induced nuclei as a relatively stable mist and a minimum amount of condensation occurs on the surface of said shale, withdrawing said relatively stable mist and accompanying gas stream from the column, and separating the shale-oil mist, including the artificially induced nuclei, from the accompanying gases.

2. A method for the destructive distillation of oil shale for the production of useful liquid products which involves the steps of continuously passing the shale as a bed of broken solids downwardly in a substantially vertical column successively through a preheating zone and a distillation zone, vaporizing aluminum chloride in a stream of heated dried gas, contacting the aluminum chloride vapors with low partial pressure water vapor, whereby hydrated aluminum oxide particles are produced, introducing said particles into stream of hot noncondensable gases, whereby the particles become dehydrated and are suspended in said gas stream, passing the gas stream containing aluminum oxide nuclei upwardly through said distillation zone, said noncondensable gas stream having a temperature sufficient to effect thermal decomposition of the oil shale, thereby producing condensable product vapors which are carried upwardly in said gas stream containing aluminum oxide nuclei, permitting said vapor containing gas stream to pass upwardly through said preheating zone, whereby the descending shale becomes progressively heated, withdrawing said gas stream from said column at a temperature sufficiently low so that substantially the entire vapor content of said gas stream containing aluminum oxide nuclei undergoes condensation within said column, whereby the major portion of the vapors condense on the artificially induced nuclei as a relatively stable mist and a minimum amount of condensation occurs on the surface of said shale, withdrawing said relatively stable mist and accompanying gas stream from the column, and separating the shale-oil mist including the aluminum oxide nuclei, from the accompany gases.

3. A method for the destructive distillation of oil shale for the production of useful liquid products which involves the steps of continuously passing the shale, as a bed of broken solids downwardly in a substantial vertical column successively through a preheating zone, a distillation zone, a sublimation zone, a combustion zone, and a residue cooling zone, withdrawing from the top of said column the products of combustion and of distillation, including normally liquid products together with a noncondensable gas relatively lean in combustibles, separating said liquid products from said lean, noncondensable gas, recycling at least a portion of said lean gas in a relatively cool condition to the lower portion of said resude cooling zone, introducing a member of the class consisting of aluminum oxide, titanium oxide and tin oxide condensation nuclei into the recycle gas, permitting the recycle gas containing said condensation nuclei to pass upwardly through said column in contact with the hot residue from said combustion zones, whereby said residue becomes cooled and said gas becomes heated, supplying an oxygen-containing gas to said column above said residue cooling zone, thereby definitely establishing the location of said combustion zone, permitting the hot gases from said combustion zone to pass upwardly through said column, thereby effecting thermal descomposition of said oil shale, and thereby producing condensable product oil vapors which are carried upwardly in said gas stream, permitting said vapor-containing gas stream to pass upwardly through said preheating zone, whereby the descending shale becomes progressively heated, and the condensation nuclei become sufficiently cooled and are suitable condensation nuclei for the oil vapors to condense upon, and the ascending mixture of gases, oil vapors, and condensation nuclei becomes progressively cooled, maintaining the exit temperature of said gas stream from said column sufficiently low so that substantially the entire vapor content of said gas stream undergoes condensation within said column, whereby the major portion of said vapors condense on the condensation nuclei as a relatively stable mist, and whereby a minimum amount of condensation occurs on the surface of the shale, withdrawing said relatively stable mist and accompanying gas stream from the column and separating the shale oil mist, including the aluminum oxide condensation nuclei, from the accompanying gases.

4. The method of claim 3 wherein the condensation nuclei comprises aluminum oxide.

5. The method of claim 3 wherein the condensation nuclei comprises titanium oxide.

6. The method of claim 3 wherein the condensation nuclei comprises tin oxide.

7. A method for the destructive distillation of oil shale for the production of useful liquid products which involves the steps of continuously passing the shale as a bed of broken solids downwardly in a substantial vertical column successively through a preheating zone, a distillation zone, a sublimation zone, a combustion zone, and a residue cooling zone, withdrawing from the top of said column the products of combustion and of distillation, including normally liquid products together with a noncondensable gas relatively lean in combustibles, separating said liquid products from said lean, noncondensable gas, recycling at least a portion of said lean gas in a relatively cool condition to the lower portion of said residue cooling zone, said lean gas containing water vapor, vaporizing aluminum chloride in a stream of heated dry gas, introducing the aluminum chloride vapors into the recycled lean gas whereby dehydrated aluminum oxide particles are formed by the reaction of aluminum chloride with water vapor, permitting the recycle gas containing hydrated aluminum oxide in suspension to pass upwardly through said column in contact with the hot residue from said combustion zone, whereby said residue becomes cooled and said gas becomes heated, supplying an oxygen-containing gas to said column above said residue cooling zone, thereby definitely establishing the location of said combustion zone, permitting the hot gases from said combustion zone to pass upwardly through said column, thereby effecting thermal decomposition of said oil shale, and thereby producing condensable product oil vapors which are carried upwardly in said gas stream, permitting said vapor-containing gas stream to pass upwardly through said preheating zone, whereby the descending shale becomes progressively heated, the aluminum oxide particles become cooled, and become suitable condensation nuclei for the oil vapors to condense upon, and the ascending mixture of gases, oil vapors, and aluminum oxide condensation nuclei becomes progressively cooled, maintaining the exit temperature of said gas stream from said column sufficiently low so that substantially the entire vapor content of said gas stream undergoes condensation within said column, whereby the major portion of said vapors condense on the aluminum oxide nuclei as a relatively stable mist, and whereby a minimum amount of condensation occurs on the surface of the shale, withdrawing said relatively stable mist and accompanying gas stream from the column and separating the shale oil mist, including the aluminum oxide condensation nuclei, from the accompanying gases.

8. A method in accordance with claim 7, wherein the gas stream is withdrawn from said column at a temperature between 115° and 175° F.

9. The method as in claim 7, wherein the heated dry gas used in vaporizing the aluminum chloride is air.

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