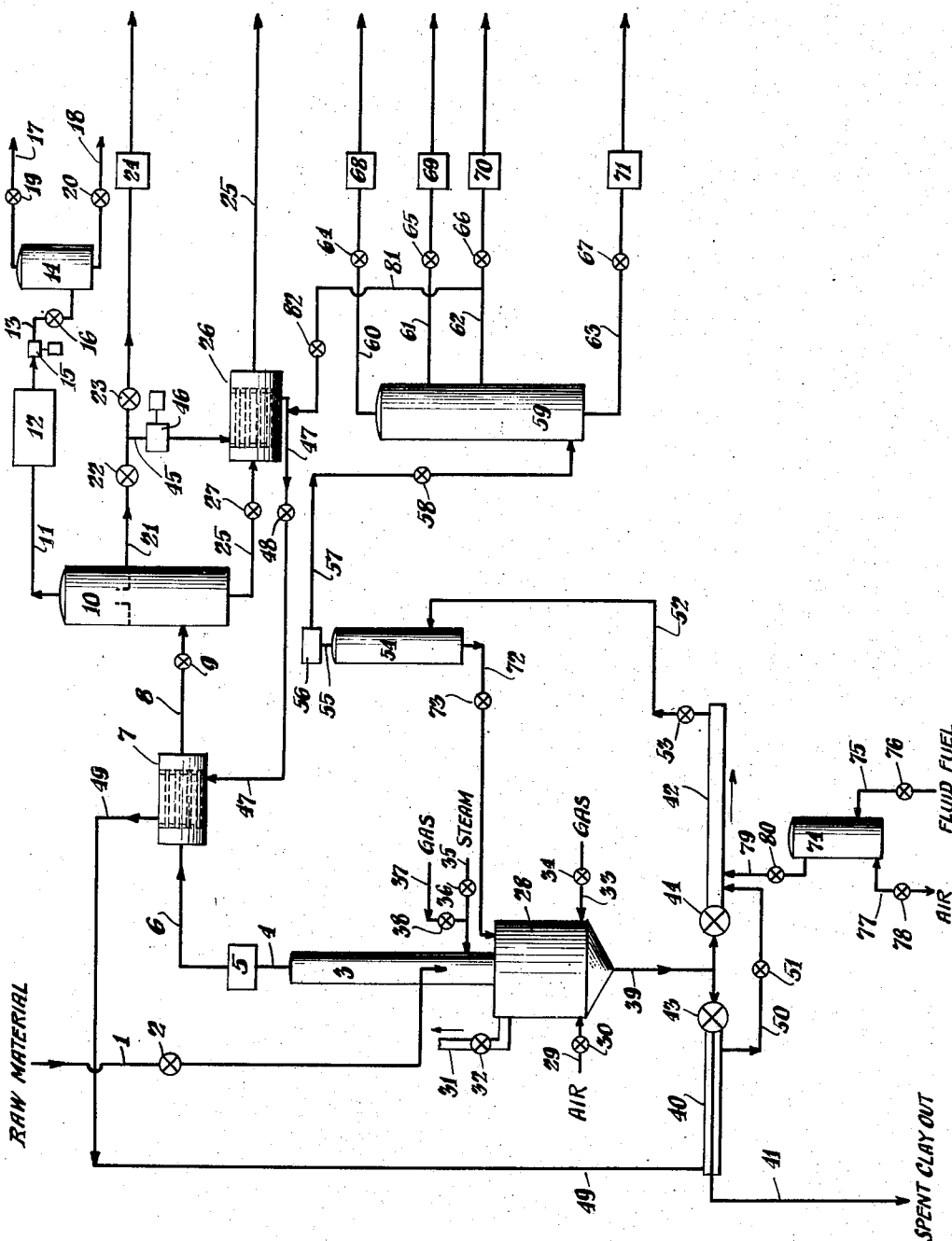


Nov. 29, 1949

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TOPPING WITH WASTE HEAT FROM
CRACKING WITH SPENT SHALE
Filed July 20, 1946

2,489,702



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2,489,702

TOPPING WITH WASTE HEAT FROM
CRACKING WITH SPENT SHALEJohn W. Coast, Dallas, Tex., assignor of one-half
to Clarence H. Dragert, Dallas, Tex.Application July 20, 1946, Serial No. 685,068
In Cuba November 30, 1945

3 Claims. (Cl. 196—50)

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My present invention relates to a process for the recovery of values from rock asphalt, oil shales and like material, which contains both hydrocarbon constituents and inorganic portions. The general object of the present invention is to recover valuable petroleum products, preferably including both straight run and cracked products, from such material.

While the present invention is deemed by me to be applicable to many different types of raw material as aforesaid, it is especially adapted to the treatment of a certain type of such material which is found in Cuba and which comprises from 50% to 60% hydrocarbon constituents, the remainder being a relatively fine volcanic ash.

Various processes for the recovery of values from material of this general type, are set forth in my copending applications in Cuba Serial Nos. 97,801, 97,802, 97,803 and 98,543, the first three of which were filed on August 4, 1945, and the last of which was filed in Cuba on September 15, 1945. The processes of these applications all included the treatment of the material originally with a solvent, so as to dissolve the hydrocarbon constituents, followed by a separation between the solution of the hydrocarbon constituents and the remaining material.

My present invention, in contradistinction to the above, contemplates the avoidance of the use of a solvent in treating the original raw material and instead, relies upon a distillation operation for effecting the original separation between the hydrocarbon constituents which are volatilized in this distillation step and the remaining material. A primary object of the present invention is to provide for such a process wherein the distillation is effected to a substantial extent at least by heat obtained from the combustion of the combustible portions of such material as remains following the distillation, i. e., of the relatively non-volatile portions of the original raw material.

Further and more specific objects of the invention include the process as above generally outlined, coupled with various refinements to aid in the carrying out of this process, such, for example, as the use of a supplemental supply of fuel to augment the fuel supply obtained from the residue from the distillation step, the use of a selected part of the products of combustion passing through the distilling chamber to act as a carrier for volatile constituents separated therein and to assist in such distillation, and the use of a gaseous fluid, specifically a hydrocarbon gas or steam or both, in the distillation chamber in assisting in the distillation therein.

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A further important object of the present invention is to provide a process as generally above set forth, wherein the straight run operations include the refining of the distillate from the distilling chamber aforesaid to separate it by more or less conventional "topping" operations into selected individually usable fractions, including a cracking stock, and wherein this cracking stock is thereafter cracked by heat derived from the same source which is used in effecting the distillation.

More specifically, the process of my present invention contemplates not merely conventional cracking by heat alone, but more specifically, cracking of a type similar to that now termed "catalytic cracking," wherein some or all of the inorganic constituents of the original raw material are used in the cracking chamber in contact with the hydrocarbon materials therein for effecting a desired type of cracking analogous to that process now conventionally termed "fluid catalyst cracking."

Further and more detailed objects of the present invention in this respect include the provision of process steps for the re-cycling of a desired amount of the inorganic material used to assist the cracking step of the process, provision for the saving and recovery of heat at various points throughout the process and other incidental provisions in order to carry the process as a whole into effect in a commercially practical manner.

Other and more detailed objects of the present invention will become apparent from the following specification and appending claims, when taken in connection with the accompanying drawing, in which

The single figure is a diagrammatic illustration of preferred apparatus and connections therebetween for carrying out a process in accordance with the present invention.

Turning now to the accompanying drawing, the raw material, which is preferably comminuted to a selected extent, for example, to an average size range of about 30 to 40 mesh, is supplied through suitable means indicated by a line 1 under control of a suitable valve mechanism or proportioning feeding means 2 therein to a distilling chamber 3, preferably intermediate the upper and lower ends thereof as generally indicated in the drawing. In the chamber 3, the material is subjected to heat in a manner hereinafter more particularly described, so as to distil therefrom any constituents which are volatile at the temperature and under the conditions existing in this chamber. The vapor from this chamber passes

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through a line 4 leading from the upper end thereof, thence through an apparatus generally indicated at 5 which serves to remove any solid particles from the vapor, this apparatus being preferably of an electrical type, such as a Cottrell separator. The vapor passes thence through a line 6 through a heat interchanger 7, wherein its temperature is reduced to a certain predetermined extent, the heat being recovered as hereinafter set forth and then passes through a line 8 under control of a valve 9 therein to a fractionating tower 10.

The fractionating tower 10 may be of a conventional type, such as the well known bubble towers now in wide use in the oil refining industry. Only a few of the tap-off lines are shown from this tower, including a line 11 for gaseous products not condensed in the tower, this line passing to and through a heat interchanger or condenser 12 and thence through a line 13 to a vapor separator 14. Interposed in the line 13 is a pump mechanism generally indicated at 15 and a valve 16 so as to control the flow. The valves 9 and 16 conjointly and with the aid of other valves in other lines from the tower 10, operate to control the pressures existing within the tower and hence to a certain extent, the operations of fractional condensation taking place therein. Leading from the vapor separator 14 is a line 17 for gaseous materials and a line 18 for liquid materials, these lines having valves 19 and 20, respectively therein. It is contemplated that some permanent gases and some products of combustion as hereinafter set forth, will pass out of the system through the line 17, while the material passing through the line 18 will be at least to a large extent the lighter, normally liquid hydrocarbon constituents, such as naphtha or gasoline.

Also leading from the tower 10 is shown a line 21 which has valves 22 and 23 therein and which has interposed therein a suitable means 24 for the cooling of material flowing through this portion of the line, this line being so disposed in respect to the operations taking place within the tower 10 that the material flowing therethrough will be in the gas oil range, i. e., this material will that normally used in the art as a "cracking stock." Also shown passing from the tower is a line 25 for heavy tarry material, which passes through a heat interchanger 26 enroute to a collection point for this material, flow of the material through this line being controlled by a valve 27 interposed therein.

The non-volatile material in the distillation chamber 3, which includes all the material other than that which vaporizes and passes through the line 4 from this chamber, in accordance with the present invention, passes downwardly through suitable means which may take the form of a grate (not shown) and which may or may not have suitable constricting means for controlling the upward flow of gases therethrough, to a combustion chamber or furnace 28. The purpose in the present instance is to provide for the burning out from this material of combustible portions thereof, which include all the remaining non-volatile hydrocarbon and/or carbonaceous constituents not volatilized in the chamber 3. To this end air is supplied to the furnace 28 through a line 29 under control of a valve 30. In accordance with the present invention not only is heat from the combustion in the furnace 28 used as a source of heat for effecting the distillation in the chamber 3, but from a broad sense this heat transmission may be indirect as through walls of

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passages with the products of combustion on one side of such a wall and the material being distilled in the chamber 3 on the other side thereof. However, the specific form of the invention presently contemplated is to pass a selected part of these products of combustion from the furnace 28 directly through the chamber 3 and thence through the remainder of the system previously described, these products of combustion passing out through the line 17 from the system and being discharged to the atmosphere at any suitable point beyond that portion of this line 17 shown in the drawing. It is contemplated that these products of combustion may aid in carrying out the desired distillation operation within the chamber 3 and serve as a carrier for the vapor from that chamber to and through the rest of the system previously described.

In accordance with the present invention, all the products of combustion may not be desired to pass through the system as above specifically set forth. For this reason there is shown in association with the furnace or combustion chamber 28 a stack 31, flow through which is controlled by a suitable valve or damper mechanism 32.

It is further contemplated that the materials supplied to the combustion chamber or furnace 28 may not have sufficient combustible material therein to supply all the heat required to be generated in this chamber or furnace. For this reason there is shown a line 33 through which a fluid fuel, such as gas or oil, may be supplied to this chamber under control of a valve 34 therein.

In effecting the distillation in chamber 3 it may be desired to supply to this chamber in addition to such products of combustion as are passed therethrough as aforesaid, some gaseous fluid, which will be effective to establish and maintain desired distillation conditions in the chamber and which will serve to augment the flow of gaseous materials through the remainder of the system previously described as may be desired under certain circumstances. It is contemplated that either steam or a hydrocarbon gas or both may be supplied to the chamber 3 for this purpose. As shown, there is a line 35 through which steam may be supplied to this chamber under control of a valve 36 therein and a branch line 37 for hydrocarbon gas joining the line 35 between the valve 36 and the chamber 3, flow through the line 37 being controlled by a valve 38 therein.

As stated in the introduction to his application, it is contemplated that the present invention may have incorporated therewith provision for the cracking of a cracking stock which, as set forth hereinabove, is derived from the straight run operations previously described and particularly from the line 21 passing from the fractionating tower 10. From a broad point of view, it is contemplated that the cracking of this material may be effected in any conventional manner and by heat generated in the combustion chamber or furnace 28.

However, while it is contemplated that some of this heat may be used in conjunction with this cracking stock for effecting conventional cracking, it is preferred to provide a system and a process wherein so-called "catalytic cracking" is effected, using the inorganic portion of the original raw material as a catalyst. For this purpose this inorganic portion, from which the combustible carbonaceous or hydrocarbon materials have been completely burned out, passes from the bottom of the combustion chamber or furnace 28 through suitable means indicated as a line 39

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and may pass thence in either of two directions. As more particularly hereinafter described, some of this material is preferably recycled to a desired extent through a circuitous path wholly within the process, while the remainder, which in continuous stabilized operation is equivalent to the amount of such inorganic material being supplied to the process in any unit of time, passes from the process to a suitable collection point for such use as it may be put. This remainder is shown in the accompanying drawing passing to the left from the lower end of the line 39 through a heat interchanger 40 and thence through a line 41 to a suitable collection point (not shown) for such inorganic material. The portion of this inorganic material, which is to assist in the cracking operations, passes from the lower end of the line 39 to a cracking chamber 42. Suitable valve mechanisms 43 and 44 control the proportionate amounts of the inorganic material flowing through the line 39 which passes to and through the heat interchanger 40 and the cracking chamber 42 respectively.

Starting now to trace the course of the cracking stock to and through the cracking system and to the delivery points for the cracked products, a selected amount of the material flowing through the line 21 or cracking stock is diverted therefrom through a line 45, intermediate the valves 22 and 23, the amount of such material flowing through the line 45 being controlled by the relative setting of these two valves. A pump mechanism generally indicated at 46 is interposed in the line 45 to insure a desired flow therethrough. This line passes then to the heat interchanger 26 previously described for the further heating of the cracking stock. It is noted, however, that this cracking stock is diverted from the line 21 prior to the cooler 24 interposed in this line, so that a maximum amount of the sensible heat in this material as it flows from the fractionating tower 10 is retained therein for subsequent use. The cracking stock picks up some heat from the heavier material flowing through the line 25 and thence through the interchanger 26 as this material is withdrawn from the tower 10 at a substantially higher temperature than that of the cracking stock. The cracking stock flows thence through a line 47 under control of a valve 48 therein to and through the heat interchanger 7, and is further heated during its course there-through. This cracking stock flows thence through a line 49 to and through the heat interchanger 40 for the further heating of the material and saving of heat, which might otherwise be lost, and then flows through a line 50 under control of a valve 51 therein to the cracking chamber 42.

All the materials supplied to the cracking chamber 42 as aforesaid, which includes both the hydrocarbon oil cracking stock and the inorganic clay type material, pass from the cracking chamber through a line 52 under control of valve 53 therein to a vapor separator 54, the valve 53 serving to control the pressure within the cracking chamber and thus to enable a desired type of cracking to take place therein, for example, to insure a wholly liquid phase cracking, if that be desired. The present invention, however, is not intended to be limited to liquid phase as against vapor phase cracking or as against some combination of the two, the means being provided as hereinabove described to permit of desired controls as may be found necessary in practice.

The vapor separated from solid materials in the vapor separator 54 passes thence through a line 55 to and through a solid particle removing apparatus 56, which may be similar to the apparatus 5 previously described, and thence through a line 57 under control of a valve 58 therein, to a fractionating tower 59.

In the fractionating tower 59 conventional operations take place for the separation by fractional condensation of the vapors supplied thereto into selected individually usable fractions having different specific gravities; these several fractions including a gaseous fraction passing through a line 60 from the top of the tower, various liquid fractions passing through lines 61 and 62 and a heavy material or tarry residue fraction passing from the bottom of the tower through a line 63, these lines having valves 64, 65, 66 and 67 therein and also having cooling means 68, 69, 70 and 71 therein, for the cooling of materials flowing there-through and for the recovery of the heat for such use as it may be put (not shown) in any desired manner. It will be understood that the lines 60 to 63 are for the flow of cracked petroleum products from the fractionating tower 59, wherein fractional condensation separation between these products takes place, to desired collecting points or points of use for the respective products.

The non-volatile material from the vapor separator 54 passes from the lower end thereof through a line 72 under control of a valve mechanism 73 therein back to the combustion chamber or furnace 28 for the re-cycling of the inorganic portion thereof, it being understood that any carbonaceous or hydrocarbon material or constituents of the material passing through the line 72 will be burned out substantially completely in the furnace or combustion chamber 28 prior to the inorganic portion of this material passing therefrom through the line 39 as aforesaid. Thus there is provided a means for the complete recycling within the process of a selected amount of the inorganic material, which acts in some manner the same as or similar to the "fluid catalyst" of the prior art, wherein the clay material used is derived from a source separate and distinct from the hydrocarbon materials being worked upon.

In some instances it may be desired to introduce more heat into the cracking chamber than that available from the hot inorganic material supplied thereto from the furnace 28 through the line 39. This additional heat may be supplied in any desired manner, but I contemplate as a preferred way of accomplishing this to supply to the interior of the cracking chamber hot products of combustion.

For this purpose there is provided a generator 74 for such products of combustion, to which a fluid fuel, such as gas is supplied through a line 75 at a selected pressure and under control of a valve 76, and air is supplied through a line 77, under control of a valve 78, preferably at a selected pressure. The products of combustion pass from the generator 74 to the entrance portion of the cracking chamber 42 through a line 79 controlled by a suitable valve 80. When this generator is used, the products of combustion pass through the cracking portion of the system previously described to and through the tower 59 and thence pass out through the line 60. They may then be discharged to the atmosphere or suitably treated for the recovery of volatile materials and subsequently discharged.

In this case as in the case of other cracking processes in my prior applications aforesaid, it may be desired to recycle a selected portion of hydrocarbon fluid material having the characteristics of cracking stock or gas oil. For this purpose, the line 62 through which this material passes from the tower 59 may be provided with a take-off line 81, controlled by a valve 82 and leading to the line 47 between the heat interchangers 26 and 7 or to some other selected point in the flow of the straight run cracking stock to the cracking chamber 42.

While there is shown and described herein but one principal embodiment of the entire invention and suggestions are made herein for contemplated variations of the process specifically disclosed, I do not wish to be limited except by the scope of the appended claims, which are to be construed validly as broadly as the state of the prior art permits.

What is claimed is:

1. The process of treating oil shales, containing both hydrocarbon and inorganic portions, to recover valuable hydrocarbon products therefrom, which comprises the steps of separating volatile materials from the shale by distillation assisted by a current of hot gases, separating the resultant vapor by fractional condensation into a plurality of straight run fractions one of which is suitable as a cracking stock, subjecting the non-volatile residue from the distillation to the action of an oxygen-containing gas at a temperature sufficient to burn out all combustible material therefrom to generate hot products of combustion and to produce a hot inorganic material suitable for use as a cracking catalyst, supplying heat from said hot products of combustion thus generated to said distillation, passing a selected part of said cracking stock and a selected part of said inorganic material cracking catalyst into a separate and distinct cracking zone, subjecting the materials aforesaid in the cracking zone to a temperature sufficient to effect catalytic cracking of said cracking stock, separating the effluent

from said cracking zone into a spent inorganic residue and a vapor portion, and separating said vapor portion into a plurality of cracked hydrocarbon fractions.

2. The process in accordance with claim 1, wherein a part of said hot products of combustion generated as aforesaid are passed through the shale in direct contact therewith as a part at least of said current of hot gases used to assist in distilling volatile materials from the shale.

3. The process in accordance with claim 1, comprising the additional step of recycling said spent inorganic residue from said cracking zone, after said vapor portion has been separated therefrom as aforesaid, to the step wherein the non-volatile residue from the distillation is subjected to the action of an oxygen-containing gas, so as to produce from both said non-volatile residue from the distillation and the recycled spent inorganic residue a hot inorganic material suitable for use as a cracking catalyst, and diverting from the recycle of the inorganic material, during the continuous operation of the process, an amount of the inorganic material cracking catalyst equivalent to the amount of inorganic material supplied to the process as oil shale, so as to maintain substantially constant the amount of inorganic material in and passing through said cracking zone.

JOHN W. COAST.

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