



## UNITED STATES PATENT OFFICE

JOHN C. BLACK, OF DESTREHAN, LOUISIANA, ASSIGNOR, BY MESNE ASSIGNMENTS, TO GASOLINE PRODUCTS COMPANY, INC., OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

## APPARATUS FOR TREATING HYDROCARBONS

Application filed May 28, 1925. Serial No. 33,553.

My invention relates more particularly to improvements in the decomposition of petroleum oils with the object of reducing the viscosity of the residuum after the distillation and for the production of an increased yield of the lighter or lower boiling point hydrocarbons from hydrocarbons possessing these characteristics in lesser degree.

In my previous Patent No. 1,456,419, I describe a process for the production of low boiling point hydrocarbons by using two separately fired heating elements placed in series—the first one of the series is used as a preheater to elevate the temperature of the hydrocarbons passing therethrough to a temperature where decomposition will take place and then passing the heated hydrocarbons through the second coil in the series where the temperature of the oil is maintained at the decomposition temperature by supplying the oil with the necessary heat of reaction which is the heat absorbed by the hydrocarbons during the decomposition period, then passing the oil to a carbon precipitating chamber and finally to a pressure relief valve to be discharged for subsequent treatment.

The present invention is an improvement over the invention disclosed in the above mentioned patent whereby the equipment is materially reduced and the formation of carbonaceous material lessened with consequent increased efficiency of operation and lowered cost of finished products as will be hereinafter disclosed.

My improved process of treating hydrocarbons consists in heating the hydrocarbons in a manner to produce the maximum decomposition products with a minimum expenditure of heat energy and under comparatively low temperature which is brought about by my method of supplying the endothermic heat of reaction in a heating element with an independently controlled heating means whereby the preheated hydrocarbons elevated to the optimum decomposition temperature are supplied with the heat of reaction and maintained at substantially the optimum decomposition temperature above referred to while passing through the reac-

tion element which is so designed as regards volumetric capacity that the proper time element will be insured to bring about the maximum decomposition of the hydrocarbon at the temperature employed. This is accomplished by using a larger number of tubular elements in the reaction coil than I have used heretofore in the practical application of my Patent 1,456,419 and I am also enabled to eliminate the carbon precipitating chamber employed in the above patent. By using a large number of tubes in the reaction coil I am enabled to extend the reaction time where the hydrocarbons are given a prolonged heat treatment without diminution of the active supply of heat necessary to obtain the substantially maximum decomposition of the hydrocarbons for the temperature employed.

In this connection I have discovered that by heating the oil to be cracked to a temperature of active decomposition to obtain a yield of, say, 20 percent of low boiling fractions, will require a temperature well above 800° F. if the oil, after passing through a heater is immediately cooled down; whereas if after heating the oil in the above mentioned heater and then passed to a secondary coil or what I denominate my reaction coil wherein heat is supplied to maintain its temperature and supply the endothermic heat of reaction, then the temperature of the oil may be reduced 50 to 100° F. and still obtain a 20 per cent yield of low boiling fraction as illustrated above. It can be readily understood by those familiar with cracking that such a reduction of temperature for a given yield very often means the difference between practical and impractical operation for the reason that at the higher temperature the tubes are more highly heated, causing coking of the tubes and also a shorter life for the tubes and increases the liability of blow-outs with its consequent danger to life and property. Furthermore the plant can be kept on stream at the lower temperature a much longer time without shutdowns for cleaning and repairs, thereby reducing the cost of the products; there is also the advantage of a saving in fuel due to the lowered temperature of operation. To ac-

comply with this purpose, I use a combination of fire heaters and heat exchangers, the heat exchangers are used as a feature of economy, employed to first preheat the hydrocarbons before they go to the fire heated preliminary tubular heating element where the desired heat of decomposition is attained or approximately so; from this heater the hydrocarbons pass to an additional separately fired an controlled heating element so designed as to permit the hydrocarbons to absorb the heat which is rendered latent by the decomposition or cracking reaction and to maintain or approximately so, its sensible heat. This secondary heating element or reaction coil is also of tubular form and is of such a volumetric capacity, in relation to the quantity of oil handled in any period of time, that as long a duration of time, as is consistent with economy or practicability, be permitted for the passage of the oil or hydrocarbon through the heater whereby the rate of decomposition is not reduced by diminution of temperature and the optimum decomposition or cracking of the hydrocarbons be obtained thereby.

In practice, I use a preliminary fire heater having steel or alloy steel tubes of three or four inches in diameter and numbering one hundred more or less, connected in series, and the secondary or reaction coil is constructed of similar tubing of approximately the same size and number although, as previously intimated, this coil should be constructed to permit of a long time duration to obtain the optimum decomposition reaction; also to obtain a sufficiently high rate of speed to materially reduce the deposition of carbonaceous material in the tubes.

The relation of these two coils as to number of tubes may be varied over a wide range, depending upon the oil treated and the decomposition or cracking required. In general the more cracking or decomposition desired, the more tubes should be used, or their size made larger to give a longer time reaction at the temperature employed.

In practice I prefer to use the same size tubes for both coils, but it can be readily understood that the size of the two sets of coils may be dissimilar within certain limits without material departure from good results.

In the operation of this process I use a pump capable of developing a pressure sufficient to hold the hydrocarbons in a liquid phase. this pressure being controlled by a pressure regulating valve located between the final heater and the discharge connection depending upon the method of subsequent handling; three methods being shown in the drawing appended thereto.

In my accompanying single figure of drawing, I show the above described features of my invention together with auxiliary apparatus to show the process complete and

clear to any one familiar with the art of refining petroleum hydrocarbons.

I will now describe the drawing of the apparatus suitable to operate my process:

The pump 1 takes its supply of petroleum from the supply tank 2 and discharges it through the pipe 3 on which is the pressure gauge 4. The pipe 5' discharges through the heat exchanger No. 1 into heat exchanger No. 2, then into the heater No. 1, thence into heater No. 2; between the two heaters, Nos. 1 and 2, is a pyrometer 5 and at the outlet of heater No. 2 is a pyrometer 6. Leading from the outlet of heater No. 2 is a pipe 7 connecting with the heat exchanger No. 2 from which leads a pipe 8 connecting with a pipe 9 having two branches, one branch controlled by valves 10 and 43 connecting to the cooler No. 1 and receiving tank 11 and the other branch connecting with the evaporator through the line 12 and valve 13. Leading from the evaporator is a residuum pipe 14 connecting with the heat exchanger No. 1 from which leads pipe 15 to the cooler No. 2 thence to the residuum tank 16. From the evaporator leads a vapor pipe 17 connecting with a fractionating tower 18. From tower 18 leads a vapor pipe 19 connecting with a condenser 20 and look box 21 and receiving tank 22. From the tower 18 leads a pipe 23 and cooler 23' connecting with the wash oil tank 24 to which is connected the pump 25 which in turn discharges through pipe 26 into the top of tower 18. From tank 24 leads an overflow pipe 27 into tank 28 from which leads a pipe 29 into the suction of the pump 30 which discharges through the pipe 31 and valve 31' into the pipe 12 connecting with the evaporator; also through pipe 42 and valve 42' to the supply tank.

Connecting with pipe 12 is a bypass pipe 32 with a valve 33 to permit the oil to bypass the heat exchanger No. 2, valves 34 and 33 being used for this purpose. Connecting with the outlet pipe of heater No. 2 is a water supply pipe 35 with a control valve 36 used for purging the heaters of oil and discharging through pipe 37 by means of valve 38 and block valve 39. Into pipe 8 is connected a pressure gauge 40 to indicate the pressure at that point and also one lettered 41 in pipe 7 to indicate the pressure at the outlet of the heaters.

I will now describe the operation of the process as depicted in the drawing. The drawing is diagrammatic only but is sufficiently clear to enable those familiar with refinery equipment to understand it; For instance, the heaters Nos. 1 and 2 are tubular elements set in a brick or other suitable setting and heated by means of a fire box situated within the setting or forming a part of it. To show the detail of the heater would only confuse the drawing and render it less clear. Likewise, the exchangers shown in diagram-

matic form may be any of the well known types of exchangers used for this purpose and to show more detail would tend to only lessen the clearness of the drawing. This would apply also to the evaporator, the fractionating tower and the condensing equipment.

The pump 1 takes its supply of petroleum from the supply tank 2, developing sufficient pressure to force the oil throughout the oil system and to maintain sufficient pressure on the hydrocarbons to substantially overcome the vapor pressure due to the temperature of the hydrocarbons while passing through the heaters and exchangers, this pressure being regulated by the valves 10, 13 or 33, depending upon the product desired. In passing through exchanger No. 1 heat is absorbed from the hot residuum leaving the evaporator and in passing through exchanger No. 2 heat is absorbed from the hot oil leaving heater No. 2. These heat exchangers are not essential to the working of the process but are employed from economical considerations and are desirable in the practical operation of the process. After the oil has passed through exchanger No. 2 it goes to the heater No. 1 where its temperature is further increased to the point of decomposition of the hydrocarbons or at least a portion of them; this temperature being observed by means of the pyrometer 5; and is usually predetermined for each particular oil undergoing treatment. When the desired temperature is reached as indicated by pyrometer 5, the oil is now passed through heater No. 2 and is maintained at that temperature or substantially so as indicated by pyrometer 6, and to so maintain the oil at the maximum point of decomposition in heater No. 2 will require additional heat from an outside source; that is to say the furnace will be required to furnish a quantity of heat sufficient to supply the heat rendered latent by the endothermic reaction of decomposition. By this regulated means of heat supply to the hydrocarbons passing through the two heaters, a greater yield of decomposition products is obtained than if the oil had been brought to the point of decomposition and then passed to exchanger No. 2 and immediately cooled off, as for instance, if the oil leaving heater No. 1 had gone direct to the exchanger instead of to heater No. 2, the sensible heat attained by the oil in both cases would be substantially the same but in undergoing decomposition, heat is rendered latent and the sensible heat is reduced with attendant reduction of decomposition products and I have found that by supplying from an outside source the heat rendered latent and maintaining the sensible heat at its maximum an increased yield of decomposition products will result.

The heated hydrocarbons leaving the heaters pass through exchanger No. 2 where a

portion of the heat may be removed, thence through valve 13 and pipe 12 to the evaporator. To regulate the heat to the desired amount a bypass may be employed as shown by pipe 32 and valve 33 whereby any desired amount of hot oil may be added to the cooled oil passing from the exchanger No. 2.

The hot oil on being discharged into the evaporator will separate into a vapor and a residuum, the vapor passing over into a fractionating tower 18 to be fractionated, the light fractions passing to a condenser and receiving tank; the heavier fractions passing out of tower 18 at the bottom and through a cooler 23' to the wash oil tank 24; a portion of this oil is recirculated by pump 25 through the tower by means of pipe 26 and is used as a condensing medium therein, the increment in the amount of wash oil due to the condensation products overflows from the tank 24 through pipe 27 into tank 28 from which it is drawn by pump 30 through pipe 29 and discharged through pipe 31 into the hot oil flowing in pipe 12 into the evaporator; in this way the temperature of the stream of synthetic crude may be modified, and any light fractions absorbed by the wash oil may be re-evaporated and recovered as a part of the light fraction going to the condenser, or the light fractions absorbed by the wash oil may be discharged to the supply tank 2 by means of pipe 42 and valve 42'.

The residuum collecting in the lower portion of the evaporator is discharged through pipe 14 to the exchanger No. 1 from which it passes by pipe 15 to cooler No. 2 and residuum tank 16.

By this method of procedure, hydrocarbons may be decomposed, forming new hydrocarbons which could not be obtained by ordinary distillation processes. For instance, I can take a heavy residuum containing practically no low boiling fractions and heat it to a temperature of 700° F. or above and a pressure sufficient to overcome its vapor-pressure and obtain therefrom new hydrocarbons having low boiling fractions of the gasoline series and also obtain a residuum having a low viscosity, and, if so desired the viscosity of the new residuum may be made lower than the original oil used if a heavy crude or viscous residuum had been used as the original stock. As an illustration, I can take a heavy Mexican crude oil containing four to five percent of gasoline, the residuum from which after the extraction of the gasoline would have a viscosity of 2000 at 122° F taken in a Furol viscosimeter and having a gravity of less than 10° Baumé, and run it through my heaters and distilling apparatus and obtain a yield of ten to twelve percent of low boiling hydrocarbons and the residuum will have a viscosity of 300 or less as compared to the 2000 of the original resid-

uum and the gravity of the new residuum will be 11 Baumé or above.

To obtain this result a temperature of 750° F. to 800° F. is used and a pressure at the pump of 600 or 700 pounds is used. If a high grade residuum is required, the temperature should not be much above 800° F. but if a larger yield of light products is desired a temperature as high as 900° F. may be used but such a temperature will cause too much decomposition of the heavy oils and the residuum would be more or less granular and would not make a suitable fuel oil for the market.

The temperature and pressure must be properly regulated for each class of oil processed and varies according to the class of products desired. If a gas oil distillate were used as the raw stock and if gasoline hydrocarbons were the desired products then a temperature of 750° F. to 950° F. should be used; in this case the pressure should be in excess of 500 pounds although lower pressures may be used.

For cracking gas oil for instance, I can produce from 30 to 40 percent of gasoline boiling point hydrocarbons by a once through operation and as high as 70 per cent by recirculating the heavy ends or condensation products from the fractionating tower. In the latter case a somewhat higher temperature is required than if a fresh or uncracked gas oil were used.

To make the handling of the heaters more easy, I install a water supply pipe with control valve and also a blow down line with a valve so that water may be forced into the heaters to displace the oil and also to assist in the removal of carbonaceous material in the tubes.

I also provide a cooler No. 1 and a receiving tank 11 connected to the pipe 9 through valve 10 to permit the oil to go to storage if it is not suitable or desirable to pass to the evaporator.

What I claim as new is:

1. An apparatus for the treating of hydrocarbon oils which comprises a furnace, a coil in said furnace, a heat exchanger, means for passing oil to be treated through said heat exchanger under superatmospheric pressure, a second heat exchanger, means for passing oil from said first heat exchanger to said second heat exchanger, means for passing oil from second heat exchanger to said coil, means for passing oil from said coil directly to said second heat exchanger, a low temperature, low pressure evaporator, means for passing oil from said second heat exchanger directly to said evaporator, means for reducing pressure on the oil in its passage from said second heat exchanger to said evaporator, means for removing the vapors from said evaporator, means for removing the unvaporized oil from said evaporator, means for

passing said unvaporized oil to said first mentioned heat exchanger, a fractionating column, a conduit for conveying vapors from the evaporator to the column, means for withdrawing reflux condensate from said column means for cooling the reflux condensate, and means for introducing withdrawn cooled condensate into the oil during its passage between the second heat exchanger and the evaporator and after the pressure reducing means.

2. An apparatus for the treatment of hydrocarbon oils which comprises a furnace, a coil in said furnace, a heat exchanger, means for passing oil to be treated through said heat exchanger under superatmospheric pressure, a second heat exchanger, means for passing oil from said first heat exchanger to said second heat exchanger, means for passing oil from said second heat exchanger to said coil, means for passing oil from said coil directly to said second heat exchanger, a low temperature, low pressure evaporator, means for passing oil from said second heat exchanger directly to said evaporator, means for reducing pressure on the oil in its passage from said second heat exchanger to said evaporator, means for removing the vapors from said evaporator, means for removing the unvaporized oil from said evaporator, means for passing said unvaporized oil to said first mentioned heat exchanger, a fractionating column, a conduit for conveying vapors from the evaporator to the column, means for withdrawing reflux condensate from said column, means for cooling the reflux condensate, means for introducing a portion of the withdrawn cooled condensate into the oil during its passage between the second heat exchanger and the evaporator and after the pressure reducing means, and means for introducing another portion of the reflux condensate withdrawn from the column into the upper portion thereof.

In testimony whereof I affix my signature.  
JOHN C. BLACK.