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PROCESS OF CRACKING HYDROCARBONS

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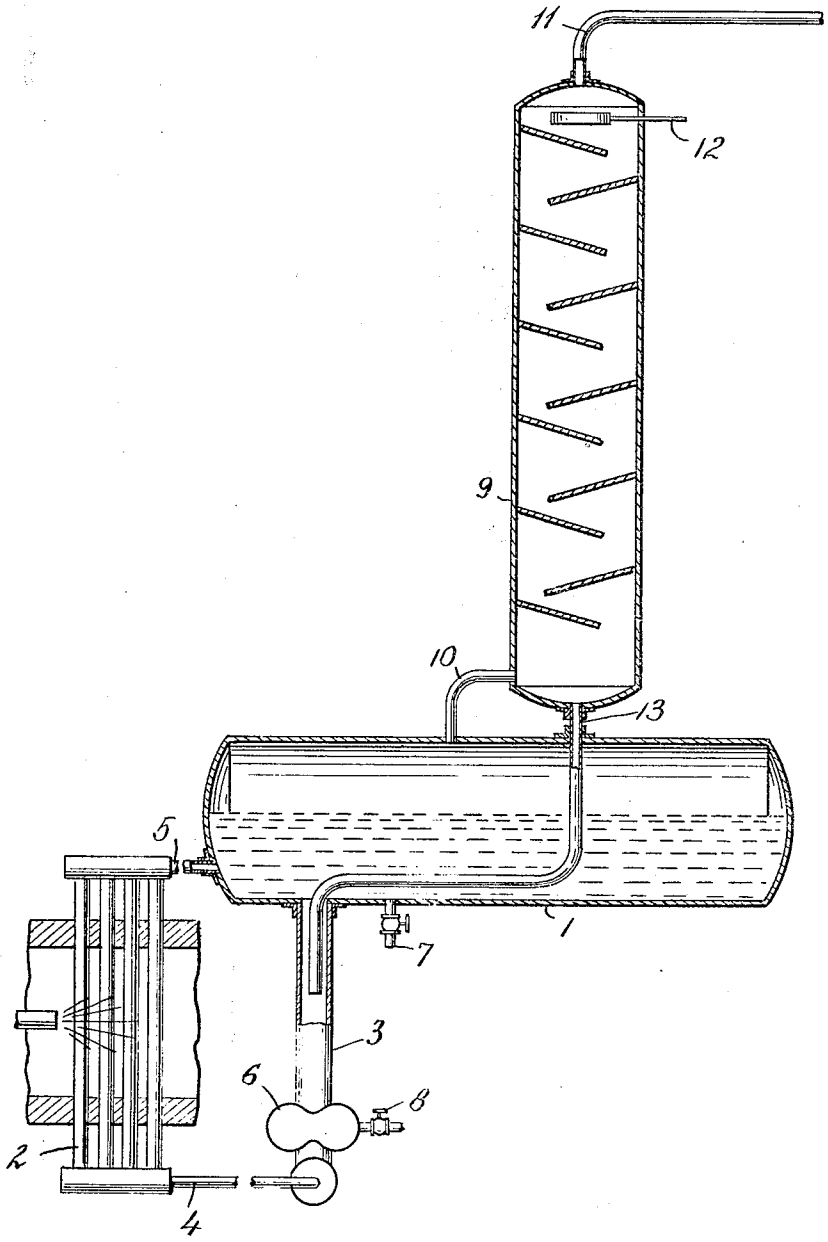

INVENTOR
Eugene C. Herthel
BY
Rector, Hibben, Davis & Macauley
ATTORNEYS

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UNITED STATES PATENT OFFICE

EUGENE C. HERTHEL, OF CHICAGO, ILLINOIS, ASSIGNOR TO SINCLAIR REFINING COMPANY, OF NEW YORK, N. Y., A CORPORATION OF MAINE

PROCESS OF CRACKING HYDROCARBONS

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My invention relates to improvements in the cracking of higher boiling hydrocarbon oils to form lower boiling hydrocarbon oils therefrom by distillation at a cracking temperature under pressure. This application is in part a continuation of my prior application filed July 12, 1922, Serial No. 574,380, and my present invention relates particularly to improvements in the treatment of relatively light hydrocarbon oils, such as kerosene, for the production of gasoline or pressure distillate or motor spirit according to the general process there described.

In carrying out the process of my said prior application, a liquid body of the hydrocarbon oil to be cracked is subjected to distillation at a cracking temperature and under superatmospheric pressure, vapors being taken off under superatmospheric pressure, and fresh oil is supplied to and tar-laden oil withdrawn from the liquid body as the operation proceeds, the supply of fresh oil to and withdrawal of tar-laden oil from the liquid body being regulated to prevent saturation of the oil in the liquid body and pitch or pitchy constituents and so that such pitch and pitchy constituents are held in solution in the oil body and in the tar-laden oil as withdrawn. As further described in my said prior application, the supply of fresh oil and withdrawal of tar-laden oil are regulated so that at no time more than 50% of the total stock, including feed oil, has been taken off as distillate. The formation of carbonaceous deposits upon the heating surfaces of the still by coking thereon of pitch or pitchy constituents precipitated from the oil is thus prevented; several important advantages being thereby secured, among which may be mentioned prolongation of the period of operation and the avoidance or retardation of the formation of carbonaceous deposits upon the heating surfaces of the still acting as an insulating layer upon these surfaces. In carrying out my present invention, likewise, the operation is conducted so that the body of oil undergoing distillation does not become saturated with pitch or pitchy constituents during the operation or at least not until just prior to the time when it is desired to terminate the operation.

My present invention relates particularly to the treatment of hydrocarbon oils of which more than about 25% boils off at 500° F. and of which not less than about 80% boils off at 600° F. upon fractional distillation under atmospheric pressure. The following distillation figures were taken from an oil typical of those to the treatment of which my present invention relates. This oil had a gravity of 36.9° Bé., an initial boiling point of 426° F., and 55.7% came off up to 500° F.

10%	off at 463° F.	Gravity of fraction	40.6° Bé.
20%	off at 471° F.	Gravity of fraction	39.9° Bé.
30%	off at 478° F.	Gravity of fraction	39.4° Bé.
40%	off at 486° F.	Gravity of fraction	38.9° Bé.
50%	off at 495° F.	Gravity of fraction	38.6° Bé.
60%	off at 507° F.	Gravity of fraction	38.0° Bé.
70%	off at 524° F.	Gravity of fraction	37.2° Bé.
80%	off at 548° F.	Gravity of fraction	36.6° Bé.
90%	off at 586° F.	Gravity of fraction	35.9° Bé.
Bottoms			31.6° Bé.

According to my present invention, a charge of such relatively light oils is distilled at a cracking temperature under a pressure upwards from 125 pounds per square inch, and fresh oil is supplied to and tar-laden oil withdrawn from the charge of oil undergoing pressure distillation during the operation, the supply of fresh oil and the withdrawal of tar-laden oil being regulated so that the amount of oil taken off as distillate does not substantially exceed about 60% of the total oil, including the original charge of oil and the fresh oil supplied during the operation. Petroleum oils of the character specified are relatively refractory and do not break down as readily as oils of lower boiling range. The tendency to formation of very heavy pitches or heavy coking of solid or semi-solid matter is materially reduced and the pitches formed are less dense. As a consequence, the concentration of pitch in the body of oil undergoing pressure distillation can be carried to a higher degree before the saturation point is reached. Thus, although the percentage of the oil taken off as distillate may be increased in carrying out the present invention, objectionable deposition of carbonaceous material within the pressure still is nevertheless avoided. Oils of the character specified also vaporize very readily and have a tend-

ency to escape as a vapor before being broken down to a sufficient extent. In carrying out my invention, this tendency is counteracted by employing pressures of 125 pounds per square inch or more. With such relatively high pressures, vaporization is retarded making more heat available for cracking and the temperature of the body of oil undergoing distillation is also increased assisting in increasing the rate at which cracking proceeds.

Likewise, in carrying out my invention, it is advantageous to subject the vapors from the pressure still to a refluxing operation by direct contact and heat exchange with fresh oil supplied to the operation at a rate substantially in excess of the rate at which oil is taken off as distillate. Fresh oil of the character to the treatment of which the invention particularly relates may, for example, be so supplied at a rate corresponding to from 170% to 200% or more of the rate at which distillate is removed. Preheating the fresh oil in this manner also tends to increase the temperature of the body of oil undergoing distillation, thus assisting in increasing the rate at which cracking proceeds. When higher pressures are employed, the rate at which fresh oil is so supplied may be decreased, and any additional fresh oil to be supplied to the operation to maintain the still charge or to maintain the rate at which distillate is taken off may be supplied directly to the operation. The refluxing effected in such operation, in carrying out my invention, may with advantage be increased by employing in conjunction with the fresh oil supplied to the refluxing operation some other refluxing medium, for example, a part of the condensed pressure distillate or a fraction of corresponding character such that it would be substantially completely vaporized in the tower with the consequent cooling and refluxing action without however, increasing the volume of oil in the pressure still. Adequate refluxing action may thus be secured without limiting the percentage of the oil which may be taken off as distillate up to the limits where objectionable deposition of carbonaceous material is involved. Oil employed as such a supplemental refluxing medium may be introduced either in admixture with the fresh oil supplied to the cracking operation or it may be separately introduced into the refluxing operation.

One form of apparatus adapted for carrying out the present invention is diagrammatically illustrated in the accompanying drawing, and the invention will be further described in connection therewith. The pressure still illustrated is of the general construction described and illustrated in Letters Patent No. 1,285,200 issued to the Sinclair Refining Company, November 19, 1918, on an application of Edward W. Isom but it will be appreciated that my invention is useful in connection with other types of pressure cracking stills.

Referring to the drawings, the pressure still proper comprises a bulk supply tank 1 adapted to contain a body of oil and located away from a battery of heating tubes 2 with circulating connections 3, 4 and 5 including a circulating pump 6 for circulating oil from the bulk supply tank upwardly through the heating tubes and back to the bulk supply tank. A connection is provided at 7 for withdrawing tar-laden oil from the body of oil in the bulk supply tank 1, and a connection is shown at 8 for supplying fresh oil directly to the stream of oil circulating through the pump 6 to the heating tubes. A reflux tower 9 is arranged above the bulk supply tank and is connected thereto by a vapor line 10 through which vapors escaping from the bulk supply tank enter the lower end of the reflux tower. The vapors escaping uncondensed from the reflux tower pass to a suitable condenser (not shown) through connection 11 where they are condensed to form the pressure distillate. The pressure within the system may be maintained by valves (not shown) located in the vapor line between the reflux tower and the condenser or by valves arranged beyond the condenser. A connection 12 is provided for introducing fresh oil directly into the upper end of the reflux tower. Any oil employed as a supplemental refluxing agent may be introduced into the reflux tower through this connection in admixture with fresh oil, or a separate connection may be provided for introducing such oil, advantageously at a point in the reflux tower above the point at which the fresh oil is introduced. Reflux and admixed fresh oil collecting in the lower end of the reflux tower are supplied to the circulating stream of oil entering the circulating pump 6 through connection 13.

In carrying out the invention in apparatus of the type illustrated, the pressure still is charged with say 8,000 gallons of a stock of which more than about 25% boils off at 500° F. and brought to a cracking temperature under a pressure upwards of 125 pounds per square inch. The introduction of fresh oil into the upper end of the tower is then begun and vapors are taken off and condensed to form the pressure distillate. Distillates may be taken off, for example, at a rate of about 750 gallons per hour and fresh oil supplied at a rate of about 1,000 gallons per hour or somewhat more. Before the concentration of pitch in the still charge reaches the saturation point, the withdrawal of tar is begun. Initially, the tar may be withdrawn at a rate of from 800 to 1,000 gallons per hour, until the still charge is reduced approximately to the amount of the charge before the introduction of fresh oil is begun and the rate then

somewhat reduced but maintained sufficient to prevent the concentration of pitch exceeding the saturation point. Any additional fresh oil required to maintain the charge in the still is introduced through the circulating pump. The amount of additional fresh oil so introduced through the circulating pump may vary over wide limits. In practice the apparatus illustrated and described in this application has been found to operate satisfactorily when additional fresh oil is introduced through the circulating pump at a rate of about 250 gallons per hour or somewhat more. Any additional refluxing required may be secured by returning and reintroducing into the reflux tower a part of the pressure distillate. An amount of pressure distillate corresponding to as much as 25% or somewhat more of the fresh oil introduced into the reflux tower may, for example, be so returned. The distillation is terminated before the percentage of the oil taken off as distillate substantially exceeds 60% of the total oil supplied to the operation, including the original charge and the fresh oil supplied during the operation. The actual length of time during which the operation is continued will vary over wide limits depending on the rate at which fresh oil including any additional fresh oil supplied through the circulating pump is introduced to the system. In the foregoing example, however, in which fresh oil including that introduced through the circulating pump, is introduced to the system at a rate of about 1250 gallons per hour and distillate is taken off at a rate of about 750 gallons per hour, the distillation may be terminated with advantage after distillate has been taken off for a period of approximately 200 hours at which time the total distillate taken off would amount to 58% of the total oil supplied to the system including the initial charge. If the major portion of the distillation has been carried out in accordance with my invention, the withdrawal of tar-laden oil may be stopped or diminished and the operation of the pressure still continued for a further brief interval to obtain an additional amount of distillate. This, however, entails danger of deposition of carbonaceous material within the still, although only at the end of the operation and just before it is terminated.

I claim:

1. A process of cracking higher boiling hydrocarbons to form lower boiling hydrocarbons, which comprises heating a liquid body of hydrocarbon oil of which more than about 25% boils off at 500° F. and not less than about 90% at 600° F. at atmospheric pressure to a cracking temperature under superatmospheric pressure upwards of 125 pounds per square inch by circulating oil from said liquid body through heating tubes and back to said body, taking off vapors from said liquid body under pressure while continuing the heating operation, supplying fresh hydrocarbon oil of the same character to and withdrawing tar laden oil from the said liquid body of oil as the operation progresses, and regulating the supply of fresh oil and the withdrawal of tar laden oil so that throughout the major portion of the operation the amount of oil taken off as final distillate exceeds 50% and does not substantially exceed about 60% of the total oil supplied to the operation including the original liquid body of oil and the fresh oil supplied during the operation.

2. A process of cracking higher boiling hydrocarbons to form lower boiling hydrocarbons, which comprises heating a liquid body of hydrocarbon oil of which more than about 25% boils off at 500° F. and not less than about 90% at 600° F. at atmospheric pressure to a cracking temperature under superatmospheric pressure upwards of 125 pounds per square inch by circulating oil from said liquid body through heating tubes and back to said body, taking off vapors from said liquid body under pressure while continuing the heating operation, subjecting the vapors to a refluxing operation in which fresh hydrocarbon oil of the same character is introduced into direct contact with the vapors and from which the admixed, refluxed and unvaporized fresh oil is returned to the said liquid body, withdrawing tar laden oil from the said liquid body as the operation progresses, and regulating the supply of fresh oil and the withdrawal of tar laden oil so that throughout the major portion of the operation the amount of oil taken off as final distillate exceeds 50% and does not substantially exceed about 60% of the total oil supplied to the operation including the original liquid body of oil and the fresh oil supplied during the operation.

3. A process of cracking higher boiling hydrocarbons to form lower boiling hydrocarbons, which comprises heating a liquid body of hydrocarbon oil of which more than about 25% boils off at 500° F. and not less than about 90% at 600° F. at atmospheric pressure to a cracking temperature under superatmospheric pressure upwards of 125 pounds per square inch by circulating oil from said liquid body through heating tubes and back to said body, taking off vapors from said liquid body under pressure while continuing the heating operation, subjecting the vapors to a refluxing operation, introducing into direct contact with the vapors in the refluxing operation fresh oil of the same character and an oil of the character corresponding to that of the distillate taken off, returning the admixed, refluxed and unvaporized components of the oil introduced into the refluxing operation to the said liquid body, withdrawing tar laden oil from the said liquid body and regulating the supply of fresh oil

and the withdrawal of tar laden oil so that throughout the major portion of the operation the amount of oil taken off as final distillate exceeds 50% and does not substantially exceed about 60% of the total oil supplied to the operation including the original liquid body of oil and the fresh oil supplied during the operation.

In testimony whereof I affix my signature.

EUGENE C. HERTHEL.