July 16, 1935. R. A. HALLORAN ET AL 2,008,550

PROCESS OF CRACKING PETROLEUM OILS

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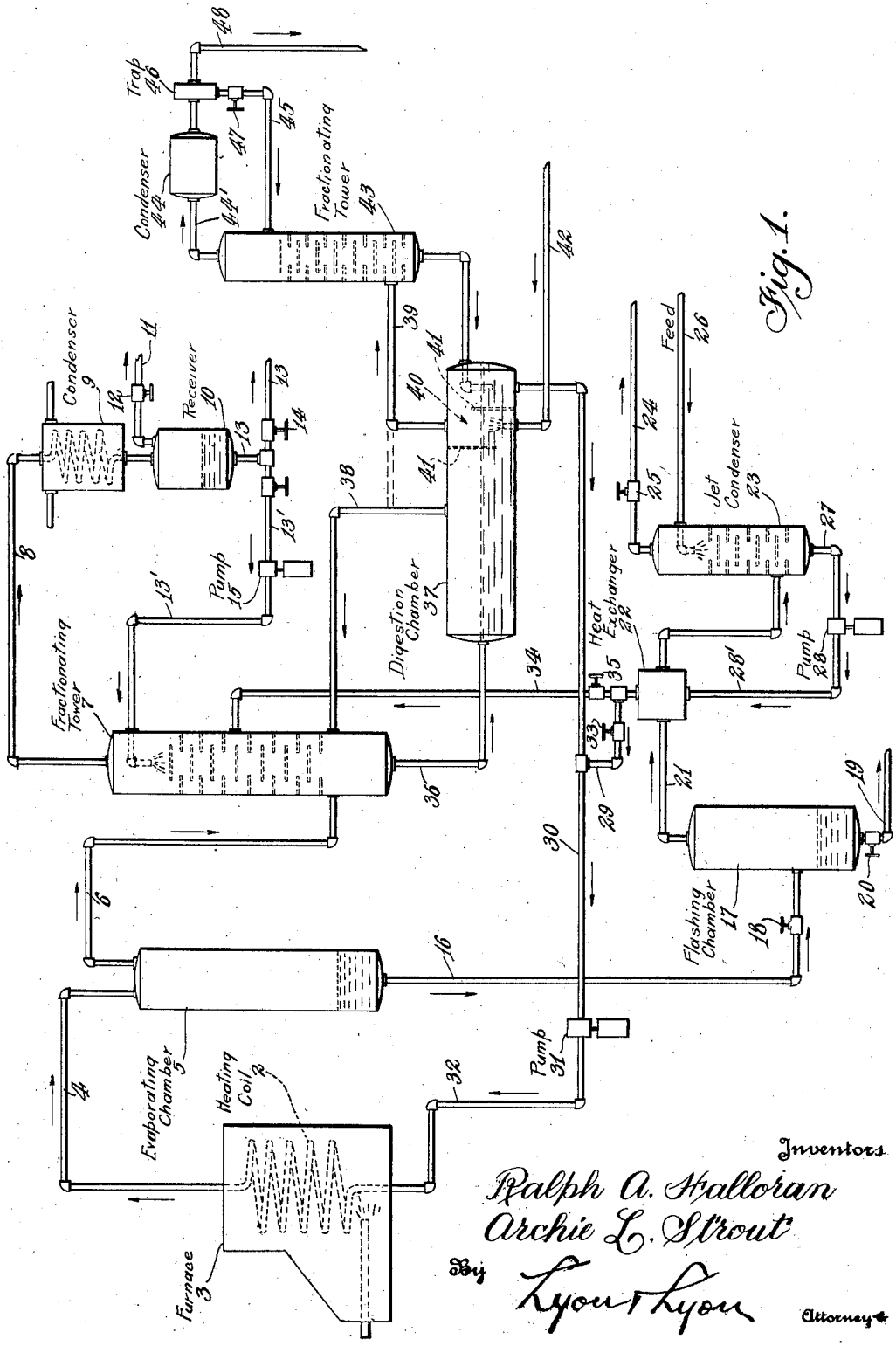


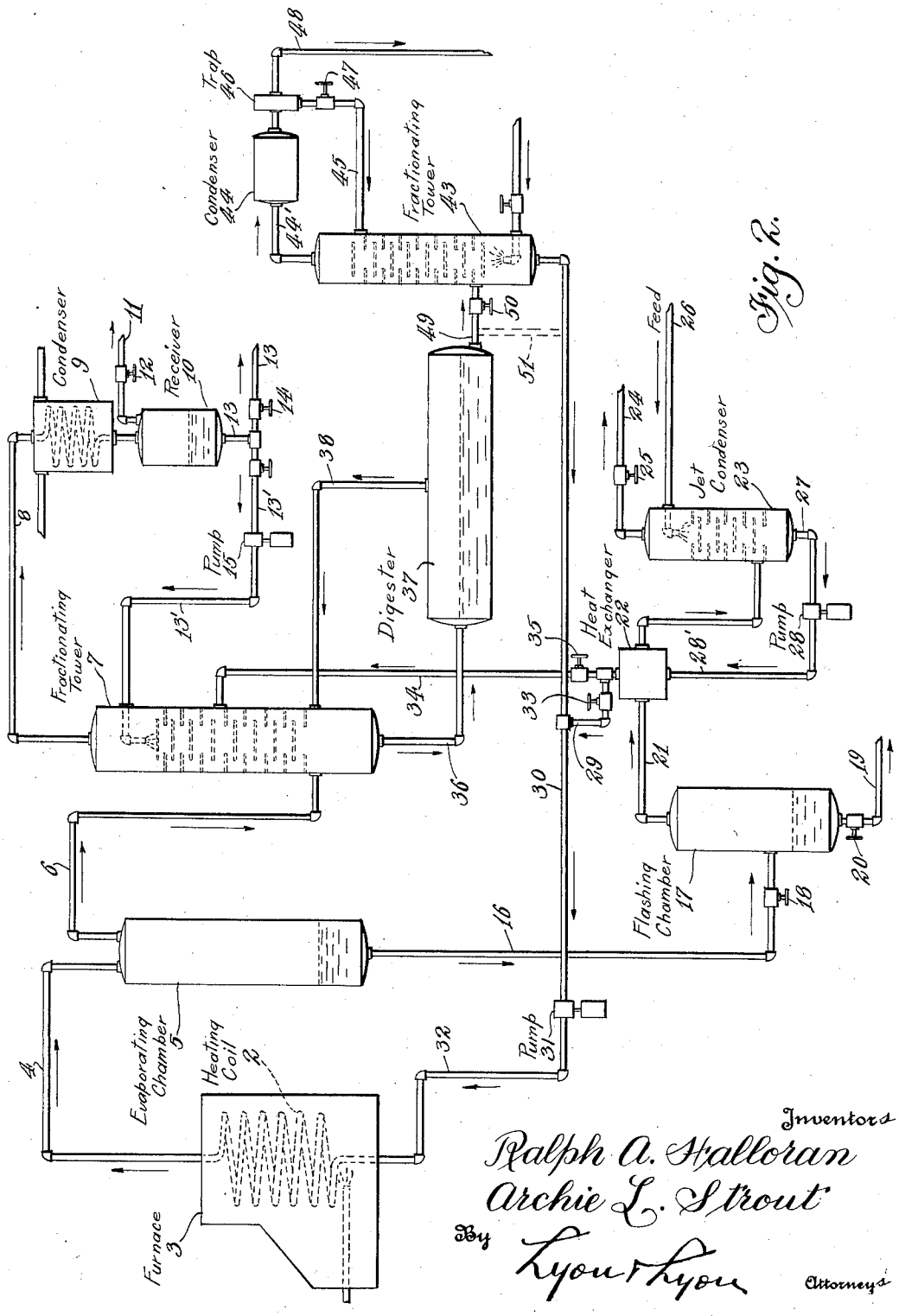
Fig. 1.

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Patented July 16, 1935 2,008,550

UNITED STATES PATENT OFFICE

2,008,550

PROCESS OF CRACKING PETROLEUM OILS

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Application October 10, 1928, Serial No. 311,467

2 Claims. (Cl. 196—51)

This invention relates to the art of decomposing or cracking oils, such as petroleum oils, by means of high temperature and pressure above atmospheric, commonly referred to as the pyrogenetic cracking of oils, to produce low boiling point, low specific gravity oils from relatively higher boiling point oils, and particularly to produce low boiling point oils adapted for use as fuel in internal combustion engines.

More specifically the invention relates to a pyrogenetic oil cracking process of the type in which oils, after being heated to a desired cracking or decomposing temperature, are passed into a vaporization zone from which the vapors are withdrawn as distillation products thus separating them from the unvaporized oils.

In cracking processes of this type, the operation has generally been so carried on that there is excessive coke or carbon formation in the evaporating chamber and the resulting residual oil withdrawn from the system contains such an amount of free carbon or sediment as to materially reduce the value of such residual oil as a commercial fuel oil.

An object of the invention is to provide a cracking process by which a high yield of low boiling point fractions may be obtained, while at the same time the production and precipitation of coke, carbon or carbonaceous material in the respective parts of the apparatus may be minimized and controlled or substantially avoided, and the sediment content of the residual oil reduced to a minimum, thereby rendering such residual oil satisfactory for a commercial fuel oil.

Heretofore it has been common practice to maintain in the evaporating chamber for relatively long periods of time a very considerable volume of the heated unvaporized oils discharged from the heating zone or coil, in order to secure a material amount of cracking reaction or conversion of such oils into lower boiling point oil. When the cracking reaction is thus allowed to continue while vaporization takes place and before the residual oil is withdrawn from the system digestion of the ingredients which are capable of yielding further low boiling products in substantial quantity takes place in the presence of the heavier derivatives of decomposition or cracking. The result has been rapid and excessive degeneration of the heavier derivatives of the cracking reaction, with the consequent production and precipitation of excessive amounts of carbon and sediment in such chamber.

This invention comprehends a process whereby oil may be rapidly raised to the reaction temperature and then the heavy residuents of the cracking or decomposing reaction separated from the oil after their formation, with sufficient celerity to avoid their degeneration into coke and the formation of sediment, while desired portions of the insufficiently cracked oils remaining after such separation may be further decomposed without supplying further heat thereto, whereby the production and the precipitation of carbon or coke or carbonaceous material in the apparatus may be substantially avoided or reduced to a minimum while recovering a high yield of the desired low boiling point oils.

An object of the invention is to provide a process whereby there is obtained a high yield of low boiling point oils without reliance, as a controlling factor for the desired high yield, upon digestion of the unvaporized oils remaining in the evaporating chamber being conducted in the presence of the heavy residuents of the cracking or decomposing reaction, thereby reducing to a minimum or substantially avoiding the production and precipitation of carbon or coke or carbonaceous material in the apparatus. The invention contemplates a process in which digestion of insufficiently cracked portions capable of yielding a further material amount of low boiling point products, i. e., their further decomposition without further heat input, is substantially confined to a condensate from vapors. The invention also contemplates the dilution, before their removal from the zone of reaction, of the heavy residuents of cracking with a portion of intermediate constituents capable of yielding a further material quantity of low boiling point products and the return of such intermediate constituents to the heating zone free from such heavy derivatives of cracking.

By the process disclosed in the pending application of Ralph A. Halloran and Archie L. Strout, Serial Number 176,990, filed March 21, 1927, the production of such carbon and sediment may be effectively controlled and reduced to a minimum or substantially avoided, thereby reducing or substantially avoiding precipitation thereof in the evaporating chamber. However, with such a process as that disclosed in said application, in order to secure the desired high yield of low boiling point oils, it has been necessary to compensate for the decrease in digestion taking place in vaporization chamber by increasing to a greater or less degree the temperature to which the oil undergoing treatment is raised in the heating zone or coil. Corrosion of the equipment is a material factor in the commercial operation

of such process. Higher coil temperatures increase corrosion. It is one of the objects of this invention to provide a process by which the same high yield may be obtained without resort to such higher coil temperature, and in fact by a reduction in the coil temperature, thus avoiding such increased corrosion or experiencing a reduction in the amount of corrosion.

Another embodiment of this invention comprehends a process or method whereby relatively high boiling point, high specific gravity oils may be economically cracked or decomposed by rapid passage through a relatively long heating coil in which such oils are subjected to pressure materially above atmospheric while being quickly raised to a relatively high cracking temperature whereby a relatively rapid cracking rate is secured within the coil and from which heating coil the intermingled oil and vapors are discharged into a vaporization or separation chamber, (preferably maintained under substantially the same pressure as the oil and vapors in said coils), wherein the vaporized fractions are quickly separated from the oil fractions unvaporized at the temperature and pressure of the operation, and in which the temperature of said unvaporized oils rapidly drops materially below the exit temperature from the coil, subjecting the resultant vapors to reflux condensation, (preferably under substantially the pressure of the operation), subjecting the liquid oils condensed thereby to digesting or cracking reaction, preferably under the contained heat thereof, and under pressure above atmospheric, recovering the vapors from such digestion or cracking operation, passing the residuum from such last named cracking or conversion operation to the heating coil for re-treatment, maintaining a substantially constant but relatively small volume of unvaporized oils in said evaporating chamber by continually discharging the unvaporized oils therefrom to a distillation chamber (preferably by maintaining a substantially uniform rate of flow into and separate discharge of vapors and unvaporized oils from said vaporizing chamber), wherein the pressure of such oils is sufficiently reduced to permit flash distillation sufficient to separate a material portion of the oils suitable for further cracking from the heavy derivatives which are unsuitable therefor, and at the same time leave a liquid residuum suitable for fuel oil, discharging the unvaporized residue, removing and condensing the resultant vapors thereby freed from such derivatives of the cracking operation as are, under the temperature and pressure of such operation, readily decomposed to coke, and returning said last named condensate together with fresh feed, either directly or indirectly, to the heating coil; preferably maintaining in such vaporizing chamber such a relation of pressure to temperature therein as to provide dilution of the heavy residuents of cracking with a proportion of lighter oils not readily decomposed into carbonaceous material under the time, pressure and temperature conditions of the operation.

An essential feature of this invention resides in subjecting the condensate from the reflux condensation of the vapors withdrawn from the evaporating chamber to digestion and returning the residuum of such reaction for further treatment in the heating coil. We have found that such a digesting operation is practical and may be employed to a considerable degree without the production of any material amount of coke or carbonaceous material in the digestion chamber and without the production of products in such residuum which when passed through the heating coil will undergo extensive decomposition to coke, carbon or carbonaceous matter or precipitation therein.

The invention may be more readily and fully understood by reference to a description of a preferred embodiment as utilized in actual practice taken in connection with the accompanying drawings diagrammatically illustrating the apparatus employed, and in which

Fig. 1 is a diagrammatic illustration of such an apparatus; Fig. 2 showing modifications of the apparatus in connection with the digestion or cracking reaction of the condensate.

In the drawings, 2 indicates a heating coil, suitably mounted within a furnace 3 to be heated thereby to the desired temperature. The furnace is fired in the usual or any preferred manner. This coil 2 is preferably of such length and dimensions and so mounted in the furnace 3 as to provide a relatively long passage of the oil through the heating zone, so that the oil to be cracked or decomposed may be rapidly forced through the coil and raised to and subjected to the desired cracking temperature while within the coil, at the same time being moved therethrough with such rapidity as to substantially prevent the formation or precipitation of coke or carbonaceous matter in the cracking coil. 4 indicates a discharge line leading from the cracking coil to a separating or evaporating chamber 5. Preferably this discharge line discharges into such chamber 5 at the top thereof. 6 indicates a vapor line by means of which the vapors are conducted from such separating or evaporating chamber 5 and discharged into a fractionating tower 7. This fractionating tower 7 may be of the ordinary or any preferred construction, such as the well-known bubble or doughnut-and-pan tower.

8 indicates a vapor line leading from the fractionating tower 7 into a suitable condenser 9 from which the condensed oil may be discharged into a suitable receiver 10. 11 represents a gas discharge line by means of which any fixed gas or uncondensed vapor may be discharged. This line 11 is provided with a valve 12, as indicated. 13 indicates a line by which the oil may be withdrawn from the receiver 10 to storage. This line 13 is controlled by a suitable valve 14. If desired a branch 13' in the line 13 may be connected to a pump 15 by which a portion of such distillate may be returned from the receiver 10 to the upper part of the fractionating tower 7 and therein used as a cooling agent for the ascending vapors. Any well-known cooling medium or means may be used, however, to control the fractionating tower 7.

16 indicates a discharge line for the withdrawal of the unvaporized oils from the vaporization chamber 5 and discharges into a flashing chamber 17. 18 indicates a suitable valve by which the release of pressure is controlled. 19 represents a discharge line from the bottom of the flashing chamber 17 controlled by a valve 20 leading to suitable storage for the fuel oil produced. 21 represents a line for drawing off the vapors from the flashing chamber 17 and leads through a heat exchanger 22 to a jet condenser 23. The heat exchanger 22 may be of any ordinary or preferred construction. Only one heat exchanger is indicated in the drawings. Any desired number may be used. The jet condenser may be of any ordinary or preferred construction

and is indicated as provided with the usual baffle plates. The condenser is provided with a line 24 controlled by a valve 25, by which the incondensible gases may be withdrawn and discharged.

26 indicates the fresh feed line through which the fresh oil to be treated may be introduced to the jet condenser and sprayed therein, thereby effecting a jet condensation of the vapors from the flashing chamber 17. 27 represents an outlet line from the jet condenser connected with the suction side of a feed pump 28 which delivers into the line 28' through heat exchanger 22 and to the branch feed line 29 which is connected with the pipe or line 30 connected to the suction side of the feed pump 31 arranged to deliver through the line 32 to the heating coil 2. Interposed in the branch feed line 29 is a suitable control valve 33. 34 indicates a second branch of the feed line 28', controlled by the valve 35 and discharging into the fractionating tower 7, thereby spraying a portion of the feed into the uprising vapors in the fractionating tower 7. It is obvious that either the branch 29 or 34 of the feed line 28' may be dispensed with and the whole stream of oil directed through the other branch.

36 indicates a discharge line for the condensate of the fractionating tower 7. This line 36 discharges into a digestion chamber 37, which may be of the ordinary or any preferred construction and may be arranged horizontally, as indicated in the drawings, or vertically. It is preferable to utilize a horizontally disposed digester 37 of comparatively small cross section and of considerable length, in order to provide directional flow through such digester, as thereby the time of treatment of the oils passing into and through such digester may be more accurately controlled. The line 30 connects the outlet end of the digester 37 with the suction of the pump 31. 38 indicates a vapor line by means of which the vapors produced in the digester 37 may be withdrawn. As indicated in the drawings, this vapor line 38 discharges into the fractionating tower 7. It is obvious that if desired a separate condenser may be used for these vapors, and they may be separately discharged to suitable storage. 40 indicates a compartment in the digester 37 formed by baffles 41. 42 indicates a line through which gas or steam may be passed to this compartment as an aid to distillation therein. 39 indicates a vapor line passing to fractionating tower 43. A line 44' leads from the fractionating column 43 to condenser 44 which may be of any practical type. 46 indicates a line for conducting condensate from condenser 44 to suitable storage or to a naphtha recovery system. Interposed in line 46 is trap 46 from which line 45 provided with valve 47 leads to fractionating tower 43 for conducting thereto a part of the condensate.

As an example of an operation of a process embodying this invention with a particular type or size of equipment, we have used as a charging stock or fresh feed to the system a 26° A. P. I. gas oil cut from California crude. This oil was pumped at the desired rate into the upper part of the jet condenser 23. In descending over the baffle plates of this condenser this cooled feed contacted with the cycle stock vapors from the distillation chamber 17 and condensed the said vapors. The commingled feed oil and condensed cycle stock were withdrawn from the condenser chamber 23 through the feed line 27 by the pump 28. Inasmuch as the cycle stock had been cooled by passage through the heat exchangers indicated at 22, and further cooled by contact with the incoming fresh feed in the chamber 23, the temperature of the mixture flowing through the pump 28 was relatively low. As this mixed feed was forced through the feed line 28' by the pump 28, it passed through the heat exchanger 22, and was raised to a temperature of approximately 500°–600° F. and passed into the fractionating tower 7. The length of the heating coil 2 was so proportioned to the furnace conditions that the oil passed therethrough with sufficient rapidity to be progressively and not too abruptly raised to the maximum temperature. By its passage through the cracking coil, the oil was raised to a temperature of about 875° F. under a pressure between 275–290 pounds. With such an operation the temperature of the vapors discharged through the transfer line 4 approximated 875° F. The evaporating chamber was suitably insulated to avoid excessive heat radiation and the temperature of the unvaporized oil collecting in the bottom of the vaporizing chamber was approximately 790° F. The fractionating tower 7 was so constructed and operated as to produce from the vapor discharged through the vapor line 8 the desired distillate. The reflux condensate from this fractionating tower had a temperature of 735° F. The pressure maintained in the fractionating tower approximated 270 pounds. The temperature of the oils entering the digestion chamber was approximately 785° F. and the residual therefrom was drawn through the pump 31 at a temperature of approximately 775° F. The pressure in the digestion chamber 37 in such operation approximated 270 pounds.

From the evaporator chamber 5 the unvaporized oils were discharged through the line 16 to the flashing chamber 17, pressure being released by the valve 18 to effect flash distillation. These oils were distilled in the flashing chamber 17 by their contained heat and all those constituents suitable for further decomposition recovered as vapors, and were utilized as a charging stock. The liquid oil, (containing the heavy derivatives of the cracking reaction) remaining from such flash distillation was discharged from the chamber 17 at a gravity of approximately 10° to 12° A. P. I. and was substantially free from sediment and carbon or coke, and available as a good liquid fuel.

With certain oils or certain operations, the entire pressure may be released upon the delivery of the unvaporized oils to the flash chamber 17 and with certain operations advantage may be had by actually creating a partial vacuum in such chamber 17 by means of a vacuum pump (not shown in the drawings), thus inducing additional distillation therein.

Degeneration of the heavy derivatives of cracking to coke and carbonaceous material was controlled by regulating the time during which the unvaporized oils from the cracking coil and the heavier derivatives of cracking were subjected to decomposition conditions in the vaporization chamber by passing such residuals out of the vaporization chamber before such excessive decomposition or degeneration could take place.

The best results were obtained by maintaining a relatively small amount of liquid oils within the vaporization chamber 5. By reducing the amount of unvaporized oils within the vaporization chamber 5 and by maintaining a substantially uniform rate of flow into and separate discharge of vapors and unvaporized oils from the vaporizing chamber 5, substantial degeneration of the heavy

residuents of cracking into a material amount of coke, carbon or carbonaceous material, or the precipitation thereof in the vaporization chamber, was prevented. A further factor in the accomplishment of this result was the maintenance of a suitable relation of the pressure maintained in the vaporization chamber to the temperature of the oils therein, so as to provide a certain dilution of the heavy residuents of cracking with a proportion of lighter oils not readily decomposed into coke, etc., under the temperature and pressure of the operation. Therefore, specific illustrations of the particular time element preferable in such operation are not given, as these must be related to the volume of oil undergoing treatment, the volumetric capacity of the apparatus, temperatures, pressures, etc. The rate of discharge of such diluted unvaporized oils from the evaporating chamber should, however, be at such rate as not to maintain any given portion thereof therein for a sufficient period of time to permit degeneration to or precipitation therein of coke, etc.

During the progress of the oil through the digester a drop in temperature occurs between the inlet and outlet ends due in part to the endothermic reaction of the cracking process and in part to the heat of vaporization absorbed in the production of vapors in this element. Inasmuch as lighter fractions are produced within the body of the oil, not all of the light fractions produced may be distilled off under the constant pressure conditions. If these fractions are not removed from the oil they pass to the heating element and may be partially cracked to gas and undesirably further broken down. Their presence in the oils passing to the cracking coil may also cause too early vaporization therein, and their vapors will exert their partial pressure effect within the system, and also, due to the formation of such vapors, will tend to cause an over-all expansion of the material passing through the coil and thereby for the same thruput shorten the time of exposure under the established temperatures. This shortening of time will tend to reduce the amount of cracking for any given temperature and for the same yield or production make it necessary to carry higher temperatures than would be the case if the lighter fractions were not present. Where such light fractions would otherwise remain in the residuum discharged from the digester **37** into the feed line to the heating coil **2**, provision is preferably made for their removal from the residuum either before the residuum is discharged from the digester **37** or before such residuum is passed into the feed to the coil. In Fig. 1 there is illustrated a method of stripping out these lighter fractions. Distillation is facilitated by the gas or steam introduced through line **42** and the vapors evolved in compartment **40** are passed through line **39** to fractionating tower **43** equipped with or accompanied by the necessary facilities for proper fractionating and for condensing the desired product from said vapors. While it is indicated in the drawings that a part of the condensate may be returned to the fractionating column **43**, it is evident that various types of fractionating tower with the return of the necessary fractions for cooling may be utilized. Reflux from the column is preferably returned to the residuum passing to the heating coil **2** as by a reflux line **45'**. Instead of utilizing a separate condenser, the vapors rising from the compartment **40** may be conducted (as indicated in dotted lines) into the vapor line **38**.

Another method of stripping the lighter fractions from the digester **37** is illustrated in Fig. 2. In this method pressure is reduced between the digester **37** and the fractionating column **43** by means of the valve **50** in line **49** which conveys residuum from the digester **37** to the fractionating tower **43**. The amount of reduction in pressure will depend on operating conditions, the type of stock handled, the amount of low boiling fractions carried in the digested stock and the amount of fractions it is desired to remove. Any practical fractionating equipment may be used for the purpose of stripping the lighter fractions while gas or steam may be used as an aid to distillation if found desirable. In the event it may not be necessary or desired to strip out these lighter fractions the fractionating tower **43** and its accompanying equipment may be omitted and the residuum from digester **37** passed directly to the heating coil as indicated by dotted line **51** of Fig. 2; or by the omission of baffles **41** shown in Fig. 1 together with the omission of fractionating equipment **43** as explained above.

By subjecting the reflux condensate of the vapors, separated from the unvaporized oil delivered from the cracking coil, to a digestion or cracking reaction and distillation, and then passing the residual of such reaction back to the cracking coil a substantial yield of low boiling point oils is obtained without the production or the precipitation from this part of the oils undergoing treatment of a material amount of coke, etc. in the cracking coil or vaporization chamber. This digestion can be effectually secured without the addition of heat to such condensate and may be conducted at substantially the pressure under which such condensate is produced or at somewhat reduced pressure, or under higher pressure, and with added input of heat if desired. As the low boiling point oils thereby produced are recovered, less cracking will be required in the heating coil and in the evaporator for the same overall yield of low boiling point oils. Therefore, it becomes practical to operate the process at lower coil temperatures reducing to an appreciable degree the corrosive difficulties experienced at the higher temperatures, particularly when treating oils containing a material sulphur content.

In the foregoing description and drawings for a more clear understanding of our invention, we have described and indicated the digester **37** as a separate mechanical element. Under some conditions of operation and installation the condensate might be permitted to collect in the bottom of the fractionating tower (as in the lower portion of the tower **7**, thus utilizing the same as a digestion chamber) and be held therein for the desired time interval during which the desired decomposition takes place before discharge of the residuum into the feed line to the cracking coil. In such case the evolved vapors of the digestion or cracking reaction distilling off would be removed before the residuum is passed to the feed line. This would also be true where the fractionating tower **7** is superposed above the evaporator **5**. In such practice, however, there would be sacrificed the advantage of controlling parallel flow through the digestion chamber, securable with the operation and apparatus heretofore described, because the lower boiling point fractions formed during digestion would rise through the liquid oils, causing agitation and rendering it impossible or difficult to withdraw

all portions of the residual oils or rediduum separately after the lapse of the established desired time. This sacrifice, however, under certain conditions may not be of sufficient magnitude to prohibit its use, particularly in consideration of the simpler equipment involved, and our invention therefore extends to and includes both these methods of operation.

We claim:

1. A process for converting heavy hydrocarbon oil into lower boiling products which comprises passing the oil in a restricted stream rapidly through a heating zone and heating the same therein to cracking temperature under superatmospheric pressure, discharging the heated oil into a reaction zone maintained under cracking conditions of temperature and pressure and separating the same therein into vapors and unvaporized oil, removing the latter from the reaction zone before any substantial quantity thereof has degenerated into coke and preventing its return to the heating zone, separately removing the vapors from the reaction zone and dephlegmating the same under superatmospheric pressure thereby forming a reflux condensate which is at cracking temperature, digesting the reflux condensate under the superatmospheric pressure and without application of heat thereto in a heat insulated digestion zone and effecting further conversion thereof by its contained heat, removing the digested reflux condensate from the digestion zone and lowering the pressure thereon thereby separating the same into vapors and residuum, supplying said residuum to the heating zone for retreatment in the process, and condensing the vapors evolved from the digested reflux condensate as well as those uncondensed by the dephlegmation.

2. The process as defined by claim 1 further characterized in that the unvaporized oil withdrawn from the reaction zone is flash distilled by pressure reduction, the flashed vapors dephlegmated, and resultant flash reflux introduced into contact with the initially separated vapors being dephlegmated and thence into the digestion zone in admixture with said reflux condensate.

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