The present invention relates to the treatment or conversion of fluids, particularly hydrocarbons, and especially relates to operations involving catalysis.

The material to be treated or starting material may, for example, comprise a high boiling hydrocarbon material such as a topped crude petroleum oil, a gas oil fraction containing heavy components, or a residual fraction. Other materials of such nature, whether of shale, coal or other origin, may also be treated according to this invention. The product or products desired may comprise low boiling hydrocarbons, such as gasoline and/or fractions higher boiling or lower boiling than gasoline, derived as products from a cracking of the starting material.

One object of this invention is advantageously to prepare a desired boiling range charge for a conversion operation, especially a catalytic cracking or transforming reaction, from a starting material of the type above indicated. Another object is to employ a fraction or fractions derived from the reaction or reactions of this invention to aid in controlling the boiling range of such charge which is to be cracked or converted. Another object is to control the process of this invention so that the size of apparatus employed may be minimized; or, conversely, so that its capacity may be increased. Another object is to obtain a high yield of desired product, such as gasoline, from a heavy high boiling starting material. A further object is to effect the heating of the starting material or charge so as to avoid the production of large amounts of deposits, such as coke, and to provide good operation of the still or other heating means. These and other objects and advantages, as well as a quick understanding of illustrative embodiments of the invention, will be readily apparent by reference to the accompanying drawings in which:

Fig. 1 schematically shows exemplary apparatus for carrying out steps of process of this invention;

Fig. 2 is a modification of the left-hand portion of the apparatus shown in Fig. 1; and

Fig. 3 is a modification of the right-hand portion of the apparatus of Fig. 1.

The modifications shown in Figs. 2 and 3 illustrate variations in certain aspects or features of the invention. It will be understood that the apparatus illustrated in Fig. 2 may be combined with that appearing in the right-hand portion of Fig. 1 or with that shown in Fig. 3. Likewise, it is contemplated that the apparatus shown in Fig. 3 may be employed in combination with that shown in the left-hand portion of Fig. 1 or that of Fig. 2.

Referring more in detail to the drawings, in the several figures of which like reference characters denote similar parts, 1 is a heater, 2 indicates separating means such as a tar separator, 3 indicates reaction or cracking chambers containing contact material or catalyst 4, and 5 is a fractionating column.

Referring especially to Fig. 1, the crude starting material or feed, e.g., a topped crude or other composite hydrocarbon material of high boiling range and containing substantial amounts of difficulty vaporizable or unvolatile components, may be forced at a high or substantial superatmospheric pressure through line 6 by pump 1 into the coils 8 within heater or furnace 1. Heated fluid leaving coils 8 (having some liquid or possibly a substantial proportion of liquid present with vapors) may pass through line 9 and be expanded or reduced in pressure by passing through pressure release valve 10 whereupon a large amount of components previously in the liquid phase are converted into vapors. The resulting mixture of vapors and liquid pass through line 11 into tar separator 2, the latter having plates or members 2a of any suitable construction, for example, flat plate, bubble plate or other fractionating devices, including suitable packing. Vapors having the boiling range desired for use as charge to the catalytic reaction cases are withdrawn as overhead from the tar separator through line 12 and are further heated, where further heating is desired, for example, by passing through coil 13 of heater 1, and then are passed through line 14 into any one or more of the several converters 3. Hydrocarbon products of reaction may be withdrawn from the converters as indicated and passed through line 15 into rectifying column or fractionating tower 5, the latter having any suitable types of plates, trays or packing so as to effect the desired fractionation and to permit withdrawal of side streams at various levels along the height of the tower. A suitable fraction, such as gasoline and gases may be withdrawn as overhead from the fractionating column through line 16, passed through cooler or condenser 17 and otherwise processed, stabilized, or sent to storage. Any required part of any desired side stream fraction or fractions may be withdrawn from column 5 and passed through line 18 to be introduced as reflux into the tar separator 2, as illustrated.

A bottoms fraction may be withdrawn from
fractionator through line 19 and sent to steam stripper 20, overhead from the steam stripper being returned to the lower end of the fractionator through line 21 and bottoms from the stripper being withdrawn through line 22 and either rejected from the system, further treated as desired, or partially or wholly sent as reflux by lines 22a and 18 to the separator 2.

Bottoms from the tar separator 2 may be withdrawn through line 23 to be further processed in any desired manner, passed through cooler 24 to store, or often preferably a desired proportion thereof, after being cooled somewhat, may be forced through line 24a back into the bottom of separator 2 in order to cool the mass of tar in the bottom of the latter sufficiently to avoid any substantial coking thereof.

The pressure under which the starting material is heated in coil 8 may be any substantial superatmospheric pressure, for example 200 pounds/sq. in. gauge or less at the outlet of coil 8, but usually at least 20 or more and ordinarily at least 40 to 50 lbs/sq. In. gauge at the outlet of the heating coils. A small amount of air is added to the starting material or feed in the coil 8 so that, after suitable reduction in pressure of the feed upon passing through pressure release valve 10, a desired temperature such, for example, as 700 to 750° F., more or less, e.g. 750 to 770° F., may be maintained in the lower portion of the tar separator 2. The pressure in the tar separator will in general be less than that existing within the coil 8 and may for example be in the range of approximately 20 to 50 lbs. per sq. In. gauge, the pressure in the tar separator being ordinarily about 25 to 75 or 100 lbs./sq. In. more or less, below that at the outlet of the coil 8, one reason for this being to avoid vaporizing in the heating coils components of the starting material which it is desired to withdraw as liquid from the tar separator, thus minimizing the size of apparatus for heating. It is important to maintain coil 8 under sufficient pressure so as to provide good operating conditions. The particular temperature and pressure conditions in coil 8 or equivalent will depend upon the starting material and type of reaction. However, with many hydrocarbon starting materials, e.g. topped crudes, if there is too high a percentage of vaporization, too much coke will be formed. This condition is also remedied or avoided by maintaining a suitably high pressure in coil 8.

The materials charged to the catalytic converters 3 through line 14 may be at a temperature of the order of 825° F. to 880° F., for example, depending upon the particular desired temperature of the contact material or catalyst 4, which may be 825° to 900° F., or, illustratively, may be about 850° or 880° F., where the catalytic material comprises an adsorptive silicious mass such as blends of silica and alumina of natural or artificial origin, or blends of silica with other suitable metalliferous materials. A selective catalyst is an active blend of silica with alumina in the weight ratio of at least approximately 31/2:1 as described, for example, in U. S. Patent No. 2,078,661, issued to Eugene J. Houdry on May 4, 1937.

While the liquid employed as reflux for the tar separator 2 may comprise various fractions, in general such reflux will be made up largely of material susceptible of vaporization in the tar separator under conditions of temperature and pressure which obtain therein. The reflux may have a boiling range approximating that of the overhead withdrawn through line 12 from the tar separator, but often it has a somewhat lower boiling range and may, for example, advantageously be a naphtha. The temperature at which the reflux is introduced into the tar separator 2 is usually (though not necessarily) at least several degrees below that of the overhead from the tar separator.

Water or steam may be introduced through line 25 into the coil 26 within the heater 1 and superheated steam withdrawn therefrom through line 27. Often some steam will be introduced into the starting material before it is introduced through coil 8, as for example through the valued line 28, so as to control mild cracking or viscosity breaking of higher boiling hydrocarbons which may, where desired, take place to some extent in the coil 8 during the heating step. Further amounts of steam may be introduced with hydrocarbons leaving coil 8, either into line 9 (preceding the pressure release valve 10) or into line 11 (following the pressure release valve 10) or partially before and partially after. Further amounts of water or other vaporizing medium or process fluid, may be introduced into the vapors passing through line 12 into coil 13 so as to provide the desired amount thereof as process fluid and/or to provide the desired degree of superheat in the charge to the catalytic cases 3.

The modification illustrated in Fig. 2 will, in a general way, be understood from the description given hereinabove in connection with Fig. 1.

In the apparatus shown in Fig. 2, a starting material or feed, which may consist of material such as topped crude petroleum oil having substantial amounts of tarry, asphaltic, or difficulty vaporizable components, may be passed through line 6 and through coil 8 of the heater 1, substantially as defined in connection with Fig. 1.

However, in the apparatus shown in Fig. 2, a portion or all of the bottoms withdrawn from separator 2 through line 23 may be forced through line 29 into a second separator or tar flashing chamber 30. The pressure within chamber 30 may be reduced by action of an ejector 31 in which starting material is provided on the line 32 by a jet of steam or the like introduced through line 33. Steam may be introduced into the separator 30 in any desired quantity through line 34 and unvaporized material may be withdrawn through line 35. The vapors leaving ejector 31 may pass through the line shown into a second separator 35 wherein a jet of heated hydrocarbons from coil 8 provides a suction or jet action thereon. Alternatively, vapors from ejector 31 may pass through line 37, either directly into the separator 2 or through the valued branch shown into line 11, therein to be admixed with heated material from coil 8. In the event that this alternative procedure is followed, heated material from coil 8 may be passed through line 38, having pressure release valve 10 therein, rather than to pass through the ejector 35 where the suction effect created thereby is not needed or desired. Steam supplied through line 27 may be introduced with the hydrocarbons either during their passage through coil 8, or following coil 8 either before or after pressure reduction.

The operation of the modification shown in Fig. 3 will be in part understood from the description given in connection with Fig. 1. However, Fig. 3 illustrates process and apparatus different in important particulars from that illustrated in Fig. 1. Heated and partially vaporized materials may be supplied to the sep-
arator 2 through line 14 from any source, as, for example, in the manner described in connection with either Fig. 1 or 2. Overhead vapors may be withdrawn through line 12, further heated at 13a or not, as may be desired, and then passed through line 14 to any one or more of the converters 3, also in the manner shown and described in connection with Fig. 1. Outgassing products from the converters 3 pass through the line 15 into rectifying tower 5 at some intermediate level along the height thereof and low boiling material such as gasoline and gases may be withdrawn as overhead through line 16, cooled or condensed in 17 and passed to storage or further treating apparatus as desired.

Any desired fraction may be passed through line 39, being withdrawn from fractionator 5 through any of branched lines 39a, 39b or 39c, as desired, and forced by the pump shown through the converter 45, which is preferably of the pyrolytic type, and from which the products pass into element 41, the latter optionally being operated as a reaction chamber to allow the cracking or viscosity breaking to proceed further, as a flash evaporator, or as a condenser. When it is desired, for example, as a flash evaporator or a reaction chamber, any heavy materials which remain as liquid may be withdrawn from chamber 41 through line 42 and vapors may pass from the chamber through line 43 and either be sent through branch 44 into partial condenser 45 (which latter may be used to transfer heat from the vapors to incoming starting material to the system as passing to coil 8 of the furnace 1 (Figs. 1 and 2), or for any other suitable purpose) or a portion or all of the vapors may be sent through the valve, line 46 and be introduced into rectifying tower 5 at any suitable level, passing through lines 46a, 46b or 46c as desired. However, at least a part of the vapors from chamber 41 usually pass into partial condenser 45 wherein heavier portions of such vapors are condensed and passed downwardly through line 47 into steam stripper 48. Overhead from steam stripper 48 may pass through line 49 and be combined with vapors leaving the partial condenser 45 and passed together through line 50 to tower 5. When the material passing through the valve, line 46 and into tower 5, any desired cooling may be effected in heat exchanger 51; also separation of any wild gases (which may be present) from liquids may be effected, if desired, in a suitable liquid-gas separator located in circuit between exchanger or cooler 51 and the point of introduction of reflux into the top of fractionator 5. However, where desired, material passing through line 50 may be introduced into tower 5 at some lower level without affecting any cooling in heat exchanger 51.

Unvaporized or liquid material passing from steam stripper 48 through line 52 may either go through line 53 and be sprayed or otherwise introduced into separator 2 separately or in admixture with materials introduced through line 14, or may be partially returned or entered partially through line 54 to be recycled downwardly through or pyrolytic converter 48. For all or such liquid may pass through the valve, branch 55 into line 10 to be sent, either alone or in admixture with other liquid withdrawn from the tower, as reflux at or near the upper end of the separator 2. Also, any desired portion of the liquid withdrawn from stripper 48 may leave the system through valve line 46.

Where vapors leaving chamber 41 pass through partial condenser 45, the latter may be operated so that fluid passing through line 50 is composed substantially completely of components such as gasoline and/or naphtha together with some hydrocarbons in the gas oil boiling range, thereby providing a blend of pyrolytically and catalytically produced lower boiling components of gasoline in tower 5. The amount of material fed from tower 5 through the still or pyrolytic converter 45 may be controlled in relation to the amount of material fed through line 14 into catalytic converters 3 so as to maintain the characteristics and anti-knock rating of low boiling hydrocarbons withdrawn from tower 5 through line 16 within desired limits.

Though not shown in the drawings, it is within the scope of my invention to send a fraction composed of insufficiently converted hydrocarbons, e.g. a gas oil fraction, from fractionator 5 into line 6 (Figs. 1 and 2) to be forced by pump 7 through coil 8. However, the ratio of such returned fraction to original starting material will ordinarily be low, e.g., 1:10 or less. Also, though not shown in the drawings, this invention comprehends condensing or compressing the overhead from separator 30 (Fig. 2) and introducing some or all of the same into line 6.

While the invention contemplates the treatment of a broad class of materials as above indicated, the treatment of a previously unconverted or virgin stock is especially contemplated. That is, this invention has particular application where the material charged through line 6 to coil 8 of the heater 1 consists wholly or predominantly of a material which has not previously been subjected to cracking or decomposition.

While the catalytic conversion step performs to best advantage on a previously untreated or virgin stock, the amount of material derived from the products of a previous catalytic or pyrolytic conversion which may be introduced into separator 2 as reflux is small in proportion to the whole charge passing to the converters 3. That is, the ratio of the reflux to separator 2 to the charge for the converters withdrawn through line 12 is ordinarily less than 1:10, i.e., less than 10%, and frequently is only of the order of 5% by weight of the vapors passing from the separator through line 12. Where the present process is being used in the production of a volatile gasoline, such as aviation gasoline having a 300° F. end point, and apparatus such as shown in Fig. 1, modified or not as indicated by Fig. 3, is employed, one advantageous procedure is to recycle a heavy naphtha having an initial boiling point above 300° F. from column 5 as reflux to separator 2.

It is to be understood that the apparatus shown in the left-hand portion of Fig. 1 and in Fig. 3 of the drawings may be used in preparing charge for other types of conversion apparatus than those shown in Figs. 1 and 3. Also, the conversion apparatus illustrated in the right-hand portion of Fig. 1 and in Fig. 3 may receive charge prepared by apparatus other than the types illustrated in Figs. 1 and 2. All adaptations and modifications within the scope of the appended claims are contemplated.
What we claim is:

1. In the production of desired low boiling hydrocarbons from a composite hydrocarbon starting material of wide boiling range containing a substantial proportion of heavy or unvaporizable components, the steps of process which comprise heating said starting material under conditions so as to retard active cracking while effecting vaporization of a large proportion of said starting material, passing the heated and partially vaporized material into a separating zone maintained at a pressure below that under which said heating is effected and wherein separating liquids from vapors, withdrawing unvaporized material from said separating zone, withdrawing vapors from said zone and effecting a superheating of the same and controlling the temperature thereof, continuously passing the resulting superheated vapors to a conversion zone containing a solid adsorptive incombustible catalytic material and maintained under conditions so as to effect a cracking of higher boiling to lower boiling hydrocarbons, passing hydrocarbon products from said conversion zone to a fractionating zone wherein desired low boiling products are withdrawn as vapors, withdrawing a higher boiling liquid fraction from said fractionating zone, subjecting it to a pyrolytic conversion, passing those portions of the products of the pyrolytic conversion which boil below approximately 500°F. into the aforesaid fractionating zone, and withdrawing therefrom a small portion of liquid having an initial boiling point higher than the end point of said desired low boiling point products and sending it to the top of the separator in order to control the boiling range of vapors passing to the catalytic conversion zone.

2. In the production of desired low boiling hydrocarbons from a composite hydrocarbon starting material of wide boiling range containing a substantial proportion of heavy or unvaporizable components, the steps of process which comprise heating said starting material under conditions so as to retard active cracking while effecting vaporization of a large proportion of said starting material, passing the heated and partially vaporized material into a separating zone maintained at a pressure below that under which said heating is effected and wherein separating liquids from vapors, withdrawing unvaporized material from said separating zone, withdrawing vapors from said zone and effecting a superheating of the same, passing a stream of the resulting superheated vapors into and through a conversion zone containing an active, adsorptive silicious catalytic material and maintained under conditions so as to effect a cracking of higher boiling to lower boiling hydrocarbons, passing fluid hydrocarbon products from said conversion zone to a fractionating zone wherein desired low boiling products are separated from higher boiling hydrocarbons, withdrawing a fraction of higher boiling hydrocarbons from said fractionating zone and subjecting it to a step of pyrolytic conversion so as to produce lower boiling hydrocarbon fractions, separating the products from said pyrolytic conversion step into lower and higher boiling fractions, sending the lower boiling fraction into the said fractionating zone, and passing a portion of the higher boiling fraction having an initial boiling point higher than the end point of said desired low boiling products to the top of the separator in order to control the boiling range of vapors passing therefrom to the catalytic conversion zone.

3. In the production of desired low boiling hydrocarbons from a composite hydrocarbon starting material of wide boiling range containing a substantial proportion of heavy or unvaporizable components, the steps of process which comprise passing said starting material through a heating zone under a substantial superatmospheric pressure but under such conditions as to prevent the production of large amounts of gasoline, whereby to partially vaporize said material, substantially reducing the pressure of material leaving said heating zone and introducing it into a separating zone, withdrawing a stream of liquid from said separating zone, passing said stream of liquid from said separating zone to a flashing chamber, introducing a vaporizing medium into said flashing chamber, withdrawing separate streams of liquids and vapors from said flashing chamber, then passing the resulting vapor stream into the separating zone and admixture with heated and partially vaporized fluid passing into the latter from said heating zone, and passing a stream of vapors from said separating zone into and through a reaction zone to convert higher boiling hydrocarbons into lower boiling products including gasoline, passing hydrocarbon products from the cracking zone to a fractionating zone, withdrawing said gasoline from the fractionating zone as vapors and withdrawing from the fractionating zone a liquid fraction having an initial boiling point greater than the end point of the gasoline and introducing it as reflux at a point adjacent the top of the separator in order to control the boiling range of vapors passing therefrom to the cracking zone.

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