

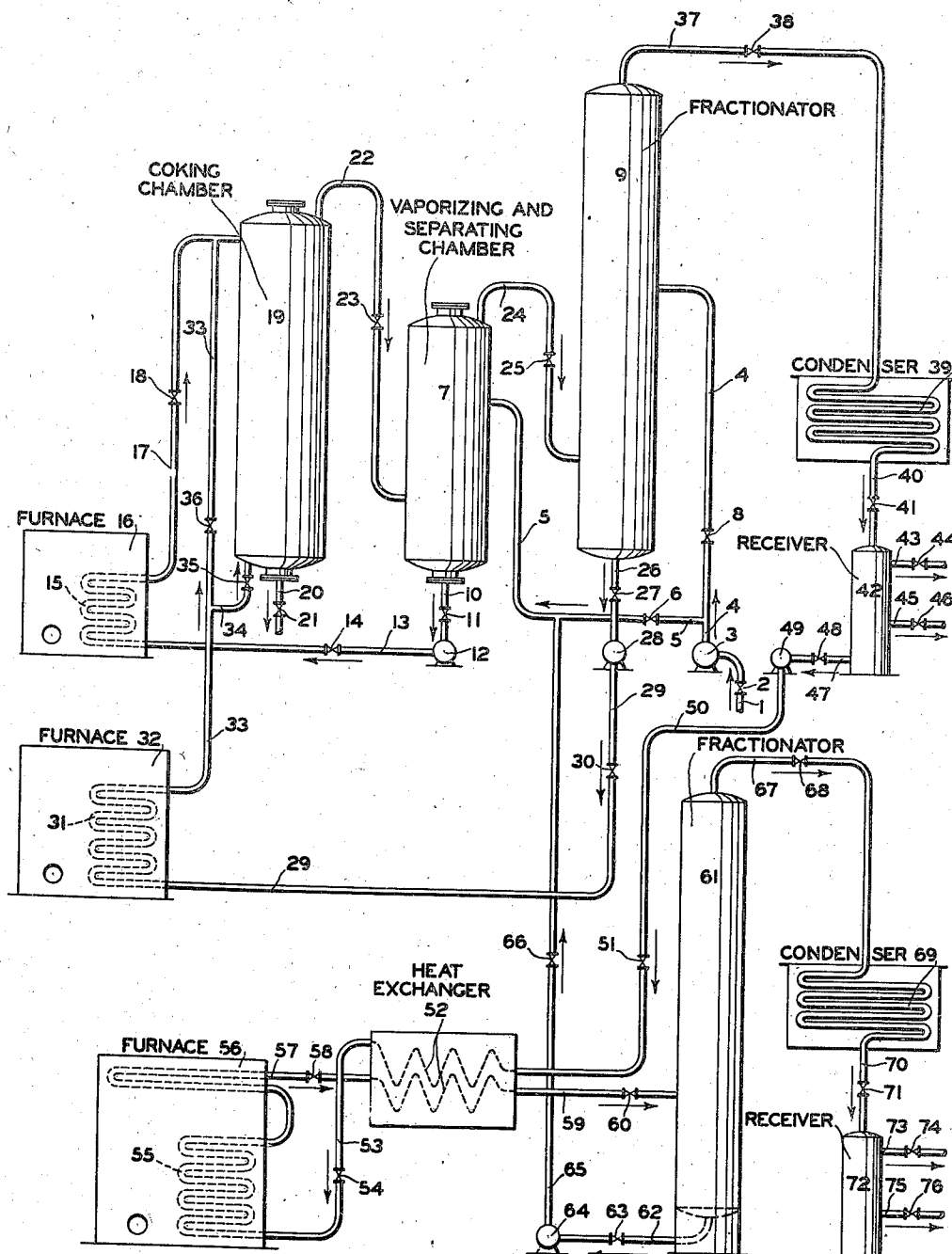
May 25, 1937.

C. H. ANGELL

2,081,348

CONVERSION OF HYDROCARBON OILS

Filed Oct. 28, 1935



INVENTOR
CHARLES H. ANGELL
BY *Lee Cary*
ATTORNEY

UNITED STATES PATENT OFFICE

2,081,348

CONVERSION OF HYDROCARBON OILS

Charles H. Angell, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application October 28, 1935, Serial No. 46,978

4 Claims. (Cl. 196—49)

This invention particularly refers to an improved process for the treatment of hydrocarbon oils which combines the steps of topping, cracking, coking and reforming in a cooperative manner to produce high yields of motor fuel of good antiknock value with minor yields of coke and gas.

While the invention is particularly advantageous as applied to the treatment of hydrocarbon oils of relatively wide boiling range, such as crude petroleum, topped crude and the like, it is also well adapted to the treatment of low-boiling, intermediate and high-boiling oils ranging from gasoline, naphtha or other light distillate to heavy residual oils.

As applied to the conversion of charging stocks containing at least an appreciable quantity of high-boiling components, the charging stock is preferably supplied to an intermediate point in the system, comprising a vaporizing and separating chamber, to which hot vaporous products from the coking zone of the system are supplied. Heat is thus supplied to the charging stock to effect vaporization of all but its high-boiling components and, at the same time, sufficient cooling of the hot vaporous products from the coking chamber is accomplished by their contact with the charging stock to effect the removal therefrom of undesirable high-boiling components including the tars, pitches and similar high coke-forming oils normally entrained in the form of liquid particles in the vaporous products from coking operations. Any high-boiling components of the charging stock remaining unvaporized in the vaporizing and separating chamber are withdrawn from this zone, together with high-boiling components removed from the vapors supplied to this zone, and the commingled high-boiling oils are passed through a heating coil, wherein they preferably are quickly heated to a high conversion temperature under non-coking conditions, and from which the heated products are supplied to the coking zone, wherein their non-vaporous high-boiling components are reduced to coke. Vaporous products from the vaporizing and separating chamber, including vaporous components of the charging stock and components of the vaporous products from the coking chamber which remain uncondensed in this zone, are subjected to fractionation for the formation of reflux condensate. The reflux condensate is subjected to independently controlled conversion conditions of cracking temperature and superatmospheric pressure and then introduced into the coking zone wherein its vaporous

and non-vaporous components are separated and the latter reduced to coke, whereby to assist the coking operation and to augment the volume of vapors supplied from the coking zone to the vaporizing and separating chamber to serve as a heat carrying medium for vaporization of the charging stock. Low-boiling products of the desired end-boiling point from the fractionating step to which vaporous products from the vaporizing and separating chamber are supplied, comprising any motor fuel components of the charging stock as well as the motor fuel conversion products resulting from the cracking and coking operations and which may also, when desired, include somewhat higher boiling oils such as heavy naphtha fractions, kerosene or kerosene distillate, pressure distillate bottoms and the like, are subjected to independently controlled conversion conditions of relatively high cracking temperature and superatmospheric pressure in a reforming state of the system for the purpose of materially improving the anti-knock value of their motor fuel components and producing high yields of good quality motor fuel from any higher boiling components. The resulting products are fractionated in a separate fractionating zone for the recovery of an overhead product comprising good quality motor fuel which is recovered from the fractionating zone of the reforming stage, and higher boiling conversion products which are returned to the vaporizing and separating chamber wherein their low-boiling components are vaporized and subjected to subsequent fractionation, together with the other vaporous products from this zone, while their higher boiling components which remain unvaporized in the vaporizing and separating chamber commingle with the other residual oils in this zone and pass therewith to further treatment and reduction to coke, as previously described.

The cooperative and interdependent nature of the various features of the invention and the advantages of the unified process of topping, cracking, coking and reforming provided by the invention will be apparent to those familiar with the cracking art from the foregoing and from the following description of the accompanying diagrammatic drawing. The drawing illustrates one specific form of apparatus in which the process of the invention may be accomplished.

Referring to the drawing, charging stock for the process, comprising any desired type of hydrocarbon oil, is supplied through line 1 and valve 2 to pump 3 by means of which it is fed through line 4 and preferably, particularly in

case it contains an appreciable quantity of high-boiling components of a high coke-forming nature, is directed through line 5 and valve 6 into vaporizing and separating chamber 7. In case the charging stock does not contain any appreciable quantity of such high-boiling material it may, when desired, be directed, in part, through valve 8 in line 4 into fractionator 9 to commingle therein with the vaporous products supplied to this zone, serving to cool and assist fractionation thereof and being thereby subjected to vaporization and fractionation therewith. It is, of course, within the scope of the invention to pre-heat the charging stock to any desired temperature below that at which any appreciable conversion thereof will occur prior to its introduction into vaporizing chamber 7 or fractionator 9. This may be accomplished, when desired, in any well known manner not illustrated in the drawing. Preferably, however, the charging stock supplied to chamber 7 is at a temperature substantially below that of the vaporous products supplied to this zone from the coking chamber.

The charging stock supplied to vaporizing and separating chamber 7 commingles therein with hot vaporous products from the coking zone of the system, which are supplied to this zone as will be later more fully described. The charging stock is thereby heated and subjected to vaporization and serves as a means of partially cooling the hot vaporous products whereby to remove therefrom high-boiling components and/or entrained heavy liquids undesirable for conversion together with the reflux condensate from fractionator 9. The non-vaporous high-boiling components of the charging stock and the high-boiling materials separated from the vaporous products from the coking zone in chamber 7 are withdrawn from the lower portion thereof through line 10 and valve 11 to pump 12 by means of which they are supplied through line 13 and valve 14 to heating coil 15.

Heating coil 15 is located within a furnace 16 of suitable form and preferably the relatively high-boiling oils supplied to this zone are quickly heated to a high conversion temperature sufficient to induce their subsequent reduction to coke without allowing them to remain in the heating coil for a sufficient length of time to permit any substantial formation and deposition of coke in the heating coil and communicating lines. The highly heated products are discharged from heating coil 15 through line 17 and valve 18 into coking chamber 19.

Coking chamber 19 is preferably operated at substantially atmospheric pressure although superatmospheric pressures up to 150 pounds, or more, per square inch may be employed in this zone, when desired. The non-vaporous high-boiling components of the heated products supplied to the coking chamber are reduced therein to substantially dry coke. The coke produced in chamber 19 may be allowed to accumulate therein until the chamber is substantially filled or until its operation is completed for any other reason following which the chamber may be cleaned and prepared for further operation. It is, of course, within the scope of the invention to employ a plurality of coking chambers similar to chamber 19, although only one is shown in the drawing. In such cases the coking chambers preferably are alternately operated, cleaned and prepared for further operation, in order to permit continuous operation of the coking stage, although two or more coking chambers may be operated si-

multaneously, when desired. Chamber 19 is provided with a suitable drain-line 20 controlled by valve 21 which may also serve as a means of introducing steam, water or other suitable cooling material into the chamber and into the bed of coke accumulated therein after operation of the chamber is completed and after it has been isolated from the rest of the system, in order to hasten cooling and facilitate removal of the coke. Hot vaporous products are withdrawn from the upper portion of the coking chamber and directed through line 22 and valve 23 into vaporizing and separating chamber 7 wherein any entrained heavy liquid particles and similar high coke-forming components are removed by contact with the relatively cool charging stock.

Vaporous products, including the vaporous components of the charging stock and the vaporous products from the coking zone remaining uncondensed in chamber 7, are withdrawn from the upper portion of this zone and directed through line 24 and valve 25 to fractionation in fractionator 9 wherein their high-boiling components are condensed as reflux condensate. The reflux condensate formed in fractionator 9 is withdrawn from the lower portion thereof through line 26 and valve 27 to pump 28 by means of which it is supplied through line 29 and valve 30 to conversion in heating coil 31.

A furnace 32 of suitable form supplies the required heat to the oil passing through heating coil 31 to subject the same to the desired conversion temperature, preferably at a substantial superatmospheric pressure, and the heated products are directed from heating coil 31 through line 33 and may be directed therefrom into coking chamber 19 at any desired point or plurality of points in this zone. Provision is made in the case here illustrated for introducing a regulated portion or all of the heated products from heating coil 31 into the lower portion of the coking chamber by means of line 34 and valve 35 or they may be directed, all or in part, through valve 36 in line 33 into the upper portion of the coking chamber.

Fractionated vapors of the desired end-boiling point are withdrawn together with uncondensable gas from the upper portion of fractionator 9 and directed through line 37 and valve 38 to condensation and cooling in condenser 39. The resulting distillate and gas passes through line 40 and valve 41 to collection and separation in receiver 42. Uncondensed gases may be released from the receiver through line 43 and valve 44. A regulated portion of the distillate collected in receiver 42 may, when desired, be withdrawn therefrom through line 45 and valve 46 to storage or to any desired further treatment, not illustrated. When, desired, regulated quantities of the distillate collected in receiver 42 may be recirculated by well known means, not illustrated in the drawing, into the upper portion of fractionator 9, to serve as a refluxing and cooling medium in this zone for assisting fractionation of the vapors and to maintain the desired vapor outlet temperature therefrom.

The distillate recovered in receiver 42 comprises any components of the charging stock within the boiling range of motor fuel as well as the motor fuel conversion products of the preceding stages of the process and it may also include, when desired, selected higher boiling oils such as, for example, naphtha, kerosene or kerosene distillate, pressure distillate bottoms and the like and, in general, comprises distillates suitable

for treatment under conditions within what may be termed the reforming range (950-1050° F. and 200 to 1000 pounds per square inch) to produce high yields of motor fuel of good antiknock value.

At least a portion if not all of this material is directed from receiver 42 through line 47 and valve 48 to pump 49 by means of which it is supplied through line 50, valve 51, heat exchanger 52, line 53 and valve 54 to heating coil 55.

It is of course, within the scope of the invention, although not here illustrated, to supply vaporous products comprising the overhead stream from fractionator 9 direct to heating coil 55 without subjecting the vapors to condensation and separating uncondensed gases from the resulting distillate supplied to the heating coil, although well known means for accomplishing this are not illustrated in the drawing. The invention also contemplates, particularly in case the vaporous products undergoing fractionation in fractionator 9 contain an appreciable quantity of materials within the boiling range of motor fuel which are of satisfactory anti-knock value, the recovery of only such materials in receiver 42 as the light distillate product of this stage of the process. In such cases somewhat higher boiling materials, including any higher boiling motor fuel components of the vapors of inferior antiknock value as well as, when desired, somewhat higher boiling materials such as naphtha, kerosene, kerosene distillate, pressure distillate bottoms and the like, are removed as condensate from one or a plurality of suitable intermediate points in the fractionator and directed by well known means, not illustrated, to heating coil 55.

The motor fuel or motor-fuel-containing distillate supplied to heating coil 55 is subjected therein to conversion conditions of cracking temperature, superatmospheric pressure and conversion time regulated to materially improve the antiknock value of the motor fuel without excessively altering its boiling range and at the same time to convert any high-boiling components of the distillate into substantial yields of good quality motor fuel. The required heat is supplied to heating coil 55 from a suitable furnace 56 and the heated products are discharged through line 57, valve 58, heat exchanger 52, line 59, and valve 60 into fractionator 61.

Heat exchanger 52 serves the purpose of preheating the distillate supplied to heating coil 55 and cooling the stream of hot conversion products discharged from this zone whereby to prevent their excessive further conversion. It will be understood, of course, that other well known means of cooling the stream of hot conversion products from heating coil 55 may be employed either alone or in conjunction with heat exchanger 52, although not illustrated, and that other cooling media may, when desired, be employed in heat exchanger 52 or this zone may, when desired, be eliminated. Preferably the superatmospheric pressure imposed upon the stream of heated products discharged from heating coil 55 is substantially reduced as they pass through valve 58 in line 57 and/or valve 60 in line 59. This pressure reduction also serves to assist cooling of the conversion products and to assist their substantial vaporization and fractionation in fractionator 61.

The components of the vaporous conversion products supplied to fractionator 61 boiling above the range of the desired final motor fuel product of the process are condensed in this zone as reflux condensate which accumulates in the

lower portion of the fractionator together with any high-boiling non-vaporous components of the conversion products supplied thereto, including residual liquid and/or heavy polymers and the like. These materials are removed from the lower portion of fractionator 61 and directed through line 62 and valve 63 to pump 64, by means of which they are directed through line 65, valve 66 and line 5 and introduced into vaporizing and separating chamber 7, wherein their non-vaporous high-boiling components commingle with the residual liquid supplied from this zone to heating coil 15 while their lower boiling components, which are vaporized in this zone, pass therefrom to fractionation in fractionator 9 together with the other vaporous products from chamber 7.

Fractionated vapors of the desired end-boiling point, comprising materials of good antiknock value within the boiling range of motor fuel and uncondensable gas, are withdrawn from the upper portion of fractionator 61 and directed through line 67 and valve 68 to condensation and cooling in condenser 69. The resulting distillate and gas passes through line 70 and valve 71 to collection and separation in receiver 72. Uncondensed gases may be released from the receiver through line 73 and valve 74. Distillate is withdrawn from receiver 72 through line 75 and valve 76 to storage or elsewhere, as desired. When desired, regulated quantities of the distillate collected in receiver 72 may be recirculated by well known means, not illustrated in the drawing, into the upper portion of fractionator 61 to serve as a refluxing and cooling medium in this zone for assisting fractionation of the vapors and to maintain the desired vapor outlet temperature therefrom.

In order to accomplish the desired results in an apparatus such as illustrated and above described, the preferred range of operating conditions for the process may be approximately as follows: The heating coil to which the reflux condensate is supplied may utilize an outlet conversion temperature ranging, for example, from 850 to 950° F. preferably with a superatmospheric pressure measured at the outlet from the heating coil of from 100 to 500 pounds, or thereabouts, per square inch. The heating coil to which the residual liquid from the vaporizing and separating chamber is supplied preferably employs an outlet conversion temperature of from 900 to 1000° F. although temperatures as high as 1050° F. may be utilized in some cases and, when desired, lower temperatures down to 800° F., or thereabouts, may be employed. The pressure employed at the outlet from this heating coil is preferably of the order of 30 to 150 pounds, or thereabouts, per square inch, superatmospheric pressure, although lower or higher pressures may be employed, when desired. The coking zone preferably employs a pressure ranging from substantially atmospheric to 150 pounds, or thereabouts, per square inch, superatmospheric pressure. The pressure employed in the coking chamber may be either substantially equalized or reduced in the succeeding vaporizing, fractionating, condensing and collecting portions of this stage of the system. The temperature employed at the outlet from the reforming coil to which the motor fuel products of the process are supplied may range, for example, from 950 to 1050° F. preferably with a superatmospheric pressure measured at the outlet from this zone of the order of 200 to 1000 pounds, or thereabouts, per square inch.

This pressure is preferably reduced in the succeeding fractionating stage to a pressure of the order of substantially atmospheric to 150 pounds, or thereabouts, per square inch, superatmospheric pressure and the temperature of the stream of conversion products entering this zone is preferably reduced to approximately 650 to 800° F.

As a specific example of the operation of the process as it may be accomplished in the apparatus illustrated and above described, utilizing as charging stock a Michigan crude of about 42° A. P. I. gravity containing approximately 40 per cent of straight-run gasoline boiling up to 400° F. having an exceptionally low antiknock value: The charging stock is supplied to the vaporizing chamber wherein it is substantially vaporized by contact with hot vaporous products from the coking zone, vaporous products from this zone being supplied to the fractionator of this stage of the system while non-vaporous residual liquid is withdrawn from the vaporizing chamber, quickly heated in a heating coil to an outlet conversion temperature of approximately 960° F. at a superatmospheric pressure, measured at the outlet from the heating coil, of approximately 150 pounds per square inch and introduced into the coking chamber which is operated at a superatmospheric pressure of approximately 60 pounds per square inch. Reflux condensate from the fractionator succeeding the vaporizing chamber to which the charging stock and vaporous products from the coking chamber are supplied is subjected in a separate heating coil to an outlet conversion temperature of approximately 940° F. at a superatmospheric pressure of approximately 350 pounds per square inch and the treated products are introduced into the coking chamber. The overhead product from this stage of the system comprises a distillate containing the straight-run gasoline recovered from the charging stock and the motor fuel conversion products of this stage of the system as well as other straight-run and cracked distillates boiling up to approximately 500° F. This material is subjected in the reforming coil to an outlet conversion temperature of approximately 980° F. at a superatmospheric pressure of about 750 pounds per square inch. The resulting heated products are cooled by indirect heat exchange with the distillate supplied to this zone and by pressure reduction to a temperature of approximately 680° F. and introduced into a fractionator operated at a superatmospheric pressure of approximately 60 pounds per square inch. Liquid products from this zone are returned to the vaporizing and separating chamber and the final motor fuel product of the process is recovered by condensation of the fractionated vapors from the last mentioned fractionating step. This operation will yield, per

barrel of charging stock, approximately 68 per cent of 400° F. end-point motor fuel having an octane number of approximately 70 by the motor method, about 35 pounds of low volatile coke and approximately 500 cubic feet of uncondensable gas.

I claim as my invention:

1. A hydrocarbon oil conversion process which comprises contacting hydrocarbon vapors with charging oil in a vaporizing zone, separately removing uncondensed vapors and unvaporized oil from said zone, distilling the unvaporized oil to coke in a coking zone, fractionating said uncondensed vapors to separate heavier from lighter fractions thereof, heating said heavier fractions to cracking temperature under pressure in a heating coil and then discharging the same into the coking zone, removing vapors from the coking zone and introducing the same to said vaporizing zone, passing at least a portion of said lighter fractions through a second heating coil and heating the same therein to higher cracking temperature than the said heavier fractions in the first-named coil, separating the resultant products into heavy and light components and introducing such heavy components into said vaporizing zone.

2. The process as defined in claim 1 further characterized in that said unvaporized oil, prior to introduction to the coking zone, is passed through an independent heating coil and heated therein to its coking temperature under pressure.

3. The process as defined in claim 1 further characterized in that said lighter fractions comprise gasoline boiling hydrocarbons which are heated in said second coil sufficiently to enhance their anti-knock value.

4. In a conversion process wherein hydrocarbon oil is distilled to coke in a coking zone, the method which comprises introducing the vapors from the coking zone to a vaporizing zone and therein contacting the same with crude petroleum containing natural gasoline, separately removing vapors and unvaporized oil from the vaporizing zone and distilling the latter to coke in the coking zone, fractionally condensing the vapors from the vaporizing zone to form a heavy reflux condensate and a lighter condensate containing low anti-knock gasoline fractions of the crude, heating the heavy reflux condensate to cracking temperature under pressure in a heating coil and then discharging the same into the coking zone, heating said lighter condensate in a second heating coil sufficiently to enhance the anti-knock value of said gasoline fractions, separating the resultant products into heavy and light components and introducing such heavy components into said vaporizing zone.

CHARLES H. ANGELL.