

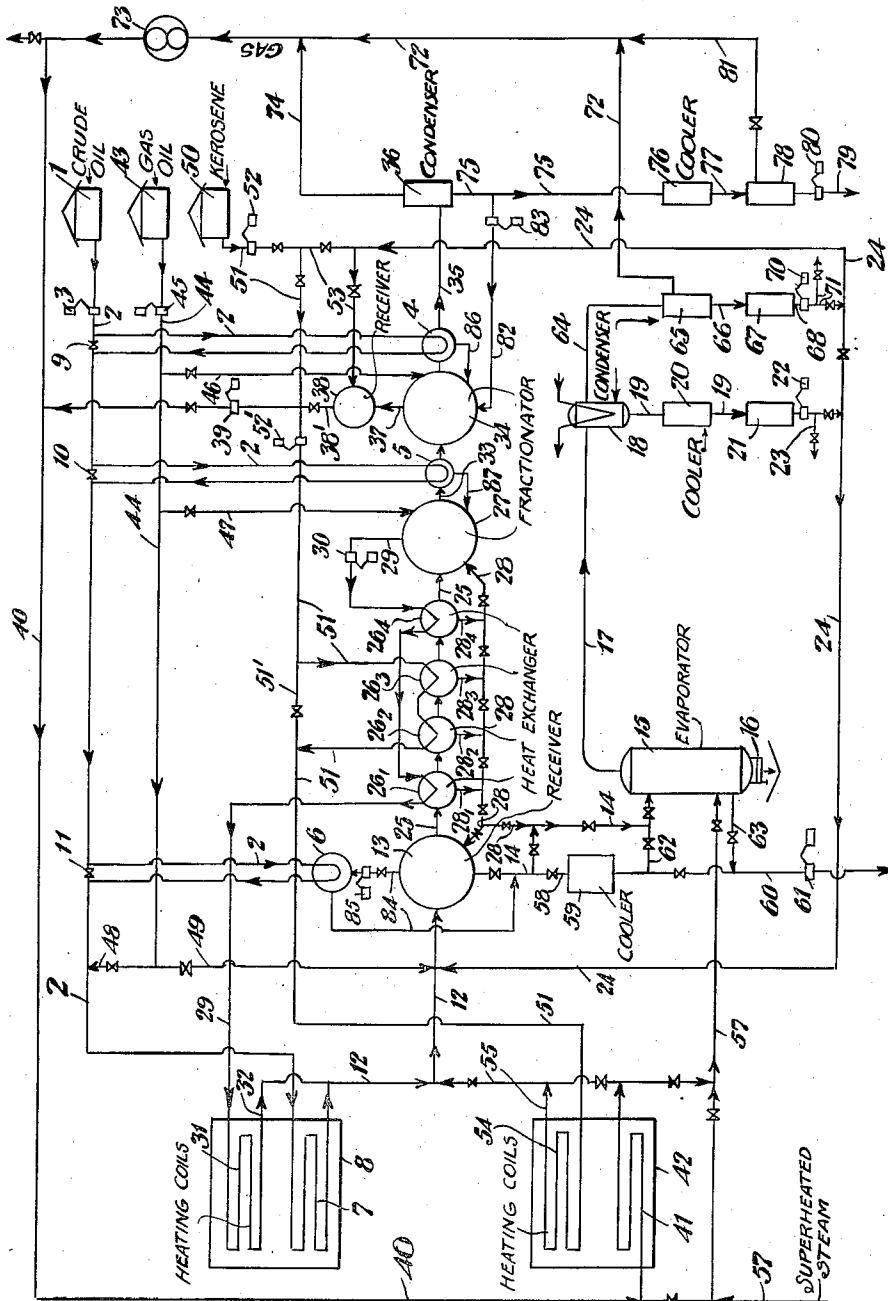
Aug. 13, 1940.

B. P. CRITTENDEN

2,210,901

PROCESS FOR CRACKING HYDROCARBON OILS

Original Filed April 4, 1932



INVENTOR
BUTLER P. CRITTENDEN

BY *Edmund G. Rorden*
ATTORNEY

UNITED STATES PATENT OFFICE

2,210,901

PROCESS FOR CRACKING HYDROCARBON OILS

Butler P. Crittenden, Shreveport, La., assignor,
by mesne assignments, to Arkansas Fuel Oil
Company, a corporation of West Virginia

Original application April 4, 1932, Serial No.
602,969. Divided and this application Febru-
ary 6, 1937, Serial No. 124,392

3 Claims. (Cl. 196—48)

This invention relates to a process of cracking hydrocarbon oils in such a manner that motor fuels are obtained which contain anti-detonating compounds. The process is applicable to crude petroleum oils and other crude hydrocarbons, such as blast furnace tar, coke house tar and hydrocarbons obtained by the destructive distillation of coal and wood, as well as the distillates and residues of such products. By this invention heat is applied to the oils or hydrocarbons in such a manner that anti-detonating motor fuels are produced together with other products which may be converted in large part into anti-detonating motor fuels. At the same time gases and other liquid products, as well as solid residues are produced.

This application is a division of application Serial No. 602,969, filed April 4th, 1932 for "Process for treating hydrocarbon oils" which in turn is a continuation in part of the applicant's earlier application Serial No. 491,101, filed October 25th, 1930 for "Combined liquid phase and vapor phase oil cracking process." The application Serial No. 491,101, discloses a combined cracking process in which vapors from the cracking operation separated out in an enlarged separating zone are passed through a plurality of fractionating zones in which a series of fractional condensates are formed of higher boiling point than the desired gasoline product. A portion of the very heavy condensate is returned to the separating zone while other reflux condensates are separately cracked in cracking coils which discharge into the enlarged separating chamber. The lighter condensate is subjected to a higher temperature than the heavier condensate. Preheated heavy oil is mixed with the transfer products from one of the coils and discharged into the enlarged separating zone in contact with the vapors and liquids therein.

An arrangement of apparatus is somewhat diagrammatically shown in the accompanying drawing by which the invention may be carried out.

In the drawing reference character 1 indicates a storage tank for crude or reduced petroleum oils, for example. A pipe line 2 in which a pump 3 is located leads from the tank 1 through heat exchangers 4, 5 and 6 to the tubular heating elements or coil 7 located in the furnace 8. Valved bypasses 9, 10 and 11 may be provided in the pipe line 2 around the heat exchangers 4, 5 and 6 so that any desired portion of the material from the tank 1 may be passed to the heating coil 7 without passing through the heat ex-

changers 4, 5 and 6. A pipe line 12 leads from the coil 7 to a receiver 13.

An outlet 14 for the heavy residues from the receiver 13 leads to an evaporator 15. An outlet 16 for coke or heavy residue is provided at the bottom of the evaporator 15.

A vapor outlet 17 extends from the upper portion of the evaporator 15 to the partial condenser 18. A condensate outlet pipe 19 leads from the lower portion of the condenser 18 through the cooler 20 to the reservoir 21. A pump 22 is provided in the outlet 23 from the reservoir 21. The outlet 23 is divided into valved branches, one of which may lead to a storage tank and the other to the pipe 24 which leads back to the receiver 13.

A vapor outlet pipe 25 leads from the receiver 13 to the first one of a series of heat exchangers of direct or indirect contact type. Four of these exchangers 26₁, 26₂, 26₃, and 26₄ are illustrated, although this number may be varied. The pipe 25 leads from the last heat exchanger of the series to a fractionating column 27 of the well-known sort. Valved outlet pipes 28₁, 28₂, 28₃ and 28₄ lead from the heat exchangers 26₁, 26₂, 26₃, and 26₄ to the pipe 28 which is provided with valves so that the material entering it can be passed to the receiver 13 or the evaporator 15 or the fractionating column 27, or selected portions may be diverted respectively to whichever of these receptacles as is desired.

An outlet pipe 29 for the heavy fraction from the fractionating column 27 is provided with a pump 30 and leads to the heating device or coil 31 through heat exchangers such as 26₄ and 26₁, for example. An outlet pipe 32 leads from the coil 31 to the pipe 12.

A vapor pipe 33 extends from the fractionating column 27 to the heat exchanger 5 and thence to a fractionating column 34 similar to the first one. A vapor pipe 35 extends from the fractionating column 34 to the heat exchanger 4 and thence to the condenser 36.

An outlet pipe 37 for condensates from the column 34 leads to a reservoir 38 from which an outlet pipe 38' provided with a pump 39 leads to a pipe 40 which leads to the heating element or coil 41 in the furnace 42.

A storage tank 43 is provided which may contain gas oil. A pipe 44 provided with a pump is also provided with branches 46, 47, 48 and 49 leading respectively to the fractionating column 34, fractionating column 27, pipe 2, and pipe 12.

A storage tank 50 is provided which may contain kerosene or heavy naphtha. A pipe 51 pro-

vided with pumps 52 and 52' leads from the tank 50 and also from line 38' and receiver 38 through the heat exchangers 26₃ and 26₂, with a valved bypass 51' around them, to tubular heating elements or coil 54 in the furnace 42. The outlet 5 from the coil 54 leads to the pipe 12. A valved branch line 53 leads from the pipe 51 and pump 52 to the reservoir 38 so that all or a portion of the material from tank 50 or pipe 10 line 24 may be passed either through line 51 or line 53.

A pipe 57 from any convenient source of superheated steam extends into the evaporator 15. The steam may be superheated to a temperature of about 1000° F. The pipe lines 40 and 55 are connected by valved connections to the steam pipe 57.

A valved branch pipe 58 extends from the outlet pipe 14 from the receiver 13 to a cooler 59. An outlet pipe 60 provided with a pump 61 extends from the cooler 59 to a storage tank (not shown) and a valved branch pipe 62 is connected from the pipe 60 to the pipe 14 near the evaporator 15. A valved pipe 63 extends from the lower portion of the evaporator 15 to the pipe 60.

A vapor outlet pipe 64 extends from the partial condenser 18 to a secondary condenser 65 from which a condensate outlet pipe 66 leads to a reservoir 67. An outlet pipe 68 provided with a pump 70 leads away from this reservoir 67. The outlet 71 of the pump is divided into valved branches one of which leads to a storage tank (not shown) and the other one to the pipe 24. An outlet pipe 72 for uncondensed gases leads 35 from the condenser 65 to a pressure pump 73 and thence to a gas storage tank (not shown).

An uncondensed gas pipe 74 also leads from the condenser 36 to the pipe 72. An outlet pipe 75 for condensates leads from the condenser 36 to the cooler 76 from which a pipe 77 leads to the reservoir 78. An outlet pipe 79 provided with a pump 80 leads away from the reservoir 78. A gas pipe 81 leads from the reservoir 78 to the pipe 72. A pipe 82 provided with a pump 83 leads from the 45 pipe 75 to the fractionating column 34.

A pipe line 84 provided with a pump 85 passes hot fuel oil from the receiver 13 through heat exchanger 6 thence to pipe 14. Pipes 87 and 86 return condensates from heat exchangers 5 and 50 4 to fractionating columns 27 and 34 respectively.

Valves are indicated in the various pipes at appropriate locations by crosses so that the apparatus can be manipulated in accordance with 55 the desired conditions of operation.

The following are given as specific examples of carrying out the invention with the arrangement of apparatus shown on the drawing, but it is to be understood that the invention is not restricted to these particular examples:

Reduced crude oil such as the fraction having an initial boiling point of about 300° F. and an end boiling point of about 850° F. from which light fractions have been distilled off is supplied 65 to the tank 1 from which it is passed through the pipe 2 by the pump 3 through the heat exchangers 4, 5 and 6 to the heating coil 7 which it reaches at a temperature of about 700° F. It passes through the coil 7 in about 4 to 5 minutes and leaves this coil at a temperature of about 70 850° F. and passes to the receiver 13 through a common pipe 12, together with material from coil 41 or 54, or both.

Within the receiver 13 there results a separation of material entering into a vapor portion

passing out through pipe 25 and a liquid portion passing out through pipe 84 and pump 85, through heat exchanger 6 into line 14. The vapors passing out through the pipe 25 are partially condensed in the heat exchangers 26₁, 26₂, 26₃ and 5 26₄ from which the condensates are withdrawn to the pipe 28. The remaining vapors pass to the fractionating column 27. The condensed residues from the column 27 having an initial boiling point of 350° F. and a final boiling point of 750° F. are 10 passed through one or more of the heat exchangers 26₁ to 26₄ and line 29 to the coil 31 which they reach at a temperature of about 700° F. They pass through this coil in about 12 to 14 minutes and leave it at a temperature of about 15 860° F. to 910° F. and thence to the receiver 13.

The vapors leaving the fractionating column 27 pass through the heat exchanger 5 and thence to the fractionating column 34. The condensate from the column 34 having an initial boiling point of about 350° F. and a final boiling point of about 700° F. passes into the receiver 38 and thence through pump 52', the line 51 and heat exchangers 26₃ and 26₂ to the coil 54 which it reaches at a temperature of about 700° F. taking 25 about 15 to 20 minutes to pass through, leaving this coil at a temperature of about 920° F. to 980° F., from which it passes to the receiver 13; or, a fraction or all of it may be diverted to the line 57 and thence to the evaporator 15. 30

Also, part of the material from the receiver 38 may be passed through pump 39 into line 40 along with some fixed gases from the process to the heating coil 41, which they reach at a temperature of about 400° F. taking about 30 minutes 35 to pass through this coil. They leave this coil at about a temperature of 975° F. to 1150° F. and pass through the pipes 55 and 12 into the receiver 13, or the efflux from the coil 41 or a portion thereof may be diverted through line 57 to 40 the evaporator 15.

The vapors leaving the fractionating column 34 pass through the heat exchanger 4 to the condenser 36. The uncondensed gases pass from the condenser 36 through the pipe 74 to the pipe 45 72 and pressure pump 73 and thence to line 40 or a gas storage tank (not shown). Condensates having an initial boiling point of 90° F. and an end point of 450° F. pass through the outlet 75 to the cooler 76 and thence to the receiver 78 from 50 which they pass to a storage tank (not shown) through the pipe 79. Uncondensed gases from receiver 78 pass through the pipe 81 to the pipe 72. A portion of the condensates leaving the condenser 36 may be passed by means of the 55 pump 83 back into the fractionating column 34.

The condensates from the heat exchangers 26₁, 26₂, 26₃ and 26₄, vary in their gravities and boiling points, the heaviest ones being from the earlier heat exchangers in the series. In actual 60 runs the boiling point of the condensates passing out through the outlet 28₁ have been found to have an initial boiling point of 440° F. and an end boiling point of 138° F., and a gravity ranging from 10° Bé. to 18° Bé.; those from 28₂ having 65 a boiling point ranging from 406° F. to 700° F. with specific gravity in range from 12° Bé. to 19° Bé.; those from 28₃ having a boiling range of 320° F. to 700° F. and a gravity range of 16° to 22° Bé. and those from 28₄ having a boiling range from 70 230° F. to 700° F. with a gravity from 16° Bé. to 24° Bé.

By manipulation of the valves in the pipe 28 such a portion of these condensates as is desired is returned to the receiver 13 and the remaining 75

portion is passed to the fractionating column 27. The portions returned to the receiver 13 are in general the heavier portions and they serve in this receiver 13 for at least two purposes. One is to absorb excess heat that had been furnished by the furnaces 8 and 42, and the other is to permit of the conversion of these condensates into materials of a desired type through admixture with the high temperature vapors from the coils heated by the furnaces 8 and 42.

The portion of the condensates from the heat exchangers which reach the pipe 28 and are passed to the column 27 are in general the lower boiling portions resulting from two sources, namely the re-boiling of the condensates diverted to the receiver 13 and the light fractions from the vapors entering the receiver 13 through line 12.

If condensates reaching the pipe 28 are found to be valueless or harmful for producing anti-detonating fuels they can be diverted by manipulation of the valves to pass either to the evaporator 15 or out of the system through the pipe 60.

With this system of apparatus, starting with reduced crude oil, the valves may be manipulated when desired in such a manner that all or a portion of the condensates reaching the pipe 28 can be passed into the evaporator 15. This may be desirable, for example, when it has been found by analyses of these condensates that so much of the hydrogen has been removed that it is inadvisable to return them to the receiver 13. When they are passed to the evaporator 15 they are therein cracked by the high temperature products received through the line 57 and as a result coke or extraordinarily heavy residues are produced and can be withdrawn through the outlet 16 while anti-detonating products and intermediate products suitable for the production of anti-detonating products are simultaneously produced and pass out through the pipe 17.

In carrying out this invention condensates leaving the condenser 18 have been found to have an initial boiling point of 288° F. and final boiling point of 800° F. and a gravity range of about 8° Bé. to about 18° Bé. The condensates from the condenser 65 had an initial boiling point of 150° F. and final boiling point of 640° F. with gravity range from about 30° Bé. to about 50° Bé.

When treating reduced crude as described above it is sometimes found desirable to introduce some gas oil from the tank 43. This may be done by passing some gas oil having an initial boiling point of 350° F. and a final boiling point of 750° F. through the pipes 46, 47 and 49 to the fractionating columns 34 and 27 and to the receiver 13 through the transfer line 12. The products from this gas oil thereby become distributed in the system, thus making it more flexible in operation.

Also, it may be advantageous to introduce into the system kerosene or heavy naphtha, or condensates from the condensers 18 and 65. The kerosene or heavy naphthas may have been obtained from crude oil which was the source of the reduced crude in the tank 1. In such cases the kerosene, etc. is introduced into the system either through the line 53 and receiver 38, or through the line 51 and heating coil 54 in such a manner that the light boiling fractions contained therein and of known poor anti-detonating characteristics will be so reacted upon by temperatures within the system that anti-detonating

compounds are produced therefrom in abundance.

Another example of carrying out the invention will be described starting with gas oil which may be introduced into the tank 43. The gas oil is passed from the tank 43 through the pipe 44 by means of the pump 45. A portion or all of this gas oil may be introduced through the pipes 45 and 47 into the fractionating columns 34 and 27. The gas oil, or the portion thereof that is not introduced into the columns 34 and 27 may be passed through the pipes 49 and 12 into the receiver 13. On the other hand, when its composition is such as to make it desirable to subject it to heat before passing into the receiver 13 it may be passed through pipes 48 and 2 and the heating coil 7 and thence through the pipe 12 into the receiver 13. Constituents in this gas oil which would make such heating desirable are heavy paraffin fractions or heavy tarry fractions which need to be heat treated before they enter the receiver 13.

The operation from the receiver 13 is similar to that already described in that condensates from the heat exchangers 26₁, 26₂, 26₃, and 26₄ may be recirculated to the receiver 13 or pass to the column 27, or to the evaporator 15, or out through the line 60, depending upon the same factors as already explained. In a similar way reduced crudes from the tank 1 and kerosene or heavy naphthas from the tank 50 may be introduced into the system when gas oil is being treated as just described, thus utilizing the reduced crude and/or kerosene for the production of additional anti-detonating compounds.

Whether reduced crude or gas oil is the main portion of the hydrocarbon that is undergoing treatment by this process, fixed gases may be passed through the pipe 40 and coil 41 into the receiver 13 or evaporator 15, and condensates from the condensers 18 and 65 may be returned through the pipes 24 and 12 to the receiver 13 or through the pipe 24 to receiver 38, or pipe line 51, or tank 50.

It has been found in operating the process that the pressure in the coil 7 should be kept at about 150 to 400 pounds per square inch; that the pressure in coil 31 should be kept at about 400 to 700 pounds per square inch; that the pressure in the coil 41 should be kept at about 100 to 300 pounds and that the pressure in the coil 54 should be kept at about 700 to 1000 pounds per square inch. The pressure in the receiver 13, fractionating columns 27 and 34 should be about 30 to 60 pounds per square inch; and the pressure in the evaporator 15 may range from about 25 inches of mercury to 60 pounds per square inch.

The gas which passes through pipe 40 may be from the system or from the gas storage tank, or it may be natural gas or industrial hydrocarbon gases.

Having thus described the invention, what is claimed as new is:

1. In the process of converting hydrocarbon oil to produce anti-detonating motor fuel in which a stream of such oil to be converted is subjected to conversion conditions of temperature and pressure in a heating and converting zone and the resulting heated products passed into a vapor liquid separating zone wherein vapors are separated from liquid products, the improvement which comprises passing the separated vapors from said separating zone through a series of at least three indirect heat exchange zones and then through a plurality of fractionating zones in series

where the vapors pass in contact with charging oil, passing the charging oil and reflux condensate from the first fractionating zone through the last and first indirect heat exchange zones of the series in heat exchange with vapors and then into said heating zone to be converted into anti-detonating products, passing condensate formed in the first indirect heat exchange zone without additional heating into said separating zone and converting a portion to anti-detonating motor fuel, independently passing a mixture of reflux condensate and charging stock from the second of said fractionating zones through an intermediate heat exchange zone of said series and independently heating the mixture to a higher temperature than that to which the oil is heated in said heating zone to convert the mixture into anti-detonating products, and passing at least a portion of the resulting heated products into said separating zone.

2. The process of converting hydrocarbon oils to produce anti-detonating motor fuel, which comprises passing a high boiling residue-containing hydrocarbon oil in a confined stream of restricted cross-section through a heating zone and heating the oil therein to a temperature of approximately 850° F., passing the resulting heated oil constituents into an enlarged separating chamber in which vapors are separated from unvaporized residual oil constituents, passing vapors produced in the cracking operation from said enlarged chamber into a tower in contact with a heavy oil charging stock, passing uncondensed

vapors from said tower into a fractionating tower in which constituents of higher point than the desired motor fuel products are condensed as reflux condensate, withdrawing unvaporized residual oil constituents from said enlarged chamber into an evaporating chamber, passing vapors from said evaporating chamber and fractionating them to produce a condensate suitable for cracking, mixing said condensate with said reflux condensate from said fractionating tower, passing the resulting mixture in a confined stream of restricted cross-section through a heating zone and heating the mixture therein to a high temperature and passing at least a portion of the resulting products while at said high temperature into contact with the unvaporized residual oil in said evaporating chamber, passing charging stock and high boiling condensate from said first-mentioned tower through a heating coil in which the mixture is heated to a cracking temperature, and mixing the resulting products with the highly heated products of said first-mentioned heating zone and thereafter introducing the resulting combined mixture into said enlarged chamber.

3. The process of converting hydrocarbon oils to produce anti-detonating motor fuel as defined by claim 2 in which a heavy condensate is produced from vapors evolved in said evaporating chamber and introducing said condensate into said resulting combined mixture passed into said enlarged separating chamber.

BUTLER P. CRITTENDEN.

CERTIFICATE OF CORRECTION.

Patent No. 2,210,901.

August 13, 1940.

BUTLER P. CRITTENDEN.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 64, for "138° F." read --738° F.--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of October, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)