

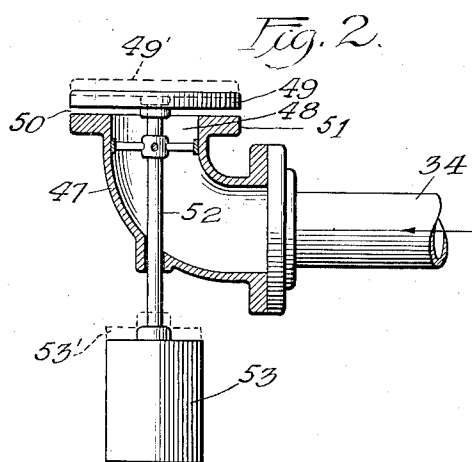
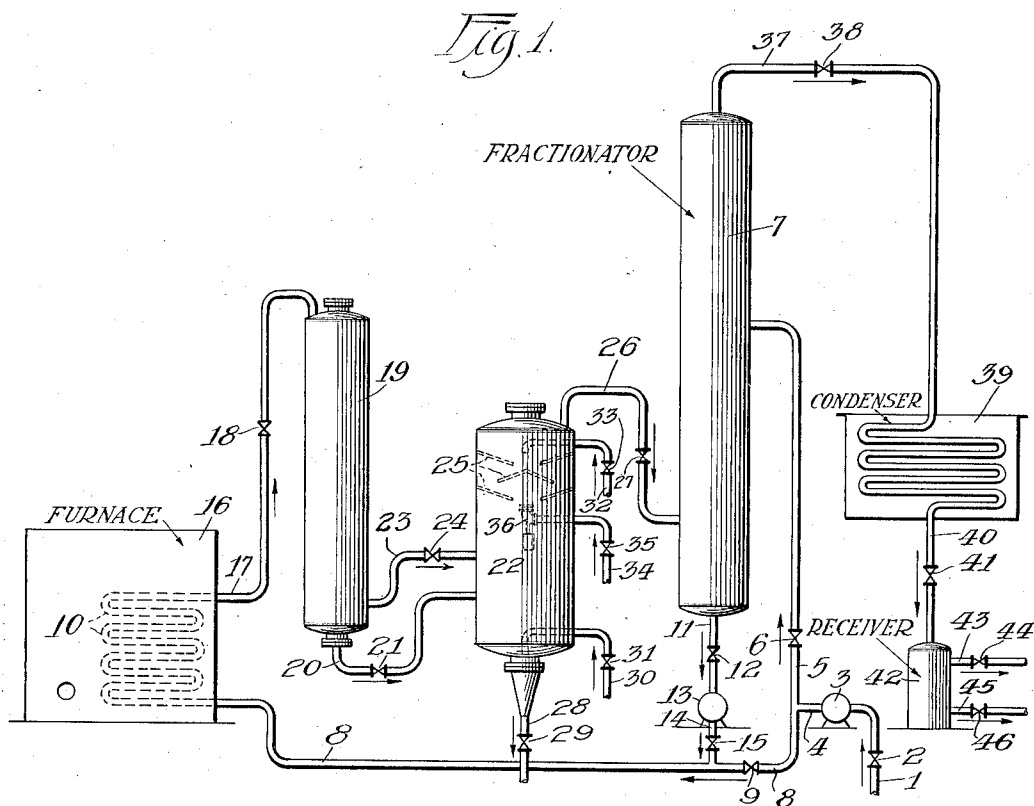
Nov. 12, 1935.

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2,020,653

CONVERSION OF HYDROCARBON OILS

Filed May 22, 1933



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UNITED STATES PATENT OFFICE

2,020,653

CONVERSION OF HYDROCARBON OILS

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Application May 22, 1933, Serial No. 672,167

1 Claim. (Cl. 196—58)

This invention refers to an improved process and apparatus for the conversion of hydrocarbon oils of the type wherein the vaporous and liquid conversion products of the process are passed from the high-pressure reaction zone into a reduced pressure vaporizing chamber in which further vaporization of the liquid conversion products is accomplished, the vapors from the vaporizing chamber being subjected to fractionation and the reflux condensate, comprising the insufficiently converted intermediate products of the cracking operation which are condensed by fractionation of the vapors, returned to further conversion in the same system. The present invention is particularly directed to improvements in this type of process for preventing the accumulation of heavy pitch-like or residual material in the reflux condensate which tend to form excessive quantities of coke when subjected to further conversion with the reflux condensate.

It is common practice in processes of the character described to withdraw all or a major portion of the vaporous conversion products from the reaction chamber with the liquid conversion products and introduce the commingled materials into the reduced pressure vaporizing chamber where the large volume of vapors relative to the volume of liquid serves to assist further vaporization of the liquid by virtue of their partial pressure effect thereon and the latent heat liberated therefrom, due to the reduction in pressure. Such processes are normally operated for the production of high yields of light liquid products such as motor fuel of high anti-knock value and minor yields of residual liquid and, under the preferred conditions of operation, a large volume of vapors is generated in the heating coil and reaction chamber relative to the volume of liquid conversion products remaining unvaporized in the reaction chamber. I have found that in many operations this practice of introducing the total vaporous and liquid conversion products into the vaporizing chamber in commingled state, causes excessive vaporization of the liquid conversion products, leaving an unnecessarily heavy residual liquid and causing the vaporization or entrainment in the vapors of heavy hydrocarbon of an asphaltic or pitchy character which, when condensed with the reflux condensate by subsequent fractionation of the vapors and returned to the heating coil of the system for further conversion, will cause the formation and deposition of excessive quantities of coke in the heating coil and/or reaction chamber, and also often results in excessively high

yields of gas at the expense of liquid products. In the present invention I avoid such excessive vaporization of the liquid conversion products by withdrawing therewith from the reaction chamber only a minor portion of the vaporous conversion products. The quantity of vapors thus withdrawn in a commingled state with the liquid conversion products is regulated to suit requirements, depending upon the degree of vaporization desired in the vaporizing chamber and may range, for example, from 5 to 40%, or thereabouts, of the total vaporous products in the reaction chamber, the remaining major portion of the vapors being separately withdrawn from the reaction chamber and preferably introduced separately into the vaporizing chamber at a point above the point of introduction of the commingled vaporous and liquid products.

It is also within the scope of the present invention to employ fractionating means in the upper portion of the vaporizing chamber which serve to remove, from the vapors leaving this zone, any entrained heavy particles of residual liquid or other heavy components of the vapors which would tend to coke upon subjection to further conversion with the reflux condensate. Rough fractionating means such as baffles assisted, when desired, by a spray or sprays of suitable refluxing material are preferred to more efficient fractionating means such as bubble trays, perforated pans or packing for this type of service as the former are not so susceptible to plugging and coking difficulties when handling heavy materials.

As a special feature of the present invention, when a spray is employed in the reduced pressure vaporizing chamber for the purpose of assisting fractionation of the vapors and, more particularly, washing the walls of the chamber, in order to prevent the accumulation of heavy residual material thereon which would tend to form coke, a special spray or wall washing device may be employed, having a weighted floating head which acts as an automatic valve regulating the size of the discharge from the spray or wall washing device, dependent upon the volume of fluid supplied to the device and serving as a means of maintaining a fairly constant discharge pressure independent of the volume of material fed through the device. It will be understood that this spray or wall washing device shown in the accompanying drawing might be advantageously employed in other parts of the apparatus or for similar service in other processes and it is not

intended to limit its application to the specific service shown and described.

Figure 1 of the accompanying diagrammatic drawing illustrates one specific form of apparatus embodying the features of the present invention and in which the process of the invention may be practiced. Figure 2 is an enlarged detail partially in cross-section of the spray or wall washing device which comprises a special feature of the present invention.

Referring to Figure 1, the raw oil charging stock to be treated is supplied through line 1 and valve 2 to pump 3 by means of which it is fed through line 4 and may pass, all or in part, as desired, either through line 5 and valve 6 into fractionator 7 or through line 8 and valve 9 direct to heating coil 10. The charging stock supplied to fractionator 7, as described, may come into direct contact in this zone with the vaporous conversion products undergoing fractionation, serving to assist their fractionation and being preheated by contact therewith. The preheated oil supplied to the fractionator collects, together with the reflux condensate, comprising the insufficiently converted components of the vapors condensed by fractionation in fractionator 7, in the lower portion of this zone from which this material is withdrawn through line 11 and valve 12 to pump 13 by means of which it is fed through line 14 and valve 15 and line 8 to conversion in heating coil 10. It will be understood that the charging stock or the combined charging stock and reflux condensate may when desired, be preheated in any well known manner not shown in the drawing, prior to its introduction into heating coil 10. As an example of one such method, the oil may pass through a heat exchanger in indirect heat exchange relation with hot vaporous conversion products of the process, passing from the vaporizing chamber to the fractionator, in which case the heat exchange serves as a means of condensing heavy components of the vapors, prior to their admission to the fractionator, so that they may be prevented from returning to the heating coil with the reflux condensate, the condensate serving a useful purpose in the operation of the process, as will be later described.

A furnace 16 of any suitable form enclosing heating coil 10 furnishes the heat required to bring the oil passing through the heating coil to the desired conversion temperature, preferably at a substantially superatmospheric pressure and the heated oil is discharged through line 17 and valve 18 into reaction chamber 19.

Chamber 19, like heating coil 10, is preferably maintained at a substantial superatmospheric pressure and although not illustrated in the drawing, it is preferably well insulated to prevent the excessive loss of heat therefrom by radiation so that conversion of the heated oil introduced into the reaction chamber, and particularly its vaporous components, may continue in this zone. In the case here illustrated the heated oil enters the upper portion of the reaction chamber and passes downward therethrough, being subjected during its passage through the reaction chamber to continued conversion under the conditions maintained in this zone. By this method of operation the vaporous conversion products are subjected to longer conversion time in the reaction chamber than the heavier liquid products, which gravitate more rapidly to the bottom of the chamber. In accordance with the features of the present invention a minor portion of the vaporous conversion products is withdrawn from

the lower portion of the reaction chamber together with the liquid conversion products, thereby insuring removal of the liquid from the reaction chamber substantially as fast as it accumulates in the lower portion of this zone and, by regulating the quantity of the vaporous products thus withdrawn with the residual liquid, the degree of vaporization to which the liquid is subsequently subjected may be regulated to suit requirements. The commingled vaporous and liquid conversion products pass from the lower portion of chamber 19 through line 20 and valve 21 into vaporizing chamber 22. The remaining vaporous conversion products not withdrawn from chamber 19 with the liquid and constituting, preferably, the major portion of the vapors is separately withdrawn from chamber 19 at any suitable point above the exit of the liquid conversion products and passes through line 23 and valve 24 from which it is separately introduced into chamber 22.

Vaporizing chamber 22 is preferably operated at substantially reduced pressure relative to that employed in chamber 19 by means of which further vaporization of the liquid conversion products introduced into this zone is accomplished, the extent of vaporization being controlled in the present case not only by the degree of pressure reduction between chambers 19 and 22 but also by the amount of vapors withdrawn with the liquid in commingled state and introduced therewith into chamber 22, as previously described. Preferably rough fractionating means such as baffle plates, indicated at 25, are provided within the upper portion of vaporizing chamber 22 to assist in separating from the vapors any entrained residual liquid or heavy components which might form excessive quantities of coke in the heating coil. The vapors pass from the upper portion of chamber 22 through line 26 and valve 27 into fractionator 7. The residual liquid remaining unvaporized in chamber 22 is withdrawn from the lower portion of this zone through line 28 and valve 29 to cooling and storage or to any desired further treatment. When desired, in order to assist in preventing coking of the residual oil in chamber 22 and restriction or plugging of the discharge line, a suitable cooling medium such as, for example, a portion of the residual liquid withdrawn from this zone and cooled to the desired temperature, by well known means not shown in the drawing, may be returned through line 30 and valve 31 to the lower portion of chamber 22 to commingle with and cool the residual liquid being withdrawn from this zone. In order to assist fractionation of the vapors in the upper portion of chamber 22 a suitable cooling and refluxing medium from any suitable source may be introduced through line 32 and valve 33. The material thus employed as refluxing medium is preferably an oil which will be substantially revaporized in chamber 22 and may comprise, for example, a portion of the raw oil charging stock or a portion of the reflux condensate from fractionator 7 or a portion of the combined feed comprising the commingled reflux condensate and raw oil supplied to heating coil 10 or any other suitable oil either from within the system or from an external source. Well known means for pumping the refluxing medium from the source of supply to line 32 are not shown in the drawing.

It is also within the scope of the present invention to wash the walls of vaporizing chamber 22 with a suitable oil, preferably of a relatively heavy

nature, to prevent the accumulation and coking of residual material thereon. The washing medium employed for this purpose is preferably an oil which will not be entirely vaporized under the conditions maintained in chamber 22 and a portion or substantially all of this material may be withdrawn from the lower portion of the chamber, together with the residual conversion product of the process. Residual liquid withdrawn from chamber 22 and cooled to the desired temperature and condensate removed from the vaporous products of the process, prior to their fractionation, in a heat exchanger not shown in the drawing but previously mentioned, are examples of oils which have been found suitable for washing the walls of the vaporizing chamber and this material or any desired oil of a similar nature may be supplied to chamber 22 through line 34 and valve 35 to be sprayed over the inner surface of the chamber walls at the desired point by means of any suitable spray or wall washing device 36, a more detailed view of one preferred form of which is shown in Fig. 2, which will be later described.

The vaporous conversion products of the process supplied to fractionator 7 are subjected to fractionation therein by the use of any suitable fractionating means, not shown, such as perforated pans, bubble trays, packing or the like or any desired combination of such means, assisted, when desired, by the introduction of all or a portion of the raw oil charging stock into the fractionator, as previously described, and/or by returning to the upper portion of the fractionator a portion of the final light distillate product of the process by well known means not shown in the drawing. In this manner the heavy components of the vapors, comprising their insufficiently converted components, are condensed as reflux condensate, the reflux condensate being returned, as already described, to heating coil 10 for further conversion.

Fractionated vapors of the desired end-boiling point pass from the upper portion of fractionator 7 through line 37 and valve 38 to condensation and cooling in condenser 39 from which the resulting distillate and uncondensable gas passes through line 40 and valve 41 to collection and separation in receiver 42. Uncondensable gas may be released from the receiver through line 43 and valve 44. Distillate may be withdrawn from this zone to cooling and storage or to any desired further treatment through line 45 and valve 46.

Referring to Figure 2, which illustrates one preferred form of spray or wall washing device 36 and is a special feature of the present invention, acting in cooperation with the other features of the invention to prevent the return of heavy coke-forming materials to heating coil 10 with the reflux condensate; a flanged L fitting 48 is attached to the end of line 34 which terminates within chamber 22, as shown in Fig. 1. The oil to be sprayed against the walls of the chamber is directed upward from the outlet end 48 of the L against a blind flange 49, which serves to spread the liquid out in a horizontal plane and direct it through the circumferential opening 50 between flanges 49 and 51 and by means of which the liquid is directed in the form of a cone-shaped spray against the inner surface of the walls of the vaporizing chamber. Devices of this general character have been previously employed, in which the relative position of flanges 49 and 51 is fixed by means of suitable spacers between the

flanges. This fixes the area of the opening between the flanges corresponding to opening 50 in Figure 2, thereby causing a variation in the pressure at which the oil is sprayed against the walls of the chamber with variations in the quantity of the oil. It will be apparent that this method of operation permits proper functioning of the spray device with only slight variations in the volume of oil which it is designed to handle but, in case it is found necessary to appreciably increase the volume of material sprayed against the walls of the chamber, the increased pressure at which it is discharged against the walls will cause excessive splashing and defeat the purpose of the larger volume of wall washing material, while, with an appreciably decreased volume the spray may fail to contact the walls of the chamber at the proper point. In the present invention, provision is made for discharging a variable quantity of fluid from the spray or wall washing device with only a slight and permissible variation in the discharge pressure. This is accomplished by the use of a floating flange 49, which acts as an automatic valve, attached to a slidable shaft 52, to the opposite end of which a predetermined fixed weight 53 is attached whereby constant pressure is exerted against the stream of oil supplied to the device. Any increase in the volume of oil tends to increase the pressure within the device and lifts the weight to a point where the increased size of opening 50 permits the passage of the greater volume of fluid, the decreased velocity and friction through opening 50 tending to lower the pressure within the device, thereby compensating for the tendency toward increased pressure and serving to maintain the discharge pressure from the device substantially uniform. The dotted lines 49' and 53' illustrate how the weight 53 and valve or flange 49 may be raised when an increased volume of liquid is supplied through line 33.

The process is preferably operated at a conversion temperature, measured at the outlet from the heating coil, within the range of 900 to 1050° F., or thereabouts, and with a superatmospheric pressure, measured at this point, of from 100 to 500 pounds, or more, per square inch. A substantially equalized or somewhat reduced superatmospheric pressure within substantially this same range is preferred in the reaction chamber and a substantially reduced pressure ranging, for example, from 100 pounds or thereabouts per square inch down to substantially atmospheric pressure is employed in the vaporizing chamber. The pressures in the fractionating, condensing and collecting portions of the system may be substantially equalized with or somewhat reduced relative to the pressure in the vaporizing chamber.

As a specific example of the operation of the process of the present invention utilizing as charging stock a mid-continent fuel oil of about 24° A. P. I. gravity, the charging stock and reflux condensate is subjected to a conversion temperature measured at the outlet from the heating coil of approximately 930° F., at a superatmospheric pressure of approximately 350 pounds per square inch. The vaporizing chamber is maintained at a reduced pressure of approximately 50 pounds per square inch which is substantially equalized in the succeeding portions of the system. About 20% of the vaporous conversion products are withdrawn from the reaction chamber with the residual liquid and supplied to the vaporizing chamber in commingled state while

the remaining 80%, or thereabouts, are separately withdrawn from the lower portion of the reaction chamber and introduced into the vaporizing chamber above the point of introduction 5 of the residual liquid thereto. A portion of the combined feed comprising raw oil charging stock and reflux condensate is sprayed over the walls of the vaporizing chamber in the manner herein disclosed, the spray being located beneath rough 10 fractionating means in the upper portion of this zone and a portion of the reflux condensate is introduced into the upper portion of the vaporizing chamber to serve as refluxing medium over the fractionating means therein. A regulated 15 portion of the residual liquid product of the process withdrawn from the lower portion of the vaporizing chamber is returned thereto after being cooled for the purpose of cooling the residual oil passing from the chamber and prevent the 20 accumulation of coke in the lines and valves through which it passes. This operation may yield, per barrel of charging stock, about 58% of 400° F. end-boiling point motor fuel having an anti-knock value equivalent to an octane number 25 of approximately 75, about 36% of Bunker B. fuel oil and about 450 cubic feet of uncondensable gas. Due to the absence of heavy high coke-forming yields in the reflux condensate this operation may be extended over a period of several 30 weeks without necessitating a shut-down, due to the deposition of coke in the heating coil.

I claim as my invention:

35 A hydrocarbon oil cracking process which comprises heating the oil to cracking temperature under pressure while flowing in a restricted

stream through a heating zone, discharging the heated oil into the upper portion of an enlarged vertical reaction zone maintained under cracking conditions of temperature and pressure, passing both vapors and unvaporized oil downwardly 5 from the upper to the lower portion of the reaction zone, removing the unvaporized oil and a minor portion of the vapors as a mixture from the bottom of the reaction zone at a rate adequate to prevent any appreciable liquid accumulation in the reaction zone, separately removing 10 the major portion of the vapors, unadmixed with unvaporized oil, from the lower portion of the reaction zone but at a point above the bottom thereof, introducing said mixture withdrawn 15 from the bottom of the reaction zone into a separating zone maintained under lower pressure than the reaction zone and separating the same therein into vapors and residue, introducing said major portion of the vapors into the separating 20 zone above the point of introduction of said mixture thereto whereby to prevent contact of these vapors with said unvaporized oil while combining them with the vapors separated in the separating zone, roughly fractionating the combined 25 vapors in the upper portion of the separating zone to remove high coke-forming components therefrom, then removing the combined vapors from the separating zone and further fractionating the same to condense insufficiently cracked 30 fractions thereof, subjecting resultant reflux condensate to further cracking treatment in the process, and finally condensing the fractionated vapors.

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