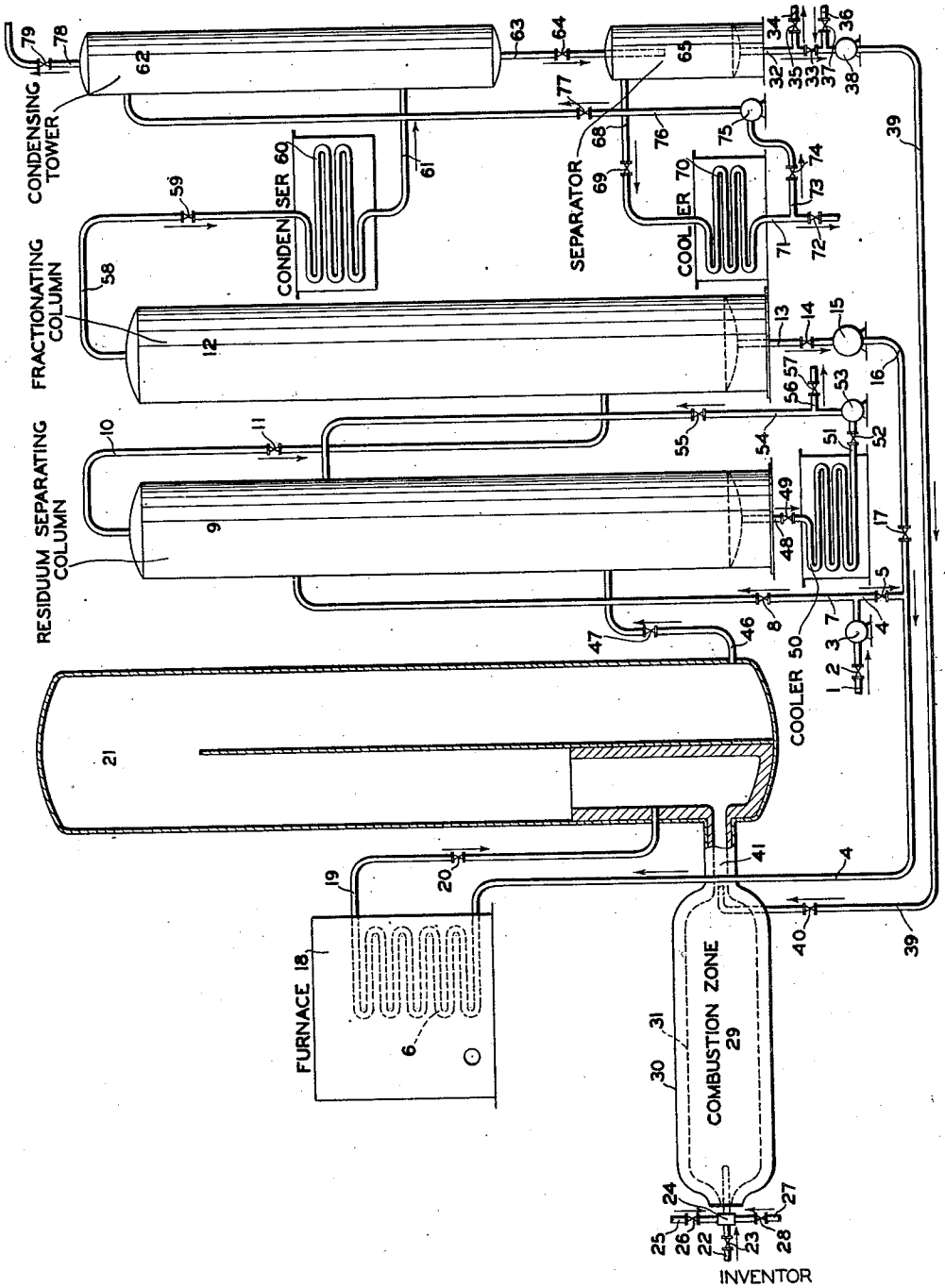
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CONVERSION OF HYDROCARBON OILS

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INVENTOR

ROBERT PYZEL

BY Frank L. Belknap

ATTORNEY

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CONVERSION OF HYDROCARBON OILS

Robert Pyzel, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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The present invention is directed to improvements in the type of cracking process and apparatus wherein hydrocarbon oil vapors are brought into direct contact and commingle with hot combustion gases to effect conversion of the oil for the production of high yields of lower boiling hydrocarbons such as motor fuel of high antiknock value.

In processes of the type mentioned, the combustion gases, which serve as a heat carrying medium for the main cracking reaction by direct contact and commingling with the oil to be treated, are preferably substantially devoid of excess air or free oxygen in order to avoid combustion or excessive oxidation of the hydrocarbon oil undergoing treatment. However, high combustion temperatures result from burning any ordinary type of fuel without great excess air and when fresh combustion products generated under such conditions are brought into direct contact with hydrocarbon oil, the reaction will result in the formation of major yields of gas and an excessive quantity of coke with a minor production of liquid products. It is the purpose of the present invention to reduce and control the temperature of the heat-carrying medium by introducing controlled quantities of water into the fresh hot combustion products, prior to their admixture with the hydrocarbon oil vapors to be treated. This results in the generation of superheated steam from the water thus introduced, which serves to dilute and cool the combustion gases to the desired temperature. There are additional advantages in the introduction of water into the heating medium, e. g., it has been found to exert a beneficial action upon the operation and the oil undergoing conversion, as well as upon the conversion products, especially the overhead distillate, rendering refining of the same much easier and resulting in the production of a sweeter and more stable light distillate product of better color, as compared with the product from the same type of process not utilizing water and/or steam. Furthermore, less carbon and pitchy matter appears to be produced under these conditions and the overhead product of the process is richer in hydrocarbons and higher in B. t. u. value and recovery of gasoline therefrom is rendered easier and more economical.

Water has been found more suitable as a diluent and cooling medium for the fresh combustion products than non-condensable gases, such as relatively cool spent combustion gases or a mixture of the same with the gaseous products of the process which have previously been used in cracking processes of the general character described, as a smaller volume of cooling medium is necessary for a given reduction in temperature when water is employed due, in part, to the latent heat of vaporization required for conversion of the water into steam. This reduces the volume of vapors handled for a given charging capacity, thereby making it possible to reduce the size of equipment required for a given capacity or vice versa, to increase the capacity of a given apparatus. The size of the scrubbing equipment required for recovery of entrained liquid products from the gaseous products of the process is particularly beneficially affected when water is utilized as the cooling medium for the combustion gases as the steam generated may be condensed to water and separated from the gases, prior to the scrubbing stage, whereas when relatively cool spent combustion products are employed as the cooling medium, the total volume of fixed gases is greatly increased. Also the cost, character and capacity of the equipment required for injecting water, as well as the operating costs of such equipment, are very much less than those required for compressing and injecting gaseous cooling media into the system.

The accompanying diagrammatic drawing illustrates one specific form of apparatus embodying the features of the present invention and wherein the process of the invention may be practiced. However, it is not intended to limit the invention to the specific form of apparatus illustrated.

Referring to the drawing, raw oil charging stock for the system is supplied through line 1 and valve 2 to pump 3 from which it may be fed through line 4 and valve 5 to heating coil 6. When desired, a portion or all of the raw oil charging stock, instead of passing directly to heating coil 6, may be diverted from line 4 through line 7 and valve 8 into the residuum separating column 9, wherein it is preheated by direct contact with the hot ascending cracked vapors, serving to assist in cooling the vapors sufficiently to condense and separate therefrom the heavy ends which form the residual liquid conversion product of the process. All or a major portion of the raw oil may be vaporized by contact with the hot conversion products in column 9 but, by introducing the raw oil into column 9, a means is afforded of separating therefrom any heavy ends which it is not desired to subject to the relatively severe conversion conditions in the mixing and conversion stages of the process, while the lower boiling portions of the raw oil, desirable as cracking stock for the major crack-

ing operation of the process, are vaporized in column 9, passing therefrom through line 10 and valve 11 to condensation in the fractionator or reflux separating column 12, to be withdrawn therefrom, together with the insufficiently converted components of the cracked vapors condensed in this column as reflux condensate, through line 13 and valve 14 to pump 15 by means of which the oil is directed through line 16, valve 17 and line 4 to heating coil 6.

Heating coil 6 is located in the furnace 18 of any suitable form capable of furnishing the heat required to bring the oil to the desired temperature under the desired pressure conditions. In all cases the oil is heated in heating coil 6 to a temperature sufficient to insure substantial subsequent vaporization and usually a relatively mild conversion temperature of the order of 850 to 950° F. is employed at the outlet from the heating coil, although any conversion which may take place in this zone is incidental to the main cracking reaction subsequently accomplished by contact between the hydrocarbon vapors and the heat carrying medium from the combustion zone. Any desired pressure ranging from substantially atmospheric to a superatmospheric pressure of several hundred pounds per square inch may be employed in the heating coil and the heated oil is discharged therefrom through line 19 and valve 20 into the mixing and reaction chamber 21.

Simultaneous with the operation above described, fresh combustion gases are generated in combustion zone 29. Any suitable fuel such as oil, gas or pulverized solid fuel is supplied to a burner 24 of any suitable form through line 22 and valve 23 while air, in an amount approximate to that theoretically required for complete combustion, is supplied through line 25 and valve 26, care being exercised to introduce no substantial amount of excess air to the combustion zone for the reasons already given. Combustion zone 29, in the particular case illustrated, comprises a metal shell 30 with suitable refractory lining 31, which is capable of withstanding super-atmospheric pressures up to 150 pounds, or thereabouts, per square inch so that combustion may, when desired, be accomplished at super-atmospheric pressure, permitting the use of a similar pressure in the mixing and reaction chamber 21. Since unusually high flame-burst temperatures result from the use of little or no excess air and super-atmospheric pressure, steam supplied through line 27 and valve 28 to burner 24 may be introduced to the combustion zone with the combustible fuel-air mixture in an amount sufficient to reduce the temperature in the combustion zone to below the fusion point of the refractory lining 31. Water is introduced through line 39 and valve 40 into direct contact with the hot combustion gases leaving combustion zone 29, serving to cool the combustion gases to the desired temperature, prior to their contact with the hydrocarbon oil vapors from heating coil 6. The resulting mixture of steam and combustion gases passes through duct 41 into the mixing and reaction chamber 21, preferably entering this zone at a temperature of the order of 1400 to 2200° F. I have found that any desired temperature within this range may be obtained by the regulated introduction of water in an amount sufficient to generate 25 to 50 percent by volume of the total heat carrying medium, comprising combustion gases and steam. As a means of comparison it should be remembered that the amount of steam ordinarily formed as a product of combustion when burning hydrocarbon fuel is of the order of only 12 percent by volume of the total combustion products.

Intimate contact and mixture of the commingled steam and combustion gases with the heated hydrocarbon vapors is accomplished in chamber 21 and the mixture is subjected at its attained temperature to a conversion time in this zone, preferably of not less than about one minute or more than about three minutes.

The mixture of conversion products, including the combustion gases and steam passes from chamber 21 through line 46 and valve 47 into the residuum separating column 9, wherein the heavy residual conversion products are condensed and separated from the vaporous conversion products, raw oil being supplied, when desired, to this zone as already described, to serve as a medium for assisting cooling and condensation of the heavy conversion products. The residual liquid separated from the vaporous conversion products in column 9 may be withdrawn from its lower portion through line 48 and valve 49 to cooling coil 50 from which it is withdrawn through line 51 and valve 52 to pump 53, passing therefrom through line 54 from which it may be directed, all or in part, to storage or to any desired further treatment through line 56 and valve 57. When desired, a portion of the cooled residual oil may be recirculated through valve 55, in line 54, to column 9 to serve as a cooling and refluxing medium.

Vapors remaining uncondensed in column 9, including all of the vaporous conversion products supplied thereto, of lower boiling point than the residual liquid and, when raw oil is introduced into column 9, all of the raw oil with the exception of any heavy components boiling within the range of the residual conversion products, pass, together with the combustion gases and steam, from the upper portion of column 9 through line 10 and valve 11 to fractionation in the fractionating or reflux separating column 12, wherein the heavy components of the vapors supplied to this zone, boiling above the range of the desired light distillate product of the system, are condensed as reflux condensate to be returned, as already described, to heating coil 6 or residuum separating chamber 9.

The fractionated vapors, combination gases and steam pass from the upper portion of column 12 through line 58 and valve 59 to condenser 60, wherein steam and a large portion of the hydrocarbon distillate product of the process is condensed, passing, together with the process gases, through line 61 into condensing tower 62, wherein further condensation to recover all but a minor portion of the desired light distillate product of the process is accomplished. The condensed hydrocarbon distillate and water passes from the lower portion of tower 62, through line 63 and valve 64 to separator 65, from the lower portion of which the water is withdrawn through line 32 while the distillate is withdrawn from the upper portion of the separator through line 68 and valve 69 to cooler 70, from which it is discharged through line 71 and valve 72 to storage or to any desired further treatment.

Preferably a subatmospheric temperature, sufficiently low to condense sustantially all of the liquids available by condensation from the vaporous products of the process, is employed in column 62 and, as an example of one means of accomplishing the desired degree of cooling in tower 62, a portion of the distillate from receiver

65, cooled to the riquired subatmospheric temperature in cooler 70, is diverted from line 71 through line 73 and valve 74 to pump 75 by means of which it is returned through line 76 and valve 77 to tower 62, where it may come into direct contact with the vapors and gases in this zone, serving to cool them to the required temperature for effecting condensation of the desired products. Uncondensed gases including both hydrocarbon and combustion gases are withdrawn from the upper portion of tower 62 through line 78 and valve 79 and may, when desired, be supplied to a suitable scrubber or absorber, not shown, of any well known form, for the recovery of additional light liquid products which may, when desired, be blended with the distillate recovered from separator 65 to form the total light distillate product of the system.

Water separated from the distillate in receiver 65 and withdrawn therefrom through line 32, as already indicated, may be removed, all or in part, from the system through line 34 and valve 35 but preferably the major portion of the water recovered passes through valve 33, in line 32, to pump 38, by means of which it is returned through line 39 and valve 40 to combustion zone 29. In this manner a continuous cycle of direct contact cooling medium is set up within the system, this system comprising one of the features of the invention. The amount of water recovered in separator 65 will normally be in excess of that required for the cycle inasmuch as it comprises the water condensed from the total steam in the process gases which include some steam which may be introduced through burner 24, as described, as well as that formed as a product of combustion when a hydrogen-containing fuel is employed. In starting the operation before the process has reached equilibrium conditions, water may be introduced to the system by means of line 36 containing control valve 37. It is to be understood that water may be introduced into the system from any outside source but that the water obtained from the receiver is preferred as it is distilled and is free from scale forming materials and pumping costs are reduced since the pressure differential may be less from the receiver to the system than from an outside source.

As already indicated, the temperature to which the hydrocarbon oil to be treated is heated and vaporized, prior to its contact with the mixture of combustion gases and steam, is preferably within the range of 850 to 950° F. and this heating is preferably accomplished at a substantial super-atmospheric pressure within the range of 100 to 500 pounds, or thereabouts, per square inch although, when desired, lower temperatures or pressures, or both, may be employed. The heat carrying medium preferably enters the mixing and reaction chamber at a temperature, as already stated, of from 1400 to 2200° F., or thereabouts, and in an amount sufficient to maintain the resulting mixture of combustion gases, steam and hydrocarbon oil vapors at a temperature within the range of 900 to 1100° F. in the mixing and reaction chamber. The conversion time afforded the mixture in the reaction chamber is preferably not less than one minute and not more than approximately three minutes and, although not illustrated in the drawing, the reaction chamber is preferably well insulated to prevent the excessive loss of heat by radiation and maintain the mixture within or not appreciably below the temperature range given during its time in this zone. Any desired pressure ranging from substantially atmospheric to a super-atmospheric pressure of 150 pounds, or thereabouts, per square inch may be maintained in the combustion zone and in the succeeding mixing and reaction chamber. The pressure employed in the succeeding portions of the system may be substantially equalized with or somewhat reduced relative to the pressure employed in the reaction chamber.

As a specific example of one operation of the process of the present invention, the charging stock is a 33° A. P. I. gravity gas oil which is supplied to the residuum separating chamber of the system, raw oil vaporized in the residuum separating chamber and subsequently condensed with the reflux condensate in the fractionator of the system is supplied, with the reflux condensate, in the proportion of about two parts of reflux to one part of raw oil condensate, to a heating oil wherein it is subjected to a relatively mild conversion temperature of approximately 900° F. at a super-atmospheric pressure of about 300 pounds per square inch, at which temperature it is introduced into the mixing and reaction chamber, which is maintained at a superatmospheric pressure of about 100 pounds per square inch. Simultaneously combustion gases are generated from the combustion of fuel oil with no appreciable excess air at a superatmospheric pressure of about 100 pounds per square inch. Sufficient steam is introduced into the combustion zone with the fuel to cool the fresh combustion products and prevent the rapid deterioration of the walls of the combustion zone. Additional water is introduced into the combustion gases, prior to their entrance into the mixing and reaction chamber, to bring the temperature of the resulting mixture to about 1500° F., about one part, by volume, of steam being required in the mixture to two parts of combustion gases. The heat carrying medium is then commingled with the hydrocarbon oil vapors with a resulting temperature of about 980° F. for the mixture which is subjected to a conversion time of approximately two minutes in the reaction chamber.

An operation such as above described may yield, per barrel of charging stock, about 64 percent of distillate containing about 94 percent of 50° A. P. I. gravity motor fuel having an antiknock value equivalent to an octane number of approximately 84. The residual oil produced amounts to about 17 percent of the charging stock and is of exceptionally good quality with respect to suspended coke and B. S., as compared with residual oil from similar operations not utilizing water or steam as a cooling medium. The remaining 19 percent, or thereabouts, based on the charging stock, is chargeable to gas, loss and a negligible amount of coke. The gasoline produced is a sweeter and more stable product and has a better color than that produced by similar methods without the use of steam and is more easily refined with less treating losses.

As a further comparison between the operation above described and similar operations wherein combustion gases are utilized as the heat carrying medium without the addition of water or steam there is, in either type of operation, about 0.3 gallon of desirable condensable hydrocarbons per thousand cubic feet of process gases, still entrained in the gases after they have been subjected to scrubbing by ordinary means. Since the process of the present invention reduces by about one-third the volume of uncondensable gases in the heat carrying medium (about one-third of

the heat carrying medium being steam) there is a corresponding reduction in the final process gases and a corresponding reduction in the loss of desirable liquid products entrained therein.

I claim as my invention:

1. A process for the conversion of hydrocarbon oils which comprises heating an oil to a relatively mild conversion temperature in a heating coil and introducing it in vaporous form into a mixing and reaction chamber, simultaneously generating fresh combustion products and introducing thereto controlled quantities of water, commingling the resulting mixture of combustion gases and steam with the hydrocarbon oil vapors in the mixing and reaction chamber wherein the hydrocarbon oil vapors are subjected at their attained temperature to a predetermined conversion time, withdrawing the resulting products from the reaction and mixing chamber and separating the residual material therefrom, subjecting the vaporous products to fractionation for the removal therefrom of insufficiently converted components which are condensed as reflux condensate, returning the reflux condensate to the heating coil for further treatment, subjecting the vaporous materials remaining uncondensed by fractionation to condensation, separating the resulting products into hydrocarbon oil distillate, water and gaseous products and commingling water condensate recovered from the operation with the freshly generated combustion gases, as heretofore described.

2. A process for the conversion of hydrocarbon oils which comprises heating an oil to a conversion temperature of 850 to 950° F. at a super-atmospheric pressure of from 100 to 500 pounds, per square inch in a heating coil and introducing it in vaporous form into a mixing and reaction chamber, simultaneously burning hydrocarbon fuel at super-atmospheric pressure, without appreciable excess air but with the controlled introduction of steam into the combustion zone with the fuel, introducing water into the freshly generated combustion products in quantities sufficient to produce a temperature of the order of 1400 to 2200° F. in the resulting mixture of combustion gases and steam, commingling the mixture with the hydrocarbon oil vapors in the mixing and reaction chamber at a super-atmospheric presure of the order of 50 to 150 pounds per square inch, subjecting the hydrocarbon oil vapors admixed with the heat carrying medium to a conversion time of from one to three minutes in the reaction chamber, withdrawing the resulting conversion products and heat carrying medium from the reaction chamber, commingling therewith raw oil charging stock for the process in a residuum separating zone and separating residual materials from the resulting mixture, subjecting vaporous materials from the residuum separating zone to fractionation, for the removal therefrom of insufficiently converted components which are condensed as reflux condensate, returning the reflux condensate to the heating coil for further treatment, subjecting the vaporous materials remaining uncondensed by fractionation to condensation, separating the resulting products into hydrocarbon oil distillate, water and gaseous products and commingling a portion of the water condensate recovered from the operation with the freshly generated combustion gases, as heretofore described.

3. In the cracking of hydrocarbons by contact with hot combustion gases, the improvement which comprises generating the gases by burning fuel at a point of combustion out of contact with the hydrocarbons to be cracked, injecting water in liquid condition into the gases beyond the point of combustion in an amount sufficient to cool the gases to below 2200° F. but insufficient to cool the gases to below the cracking temperature of the hydrocarbons, and subsequently commingling the resultant mixture of combustion gases and steam with the hydrocarbons in sufficient quantity to crack the latter, condensing the cracked vapors and steam and separating the oil condensate from the water condensate, and utilizing such water condensate to cool the combustion gases as aforesaid.

ROBERT PYZEL.