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CONVERSION OF HYDROCARBON OILS

Filed Jan. 28, 1933

2 Sheets-Sheet 1

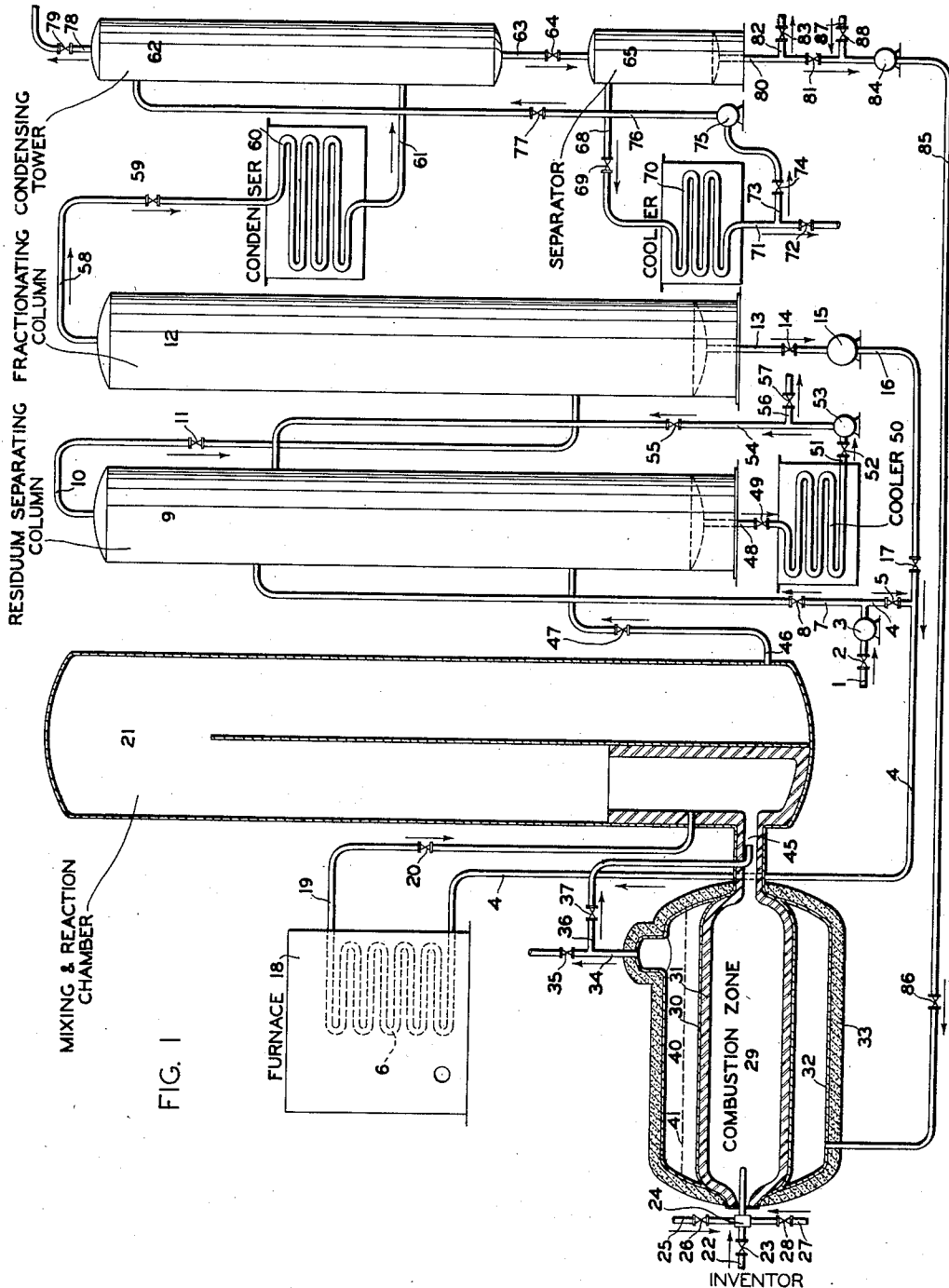


FIG. 1

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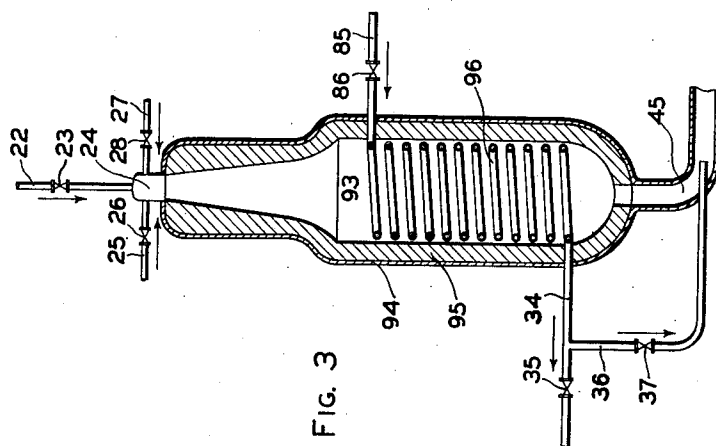


FIG. 3

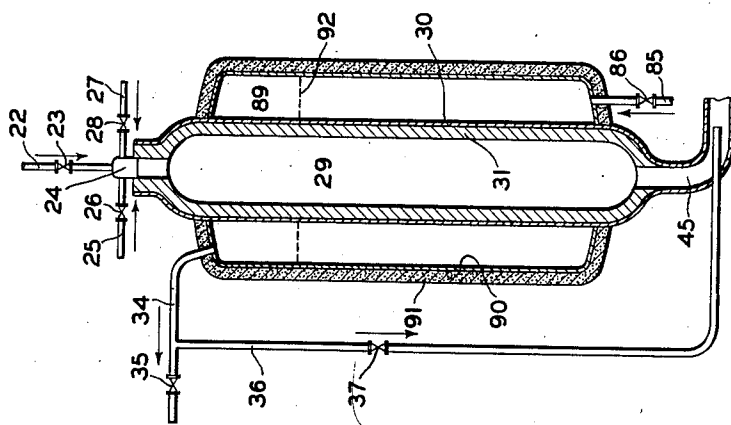


FIG. 2

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CONVERSION OF HYDROCARBON OILS

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8 Claims. (Cl. 196—67)

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 commingled 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 anti-knock 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, preferably are substantially devoid of air or free oxygen in order to avoid combustion or excessive oxidation of the hydrocarbon oil undergoing treatment. It is also preferable to effect conversion of the oil at super-atmospheric pressure which necessitates generation of the combustion gases which comprise the heat carrying medium at superatmospheric pressure. The high flame-burst temperatures resulting from combustion of ordinary fuels under such conditions are destructive to any known metals or refractories readily available at the present time and the walls of the combustion zone are therefore subject to rapid deterioration. Furthermore, when fresh combustion products are brought into direct contact with hydrocarbon oil without being first diluted and cooled with large quantities of excess uncondensable gases or other suitable cooling medium, 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.

The present invention provides an improved method and means of controllably cooling both the combustion gases and the walls of the combustion zone, thereby obviating the use of non-condensable diluents in a heat carrying medium and special mixing devices to overcome localized overheating of the hydrocarbon vapors and also greatly prolonging the life of the apparatus. Moreover, by controlling the temperature of the heat carrying medium, prior to its contact with the hydrocarbon vapors, an additional means is provided for positively controlling the conversion conditions to which the hydrocarbon vapors are subjected.

Primarily the invention comprises bringing the hot combustion gases, during their generation into indirect contact with water which is thereby converted into steam, with or without substantial super-heating, and all or a portion of the steam generated is then utilized to further cool the combustion gases to the desired temperature, by

introducing the steam in controlled amounts into direct contact and allowing it to intimately commingle with the combustion gases, prior to their contact with the hydrocarbon vapors to be treated. This not only provides a positive method and means of cooling the walls of the combustion zone to prevent their rapid destruction but also provides for the recovery of at least a portion of the heat lost by the combustion products in the form of latent and sensible heat in the steam generated. This heat recovery is accomplished, in part, by the use of such steam as a component of the heat carrying medium and, as a matter of further heat economy within the process, steam generated in excess of that required as a direct cooling medium for the combustion gases may be utilized for the operation of pumps, compressors, etc., for the preheating of oil or vaporization of fuel or similar uses for which steam is ordinarily required in the operation of the process.

Steam is more suitable as a diluent and cooling medium for the combustion gases than non-condensable gases, such as relatively cool spent combustion gases or a mixture of the same with gaseous products of the process, which have previously been used in cracking process of the general character described. The use of steam greatly reduces the total volume of non-condensable gases in the heat carrying medium, thereby facilitating the recovery of liquid hydrocarbons from the final process gases and vapors, due to the ease with which the steam is condensed and the smaller volume of condensable hydrocarbons which may be entrained by the decreased amount of non-condensable gases. The relatively small amount of non-condensable gases resulting from the operation of the process of the present invention also permits the use of scrubbing equipment of decreased size and capacity for the recovery of entrained liquids from the gaseous products. The use of steam, in the manner described, as a cooling medium, also eliminates costly equipment of large capacity required for the compression and injection of gaseous cooling media into the system, thereby reducing both equipment and operating costs. In addition there are other advantages in the introduction of steam into the heat carrying medium, for example, it has been found that a beneficial action is exerted upon the operation and the oil undergoing conversion, as well as upon the conversion products by contacting steam with the oil undergoing treatment. This is particularly evidenced in the quality of the light distillate product of the

process which is rendered sweeter, more stable and of better color than a product of the same type of process not utilizing steam. Furthermore, it is apparent that less carbon and pitchy matter are produced under the conditions of operation of the present invention and the gaseous products of the process are richer in hydrocarbons and of greater calorific value, as compared with similar operations not utilizing steam.

Fig. 1 of the accompanying diagrammatic drawings illustrates one specific form of cracking apparatus embodying the features of the present invention. Figs. 2 and 3 illustrate certain modified forms of that portion of the apparatus wherein the combustion gases of controlled temperature are generated. The drawings are given solely for the purpose of more clearly illustrating the features of the invention and not intended to limit it to the specific forms of apparatus shown.

Referring first to Fig. 1, 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 vaporous products of the process, 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 cracking 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 a 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 in the mixing and reaction chamber 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 de-

scribed, a suitable fuel, such as oil, gas or pulverized solid fuel or a mixture of such fuels, is supplied through line 22 and valve 23 to a burner 24 of any suitable form, to which a suitable vaporizing and combustion-supporting medium, such as air, is supplied through line 25 and valve 26. Line 27 and valve 28 is provided for the introduction of steam which may, when desired, be introduced in relatively small regulated amounts to assist in reducing the flame-burst temperature in the combustion zone and prevent fusion and slugging of the refractory lining of this zone. The combustible mixture is supplied to combustion zone 29 wherein the hot combustion gases to be utilized in the process are generated.

In the case here illustrated, the combustion zone is constructed to operate at superatmospheric pressure and comprises a metal shell 30 lined with suitable refractory material 31 and the combustion zone is surrounded by a vaporizing zone 40, the outer walls of which comprise a metal shell 32 covered with suitable insulating material 33, and this zone is also constructed to operate at substantial superatmospheric pressure. Water may be supplied to the vaporizing zone through line 35 and valve 36 and a suitable liquid level, indicated by line 41, may be maintained in the vaporizing zone. The steam generated is withdrawn through line 34 and the excess, if any, over that required for further cooling of the combustion gases passes through valve 35 to be used in any desired manner, such as, for example, the operation of the various pumps utilized in the process, for the vaporization of fuel supplied to the combustion zone, for preheating the raw oil or in any other suitable manner, not illustrated in the drawings. However, at least a portion of the steam generated in vaporizing zone 40 is directed from line 34 through line 36 and valve 37 to be directly commingled with the combustion gases, prior to their contact with the hydrocarbon oil vapors in the mixing and reaction chamber. In the case illustrated the steam is commingled with the combustion gases in duct 45 leading from the combustion zone to the mixing and reaction chamber.

The combustion gases from combustion zone 29, after being cooled by indirect contact with the cooling medium in the surrounding vaporizing zone 40 and further, by the direct introduction of steam, as described, preferably to a temperature of the order of 1400 to 2200° F., pass through duct 45 into mixing and reaction chamber 21 to which the hydrocarbon oil is also supplied in vaporous state, as already described.

The mixture of conversion products, and heat-carrying medium, 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 and from the raw oil introduced into this zone, when residual materials are contained in the raw oil, 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 de-

sired, 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.

The fractionated vapors, combustion 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 are 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 pass 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 83 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 substantially 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 required 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 80, as already indicated, may be removed, all or in part, from the system through line 82 and valve 83. Preferably, however, at least a portion of the water recovered passes through valve 81, in line 80, to pump 84 by means of which it is returned through line 85 and valve 86 to the vaporizing or steam generating zone 40. In this manner a continuous cycle of cooling medium is set up within the system and comprises one of the features of the invention. The amount of water recovered

from the process will normally be in excess of that required, in the form of steam, as cooling medium to be commingled with the combustion gases as it comprises the water condensed from the total steam in the process gases which includes any steam which may be introduced through burner 24, as described, as well as that formed as a product of combustion, when hydrogen-containing fuel is employed. In starting the operation, before the process has reached equilibrium conditions, and when water, in excess of that recovered, is desired as an indirect cooling medium around the combustion zone and for the generation of excess steam, water may be introduced to the system by means of line 87 containing control valve 88. It will be understood that water may be supplied to the system from any desired external source but water recovered, as described, from within the system is preferred as it is a distilled product substantially free from calcareous or other scale-forming materials and, in addition, pumping costs may be reduced since the pressure differential may be less between receiver 65 and chamber 40 than between chamber 40 and the external source of supply.

Fig. 2 of the attached drawings illustrate a modified form of the steam generating zone illustrated in Fig. 1. Combustion zone 29, as well as the burner arrangement, etc., are the same in both figures except that in Fig. 2 the combustion zone is vertically instead of horizontally disposed. The vaporizing zone or steam generating zone 89, to which water is supplied through line 85 and valve 86, comprises a metal shell 90 which may be covered with suitable insulating material, as indicated at 91. In the case of the apparatus illustrated in Figure 2, the liquid level, which is indicated by line 92, does not entirely cover the walls of the combustion zone. In this manner the steam generated by the heat recovered from the combustion gases may be super-heated before it is withdrawn from the vaporizing zone through line 34. Although Fig. 2 shows the combustion zone fired from the top in such a manner that the hottest combustion gases impart heat to the steam in the upper portion of vaporizing zone 89, the combustion zone may, when desired, be fired from the bottom so that the steam will be super-heated by the partially cooled combustion gases. In the apparatus shown in Figure 2 as well as that shown in Fig. 1 the partially cooled combustion gases pass from combustion zone 29 through duct 45 to the mixing and reaction chamber and succeeding portions of the cracking system, not shown in Fig. 2, and steam, diverted from line 34 through line 35 and valve 37, is introduced into direct contact with the combustion gases passing through duct 45 in order to bring the heat carrying medium to the desired temperature, prior to its contact with the hydrocarbon oil vapors.

Still another form of combustion zone and steam generator is shown in Fig. 3 of the accompanying diagrammatic drawings. In this case, as in Fig. 2, the combustion zone is vertically disposed and is fired by means of the same type of burner arrangement illustrated in Figs. 1 and 2 and described in connection therewith. Combustion zone 93 comprises a metal shell 94 lined with suitable refractory material 95 and the cooled combustion gases pass, as in Figs. 1 and 2, through duct 45 into the mixing and reaction chamber, not shown in Fig. 3. In Fig. 3, instead of providing a steam generating zone surrounding

the combustion zone, a steam generating coil 96 is provided within the combustion zone and is preferably located adjacent to the refractory walls 95 of this zone in order to reduce the temperature of the refractory surface of these walls and, in this type of apparatus, a relatively small regulated quantity of steam is preferably supplied to the combustion zone through burner 24, as previously described, in order to reduce the flame-burst temperature of the combustion products and assist in protecting the refractory walls, particularly in that portion of the combustion zone where the walls are not protected by heating coil 96. Water is supplied to heat coil 96 through line 35 and valve 36 and the steam is discharged therefrom through line 34 passing, in part, when desired, through valve 35 for use, as already described, within the process or elsewhere. However, at least a portion of the steam generated in coil 96 passes through line 36 and valve 37 into duct 45, to commingle with the partially cooled combustion gases from combustion zone 93 for the purpose of reducing the temperature of the heat carrying medium to the desired degree.

As already indicated, the temperature to which the oil is heated and vaporized, prior to its direct contact with the heat carrying medium in the mixing and reaction chamber, is preferably within the range of 850 to 950° F. and preferably this heating is accomplished at a super-atmospheric pressure which may range, for example, from 100 to 500 pounds or more per square inch although, when desired, lower pressures or temperatures, or both, may be employed. The commingled combustion gases and steam, comprising the heat-carrying medium, preferably enter the mixing and reaction chamber at a temperature, as already stated, of from 1400 to 2200° F., or thereabouts, and the heat carrying medium and hydrocarbon vapors are preferably admixed in such proportion that the temperature of the resulting mixture is within the range of 900 to 1100° F. The conversion time afforded the mixture in the reaction chamber is preferably not less than about one minute and not more than approximately three minutes, and although not illustrated in the drawings, the reaction chamber is preferably well insulated to prevent the excessive loss of heat by radiation and maintain the mixture within or not greatly 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 more per square inch may be maintained in the combustion zone and in the succeeding mixing and reaction chamber, a substantial super-atmospheric pressure being preferred. The pressures 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 of the many operations of the process of the present invention which may be practiced in an apparatus such as illustrated and above described, the charging stock is a 36° A. P. I. gravity mid-continent gas oil which is subjected, together with reflux condensate from the reflux separating column, to a temperature of about 900° F. at a super-atmospheric pressure of about 200 pounds at the outlet from the heating coil, prior to its introduction into the mixing and reaction chamber. The combustion gases in the combustion zone are cooled by indirect contact with the water in the

steam generating zone to a temperature of approximately 1800° F. and a sufficient quantity of steam is then commingled with the combustion gases to bring the temperature of the resulting heat carrying medium to approximately 1500° F., prior to contact of the heat carrying medium with the hydrocarbon oil vapors in the mixing and reaction chamber. The resulting temperature in the reaction chamber is in the neighborhood of 1000° F., and a super-atmospheric pressure of approximately 100 pounds per square inch is employed in this zone and is substantially equalized in the succeeding portions of the system. This operation may yield, per barrel of charging stock, about 62 per cent of distillate containing over 90 per cent of motor fuel having an antiknock value equivalent to an octane number of approximately 85. Residual oil of about 10° A. P. I. gravity amounting to about 18 per cent of the charging stock may also be produced, the remaining 20 per cent, or thereabouts, based on the raw oil charged to the system, being chargeable, principally, to uncondensable gas and loss.

I claim as my invention:

1. In a process for the conversion of hydrocarbon oil wherein the oil is commingled with hot combustion gases generated without appreciable excess air, the improvement which comprises generating the combustion gases in a combustion zone whose major portion is surrounded with water, which is thereby converted into steam, and commingling regulated quantities of the steam with the partially cooled combustion gases for the purpose of further cooling them, prior to commingling them with the hydrocarbon oil.

2. In a process for the conversion of hydrocarbon oil wherein the oil is heated and introduced, substantially in vaporous state, into direct contact with hot combustion gases, generated without appreciable excess air, the improvement which comprises generating the combustion gases in a combustion zone whose major portion is surrounded with water, which is thereby converted into steam, and commingling controlled amounts of the steam with the partially cooled combustion gases for the purpose of further cooling them, prior to their contact with the hydrocarbon oil vapors.

3. In a process for the conversion of hydrocarbon oil wherein the oil is heated to a relatively mild conversion temperature at super-atmospheric pressure thereby forming vapors and the vapors then commingled with hot combustion gases substantially devoid of free oxygen whereby the hydrocarbon oil vapors are heated to a higher conversion temperature, the improvement which comprises partially cooling the combustion gases, during their generation, by indirect heat exchange with water, which is thereby converted into steam, and commingling controlled amounts of the steam with the partially cooled combustion gases for the purpose of further cooling them to the desired temperature, prior to their contact with the hydrocarbon oil vapors.

4. In a process for the conversion of hydrocarbon oil wherein the oil is heated, the heated oil introduced, substantially in vaporous state, into a mixing and reaction chamber and combustion gases, generated within a combustion zone, without appreciable excess air, are commingled at superatmospheric pressure with the hydrocarbon oil vapors, the improvement which comprises circulating water adjacent at least the major portion of the walls of the combustion zone in indirect heat exchange with the combustion

tion gases whereby to partially cool the combustion gases and the walls of the combustion chamber and convert the water into steam and then commingling regulated quantities of the steam generated with the partially cooled combustion gases whereby a heat carrying medium of controlled temperature, comprising a mixture of steam and combustion gases, is formed to effect pyrolytic conversion of the hydrocarbon oil by subsequent direct contact therewith.

5. A process for the conversion of hydrocarbon oil which comprises heating an oil to a relatively mild conversion temperature in a heating coil thereby forming vapors and introducing the vapors into a mixing and reaction chamber, simultaneously generating fresh combustion products substantially devoid of free oxygen and partially cooling them during generation by indirect contact with water from which steam is thereby generated, commingling regulated quantities of the steam generated with the partially cooled combustion gases whereby a heat carrying medium of controlled temperature, comprising a mixture of combustion gases and steam, is produced, commingling the heat carrying medium with the hydrocarbon oil vapors in the mixing and reaction chamber whereby the oil is subjected at conversion temperature to a predetermined conversion time, withdrawing the resulting products from the mixing and reaction chamber and separating the residual material therefrom, subjecting the cracked vapors 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 vaporous materials remaining uncondensed by fractionation to condensation, separating the resulting products into hydrocarbon oil distillate, water and gaseous products and returning water recovered from the operation to indirect contact with the combustion gases for the generation of steam.

6. A process for the conversion of hydrocarbon oils which comprises heating an oil to a conversion temperature of 850 to 950° F., at a superatmospheric pressure of from 100 to 500 pounds per square inch in a heating coil thereby forming vapors and introducing the vapors into a mixing and reaction chamber, simultaneously generating combustion gases substantially devoid of free oxygen in a combustion zone maintained at super-atmospheric pressure and cooling the walls of the combustion zone and the combustion gases, during their generation, by indirect contact with water, from which steam is there-

by generated, further cooling the combustion gases by the introduction thereto of controlled quantities of the steam generated, whereby a heat carrying medium of controlled temperature, comprising a mixture of combustion gases and steam, is produced, commingling the heat carrying medium at a temperature of from 1400 to 2200° F., and a superatmospheric pressure of from 50 to 150 pounds per square inch with the hydrocarbon oil in the mixing and reaction chamber, subjecting the resulting mixture to a conversion time of the order of one to three minutes at a temperature of from 900 to 1100° F., 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 the 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 a hydrocarbon oil distillate, water and gaseous products and returning water recovered from the operation to indirect contact with the combustion gases for the generation of steam.

7. In the cracking of hydrocarbon oil by direct contact with combustion gases, the improvement which comprises generating the combustion gases by the burning of fuel in a combustion zone whose major portion is surrounded with water, commingling resultant steam with the combustion gases and thereafter contacting the mixture of combustion gases and steam with the oil to be cracked.

8. In the cracking of hydrocarbon oil by direct contact with combustion gases, the improvement which comprises generating the combustion gases by the burning of fuel in a combustion zone whose major portion is surrounded with water, commingling resultant steam with the combustion gases, and thereafter contacting the mixture of combustion gases and steam with the oil to be cracked, condensing the cracked vapors and steam and separating the oil condensate from the water, and recycling the latter into indirect heat exchange relation with the combustion gases being generated.

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