My invention relates to a process for the treatment of petroleum hydrocarbons to produce therefrom primarily lower molecular weight hydrocarbons by thermal decomposition and synthesis of the hydrocarbons undergoing treatment and, more particularly, so to conduct such treatment as to produce not only lower molecular weight gasoline-like hydrocarbons suitable for use as a motor fuel of high anti-knock qualities, but in addition to secure an increased yield of hydrocarbons of the aromatic series including naphthalene, benzol, xyloil and toluol.

When fuel is burned with no excess of air, the temperature of combustion is between 3000° F. and 4000° F. Such temperatures are too high for the proposed thermal treatment productive of the desired products and accordingly this temperature must be brought down considerably in order to produce most efficiently the greatest yield of the desired products.

In my co-pending applications Serial No. 598,503 filed March 12, 1932, now Patent No. 2,046,504, issued July 7, 1936, to Maurice B. Cooke, and Serial No. 598,504, filed March 12, 1932, now Patent No. 2,046,505, issued July 7, 1936, to Maurice B. Cooke, I have disclosed a process for the thermal treatment of petroleum hydrocarbons for the production of lower molecular weight gasoline-like hydrocarbons by the direct commingling of hot combustion gases with the hydrocarbons being treated. I have shown therein that the temperature of from 3000° F. to 4000° F. obtained by the generation of these gases may be lowered to a temperature more favorable for the treatment of the hydrocarbons by tempering or cooling the gases with steam which may be condensed in a prefractionating condensing zone with considerable advantages being obtained in permitting a reduction in the size of fractionating and recovery equipment over that required where normally incondensible inert tempering gases are employed. In addition, I have shown that the combustion gases may be tempered in part by passing oil to be heated for various ancillary related steps of the process in indirect heat exchange with the hot gases. In particular, I have disclosed: the indirect heating of a relatively heavy petroleum oil to prepare it for a topping operation; the indirect heating of the topped oil to enable the formation of hydrocarbon vapors for subsequent direct thermal treatment with the tempered combustion gases; and the indirect heating of a cooled condensate of the thermally treated vapors to effect distillation and permit subsequent fractionating of the distillate vapors for ultimate recovery of the desired products.

The character of the liquid ultimately produced as a desired product from petroleum hydrocarbons as disclosed in the processes of the foregoing applications, is essentially dependent upon the time, temperature and pressure conditions employed.

It is an object of my invention to produce low molecular weight hydrocarbon products including liquid aromatic products such as naphthalene, benzol, xyloil and toluol from heavier petroleum hydrocarbons by the direct thermal treatment of such heavier hydrocarbons with hot combustion gases under closely controlled conditions of time, temperature and pressure.

It is another object of my invention to extract the desired products from the mixture of thermally treated hydrocarbons and combustion gases with fractionating and separating equipment no greater in size than is normally employed for the extraction of such products from thermally treated petroleum hydrocarbons not admixed with combustion gases.

It is another further object of my invention to effect in the same thermal treating zone, a secondary or final conversion into desired products, of such hydrocarbons lower boiling than the desired products as are recovered from the products of the thermal treating operation and recycled to the treating zone.

It is another object of my invention to coordinate the thermal treatment of petroleum hydrocarbons occurring when such hydrocarbons are directly commingled with hot combustion gases, with distillation of the liquid petroleum hydrocarbons for the production of hydrocarbon vapors to be treated, and the tempering or cooling of the combustion gases to the desired treating temperature.

It is a further object of my invention to secure an increased yield of desired liquid aromatic and low molecular weight hydrocarbon products by close control of the character and quantity of the recycle oil returned to the primary thermal treating zone for retreatment with fresh oil.

Other and further objects of my invention will appear from the following description and the appended claims.

The accompanying drawing which forms part of the Instant specification and is to be read in conjunction therewith is a schematic showing in elevation with parts in section of one form of apparatus capable of carrying out the process of my invention.
In general, I propose to generate hot gases of combustion by the admixture of combustible gases with no excess of oxygen and the burning of such mixture. The resultant temperature of from 3000° F. to 4000° F. being too high for the efficient thermal treatment of hydrocarbon vapors to be subsequently mixed with the gases, I propose to reduce this temperature partially by the addition of a cooler inert gas such as steam and partially by passing the gases in indirect heat exchange with cooler liquid petroleum hydrocarbons.

Crude oil is passed in indirect heat exchange with the hot combustion gases whose temperature is thereby lowered while the reduced crude is heated, the heated crude then being subjected to a topping operation in which the depth of the cut may vary within wide limits. The topped crude, together with light and heavy recycle oil, forms the charge to a vaporizing coil through which it passes in indirect heat exchange with the gases, the heated oil then being flashed into vapors. Preferential heating in the vaporizing coil is locationally in the hottest portion of the zone through which the combustion gases are being passed. In view of the quantity of oil passing through this coil, it may be necessary to employ external heating means auxiliary to the combustion gases to secure the desired vaporization.

The vapors resulting are directly commingled in a mixing zone with the combustion gases which, on entering this zone, have been tempered or cooled to a temperature of from about 1500° F. to about 2500° F., the temperature preferably being from about 1800° F. to about 2000° F. The mixture of hydrocarbon vapors and combustion gases, which for convenience I shall hereinafter call the reactant, passes through a primary treating zone of a length sufficient to provide the time element necessary to effect decomposition of heavier hydrocarbons of the reactant into lighter hydrocarbons into desired aromatic products. The reactant is preferably subjected to the action of the hot combustion gases in this primary zone for a period of from about one second to about three seconds, depending upon whether the temperature of these gases is at 2500° F. or a lower temperature of around 1500° F. respectively.

The reactant passes from the primary treating zone into a secondary treating, or soaking zone, wherein the reactant is cooled to a temperature of from about 1050° F. to about 1800° F. by the spraying into the reactant of a cooler recycle oil substantially completely vaporizable at the resulting temperature, or by indirect heat exchange with a cooler oil. In this secondary treating zone the recomposition and synthesis of hydrocarbons proceeds to form not only lower molecular weight gasoline-like hydrocarbons, but by reason of the lower temperature, a substantial quantity of hydrocarbons of the aromatic series including naphthenalene, benzol, toluol and xyol. The time of reaction in this zone will vary from about one second to about ten seconds, depending upon whether the temperature of the reactant is about 1800° F. or 1050° F. respectively.

From the secondary treating zone, the reactant passes into a combined quenching and separating zone wherein a cooler hydrocarbon oil is sprayed into the reactant whose temperature is quickly reduced to around 600° F. to 700° F. At the same time and as the result of this quenching operation, the heavy polymers, tars, gums and fuel oil present are condensed and are then withdrawn from the quenching zone and the process. The uncondensed portion of the reactant is then cooled further by passing in indirect heat exchange with clean water which is utilized for initially tempering the combustion gases, and as process steam for stripping in the main fractionator. The further cooling of the reactant takes place in a series of separate zones in which the heavier hydrocarbons of the reactant are condensed and from which they may be selectively withdrawn. A portion or all of the heavy condensate formed in these separate condensing zones is returned to the quench zone as reflux for end point control and another portion of this heavy condensate is passed to the main fractionating tower. The uncondensed lower boiling portion of the reactant which may be, for example, a 200° F. to 250° F. end point naphtha plus all lighter hydrocarbons and the combustion gases, is further cooled by indirect heat exchange to condense preferably substantially all the normally liquid hydrocarbons. The water resulting from condensation of steam in the mixture is withdrawn from the separating zone to which the cooled reactant is passed and the liquid hydrocarbons of the reactant are regeneratively reheated by passing in indirect heat exchange with the reactant and then by passing in indirect heat exchange with the hot combustion gases, the liquid reactant being raised thereby in a distillation coil to a temperature sufficient to permit vaporization at the substantially atmospheric pressure under which the process is conducted. On issuing from this distilling coil, the reactant passes directly to the main fractionator.

In the main fractionator relatively heavy cracked gas oil is withdrawn as a bottom product, light gas oil is withdrawn as a sidestream, and the overhead product of the fractionator consists of lower molecular weight gasoline-like hydrocarbons and/or hydrocarbons of the aromatic series including naphthenalene, benzol, toluol and xylol which are cooled, condensed and removed from the accumulator-separator as the desired distillate product. The uncondensed portion of the fractionator overhead which will include saturated and unsaturated hydrocarbons of the paraffin series such as propane-propylene, butane-butylene, ethane-ethylen, as well as some hydrogen, methane and entrained gasoline-like hydrocarbons is combined with the uncondensed portion of the reactant, compressed and the light condensate resulting separated from the gases uncondensed by the compression and cooling. The light condensate is recycled to the flash tower vaporizing coil as part of the charge to that coil, is vaporized, and then admixed with the hot combustion gases for further thermal treatment and the production of additional desired lower molecular weight hydrocarbons, particularly aromatics, since a large percentage of unsaturates will be present in this recycle condensate.

The gases remaining uncondensed after the compression and cooling operation are passed to an absorber wherein they are contacted under pressure with cooled light absorber oil withdrawn as a sidestream from the main fractionator, the unabsorbed gases particularly the combustion gases and methane being released to a fuel gas main and the rich absorption oil being recycled to the vaporizing coil as part of the charge to?
that oil for further thermal treatment by the hot combustion gases.

Referring now more particularly to the drawing, I charge a crude by means of a pump 1 across the pipe 2, heat exchangers 3 and 4, heating coil 5 and transfer pipe 6 into fractionating tower 7.

Fuel gas is drawn by the compressor 8 through the pipe 9 adapted to take fuel gas from the recycle tail gas main 10 or valved fuel gas inlet pipe 11, and discharged through pipe 12 into the fuel gas supply tank 13. The fuel gas is discharged from the supply tank 13 through the valved pipe 14 into the mixing chamber 15 wherein it is mixed with air fed through a valved pipe 16 in quantities sufficient to produce complete combustion of the gas without excess of oxygen. The combustible mixture forms a plume with surface combustion on the granules of refractory material 17 to form hot combustion gases in the combustion chamber 18. These hot gases will be at a temperature of from 3000° F. to 4000° F. which is too high for the efficient thermal treatment of hydrocarbon vapors in accordance with my process.

The temperature of these gases may be reduced in part by admixing therewith cooler steam fed into the gases through the valved pipe 19 at a point 20 in the combustion chamber 18 where complete combustion of the gas fuel air mixture has taken place. The steam thus supplied will act as an additional heat carrier medium with the combustion gases, and has the advantage of being condensable and separable from the combustion gases and hydrocarbon vapors at normal atmospheric conditions of temperature and pressure. For this reason I am enabled to reduce the quantity of vapor to be passed through the main fractionating tower. The combustion gases partially cooled by the steam, if such cooling is desired at this time, flow into the chamber 21 and across the tubes forming the heating coil 5. The relatively cool oil passing through the heating coil 5 assists in reducing the temperature of the combustion gas and is at the same time heated. These gases are prepared to fractionation in the fractionating tower 7.

Obviously, the heating effected in the coil 5 may be supplemented by an external tube still (not shown) and if no topping operation is necessary or if the cooling effect of the coil 5 on the combustion gases is not deemed necessary, this coil may be dispensed with entirely.

In the fractionating tower 7 the vapors formed are fractionally separated and the overhead products of desired end point flow through vapor pipe 22, vapor heater exchanger 8 and water cooler 23 into accumulator 24 from which reflux is returned through pipe 25 by pump 26 to the fractionating tower 7 for end point control of the fractionator overhead. Any steam condensed in a vapour temperature is withdrawn from the accumulator 24 through the valved pipe 27 and the distillate is discharged to storage through the valved pipe 28.

The topped crude accumulating in the base of the tower 7 is withdrawn therefrom through a pipe 29 by means of pump 30 and passes through heat exchanger 31 and water cooler 32 into a topping coil feed tank 33. All or part of the oil in the pipe 29 may be diverted therefrom by suitable manipulation of a valve 34 in the line 29 thus causing the oil to flow through a pipe 35 in which valve 36 is opened and through cooler 37 into a topped oil accumulator 38 from which the oil may be withdrawn through pipe 39 by means of a pump 40 discharging into the feed pipe 29 connecting with feed tank 33 as previously described.

The feed tank 33 contains the oil which is to be heated in a vaporizing coil and after vaporization thermally treated by direct contact with combustion gases of proper temperature, and in the case where the initial charge oil has been subjected to an initial topping operation as previously described, consists of this topped oil such as heavy gas oil, and cracked recycle gas oil recovered in the operation of the process as will be more fully described.

The oil to be treated is withdrawn from the feed tank 33 through the pipe 41 by means of the pump 42 which forces the oil through the pipe 43, through the valves 44 and 45 in the pipe 46, through the vaporizing heating coil 47 in the chamber 21 from which the heated oil is transferred through the pipe 48 into the flash tower 49. The oil circulating through the coil 46 is heated during transit to a vaporizing temperature and at the same time the combustion gases are partially cooled by indirect heat exchange with the colder oil. In view of the relatively large quantity of oil passing through this heating coil, I may deem it necessary to provide additional means for heating the oil such as a tube still (not shown) externally of the chamber 21, connected into the pipe 42. By such means, I can obtain a very close control of the temperature change of the combustion gases by the coil 46. A pipe 49 controlled by a valve 50 connects the pipe 43 and 47 in order that all or part of the oil from pipe 43 may be passed directly into the flash tower 48 as operating conditions with respect to temperature may dictate.

The coil 46 is preferably placed in the chamber 21 in such position as to come in contact with the combustion gases at their highest temperature, although the exact positioning and arrangement of the tubes forming the coil 46 will be governed by the furnace design and by the amount of tempering of the combustion gases contemplated.

In the flash tower 48, the heated oil from pipe 47 is flashed into vapors and unvaporized oil, which latter forms a fuel oil and is withdrawn through the pipe 51, valve 52, heat exchanger 53 and cooler 54 by the pump 55 which discharges the fuel oil to storage 56.

The hydrocarbon vapors formed in the flash tower 48 discharge therefrom at substantially atmospheric pressure through the pipe 57 into the mixing chamber 58 wherein they are mixed with the combustion gases issuing from the chamber 21.

The combustion gases entering the mixing chamber 57 will have been reduced in temperature by the steam and indirect heat exchange to a temperature between about 1500° F. to about 2500° F., and preferably to a temperature such that the mixture of hydrocarbon vapors and combustion gases will be at a temperature of from about 1800° F. to about 2000° F. which I have found is most favorable for the primary thermal decomposition or cracking of the heavier hydrocarbons of the 31, and molecular weight gasoline-like hydrocarbons and the simultaneous synthesis of unsaturated hydrocarbons present into desired aromatic products.

The mixture of combustion gases and hydrocarbon vapors, which I have termed the reaction for the sake of convenience, passes from the cracking zone 57 into the primary treating or cracking 75.
zone 58, the time of passage of the reactant through which varies from between about one second at 2500° F. to about three seconds at 1500° F.

The reactant leaves the primary thermal treating zone 58 after an interval and enters the secondary thermal treating or polymerizing zone 59 wherein the reactant is cooled to a temperature between about 1050° F. to about 1800° F. by intimate physical commingling of a cooler oil which is sprayed into the hot reactant through a spray nozzle or other suitable means 60. The zone 59 acts as a soaking zone for the final decomposition of the heavier hydrocarbons present in the reactant and at the same time the temperature conditions existing are those which I have found are most favorable for the production of desired aromatic products from the unsaturated low molecular weight hydrocarbons present in the reactant. The time of passage of the reactant through the secondary treating zone will vary from about one second at 2000° F. to about five seconds at 1400° F. to about ten seconds at 1200° F.

The reactant on leaving the secondary treating zone 59 enters a separator 61 wherein the temperature is quickly lowered to around 600° F. to 700° F. to substantially terminate further reaction by spraying into the reactant a cooler oil through a suitable quench nozzle 62. The heavy polymers, tars and gums of the nature of fuel oil which are condensed in the separator 61 are discharged through the cooled pipe 63 into the pipe 51 and sent to storage with the fuel oil from flash tower 48.

The uncondensed portion of the reactant rises upwardly through a plurality of fractionating trays 64 countercurrent to downflowing cooler reflux oil. The reactant of desired end point discharges from the separator 61 through the pipe 65 into condensing vessel 66.

The condensing vessel 66 is provided with a cooling coil 67 into which clean cool water is passed by pump 68 through pipe 69 and cooler 70.

The water is heated in the coil 67 by exchange with the hot reactant and the steam formed is discharged through the pipe 71 into the steam supply tank 72 from which tempering steam is withdrawn at will through the pipe 73. The reactant in the condensing vessel is cooled to an extent sufficient to condense the heavier hydrocarbons which accumulating as fractional condensate in the condensate basins 74, 75 and 76 may be withdrawn therefrom through the pipes 77, 78 and 79 respectively, and returned in suitable proportions through the pipe 78 to the separator 61 as reflux by suitable manipulation of the valves 80, 81 and 82.

The uncondensed portion of the cooled reactant in the condensing vessel 66 will preferably have as its heavier fraction a hydrocarbon distillate having about a 200° F. to 250° F. end point and discharges from the condensing vessel 66 through a pipe 83, through coolers 70, 84 and 85, and through pipe 86 into separator 87.

In the separator 87, the condensate resulting from the cooling operation will preferably consist primarily of hydrocarbons boiling above the pentane or C5 hydrocarbons. The water resulting from condensation of the tempering steam is withdrawn from the separator 87 through the valve pipe 88.

The temperature of the thermal treating zones is maintained at the low or substantially atmospheric pressure which I have found is most desirable for the production of the desired aromatic products. The uncondensed portion of the reactant in the separator 87 will therefore consist of a mixture of those saturated and unsaturated hydrocarbons which are normally gaseous under normal atmospheric temperatures and pressures, and which are those from which the desired aromatic products are obtained. The temperature and pressure of the exit gas from the separator 87 is controlled by the condenser 66.

The condenser portion of the reactant in the separator 87 is withdrawn therefrom through the pipe 90 by the pump 91 and is charged thereby through the pipe 92, cooler 94, valve pipe 95, heat exchanger 96, pipe 97 and pipe 98 to the distillation coil 97 in the chamber 98. If desired, the heat exchanger 94 may be by-passed to the pipe 99 through the valve pipe 99 and, likewise, a portion of the condensate in the pipe 98 may be by-passed through the valve pipe 99 into the pipe 97 leading to the vaporizing coil 96 by suitable manipulation of the valves 100 shown. A valve pipe 109 connecting the pipes 99 and 100 permits the by-passing of a portion of the condensate issuing from the heat exchanger 94 into the oil flowing through the pipe 92 to the vaporizing coil 46.

The reactant condensate flowing through the distillation coil 97 is heated therein to a temperature sufficient to permit vaporization of the heated oil at low or substantially atmospheric pressure and is discharged through the transfer pipe 101 to the main fractionator 102.

The heavy condensate separated from the reactant in the condensing chamber 95 may be transferred in whole or in part through the pipe 103 controlled by the valve 104 by suitable manipulation of the valves 101, 102 and 104. In thus returning the heavy condensate from the pipe 103 to the fractionating tower 102, I am enabled to effect sharp separation of suitable recycle stock such as heavy fuel oil from the condensing vessel and which is cooled in the condensing coil 67, and to vaporize the steam coming from the condenser tank 71. The valve 105 may be opened at will to allow the heavy condensate to be injected into the fractionator 102 through the pipe 105 by opening the valve 206.

From the fractionator 102 there is withdrawn a relatively heavy recycle oil such as cracked gas oil through the pipe 106 by means of the pump 107, the oil being cooled by the heat exchanger 32, and cooler 108. A portion of the oil in the pipe 106 passes through the pipe 109 controlled by the valve 110 into the pipe 111 of the separator 60 for use as quench oil. A portion of the oil in the pipe 106 is passed through the pipe 112 controlled by the valve 113 into the spray tank 114 from which it is discharged to control the temperature of the reactant in the secondary treating zone 68.

The relatively heavy oil withdrawn from the fractionator 102 through the pipe 106 is most suitable as recycle oil and, the greater quantity of this oil passes through the pipe 106 and from thence through the pipe 113 controlled by the valve 114 into the feed tank 115 from which a vapor return line 116 leads to the main fractionator 102. I have found that for most satisfactory operation of my process, the ratio of heavy
A process for thermally treating petroleum hydrocarbons including the steps of generating combustion gases having a substantially complete absence of oxygen, cooling the hot gases to a temperature of from about 1500°F. to about 2500°F., admixing dry hydrocarbon vapors with the cooled gases to form a reactant at cracking temperature, soaking the reactant at substantially cracking temperature for from about one to about three seconds to form normally gaseous, unsaturated hydrocarbons, cooling the reactant to a lower and polymerizing temperature of from about 1050°F. to about 1800°F., maintaining the reactant at the lower temperature for from about one to about twelve seconds to polymerize normally gaseous, unsaturated hydrocarbons to higher molecular weight, aromatic hydrocarbons, quenching the reactant to a temperature below 700°F. and recovering aromatic hydrocarbons from the quenched reactant.

A process for thermally treating petroleum hydrocarbons including the steps of generating combustion gases having a substantially complete absence of oxygen, cooling the hot gases to a temperature of from about 1200°F. to about 1800°F., admixing dry hydrocarbon vapors with the cooled gases to form a reactant at cracking temperature, soaking the reactant at a temperature below 700°F. to substantially terminate further reaction and recovering aromatic hydrocarbons from the quenched reactant.

A process for thermally treating petroleum hydrocarbons including the steps of generating combustion gases having a substantially complete absence of oxygen, cooling the hot gases to a temperature of from about 1200°F. to about 2500°F., admixing dry hydrocarbon vapors with the cooled gases to form a reactant at cracking temperature, soaking the reactant at substantially cracking temperature for from about one to about three seconds to form normally gaseous, unsaturated hydrocarbons, cooling the reactant to a lower and polymerizing temperature of from about 1050°F. to about 1800°F., maintaining the reactant at the lower temperature for from about one to about twelve seconds to polymerize normally gaseous, unsaturated hydrocarbons to higher molecular weight, aromatic hydrocarbons, quenching the reactant to a temperature below 700°F. and recovering aromatic hydrocarbons from the quenched reactant.
actant to a polymerizing temperature of from about 500° F. to about 1800° F., maintaining the reactant at the polymerizing temperature for from about one to about twelve seconds to polymerize the normally gaseous, unsaturated hydrocarbons to higher molecular weight aromatic hydrocarbons, quenching the reactant to a temperature below 700° F. and cooling the quenched reactant and separating therefrom a light condensate comprising mainly normally liquid hydrocarbons of gasoline boiling range and a heavy condensate comprising mainly hydrocarbons boiling above the gasoline boiling range, fractionating the condensates to obtain a plurality of successively higher boiling hydrocarbon fractions, recovering from one of said fractions desired aromatic hydrocarbons, vaporizing another of said fractions and admixing the vapors formed with said first mentioned cooled gases as dry hydrocarbon vapors.

4. A process for thermally treating petroleum hydrocarbons including the steps of generating combustion gases having a substantially complete absence of oxygen, cooling the hot gases to a temperature of from about 1500° F. to about 2500° F., admixing dry hydrocarbon vapors with the cooled gases to form a reactant at cracking temperature, soaking the reactant at substantially the mixing temperature for from about one to about three seconds to form lower molecular weight hydrocarbons including normally gaseous, unsaturated hydrocarbons, cooling the reactant to a lower and polymerizing temperature of from about 1050° F. to about 1800° F., maintaining the reactant at the lower temperature for from about one to about twelve seconds to polymerize said normally gaseous, unsaturated hydrocarbons to normally liquid aromatic hydrocarbons, quenching the reactant to a temperature below 700° F. and recovering liquid aromatic hydrocarbons from the quenched reactant.

5. A process for thermally treating petroleum hydrocarbons including the steps of generating combustion gases having a substantially complete absence of oxygen, cooling the hot gases to a temperature of from about 1800° F. to about 2000° F., admixing dry hydrocarbon vapors with the cooled gases to form a reactant at cracking temperature, maintaining the reactant at substantially the mixing temperature for from about one to about three seconds to form lower molecular weight hydrocarbons, including mainly a gaseous, unsaturated hydrocarbons, cooling the reactant to a lower temperature of from about 1200° F. to about 1800° F., polymerizing the reactant at lower temperature for from about one to about twelve seconds to form normally liquid aromatic hydrocarbons from said normally gaseous, unsaturated hydrocarbons, quenching the reactant to a temperature below 700° F. to substantially terminate further reaction and recovering liquid aromatic hydrocarbons from the quenched reactant.