Nov. 15, 1932. C. P. DUBBS 1,888,028

PROCESS FOR HYDROCARBON OIL CONVERSION

Filed April 4, 1927 2 Sheets-Sheet 1

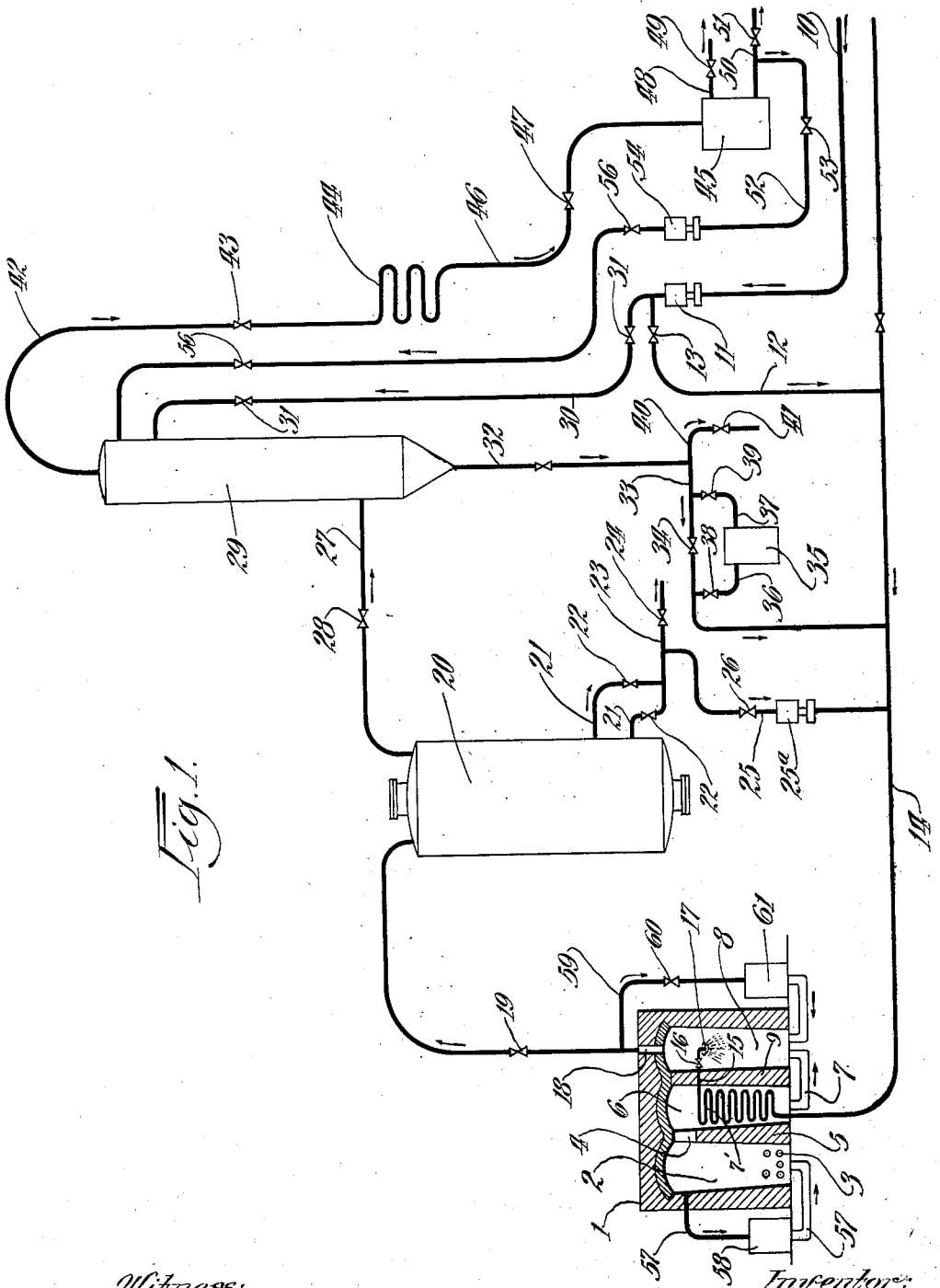


Fig. 1.

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Fig. 2.

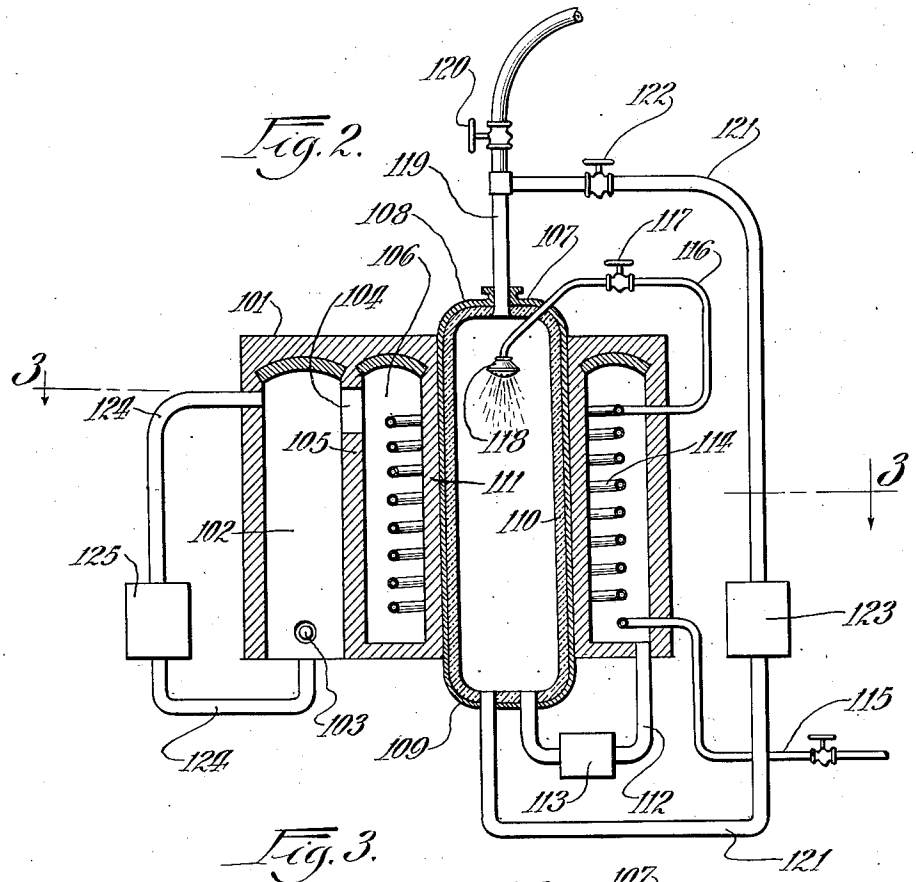
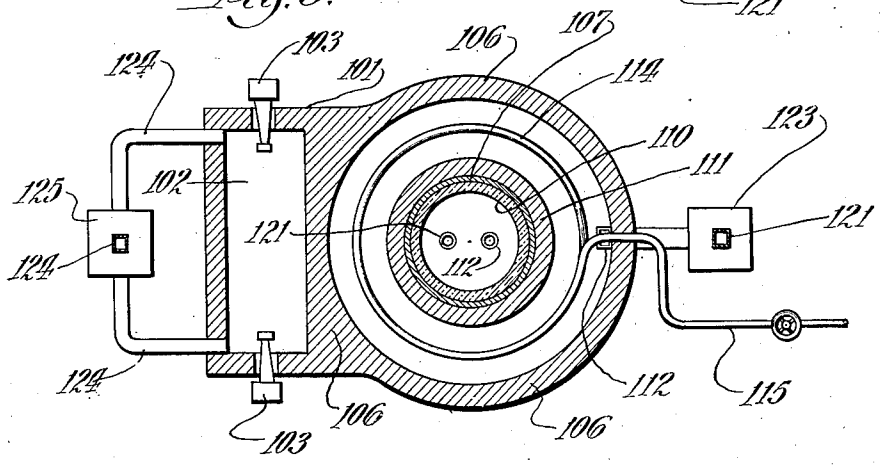


Fig. 3.



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UNITED STATES PATENT OFFICE

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PROCESS FOR HYDROCARBON OIL CONVERSION

Application filed April 4, 1927. Serial No. 180,687.

This invention relates to improvements in the conversion of heavier hydrocarbon oil into lighter oils, and more particularly into products having high anti-knock properties, or products containing substantial amounts of aromatic and unsaturate compounds.

More particularly, the invention relates to a process wherein the oil is treated in direct contact with combustion gases whereby it is vaporized and converted, and wherein the constituent gases of the combustion assist in the reaction for the production of the hydrocarbons of the characteristics desired.

I am aware that the treatment of hydrocarbon oils in direct contact with combustion gases has been considered in the prior art, but the processes which have attempted to utilize this method of conversion have not had the advantages which characterize the present invention, i. e., flexibility and the elimination of the severe conditions of temperature to which the oil was subjected.

To operate this type of process without an extremely high proportion of loss in fixed gases and coke, and at the same time to obtain the maximum obtainable proportion of products having the desired boiling point and characteristics, it is necessary that the conditions of operation of the process be regulated to a nicety, and particularly that the degree of heat and temperature to which the oil is subjected in contact with the combustion gases be so regulated that a relatively mild condition exists, while at the same time the oil and combustion gases are subjected to necessary heat for as long a time as is necessary to produce the degree of conversion desired without utilizing obnoxious temperatures.

These features are present in the process of the invention as will appear more clearly from the following description.

It is understood that the process object of the invention may be carried out in a number of ways and in a variety of apparatus, but to permit a clear understanding of the invention, I have illustrated in the accompanying drawings two forms of apparatus in which the process may be carried out.

Fig. 1 is a diagrammatic drawing, partly in elevation and partly in section, of apparatus.

Fig. 2 is a diagrammatic fragmentary vertical sectional enlarged view illustrating a slightly modified form of furnace.

Fig. 3 is a cross sectional view taken on line 3—3 of Fig. 2.

Referring to Fig. 1, 1 designates a furnace setting which may be of brick supported by a suitable frame work, which furnace is divided into three parts by the partitions 5 and 9 to produce a combustion chamber 2, heated by burners 3, wherein combustion of a fuel is effected and from which the hot combustion gases pass through flue 4 provided in the upper portion of baffle wall or partition 5, into preheating chamber 6. In preheating chamber 6 is positioned a preheating coil 7′, through which the oil to be treated may be passed, as hereafter described. The combustion gases, after passing over said preheating coil 7′ in the preheating chamber 6, where they are somewhat lowered in temperature, pass out through flue 7 into the lower portion of the third compartment 8 of the furnace, maintained entirely separate from the other compartments, except for the flue 7, through the medium of a separating wall or partition 9. The separating wall 9 is preferably made of radiating material so that a portion of the heat of the combustion gases passing through the preheating chamber 6 is radiated into the chamber 8 through the wall 9. It is understood that the characteristics of the material of which the wall is made and the thickness of the wall, may be changed so that the amount of heat radiated through said wall can be controlled.

The material to be treated, which may be crude oil or any fraction thereof or which may be a paste-like mixture of solid hydrocarbon-containing material, such as powdered coal, coal tar and the like, with a controlled proportion of liquid oil, is charged into the system from storage means (not shown) through line 10, and pump 11, from which it may be diverted into line 12 controlled by a valve 13, and through line 14 into the lower bank of tubes of the preheating coil 7′. The oil passing through the preheating coil 7′ is heated to a temperature

which is preferably below conversion temperature, and then passed through transfer line 15, controlled by valve 16, into an injecting nozzle or perforated pipe 17, positioned in the upper part of the chamber 8. The injector or perforated pipe 17 may be of any desired construction, and the injection of the raw oil may be confined to one point of the chamber or may be divided over the length of the chamber 8 by extending the injector 17 through the length of said chamber.

As will be noted, the oil passing through the preheating coil 7′ may, if desired, be maintained therein under a pressure higher than the pressure maintained in the chamber 8, by means of the pump 11 and valve 16, so that the oil will be preheated while in a substantially liquid form at the temperature required, and will vaporize only when it is injected into the chamber 8.

In said chamber 8, the oil sprayed downwardly through injector 17 comes in contact with the ascending combustion gases entering said chamber through flue 7. The gases and the oil are thus brought into intimate contact, the oil is vaporized and receives the heat required for conversion from the combustion gases in the chamber as well as from the radiating wall 9.

The hydrocarbon vapors, noncondensible gases and combustion gases from the heating chamber 8, pass off the top of the chamber through vapor line 18 controlled by valve 19 through which they are discharged into a reaction chamber 20. In the reaction chamber the reaction is completed and the heavier liquid and solid products of the reaction separate and are entrapped.

The heavy liquid products, if such are made, are withdrawn, preferably continuously from the reaction chamber 20, through one or more of the lines 21, controlled by valves 22 and through line 23, controlled by valve 24, and passed to storage or to other treating zones. Or, these liquid products may be returned to the heating coil 7′ and heating chamber 8 for retreatment through line 25, in which is interposed pump 25*a* and valve 26, which line is connected with the main charging line 14. The vapors and gases separated in the reaction chamber pass off through vapor line 27 controlled by valve 28 and are directed into dephlegmating column 29, which is provided with suitable fractionating means, such as bubble trays, plates, or the like, wherein the vaporized products of reaction undergo fractionation. The fractionation may be assisted by introducing therein cooling mediums. For instance, all or any regulated portion of the raw oil from pump 11 can be directed into the top of the dephlegmator 29 through line 30, controlled by valve 31 instead of passing directly to the heating tubes through line 12, or a portion of the raw oil may be passed directly to the heating zone and the other portion may be charged to the dephlegmator.

The reflux condensate and the preheated raw oil which does not vaporize in the dephlegmator are withdrawn from the bottom thereof through the line 32 connected to line 33, which latter is controlled by valve 34, connected at its other end with main charging line 14, whereby said condensed products may be returned to the system for retreatment. A pump 35 is interposed in by-pass lines 36 and 37 controlled by valves 38 and 39 and connected to the reflux line 33, whereby said pump may be utilized to return the oil from the dephlegmator to the heating coil. The line 32 may also be provided with a branch 40, controlled by valve 41, whereby any portion of, or all, the oil from the dephlegmator may be withdrawn from the process.

The vapors which have not been condensed in the dephlegmator 29 pass out therefrom through vapor line 42, controlled by valve 43, thence into condenser 44, from which the condensed and uncondensed products are directed into receiver 45 through line 46, controlled by valve 47. The receiver is provided with gas release line 48 controlled by valve 49 and the liquid drawoff 50, controlled by valve 51. If desired, a portion of the liquid products collected in receiver 45 may be returned to the dephlegmator 29 as a cooling agent through line 52, in which may be interposed valve 53, pump 54 and valve 56.

As a further feature of the invention, a portion of the combustion gases evolved in the combustion chamber 2 of furnace 1 may be withdrawn from the furnace, after they have travelled therethrough for some length, and have thereby been cooled to some degree, and returned to the hottest zone of the combustion chamber relatively close to the burners 3. For instance, this can be effected by drawing off a portion of the gases of combustion from the end of the combustion chamber 2 opposite that where the burners are positioned, and as illustrated in the drawings, from the top of chamber 2 through flue 57 on which is interposed a gas pumping means such as a fan 58, whereby this portion of relatively cooler gas is returned into the hottest combustion gases in chamber 2. In this manner it is possible to regulate accurately, by means of the mixture of the relatively colder gas in a controlled amount with the hotter gas of combustion, the temperature of the latter, as well as the composition of the combustion gases through the various parts of the furnace.

In this manner, by combining the control of the temperature and composition of the combustion gases through the recirculation of a portion thereof through flue 57 with the control of the amount of heat radiated through the partition 9 and that given to the oil in

the preheating coil 7', it is possible to control accurately the temperature and the composition of the combustion gases entering the heating chamber 8 and coming in contact with the oil which is atomized therein, so that the desired results may be produced.

As a further feature of my invention, to combine the proper time element under which the materials undergoing reaction are maintained under proper temperature with the regulation of said temperature, the mixture of combustion gases and vapors and incondensible gases produced in the heating chamber 8 and withdrawn therefrom, are returned, preferably in a continuous manner, to said chamber in a local cycle, for instance, as shown in the drawings through circulating line 59, controlled by valve 60 and on which is interposed the circulating vapor or gas pump or fan 61.

By controlling the circulation of the vapors leaving the heating chamber 8 by valves 19 and 60, I am able to control to a nicety the length of time during which the oil is subjected to the proper temperature and treatment in contact with the combustion gases.

Although I have shown in the drawings that portions of the combustion gases produced in combustion chamber 2 may be withdrawn from the top of the combustion chamber and returned to the hottest zone of combustion near the burners 3, it is understood that the point at which a part of said gas may be withdrawn for recirculating can be varied according to the conditions of operations and result desired. For instance, the flue 57 may be connected to the top of the preheating chamber 6 or to any point in the path of the combustion gases instead of being connected to the top of the chamber 2.

In the same manner the point to which the vapors and combustion gases, withdrawn from chamber 8 are returned may be varied, but they are preferably returned to such a point of this chamber that the returned mixture of vapors and combustion gases has to pass again, during its recirculation, through the length of the heating chamber 8 for better efficiency of the heating process.

It can be seen that by means of the process object of the invention the oil can be subjected to the treatment of the combustion gases in intimate mixture therewith at such temperature as is best to produce the desired results. The composition of the gas in contact with the oil, and particularly the amount of carbon monoxide present in said gas will be governed by the degree of incomplete combustion of the fuel consumed and the rate of recirculation of the flue gases. The temperature to which the oil is subjected will also be governed by the amount of flue-gas circulated in the combustion chamber as well as the degree of convection and radiation into coil 7' and through partition 9 so that no portion of the oil is subjected to a temperature higher than desired. Furthermore, the circulation of the oil vapors, flue gases and uncondensible gases in admixture from and to the heating chamber 8 should hold this mixture at the desired temperature for the desired length of time and this will depend upon the rapidity of the circulation.

I can, by means of this process, and particularly by the control of the temperature of the combustion gases, control the degree of preheating given to the oil in the coil 7' and I can also control the temperature to which the oil is subjected when discharged into the combustion gases in heating chamber 8.

As another feature of the invention the temperature to which the oil is subjected in the heating chamber 8 is dependent upon the condition of the gas, and particularly the content of carbon monoxide in said gas. In some instances, it may be desired to maintain the temperature in this heating chamber 8 sufficiently high to produce in said chamber a substantial conversion of the oil into gasoline which I find readily unites with the carbon monoxide to form anti-knock compounds.

Any one skilled in the art will understand that different oils will not react at the same temperature to the same degree, nor that the different fractions of an oil will react at the same temperatures, so that the best conditions suited to the oil being treated will be determined preferably by making a pilot run with the oil being treated.

The pressure maintained on the system or on the various parts thereof will depend upon the characteristics of the material treated, and while I consider maintaining upon the preheating coil 7' a superatmospheric pressure which will prevent substantial vaporization of the oil therein under the temperature used, the balance of the system from the heating chamber 8 on may be preferably operated under atmospheric pressure.

When it is necessary, to assist in producing draft for the combustion in the furnace and motion of the vapors and gases through the system, a vacuum pump may be connected to any desired point thereof, for instance, it may be connected to the receiver 45 or to the outlet of the condenser 44.

While I have described heretofore a method suitable to carry out my invention under atmospheric pressure or subatmospheric pressure, it may be desirable to operate under superatmospheric pressure, particularly, for instance, when production of aromatics is desired. While the principle of the invention will remain the same, the apparatus to carry it out may be somewhat modified, and I have shown in Figs. 2 and 3 a suitable modified form of apparatus which can be used to carry out the process under superatmospheric pressure.

For the sake of clearness I have not illus-

trated in Figs. 2 and 3 other parts than those which have to be substituted for the furnace and piping directly connected therewith in Fig. 1, the balance of the system may be the same as that illustrated in Fig. 1, or of any other suitable type.

Referring to Figs. 2 and 3, the furnace 101 comprises a combustion chamber 102 heated by burners 103. The combustion gases evolved in said chamber pass through opening 104 above a separating wall 105, into convection chamber 106. The convection chamber 106 is preferably circular such as shown in section in Fig. 3. Inside said convection chamber 106 and concentrically disposed relative thereto, may be positioned tank 107, the metal walls of which are designed to withstand the operating pressure. The upper and lower ends of vertical tank 107 are preferably outside the convection chamber 106, so as to receive no heat, as shown at 108 and 109.

The part of the wall of the chamber 107 which is inside the chamber 106 is preferably protected by a refractory material at the inside and outside, such as shown respectively at 110 and 111. This material is preferably of such characteristics as will radiate heat so that a portion of the heat contained in the combustion gases formed in chamber 102 and passing through chamber 106 around chamber 107 will radiate from the former to the latter. If metal can be used for chamber 107 which will resist heat at the pressure used, it may not be necessary to use brick material, although this is preferable. The thickness of the brick protection inside and outside chamber 107 may be varied so as to regulate the amount of heat radiated.

The combustion gases, after passing through the chamber 106, are directed therefrom through the flue 112 into the inside of the chamber 107. To permit the injection of said gases in the chamber when superatmospheric pressure is maintained, mechanical means are provided and interposed in flue 112, such as shown at 113, whereby said gases may be withdrawn from the furnace and compressed to the pressure desired. This mechanical means is made of material that will resist heat and corrosion.

As a further means to increase the efficiency of the process, the material which is to be treated therein may be preheated by the heat of the gases passing through chamber 106, and this is effected by positioning in said chamber a preheating coil shown at 114. The oil to be treated and which is formed of the same materials that have been mentioned here in the description of the operation relating to Fig. 1, and which has been made up in the same manner, may be introduced through line 115 into the coil 114 where it is preheated to the proper temperature, preferably short of conversion from which it is passed through line 116, controlled by valve 117, and injected into the upper portion of vertical inner heating chamber 107 through nozzle 118. The combustion gases and the oil combine and undergo the desired degree of reaction in said chamber after which the vapors, noncondensible gases and combustion gases pass off the top of chamber 107 through line 119, controlled by valve 120.

As has been described in connection with the operation of the process in Fig. 1, the degree of conversion and time element required therefor may be controlled by recirculating portions of products from chamber 107 in controlled manner to said chamber through line 121, controlled by valve 122, and on which is interposed a recirculating mechanical means 123.

The means illustrated in Fig. 1 for controlling the temperature of the combustion gases at the point where their heat is passed into the oil can also be used in this method of operation, and the partly cooled combustion gases can be recirculated from any part of the combustion of convection chambers 102 or 106, into the hottest part of the furnace somewhat close to and in front of the burners 103 and means for doing this are shown in Figs. 2 and 3 at 124 and 125.

The lines 115 and 119 of Figs. 2 and 3 are connected to the balance of the system in the same manner as shown in Fig. 1. The method of operation of the system, the degree of conversion, the temperature of the gases passing through the various parts of the system, and the temperature of the oil when it comes in contact with the combustion gases for reaction, are all controlled exactly in the same manner as has been described for the operation of the process shown in Fig. 1. By means of the valves and pumps shown, any super-atmospheric pressure may be maintained on the oil in the preheating coil 114 and in the heating chamber 107, and on the balance of the system.

The incondensible gases produced in the system may be passed through an absorption tower (not shown) for the recovery of any liquid content. Said gases may be sent back to the furnace for use as fuel before or after passing through the absorption tower.

As a further feature of my invention, water in the form of liquid or vapor may be injected into the oil undergoing treatment, either into the oil passing through the preheating coil 6, or into the heating chamber 8. The steam may be heated to the required temperature, and in such case may be used as a further means to modify and control the temperature of the materials undergoing treatment in the chamber 8. In other cases, it may be desirable to decompose the steam before or while it is in contact with the oil, so that the hydrogen and oxygen may enter

directly in chemical combination with the oil vapors.

When the oil which is treated contains sulphur which forms products which would corrode the system and form objectionable compounds in the distillates and gases, I may add to the oil a caustic material such as lime, soda, potash, baryta or the like, either in pulverized form, or as an aqueous solution. This caustic material may be added to the oil before it enters the heating chamber 8.

In this manner, the caustic is brought into intimate contact with the fine particles of the oil atomized through nozzle or perforated pipe 17, and the reaction between the caustic and the sulphur or sulphur compounds is more complete.

In another method of operation, water-gas or producer gas may be injected into the heating chamber 8, or at any point in the passage of combustion gases through the furnace 1, whereby additional reaction will occur, causing enrichment of the producer gas and formation of aromatic, ethylenic, alklyl compounds and the like.

While I have shown and described heretofore a process wherein all of the combustion gases formed in the furnace are brought in contact with the oil to be treated for heating and converting it, it is understood that only a part of the combustion gases formed may be so utilized. In this case, a by-pass flue to the stack is branched on the flues 7 and 112 and suitable dampers are provided to control the proportion of combustion gases evacuated.

I claim as my invention:

1. A process for converting liquid hydrocarbons, which comprises raising the temperature of said liquid hydrocarbons by subjection to indirect heat conductive relationship with combustion gases, in subsequently introducing the heated hydrocarbons into direct contact with said combustion gases to cause substantial vaporization, in removing said vapors and subjecting same to cracking reaction in an enlarged reaction zone, in removing vapors from said reaction zone and subjecting same to dephlegmation, in removing the reflux condensate from said dephlegmation and returning same to the heating zone for retreatment, in controlling the degree of conversion taking place by locally recirculating, through the oil being contacted with combustion gases, regulated portions of the vapors passing to the enlarged reaction zone.

2. A process for converting liquid hydrocarbons, which comprises generating combustion gases in a gas generating zone and raising the temperature of said liquid hydrocarbons by subjection to indirect heat conductive relationship with the combustion gases, in subsequently introducing the heated hydrocarbons in finely divided condition into direct contact with said combustion gases to cause substantial vaporization, in removing said vapors and subjecting same to cracking reaction in an enlarged reaction zone, in removing vapors from said reaction zone and subjecting same to dephelgmation, in removing the reflux condensate from said dephlegmation and returning same to the process for retreatment, in controlling the degree of conversion taking place by locally recirculating through the oil being contacted with combustion gases regulated portions of the vapors passing to the enlarged reaction zone, and in regulating temperature conditions within the gas generating zone by locally recirculating therethrough regulated portions of the combustion gases.

3. A process of hydrocarbon oil conversion consisting in heating the oil in indirect contact with gases of combustion in a heating zone, passing the heated oil and gases of combustion into a second heating zone in direct physical contact to vaporize the oil, and recirculating regulated portions of the resultant mixture of vapors and gases in a local cycle through said second heating zone.

4. A process of hydrocarbon oil conversion consisting in generating gases of combustion in a gas generating zone, heating the oil in indirect contact with the gases of combustion, passing the heated oil and gases of combustion into a second zone in direct physical contact attended by vaporization of the oil, and recirculating regulated portions of the contents of said zones in a local cycle respectively through each of said zones.

5. A process for cracking hydrocarbon oil which comprises first heating the oil by passing the same through a heating zone in indirect heat conductive relationship with hot combustion gases, discharging the heated oil from said heating zone into a conversion zone maintained under cracking conditions of temperature and causing the oil to mingle with said combustion gases in said conversion zone thereby effecting cracking of the oil, removing vaporous products of the cracking and combustion gases from said conversion zone, and returning a portion of the removed vaporous products and combustion gases directly to said conversion zone without passage through said heating zone.

6. A process for cracking hydrocarbon oil which comprises first heating the oil by passing the same through a heating zone in indirect heat conductive relationship with hot combustion gases, discharging the heated oil from said heating zone into a conversion zone maintained under cracking conditions of temperature and causing the oil to mingle with said combustion gases in said conversion zone thereby effecting cracking of the oil, removing vaporous products of the cracking and combustion gases from said conversion zone, returning a portion of the removed vaporous

products and combustion gases directly to said conversion zone without passage through said heating zone, dephlegmating vapors removed from said conversion zone thereby forming reflux condensate, and returning said condensate to the process for retreatment.

7. A process for cracking hydrocarbon oil which comprises generating hot combustion gases at a point remote from the oil to be cracked, passing the oil in indirect heat conductive relationship with said combustion gases, then bringing all of the oil thus heated into direct physical contact with said combustion gases under cracking conditions of temperature in a conversion zone and thereby effecting cracking of the oil, removing vapors and gases from said zone, and continuously returning a portion of the removed vapors and gases directly to said zone.

8. A hydrocarbon oil conversion process which comprises cracking the oil by directly contacting the same with a gaseous heating medium in a conversion zone, removing the resultant mixture of vapors and gases from said zone, and recirculating regulated portions of said mixture in a local cycle through said zone.

9. A hydrocarbon oil conversion process which comprises cracking the oil by directly contacting the same with hot combustion gases in a conversion zone, removing the resultant mixture of vapors and gases from said zone, and recirculating regulated portions of said mixture in a local cycle through said zone.

In testimony whereof I affix my signature.

CARBON P. DUBBS.