Dec. 27, 1932. E. W. REMBERT 1,892,534

PROCESS FOR DISTILLATION AND CONVERSION OF MINERAL OILS

Filed May 11, 1929 3 Sheets-Sheet 1

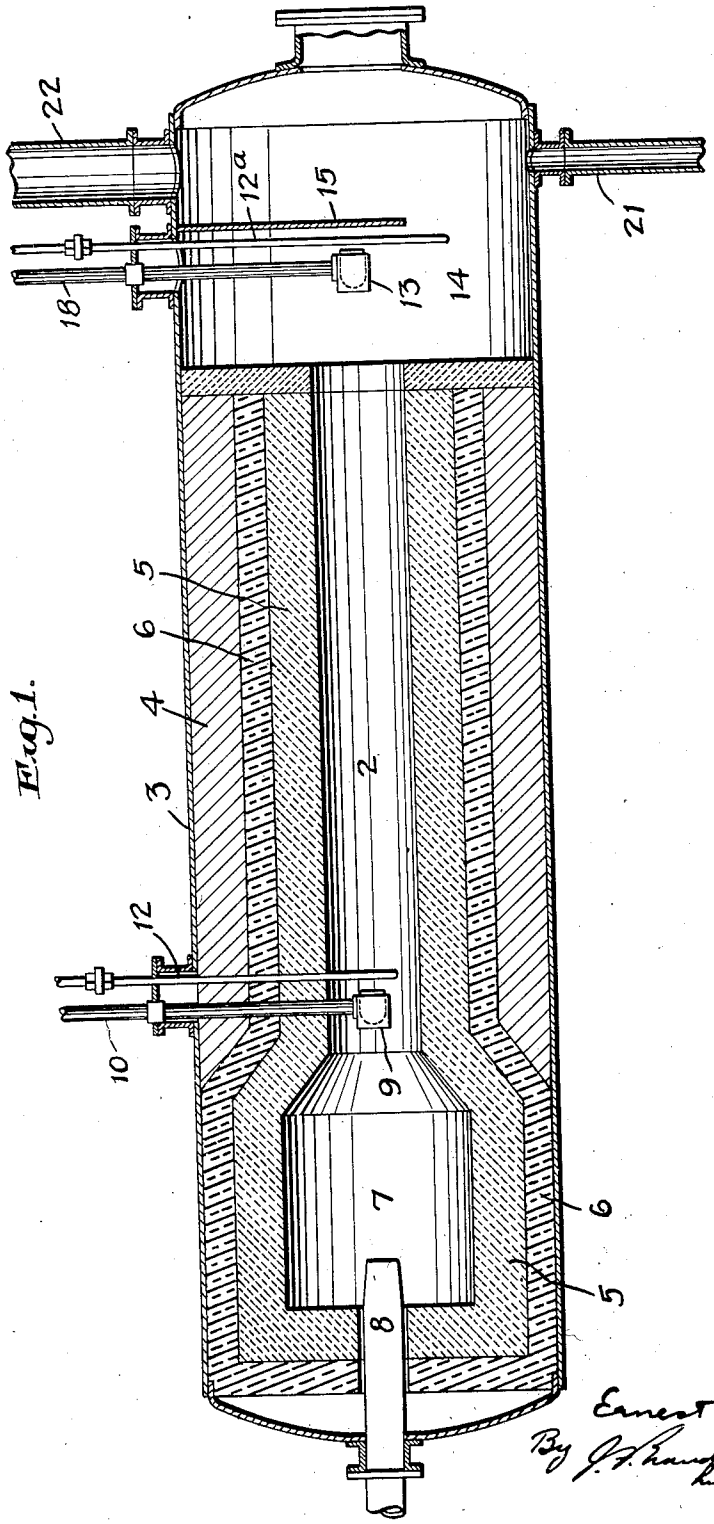


Fig. 1.

INVENTOR
Ernest Wayne Rembert
By J. F. Brandenburg
his ATTORNEY

Dec. 27, 1932. E. W. REMBERT 1,892,534

PROCESS FOR DISTILLATION AND CONVERSION OF MINERAL OILS

Filed May 11, 1929 3 Sheets-Sheet 2

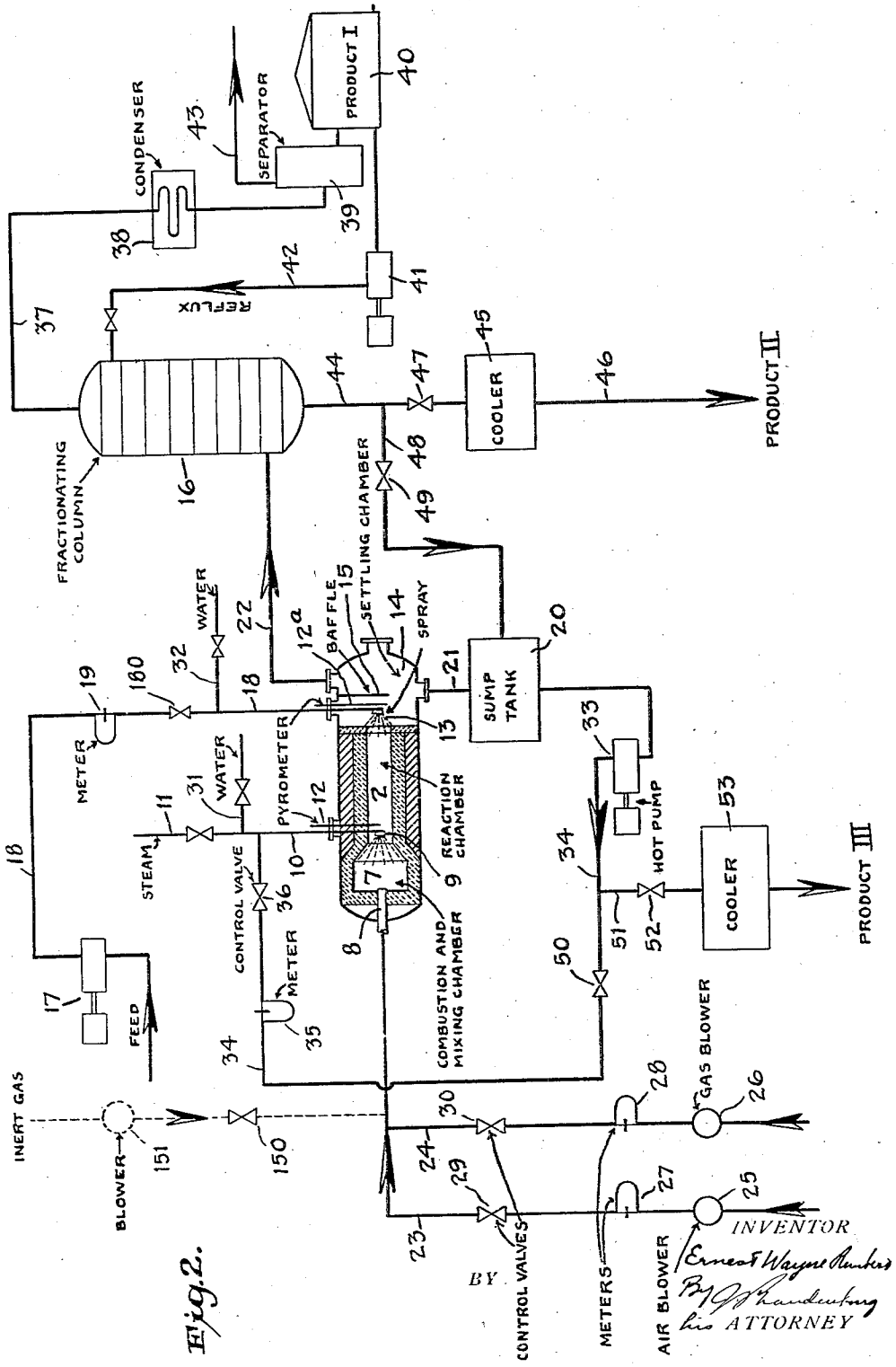


Fig. 2.

INVENTOR
Ernest Wayne Rembert
BY
his ATTORNEY

Dec. 27, 1932. E. W. REMBERT 1,892,534

PROCESS FOR DISTILLATION AND CONVERSION OF MINERAL OILS

Filed May 11, 1929 3 Sheets-Sheet 3

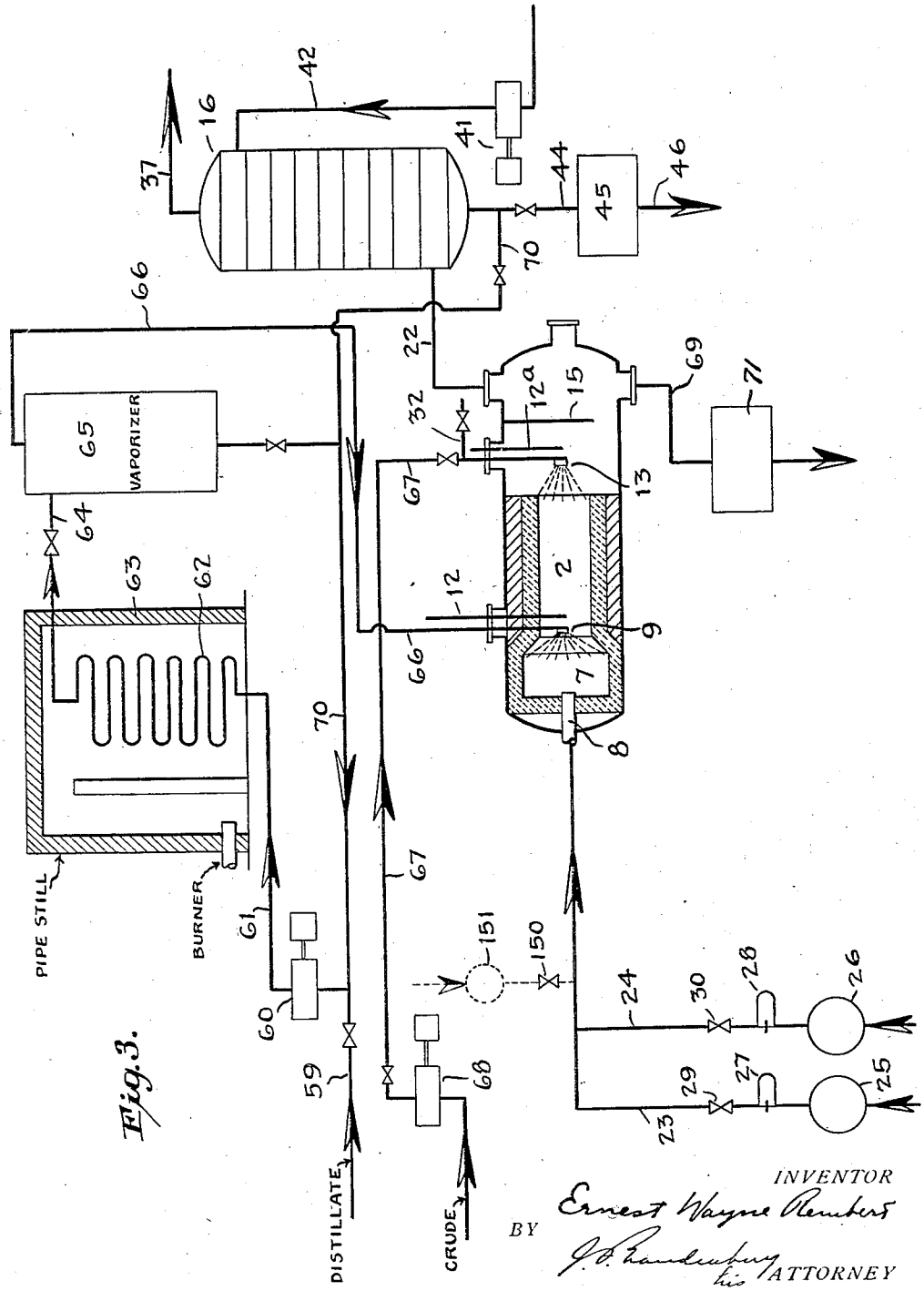


Fig. 3.

INVENTOR
Ernest Wayne Rembert

BY J. B. Vandenburg his ATTORNEY

Patented Dec. 27, 1932

1,892,534

UNITED STATES PATENT OFFICE

ERNEST WAYNE REMBERT, OF BAYONNE, NEW JERSEY, ASSIGNOR OF THREE-FOURTHS TO TIDE WATER OIL COMPANY, OF BAYONNE, NEW JERSEY, A CORPORATION OF NEW JERSEY

PROCESS FOR DISTILLATION AND CONVERSION OF MINERAL OILS

Application filed May 11, 1929. Serial No. 362,192.

This invention relates to the distillation of mineral oils and similar materials in continuous process, including operations of this character in which thermal decomposition and recomposition of hydrocarbons is effected in the vapor phase, to produce oils and/or liquids containing compounds of the same or different chemical series from those treated, and more especially to produce lower boiling oils and liquids such as motor fuel products, gasoline and the like, from higher boiling oils. A particular application of the invention is in the production of motor fuels or motor fuel material having excellent anti-knock properties. The invention comprises process and apparatus for effecting such operations.

One of the objects of the invention is to accomplish the thermal conversion of hydrocarbons such as petroleum, its residues or heavier distillates, in such a way that no solid coke need be formed in the apparatus, and that very little, if any, free carbon is produced even in the cracking of crude oil, topped crudes, reduced crudes, residuums, or residual oil such as fuel oil, all of which may be classed as crude or residual oils, in contradistinction to distillates. This avoids the expense and delay occasioned by the usual necessity for periodic shut-downs and cleaning out of units, besides effecting a marked saving in maintenance costs. Another object is to effect thermal conversion of the hydrocarbon mixtures in such a way that little or no tar need be produced as a product of the process.

Another object is to reduce the loss of liquid products through production of fixed gas to a minimum.

Another object is to secure maximum yields of desired products.

Another object is to produce, through thermal decomposition and recomposition of constituents of such hydrocarbon mixtures, low-boiling mixtures containing relatively large quantities of aromatic hydrocarbons, or similar hydrocarbons, such as, for example, naphthenes. In this connection, an important object is to obtain, after appropriate separation, if necessary, a motor fuel, or a product for blending with motor fuels, having a high anti-knock value.

An important object of the invention is to secure definite control of the reaction time and the reaction temperature, while obviating injurious local overheating of the hydrocarbons undergoing treatment.

Another object is to vaporize the oil with extreme rapidity, so that cracking in the liquid phase or at the moment of passing from the liquid to the vapor phase, such as would be attended by the production of coke or carbon, is not permitted to occur, and thereupon immediately to superheat the vapors to the desired conversion temperature and to keep them substantially at that temperature for a precise, limited period of time, whereupon the reactions are immediately retarded to a negligibly low rate, so that the reactions are thereupon virtually stopped.

Another object of the invention is to provide a process whereby a crude oil or reduced crude (residuals, heavy fuel oil and the like) can be easily and successfully treated for the purposes indicated. As far as I am aware, the vapor phase cracking processes which have been commercially exploited require an oil that can be easily vaporized as a charging stock, that is to say a distillate, for their economic operation.

Another object of the invention is to effect the desired conversion in a relatively inexpensive way, with the use of apparatus involving low first cost and occupying little space. A further object is greatly to reduce maintenance charges and to avoid the hazard which exists when apparatus fails.

In the mode of executing the invention which is particularly advantageous for the treatment of crudes and residuals, the oil to be cracked is introduced in a finely divided state into a stream of hot and preferably non-oxidizing gas produced by the combustion of fuel and air in a closed chamber adjoining the cracking chamber, the oil is thereby suddenly vaporized and superheated to the desired cracking temperature, the conditions being such as to secure rapid and thorough mixing and therefore an extremely rapid transfer of heat from the heating medium

to all portions of the material to be treated, so that thermal equilibrium is at once established the mixture of hot gas and superheated vapor is passed at predetermined speed through a conduit-like cracking chamber, preferably heat insulated and lined with refractory material, the length and diameter of this conduit being governed by the capacity desired for the unit and the intended reaction time, and at a point spaced from the point of mixing by an exact distance, depending upon the length of the conduit and the speed of travel, all portions of the mixture are suddenly cooled by contact with a quenching liquid down to a temperature which will practically halt the reactions.

The reaction time is determined by the speed of travel and the distance from the point where the vapors are quickly superheated to the predetermined cracking temperature to the point where they are quickly quenched, and the speed of travel is controlled by regulating the amount of heating medium supplied to or produced in the unit and/or the amount of material for treatment which is introduced, per unit of time. The reaction time for virtually all portions of the vapors is controllable with an exactitude on the order of one one-hundredth of a second. The reaction temperature is readily and exactly controlled by regulating the amount and temperature of the heated inert gas and/or by regulating the proportion and/or degree of preheat of hydrocarbon material fed in to be vaporized and/or superheated by the heating medium.

To illustrate what is meant by controlling the reaction time with an accuracy on the order of one one-hundredth of a second, a desired reaction time of about 1/5 second and a desired reaction temperature of about 1100° F. may be taken by way of example. The process in this case can give an actual cracking time of 1/5 second plus about 1/100 second as measured from and to temperature ranges below any cracking temperature. In other words, the stock would be raised from, say, 650° F. to 1100° F., held at 1100° F. for 1/5 second and then cooled to about 650° F., all in a time of 1/5 second plus about 1/100 of a second.

Not only are the reaction time and the reaction temperature positively controlled, but local overheating is eliminated or substantially eliminated. In vapor phase processes in which the vapors are superheated in externally heated metal tubes (indirect heating), local overheating with excessive cracking and corresponding high production of coke, carbon and fixed gas occurs, and it is not possible to control the reaction in the manner that is characteristic of this invention, since, with indirect heating, different portions of vapor in the same cross-section of the stream are heated to different temperatures.

I am aware that it has been proposed to crack mineral oils in the vapor state with the direct heat of combustion gases, but such proposed processes, as far as I know, have not provided for the positive control of optimum reaction time and optimum reaction temperature, together with avoidance of local overheating, as contemplated herein.

The substantially instantaneous vaporization of the oil, and immediate superheating of the vapors to the cracking temperature at which they are kept for a definitely limited time, is very important for the treatment of materials which contain constituents which ordinarily crack in the liquid phase with the formation of coke and carbon, at temperatures below the temperature at which they vaporize. A time element is involved, and I therefore seek to vaporize the oil so suddenly that cracking at this stage and of this nature is avoided. In other words, I carry out the process of vaporization as rapidly as possible with respect to the process of cracking.

Not only this result, but also the immediate formation of a uniform mixture wherein the heavy hydrocarbons are superheated to and maintained at the cracking temperature without detrimental local overheating, can best be obtained by introducing the oil into the stream of hot gas in a finely atomized or fog-like delivery, projected across the oncoming stream of heated gas or superheated vapor, the arrangement being such that a tenuous issue of the material completely intersects or is intersected by the blast. Causing the fine oil particles to change their course as they meet the hot gases promotes turbulence and aids in securing the desired prompt and perfect mixing. The most desirable disposition is one in which the fog, or very fine spray, is delivered, or tends to be delivered, in the form of a very thin sheet or curtain across the direction of flow of the heating medium.

When distillates are employed as the feed stock, or even when certain kinds of crude materials are to be treated, they may be vaporized outside the reaction apparatus and be mixed with the hot gas in the form of vapor. In that case, the vapors are introduced as a cross stream in the path of the hot gas in order to secure rapid mixing, substantially as described in connection with liquid material, the effect being the same as regards mixing and transfer of heat.

This variation of the invention employs the same features of quickly superheating the hydrocarbon mixture by direct heat to the desired cracking temperature, under conditions insuring prompt and uniform mixing with the superheating agent, so that thermal equilibrium is immediately obtained, allow-

ing the reaction to proceed for a strictly limited period of time which will give the maximum yields of the desired products, all so conducted that local overheating is avoided, and then instantly arresting or checking the reactions by quenching with a cold, or relatively cold, or vaporizable medium.

Where the oil to be treated is a crude, or similar material containing some natural low-boiling constituents, the crude oil is preferably employed as the chilling agent. In this way the heat abstracted from the gaseous and vaporous mixture at the moment of arresting the reaction is utilized to strip the crude, by vaporizing off its natural gasolene or low-boiling constituents.

In any case, whether the feed stock is crude, topped or reduced crude, or other residual material, or a distillate, it is desirable to employ the feed stock for cooling down the flow of gases and vapors, the material to be converted being thereby preheated.

However, any other suitable liquid, such as water, may be used for chilling. In the case of a liquid quenching medium, a portion, all or none of the quenching liquid may be vaporized.

By the term inert gas is meant one which is not oxidizing. It is desirable that the combustion gases contain substantially no uncombined oxygen.

The cracking temperatures employed in the process are upwards of 900° F., and the reaction time may range, consistently with other conditions, from a fraction of a second up to a fraction of a minute, but I wish to emphasize that the best results are obtainable with conditions adjusted to a very short reaction time.

In order to obtain a product having any material content of aromatics, it is necessary to employ in the process reaction temperatures upwards of about 900° F., and to be effective in the sense of producing a motor fuel oil having a good anti-knock rating, the temperatures should be upwards of 950° F., and preferably not above 1400° F., though with extremely short reaction time, temperatures even higher may be used. For the production of gasolene having an excellent knock rating, reaction temperatures between 1000° F. and 1100° F. have been found to be the most practical and beneficial. Reaction temperatures can not be more definitely limited because there is a reciprocal relation between the factors of time and temperature, as I have demonstrated by passing a mixture of heating medium and hydrocarbon vapors from the point of commingling to the point of quenching so rapidly that, notwithstanding the hydrocarbons were exposed to a temperature far above the accepted cracking range, no alteration in the structure of the hydrocarbons was discoverable.

In cracking crudes, fuel oil or the like to obtain materials having a low hydrogen-carbon ratio, the cracking temperature should be above about 1050° F., to avoid the deposition of coke or the formation of any material amount of lamp black.

Dependent upon the other conditions, the reaction time for the production of aromatics or other anti-knock bodies should be brief. Such reaction times are accompanied by the best results. Reaction times that are most favorable are on the order of a fraction of a second to a few seconds, and better still small fractions of a second. With reaction times under one second the production of fixed gas from the material treated is very greatly reduced.

Example 1

As an illustration, a mixture of reduced crude from Venezuela and California crudes, having a gravity of 14.0° A. P. I., Saybolt viscosity 330 sec. at 122° F., flash 305° F., and initial boiling point of 480° F. with 6% off at 600° F., has been cracked in accordance with the invention, being first preheated to about 400° F. Using a reaction time of approximately one-tenth of a second and a reaction temperature of 1400° F., and quenching below 700° F., it was found that between 30% and 35% of gasoline could be produced from the reduced crude on a single pass through the unit, which gasoline on analysis was shown to contain 70% of aromatic hylrocarbons and 30% unsaturated hydrocarbons. This gasoline was entirely soluble in concentrated sulfuric acid, indicating the absence of paraffin hydrocarbons. It is reasonable to expect that it would be possible to obtain a low-boiling product suitable for motor fuel, or for blending with motor fuel, or for other purposes, consisting altogether, or almost wholly, of aromatics or cyclic hydrocarbons, if that should be desired.

Naturally if the gas oil, or other relatively high-boiling part of the liquid products of the reaction, is recycled, the yield of gasoline or other low-boiling liquid product will be increased. Whether the gas oil is recycled in whole or in part will depend on economic considerations, such as the price obtaining for gas oil.

The following additional examples of the process are illustrative of yields on a recycling basis, but it will be understood that high anti-knock ratings are obtained with or without recycling. The last line of the table is for comparison in knock-rating with benzol.

Example 2

When charging Mid-Continent gas oil (grav. 31.4, I. B. P. 392° F., 28% off at 600° F.) and cracking at 1080° F. with a reaction time of ¼ second, a yield of 81.3% gasoline

on a complete recycle basis is obtained. This gasoline has a knock rating equivalent to a blend of 6 c. c. lead tetraethyl with 1 gal. of Pennsylvania Navy gasoline, this being better than Ethyl Standard, which is 5 c. c. of lead tetraethyl in 1 gal. of Pennsylvania Navy gasoline.

Example 3

When charging West Texas crude of 30.2 A. P. I. gravity containing 30% of natural gasoline, removing the light products from the crude in the quencher to give a 22.9 gravity residue, which is cracked at 1060° F. and a reaction time of 1/5 second, a yield of 75% gasoline is obtained, based on the reduced stock, on a complete recycle basis. The composite gasoline from the unit has a knock rating equivalent to 3 c. c. of lead tetraethyl in Pennsylvania gasolene, while the natural gasolene from the crude has a knock rating equivalent to Pennsylvania gasolene.

It is possible with this process to produce gasoline having a knock-rating equivalent to pure benzol, by regulation of the reaction time and reaction temperature. It may be noted that in obtaining exceedingly high knock ratings the yield of gasoline is not so high as when the process is conducted to obtain lower but very excellent knock ratings. The following table is illustrative of variation in knock rating with yield, the knock rating being expressed in c. c./gallon of lead tetraethyl in Pennsylvania Navy gasoline:

Yield of gasoline	Knock rating
81.3%	6
65.6%	6.5
56.0%	7.1
49.5%	9.5
Benzol	9.5

It will be understood that by varying the precise conditions, the converted materials may comprise low-boiling hydrocarbons of the benzene, naphthene, or similar series, the paraffin series, and/or the olefine or similar series, or varying combinations of two or more of these kinds of hydrocarbons.

As previously stated, the desired conversion temperature is controlled by the amount, temperature and composition of the inert gas and the amount and temperature of oil or oil vapor introduced to the gas. As is well known, complete combustion of ordinary fuel gases produces flame temperatures in excess of 2500° F. or even 3000° F. (see Handbook of Chemistry and Physics, 16th edition, page 682—"Heats of combustion and composition of manufactured and natural gases, theoretical flame temps."—published by Chemical Rubber Publishing Company, Cleveland, Ohio). Because of the extreme rapidity and uniformity of the mixing of the heating agent and the hydrocarbons, the non-oxidizing combustion gases, which are obtained at a high temperature, can be, and are, used at such temperature, and in any event at temperatures over 2500° F., without danger of injurious overheating of the hydrocarbons in the mixing step, so quickly is thermal equilibrium attained. In practice, the products of substantially complete combustion of hydrocarbon fuel and air, the temperature of which is much above 2500° F., are mixed directly with the finely divided oil or the oil vapor to be cracked, without any preliminary tempering of the gases by the introduction of relatively cool fluid, or otherwise. The fact that very hot gases are successfully mixed with the material to be converted is an important practical advantage of the process, not only because, for a given capacity, the reaction unit, fractionating column, etc. can be of minimum size and therefore relatively inexpensive, but also because the relative smallness of the volume of hot gas that is required favors the rapidity of the mixing and the superheating of the hydrocarbons to the maximum reaction temperature, facilitates the quenching down of the mixture from this maintained temperature, and materially simplifies the ensuing reflux fractionation and separation operations which have to be performed in the presence of the combustion gases. The less of these gases to be handled, the better, and it is one of the features of the invention that their volume is strictly limited. Naturally, there may be some dilution of the combustion gases without departing from this aspect of the invention.

In converting certain oils, it may likewise be desirable to introduce steam or some other inert gas or vapor along with the oil so as to form a protective film around the liquid particles, to guard them further against local overheating during vaporization. Steam may be employed to atomize the oil to be cracked, but a fog or extremely fine spray can be secured without steam, by forcing the oil under pressure through a nozzle of appropriate and available design.

The cracking operation may be carried out below at or above atmospheric pressure, and up to 1000 lbs. per square inch. The use of pressures above atmospheric may increase the yields and decrease the size of equipment required for a given throughput. Operating pressures on the order of about 5–50 lbs. per square inch are economic in this process. Pressures of this order have little, if any, real influence on conversion. The process is not dependent on the pressure factor, since any convenient operating pressure may be used.

In the accompanying drawings forming part hereof:

Fig. 1 is a longitudinal section through a

preferred form of unit constituting a part of the apparatus;

Fig. 2 is a schematic view illustrating a system of equipment and operations employing the unit illustrated in Fig. 1; and

Fig. 3 is a schematic view illustrating another mode of applying and carrying out the invention.

Referring to Figs. 1 and 2, the apparatus shown in these views comprises a cylindrical reaction chamber 2 built of refractory and insulating material surrounded by a tight steel shell 3 capable of holding the pressure, if any, desired and of retaining the gases and vapors by which the refractory and insulating lining would naturally be penetrable. The lining may consist of a cylindrical wall 4 of ordinary brick next to the shell, an inner wall 5 of fire-brick, with an intermediate layer 6 of insulating material. The refractory conduit 5 is capable of withstanding the action of the hot vapors and gases, and the insulating layer 6 reduces heat losses so as to insure practical maintenance of the desired reaction temperature.

While the reaction chamber may be made of other materials, for example, such as heat resisting alloys, the construction illustrated is especially advantageous because of its low first cost and low maintenance expense and its safety.

At one end of the reaction chamber there is a combustion and mixing chamber 7, which may be enclosed in an extension of the same shell 3. This chamber may be larger in diameter than the reaction chamber, and is lined by the refractory and insulating walls or layers 5 and 6.

Through the outer end of the combustion chamber there project one or more burners 8. These burners may be of any suitable character adapted to burn fuel and air in proper proportions so as to produce a blast of hot combustion gases of neutral, that is to say non-oxidizing, character. The fuel might be oil, but is preferably a gas containing little or no non-combustible constituents other than air.

At the opposite end of the combustion chamber, or within the end of the reaction chamber where it joins the combustion chamber, there is a spray nozzle 9, the pipe 10 leading to this nozzle passing through the shell and lining at right angles to the axis of the reaction chamber.

The material to be cracked is delivered to this nozzle under pressure, with or without steam or other gas or vapor which may be employed for the purposes heretofore indicated. Such additional fluid may be supplied to the pipe 10 through a valved pipe 11 leading from a suitable source of supply.

The nozzle is preferably so designed and placed as to deliver a very fine spray obliquely toward and across the oncoming stream of combustion gases proceeding from the burners. It preferably emits a curtain-like spray of hollow conical form which has its apex or origin at the center of the throat of the reaction chamber and which diverges into the combustion chamber across the blast of heating fluid. The form of the spray is naturally modified by the gas stream, which turns the exceedingly fine particles of oil and carries them toward the reaction zone, so that very thorough mixing with the hot gas is obtained. Vaporization and mixing can be regarded as being complete a very short distance behind the spray nozzle 9, by which time the vapors have been superheated to the predetermined reaction temperature.

The extremely rapid vaporization of the oil, the intimate and uniform mixing of the hydrocarbons to be converted with the hot gases, the promptness with which the mixing is effected, and the rapidity with which the vapors are superheated to the cracking temperature are important factors of the operation.

In regard to the dimensions of the chamber 2, it has been proven desirable to maintain a velocity of 50–200 feet per second through the conduit, which is ample to keep the stream in a turbulent motion, and therefore of uniform temperature. The length of the conduit is chosen consistent with the throughput and reaction time necessary to produce the desired yield and quality of product. In the case of a unit designed to crack 250 barrels of fuel oil per day in the vapor phase, a reaction conduit one foot in diameter and ten feet long has been found to be satisfactory, but it will be understood that this is given by way of one concrete example and that the width and length of the chamber can be varied and are to be selected to allow the desired reaction time for any desired throughput.

The flow through the reaction chamber should be such as to avoid delaying portions of the stream more than other portions with the result of causing portions thus delayed to become over-cracked.

It may be understood that complete vaporization of all the oil delivered into the hot gases at the point 9 is contemplated.

The superheated vapors are mixed with the hot gases and conducted through the reaction chamber 2, the length and width of which are proportioned according to the capacity of the unit and these proportions being such as to accord with a reaction time to give the maximum conversion to desired products. Owing to the thoroughness with which the material is vaporized and mixed with the hot gases at the entrance to the reaction conduit and the velocity at which the mixture is passed, and also to some extent to the heat insulation, the cracking temperature is uniform, or substantially uniform, throughout this chamber.

A pyrometer 12 registers the temperature in the reaction zone, and another pyrometer 12[a] registers the temperature at a region close behind the point where the hot mixture of gases and vapors is suddenly cooled to arrest the reactions.

At the outlet end of the conduit-like reaction chamber there is a second spray nozzle 13, which faces in the same direction as the nozzle 9 and which delivers a conical curtain-like spray across the path of the mixture of gases and vapors issuing from the reaction zone. This nozzle is preferably located in a settling chamber 14, which may be formed by an extension of the same tight shell 3, this chamber containing a baffle 15 to prevent liquid from the spray being carried onward to a fractionating column 16. The spray produced by the nozzle 13 is finely divided so as to provide a large surface of contact. However, the liquid particles should not be so exceedingly fine as to be carried over into the fractionating column.

The function of this spray is to lower the temperature of the stream of vapor and hot gas quickly to a temperature below that at which cracking occurs to any appreciable or undesired extent, and the quantity of the quenching liquid is adjusted to that end.

The mixture is cooled to such point below about 750° F. as to bring the mixture practically to the dew point.

The precise temperature to which the mixture is cooled by this spray will depend upon the other operating conditions, the material treated, and the products which are sought. The object being to cool the mixture sufficiently to arrest the reactions definitely for each successive portion of the flow at the conclusion of the predetermined reaction time, the cooling need not, and preferably is not, carried below the temperature which will bring about this result and will cause the mixture of gases and vapors which proceed to the fractionating column to be saturated. For efficient operation of the fractionating equipment, it is desirable to throw as much heat into the base of the tower as is consistent with the attainment of these objects. Condensation of any part of the vapors carried by the gas, though not necessarily excluded, is not an object.

The quenching medium may be cold, or relatively cold, oil, water or other liquid. It is supplied to the spray nozzle 13 by a pump 17 through a pipe 18 provided with a meter 19 and a control valve 180.

The purpose of the settling chamber is to trap unvaporized liquid from the spray nozzle 13. This liquid settles out into a sump tank 20 located below the settling chamber and connected with it by a pipe 21. The gases and vapors pass out from the upper part of the settling chamber, beyond the baffle 15, through a pipe 22 to the fractionating column 16, which is provided with suitable condensers and coolers.

Pipes 23 and 24 are indicated for supplying the burner 8 with air and gas, respectively, these pipes containing blowers 25 and 26, meters 27 and 28 and control valves 29 and 30.

In actual operation, the burner is lighted and the ratio of fuel to air is so adjusted as to give a flue gas containing substantially no uncombined oxygen. As soon as the temperature directly behind the first spray nozzle 9 reaches that which is desired for normal operation, water is started through this spray nozzle in just sufficient quantity to maintain this desired temperature, and firing is continued until the temperature behind the second spray nozzle 13 indicates that which it is desired to maintain at that point, water being also delivered through this nozzle at this time. For the supply of water to the two nozzles, valved pipes 31 and 32 connecting with the pipes 10 and 18 are indicated.

Then, if the crude oil or any other stock which it is desired to treat is to be used as the quenching medium, water is turned off from the second spray and the feed stock is started through the second spray in sufficient quantity to maintain the desired temperature at that region. If crude is charged, a portion will be vaporized and will pass on to the fractionating and condensing equipment, while the remainder will fall into the sump. As soon as sufficient stock, preheated by its contact with the hot gases, is accumulated in the sump, water is cut out of the front spray and the residual is started through this spray in such quantity as to maintain the optimum cracking temperature. Thereafter the normal operation of the unit proceeds continuously without necessity of shut-down since coke is not formed and little if any carbon in the form of lamp black.

The apparatus shown in Fig. 2 is especially adapted for the processing of low-grade crudes and reduced crudes, fuel oil and the like, or gas oil.

Assuming that the feed stock is a crude, this material is forced through the pipe 18 by the pump 17 to the spray nozzle 13. Where it serves as the quenching medium. The crude is there topped or deprived of its natural gasoline content, and the residual which collects in the sump tank 20 is continuously withdrawn by a hot pump 33 and forced through piping 34, provided with a meter 35 and a control valve 36, to the pipe 10 of the spray nozzle 9, from which it is projected in a state of fine division into the stream of hot flue gases from the burner.

The vapors and gases which leave the top of the fractionating column 16 pass through a pipe 37 to a condenser 38, from which the light condensate passes to a separator 39, the

light condensate being collected in a tank 40. From this tank a portion of the liquid may be supplied by a pump 41 through a pipe 42 to the top of the fractionating column, where it flows downward over the plates in contact with the ascending gases and vapors, to serve as a fractional condensing medium.

The tank 40 is marked "Product I" on the drawings, this product being, for example, gasoline or gasoline material. The fixed gases are conducted through a pipe 43 to the gasolene recovery plant.

Assuming the particular case in which a reduced crude has been cracked to gasoline and gas oil, the gas oil is withdrawn from the bottom of the fractionating column through a pipe 44 to a cooler 45, from which it may be delivered through a pipe 46 to a suitable point of collection. This pipe is marked Product II in the drawings.

The fractionating and condensing equipment which have been illustrated are consistent with approved practice, and are susceptible of variation.

The operation preferably consists of a single pass. In some cases economic advantages may be realized by recycling all or a portion of the gas oil, or other relatively heavy condensate, through the cracking chamber. For that purpose the pipe 44 is shown provided with a valve 47, while between this valve and the bottom of the fractionating column a pipe 48 provided with a valve 49 leads to the sump tank 20. The arrangement shown permits either liquid from the spray 13 or a mixture of this liquid and heavy distillate from the fractionating equipment to be introduced into the reaction chamber. Or, the distillate designated as Product II may be charged, with or without cooling to a second similar unit operated under proper conditions for the treatment of gas oil or the like.

Provision is made for withdrawing fuel oil from the system. In that connection there is shown a valve 50 in the line 34 and a pipe 51 leading off from this line behind said valve, the pipe 51 having a valve 52 and a cooler 53 connected therein. By closing the valve 50 and opening the valve 52, a portion of this material can be removed from the system, this product being designated Product III.

Instead of the single sprays 9 and 13 indicated in the drawings, multiple sprays may be used at one or both of these points.

A valved line 150 containing a blower 151 is indicated. Through such a line any suitable inert gas may be introduced in proper proportion through the burner or into the mixing chamber to moderate the temperature slightly, though that is neither necessary nor desirable.

A modification of the invention employs an external, indirect heating means for vaporizing all or a part of the feed to the vapor phase reaction chamber. This vapor or mixture of vapor and liquid is then passed in through the spray nozzle 9 into the blast of hot gas from the burner 8, in such proportions as to give a resulting temperature equal to that required for a maximum conversion to the desired products. In a plan of this kind, water, the feed, any stock to be topped, or in fact any suitable relatively cold liquid can be used as the quenching medium.

Fig. 3 represents a system illustrating these matters.

The feed, or a part of the feed, is supplied through a valved pipe 59 and forced by a pump 60 through a pipe 61 to and through the coil 62 of a pipe still 63. This liquid may be understood to be a distillate. The coil 62 is connected by a valved pipe 64 with a vaporizer chamber 65. From the top of this chamber the vapors are conducted through a pipe 66 to the nozzle 9. By this nozzle the vapors are delivered, preferably in a form which tends to be that of a conical curtain or sheet, or fine jets corresponding to such general description, into the combustion and/or mixing chamber 7, where they are encountered and turned toward the throat of the reaction chamber 2 by the stream of hot gases proceeding from the burner 8. In either case, an intimate and uniform mixture of the vapors to be treated and of the hot gas is formed, and the hydrocarbon vapors are superheated to the predetermined cracking temperature in the briefest possible time.

The quenching spray 13 may be supplied with water or other liquid through a valved pipe 32.

On the other hand the feed or a part of the feed to the system may be introduced through the spray 13, to serve as the quenching medium and to be preheated. This feed material may be a distillate, or it may be a crude to be topped, or it could be a reduced crude or residual. 67 is a valved pipe connected with the quenching spray, through which this stock can be supplied from a suitable source by a pump 68.

The liquid settling out in the settling chamber 14 is drawn off through a pipe 69 and a cooler 71.

The reflux from the fractionating column 16 may be drawn off through a valved pipe 44 and a cooler 45, or this reflux may be conducted through a valved pipe 70 to the inlet side of the feed pump 60 connected with the coil of the pipe still 63.

The feed to the system may be taken entirely through the feed line 59, or it may be taken entirely through the feed line 67 and be delivered through the quenching spray. In the latter case, the reflux from the fractionating column supplies the pump 60 and the coil of the pipe still 63. Again, a

part of the feed may be taken from one source through the line 59, and another part of the feed may be taken, from the same or a different source, through the line 67. Again, the liquid supplied to the quenching spray may be a crude to be topped. In these cases, also, part or all of the reflux from the fractionating and condensing equipment may be recycled through the pipe still, the vaporizer, the nozzle 13, and the mixing and reaction chambers.

I appreciate that there are numerous other possible modifications of the invention and numerous other possible combinations and arrangements of apparatus and operations for carrying out the invention, and consequently I do not wish to be limited to the particular forms and modes of execution chosen for purpose of illustration.

The gasoline, motor-fuel or other liquid low-boiling end product will consist entirely or mainly of saturated and/or unsaturated hydrocarbons of the chain type, if a proper reciprocal relation of reaction time and reaction temperature are observed. Aromatic compounds are not produced in appreciable quantities below a certain temperature even over relatively long reaction periods. If the reaction temperature is above 850° F.–900° F. and if the reaction time, though brief, is sufficient, aromatic or ring-type hydrocarbons are formed, while between about 950° F.–1200° F., or higher with the proper corresponding reaction time, motor fuels having excellent antiknock properties, owing to the presence of such compounds in significant quantity, are obtainable.

By carrying the process further a low-boiling product consisting almost wholly of aromatic and unsaturated hydrocarbons can be separated.

I am not prepared to state that the bodies which give valuable anti-knock properties to motor fuel obtainable with the process and apparatus above described need be entirely or predominantly aromatic and unsaturated hydrocarbons, since it is believed that other bodies are produced which have a like effect.

It will be apparent that the invention is applicable to various hydrocarbon materials to be treated for the obtaining of various specific products.

The process and apparatus herein disclosed may be operated with or without the use of catalysts. For example, the apparatus lends itself readily to the placing of catalytic material in the reaction chamber or to the use of a wall for the chamber which will itself exert a catalytic influence for the promotion of the reactions.

What I claim as new is:

1. A continuous process for effecting thermal conversion of hydrocarbon oils and similar materials, which comprises continuously producing hot and substantially non-oxidizing combustion gases at a temperature above 2500° F. and, without previously altering the temperature of these gases, continuously introducing in fine division the hydrocarbons to be converted and mixing them with the hot gases so intimately that thermal equilibrium at a temperature above 950° F. is attained in all portions of the mixture practically instantaneously, passing the mixture at this temperature through an elongated reaction zone, and then instantly reducing the temperature to one at which the reactions are definitely arrested, by bringing the mixture into direct contact with finely divided cooling liquid, the entire time of mixing, attainment of thermal equilibrium, conversion and cooling being not in excess of one to a few seconds.

2. A continuous process for effecting thermal conversion of hydrocarbon oils and similar materials, which comprises continuously producing hot and substantially non-oxidizing combustion gases at a temperature above 2500° F. and, without previously altering the temperature of these gases, continuously introducing in fine division the hydrocarbons to be converted and mixing them with the hot gases so intimately that thermal equilibrium at a temperature above 950° F. is attained in all portions of the mixture practically instantaneously, passing the mixture at this temperature through an elongated reaction zone, and then instantly reducing the temperature to one at which the reactions are definitely arrested, by bringing the mixture into direct contact with the finely divided cooling liquid, the entire time of mixing, attainment of thermal equilibrium, conversion and cooling being not in excess of one to a few seconds, of which total time the time in attaining thermal equilibrium and the time of cooling are together less than one-fifth of the total time.

3. A process as defined in claim 1, further characterized in that the hydrocarbons are introduced in the state of vapor.

4. A process as defined in claim 1, further characterized in that the hydrocarbons are introduced in the liquid phase.

5. A continuous process for effecting thermal conversion of hydrocarbon oils and similar materials, which comprises continuously producing hot and substantially non-oxidizing combustion gases at a temperature above 2500° F. and, without previously altering the temperature of these gases, continuously introducing in fine division the hydrocarbons to be converted and mixing them with the hot gases so intimately that thermal equilibrium at a temperature above 1000° F. is attained in all portions of the mixture practically instantaneously, passing the mixture at this temperature through an elongated reaction zone, and then instantly reducing the temper-

ature to one at which the reactions are definitely arrested, by bringing the mixture into direct contact with finely divided cooling liquid, the entire time of mixing, attainment of thermal equilibrium, conversion and cooling being less than approximately one second.

6. A continuous process for effecting thermal conversion of heavy oils such as reduced crude, which comprises bringing a continuous stream of finely divided liquid particles of this oil into such intimate contact with all portions of a flow of hot gas at a temperature above 2500° F., this flow being independently controlled, that the oil particles are immediately and completely vaporized and the vapors are uniformly superheated to a temperature above 900° F., maintaining all portions of the flowing vaporous and gaseous mixture at this cracking temperature for a reaction time on the order of a small fraction of a second to a few seconds and not in excess of a few seconds, and then, before any polymerization to tars condensable in the reaction chamber takes place, instantly quenching all portions of the mixture by direct contact with finely divided cooling liquid.

ERNEST WAYNE REMBERT.