Nov. 1, 1938. P. OSTERGAARD 2,135,109

ART OF CRACKING PETROLEUM OILS

Filed Dec. 2, 1936 8 Sheets-Sheet 1

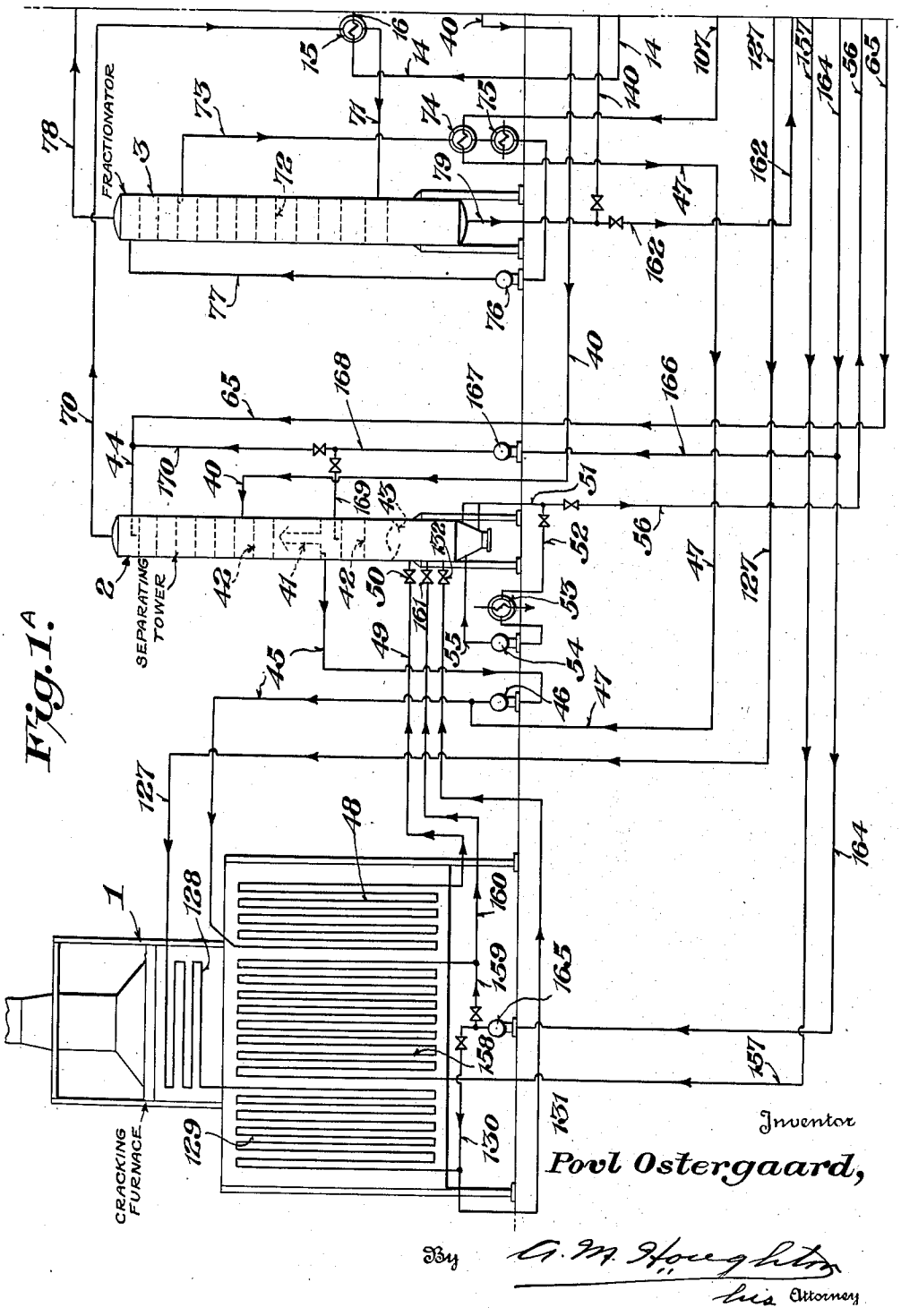

Fig. 1A.

Inventor
Povl Ostergaard,

By G. M. Houghton
his Attorney

Nov. 1, 1938. P. OSTERGAARD 2,135,109

ART OF CRACKING PETROLEUM OILS

Filed Dec. 2, 1936 8 Sheets-Sheet 2

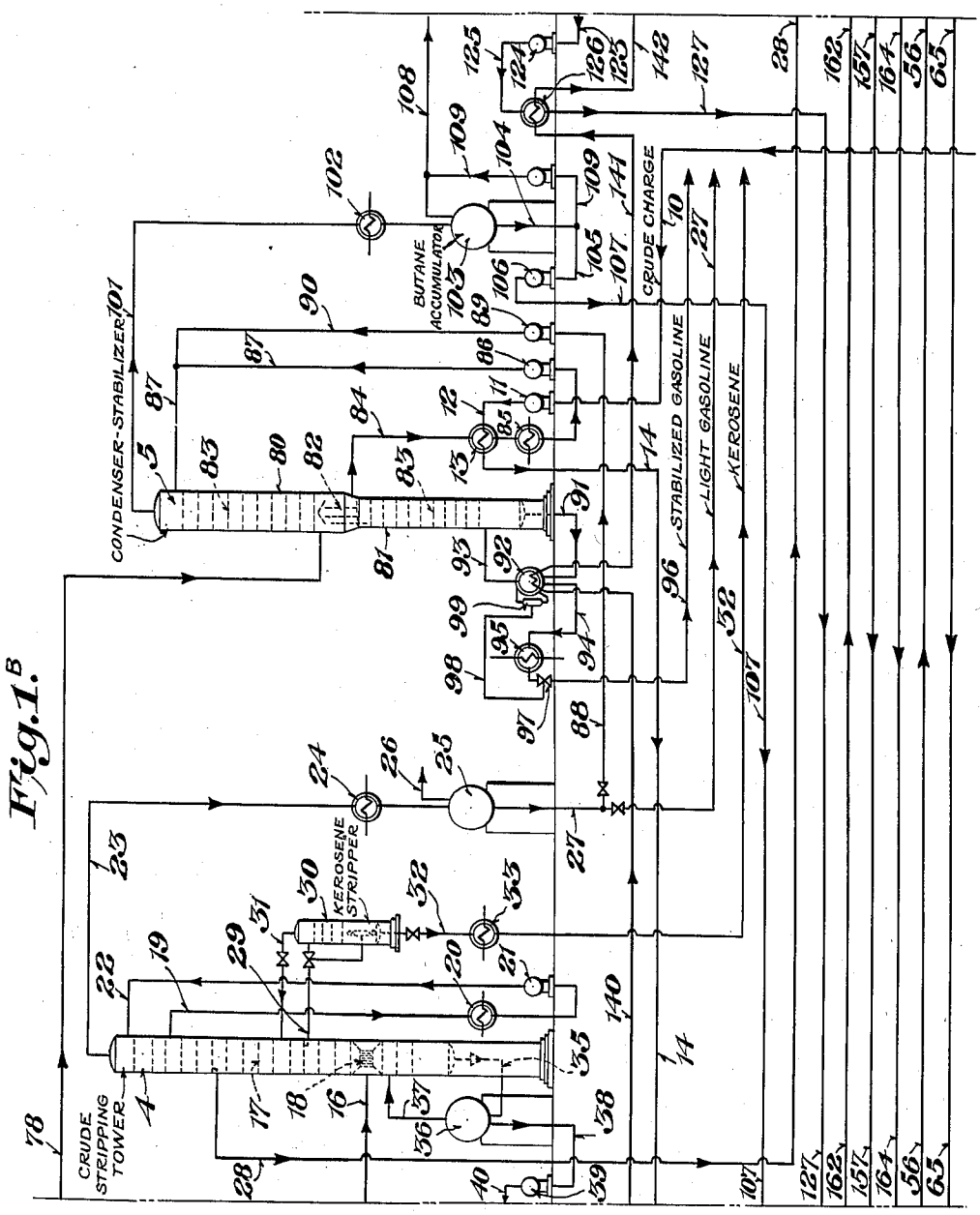

Fig. 1.B

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Nov. 1, 1938. P. OSTERGAARD 2,135,109

ART OF CRACKING PETROLEUM OILS

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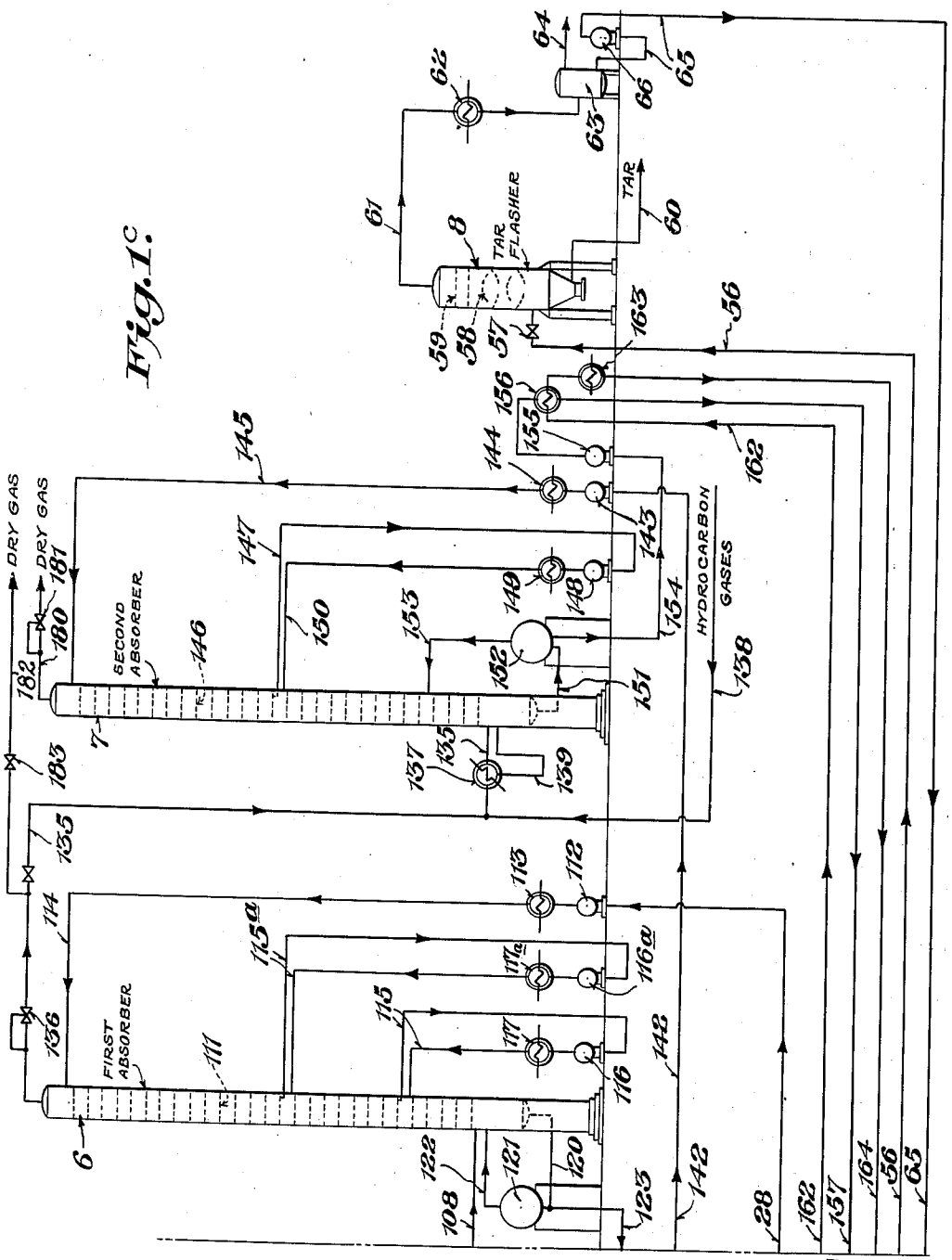
Fig. 1C.



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By G. M. Houghton Attorney

Nov. 1, 1938. P. OSTERGAARD 2,135,109

ART OF CRACKING PETROLEUM OILS

Filed Dec. 2, 1936 8 Sheets-Sheet 4

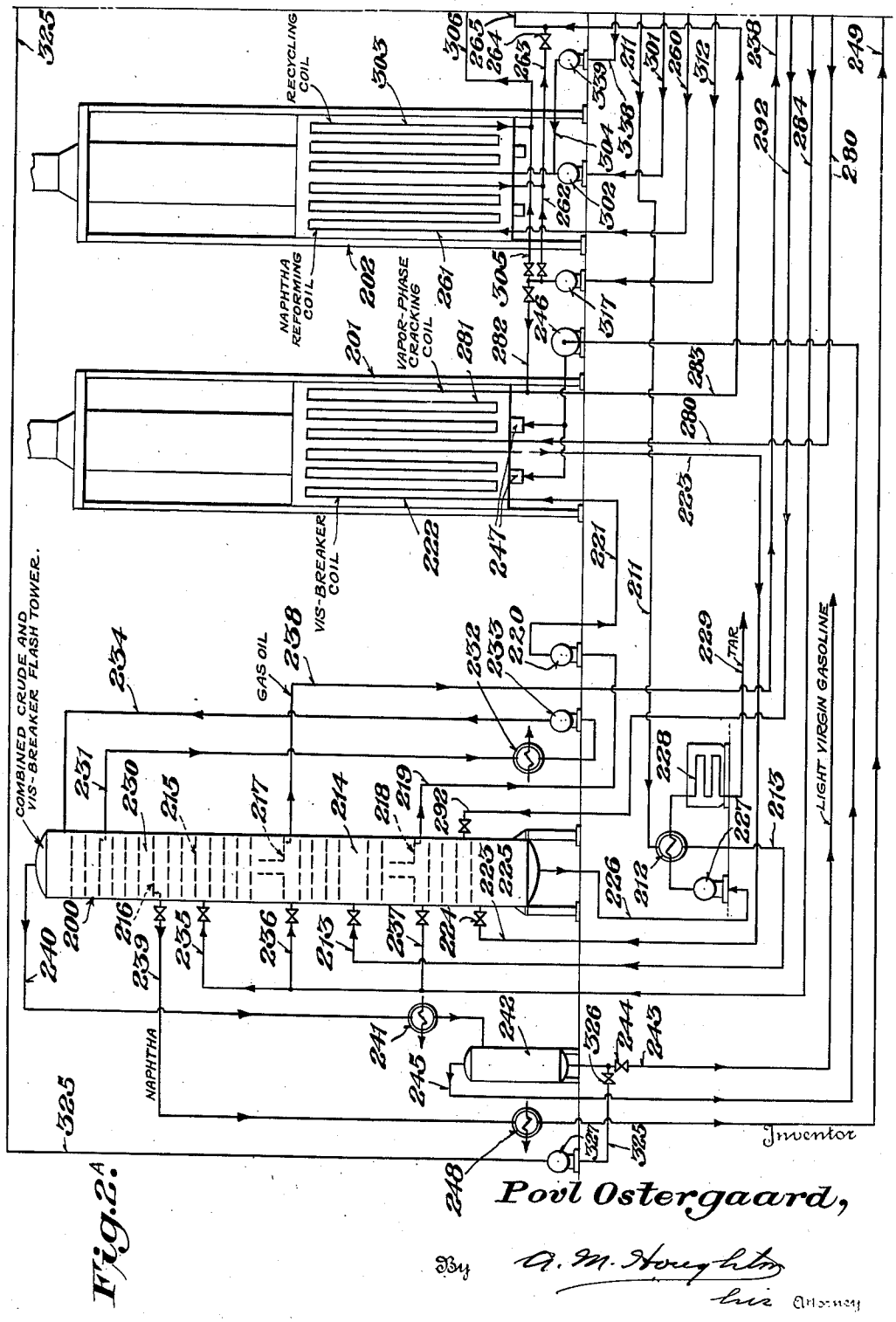

Fig. 2A.

Inventor

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Nov. 1, 1938. P. OSTERGAARD 2,135,109

ART OF CRACKING PETROLEUM OILS

Filed Dec. 2, 1936 8 Sheets-Sheet 5

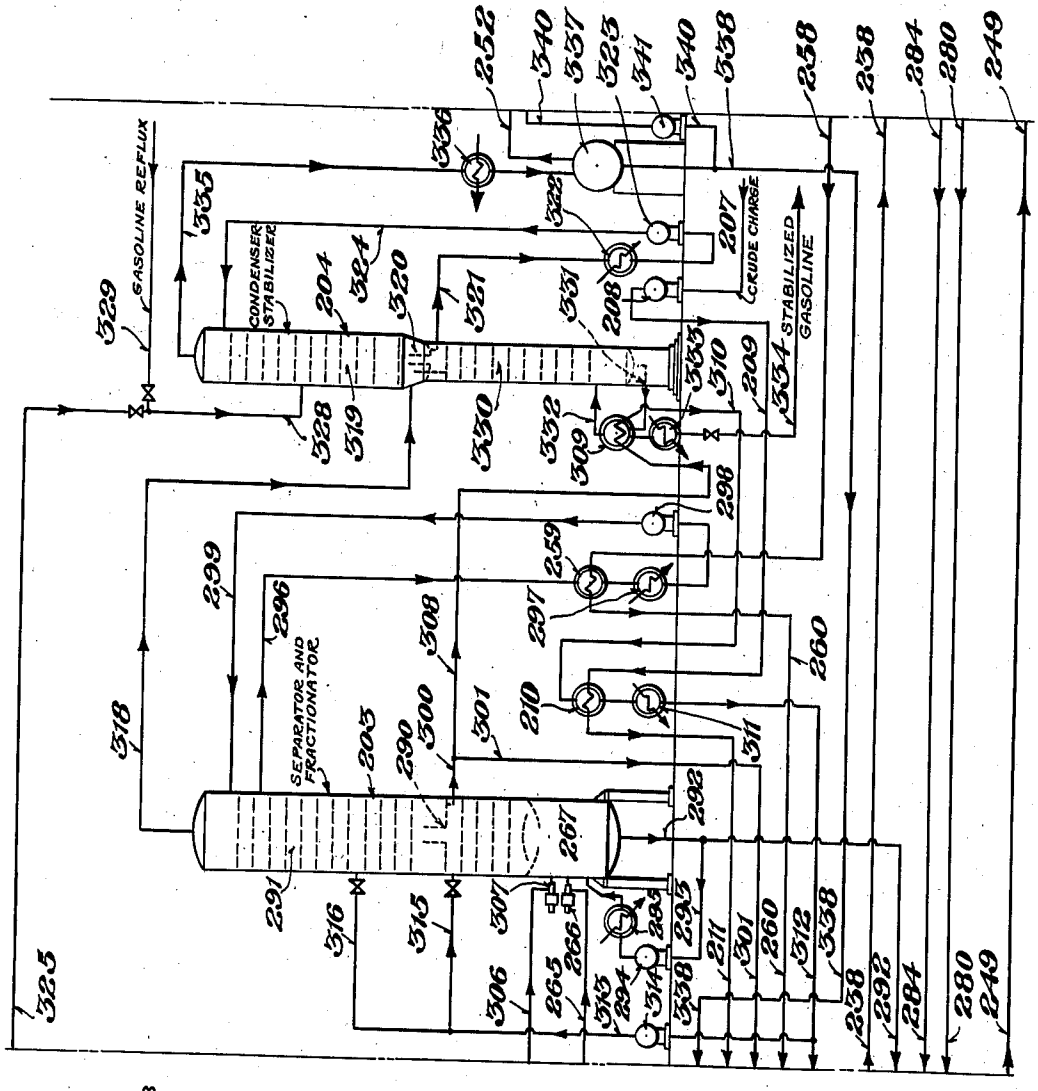

Fig. 2.B

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Nov. 1, 1938. P. OSTERGAARD 2,135,109

ART OF CRACKING PETROLEUM OILS

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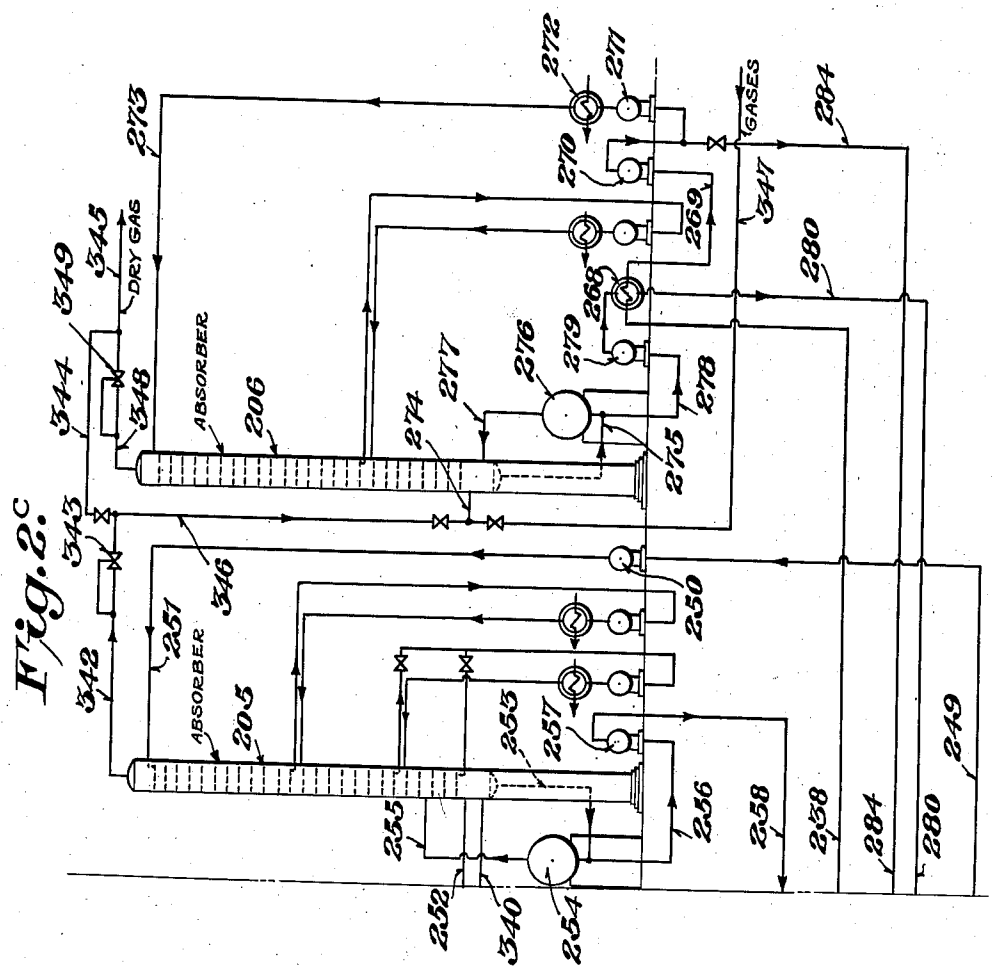

Fig. 2c.

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Attorney

Nov. 1, 1938. P. OSTERGAARD 2,135,109

ART OF CRACKING PETROLEUM OILS

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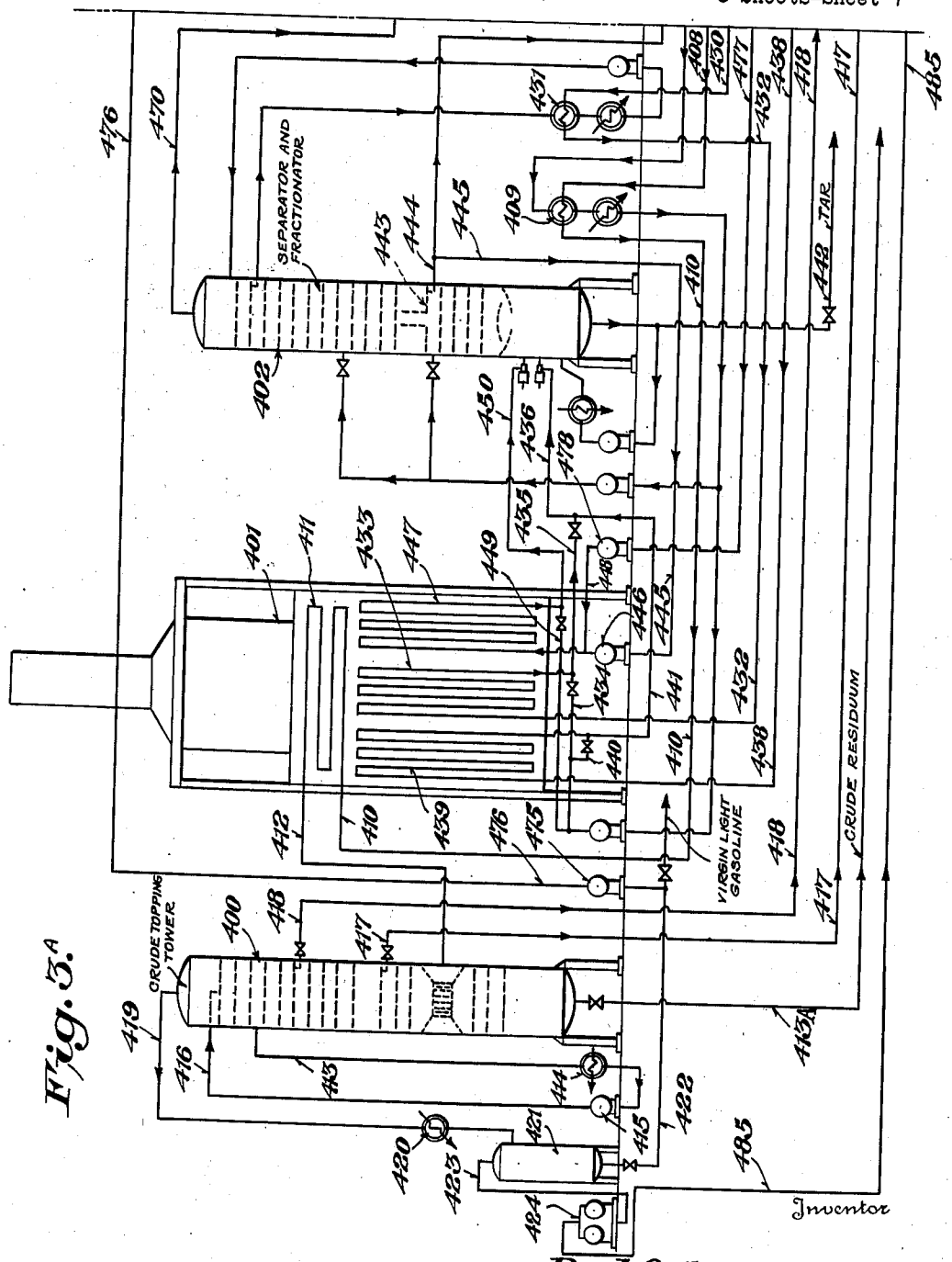

Fig. 5A

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ART OF CRACKING PETROLEUM OILS

Filed Dec. 2, 1936 8 Sheets-Sheet 8

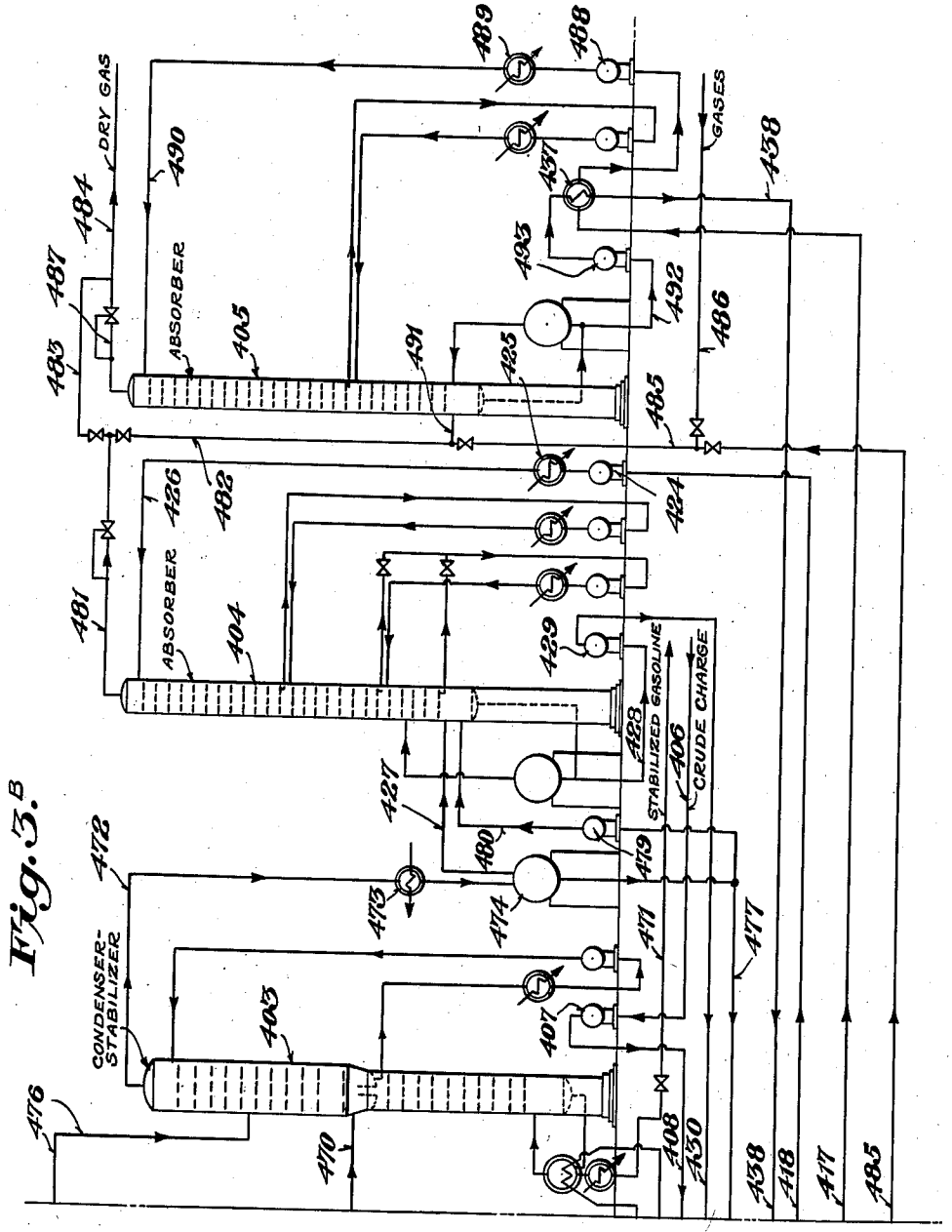

Fig. 3.B

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By G. M. Stanley Attorney

Patented Nov. 1, 1938 2,135,109

UNITED STATES PATENT OFFICE

2,135,109

ART OF CRACKING PETROLEUM OILS

Povl Ostergaard, Mount Lebanon, Pa., assignor to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

Application December 2, 1936, Serial No. 113,906

8 Claims. (Cl. 196—9)

This invention relates to the art of cracking petroleum oils and it comprises a process of making motor fuel or gasoline of high anti-knock value from hydrocarbon oil as well as normally gaseous hydrocarbons, such as those produced in cracking hydrocarbon oils, and such as natural gases and the like.

In my copending applications, Serial No. 52,717, filed December 3, 1935, and Serial No. 97,295, filed August 21, 1936, of which applications this application is in part a continuation. I disclosed a process of cracking hydrocarbon oil, such as naphtha or relatively heavy oil, wherein the oil is subjected to thermal conversion in the presence of normally gaseous hydrocarbons containing 3 to 4 carbon atoms per molecule, such hydrocarbons including those formed as a result of the cracking of the hydrocarbon oil as well as, where desired, normally gaseous hydrocarbons from an extraneous source. As disclosed in the aforesaid copending applications, the process is advantageously conducted by employing the hydrocarbon oil charging stock as an absorption medium for recovering the desired normally gaseous hydrocarbons from hydrocarbon gases containing them in addition to fixed gases such as hydrogen and methane. As disclosed in my application Serial No. 97,295, the operation is so conducted that the hydrocarbon oil is subjected to a higher degree of conversion per pass, in the presence of the normally gaseous hydrocarbons, than can be attained in similar apparatus when cracking the same oil alone and without the presence of the normally gaseous hydrocarbons. Under such conditions the degree of conversion per pass, or the "crack per pass", may be increased over that which could be obtained under practical conditions in the conversion of the oil alone. The resultant gasoline product represents a material of extremely high anti-knock value, the major portion of the increase in anti-knock value obtained resulting from the increased conversion of the oil and the balance of the increase in octane number of the gasoline being due to polymerization of gas constituents and inter-reaction between gas constituents and the oils or products of conversion thereof.

The specific processes described and illustrated in the above-mentioned copending applications are of the "single coil" type and are preferably, although not necessarily, of the "once-through" type, i. e. they are operations which are preferably conducted without recycling oil to the conversion coil.

I have found that whereas straight-run gas oils can be cracked by themselves to between 15 to 30 per cent crack per pass, the same gas oils diluted with normally gaseous hydrocarbons containing 3 to 4 carbon atoms per molecule can be cracked in similar apparatus to from 25 to 60 per cent conversion per pass. Similarly, whereas a residual petroleum oil such as a reduced crude may be cracked by itself to from 5 to 12 per cent crack per pass, the same oil, diluted with liquefied normally gaseous hydrocarbons containing 3 and 4 carbon atoms per molecule may be cracked to from 10 to 25 per cent conversion per pass. Similarly, naphthas with boiling ranges lying between approximately 200° and 500° F. may be cracked to a higher degree of conversion per pass in the presence of liquefied normally gaseous hydrocarbons containing 3 and 4 carbon atoms per molecule than when cracked alone. In each instance, while the gasoline-like polymers resulting from the straight polymerization of the normally gaseous hydrocarbons are included in figuring the degree of conversion per pass or the degree of crack per pass, the ultimate conversion per pass or crack per pass is in excess of that obtained by simply considering the normal production of gasoline from the oil alone and the normal production of polymers from the normally gaseous hydrocarbons alone, when these oils and normally gaseous hydrocarbons are separately subjected to conversion; the results are better than the sum of the results obtained by separately cracking the oil and polymerizing the gases.

Moreover, the production of tar is materially reduced, due probably to the fact that nascent products of conversion of the hydrocarbon oil, which would otherwise undergo polymerization to form tar, react with saturated or unsaturated gaseous compounds to a much greater extent than is true when oil is cracked alone and in the absence of added normally gaseous hydrocarbons. The products of such reaction tend to be rich in aromatics and have lower molecular weights and lower boiling points than the oils which would be formed by a combination of cyclic compounds produced in the cracking of the oil alone; these products of reaction in some instances represent compounds within the desired motor-fuel boiling point range and in other instances represent compounds which are readily cracked in the process described herein to yield gasoline-like products of high anti-knock value.

In the process disclosed in the present application, I have applied the general teachings and principles of the inventions disclosed in the aforementioned copending applications to the cracking of hydrocarbon oil in a so-called "combination unit" of the multi-coil type, with advantageous results. In such a unit, the starting material is usually a crude petroleum oil. The crude oil is first stripped to recover segregated fractions of definite boiling-point ranges as well as a stripped or reduced crude, and a number or all of the segregated fractions are cracked under optimum conditions for their conversion, the hot cracked products thus obtained being combined in such manner as to simplify recovery of the products and segregation of the various charging and recycle stocks. Where desired, the topped or reduced crude may be subjected to a mild cracking or so-called "viscosity-breaking" operation for the purpose of producing a clean charging stock for subsequent cracking of gasoline rather than for the production of a high yield of gasoline directly by cracking the reduced crude under more severe conditions.

In one specific type of operation described in detail hereinbelow and especially applicable to crude petroleum of relatively low sulfur content, the crude is heated, preferably by heat exchange in the system, and discharged into an atmospheric stripping tower where light gasoline boiling up to about 200° F., naphtha boiling from 200° to 400 or 500° F. and, if desired, kerosene, are removed and recovered. The stripped petroleum is then charged into the upper portion of a separating tower receiving hot cracked products from a number of cracking operations, and by direct heat exchange with these hot cracked products is further reduced. The reduced crude, commingled with normally gaseous hydrocarbons, is cracked in a suitable coil and the hot cracked products are discharged into the lower portion of said separating tower. The vapors from the separating tower are fractionated to remove gas oil constituents boiling between about 300° and 700° F. and are then introduced into a condensing and stabilizing system for the eventual recovery of stabilized gasoline, having an end point of from 320° to about 400° F., and free from butanes and the like to a large extent. The vapors and gases leaving the condensing and stabilizing system are further condensed to provide a liquid fraction consisting largely of hydrocarbons having 4 carbon atoms per molecule, this liquid fraction being commingled at least in part with the reduced crude about to be cracked. The naphtha recovered in the crude stripping tower is used as an absorbent to remove the higher boiling constituents of the gases remaining after the aforesaid condensation, and the thereby enriched naphtha is reformed in a separate heating coil, the hot reformed products being delivered to the lower portion of the separating tower. The gas-oil recovered as described hereinabove is employed as an absorbing medium in a second absorber which may receive gases from an extraneous source, or gases leaving the first-mentioned absorber, or both, and the thereby enriched gas-oil containing dissolved hydrocarbons having 3 to 4 carbon atoms per molecule is delivered to a third cracking coil, the hot cracked products therefrom passing to the separating tower along with the hot cracked products from the reduced crude cracking coil and the reforming coil.

In a second type of operation described in detail hereinbelow, the crude charging stock is first distilled in a crude stripping tower, light gasoline, naphtha and gas-oil fractions being recovered from this tower. The reduced crude is subjected to a mild cracking or viscosity-breaking operation and the hot viscosity-broken products are discharged back into a lower portion of the crude stripping tower, tar being separated and the vapors passing into the upper portion of the crude stripping tower for recovery and fractionation along with the initially heated crude oil. The naphtha and gas-oil fractions thus recovered, after passing through separate absorbers wherein they are enriched with normally gaseous hydrocarbons, are reformed and cracked, respectively, in separate coils, and the cracked products, after quenching, are delivered to a separator from which tar and vapors are separately removed. The vapors are fractionally condensed to remove gas-oil, stabilized gasoline and a liquid "butane" fraction. The gas-oil and the "butane" fraction are combined and delivered to a separate recycling coil from which the hot cracked products pass into the separator along with the products from the reforming coil and the virgin gas-oil cracking coil. The remaining gases and vapors pass through the naphtha absorber and either resultant scrubbed gases or gases from an extraneous source, or both, then pass through the gas-oil absorber. This type of operation is especially suitable for crude petroleum stocks of relatively high sulfur content.

In a third type of operation also described in detail hereinbelow and especially adapted to the treatment of crude oil from which it is desired to recover lubricating oil constituents, the crude oil is first topped to recover light virgin gasoline, heavy naphtha and gas-oil fractions, the topped crude being withdrawn from the system and substantially treated for the recovery of the lubricating oil constituents contained therein. The heavy naphtha and gas-oil fractions thereby recovered are used as absorption media in separate absorbers for the recovery of normally gaseous hydrocarbons from mixed hydrocarbon gases produced as hereinafter set forth, and the enriched fractions are then subjected to reforming and cracking, respectively, in separate coils. The hot cracked products from these coils are then discharged together into a vapor-separator from which tar is removed. The vapors are fractionated to recover gas-oil cycle stock and stabilized gasoline. The remaining gases and vapors are passed to the absorption system. The gas-oil cycle stock is recycled to a separate coil, preferably in admixture with hydrocarbons having 3 to 4 carbon atoms per molecule obtained by subjecting the cracked gases to condensation between the gasoline condensation stage and the absorption stage. The hot cracked products from the recycling coil are also delivered to the vapor separator, together with the products from the reforming and cracking coils.

It is a characteristic of my process described herein, in certain of its embodiments, that the virgin or uncracked stocks are largely or wholly subjected to conversion in a once-through manner, that is to say, without recycling, whereas cracked gas oil constituents from the various operations are largely or wholly segregated and subjected to conversion in a recirculatory or cyclic manner; in short, recycling operations are primarily confined to a single coil, which coil receives only previously cracked products. In the case of each stock, the conversion is, however, conducted

in the presence of recycled normally gaseous hydrocarbons, the ratio of normally gaseous hydrocarbon to oil varying somewhat according to the nature of the particular oil, the degree of conversion desired and the conditions of temperature and pressure employed in the conversion. In general, however, any gas oil recovered by merely viscosity-breaking a reduced crude under extremely mild conditions may be treated for the purposes of this invention as though it were a virgin or uncracked stock, that is to say, it is cracked, either alone or with strictly virgin gas-oil, in a once-through manner, while such products of the more drastic cracking as fall within the gas-oil boiling-point range are recycled to a separate coil. I have found that this principle of operation, particularly in conjunction with the recycling of normally gaseous hydrocarbons and the regulation of the gas-recycle ratios, makes it possible to obtain better results than can be obtained when operating a combination unit without benefit of my invention.

Important objects achieved in the utilization of my invention are the production of a high yield of gasoline of high anti-knock value when used as a motor fuel, reduction in the amount of tar produced, thermal economy, and the utilization to the best advantage of the gases produced in the operation.

My invention has for further objects, however, such additional operative advantages and improvements as may hereinafter be found to obtain.

In order that my invention may be fully set forth and understood, I now describe, with reference to the drawings accompanying and forming part of this specification, various preferred forms and manners in which my invention may be practiced and embodied. In these drawings,

Figures 1A, 1B and 1C are vertical elevational views of various portions of an assembly of apparatus adapted for the performance of the process of my invention, the apparatus being shown in more or less diagrammatic form. In examining the drawings and applying the descriptive matter of the specification thereto, Figures 1A, 1B and 1C are intended to be placed side by side in the order indicated, reading from left to right; when thus arranged these figures form a single figure illustrating the entire apparatus assembly used in the process;

Figs. 2A, 2B and 2C are similar views of various portions of an alternative form of apparatus adapted for the performance of the process of my invention in a somewhat different embodiment; and

Figs. 3A and 3B are similar views of a further type of apparatus for carrying out the process of my invention in a still further embodiment thereof.

Similar reference numerals designate similar parts in all the several views of the drawings.

Referring now to the drawings, and more particularly to Figs. 1A, 1B and 1C thereof, the principal apparatus elements consist of a furnace 1 provided with several sets of cracking coils to be described hereinbelow, a separating tower 2, a fractionating tower 3, a crude stripping tower 4, a vapor-feed condenser and stabilizer 5, absorbers 6 and 7 and a tar flasher 8, together with various pipes, separators, accumulators, pumps, valves, heat exchangers and other incidental equipment. The function and purpose of the various units will be made more clear from the description set forth hereinbelow.

Crude petroleum oil is introduced into the system through a line 10 and is forced by a pump 11 through a line 12, a heat exchanger 13, a line 14, a heat exchanger 15 and a line 16 into the atmospheric-pressure crude stripping tower 4 at an intermediate level therein. The crude stripping tower 4, which receives the crude oil preheated in the heat exchangers 13 and 15, is provided with conventional plates or trays 17 and may also be provided as shown with an entrainment separator 18 at the point of introduction of the heated oil thereto.

In the crude stripping tower 4 the crude oil, which has been heated to an elevated temperature of from 300° to 700° F., preferably about 500° F., in heat exchangers 13 and 15, is partially vaporized and the vaporized portions are subjected to fractional condensation and rectification. In order to assist in the condensing and rectifying action some cooling is necessary. This cooling may be provided by locating an indirect heat exchanger or cooling coil in the upper part of the crude stripping tower 4 or by supplying to the top of the crude stripping tower 4 a cool liquid reflux medium. In a preferred instance shown, a side stream is withdrawn from a point near the top of the tower 4 through a line 19, this side stream passing to a cooler 20 and then being returned by means of a pump 21 and a line 22 to the top of the stripping tower 4 to serve as a cooling and refluxing medium therefor. It will be obvious to those skilled in the art that while the particular form of cooling and refluxing means disclosed is preferred, various other expedients may be employed for the purpose of providing the necessary cooling and refluxing in the tower 4.

The lowest boiling constituents, consisting of light virgin gasoline, pass uncondensed from the top of the crude stripping tower 4 through a line 23 to a cooler or condenser 24 and thence to a separator 25 having a vent 26. The condensate collecting in the separator 25 may be withdrawn therefrom through a line 27 and removed from the system, or it may be used in whole or in part as a refluxing and condensing medium elsewhere in the system.

A naphtha side stream, consisting of somewhat higher boiling condensed naphtha constituents, having a boiling range of for example from 200° to 500° F., is withdrawn from the upper portion of the tower 4 through a line 28, while a still heavier side stream consisting primarily of kerosene or furnace oil constituents is withdrawn from the tower 4 through a line 29 and delivered to a kerosene stripper 30. Vapors removed in the stripper 30 are returned to the tower 4 through a vapor-return line 31, while the stripped kerosene or furnace oil is withdrawn from the stripper 30 through a line 32, passing through a cooler 33 on its way out of the system.

The remaining portion of the partially distilled crude, which will henceforth be referred to as stripped crude, is removed from the bottom of the stripping tower 4 through a line 35 and passes to an accumulator 36, which is provided with a vapor line 37 leading back into the stripping tower 4. It will be understood that in this instance the virgin gas-oil constituents present in the original crude remain largely in the stripped crude.

The stripped crude from the accumulator 36 is then delivered through a line 38, a pump 39 and a line 40 to the upper portion of the separating tower 2. The separating tower 2 is pro-

vided with a trap-out tray or accumulator tray 41 at an intermediate level therein, with plates or trays 42 located above and below the tray 41, and with suitable baffles 43 in the lower portion thereof, and receives hot cracked vapors from the furnace 1 through transfer lines which will be described hereinbelow. These vapors pass upward through the trap-out tray 41 and effect a further distillation of the stripped crude delivered through the line 40. The fractionation is assisted by means of reflux supplied to the top of the tower 2 through a line 44.

The reduced crude accumulating on the tray 41 is withdrawn therefrom through a line 45, wherein is located a pump 46, and is then admixed with liquefied normally gaseous hydrocarbons, primarily butane and butylene, introduced to the line 45 through a line 47 from a source to be described hereinbelow. The mixture of reduced crude and liquefied normally gaseous hydrocarbons then passes through a heated coil 48 located within the furnace 1. The coil 48 advantageously consists of an initial heating section having a high heat input, and a soaking section with a lower heat input. The percentage by volume of the liquefied gaseous hydrocarbons will ordinarily amount to between 10 and 100 per cent of the reduced crude.

In the heating coil 48 the mixture of reduced crude and normally gaseous hydrocarbons is subjected to conversion at a temperature of from 800° to 1000° F. and under a pressure varying between 100 and 1000 pounds per square inch, the conditions being such that the degree of conversion per pass or crack per pass obtained is higher than could be obtained in the same apparatus if the reduced crude were charged through in the absence of added normally gaseous hydrocarbons. In a typical instance the operating conditions may be such as to give a coil-outlet temperature of about 925° F. and a coil-outlet pressure of about 750 pounds per square inch, the ratio of volume of liquefied gas to the liquid volume of the reduced crude under atmospheric conditions being approximately 1:3 and the reduced crude being one which could not well be subjected to a coil-outlet temperature of more than about 875° F. in the same coil in the absence of the added normally gaseous hydrocarbons.

In the heating coil 48 the reduced crude and such heavy recycle oil as may have been accumulated therewith in the separating tower 2 is cracked in the presence of the normally gaseous hydrocarbons; the degree of conversion per pass being from 10 to 25 per cent. The gases themselves manifest some tendency to crack and polymerize and to combine with products obtained in cracking the heavy oil, the tendency being to form a greater percentage of hydrocarbons boiling below 700° F. and a smaller percentage of hydrocarbons boiling above 700° F. than would be the case if the heavy oil were cracked by itself. The reactions which take place are involved and complex but actual experiments in commercial scale operation have proved that these reactions do take place.

The hot cracked products from the coil 48 then pass through a transfer line 49 and a pressure reducing valve 50 into the lower portion of the separating tower 2, where they separate into vaporous and liquid products. The vapors pass upward into the upper portion of the separating tower as aforesaid while the separated liquid or tar is withdrawn through a line 51. A portion of the tar may be returned through a line 52, a cooler 53, a pump 54 and a line 55 to the bottom of the separating tower 2 in order to minimize or prevent the formation of coke therein while the remaining portion passes through a line 56 and a valve 57 into the tar flasher 8, the interior of which is provided with baffles 58 and a suitable number of plates or trays 59. Flashed tar is withdrawn from the bottom of the tar flasher 8 through a line 60 while the liberated vapors pass through a line 61 to a cooler or condenser 62 and thence to a separator 63 having a gas vent 64. The condensate recovered in the separator 63 is advantageously returned by means of a line 65 and a pump 66 to the line 44, thus entering the upper portion of the separating tower 2 as a cooling and refluxing medium therefor.

The substantially tar-free vapors leaving the top of the separating tower 2 pass through a vapor line 70, the heat exchanger 15 and a line 71 to the lower portion of the main fractionating tower 3, the purpose of which is to remove constituents boiling above the boiling point range of the desired gasoline fraction subsequently to be condensed, i. e. to remove clean charging stock or gas oil constituents, including such products of reaction between gases and products of conversion of the oils as fall within the gas-oil range. For this purpose the fractionating tower 3 is provided with suitable cooling and refluxing means. In the instance shown this means comprises a side stream withdrawal line 73 which serves to withdraw a liquid side stream from a point near the top of the fractionator 3. This side stream then passes through a heat exchanger 74 and a cooler 75 and is then returned by means of a pump 76 and a line 77 to the top of the fractionator 3. Gasoline vapors and lighter constituents uncondensed in the fractionator 3 are withdrawn through a vapor line 78 while gas-oil condensate, having a boiling range of for example from 400° to 700° F., is withdrawn from the bottom of the fractionator 3 through a line 79.

The gasoline vapors and gases leaving the tower 3 through the line 78 pass to a vapor-feed condenser and stabilizer 5 which consists of a condensing section 80 and a stabilizing section 81 separated by a trap tray or weir device 82. The sections 80 and 81 are interiorly provided with suitable plates or trays 83. Unstabilized gasoline condensate is withdrawn from the tray 82 through a line 84 and passes through the heat exchanger 13 and a cooler 85, being then returned to the upper portion of the condensing section 80 by means of a pump 86 and a line 87, thus serving as a cooling and refluxing medium for the condensing operation. As shown in the drawings, the reflux so supplied may be supplemented by a portion of the light gasoline collected in the accumulator 25, this portion passing from the accumulator 25 through the line 27, a line 88, a pump 89, a line 90 and the line 87 into the condensing section 80 of the condenser and stabilizer 5.

The remaining portion of the unstabilized condensate passes downward into the stabilizing section 81 where it is subjected to distillation and rectification for the purpose of removing undesirably light constituents. The vaporized constituents thereby liberated return in vapor form to the condensing section 80 while the thereby stabilized gasoline passes from the bottom of the stabilizer 81 through a line 91 into a reboiler 92 having a vapor-return line 93 leading back into

the stabilizing section 81. The stabilized gasoline leaving the reboiler 92 through a line 94 passes through a cooler 95 and thence through a line 96 having a valve 97 to storage. The valve 97 is preferably connected by means of operating mechanism 98 to a float or level device 99 attached to and forming part of the reboiler 92.

As will be clear from the above, the operation of the condenser and stabilizer is so conducted as to effect the recovery from the gases and vapors passing through the line 78 of stabilized gasoline hydrocarbon and fixed gases. The vapor-feed condenser and stabilizer is a highly advantageous feature of the apparatus illustrated, in that a vapor-feed condenser and stabilizer of this type is especially advantageous in the recovery of stabilized gasoline from vapors containing a high percentage of normally gaseous constituents and fixed gases. The operation and details of this condenser and stabilizer are further disclosed in my copending applications Serial No. 52,717, filed December 3, 1935, Serial No. 97,295, filed August 21, 1936, and Serial No. 103,947, filed October 3, 1936, the last mentioned application dealing primarily with the condenser and stabilizer itself, independent of a combined oil-cracking and gas-recycling unit, while the two earlier applications disclose the use of this vapor-feed condenser and stabilizer in conjunction with combined oil-cracking and gas-recycling units.

The vapor-feed condenser and stabilizer 5 is advantageously operated, insofar as the present process is concerned, at a pressure of between 100 and 350 pounds per square inch, the preceding towers 3 and 2 being maintained under slightly higher pressures.

The vapors which leave the top of the condensing section 80 through a line 101 consist of low-boiling hydrocarbons ranging from methane on the one hand to butanes and butylenes on the other hand, and they may also contain some hydrogen. The hydrocarbons of lower molecular weight such as methane, ethane and ethylene are not sufficiently reactive to warrant recycling them to the conversion units. Butanes and butylenes are, however, extremely reactive and it is desirable to recycle all of these constituents to the conversion units, as well as, to some extent at least, propane and propylene. I have found that it ordinarily does not pay commercially to return ethane and ethylene nor to try to effect the recovery and recycling of all of the propane and propylene; it is desirable, however, to recover and return a considerable portion of the latter. In any event, the recovery and recycling of the normally gaseous hydrocarbons is so regulated as to avoid accumulation of these gases in the system and to prevent the escape from the system of the butanes and butylenes.

A portion of the normally gaseous hydrocarbons, primarily butanes and butylenes, contained in the vapors passing through the line 101 may conveniently be recovered, under the operating pressures mentioned, by simply condensing the vapors. For the purpose I provide a cooler or condenser 102 located in the line 101, and an accumulator or separator tank 103. A portion or all of the condensate thereby obtained may be delivered through a line 104, a branch line 105, a pump 106 and a line 107 to the heat exchanger 74 and thence through the line 47 to the inlet pipe 45 leading to the cracking coil 48, as described hereinabove.

The vapors separated in the separator 103 pass through a line 108 into the lower portion of the absorber 6. The remaining portion of the condensate from the separator 103 may also be delivered to the absorber 6 through a branch line 109 communicating with the pipe 104, having a pump 110 and terminating in the vapor line 108. This arrangement provides for a certain flexibility of operation, the condensate from the separator 103 being divided between the lines 105 and 109 in such manner as to give proper recycle ratios in the various cracking coils.

In the absorber 6, the interior of which is provided with suitable plates or trays 111, the vapors and gases are scrubbed with a suitable hydrocarbon liquid absorption medium, preferably a low-boiling oil such as naphtha, for the recovery therefrom of hydrocarbons containing 3 and 4 carbon atoms per molecule. In the preferred instance illustrated, the virgin naphtha removed as a side stream from the crude stripping tower 4 through the line 28 is advantageously employed as the absorption medium in the absorber 6. This naphtha side stream passes through the line 287 to a pump 112 and thence through a cooler 113 and a line 114 to the upper portion of the absorber 6. In descending through the absorber 6 the cooled naphtha thus introduced effects a selective absorption of the higher boiling components of the gases and vapors also traversing the absorber 6. At one or more points in the tower, as shown, suitable side streams may be withdrawn through lines 115 and 115a wherein are located pumps 116, 116a and coolers 117, 117a, respectively, and then returned to the absorber 6. This arrangement, which may be repeated at convenient intervals throughout the length of the absorber 6, provides for the dissipation of the heat of absorption of the normally gaseous hydrocarbons in the liquid absorbing oil.

The enriched naphtha, containing dissolved normally gaseous hydrocarbons having 3 and 4 carbon atoms per molecule, leaves the bottom of the absorber 6 through a line 120 which communicates with an accumulator 121 having a vapor return line 122 leading back into the absorber 6. The enriched naphtha from the line 120 and the accumulator 121 then passes through a line 123, a pump 124, a line 125, a heat exchanger 126 and a line 127 into a preheating coil 128 located in the convection section of the furnace 1 and thence through a cracking coil 129 located in a hotter portion of the furnace 1. The cracking coil 129 is preferably composed of a heating section arranged for high heat input and a soaking coil arranged for a lower heat input.

As has been described in connection with the cracking coil 48, the mixture of oil and normally gaseous hydrocarbons traversing the coils 128 and 129 is subjected to cracking under conditions effective to give a higher degree of conversion per pass than could be obtained if the oil were separately passed through the same apparatus in the absence of the normally gaseous hydrocarbons. In general, sufficient heat will be supplied to give a coil-outlet temperature between 900° and 1450° F., the pressure varying between 300 and 3000 pounds per square inch. Typical operating conditions which have been carried out in practice include coil-outlet temperatures of 1020° to 1030° F. and coil-outlet pressures of from 1000 to 1200 pounds per square inch, the ratio of the volume of liquefied gases to the volume of naphtha in the furnace feed, measured at atmospheric temperature, being approximately 1:1. The gas recycle ratio may, however, vary considerably.

More detailed operating conditions are fully disclosed in my copending application Serial No. 97,295 referred to hereinabove.

The hot cracked products leaving the coil 129 are first quenched by means of oil introduced through a line 130, to a temperature below an active conversion temperature, or at least to a temperature sufficient to prevent deposition of carbon in the transfer line, and then passed through a transfer line 131 having a pressure-reducing valve 132, into the lower portion of the separating tower 2, the subsequent treatment of the separated vapors and liquid being as described hereinabove.

Where the gases leaving the top of the absorber 6 still contain hydrocarbons having 3 or 4 carbon atoms per molecule, these gases are passed through a line 135 having a pressure regulating valve 136 and a cooler 137, into a second absorber 7, where they are subjected to further absorption. Hydrocarbon gases from an extraneous source, such as cracking plant gases, natural gas or other gases containing hydrocarbons of 3 and 4 carbon atoms per molecule may be introduced into the absorber 7 through a line 138 which terminates in the line 135 prior to the cooler 137. Any condensate removed in the cooler 137 passes through a trap 139 into the lower part of absorber 7.

In the absorber 7 the rising gases are subjected to a descending flow of a suitable absorbing oil for the purpose of recovering the higher boiling constituents of the gases, primarily hydrocarbons having 3 and 4 carbon atoms per molecule. In the instance shown in the drawings the absorbent oil employed in the absorber 7 comprises gas-oil condensate recovered in the fractionator 3. This gas-oil condensate is withdrawn from the bottom of the fractionator 3 through a line 79 and a portion thereof passes through a line 140, the reboiler 92, a line 141, the heat exchanger 126, a line 142, a pump 143, a cooler 144 and a line 145 into the upper part of the absorber 7, thence descending through the absorber 7 as an absorbing medium. It will be observed that with this method of operation the sensible heat of the hot gas-oil condensate is advantageously used to supply heat for reboiling in the stabilizer section 81 of the condenser and stabilizer 5 and further heat exchange between this gas-oil and the enriched absorbent from the absorber 6 is also provided for.

The interior of the absorber 7 is conveniently provided with suitable plates or trays 146. In order to dissipate the heat of absorption of the normally gaseous hydrocarbons in the absorbent oil, a liquid side stream may be withdrawn at an intermediate point from the absorber 7 through a line 147, this side stream being then delivered by means of a pump 148, a cooler 149 and a line 150 back into the absorber 7. As in the case of absorber 6, this arrangement may be repeated at various levels in the absorber 7.

In passing into the absorber 7 the gas-oil picks up the higher boiling constituents of the hydrocarbon gases traversing the absorber. The enriched gas-oil then passes from the bottom of the absorber 7 through a line 151 into an accumulator 152 having a vapor-return line 153 leading back into the absorber 7. The enriched gas oil accumulating in the accumulator 152 then passes through a line 154 having a pump 155 into a heat exchanger 156 and thence through a line 157 into a cracking coil 158 located in the furnace 1. As described in connection with cracking coils 48 and 129, the cracking coil 158 advantageously comprises a heating section of high heat input and a soaking section of relatively low heat input.

In traversing the cracking coil 158 the mixture of gas-oil and normally gaseous hydrocarbons is subjected to extremely high cracking temperatures under pressure, the conditions being regulated so as to give a crack per pass of from 20 to 50 per cent. The coil outlet temperatures will vary from about 900° to 1,250° F. and the pressures from about 300 to 3,000 pounds per square inch, while the ratio of the volume of the liquefied gases to the liquid volume of the recycle oil measured at atmospheric temperature will vary from 1:5 to 2:1, depending to some extent upon the quantity of extraneous gases introduced into the absorber 7 through the line 138. As described in connection with the cracking operations taking place in the coils 48 and 129, the cracking of the gas-oil and absorbed normally gaseous hydrocarbons involves a cracking of the gas oil under conditions more drastic than could be obtained if the oils were cracked alone, cracking and polymerization to some extent of the normally gaseous hydrocarbons, and inter-reaction between normally gaseous hydrocarbons and the products of conversion of the oil undergoing cracking. The result is the production of a high yield of gasoline of high anti-knock value and a reduction in the amount of tar formed in the conversion operation, as compared with operations in which gas oil is cracked in the absence of normally gaseous hydrocarbons. The desired advantageous results are not, however, fully obtained unless the conditions of conversion are so regulated as to effect a higher crack per pass of the gas oil than could be obtained in the same apparatus without the presence of the normally gaseous hydrocarbons.

The hot cracked products leaving the outlet of the coil 158 are then quenched by means of relatively cool oil introduced through a line 159 to a temperature below an active conversion temperature or at least to such extent as to prevent undesirable deposition of carbon in the transfer line and then pass through a transfer line 160 having a pressure-reducing valve 161 into the lower portion of the separating tower 2, the subsequent treatment of the separated vapors and liquid being as described hereinbelow.

That portion of the hot gas-oil condensate withdrawn from the fractionator 3 which is not delivered to the aosorber 7 passes through the line 79 and a line 162 to the heat exchanger 156 and thence, if desired, through a cooler 163. The portion of the cooled gas oil is then delivered through a line 164 to a pump 165 which in turn delivers it in any desired ratio to the quenching lines 130 and 159, for use in quenching the hot cracked products leaving the coils 129 and 158, respectively. The remaining portion of the cooled gas-oil leaving the heat exchanger 163 passes through the line 164 and through a branch line 166 to a pump 167. The pump 167 forces this portion of the cooled gas-oil through a line 168 terminating in two valved branch lines 169 and 170 leading to the lower portion and the upper portion, respectively, of the separating tower 2. Streams of cooled gas-oil may thus be delivered in any desired proportions to the upper and lower sections of the separating tower 2, respectively, as reflux.

The dry gases from the absorber 7, comprising largely methane, ethane, ethylene and hydrogen, are removed from the top of the latter through a line 180 having a presssure controlling valve 181

and may be used for fuel gas or otherwise disposed of. Moreover, any portion or all of the dry gases from the absorber 6 may be removed from the system through a line 182 having a valve 183, instead of passing to the absorber 7.

It will be observed that the system described hereinabove provides for the segregation of crude petroleum oil into various fractions, and the separate cracking of those fractions, in the presence of normally gaseous hydrocarbons, with little or no oil-recycling, together with recycling of the gas-oil condensate obtained in the various operations to a separate cracking coil also in the presence of normally gaseous hydrocarbons. In each case, the cracking or conversion treatment is so carried out as to give a higher degree of conversion per pass, or a higher crack per pass, than could be obtained in the same apparatus if the individual oil were cracked in the absence of the normally gaseous hydrocarbons and under temperatures which will ordinarily run from 25° to 300° F. higher than the maximum temperature to which the same oils could be subjected alone without undue deposition of carbon, other factors being the same. All of the gasoline condensate obtained in the system is collected in stabilized form in one point in the system and this gasoline condensate represents a high yield of a product having an exceptionally high anti-knock value when employed as motor fuel.

The process described above in connection with Figs. 1A, 1B and 1C represents one desirable type of operation which is especially suitable for the treatment of crudes containing a low or medium sulfur content. Where a high-sulfur crude is handled, it may be more advantageous to employ a modified type of operation in order to avoid corrosion effects.

Thus, in Figs. 2A, 2B and 2C there is shown an apparatus for handling a crude of high-sulfur content, such as West Texas crude.

In the apparatus illustrated in Figs. 2A, 2B and 2C, the primary apparatus elements consist of a combined crude and viscosity-breaker flash tower 200, furnaces 201 and 202, a vapor-separator and fractionator tower 203, a combined condenser and stabilizer 204, and absorbers 205 and 206. In this instance, the crude is introduced into the system through a line 207 (Fig. 2B) and is delivered by a pump 208 through a line 209 to a heat exchanger 210, wherein it is heated to some extent. The partially heated crude then passes through line 211 to a heat exchanger 212 wherein it is further heated to a temperature of the order of 500° F. The hot crude is then discharged through a line 213 into an intermediate section 214 of the combined crude and viscosity-breaker flash tower 200. The tower 200 is internally provided with suitable plates or trays 215, a trap tray 216 and trap-out trays or accumulator sections 217 and 218, the section 214 being located between the trap-out trays 217 and 218. In the section 214 the heated crude is distilled at substantially atmospheric pressures by means of hot vapors and its own sensible heat, to remove virgin naphtha and gas-oil constituents. The topped crude collecting in accumulator section 218 is withdrawn through a line 219 and is delivered by pump 220 through a line 221 to a viscosity-breaker coil 222 located in the furnace 201 and wherein the topped crude is heated under a mild cracking temperature and under conditions effective to reduce the viscosity of the crude and to produce clean constituents capable of further conversion to gasoline under drastic cracking conditions, but not for the purpose of producing a large amount of gasoline in this operation. In other words, instead of attempting to crack this residual stock to gasoline in one operation, it is thus mildly cracked or viscosity-broken in order to produce a relatively large amount of naphtha and gas-oil constituents suitable for further conversion to gasoline, dirty or residual constituents being separated out.

The temperatures employed in the viscosity-breaker coil will vary somewhat in accordance with the nature of the crude and the reaction time employed, but, in general, coil-outlet temperatures of from 800° to 950° F. are suitable, while back pressures of 100 to 500 pounds per square inch or higher may be employed. The hot products from the coil 222 then pass through line 223 having a back-pressure valve 224 into the bottom or vapor-separating section 225 of the tower 200 lying below the trap-out tray 218. In the section 225 separation of vapors and residual products (tar) is effected, the tar being removed through line 226 and passing through a tar pump 227 and a heat exchanger 212 to a cooler 228 before being removed from the system through a line 229. The hot vapors liberated in the section 225 pass upward through the section 214, where they mingle with the crude introduced through the line 213 and assist in the distillation and fractionation of the crude. Vapors of gas oil and lighter constituents then pass through the trap-out tray 217 into the upper section 230 of the tower 200 and are there subjected to fractional condensation. For this purpose, suitable cooling must be supplied; in the instance shown, a portion of this cooling is supplied by removing a side stream near the top of the section 230 through a line 231. The side stream passes through a cooler 232 and is then delivered by means of a pump 233 to a reflux line 234 back into the top of the section 230. Additional cool reflux is also supplied to the sections 230, 214 and 225 through reflux lines 235, 236 and 237, respectively, in such quantities as are required.

A gas-oil condensate, having a boiling range of for example from 400° to 700° F., is withdrawn from the trap-out tray 217 through a line 238, while a naphtha cut, having a boiling range of, for example, from 200° to 500° F., is withdrawn from the trap 216 through a line 239. Light gasoline vapors and gases uncondensed in the tower 200 are removed therefrom through an overhead line 240 and pass to a condenser 241 and a separator 242. If desired, the light virgin gasoline separated in the separator 242 may be withdrawn from the system through a line 243 having a valve 244, while the gases removed from the separator 242 may be removed from the system, or as in the instance shown, may be removed through a line 245 having a fan or blower 246 which in turn delivers the gases to burners 247 located in the furnace 201. It will be understood that such use of the gases from the separator 242 as a fuel is not necessarily confined to the furnace 201, as these gases might also be used in the furnace 202 or if available in sufficiently large quantities in both furnaces 201 and 202.

In any event my invention does not in any sense depend upon the use of these gases as fuel, such use being simply illustrated as a convenient method of utilizing these gases. However, the gases removed from the separator 242, in view of the nature of the original crude charging stock, will contain relatively large amounts of hydrogen sulfide and on this account are not regarded as

suitable for recycling to any of the cracking coils because of the resultant high sulfur content which would necessarily obtain in the gasoline produced in any cracking coil to which these gases were delivered. For that reason it is better to remove these gases from the system or to employ them as fuel, whereas other gases produced in the later stages of the operation, or at least fractions thereof consisting primarily of hydrocarbons having 3 to 4 carbon atoms per molecule, are recycled to the various cracking operations as described hereinbelow.

In the operation of the system as described hereinabove, it will be understood that the oil removed through the line 219 and delivered to the viscosity-breaker 222 will contain residual crude constituents and heavy constituents obtained from the vapors entering the section 214 from the section 225. The ratio of recycled heavy oil condensate obtained from the vapors to reduced crude will ordinarily be from .5:1 to 2:1.

The naphtha fraction removed through the line 239 passes to a cooler 248 where it is cooled to approximately atmospheric temperature and thence through a line 249 to a pump 250 (Fig. 2C) which in turn delivers it through a line 251 to the absorber 205 which receives cracked gases (produced as hereinafter set forth) through a line 252. In the absorber 205, the naphtha fraction acts as an absorption agent to remove from the gases the heavier normally gaseous hydrocarbons contained therein, primarily hydrocarbons having 3 to 4 carbon atoms per molecule. Provision for withdrawing, cooling and returning side streams at a plurality of points in the absorber 205 is illustrated, this apparatus being similar to that provided in connection with the absorber 6 illustrated in Fig. 1C.

The enriched naphtha, containing absorbed normally gaseous hydrocarbons, passes from the bottom of the absorber 205 through a line 253 to an accumulator 254 having a vent line 255 returning to the absorber 205. Enriched naphtha from the accumulator 254 then passes through a line 256 to a pump 257 which delivers it through a line 258 to a heat exchanger 259 (Fig. 2B) and thence through a line 260 to a heating coil 261 located in the furnace 202 (Fig. 2A). In the heating coil 261 the enriched naphtha is subjected to a high cracking temperature in order to crack or reform the same, under conditions effective to give a higher degree of conversion per pass than would be possible, without carbon stoppage, if the naphtha were heated alone and in the absence of the absorbed normal gaseous hydrocarbons. Suitable coil-outlet temperatures for the coil 261 are from 900 to 1450° F., and coil outlet pressures of 300 to 3000 pounds per square inch may be employed. Typical operating conditions which I have employed in practice are from 1020° to 1030° F. and from 1000 to 1200 pounds per square inch, the liquid volume of the absorbed gases to the volume of naphtha in the furnace charge, measured at atmospheric temperature, being of the order of 1:1.

The hot cracked products leaving the coil 261 are quenched by means of gas oil introduced through a valve-controlled line 262 and then pass through a line 263 having a valve 264 and thence through a transfer line 265 having a reducing valve 266 into a vapor-separator section 267 located in the bottom of the tower 203.

The virgin gas-oil fraction recovered in the trap-out tray 217 of the tower 200 (Fig. 2A) is withdrawn therefrom through the line 238 and passes to a heat exchanger 268 (Fig. 2C) where it gives up part of its heat, and thence through a line 269 to a pump 270. A portion of this gas-oil is then delivered by means of a pump 271 to a cooler 272 and thence through a line 273 to the top of the absorber 206 which receives gases containing hydrocarbons having 3 to 4 carbon atoms per molecule, as well as lower-boiling hydrocarbons, through a line 274. In the absorber 206, an absorption of hydrocarbons having 3 to 4 carbon atoms per molecule in the cooled gas-oil absorption medium takes place. The thereby enriched absorbent passes through a line 275 to an accumulator 276 having a vapor-return line 277 leading back to the absorber 206. The enriched virgin gas-oil then passes through a line 278 to a pump 279 which delivers it through the heat exchanger 268 and a line 280 to a cracking coil 281 located in the furnace 201, and wherein the enriched gas-oil is subjected to a high cracking temperature under conditions effective to produce a higher crack per pass than could be obtained if the gas-oil alone were cracked in the coil 281 in the absence of the absorbed normally gaseous constituents recovered in the absorber 206. The coil-outlet temperatures for the coil 281 will run from 900° to 1250° F. and the outlet pressures from 300 to 3000 pounds per square inch, the cracking operation being conducted essentially in the vapor phase. The ratio of liquid volume of absorbed normally gaseous hydrocarbons to the liquid of the gas-oil, measured at atmospheric temperture, will vary from 1:5 to 5:1, depending somewhat upon the character and quantity of the gases introduced into the absorber 206.

The hot cracked products leaving the coil 281 are quenched by means of cool gas-oil introduced through a line 282 and then pass through a transfer line 283 to the transfer line 265, through which they are introduced into the vapor-separating section 267 of the tower 203 (Fig. 2B).

That portion of the virgin gas-oil leaving the heat exchanger 268 and pump 270, which is not employed as an absorbing medium in the absorber 206, is delivered by the pump 270 through a line 284 to the reflux lines 235, 236 and 237 leading into the tower 200 (Fig. 2A), where it is employed as a reflux in the manner stated hereinabove.

In the vapor-separator 267 (Fig. 2B) a separation of vapors and residual products or tar occurs, the vapors passing upward to a trap-out tray and accumulator section 290 into a fractionator section 291 occupying the upper part of the tower 203, while the residual constituents are withdrawn from the bottom of the section 267 through a line 292. Some of the tar thus withdrawn is preferably recirculated by means of a line 293 to a pump 294, through a cooler 295 and thence back into the section 267, in order to maintain the section 267 free from coke deposition. The remaining portion of the tar withdrawn from the line 292 is either withdrawn from the system or, as shown, is delivered through the line 292 to the section 225 of the tower 200 where it is flashed for the recovery of such vaporizable products as may be retained therein. Any vapors liberated pass into the section 214 while residual constituents are withdrawn as a portion of the tar through line 226.

Suitable provision is made for cooling the fractionator section 291, and this may comprise in part, as shown, the withdrawal of a side stream through a line 296, the cooling of this side stream

in the heat exchanger 259 and a cooler 297, and the return of the cooled side stream by means of a pump 298 and a reflux line 299 to the top of the fractionator section 291. Under the influence of the cooling thus supplied, as well as such additional cooling or refluxing as may be provided for, the cracked vapors rising through the section 291 are fractionated for the recovery of constituents lying above the desired gasoline boiling-point range and comprising gas-oil cycle stock. This cycle stock is withdrawn from the trap-out tray 290 through line 300. A portion of this cycle stock is then passed through a line 301 to a hot recycle pump 302, from which it is delivered to a recycling coil 303 located within the furnace 202. Before being delivered to the coil 303, however, the gas-oil recycle stock is admixed with normally gaseous hydrocarbons containing 3 to 4 carbon atoms per molecule, recovered as hereinafter set forth and introduced into admixture with the cycle stock through a line 304.

In the coil 303 the thereby enriched gas oil cycle stock is subjected to a high cracking temperature under conditions effective to give a higher crack per pass than could be obtained in the absence of the gases. Suitable coil-outlet temperatures for the coil 303 are from 900° to 1250° F. Pressures of 300 to 3000 pounds per square inch are suitable. It will be observed that these conditions are similar to those employed in the coil 281 but the times of contact in the coils 281 and 303 may be varied in accordance with the different degrees of refractoriness of the oil stocks charged thereto and also in accordance with the amount and character of the normally gaseous hydrocarbons introduced to the respective coils. In the charging stock introduced into the coil 303, the liquid volume of normally gaseous constituents, measured at atmospheric temperature, ordinarily run from 20 per cent to 200 per cent of the liquid volume of the recycled oil.

The hot cracked products leaving the coil 303 are quenched immediately after leaving the coil by means of gas-oil quenching stock introduced through line 305 and then pass through a transfer line 306 having a reducing valve 307 into the vapor-separator section 267 of the tower 203, thus completing the cycle.

That portion of the gas-oil removed from the tower 203 to the line 300 which is not delivered directly to the coil 303 passes through the line 308 to heat exchanger or re-boiler 309 where a portion of the sensible heat of this oil is transferred to the oil in the bottom of the condenser-stabilizer 204 and used for the purpose of supplying the heat necessary for stabilization of gasoline distillate. The partially cooled gas oil then passes through a line 310 to the heat exchanger 210 and a cooler 311 where it is further cooled, leaving the cooler 311 through a line 312. A portion of this cooled gas-oil may be diverted from the line 312 through a line 313 having a pump 314 and leading to reflux lines 315 and 316 which in turn communicate with sections 267 and 291, respectively, of the tower 203. In this manner the necessary refluxing in the tower 303 over and above that supplied by means of the line 299, is provided for.

The remaining portion of the cooled gas oil passing through the line 312 is delivered to a pump 317 (Fig. 2A) which in turn communicates with quenching lines 262, 282 and 305, each of which is provided with a suitable regulating valve. This portion of the gas-oil is thereby divided into three streams for quenching the products leaving the coils 261, 281 and 303, respectively.

Returning to Fig. 2B, the vapors leaving the top of the tower 203 through a vapor line 318 consist of gasoline, fixed gases and intermediate constituents. These vapors pass through the line 318 into a vapor-feed condensing section 319 located in the upper part of the tower 204. Unstabilized condensate recovered in the section 319 is withdrawn from an accumulator section or trap-out tray 320 to a line 321 and passes to a cooler 322 to a pump 323 which in turn delivers the cooled condensate through a line 324 into the upper part of the section 319, thereby providing a cooling and refluxing medium and assisting in the condensation of the gasoline constituents in the vapors traversing in the section 319. As shown in the drawings, a portion or all of the light virgin gasoline recovered in the accumulator 242 (Fig. 2A) may also be delivered by means of a line 325 having a valve 326 and a pump 327, to a reflux line 328 leading into the section 319. Wherever the light virgin gasoline is insufficient to supply the desired amount of reflux for the section 319 over and above that supplied through the line 224 or wherever it is desired to segregate the light virgin gasoline from the cracked gasoline and additional refluxing is required for the section 319, suitable gasoline reflux stock from an extraneous source may be supplied to the section 319 through a line 329 communicating with the reflux line 328.

That portion of the unstabilized condensate not withdrawn through the line 321 passes downward into a stabilizing section 330 occupying the lower part of the tower 204 and communicating through a liquid line 331 and a vapor line 332 with the reboiler 309. Sufficient heat is supplied to the reboiler 309 to effect stabilization of the gasoline distillate, the liberated vapors passing upward into the section 319 while the stabilized gasoline passes through a cooler 333 and thence out of the system through a line 334. The pressures maintained in the towers 203 and 204 will run from 100 to 500 pounds per square inch, and, depending upon the particular pressure employed, the temperature in the upper part of the tower 204 will run from 60° to 200° F.

The vapors leaving the section 319 of the tower 204 consist of a mixture of normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, together with varying quantities of lower-boiling constituents such as ethane, ethylene and methane and, it may be, some hydrogen. These vapors leave the top of the tower 204 through a line 335 and pass to a condenser 336 where they are cooled to approximately atmospheric temperature, thereby resulting in the condensation of a portion of the normally gaseous hydrocarbons contained therein, primarily butanes and butylenes, together with such small amounts of heavier hydrocarbons as may have escaped condensation in the section 319. This butane-containing condensate is collected in an accumulator 337 and a portion or all thereof, depending upon the amount recovered, is delivered through a line 338 to a pump 339 and thence through a line 304 for admixture with the oil about to enter the recycling coil 303, as described hereinabove. The uncondensed vapors and gases leaving the accumulator 337 pass through the line 252 into the absorber 205. That portion of the condensate from accumulator 337 which is

not returned to the coil 303 as aforesaid may also be delivered by means of a line 340 having a pump 341 into the absorber 205.

In traversing the absorber 205, the gases, as aforesaid, are scrubbed with cooled naphtha introduced through the line 251 and they are thereby deprived of all or the major portion of the heavier constituents thereof, namely hydrocarbons having from 3 to 4 carbon atoms per molecule. The absorption is so conducted as to remove butanes and butylenes as completely as possible, as well as a portion or all of the propane and propylene. The remaining gases then pass from the absorber 205 through a line 342 having a back-pressure valve 343 and may either be withdrawn from the system through lines 344 and 345 or may be delivered in part or entirely to the absorber 206 through a line 346 which communicates with the inlet line 274. Hydrocarbon gases from an extraneous source containing hydrocarbon having 3 to 4 carbon atoms per molecule are conveniently and advantageously introduced into the absorber 206 through a line 347 which also communicates with the inlet line 274. In traversing the absorber 206 the gases which may comprise residual gases from the absorber 205, or gases from an extraneous source, or both, are scrubbed as aforesaid with cooled gas oil in order to deprive them of their heavier constituents. As in the absorber 205, the operation is so conducted as to remove all butanes and butylenes as well as all or a portion of the propane and propylene. The remaining constituents, comprising largely ethane, ethylene and methane, then pass through a line 348 having a back-pressure valve 349 into the dry gas main 345, by means of which they are removed from the system.

As in the instance of the absorbers illustrated in Fig. 1C, provision may be made at one or more points in absorbers 205 and 206 for removing a side stream, cooling it and returning it to the absorber, in order to dissipate the heat of absorption and maintain the temperature of the absorbers as low as possible.

The pressure in the absorber 205 will ordinarily run from 100 to 500 pounds per square inch while that in the absorber 206 may be the same, or somewhat lower, over a range of from 50 to 500 pounds per square inch. These pressures are maintained by means of the valves 343 and 349, respectively.

In the system described hereinabove in connection with Figs. 2A, 2B and 2C, and in which the charge stock has been described as a crude of high sulfur content, corrosion is limited to the tower 200 and the viscosity-breaker coil 222; the sulfur compounds in the crude are largely broken up in the coil 222 and leave the tower 200 as hydrogen sulfide in the gases passing to the accumulator 242.

It will be observed that the oils charged to the coils 261 and 281 are virgin stocks in the sense that these stocks have not been subjected to previous conditions as drastic as those employed in coils 222 and 303. It will be understood that for the purposes of this specification at least, distillates recovered from the viscosity-breaking operation conducted in the coil 222 may be regarded as virgin stocks. The coils 261 and 281 therefore operate in a once through or non-recycling manner. The coil 303, however, receives previously cracked stock and is operated, as will be understood from the description set forth hereinabove, as a recycle coil. In other words, in the operation as described, virgin and cracked stocks are segregated and only the cracked stock is recycled; the recycling is confined to a single coil and to cracked stock.

The apparatus illustrated in Figs. 3A and 3B may be employed for treating various stocks that are especially suitable for the handling of crude oils containing lubricating oil constituents which it is desired to recover as such. The principal elements in Figs. 3A and 3B are a crude topping tower 400, a furnace 401, a combined vapor-separator and fractionator 402, a combined condenser and stabilizer 403 and absorbers 404 and 405.

In the operation of this apparatus the crude charging stock is introduced through a line 406 to a pump 407 and passes through a line 408 through a heat exchanger 409 and thence through a line 410 into a preheating coil 411 located within the furnace 401, wherein the crude oil is heated to a temperature of from 300° to 800° F. The specific temperature should be such as to permit subsequent vaporization of gas oil and lighter constituents.

The preheated crude then passes through a line 412 into the crude topping tower 400, which is operated at substantially atmospheric pressure, and wherein distillation of the preheated crude takes place. The liberated vapors pass upward through the tower and are subjected to fractional condensation, while the crude residuum, containing lubricating-oil constituents, is removed from the bottom of the tower 400 through a line 413A for subsequent working up into lubricating stock or stocks. The necessary cooling in the crude topping tower 400 is conveniently provided by withdrawing a side stream through a line 413, cooling this side stream in a cooler 414 and returning the cooled side stream by means of a pump 415 to a reflux line 416 to the top of the tower 400.

A virgin gas-oil cut, having a boiling range of for example from 400° to 700° F., is removed as a side stream through a line 417, while a virgin naphtha cut, having a boiling range of for example from 200° to 500° F., is removed as a side stream through the line 418. The vapors remaining uncondensed, and consisting of gases and light virgin gasoline, pass through a vapor line 419 to a condenser 420 and thence to a separator 421 from which virgin light gasoline condensate is removed through a valved line 422. Gases are removed through a line 423.

The naphtha side stream removed through the line 418 is delivered by means of a pump 424 to a cooler 425 where it is cooled to approximately atmospheric temperature and then passes through a line 426 into the absorber 404 which receives gases, formed as hereinafter described, through a line 427. The thereby enriched naphtha, containing absorbed hydrocarbons having 3 to 4 carbon atoms per molecule, then passes through a line 428 to a pump 429 and is delivered through a line 430 to a heat exchanger 431, passing thence through a line 432 to a cracking or reforming coil 433 located in the furnace 401. The conditions maintained in the coil 433 are similar to those described hereinabove in connection with the operation of coil 261 of Fig. 2A. The products leaving the coil 433 are quenched by cool gas oil introduced through a quenching line 434 and then pass through transfer lines 435 and 436 into the lower section of the tower 402.

The virgin gas oil fraction recovered in the tower 400 passes through the line 417 to a heat exchanger 437 and thence to a pump 488 which delivers it through a cooler 489 and a line 490

to the absorber 405, which receives gas through a line 491. In the absorber 405, the cooled gas oil absorbs hydrocarbons having from 3 to 4 carbon atoms per molecule, as in the instances previously described. The thereby enriched gas-oil then passes through a line 492 wherein is located a pump 493 to the heat exchanger 437 and thence through a line 438 to a cracking coil 439 located in the furnace 401. The cracking operation conducted in the coil 439 is similar to that described hereinabove in connection with cracking coil 281 of Fig. 2A.

The hot cracked vapors leaving the coil 439 are quenched by means of cooled gas-oil introduced through a line 440 and then pass through a transfer line 441 and the transfer line 436 into the lower section of the tower 402.

In the lower section of the tower 402 a separation of vapors and residual constituents or tar takes place, the tower 402 being similar in construction and operation to the tower 203 of Fig. 2B. Tar is withdrawn through a line 442 and in this instance is removed from the system or delivered to a tar flasher for the recovery of vaporizable constituents.

In the tower 402, condensation of constituents heavier than gasoline is effected, the condensate comprising a gas-oil or recycle stock. This condensate is withdrawn from a trap-out tray 443 through a line 444, and a portion of the condensate is delivered through line 445 to a pump 446 which in turn delivers it to a recycling coil 447 located within the furnace 401. Before entering the cracking coil 447 the recycle stock is commingled with liquefied hydrocarbons containg 3 to 4 carbon atoms per molecule introduced through a line 448. The operation conducted in the coil 447 is similar to that described hereinabove in connection with coil 303 of Fig. 2A.

The hot cracked products leaving the coil 447 are quenched by means of cooled gas-oil introduced through a line 449 and then pass through a transfer line 450 into the lower section of the tower 402. The remaining portions of the gas-oil removed from the trap-out tray 443 are employed as quenching stock and as reflux and also if desired for supplying heat for the gasoline stabilization in the manner described in connection with the operation illustrated in Figs. 2A, 2B and 2C. Apparatus for these purposes has been illustrated and is similar to that shown in Figs. 2A, 2B and 2C.

The vapors, freed from constituents heavier than gasoline, which emerge from the top of the tower 402, pass through a vapor line 470 to the upper or condensing section of the tower 403. In the tower 403, condensation and stabilization of gasoline constituents takes place as in the manner previously described, stabilized gasoline being withdrawn from the system through a line 471 while the uncondensed vapors pass through a line 472 to a condenser 473 to a separator or accumulator 474.

A portion or all of the virgin light gasoline recovered in the separator 421 may be delivered by means of a pump 475 to a line 476 to the upper part of the tower 403 as reflux.

The pressure condensate collected in the accumulator 474 is delivered in part or entirely through a line 477 to a pump 478 and thence through a line 448 into the coil 447 as described hereinabove. Any portion of the condensate recovered in the accumulator 474 which is not so delivered to the coil 447 is delivered by means of a pump 479 to a line 480 into the absorber 404, together with gases separated in the accumulator 474 which pass into the absorber 404 through the line 427.

The dry gases leaving the absorber 404 through a line 481 may pass through a line 482 and the line 491 into the absorber 405 or they may be removed from the system through lines 483 and 484.

The gases recovered in the distillation of the crude are in this instance delivered to the line 423 to a compressor 424 which in turn delivers them through a line 485 and the line 491 into the absorber 405. Additional gases, from an extraneous source, such as refinery gas or natural gas, containing hydrocarbons having 3 to 4 carbon atoms per molecule, is introduced where desired through a line 486, passing thence through the lines 485 and 491 to the absorber 405. The stripped gases leaving the absorber 405 pass through a line 487 into the dry gas main 484.

The operation of the various units illustrated in Figs. 3A and 3B, but not specifically described in conjunction therewith, will be readily understood in conjunction with the description accompanying the preceding figures and particularly Figs. 2A, 2B and 2C.

While I have described my invention hereinabove with respect to various specific illustrative examples and embodiments, it will be readily understood by those skilled in the art that my invention is not in its broadest aspects limited to the details of such exemplifications or embodiments, but may variously be practiced and embodied within the scope of the claims hereinafter made.

What I claim is:—

1. In a process of making low-boiling cracked distillate of high antiknock value when used as a motor fuel, from a crude petroleum, in apparatus of the combination-unit type wherein a crude petroleum is distilled to recover a naphtha fraction and at least one heavier fraction, said naphtha and said heavier fraction are separately cracked, the cracked products are combined for the recovery of tar, cracked gasoline and an intermediate fraction heavier than gasoline, said intermediate fraction is cracked and the thereby cracked products are combined with the above-mentioned cracked products for recovery as aforesaid, the improvement which comprises condensing the combined cracked vapors remaining after condensation of cracked gasoline, under pressure, to recover a liquid butane fraction consisting predominantly of hydrocarbons having 3 to 4 carbon atoms per molecule, thereafter scrubbing the gases remaining uncondensed with the aforesaid naphtha fraction, prior to cracking the same, to remove normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule by absorption in said naphtha, cracking the thereby enriched naphtha as aforesaid, and delivering butane condensate, condensed as aforesaid, for admixture with at least one of the other above-mentioned fractions about to be cracked as aforesaid.

2. In a process of making low-boiling cracked distillate of high antiknock value when used as a motor fuel from a crude petroleum, in apparatus of the combination unit type wherein a crude petroleum is distilled to recover a naphtha fraction and a reduced crude fraction, said naphtha and said reduced crude fraction are separately cracked, the cracked products are combined for the recovery of tar, cracked gasoline and an intermediate fraction heavier than gaso-

line, said intermediate fraction is cracked and the thereby cracked products are combined with the above-mentioned cracked products for recovery, as aforesaid, the improvement which comprises condensing the combined cracked vapors remaining after condensation of cracked gasoline, under pressure, to recover a liquid butane fraction consisting predominantly of hydrocarbons having 3 to 4 carbon atoms per molecule, thereafter scrubbing the gases remaining uncondensed with the aforesaid naphtha fraction, prior to cracking the same, to remove normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule by absorption in said naphtha, cracking the thereby enriched naphtha as aforesaid, and delivering butane condensate having 3 to 4 carbon atoms per molecule, condensed as aforesaid, for admixture with said reduced crude fraction about to be cracked as aforesaid.

3. In a process of making low-boiling cracked distillate of high antiknock value when used as a motor fuel from a crude petroleum, in apparatus of the combination unit type wherein a crude petroleum is distilled to recover a naphtha fraction and a heavier fraction, said naphtha and said heavier fraction are separately cracked, the cracked products are combined for the recovery of tar, cracked gasoline and an intermediate fraction heavier than gasoline, said intermediate fraction is cracked and the thereby cracked products are combined with the above-mentioned cracked products for recovery as aforesaid, the improvement which comprises condensing the combined cracked vapors remaining after condensation of cracked gasoline, under pressure, to recover a liquid butane fraction consisting predominantly of hydrocarbons having 3 to 4 carbon atoms per molecule, thereafter scrubbing the gases remaining uncondensed with the aforesaid naphtha fraction, prior to cracking the same, to remove normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule by absorption in said naphtha, cracking the thereby enriched naphtha as aforesaid, and delivering butane condensate, condensed as aforesaid, for admixture with said intermediate fraction about to be cracked as aforesid.

4. The process of making low-boiling cracked distillate of high anti-knock value when used as a motor fuel, from a crude petroleum, which comprises distilling said crude to recover a virgin naphtha fraction and a heavier fraction, passing said heavier fraction in admixture with normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule through an elongated conversion zone of restricted cross-sectional area, under superatmospheric pressure, and there cracking the admixture, delivering the hot cracked products to a vapor-separating zone; removing tar and vapors from said zone, fractionating the vapors to recover gas-oil and gasoline fractions, scrubbing the remaining gases with said naphtha fraction to recover hydrocarbons having 3 to 4 carbon atoms per molecule therefrom, passing the thereby enriched naphtha through an elongated zone of restricted cross-sectional area and there cracking it, and delivering resultant hot cracked products to said vapor-separating zone; the temperatures to which said admixture and said enriched naphtha are subjected in said conversion zone each being substantially in excess of the maximum temperature to which the respective oil alone and without admixture of normally gaseous hydrocarbons could be subjected in identical apparatus and under otherwise identical conditions of conversion without such excessive deposition of carbon as to prevent continuous operation of the unit for extended periods of time.

5. The process of making low-boiling cracked distillate of high anti-knock value when used as a motor fuel, from a crude petroleum, which comprises distilling said crude to recover a plurality of fractions of different boiling ranges, separately cracking said fractions, combining the hot cracked products and delivering them to a vapor-separating zone, removing tar and vapors from said zone, fractionating the vapors to recover gas-oil and gasoline fractions and hydrocarbons having 3 to 4 carbon atoms per molecule, cracking said gas-oil and delivering the hot cracked products to said vapor-separating zone, each of said cracking operations being conducted in the presence of returned hydrocarbons having 3 to 4 carbon atoms per molecule in an elongated zone of restricted cross-sectional area under superatmospheric pressure and at a temperature substantially in excess of the maximum temperature to which the respective oil alone and without admixture of said normally gaseous hydrocarbons could be subjected in identical apparatus and under otherwise identical conditions of conversion without such excessive deposition of carbon as to prevent continuous operation of the unit for extended periods of time.

6. The process of making low boiling cracked distillate of high anti-knock value when used as motor fuel from a crude petroleum which comprises fractionally distilling a crude petroleum to recover a naphtha fraction, further reducing the thereby topped crude by contact with hot cracked vapors, cracking the thereby reduced crude in the presence of a liquid butane fraction recovered as set forth hereinbelow, fractionating the resultant cracked products to separate and recover tar, gas-oil, gasoline and liquid butane fractions, scrubbing the remaining gases with said naphtha fraction to remove normally gaseous constituents having 3 to 4 carbon atoms per molecule, reforming the thereby enriched naphtha and combining the hot reformed products with the first-mentioned cracked products for reduction of the topped crude and fractionation as aforesaid, cracking said gas-oil in the presence of normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule and combining the resultant hot cracked products with the first-mentioned cracked products and said reformed products for reduction of the topped crude and fractionation as aforesaid, each of said cracking and reforming operations being carried out under superatmospheric pressure and at a temperature substantially in excess of the maximum temperature to which the respective oil alone and without admixture of said normally gaseous hydrocarbons could be subjected in identical apparatus and under otherwise identical conditions of conversion without such excessive deposition of carbon as to prevent continuous operation of the unit for extended periods of time.

7. The process of making low boiling cracked distillate of high anti-knock value when used as motor fuel from a crude petroleum which comprises fractionally distilling a crude petroleum to recover a virgin naphtha fraction, a virgin gas-oil fraction and a reduced crude, viscosity-breaking the reduced crude and commingling resultant vapor with the crude undergoing distillation, cracking the virgin gas-oil fraction in the presence of normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, frac-

tionating the resultant cracked products to separate and recover tar, recycle gas-oil, gasoline and liquid butane fractions, scrubbing the remaining gases with said virgin naphtha fraction to remove normally gaseous constituents having 3 to 4 carbon atoms per molecule, reforming the thereby enriched naphtha and combining the hot reformed products with the first-mentioned cracked products for fractionation as aforesaid, separately cracking said recycle gas-oil fraction in the presence of said butane fraction and combining the resultant hot cracked products with the first-mentioned cracked products and said reformed products for fractionation as aforesaid, each of said cracking and reforming operations being carried out under superatmospheric pressure and at a temperature substantially in excess of the maximum temperature to which the respective oil alone and without admixture of said normally gaseous hydrocarbons could be subjected in identical apparatus and under otherwise identical conditions of conversion without such excessive deposition of carbon as to prevent continuous operation of the unit for extended periods of time.

8. In a process of making low-boiling cracked distillate of high anti-knock value when used as a motor fuel, from a crude petroleum, in a unit of the so-called combination-unit type, in which said crude is distilled to recover a plurality of fractions, said fractions are separately cracked at different cracking temperatures, the hot cracked products are delivered to a vapor-separating zone, tar and vapors are removed from said zone, the vapors are fractionated to recover gas-oil and gasoline fractions, the improvement which comprises condensing the remaining gases and vapors under pressure to recover a liquid butane fraction containing normally gaseous hydrocarbons having 4 carbon atoms per molecule, and commingling said butane fraction with one of the first-mentioned fractions for cracking as aforesaid, and scrubbing the remaining gases with another of said first-mentioned fractions to enrich the latter with normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule before cracking it as aforesaid, each of said cracking operations being carried out in an elongated zone of restricted cross-sectional area under superatmospheric pressure and at a temperature substantially in excess of the maximum temperature to which the respective oil alone and without admixture of said normally gaseous hydrocarbons could be subjected in identical apparatus and under otherwise identical conditions of conversion without such excessive deposition of carbon as to prevent continuous operation of the unit for extended periods of time.

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