Nov. 1, 1938. P. OSTERGAARD 2,135,014

CRACKING HYDROCARBON OILS

Filed July 2, 1937 4 Sheets-Sheet 1

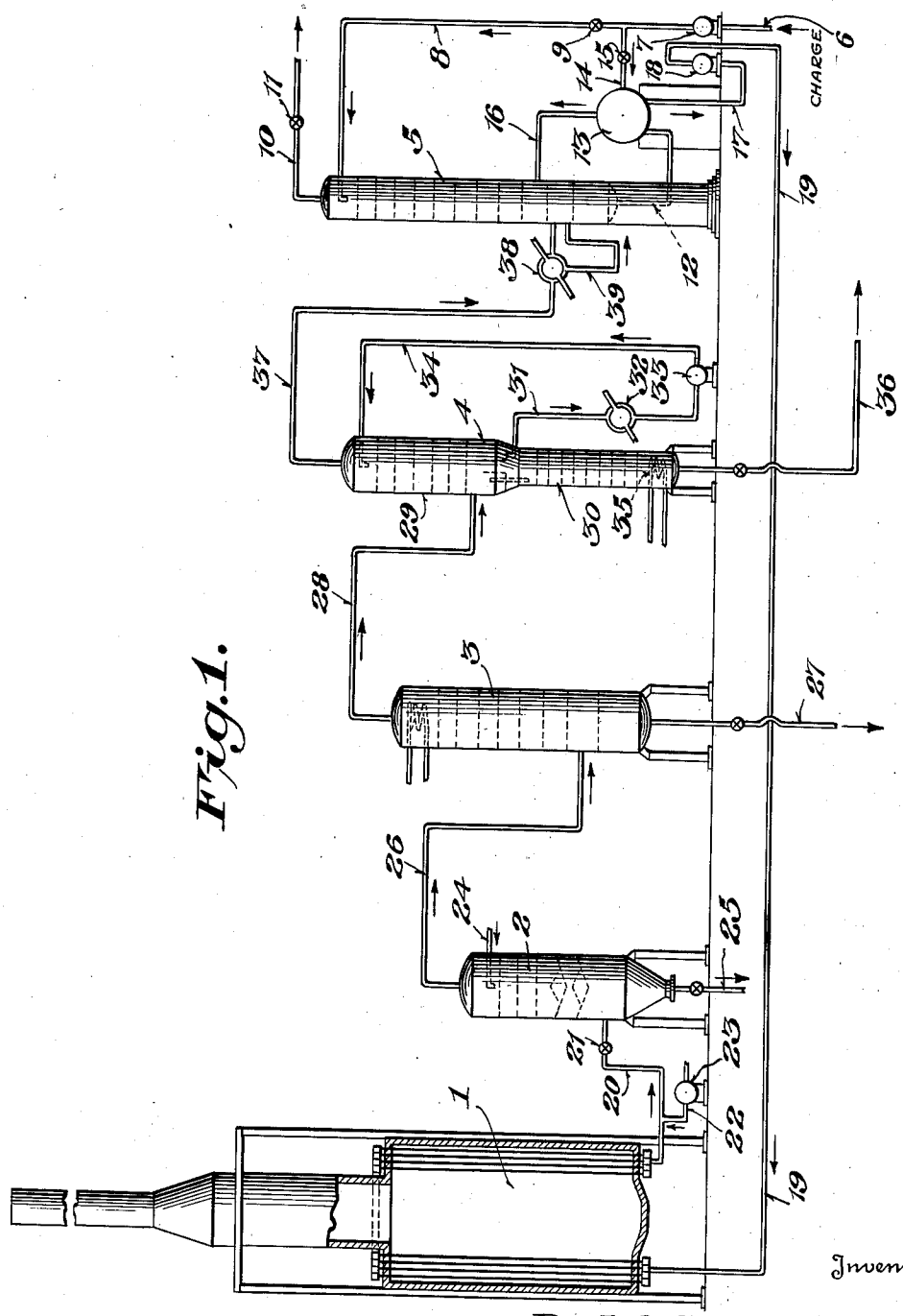


Fig. 1.

Inventor

Povl Ostergaard,

By G. M. Houghton Inc Attorney

Nov. 1, 1938. P. OSTERGAARD 2,135,014

CRACKING HYDROCARBON OILS

Filed July 2, 1937 4 Sheets-Sheet 2

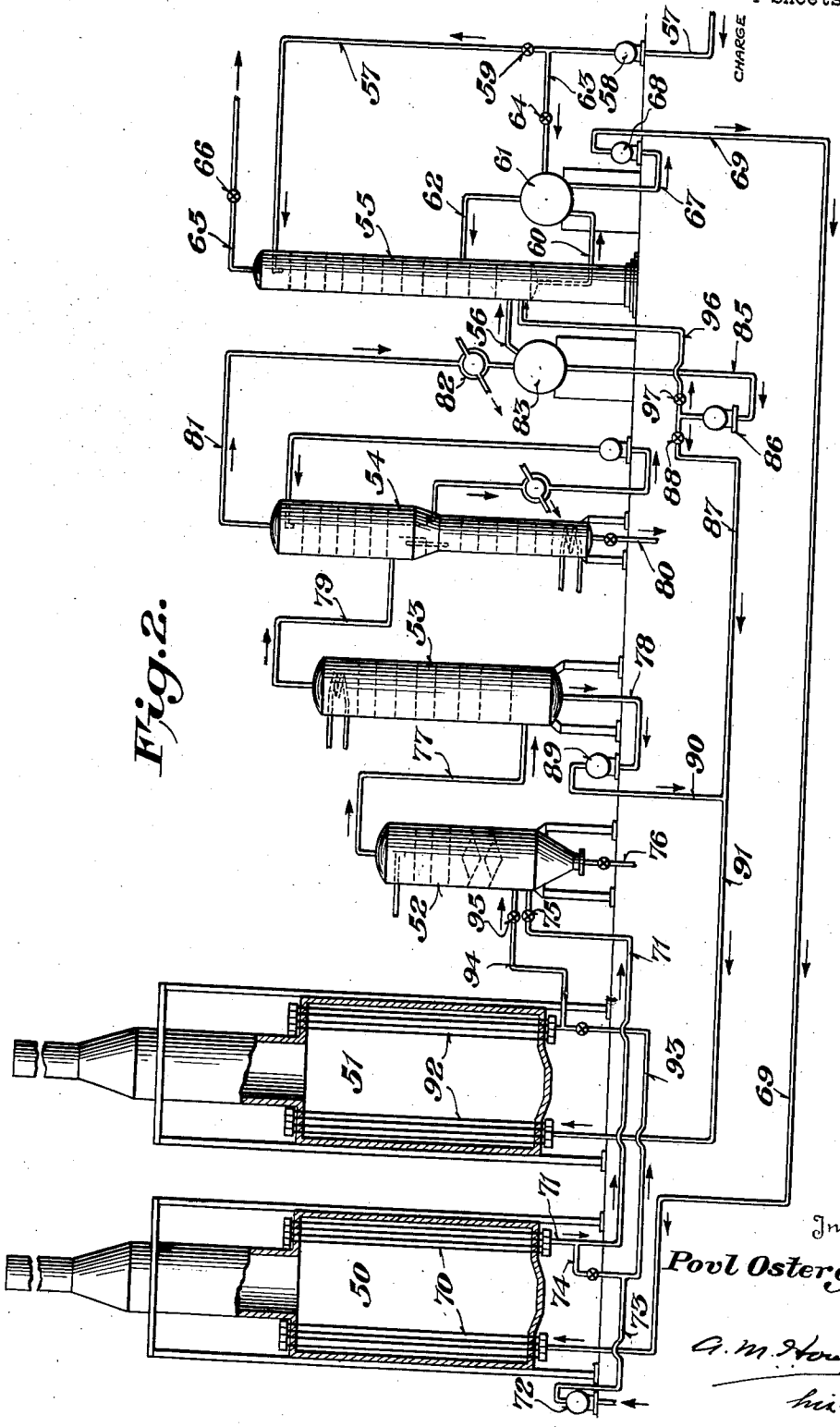


Fig. 2.

Inventor
Povl Ostergaard,
A. M. Houghton
his Attorney

Nov. 1, 1938. P. OSTERGAARD 2,135,014

CRACKING HYDROCARBON OILS

Filed July 2, 1937 4 Sheets-Sheet 3

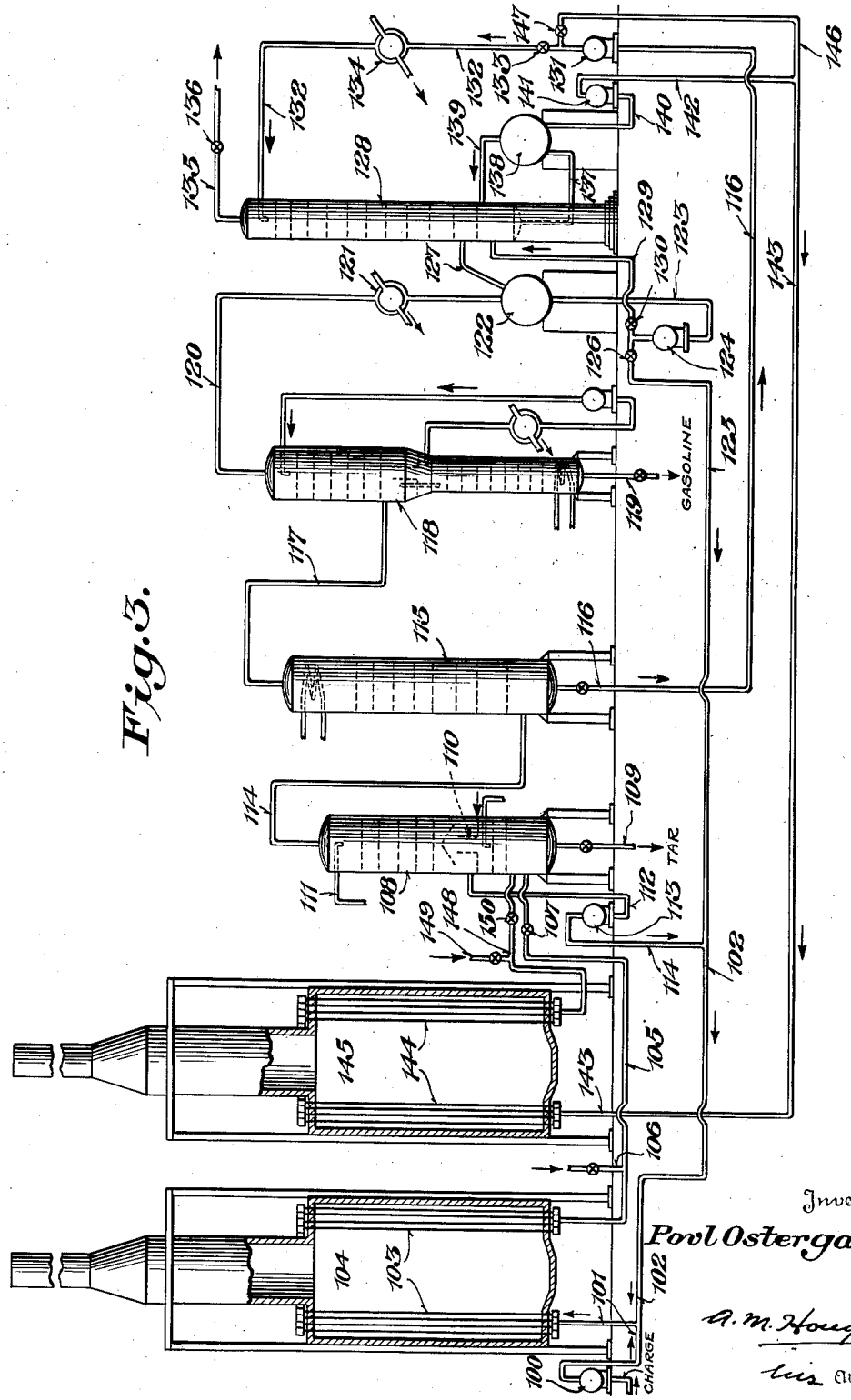


Fig. 3.

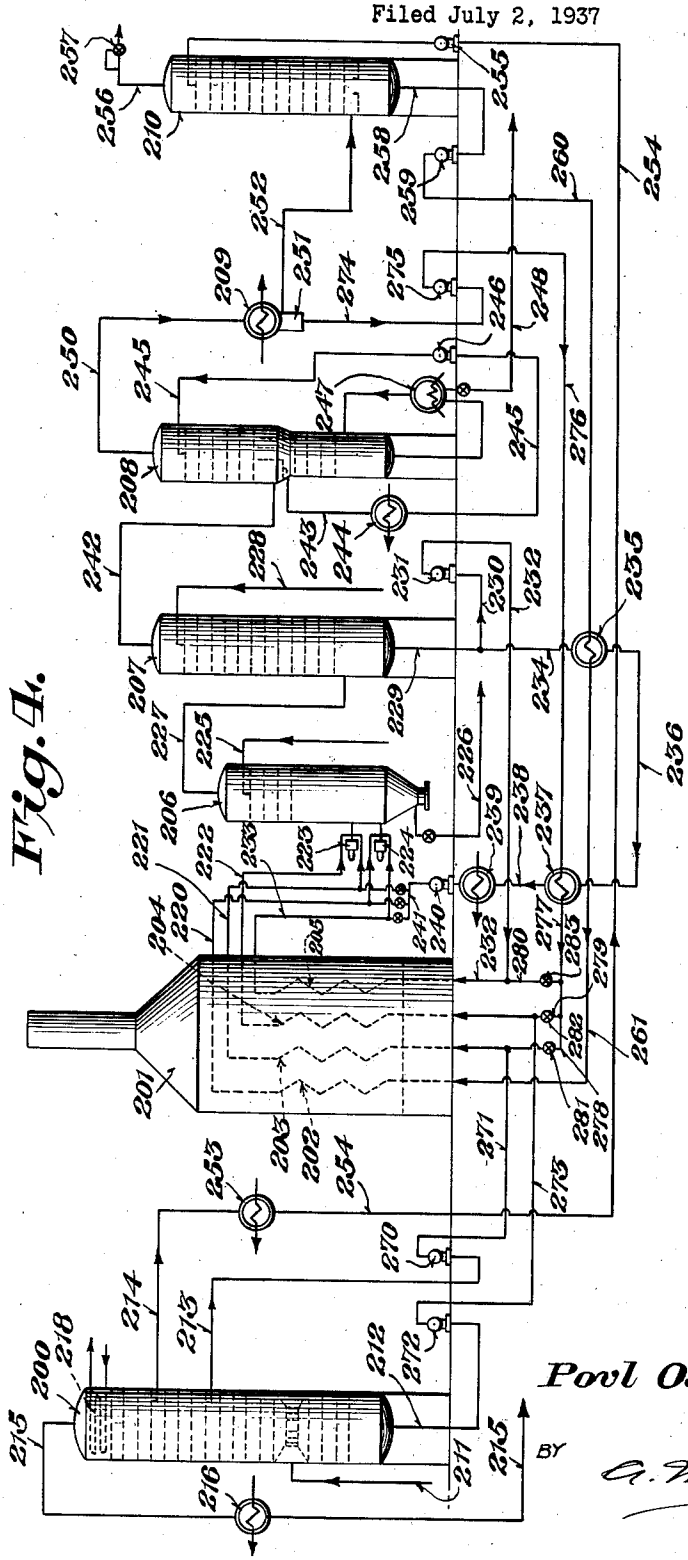
Inventor
Povl Ostergaard,
A. M. Houghton
his Attorney

Nov. 1, 1938. P. OSTERGAARD 2,135,014

CRACKING HYDROCARBON OILS

Filed July 2, 1937 4 Sheets-Sheet 4

Fig. 4.



Inventor
Povl Ostergaard,
BY
A. M. Houghton
his Attorney

Patented Nov. 1, 1938 2,135,014

UNITED STATES PATENT OFFICE

2,135,014

CRACKING HYDROCARBON OILS

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

Application July 2, 1937, Serial No. 151,743

6 Claims. (Cl. 196—9)

This invention relates to a process of cracking hydrocarbon oils for the production of gasoline of high anti-detonating value when used as a motor fuel, and more particularly to a process of such character wherein normally gaseous hydrocarbons having from 3 to 4 carbon atoms per molecule, such as those produced in the conversion of the oil, or similar hydrocarbons from an outside source, or both, are passed through the conversion zone in admixture with the oil being cracked, and wherein the degree of conversion per pass of the oil is carried to a greater extent than would be possible if the oil were cracked alone, with advantageous results; all as more fully set forth hereinafter and as claimed.

In all oil-cracking operations, the ultimate primary purpose today is to produce motor fuel or gasoline. It is desirable to produce as large a yield of gasoline as possible and it is also highly desirable that the gasoline be of high quality, especially with respect to its anti-detonating or anti-knock value, measured in terms of "octane number". All oil-cracking operations represent a compromise between yield and quality. More drastic cracking of relatively heavy stocks tends to result in higher yields of gasoline, while more drastic cracking of relatively light stock, such as naphtha, tends to reduce the yield of gasoline. It is known that the octane number of the gasoline rises with the degree of conversion per pass, and that the reaction velocity of cracking rises sharply with temperature. But more drastic cracking always tends to increase the yield of normally gaseous hydrocarbons (i. e. those which are vaporous or gaseous at atmospheric temperature and pressure), and there are definite factors which limit the maximum temperature at which cracking of any given stock can be selected. The principal limiting factor is that of carbon deposition in the conversion zone. Cracking processes, in order to be practicable, must be capable of operation for long periods of time without serious deposition of carbon in the cracking coil.

In cracking any given oil in any given cracking coil there will be found a maximum permissible degree of conversion per pass and, other factors such as pressure and contact time being the same, a maximum permissible cracking temperature, at which the stock can be cracked without giving rise to such excessive carbon deposition as would prevent continuous operation of the unit over commercially satisfactory operating periods of, for example, 1000 hours or more. Any substantial further increase in the degree of conversion per pass above this maximum point, and (other conditions remaining the same) any substantial increase in temperature over the aforesaid maximum temperature, will result in serious carbon deposition in the tubes of the heating element, reducing the possible operating period down to a matter of only a few days or even hours. The reduction of the operating period due to this excessive carbon formation is out of all proportion to the corresponding rise in the degree of conversion per pass or to the corresponding rise in the cracking temperature.

I define the degree of conversion per pass as the amount of products having boiling point ranges above and below the boiling point range of the charge oil, in per cent of the charge oil, produced from the oil in one passage through the conversion zone. This method of determination is given as a practical method of determining reaction-velocity constants of oil cracking in an article by Geniesse and Reuter, in "Industrial and Engineering Chemistry", February 1932; vol. 24, No. 2; pp. 219 to 222.

Inasmuch as the "octane-number" or anti-knock value of the final cracked gasoline from any given stock is largely a function of the degree of conversion per pass, it is of course desirable to operate at as high a degree of conversion per pass as possible, provided the yield and quality in other respects of the gasoline product are satisfactory. Modern advances in the art, particularly with respect to design of equipment and methods of treating the gasoline product, have made it possible in most instances to push the degree of conversion in oil-cracking units to the maximum extent permissible without undue deposition of carbon. No marked further improvement can well be obtained without radical alteration of the cracking processes themselves.

For the purposes of this application it will be convenient to consider oils commonly subjected to cracking in three categories, which are roughly represented by the naphtha, gas oil and residuum ("reduced crude") obtained when a crude petroleum is distilled under non-cracking conditions to separate it into fractions suitable for cracking separately.

Reduced crudes and other stocks of high average molecular weight, high critical temperatures (e. g. above 900° F.) and high carbon residue values (Conradson carbon numbers) are extremely limited with respect to the maximum permissible degree of conversion per pass and the maximum permissible cracking temperature. Usual-

ly the cracking of such heavy or residual stocks is carried out today under relatively mild cracking conditions and at low cracking temperatures from around 800° to around 900° F., this type of operation being generally known as "viscosity-breaking". The yield and quality of gasoline thus directly obtained are not high but by proper separation and fractionation of the cracked vapors, the residual constituents can, so to speak, be segregated into a tar or fuel-oil fraction, while simultaneously recovering a relatively large amount of clean charging stock or gas oil, which is then separately cracked under more drastic cracking conditions, i. e. at a high degree of conversion per pass and at a high cracking temperature in order to produce a good yield of gasoline of high quality. When the entire operation is considered, however, it will be apparent that the ultimate purpose is to obtain the highest possible yield of the highest quality gasoline.

In cracking gas oils and other oils heavier than gasoline, but substantially free from residual constituents, and having critical temperatures lying above 800° F., the cracking operation is usually regulated to give the maximum degree of conversion per pass which may safely be maintained in a given apparatus for periods of from 1000 to 1500 hours.

During recent years, due to the demand for gasoline of high octane number, it has also been common in many instances to crack or "re-form" naphthas, and particularly straight-run (uncracked) naphthas, that is to say, naphthas of relatively low octane number. By "naphtha" I mean a stock consisting largely or predominantly of constituents boiling within the gasoline boiling range and having a critical temperature below 800° F. Such cracking or reforming results in the production of (1) a reduced yield of gasoline, (2) a relatively small amount of constituents higher boiling than the original stock, i. e. a fraction corresponding to tar or gas oil, and (3) a considerable amount of normally gaseous hydrocarbons. The reduction in the yield of gasoline is balanced by the fact that the gasoline has an increased octane number. Since the octane number of the final gasoline is largely a function of the degree of conversion per pass, such operations are ordinarily so conducted as to obtain as high a degree of conversion per pass as is consistent with operability over a commercial period of time and to obtain that yield of gasoline which corresponds to the highest octane number of the gasoline produced.

It will be evident that all such prior cracking processes have been limited by definite relations between the yield and quality of the gasoline, and by the factor of carbon deposition in the heating unit. The latter factor is especially important due to the fact that commercial cracking operations are ordinarily and advantageously carried out in tubular or coil-type conversion units, of restricted cross-sectional area.

Inasmuch as the tendency in recent years to employ high cracking temperatures has been accompanied by an increase in the amount of gases produced, as well as some increase in the proportion of unsaturated constituents present in these gases, considerable attention has been devoted in recent years to processes for polymerizing such gases to gasoline-like polymers suitable for blending with the cracked gasoline. However, such polymerization processes are in general expensive because of the additional heat and apparatus required, and are justified, if at all, only because of the relatively high anti-knock value of the polymerized gasoline thus obtained.

Probably the most successful separate gas-polymerizing processes to date have been those of the catalytic type. These processes are more or less limited to the conversion of unsaturates, particularly butylenes, and the polymer gasolines produced in these processes have in some instances been disappointing in character, by reason of their low "lead susceptibility"; that is to say, when these gasolines are blended with other gasolines of lower octane number, the amount of tetraethyl lead required to bring the octane number of blend up to the market standard is not reduced to as great an extent as would be expected from the apparent octane numbers and so-called "blending values" of these polymer gasolines alone.

In the past, some attempts have been made to recycle gases produced in cracking operations. In the earlier of these attempts, no effort was made to segregate the more refractory constituents and the less refractory constituents of the gases, respectively, before recycling; these attempts were predicated upon a now discredited theory of equilibrium or "mass action", it being thought that the presence of the recycled gases would tend to restrain the formation of additional gases.

In later attempts of this character, the gases were fractionated before recycling to remove hydrogen and methane, which were then discarded, the remaining constituents of the gases being recycled. Removal of hydrogen and methane before recycling was undoubtedly a step in the right direction, yet nevertheless little improvement was effected by this manner of operation, and such processes attained no commercial importance. Under such conditions, there were obtained slight increases in yield of gasoline, without any substantial increase in the anti-knock values of the final gasoline products, and without any substantial reduction in the yield or any substantial improvement in the quality of the tar produced. It was not, however, realized that further improvement was possible with regard to the cracking of the oil itself or with regard to the conversion of the gases. Moreover, prior references disclosing such gas recycling contain no adequate information as to the proper extent of gas dilution or gas recycling which should be maintained under different operating conditions and with different cracking stocks.

The primary object realized by my invention is the provision of an oil-cracking process wherein a more favorable balance between the yield and quality of the ultimate gasoline is obtained than has been possible heretofore, under commercially satisfactory operating conditions, and without requiring the use of unnecessarily complicated apparatus. Numerous other objects and advantages realized by my invention will be made clear hereinbelow.

My process essentially contemplates the cracking of hydrocarbon oil in the presence of diluent gases having 3 to 4 carbon atoms per molecule, under conditions effective to give a degree of conversion per pass of the oil substantially higher than could be effected if the oil were cracked alone in the absence of the gases in similar apparatus without encountering excessive deposition of carbon in the tubes of the heating element. This is a fundamental feature of my invention.

Others who have proposed to recycle gases in oil-cracking operations appear to have contented

themselves with subjecting the oil to conditions effective to give substantially the same degree of conversion per pass of the oil as though no gases were introduced or recycled. However, I have discovered that by forcing the cracking of the oil to or toward the new maximum permissible under the conditions of my process, while controlling the character and relative amount of normally gaseous constituents present with the oil in the conversion zone, results are obtained which represent a marked and valuable improvement over the prior art, and without encountering serious carbon deposition in the conversion zone. Thus I have succeeded in obtaining a substantially higher yield of gasoline or a gasoline product of increased anti-knock value, and in most cases both, and also a lower yield of tar or a better quality of tar, than has heretofore been possible. The over-all results, in terms of yield times quality, are vastly improved; they are better than could be obtained by cracking the oil in one unit and polymerizing the resultant gases in another unit. Also, less apparatus is required; the entire operation is conducted in a single unit.

The process of my invention effects a simultaneous cracking of the oil to a higher degree of conversion than is possible when the oil is cracked by itself, while at the same time there is effected a substantial conversion of C_3 and C_4 hydrocarbons to gasoline-like products.

It should be recognized that the C_3 and C_4 hydrocarbons include both saturated and unsaturated constituents. The unsaturated constituents (propylene and butylenes) are susceptible to direct polymerization at fairly low temperatures, for example as low as 800° F., provided the pressures are sufficiently high. However, the saturated constituents (propane and butane) are not converted into normally liquid hydrocarbons to any substantial extent at temperatures below about 900°–950° F. These saturated constituents do not form normally liquid hydrocarbons by simple polymerization, and consequently require higher temperatures for conversion. Such conversion may proceed through the mechanism of a preliminary cracking of the saturated constituents to form unsaturated constituents which then polymerize, or it may proceed to some extent through other mechanisms of reaction, for example, through some sort of alkylation or other reaction with other hydrocarbons present. I do not desire to limit my invention to any particular theory or explanation but simply desire to point out that effective conversion of the saturated normally gaseous constituents requires a higher operating temperature, other factors being the same, than is required for a corresponding degree of conversion of the corresponding unsaturated constituents.

One of the great advantages of my process resides in the fact that, since the operating temperatures for any given oil when cracked in gas dilution in accordance with my invention are substantially higher than could safely be maintained when cracking the same oil without gas dilution, the degree of conversion per pass of the saturated normally gaseous constituents, propane and butane, is high. It is this high degree of conversion of the saturated normally gaseous constituents, combined with the increased degree of conversion per pass of the oil stock, which results in the ultimate increase in yield and quality of the gasoline produced. Of course, in the case of very heavy oils, such as an oil having a critical temperature of higher than 1000° F., the actual cracking temperature, even when the cracking is conducted in accordance with my invention, may be as low as 875° to 950° F., as such oils cannot be cracked alone in coil-type apparatus without serious carbon deposition at a cracking temperature of above 850° F. In the application of my process to such oils, comparatively little conversion of the saturated normally gaseous constituents, especially propane, can be expected; here the improved results flow almost entirely from the increased degree of conversion per pass of the heavy oil made possible in accordance with my invention, as well as from some polymerization of the unsaturated normally gaseous constituents, especially butylenes.

In all cases, however, the improved results obtained in accordance with my invention primarily flow from the increased degree of conversion per pass of the oil made possible when operating in accordance with my process, and my process is to that extent primarily an oil-cracking process.

I have discovered that in cracking oils in accordance with my process, there is a certain minimum limit of gas dilution which is necessary in order to obtain substantially improved results. Specifically, I have found that the amount of C_3 and C_4 hydrocarbons added to the oil traversing the conversion zone should be at least such that the critical temperature of the mixture lies below the maximum permissible cracking temperature for the oil alone in the same cracking apparatus and under otherwise similar conditions. This definite minimum must be maintained in order to obtain a substantial increase in the degree of conversion per pass of the oil, and without which the substantial improvements of my invention are not attained. This is especially important with respect to oils having critical temperatures above 800° F.

I believe that the necessity underlying this minimum point is due to the following facts. When the temperature of an oil traversing a cracking tube is below the critical temperature of the oil, and the pressure upon the oil is higher than the critical pressure of the oil, there always exists a liquid phase, either alone or with a vapor phase. Due to turbulence in the tube, the oil particles existing in the liquid phase tend to be brought into contact with the walls of the tube. This results in covering the inner wall of the tube with a thin liquid oil film primarily composed of the heavier components of the oil. As the heat transmitted through the tube wall to the mixture of vapor and liquid oil in the tube must be transmitted through this oil film, the coking characteristics for the mixture are largely determined by the coking characteristics of this relatively heavy oil film. As long as this liquid oil film exists, the mixture of hydrocarbons passed through the tube cannot be subjected to conditions effective to give a substantially higher degree of conversion per pass than would be possible if the heaviest constituents alone were present.

I have found that by diluting a relatively heavy oil of high molecular weight with a sufficient amount of C_3 and C_4 hydrocarbons, the critical temperature of the mixture can be reduced to a point lying below the temperature at which the oil can be cracked by itself.

Under such conditions I have discovered that a heavy oil may be cracked to a substantially higher degree of conversion per pass than would be possible otherwise. Below this minimum point,

it is not possible to accelerate the conversion of the heavy oil beyond the maximum permissible conversion for the cracking of the oil by itself.

This minimum amount of diluent required may be as high as approximately 100 per cent of the oil for a heavy oil having a critical temperature of approximately 1400° F. and an average molecular weight of 500 or more, and will of course be less with respect to oils having lower average molecular weights and lower critical temperatures.

In the past, light stocks such as naphtha and other normally liquid but relatively low-boiling hydrocarbons have sometimes been added to relatively heavy stocks, with the result that the critical temperatures of the mixtures were lowered to points considerably below those of the relatively heavy stocks themselves. However, my invention is to be distinguished from such prior art practice. In the first place, the effect on the critical temperature of the resultant mixture, when even a light naphtha is added to a relatively heavy stock having a high critical temperature, is considerably less than when normally gaseous hydrocarbons are added to the same relatively heavy stock in the same amount. Moreover, when a normally liquid hydrocarbon charging stock is thus used as a diluent, the over-all results, while perhaps improved with respect to the relative heavy stock, represent a serious impairment of the cracking efficiency with respect to the relatively light stock itself. In my process, however, no such sacrifice is entailed because of the very nature of the normally gaseous diluent employed and the type of conversion to which it is subjected.

With oils having critical temperatures below 800° F., the maximum permissible cracking temperature for the oil alone is usually higher than the critical temperature of the oil, and under such conditions it is no longer necessary to add a diluent merely for the purpose of reducing the critical temperature of the mixture to a point where homogeneous vapor-phase conditions would obtain in the conversion zone.

I have discovered, however, that it is in all cases necessary to add to the oil undergoing conversion the normally gaseous diluent (considered in liquefied form) in the amount of at least 15 per cent by volume of the oil; lower degrees of dilution do not result in sufficient acceleration of the conversion to give substantially better results.

I have referred above to the "critical temperatures" and "critical pressures" of hydrocarbon oils or hydrocarbon mixtures. These may be readily determined for any given oil or mixture by methods well known in the art. They are sometimes known as "pseudo-critical" values, and they depend upon the molecular weight or average molecular weight of the hydrocarbons or hydrocarbon mixtures and also upon what is known as the "characterization factor" of the hydrocarbons or hydrocarbon mixtures concerned. This characterization factor is in substance an indication of the type of molecular structure of the oil, that is to say, an indication of whether the individual hydrocarbon constituents of the oil are largely of the paraffinic type, the aromatic type or the "naphthenic" type. More specifically, this "characterization factor" has been defined as being equal to the cube root of the molal average boiling point, in degrees Rankine, divided by the specific gravity at 60/60° F. Thus an oil having a characterization factor of 13 and an average molecular weight of 200 will have a critical temperature of approximately 800° F. and a critical pressure of approximately 235 pounds per square inch, while an oil having a characterization factor of 10 and an average molecular weight of 140 will have a critical temperature of approximately 800° F. and a critical pressure of approximately 430 pounds per square inch.

Additional data on the "pseudo-critical" points of hydrocarbon mixtures will be found in an article entitled "Density of hydrocarbon gases and vapors" by W. B. Kay, in "Industrial and Engineering Chemistry", vol. 28, pages 1014–1019, Sept., 1936.

While I have stated above certain definite minimum limits for gas dilution, below which substantially improved results cannot be obtained, I prefer in all cases to add to any oil undergoing conversion in accordance with my invention normally gaseous diluent consisting largely or entirely of C_3 or C_4 hydrocarbons, (considered in liquefied form) in the amount of at least 30 per cent by volume of the oil, thereby making it possible to push the degree of the conversion of the oil to a point definitely higher than would be possible were the gas dilution reduced to the minimum set forth hereinabove.

The extent of gas dilution, especially when normally gaseous hydrocarbons from an extraneous source are introduced into the system, in addition to the gases produced in the system and recycled, may be increased to such a point that the mixture introduced into the coil will represent as much as eight volumes of liquefied normally gaseous constituents per unit volume of oil charging stock.

While normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule may be supplied from any suitable source for admixture with the oil about to undergo cracking, it is ordinarily advantageous and desirable to employ gases of this character which are produced in the cracking of the oil itself. This is accomplished by first fractionating the cracked products leaving the conversion zone to remove gasoline and heavier products, and then fractionating the remaining gases and vapors to recover a first fraction consisting of or predominating in C_3 or C_4 hydrocarbons, or both, and a second or residual gas fraction consisting of gaseous constituents of lower molecular weight, such as ethane, ethylene, methane and hydrogen. The first fraction containing hydrocarbons having 3 to 4 carbon atoms per molecule is then recycled for admixture with the oil entering the conversion zone or zones. This fractionation may be carried out in various manners but is advantageously effected by employing the oil charging stock as an adsorbent medium, the thereby enriched oil being delivered to the conversion or cracking zone. The normally gaseous hydrocarbons produced in the system and thus recycled may be augmented by the addition of similar hydrocarbons from an extraneous source, where such are available.

In a single-coil unit, in which no normally gaseous hydrocarbons from an extraneous source are introduced into the system, the normally gaseous hydrocarbons employed as a diluent are derived solely from the cracking of the oil itself. The gases produced are fractionated to segregate a fraction consisting largely of C_3 and C_4 hydrocarbons from the gaseous constituents of lower molecular weight, and the thus segregated fraction is delivered to the cracking coil in admixture with the oil charging stock. In operating such a unit on oils having critical temperatures of 800° F.

or less, high cracking temperatures and relatively high degrees of conversion per pass are possible, and the amount of gas produced is relatively high, but on the other hand the relatively drastic cracking conditions tend to give higher degrees of conversion per pass of the recycled gases, which tends to reduce to some extent the extent of gas recycling required in order to effect the desired ultimate degree of conversion of the gases produced in the system. The preferred range of gas dilution, in this instance, is from 100 to 200 percent by volume on the oil charging stock.

In operating a similar unit, that is to say a single-coil unit in which no gases from an extraneous source are introduced, on an oil having a critical temperature higher than 800° F., the preferred range of gas dilution is from 30 per cent to 150 per cent by volume on the oil charging stock.

Where the temperatures in any case are sufficiently high to effect a substantial degree of conversion per pass of the saturated normally gaseous constituents, the fractionation of the normally gaseous hydrocarbons for recycling and the extended recycling should be such as to secure an ultimate conversion to gasoline of all of the C_4 hydrocarbons produced (other than such amounts thereof as are removed from the system in the gasoline in order to meet gasoline vapor pressure specification) and, if the operating temperatures are sufficiently high, to secure an ultimate conversion of all of the propane produced. Ethane and ethylene are not in themselves desirable constituents for recycling, except under extremely high cracking temperatures, for example in excess of 1200° F., because of the relatively refractory character of these hydrocarbons. Methane, which is even more refractory, should not be recycled at all.

Normally gaseous hydrocarbons having 3 and 4 carbon atoms per molecule may also be introduced from an extraneous source into such a single-coil unit, but there is comparatively little advantage to be gained in thus introducing such hydrocarbons from an extraneous source (in addition to recycling gases produced in the unit) in a single-coil unit operating on a relatively heavy or residual oil stock, such as an oil having a critical temperature of 1000° F. or higher. The extent of introduction of such gases will in all cases be governed largely by the composition of such gases (that is to say, whether they predominate in C_4 hydrocarbons or C_3 hydrocarbons) and by the cracking characteristics of the oil and the operating conditions employed. In cracking relatively light oils and under relatively drastic cracking conditions, relatively large amounts of extraneous gases, if available, may be introduced and such gases may contain relatively large quantities of C_3 hydrocarbons. The extent of such introduction should, however, be so controlled that the admixture of normally gaseous hydrocarbons and oil entering the conversion zone does not in any event contain more than eight volumes of liquefied normally gaseous hydrocarbons per unit volume of oil, as aforesaid.

In combination units, that is to say, units in which a plurality of cracking coils are employed, the products of cracking being delivered into a single fractionating system, it is necessary to distribute the available gases to the several coils. Without introduction of gases from an extraneous source, and where at least one of the coils is employed for the cracking of relatively light stock, such as light gas oil or naphtha, the overall recycle ratio should be such as to return to the unit for conversion at least all of the C_4 hydrocarbons produced in the unit (and not required to be removed as such in the gasoline), and may be increased to such a point as to represent a return of most or all of the C_3 hydrocarbons produced. In distributing the recycled normally gaseous hydrocarbons between the various coils, consideration must be given to the nature of the individual oil charging stocks being delivered to these coils. With respect to the cracking coils operating on relatively heavy oils, it is normally desirable to deliver to these coils such quantities of the available normally gaseous hydrocarbons as to maintain a degree of gas dilution therein lying between limits set forth hereinabove with respect to the various types of oils. The remaining gases available for recycling should be recycled to the coil or coils receiving relatively low-boiling oil charging stocks and operating at relatively high temperatures, for example, into the gas-oil cracking or naphtha re-forming coil. Such gas distribution may be readily effected in accordance with my invention and when employing the apparatus and procedure illustrated hereinbelow with reference to multi-coil units.

In single-coil units, operating on relatively low-boiling oils, I have found it advantageous to employ the charging stock as an absorbent for the gases from which gasoline and heavier constituents have been removed, regulating the conditions of absorption in order to obtain the desired recycle ratio and the proper degree of dilution. In multi-coil units, a condenser is advantageously employed between the point of gasoline removal and the absorber, in which a considerable portion of the C_3 and C_4 hydrocarbons may be condensed under pressure. The condensate thus obtained is delivered to an accumulator from which it may be distributed to the coil or coils operating on relatively heavy oil stock, while the remaining gases pass to the absorber, the absorption medium employed in the absorber consisting of the lightest oil charging stock delivered to any of the coils, for example, naphtha. While other gas-fractionating and distributing systems may be employed, this system is especially advantageous in connection with multi-coil units and will be described in further detail hereinbelow.

When C_3 and C_4 hydrocarbons from an extraneous source are charged into such a unit, they may either be segregated as introduced, and delivered to one or more of the coils, or they may be combined with the gases produced in the unit for fractionation and distribution as, for example, by delivering them to the gases ahead of the above-mentioned condenser, or into the above-mentioned absorber, or into a second absorber in which one of the other available oil stocks (suitably cooled for this purpose) may be employed as the absorbent.

I have discovered that it is in many cases advantageous to accomplish the ultimate conversion of a petroleum crude to gasoline, to separate the original crude into fractions composed of constituents of fairly uniform cracking characteristics for cracking in separate coils, and to avoid the cracking of mixtures of straight-run oils and cracked oils (recycle stocks) wherever possible. I describe hereinbelow a unit in which a petroleum crude is first distilled to separate it into a plurality of fractions, for example, naphtha, gas

oil and reduced crude, and wherein each of these fractions is cracked under appropriate conditions and in gas dilution as aforesaid and under the conditions hereinabove set forth, the various cracked products being combined for fractional separation into fuel oil or tar, gas oil, charging stock, gasoline, recycle gases predominating in C_3 and C_4 hydrocarbons, and residue gases, consisting largely of hydrogen, methane and C_2 hydrocarbons. The gas oil (recycle stock) thus recovered is preferably cracked in a separate coil, also in gas dilution and in the manner set forth hereinabove, the products being delivered to the common recovery system. The normally gaseous hydrocarbons available for recycling, with which may be included similar hydrocarbons from an extraneous source, are distributed to the several cracking oils, in the manner set forth herein. My invention may, however, be applied with advantageous results to other types of multi-coil units, including those in which one of the cracking coils receives a mixture of straight-run stock and recycle stock as well as normally gaseous hydrocarbons, and also to multi-coil or "combination" units which include a separate coil for "viscosity-breaking" the reduced crude from the crude distilling or stripping unit, without gas dilution, as described in my copending application Serial No. 113,906, filed December 2, 1936.

The cracking temperatures employed in my process will ordinarily run from 50° to 300° F. higher, for any given oil, than the maximum temperature to which the oil could be subjected in similar apparatus without serious carbon deposition, if cracked alone. I have found, however, that temperatures as low as 25° to 50° F. in excess of the aforesaid maximum cracking temperature for the oil alone are sometimes suitable. For example, in re-forming or cracking naphthas and some other oils, it is desirable to conduct the cracking in a cracking coil having an initial heating and cracking section of relatively high input and a "soaking" section of relatively low heat input, the total time to which the oil is subjected to cracking conditions being relatively long. Under such conditions, it is in many instances desirable to avoid excessive soaking of the entire products or cracking the admixture of oil and normally gaseous hydrocarbons at excessively high temperatures. Where the cracking coil contains no soaking section of relatively low heat input, or only a relatively short soaking section, the cracking temperatures in the operation of my process may be increased to temperatures of from 50° to 300° F. higher than the maximum cracking temperature which would otherwise be permissible in the same apparatus, when cracking the same oil alone.

In the application of my invention to heavy oils from which, when cracked by themselves in the manner of the prior art, maximum yields of gasoline of from 5 to 15 per cent per pass can be obtained, I obtain yields of gasoline per pass of from 15 to 30 per cent by volume of the original oil charging stock. With respect to oils, such as gas oil, from which there can be obtained, when these oils are cracked alone in the manner of the prior art, yields of from 15 to 30 per cent of gasoline per pass, I obtain gasoline yields amounting from 25 to 60 per cent per pass, in terms of the original oil charging stock on a volume basis. I also obtain a yield of gasoline per pass, when cracking or re-forming a naphtha in accordance with my invention, higher than that yield which is obtained in cracking the same naphtha in the manner of the prior art to obtain gasoline of the maximum octane number. In all cases, the octane number of the gasoline produced is higher, for example from 3 to 15 octane numbers higher, when operating in accordance with my invention, than the maximum octane number possible when cracking the same oil in the manner of the prior art, under conditions which do not result in excessive carbon deposition in the cracking coil. Units operating in accordance with my invention can be continuously operated for extended periods of time of from 1000 to 2000 hours, or even more, without serious carbon deposition.

In order that my invention may clearly be 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, by way of example and illustration. In these drawings,

Figs. 1, 2, 3 and 4 are more or less diagrammatic elevational views of four forms of apparatus suitable for cracking hydrocarbon oil in accordance with my invention.

In these drawings, which are intended to serve primarily as flow sheets, many apparatus details such as heat exchangers and the like are omitted or shown in more or less diagrammatic or conventional form, since a complete showing of such apparatus details as would readily suggest themselves to one skilled in the art is unnecessary insofar as concerns exemplification and illustration of my invention.

In describing the operations conducted in the operations described herein in connection with these drawings, it will be convenient to discuss the extent of gas dilution and the rate of recycling of the C_3 and C_4 hydrocarbons in terms of a "recycle ratio", which, with respect to any cracking coil, may be defined as the ratio of the total charging stock (the sum of the liquid volumes of the oil charging stock and the normally gaseous hydrocarbons in admixture with the oil, considered as in liquefied form) to the liquid volume of the oil charging stock alone. Thus, in referring to a recycle ratio of 2:1 in connection with the cracking or re-forming of a naphtha, I mean to indicate that the sum of the liquid volumes of the naphtha charging stock and the liquefied normally gaseous hydrocarbons introduced into the coil in admixture with the naphtha is double the liquid volume of the naphtha alone. The "recycle ratio", as thus defined, offers a convenient method for determining the proper conditions to be employed in connection with the process of my invention, but differs somewhat from the terminology employed in ordinary oil cracking operations, in which a similar term is sometimes employed to designate the ratio of the total feed (combined fresh charging stock and recycle stock) to the fresh charging stock alone.

In Fig. 1, I have illustrated apparatus suitable for cracking light hydrocarbon oil in a once-through manner, that is to say, without recycling intermediate condensate oils, but provided with means for recycling hydrocarbons having 3 to 4 carbon atoms per molecule formed in the cracking of the oil. While this system may be applied to the cracking of various types of oil, it is especially suitable for the cracking or re-forming of straight-run naphtha.

I have found that in re-forming naphtha in accordance with the principles of my invention, especially advantageous results are obtained. The

over-all improvement is greater than could be obtained by cracking the oil and polymerizing the resultant gas in separate units. In my process, the degree of conversion per pass is higher than in an ordinary naphtha-re-forming operation, but the yield of gasoline is actually increased, due to the conversion of the gases produced in the operation. Less apparatus is required, and the yield of heavy oil is materially reduced in most instances.

In the apparatus illustrated diagrammatically in Fig. 1, cracking takes place in a suitable pipe coil in a furnace 1. The cracked vapors then pass through an evaporator 2, a fractionator 3 and a vapor-feed condenser-stabilizer 4, for the removal of tar, gas oil and stabilized gasoline, respectively. The gases and vapors remaining after the removal of the stabilized gasoline in the condenser-stabilizer 4 ordinarily contain varying quantities of hydrogen, ethane, methane, ethylene, propane, propylene, butane and butylenes, and may contain very small quantities of normally liquid higher-boiling hydrocarbons. These gases, at a controlled temperature, are introduced into an absorber 5 where they are scrubbed with fresh naphtha charging stock brought through a line 6 from a suitable source (not shown) and which is delivered by means of a pump 7 and a line 8 having a valve 9 into the upper part of the absorber 5. In the absorber 5, the naphtha charging stock descends countercurrent to the rising gases and vapors and absorbs therefrom hydrocarbons containing 3 and 4 carbon atoms per molecule, as well as any higher boiling hydrocarbons which may be present in small quantities in the entering gases. The dry gases, consisting largely of hydrogen, methane, ethane, ethylene, and in some instances some propane and propylene, leave the top of the absorber 5 through a gas line 10 having a back-pressure valve 11. The enriched naphtha charging stock passes from the bottom of the absorber 5 through a line 12 into an accumulator tank 13. A portion of the naphtha charging stock may be by-passed around the absorber 5 through a line 14 having a valve 15 leading from the pipe 8 directly into the accumulator 13. A vapor-return line 16 is usually provided, communicating between the top of the accumulator 13 and the interior of the absorber 5.

From the accumulator 13, the enriched naphtha charging stock containing absorbed normally gaseous hydrocarbons having 3 and 4 carbon atoms per molecule passes through a line 17 to a pump 18 which delivers it through a line 19 into and through the tubes of the cracking furnace 1. In the cracking furnace 1, the naphtha is cracked in the presence of the absorbed gases to obtain a higher degree of conversion per pass than could be obtained without serious carbon deposition in similar apparatus if the oil were cracked alone (that is to say, in the absence of the absorbed hydrocarbons). The temperatures employed will run from 25° to 300° F. higher than the maximum permissible temperature which could be employed for cracking the same naphtha alone in similar apparatus, and with similar times of contact and at the same pressure, without resulting in serious carbon deposition. The specific coil-outlet temperature used will obviously vary under different conditions, as will be readily understood by those skilled in the art, and will in particular vary with the character of the charging stock cited. However, whereas when operating in similar apparatus in the manner of the prior art, I have found that maximum re-forming temperatures for different naphtha stocks will ordinarily vary between 950° and 1150° F., temperatures of from about 975° to as high as 1450° F. are not only possible but desirable in practising my invention. I therefore use temperatures within the latter range, for example a temperature of from 1030° to 1050° F. Unless the temperature of cracking and degree of conversion per pass of the naphtha are substantially increased over those which would represent a practical maximum for the same stock when reformed in the conventional manner of the prior art, the full advantages and results of my invention are not realized. Naturally, some polymerization of the unsaturated gases may be expected in either event, but the advantages of my process flow not only from the cracking and polymerization of the absorbed gases but from the improved cracking of the oil itself made possible in accordance with my invention. Coil-outlet pressures ranging from about 500 to 2000 pounds per square inch are suitable; for example I have used an outlet pressure of about 1250 pounds per square inch with good results.

The cracked products leaving the furnace 1 pass through a transfer line 20 having a valve 21 into the lower part of the evaporator 2. It is ordinarily desirable to introduce a suitable quenching oil into the transfer line 20, at a point close to the furnace coil outlet, and I have shown a line 22 and a pump 23 for introducing such quenching oil. The purpose is, of course, to arrest or retard the cracking and to prevent excessive contact or soaking times at the high cracking temperatures employed.

By means of the valve 21, the pressure of the converted hydrocarbons is ordinarily reduced as they enter the evaporator 2, for example, to from 200 to 500 pounds per square inch. In the evaporator 2, into which a reflux or cooling oil may be delivered through a line 24 if desired, high-boiling or residual constituents, of a tarry nature, are separated. The tar is removed from the evaporator 2 through a valved tar line 25 and withdrawn from the system.

The tar-free vapors then pass through a vapor line 26 into the fractionator 3 which, as shown, may be of conventional design and wherein the vapors are fractionated to condense and remove intermediate oils, that is to say, oils boiling above the desired gasoline boiling point and not previously removed in the evaporator 2, i. e. gas oil. The gas oil thus condensed is removed from the fractionator 3 through a valved line 27 and, in the instance shown, passes out of the system for cracking elsewhere or for whatever disposal may be desired. In re-forming naphtha in the manner illustrated in Fig. 1, it is ordinarily not worth while to provide a separate cracking coil as a part of the unit for effecting the conversion of the relatively small amount of gas oil recovered, but as will readily be understood by those skilled in the art, this gas oil, if the quantity thereof is sufficiently large, may be cracked in a separate coil and the cracked products resulting therefrom may be combined from the cracked products from the furnace 1. This cycle stock may, after suitable cooling, be employed for scrubbing gases introduced from an outside source for the removal of C_3 and C_4 hydrocarbons therefrom and then either returned to the system as reflux or cracked in the presence of the absorbed hydrocarbons. This will be more fully understood in connection with subsequent figures illustrating operations in which relatively large

amounts of cycle stock are produced, and with reference to my prior copending applications showing various operating cycles.

The remaining vapors then pass through a vapor line 28 into the vapor-feed condenser-stabilizer 4.

The condenser-stabilizer 4 essentially consists of an upper or condensing section 29, wherein condensation of unstabilized gasoline condensate is effected, and a communicating stabilizer section 30, in which the gasoline condensate is reboiled and rectified to effect stabilization. One portion of the unstabilized condensate flows downward into and through the stabilizer section 30. Another portion is removed through a line 31, wherein is located a suitable liquid-to-liquid heat exchanger or cooler 32, and the cooled unstabilized condensate is then returned by means of a pump 33 and a reflux line 34 into the upper portion of the condensing section 29. The cooling necessary for condensation is provided in the cooler 32, while such heating as is necessary to effect stabilization of the gasoline condensate is supplied to the stabilizer section 30 in a suitable manner, as for example by means of a heating coil 35. Stabilized gasoline condensate is withdrawn from the stabilizer section 30 through a valved line 36. Vapors liberated in the stabilization of the gasoline pass upward into the condenser section 29.

The gases and vapors, from which gasoline has thus been removed, then pass from the top of the condenser-stabilizer 4 through a line 37 into the lower part of the absorber 5, for recovery of C_3 and C_4 hydrocarbons therefrom. A suitable cooler 38 is shown in the line 37, this cooler being provided with a condensate line 39 for delivering to the absorber 5 any condensate formed as a result of the cooling.

The pressures throughout the units 2, 3, 4 and 5, are maintained by means of the back-pressure valve 11 and these pressures will ordinarily be between about 200 and 500 pounds per square inch.

In the operation of a system of this character and when cracking a low-boiling oil, such as naphtha, it is desirable to control the recycling of the gases between certain limits, as set forth hereinabove. The extent to which the normally gaseous hydrocarbons are recycled in the process is controlled by adjusting the conditions existing in the absorber 5, that is to say, by regulating the extent to which constituents of the gases are picked up and absorbed in the naphtha charging stock for delivery to the cracking furnace 1. The extent of absorption is regulated and controlled by governing the amount of naphtha charging stock which is permitted to pass through the absorber 5, the pressure maintained in the absorber 5, and the temperature of absorption, which in the instance shown is subject to regulation through controlled operation of the cooler 38 and the temperature of the entering naphtha and gases.

I have found that in re-forming naphtha in accordance with my invention and where no gases are introduced from an outside source, exceptionally good results are obtained when conditions in the absorber 5 are so regulated that the recycle ratio, as above defined, is from 2:1 to 3:1. With lower recycle ratios, hydrocarbons containing 3 carbon atoms per molecule will be permitted to escape from the system to an undesirable extent and optimum cracking of the oil is not realized. On the other hand, due to the relatively refractory character of ethane, ratios higher than about 3:1 are not ordinarily desirable. Higher recycle ratios tend to build up excessive quantities of ethane and ethylene in the system. A recycle ratio, as thus defined, of about 2:1, however, represents the most desirable operation in most instances, favoring high over-all yields and high quality of gasoline product. I have obtained especially favorable results operating at a cracking or re-forming temperature of about 1030° F. and 1250 pounds per square inch pressure, with a recycle ratio of 2:1, and ordinarily I do not find it desirable to increase the recycle ratio above this point except when extremely high octane numbers of the distillate or complete conversion of the C_3 constituents is desired, in which case somewhat higher recycle ratios up to 3:1 may be employed.

In a system of the character illustrated in Fig. 1, it is often desirable to introduce C_3 and C_4 hydrocarbons from an external source. These hydrocarbons are, of course, present in refinery gases, natural gases and the like, which may be available to the refiner, and which may be utilized to considerable advantage in a process of the character set forth. Such gases may be introduced into the absorber 5 through a suitable connection (not shown) and scrubbed with the incoming oil charging stock along with the gases leaving the condenser-stabilizer 4, or they may be scrubbed in a second absorber for recovery of the C_3 and C_4 hydrocarbons contained therein. The absorbent in the latter case may be such portion of the charging stock as is not required in the first absorber 5, or it may comprise recycle stock recovered from the fractionator 3 (which will of course be suitably cooled before use as an absorbent), or both. Where recycle stock is thus employed for the purpose of scrubbing gases from an external source, the enriched recycle stock is then preferably returned to the system as reflux or quenching oil, or cracked in a separate coil under such cracking conditions as will be optimum for this type of stock, as distinguished from the fresh stock cracked in the furnace 1, and under such conditions as to effect a higher degree of conversion per pass than could be obtained without serious carbon deposition if the recycle stock were cracked alone.

Inasmuch as such recycle stock will correspond fairly closely to other recycle stocks produced in the processes illustrated in Figs. 2 and 3 and subsequently described herein, it is believed that the manner of handling such recycle stocks, when separately cracked as aforesaid, will readily be understood from consideration of the subsequent portions of this specification, without requiring extensive discussion at this point.

As set forth hereinabove, the recycle ratio, when gases are introduced as aforesaid from an outside source, will be governed in accordance with the operating conditions used in the cracking coil and the degree of conversion per pass of the various hydrocarbons contained in such gases and brought into the system by absorption, under the existing conditions. In such instance, as hereinbefore set forth, the recycle ratio should be within the range of from 2:1 to about 9:1, the lower limit corresponding to that employed in re-forming naphtha as aforesaid, and representing a condition in which little or no normally gaseous hydrocarbons from an outside source are introduced, and the upper limit representing the maximum extent to which normally

gaseous hydrocarbons from an outside source may advantageously be introduced. It may be remarked, however, that due to the high temperatures commonly employed in re-forming naphtha, an upper limit of about 4:1 when determined in accordance with the formula given hereinabove, will rarely need to be exceeded on account of the high degrees of conversion per pass of C_3 and C_4 hydrocarbons effected under such conditions.

The apparatus illustrated in Fig. 1 may also be employed for the cracking of other oils, so long as such oils are capable of use as absorbents in absorber 5.

In Fig. 2, however, I have illustrated apparatus especially suitable for cracking an oil heavier than a naphtha but having a Conradson carbon residue number below 0.05, a pour point below 60° F. and a crtical temperature below 900° F. in other words, a stock of higher boiling point than gasoline but containing substantially no residual constituents—an "overhead" or "clean" stock. This system is especially useful for the cracking of a straight-run gas oil or a gas oil condensate recovered from the "viscosity-breaking" or mild cracking of a heavy residual oil.

The system provides for cracking the fresh oil charging stock in a once-through manner and the separate cracking of recycle stock produced in the operation, both cracking operations being conducted in the presence of recycled normally gaseous hydrocarbons containing from 3 to 4 carbon atoms per molecule. The apparatus includes cracking furnaces 50 and 51, a tar-separator or evaporator 52, a fractionator 53, a vapor-feed condenser-stabilizer 54 (similar to condenser-stabilizer 4 of Fig. 1) and an absorber 55.

The absorber 55 receives, through a line 56, gases produced in the operation and not previously condensed. These gases contain hydrocarbons having 3 and 4 carbon atoms per molecule, as well as constituents of lower molecular weight. As shown, fresh gas oil charging stock is introduced into the top of the absorber 55 through a line 57 by means of a pump 58. A valve 59 is provided in the line 57. The oil passes downwardly through the absorber 55 and absorbs normally gaseous hydrocarbons containing 3 to 4 carbon atoms per molecule to the desired extent. The thereby enriched charging stock passes through a line 60 into an accumulator 61 having a vapor-return line 62 communicating with the absorber 55. The accumulator 61 is also in communication with the line 67. Through a line 63 having a valve 64, any desired proportion of the charging stock may be delivered to the absorber 55, while the remainder passes directly to the accumulator 61.

The dry gas leaving the top of the absorber 55 consists largely of hydrogen, methane, ethane, and ethylene, but ordinarily contains some propane and propylene, and is removed from the system through a dry-gas line 65 having a back-pressure valve 66.

From the accumulator 61, the enriched charging stock passes through a line 67 to a pump 68 and is delivered by means of the pump 68 through a line 69 into and through a cracking coil 70 located within the furnace 50. In this coil 70, the oil is cracked in the presence of the absorbed normally gaseous hydrocarbons, to a greater extent than could be realized were the oil cracked alone, in the absence of the normally gaseous hydrocarbons, and without serious carbon deposition. The cracking temperatures are preferably from 25° to 200° F. higher than would be permissible for the cracking of the oil alone in the same apparatus other conditions being the same. Thus, for a gas oil stock which would ordinarily be cracked at temperatures between 900° and 1000° F., I have found that temperatures of from 930° to 1200° F., are suitable. Coil-outlet pressures of from 500 to 2000 pounds per square inch are suitable. It will be understood that, in general, the lighter the cracking stock, the higher the permissible temperature will run, varying somewhat in different instances with the character and amount of the normally gaseous hydrocarbons present and with the specific nature of the oil, i. e. the "refractoriness" and carbon-depositing tendency of the oil.

The cracked products leaving the coil 70 through a pressure line 71 are preferably quenched by means of suitable quenching stock introduced by means of a pump 72, a line 73 and a valved connection 74, in the usual manner, and then pass through a pressure-reducing valve 75 into the lower portion of the evaporator 52, where they are reduced in pressure and cooled to effect separation of tarry or residual constituents, the latter being removed through a valved line 76. The vapors leaving the evaporator 52 then pass through a line 77 into the fractionator 53, where they are cooled and condensed to remove cycle stock or gas oil, i. e. condensate substantially free from residual constituents but having a boiling range above the desired gasoline end-point. This recycle stock or gas oil is removed from the bottom of the fractionator 53 through a line 78. Its further disposition will be set forth hereinbelow.

The vapors, now freed from substances heavier than gasoline, then pass through a vapor line 79 into the upper part of the condenser-stabilizer 54, in which gasoline constituents are condensed and stabilized, as previously described in connection with condenser-stabilizer 4 of Fig. 1. Stabilized gasoline is withdrawn through a valved line 80 and the remaining gases and vapors pass through a line 81 to a condenser 82 and then into an accumulator 83, which serves to accumulate such portions of the C_3 and C_4 hydrocarbons as are condensed on account of the cooling effect in the condenser 82. The uncondensed gases and vapors are then passed through the line 56 into the absorber 55.

In the present instance, in which no gases from outside the system are introduced, it is, of course, preferable to deliver the gas oil recycle stock to a cracking coil without cooling this stock to such temperature as would be necessary to enable it to be first used as an absorbent, and it is also desirable, as will be understood, to admix normally gaseous hydrocarbons with this recycle stock before re-cracking. Consequently, a portion or all of the normally gaseous hydrocarbons condensed and liquefied in the accumulator 83 are withdrawn therefrom through a line 85 to a pump 86, which delivers them through a line 87 having a valve 88 for admixture with the recycle stock condensed in the fractionator 53. The recycle stock passes through the line 78 to a pump 89 and thence through a line 90 which communicates with the line 87. The combined gas oil recycle stock and normally gaseous hydrocarbons thus delivered through the lines 90 and 87, respectively, and admixed at the juncture of these lines, then pass through a line 91 into a coil 92 located within the furnace 51, and wherein

the oil is cracked in the presence of the admixed normally gaseous hydrocarbons under conditions more drastic than could be employed if the oil were cracked alone. The range of temperatures employed may be, and usually is, quite similar to the range employed in the coil **70**, for example, from 930° to 1200° F. Also approximately the same range of pressures, of from 500 to 2000 pounds per square inch, is employed. However, it will be understood that the specific conditions employed in the coil **92** for a given stock may be and usually are somewhat different from those employed in the coil **70**, depending upon the relative characteristics of the fresh oil and the gas oil recycle stock, respectively; the cracking temperature employed in the coil **92** may usually be higher than that employed in the coil **70**, in any given unit.

The cracked products leaving the coil **92** are quenched by means of suitable quenching oil introduced through a valved line **93**, and then pass through a transfer line **94** having a pressure-reducing valve **95** into the evaporator **52**.

In the operation of a system of the character just described, in which no gases from an extraneous source are introduced into the system, recycle ratios of from 1.3:1 to 2.5:1 give the best results, with respect to both conversion coils.

The desired recycle ratios are maintained by suitable control of the conditions existing in the condenser **82** and the absorber **55**. The conditions subject to control include: (*a*) pressure, which will ordinarily run from 200 to 500 pounds per square inch, (*b*) the temperature to which the gases are reduced in the condenser **82**, (*c*) the amount and temperature of the oil introduced as an absorbent into the absorber **55**, and (*d*) the proportion of the liquefied products delivered from the accumulator **83** for admixture with the recycle stock leaving the fractionator **53**. With regard to the last factor, a line **96** having a valve **97** is provided for the purpose of delivering to the absorber **55** any portion of the liquefied light condensate recovered in the accumulator **83** which it is not desired to admix with the recycle stock entering the coil **92**.

In such a system as is illustrated in Fig. 2 and described above, the distribution of the normally gaseous hydrocarbons available for recycling between the coils **70** and **92** will, of course, depend upon the relative conditions maintained in those coils; it is more advantageous to introduce the major portion of the normally gaseous hydrocarbons available for recycling into that coil which can be and is operated under the most drastic conditions, so as to obtain the maximum conversion of the normally gaseous hydrocarbons to gasoline. However, the minimum limits for gas dilution set forth hereinabove, and better still the preferred lower limit corresponding to a 30 per cent dilution of the oil, should be maintained with respect to both the coils **70** and **92**.

In a system of the general character illustrated in Fig. 2, when it is desired to introduce normally gaseous hydrocarbons from an extraneous source, the proper distribution of the gases available for introduction into the coils **70** and **92** may be effected in different manners. For example, such gases from an extraneous source may be introduced to the absorber **55**, all or a portion of the condensate from the accumulator **83** being introduced into the coil **92** while the fresh normally gaseous hydrocarbons from an extraneous source are absorbed in the absorber **55** and passed to the coil **70**. Alternatively, the condenser **82** may be omitted, or if it is used, all the liquefied hydrocarbons which collect in the accumulator **83** may be delivered to the absorber **55**, and a portion or all of the cycle stock recovered from the fractionator **53** may there be cooled and delivered to a second absorber (not shown) similar to the absorber **55**, and into which such extraneous gases are introduced for absorption. The thereby enriched oil recycle stock is delivered to the coil **92** or is used as a quenching oil.

In such instance, that is to say when C_3 and C_4 hydrocarbons from an extraneous source are introduced, the over-all recycle ratio for the entire system should be maintained between 1.15:1 and 9:1, and in each coil the recycle ratio should be maintained within the same limits; best results are obtained when the recycle ratios are maintained in excess of 1.3:1, however, as aforesaid. Moreover, the distribution of the normally gaseous hydrocarbons available for recycling to the coils **70** and **92**, respectively, will be influenced and governed to some extent by the relative cracking characteristics of the respective oil charging stocks delivered to these coils and the operating conditions maintained therein, as has been described hereinabove with respect to the operation of a similar system in which no gases from an extraneous source are introduced.

In Fig. 3, I have illustrated apparatus for cracking a heavy hydrocarbon oil having a Conradson carbon residue number higher than 0.05 and a critical temperature lying above 900° F.; for example, a heavy gas oil or reduced crude. Inasmuch as such heavy stocks are not ordinarily suitable for use as absorption media, this system provides for direct admixture of the charging stock with C_3 and C_4 hydrocarbons and the use of a recycle stock as an absorbent medium for the gases produced in the system.

Referring to Fig. 3, the charging stock, such as a heavy gas oil or a reduced crude, is introduced by means of a pump **100** through a line **101** and is admixed with liquefied normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, as well as heavy recycle oil, both of which enter the line **101** through a line **102**. The mixture of oil and gases then passes into and through a pipe coil **103** located in a furnace **104**, wherein it is cracked at a temperature preferably from 25° to 100° F. higher than the maximum permissible operating temperature for the same oil, when cracked alone in the same apparatus and under otherwise similar conditions. Thus, for oils for which the maximum cracking temperatures would run from 800° to 950° F. when cracked alone, I have found that cracking temperatures of from 825° to 1050° F. are suitable when admixed with normally gaseous hydrocarbons in accordance with my invention. Coil-inlet pressures of from 500 to 2000 pounds per square inch are suitable.

The cracked products leaving the coil **103** pass through a transfer line **105**, where they may be quenched by means of suitable quenching oil introduced through a valved line **106**, and the cracked products then pass through a pressure-reducing valve **107** into a combined evaporator and fractionator tower **108**. In the lower portion of this tower a separation of tarry or residual constituents is effected, these constituents being removed through a valved line **109**, while the separated vapors pass upward into the upper or

fractionating section of the tower 108, that is to say, that portion lying above a trap-out tray 110. In the upper section of the tower 108, the vapors are suitably cooled, as for example by means of reflux oil supplied through a line 111, as well as by indirect cooling means, if desired, for the separation of heavy recycle stock, such as a condensate 90 per cent of which boils above 600° F. This heavy recycle stock is removed from the trap-out tray 110 through a line 112 and, in the instance shown, is delivered by a pump 113 through a line 114 and the line 102 to the line 101 for delivery to the coil 103 to be cracked in the presence of the fresh charging stock and admixed normally gaseous hydrocarbons. Alternatively, this heavy cycle stock may be cracked in a separate coil.

It may be observed at this point that the amount of heavy recycle stock removed and returned to the coil 103, when such recycling is practiced, will ordinarily vary from about one-quarter to one times the amount of fresh oil stock introduced into the coil 103 from the pump 100, the ratio of total oil feed to fresh oil feed for the coil 103 therefore lying between 1.25:1 and 2:1, without reference to the normally gaseous hydrocarbons present.

The vapors leaving the tower 108 pass through a vapor line 114 into a second fractionator 115 of conventional design, wherein a relatively light recycle stock is recovered. This recycle stock is removed through a valved line 116. The remaining vapors then pass through a line 117 to a vapor-feed condenser-stabilizer 118 (similar to the condenser-stabilizers 4 and 54 of Figs. 1 and 2, respectively) wherein gasoline constituents are condensed and stabilized. The stabilized gasoline is removed through the line 119. The remaining gases pass through a line 120 and a cooler 121 to an accumulator 122. In the cooler 121, a certain amount of normally gaseous hydrocarbons is liquefied under the conditions prevailing at this point and these are separated out in accumulator 122. The liquefied products are removed from the accumulator 122 through a line 123 and pass to a pump 124. The pump 124 is in communication with the line 102 through a line 125 having a valve 126, and all or a portion of the liquefied light condensate from the accumulator 122 is delivered through the lines 125, 102 and 101 for admixture with the fresh charging stock and heavy recycle stock going to the coil 103.

The uncondensed gases from accumulator 122 pass through a line 127 into an absorber 128, which is also in communication with the pump 124 through a line 129 having a valve 130, and is thus adapted to receive any portion of the condensate collected in the accumulator 122 that is not delivered to the coil 103.

The absorbent used in the absorber 128 in this instance comprises all or a regulated portion of the light cycle stock withdrawn from the fractionator 115. This recycle stock passes through the line 116 to a pump 131 and thence through a line 132 having a valve 133 and a cooler 134 into the top of the absorber 128. During this passage downward through the absorber 128, this oil picks up and absorbs hydrocarbons having from 3 to 4 carbon atoms per molecule from the gases traversing the absorber, as in the previous instances described above. The remaining dry gases are removed from the system through a line 135 having a back-pressure valve 136, which is ordinarily set to maintain a pressure of between 200 and 500 pounds per square inch in the absorber 128 and the preceding towers.

The enriched oil passes from the bottom of the absorber 128 through a line 137 into an accumulator 138 having a vapor-return line 139, and is then delivered by means of a line 140, a pump 141, a line 142 and a line 143 to a cracking coil 144 located within a furnace 145. Any portion of the recycle stock not required for absorption purposes in the absorber 128, may be by-passed around the absorber 128 through a line 146 having a valve 147 and communicating between the lines 132 and 143.

In the pipe coil 144, the admixed recycle stock and normally gaseous hydrocarbons are cracked, the cracking being conducted (as in the other instances previously stated) under conditions more drastic than could be tolerated were the oil cracked alone. For example, cracking temperatures of from 930° to 1200° F. and pressures of from 500 to 2000 pounds per square inch are suitable. The cracked products leaving the coil 144 pass through a transfer line 148, which is provided with a quench oil line 149 and a pressure-reducing valve 150, into the lower part of the tower 108.

In the operation of a system as set forth in the aforesaid Fig. 3, for the cracking of high-boiling stocks, such as oils having critical temperatures lying above 900° F., the distribution of the gases available for recycling to the coils 103 and 144, respectively should be such that the extent of gas dilution in the coil 103 is sufficient to lower the critical temperature of the admixture of oil and normally gaseous hydrocarbons to a value below the maximum temperature to which the oil charging stock alone could be subjected in similar apparatus and under otherwise similar conditions without excessive carbon deposition. Moreover, the recycle ratio for the coil 103 should always lie between 1.15:1 and 9:1 and preferably between 1.3:1 and 2.5:1, as will be clear from the general discussion given hereinabove. The same gas dilution limits will apply to the coil 144, but in view of the relatively clean character of the oil recycle stock delivered to the coil 144, and the relatively drastic conditions which may therefore be maintained therein, the major portion of the normally gaseous hydrocarbons available for recycling should be delivered to the coil 144.

The same considerations apply when normally gaseous hydrocarbons are introduced into the system from an extraneous source. Such hydrocarbons may be introduced to the system in various manners, as for example by delivering them into the absorber 128, or by delivering them to a second absorber which is supplied with such portion of the recycle stock as is not recycled for absorption in the absorber 128. The enriched oil from this second absorber may be passed directly to the coil 144 or it may be used as a quenching oil by introducing it through the lines 106 or 149 or both. By properly controlling the valves 136 and 130, as well as the conditions maintained in the condenser and the absorber or absorbers, the desired distribution of the normally gaseous hydrocarbons available for recycling to the coils 103 and 144, respectively, may be readily effected. The introduction of such gases from an extraneous source will increase the recycle ratio for the coil 144, while comparatively small recycle ratios for the coil 103 should still be employed, inasmuch as better conditions for obtaining conversion of the normally gaseous

hydrocarbons will be maintained in the coil 144 than in the coil 103, and the advantages of strongly increasing the extent of conversion per pass of the oil traversing the coil 144 are greater than in the coil 103.

The following table will serve to illustrate the advantageous character of the results obtainable in accordance with my invention, when cracking various typical oil charging stocks in the manners set forth hereinabove, in comparison with the results which can be obtained when cracking similar oils alone in the manner of the prior art:

TABLE I

	(1) Venezuela reduced crude		(2) Mid-Continent stock		(3) Venezuela recycle stock		(4) Mid-Continent naphtha	
Specific gravity: (°A. P. I.)	19.3		34.0		27.1		50.0	
Assay distillation:								
Over point (°F.)	238		176		250		270	
10% at	496		384		434		302	
50% at	715		595		522		336	
90% at	1015		770		664		378	
Average molecular weight	284		230		201		125	
Critical temperature (°F.)	1030		920		880		653	
Characterization factor	11.0		11.7		11.1		11.8	
Volume percentage of C_3 and C_4 hydrocarbons	A None	B 25	A None	B 53.8	A None	B 44.2	A None	B 49.2
Cracking temperature (°F.)	840	890	900	985	950	1000	1000	1030
Pressure (lbs. per sq. in. gauge)	500	600	200	750	500	1000	1100	1100
Maximum percentage of gasoline produced per pass	9.0	15	18	41.3	16.3	30.5	68.9	75.5
Octane number of gasoline made	64.0	68	62	68	72	81	71.7	75.1

The Mid-Continent pressure-still stock (2) referred to was a conglomeration of uncracked (straight run) overhead distillates. The Venezuela recycle stock (3) was a stock recovered as a condensate from cracking Venezuela reduced crude (1) as set forth in column 1A.

With respect to the foregoing table, it may be observed that the values of 68.9 and 75.5 given for the maximum per cent of gasoline per pass, (A) when cracking Mid-Continent naphtha without gas dilution and (B) when diluted in accordance with my invention, respectively, represent the yields corresponding to the maximum octane numbers obtainable i. e. the points at which the product of the yield times octane value are highest.

It will further be noted from the above table that stocks (1) and (2) have critical temperatures above those at which these oils can be cracked alone and without admixture of normally gaseous diluent.

It will be observed that with respect to all of the stocks mentioned in the foregoing table, both the yield and the octane number of the gasoline produced are considerably higher, when operating in accordance with my invention, (see columns headed "B") than the yields and octane numbers of the gasolines which can be produced by cracking the same stock alone in the manner of the prior art (see columns headed "A").

Referring now to Fig. 4, the apparatus illustrated consists primarily of a distilling or fractionating tower 200, a furnace 201 in which are located a plurality of pipe coils 202, 203, 204 and 205, an evaporator or separator tower 206, a fractionating column 207, a condenser-stabilizer tower 208, a water-cooled condenser 209 and an absorber 210. Crude petroleum oil, preheated to a temperature of the order of 700° F. is introduced through a line 211 into the distilling tower 200, which is ordinarily maintained at atmospheric pressure. In this tower a separation of the preheated crude into vapors and residual liquid or reduced crude is effected, the reduced crude being removed from the bottom of the tower 200 to a line 212. Gas oil and naphtha condensates are removed as side streams through lines 213 and 214, respectively, while uncondensed vapors and gases pass through a line 215 to a condenser 216. The proportions of the total naphtha removed through the line 214 and condensed in the condenser 216, respectively, may be regulated by controlling the extent of cooling at the top of the tower 200. A cooling coil 218 is conveniently provided for this purpose.

As will be shown hereinbelow, the naphtha, gas oil and reduced crude removed through the lines 214, 213 and 212 are eventually cracked in suitable dilution with normally gaseous hydrocarbons, in the coils 202, 203 and 204, respectively, at elevated pressures of from 200 to 2000 pounds per square inch. The cracked products from these coils pass through vapor lines 220, 221 and 222, respectively, and through pressure-reducing valves 223 and 224 into the lower part of the separator 206, the pressure at this point being reduced to from 200 to 500 pounds per square inch. A suitable reflux may be supplied to the separating tower 206 through a line 225, and under the influence of the cooling and reduction of pressure effected in the separator 206, heavy residuum or tar is separated from the vapors and is removed through a valved line 226. This tar may be subsequently flashed to a lower pressure to recover the more volatile constituents thereof, if desired.

The tar-free vapors pass through a vapor line 227 into the main fractionator 207 where they are suitably cooled and fractionated as, for example, by means of cool reflux oil introduced into the top of the fractionator 207 through a line 228. In the tower 207 there is condensed and removed a gas-oil condensate substantially free from tar or residual constituents and from constituents within the desired gasoline boiling-point range. This gas-oil condensate or recycle stock is removed from the bottom of the tower 207 through a line 229. A suitable portion of this recycle stock is delivered by means of a line 230, a pump 231, and a line 232 into the coil 205, where it is cracked in suitable dilution with normally gaseous hydrocarbons, as will be explained hereinbelow. The cracked products from the coil 205 then pass through a transfer line 233 and the reducing valve 224 into the separator 206. The remaining portion of the condensate withdrawn through the line 229 passes through a line 234, a heat exchanger 235, a line 236, a second heat exchanger 237, a line 238 and a cooler 239 to a pump 240 which delivers it through a valved manifold 241 into the transfer lines 233, 220 and 221, respectively, the purpose being to effect a quenching or shock cooling of the cracked products passing from the furnace 201 into the separator 206, thereby arresting the cracking reactions initiated in the coils 205, 202 and 203, respectively.

The vapors leaving the tower 207, and from which constituents heavier than gasoline have thus been removed, then pass through a line 242 into the upper portion of the condenser-stabilizer 208, the operation of which will be clear from the description of the preceding figures. Unstabilized condensate is collected in the upper or condensing section of the tower 208 and a portion of this is withdrawn through a line 243, passing to a cooler 244 and thence through a line 245 having a pump 246 into the upper portion of the tower 208. The remaining portion of the unstabilized condensate thus condensed through the cooling effect supplied by the cooler 244 passes downwardly into the lower or stabilizing portion of the tower 208, with which is associated a re-boiler 247, and is thereby stabilized to reduce the vapor pressure of the gasoline to the desired market specifications. Stabilized gasoline condensate then passes out of the re-boiler 247 through a valved line 248.

The remaining gases and vapors pass through a line 250 to the condenser 209, where they are cooled under pressure to effect the recovery of a liquid fraction consisting predominantly of hydrocarbons having 3 to 4 carbon atoms per molecule. This condensate is collected in an accumulator 251, while the uncondensed vapors and gases pass through a line 252 into the absorber 210.

The absorbent oil employed in the absorber 210 consists of the naphtha removed from the tower 200 through the line 214. This naphtha is first cooled to a suitable extent in a cooler 253 and is then passed through a line 254, wherein is located a pump 255, into the upper portion of the absorber 210. In flowing downwardly through the absorber 210, the cool naphtha absorbent oil removes from the vapors and gas passing upwardly through the tower 210 normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule. The extent of absorption is so regulated as to remove at least all of the C_4 hydrocarbons, and, if desired, all or substantially all of the C_3 hydrocarbons as well. The remaining gases, consisting of hydrogen, methane, ethane and ethylene, then pass out of the absorber 210 through a gas line 256 having a back-pressure valve 257, the purpose of which is to maintain the desired pressure of from 200 to 500 pounds per square inch in the towers 206, 207, 208 and 210.

The enriched naphtha absorbent, consisting of naphtha and C_3 and C_4 hydrocarbons dissolved therein, is removed from the bottom of the tower 210 to a line 258 and passes to a pump 259 which delivers it through a line 260, the heat exchanger 235, and the line 261 to the coil 202 located in the furnace 201.

The liquefied C_3 and C_4 hydrocarbons which collect in the accumulator 251 are employed to dilute the oils being cracked in the coils 203, 204 and 205. The coil 203 is employed for the cracking of gas oil removed from the tower 200 through the line 213, and which is delivered to the coil 203 by means of a pump 270 and a line 271. The coil 204 receives reduced crude withdrawn from the bottom of the tower 200 through the line 212 and delivered to the coil 204 by means of a pump 272 and a line 273. As set forth hereinabove, the coil 205 receives recycle stock condensed in the tower 207, this recycle stock being delivered to the coil 205 through the line 232. For admixture with the oils entering the cracking coils 203, 204 and 205, the liquid fraction collecting in the accumulator 251 is withdrawn from the latter through a line 274 and then delivered by means of a pump 275 and a line 276 to the heat exchanger 237, where it is preheated by indirect contact with the hot oil passing through the line 236. The preheated C_3 and C_4 hydrocarbons then pass through a line 277 into lines 278, 279 and 280, provided with valves 281, 282 and 283, and communicating with the feed lines 271, 273 and 232, leading to the coils 203, 204 and 205, respectively. By proper regulation of the temperature and pressure in the condenser 209 and the settings of the valves 281, 282 and 283, the proper distribution of a normally gaseous diluent to the coils 203, 204 and 205 is readily effected.

The general limits for the operation of the various cracking coils 202 to 205, inclusive, will readily be understood from the earlier portions of this specification. However, the following figures may be given as illustrative of a typical operation:

In this instance a West Texas crude petroleum is supplied to the tower 200 and there distilled to recover a reduced crude representing 30 per cent by volume of the original crude oil, a virgin gas oil fraction and a virgin heavy naphtha fraction. The characteristics of these stocks are given in the following Table II:

TABLE II

Properties	Reduced crude	Virgin gas oil	Naphtha
Specific gravity	14.3° A. P. I.	34.3° A. P. I.	48.0° A. P. I.
Assay distillation:			
Over point	626° F.	440° F.	245° F.
10% at		470° F.	285° F.
50% at		535° F.	340° F.
90% at		618° F.	425° F.
Viscosity at 210° S. U. V.	369° seconds		
Molecular weight	450	217	120
Critical temperature	1,250° F.	870° F.	660° F.

Operating without benefit of my invention; that is to say, without gas dilution, these stocks can be cracked under the maximum conditions set forth in the following Table III to give the gasoline yields also set forth therein:

TABLE III

Properties	Reduced crude	Virgin gas oil	Naphtha
Volume present liquefied C_3 and C_4 hydrocarbons.	None	None	None
Cracking Temperatures	840° F.	910	1,000
Gauge pressure	250 lbs. per sq. in.	650 lbs. per sq. in.	1,000 lbs. per sq. in.
Yield of gasoline per pass	9%	25%	70%
Octane number of gasoline	62	66	69

There is recovered from the combined cracked vapors thereby produced, when these stocks are cracked without benefit of my invention as aforesaid, a recycle stock having the characteristics shown in the following Table IV:

TABLE IV

Properties	Recycle stock
Specific gravity	25.1° A. P. I.
Assay distillation:	
Over point at	400° F.
10% at	442° F.
50% at	518° F.
90% at	652° F.
Molecular weight	200
Critical temperature	890° F.

This recycle stock can be cracked without benefit of my invention, that is to say, without gas dilution under temperatures and pressures as set forth in the following Table V, giving a yield of gasoline as also set forth therein.

TABLE V

Properties	Recycle stock
Liquefied C_3 and C_4 hydrocarbons	None.
Cracking temperature	950° F.
Gauge pressure	500 lbs. per sq. in.
Yield of gasoline per pass	16%
Octane number of gasoline	71

In operating in accordance with my invention, each of these stocks is cracked in the presence of C_3 and C_4 hydrocarbons, in the manner and under the conditions set forth hereinabove. The furnace feeds, their compositions, molecular weights and critical temperatures are set forth in the following Table VI:

TABLE VI

Furnace feeds, their composition, molecular weight, critical and cracking temperatures

	Specific gravity	Barrels per hr.	Volume percent present	Molecular wt.	Critical temp.
					°F.
Reduced crude coil:					
30% reduced crude	14.3	275	60.0	450	1250
C_3 and C_4 hydrocarbons	---	184	40.0	50	---
Total	48.7	459	100.0	134	650
Virgin gas oil coil:					
Virgin gas oil	34.3	366	57.0	217	870
C_3 and C_4 hydrocarbons	---	275	43.0	50	---
Total	69.1	641	100.0	98	510
Recycle coil:					
Recycle stock	25.1	458	55.7	200	890
C_3 and C_4 hydrocarbons	---	366	44.3	50	---
Total	62.6	824	100.0	96	520
Naphtha coil:					
Naphtha	48.0	184	33.6	120	660
C_3 and C_4 hydrocarbons	---	366	66.4	45	---
Total	103.5	550	100.0	61	405

Operating in accordance with my invention, the following results are obtained:

TABLE VII

Properties	Reduced crude	Virgin gas oil	Recycle stock	Naphtha
Volume present liquefied C_3 and C_4 hydrocarbons	40.0	43.0	44.3	66.4
Cracking temperature	900° F.	975° F.	1,000° F.	1,050° F.
Gauge pressure	600 lbs.	600 lbs.	1,250 lbs.	1,250 lbs. per sq. in.
Yield of gasoline per pass	15%	42%	31.0%	75%
Octane number of gasoline	68	70	76	75

The advantageous results secured in accordance with my invention will be made clear from consideration of the foregoing tables.

In comparing the effect of cracking a heavy residual oil in the presence of normally gaseous diluent in accordance with my invention with the prior art practice of cracking such material in dilution with normally liquid but relatively low-boiling oil, the following comparison will serve to illustrate the advantages of my process. This comparison is based upon the cracking of a reduced crude having an average molecular weight of approximately 400 and a critical temperature of 1230° F. This heavy reduced crude cannot be subjected to a cracking temperature substantially in excess of 840° F. without encountering excessive carbon deposition, and when cracked at 840° F. there is obtained a gasoline yield of 9 per cent by volume on the original oil, the gasoline having an octane number of 62. It has been common to crack such heavy reduced crude in dilution with an approximately equal volume of heavy recycle stock (gas oil). When the heavy reduced crude referred to is thus diluted with an equal volume of a recycle stock having an average molecular weight of 250 and a critical temperature of 1000° F., the critical temperature of the mixture is reduced to 1100° F. and consequently this mixture has to be cracked at the same temperature as the reduced crude alone, in order to avoid excessive carbon deposition. The cracking of this mixture at 840° F. will produce a yield of gasoline equal to 7.5 per cent by volume of the total charging stock, the octane number of the gasoline being the same as above, namely 62.

On the other hand, when the same reduced crude is admixed (by recycling gases produced in the system) with only one-half its volume of liquefied C_3 and C_4 hydrocarbons having an average molecular weight of approximately 50, the critical temperature of the mixture is reduced to 780° F. The mixture can then be cracked without excessive carbon deposition at a temperature of 880° F., and when cracked at that temperature there is produced a yield of gasoline equal to 15 per cent by volume of the reduced crude charging stock, the gasoline having an octane number of 68.

These figures show that the reduced crude can be cracked in accordance with my invention far more intensely and with the production of a higher yield of gasoline of higher octane number, than would be possible if the reduced crude were cracked by itself. Moreover, the percentage of recycle stock available for subsequent cracking is considerably increased, and there is obtained a lower yield of tar, the tar having a lower viscosity, a lower pour point and a lower "B. S." content than could be obtained had the reduced crude been cracked by itself. These results cannot be achieved by diluting the reduced crude with recycle stock in the ordinary manner, a procedure which is inherently disadvantageous

in that such recycle stock could be cracked separately with more profitable results.

It will be understood that in referring to "normally gaseous constituents" throughout the foregoing, I have had in mind such constituents as propane, propylene, butane and butylene which, in the absence of substantial quantities of hydrocarbons of higher molecular weight, are gases or vapors under atmospheric conditions of temperature and pressure. However, in referring to the volumes of these constituents delivered to the various cracking coils, I mean the volumes of such constituents when reduced to liquefied form, by suitable pressures. It will further be understood that these constituents may either be in liquid form or in gaseous or vapor form at the actual point of entry into the various cracking coils, when thus introduced in admixture with normally liquid hydrocarbons, depending upon the proportions of the constituents of the mixtures and the temperatures thereof. As the mixtures traverse the various heating coils and their temperatures are increased, they rapidly assume a gaseous or vaporous form; in all cases the mixtures are eventually subjected to temperatures in excess of their critical temperatures, and during their passage through the remaining portions of the heating coils they exist in a substantially homogeneous vapor state.

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

Thus, in the various systems illustrated and described hereinabove, it will be understood that various improvements in heat exchange may be secured at various points, as for example by employing hot oil produced in the system to preheat charging stocks going to the various cracking coils or to supply the heat required for stabilizing the gasoline produced. Further modifications in detail will undoubtedly suggest themselves to those skilled in the art, it being understood that the drawings accompanying this specification are intended to illustrate typical cracking systems more or less diagrammatically with as little attention to incidental specific detail as is consistent with adequate illustration and exemplification of my invention. This is especially true with respect to Fig. 4, it being understood, for example with reference to this figure, as well as Figs. 2 and 3, that the various cracking coils illustrated therein may be located either in a single furnace or in a plurality of separate furnaces, as may be desired, without departing from my invention.

What I claim is:

1. The process of cracking hydrocarbon oil to obtain gasoline of high anti-knock value and to avoid carbon deposition to such extent as would prevent continuous operation for extended periods of time, which comprises passing such oil 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 super atmospheric pressure, and there subjecting the admixture of oil and normally gaseous hydrocarbons to a high cracking temperature substantially in excess of the maximum temperature to which the oil alone and without admixture of said 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, said temperature being sufficiently high to effect an increased degree of conversion of the oil but not so high as to cause such excessive deposition of carbon as aforesaid, fractionating the resultant products to separate and recover constituents heavier than gasoline, gasoline, an intermediate fraction mainly comprising normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, and a fraction mainly comprising hydrogen and normally gaseous hydrocarbons having 1 and 2 carbon atoms per molecule, and returning said intermediate fraction to said conversion zone in admixture with the oil introduced to said zone for conversion therein as aforesaid.

2. The process of cracking hydrocarbon oil to obtain gasoline of high anti-knock value and to avoid carbon deposition to such extent as would prevent continuous operation for extended periods of time, which comprises passing such oil 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 subjecting the admixture of oil and normally gaseous hydrocarbons to a high cracking temperature of from 50° to 300° F. higher than the maximum temperature to which the oil alone and without admixture of said 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, thereby effecting an increased degree of conversion of said oil per pass, but without such excessive deposition of carbon as aforesaid, fractionating the resultant products to separate and recover constituents heavier than gasoline, gasoline, an intermediate fraction mainly comprising normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, and a fraction mainly comprising hydrogen and normally gaseous hydrocarbons having 1 and 2 carbon atoms per molecule and returning said intermediate fraction to said conversion zone in admixture with the oil introduced to said zone for conversion therein as aforesaid.

3. The process of cracking hydrocarbon oil to obtain gasoline of high anti-knock value and to avoid carbon deposition to such extent as would prevent continuous operation for extended periods of time, which comprises passing such oil 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 subjecting the admixture of oil and normally gaseous hydrocarbon to a high cracking temperature substantially in excess of the maximum temperature to which the oil alone and without admixture of said 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, thereby effecting an increased degree of conversion of said oil per pass, but without such excessive deposition of carbon as aforesaid, fractionating the resultant products to separate and recover constituents heavier than gas-

oline and gasoline, scrubbing the residual gases and vapors with incoming fresh oil to recover normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule by absorption in said oil, the amount of normally gaseous constituents thus absorbed being limited to from 30 to 200 per cent of the amount of oil entering the conversion zone, on a liquid-volume basis, and delivering the thereby enriched oil to the conversion zone as aforesaid.

4. The process of cracking naphtha to obtain gasoline of increased anti-knock value and to avoid carbon deposition to such extent as would prevent continuous operation for extended periods of time, which comprises passing such naphtha 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 subjecting the admixture of naphtha and normally gaseous hydrocarbons to a high cracking temperature substantially in excess of the maximum temperature to which the naphtha alone and without admixture of said 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, thereby effecting an increased degree of conversion per pass of said naphtha and at the same time an increased yield of high anti-knock gasoline, but without such excessive deposition of carbon as aforesaid, fractionating the resultant products to separate and recover constituents heavier than gasoline, gasoline, an intermediate fraction mainly comprising normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, and a fraction mainly comprising hydrogen and normally gaseous hydrocarbons having 1 and 2 carbon atoms per molecule and returning said intermediate fraction to said conversion zone in admixture with the naphtha introduced into said zone for conversion therein as aforesaid.

5. A process as claimed in claim 1 wherein the hydrocarbon oil is a heavy oil which does not have a critical temperature below a temperature at which active decomposition occurs, and wherein the amount of normally gaseous hydrocarbons delivered in admixture with the oil to the conversion zone is such that the critical temperature of the admixture is below the maximum temperature to which the oil alone and without admixture with 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, and is in any event equal to at least 15 per cent of the oil on a liquid-volume basis.

6. A process as claimed in claim 1, wherein the temperature to which the admixture of oil and normally gaseous hydrocarbons is subjected in the conversion zone is from 25° to 50° F. in excess of the maximum temperature to which the oil alone and without admixture with said 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.

POVL OSTERGAARD.