Sept. 12, 1944. P. OSTERGAARD 2,358,183

CRACKING HYDROCARBON OILS

Filed Feb. 3, 1939 2 Sheets-Sheet 1

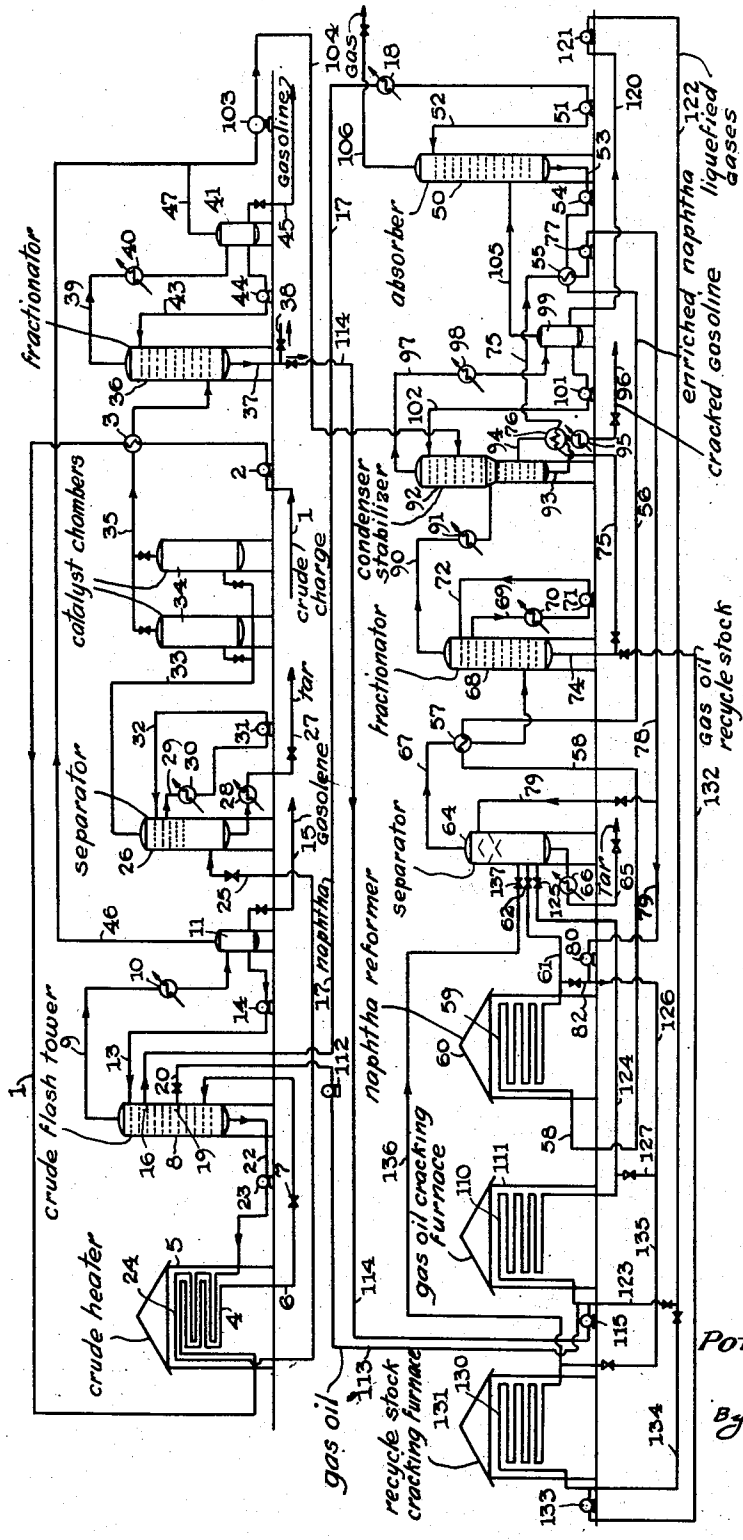


Fig. 1.

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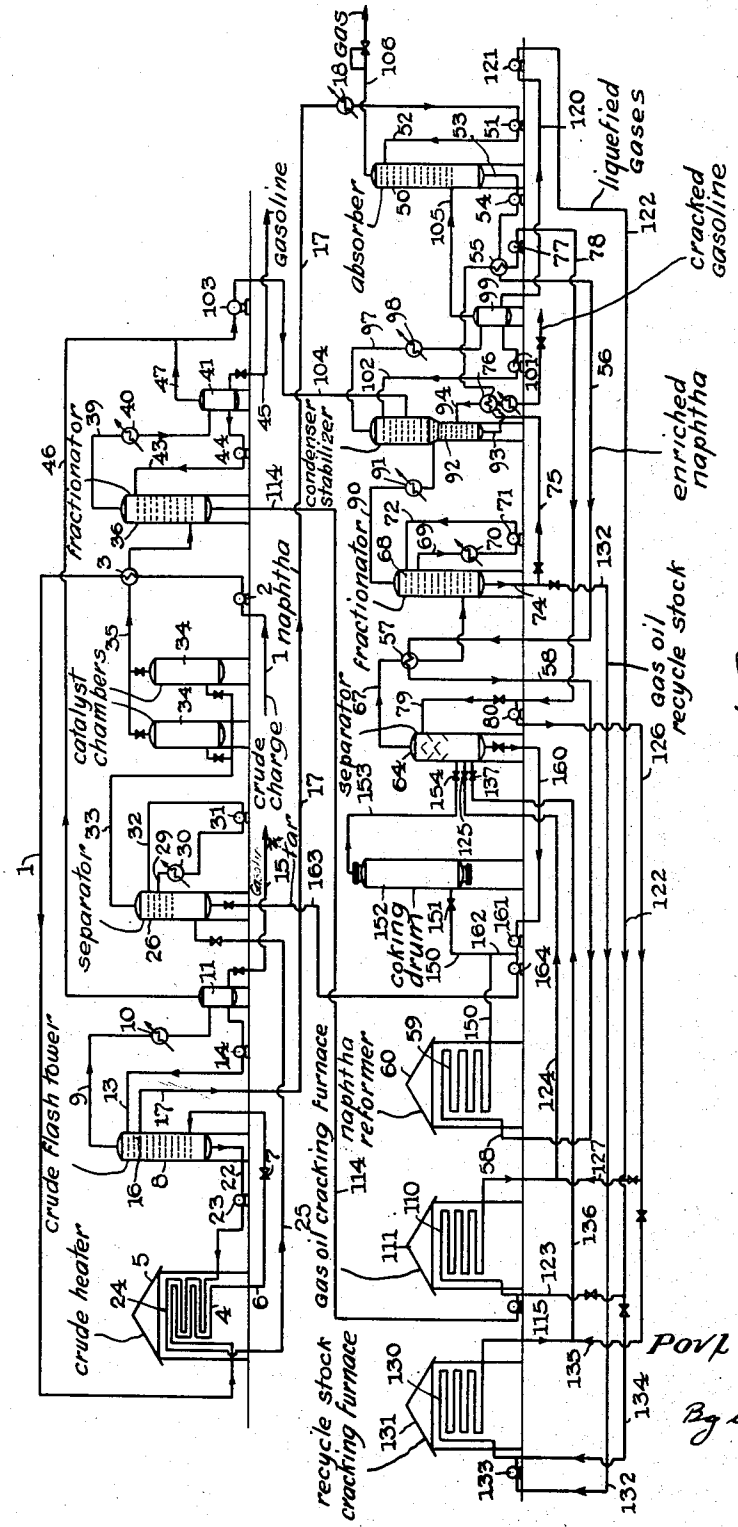


Fig. 2.

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UNITED STATES PATENT OFFICE

2,358,183

CRACKING HYDROCARBON OILS

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Application February 3, 1939, Serial No. 254,487

7 Claims. (Cl. 196—9)

My invention relates to processes for cracking hydrocarbon oils to obtain gasoline hydrocarbons useful as motor fuel and having high anti-knock value when so used. It relates more particularly to improved methods of obtaining gasoline hydrocarbons from crude petroleum stocks, wherein such stocks are first distilled in order to recover a plurality of fractions of different boiling-point ranges, one of these fractions is segregated and subjected to catalytic cracking, while another fraction is subjected to thermal cracking, and normally gaseous hydrocarbons thereby produced are recovered and delivered to the thermal cracking operation in order to promote the degree of cracking obtained therein and to effect a conversion of said gaseous hydrocarbons to gasoline-like hydrocarbons of high anti-knock value; all as more fully set forth and described hereinbelow.

Within the past few years, great strides have been made in the art of cracking petroleum oils. These advances, for the most part, derive from the ever-increasing incentive to produce a maximum yield of motor fuel of maximum anti-knock value. Those processes which are believed to have made substantial progress in this direction may in general be divided into two categories; first, processes involving conversion or polymerization of the normally gaseous hydrocarbons produced in oil-cracking operations, and second, catalytic oil-cracking processes. But while much thought and time has been expended in the development of these individual types of processes, comparatively little thought has been given to methods of combining them advantageously in a unitary conversion operation.

A considerable number of gas-polymerization processes have been proposed and some have been operated on a large scale. The opinion is growing, however, that such processes are likely to find their greatest utility either for the recovery of gasoline-like hydrocarbons from natural gases or, as in the case of certain catalytic-type polymerization processes, for the manufacture on a relatively small scale of special fuels, such as isooctane, the market for which is still comparatively limited. In so far as gases derived from refinery cracking operations are concerned, it is believed that the greatest advance in the art has been made in the development of oil-cracking processes of the so-called gas-reversion type, in which normally gaseous hydrocarbons produced in cracking the hydrocarbon oil are recirculated to the conversion zone.

A successful and widely adopted process of this character is that disclosed in my prior U. S. Patents Nos. 2,135,014, 2,135,108 and 2,135,109.

Others prior to me had proposed to recirculate C_3 and C_4 hydrocarbons to the cracking zone of an ordinary oil-cracking operation, but, at least in such cases as involved the return of these gases for reaction purposes and without the presence of non-reactive or diluent gases, had confined themselves to operations conducted under the ordinary oil-cracking conditions which would have obtained for the same oil. In my prior patents referred to above, I disclosed a process of this general type, in which the degree of conversion per pass and the operating temperature are increased above those which would normally obtain and in fact above those which could be maintained under otherwise similar conditions and without undue carbon deposition, if the same oil were cracked in the same apparatus without recirculation of the reactive normally gaseous hydrocarbons.

My aforesaid process has been successfully applied to a wide variety of cracking stocks, with highly advantageous results. Strikingly enough, however, it has been found that the optimum advantages of gas-reversion type of system generally are obtained when the process is applied to the cracking or re-forming of naphthas and similar light stocks containing substantial amounts of hydrocarbons within the gasoline boiling-point range. On the other hand, my aforesaid process has also been successfully and advantageously applied to the cracking of heavier stocks, such for example as gas oil and reduced crudes.

As distinguished from thermal cracking processes, a large number of catalytic cracking processes have been proposed, all characterized by the presence of a catalyst of one type or another in the conversion zone, and usually by the employment of relatively low pressures. The so-called Houdry process, employing as a typical catalyst an activated hydrosilicate of alumina or the like, is perhaps the best known of these catalytic processes, and its adoption is being widely advocated. On account of the necessary periodic interruption of this type of process, in order to effect periodic regeneration of the catalyst employed, and for certain other reasons, the pressures employed in these catalytic processes are for the most part extremely low, rarely if ever exceeding 50 pounds per square inch in the catalyst contact zone. For this reason it is somewhat difficult to combine gas recirculation with such catalytic cracking operations in an efficient and effective manner.

Moreover, these types of processes in general tend to produce rather high yields of normally gaseous hydrocarbons (as is true of low-pressure operations generally), and they are for the most part lacking in ultimate economy and advantages with respect to the cracking or re-forming of naphthas and similar light stocks. That is especially true in instances where the "lead susceptibility" of the cracked gasoline product is low, as is usually the case. Moreover, such catalytic processes do not, as a general rule, lend themselves very readily to the recycling of intermediate cracked products, such as gas oil. In order to effect cracking of gas oils and other intermediate products produced in catalytic cracking operations of this type, it is ordinarily preferable to withdraw such oil as produced from the catalytic cracking unit, and to subject it to conversion to gasoline in a separate thermal cracking unit.

In accordance with my invention, the maximum advantages and economies of both types of processes described hereinabove are secured together with advantages and economies which could not be obtained with respect to either type of operation considered alone.

My invention contemplates the separation, by distillation, of a crude petroleum into a plurality of fractions of different boiling-point ranges, including a naphtha fraction suitable for re-forming to high anti-knock gasoline motor fuel, and at least one heavier fraction. The naphtha thus recovered is re-formed in a gas-reversion type operation (preferably conducted in accordance with the disclosures of my prior patents referred to above) in which the naphtha is subjected to thermal conversion in the presence of recirculated normally gaseous hydrocarbons containing 3 to 4 carbon atoms per molecule, a considerable portion of which are produced in the re-forming operation itself. A heavier fraction recovered from the distillation of the original crude is subjected to separate catalytic cracking, ordinarily at low pressures, and normally gaseous hydrocarbons containing 3 to 4 carbon atoms per molecule produced in this operation are delivered to the naphtha re-forming operation referred to hereinabove.

As will be shown below, the heavy fraction thus subjected to catalytic cracking will ordinarily comprise a residual fraction, such as a reduced or topped crude, which may or may not contain virgin gas-oil constituents. In some instances, it is desirable, as shown hereinbelow, to recover virgin gas-oil contained in the original crude as a separate fraction, and to subject this fraction to thermal conversion in the presence of recirculated C_3 and C_4 hydrocarbons. The products of this cracking step are conveniently combined with the products from the naphtha re-forming step for ultimate fractionation and recovery. Gas-oil recovered in the catalytic cracking unit may also be cracked in a similar manner. Provision is also made for separately cracking gas-oil recovered as an intermediate condensate in any and all of the thermal conversion units, the products from this operation being combined with the other thermal cracking products for fractionation and recovery.

I have found it highly advantageous in a system of this character to effect the recovery of stabilized gasoline from the thermal cracking unit by rectification in place of condensation in the ordinary manner. The remaining products are then subjected to further condensation for the recovery of C_3 and C_4 hydrocarbons and after separation of the condensate thereby obtained are passed to an absorber where the remaining C_3 and C_4 hydrocarbons are picked up in the fresh naphtha or other charging stock entering the thermal cracking unit and thereby transferred to the conversion zone of the latter. Ordinarily, naphtha is used as the absorbent, and the absorbed C_3 and C_4 hydrocarbons enter the naphtha re-forming zone. Condensate recovered between the rectifying stage and the absorber is delivered to the other thermal conversion zones in proportion to the requirements of each.

As will be shown in further detail hereinbelow, I prefer to introduce the gases produced in the catalytic cracking unit into the thermal cracking unit at a point prior to the aforesaid step wherein is effected the preliminary condensation of C_3 and C_4 hydrocarbons; more specifically I introduce these gases (as well as any gases recovered in the initial crude distillation) into the rectifying zone of the thermal catalytic unit, wherein condensation and removal of stabilized gasoline is effected. This procedure permits the recovery of any gasoline constituents contained therein, as well as a portion of the C_3 and C_4 hydrocarbons present, prior to the absorber, and lightens the load carried by the absorber.

While various specific modifications of the thermal cracking units are possible, I disclose hereinbelow, as illustrative examples, two general types of thermal cracking units, namely, the conventional type in which tar, gas-oil and gasoline are recovered as individual fractions, and the so-called "pressure coking" type, wherein coke and gasoline represent the ultimate products recovered. In connection with the latter type of operation, I have found it advantageous to introduce heavy residual or tarry bottoms, separated from the heated charging stock entering the catalytic cracking unit prior to the passage of the separated vapors through the catalyst, into the coking zone of the thermal cracking unit. By thus delivering the aforesaid bottoms, along with intermediate condensates from the thermal and catalytic units, to the thermal conversion unit, it is possible to run the entire system to ultimate yields of gasoline, coke and dry gas, the latter being substantially free from C_3 and C_4 hydrocarbons.

My invention also contemplates such operating details and modifications, and such additional operative advantages and economies, as will hereinafter be found to obtain.

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

Figure 1 is a more or less diagrammatic elevational view of apparatus for manufacturing gasoline of high anti-knock fuel from petroleum oil in accordance with my invention, and including apparatus for separately subjecting individually selected fractions to catalytic cracking and thermal cracking, respectively; and

Figure 2 is a similar view of a modified form of apparatus wherein the thermal cracking unit is of the so-called "pressure-coking" type.

These drawings are primarily diagrammatic in character and have been simplified in order to show essential details of operation without encumbering this disclosure with description and explanation of many more or less obvious minor

modifications, the application of which will be obvious to those skilled in the art.

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

Referring to the system illustrated in Fig. 1, a crude petroleum charging stock is introduced into the system through a pipe 1 by means of a pump 2, and is preheated in a suitable manner, as, for example, by means of a heat exchanger 3 and a pipe coil 4 located within a furnace 5, to a suitable distilling temperature. The temperature employed is high enough to effect distillation of the crude, without being so high as to cause substantial cracking. Typical preheating temperatures are of the order of 700° to 750° F. The preheated crude then passes through a line 6 having a valve 7 into a distilling column or flash tower 8 of more or less conventional design. Gases and vapors leaving the top of the tower 8 pass through a line 9 to a condenser 10 and thence to a separator 11 from which cool reflux oil (naphtha) is returned to the top of the tower 8 through a line 13 having a pump 14.

By reason of the heat imparted to the crude oil and the low or atmospheric pressure maintained in the column 8, distillation takes place, and a considerable portion of the crude oil is vaporized, while condensation and rectification in the column 8 is effected by means of the reflux supplied through the line 13 or in any other suitable manner. Light virgin gasoline removed in the distillation collects in the separator 11 and is withdrawn therefrom through a line 15. Heavy virgin naphtha, suitable for re-forming, is withdrawn as a side stream from a trap-out tray 16 and passes through a line 17 to a cooler 18.

In addition to the naphtha fraction withdrawn from the trap-out tray 16 various other fractions may be withdrawn as side streams from the tower 8. Thus a virgin gas-oil fraction may be withdrawn from a suitably located trap-out tray 19 through a line 20.

Regardless of the number or character of fractions thus withdrawn as side streams from the tower 8, the residual fractions of the crude are withdrawn from the bottom of the tower 8 through a line 22 having a pump 23, and are delivered to suitable heating means, such as a still or pipe coil 24 conveniently located within the furnace 5. In passing through the coil 24 the reduced crude is heated to a temperature sufficient to provide for vaporization of all but the very heaviest constituents thereof, and to promote conversion in the presence of the catalyst with which the vaporized portions of the oil are subsequently brought into contact. In the instance shown, in which the cracking of this stock is effected in accordance with the so-called Houdry process, the reduced crude ordinarily leaves the coil 24 at a temperature of around 880° F. At this temperature, the reduced crude passes from the coil 24 through a valved transfer line 25 into a separator or vaporizer 26 maintained at a low pressure ranging from atmospheric to about 50 pounds per square inch gauge. Tar bottoms are withdrawn from the vaporizer 26 through a valved line 27, wherein is located a cooler 28.

Where it is necessary to provide cooling in the vaporizer 26, a side stream may be withdrawn near the top of the tower through a line 29 leading to a cooler 30 and a pump 31, whence the cooled oil is returned to the top of the vaporizer 26 through a line 32.

The vapors liberated in the vaporizer 26 pass through a valved manifold vapor line 33 into one of a plurality of catalyst cases 34. These catalyst cases are provided internally with suitable catalytic contact masses, disposed in any desirable manner, and they are also provided with inlet and outlet manifold connections substantially as shown, in such a manner that they may be alternated as desired. Ordinarily only one of the cases is kept "on stream," while the other case is disconnected for cleaning, regeneration or replacement of the catalyst contained therein.

While I do not desire to limit myself to any particular catalyst or to any specific conditions of temperature or pressure, it may be stated that a suitable catalyst comprises an activated hydrosilicate of alumina and that typical conditions of temperature and pressure are from 800° to 900° F. and from atmospheric to 20 pounds per square inch gauge pressure, respectively. Various details of the Houdry process, applicable to this unit, are disclosed in an article entitled "Catalytic processing by the Houdry process," found at page R-570 of the National Petroleum News for November 30, 1938, and in the patents listed in that article, while various other catalytic processes are described in prior patents and in the literature.

Under the influence of the catalyst and the heat applied to the oil, conversion takes place, resulting in the formation of gasoline and other useful hydrocarbons. The other vapors leave the "on stream" catalyst case 34 through a manifold line 35 and pass through the heat exchanger 3 into a more or less conventional fractionating column 36, which is operated to condense and recover intermediate constituents to such extent as will leave uncondensed a gasoline fraction of the desired end boiling point. The gas-oil condensate thus obtained is removed from the bottom of the column 36 through a line 37 and where desired may be removed from the system through a valved branch line 38. The gasoline and lighter vapors and gases pass through a line 39 to a condenser 40 and thence to a separator 41.

A portion of the cracked gasoline condensate accumulating in the separator 41 is conveniently returned to the tower 36 through a line 43, wherein is located a pump 44, as a refluxing and cooling medium for the tower 36. The cracked gasoline not required for refluxing purposes in the column 36 is withdrawn from the separator 41 through a line 45.

Uncondensed gases are withdrawn from the separators 11 and 41 through lines 46 and 47, respectively. The subsequent disposition and utilization of these gases will be described in detail hereinbelow, but for the present it will be sufficient to state that a portion of these gases ultimately enters an absorber 50 forming a part of the thermal cracking unit subsequently to be described, along with gases produced in the latter unit.

The naphtha side stream withdrawn from the column 8 through the trap-out tray 16 and the line 17, after passing through the cooler 18, is delivered by means of a pump 51 and a line 52 into the upper portion of the absorber 50, and in passing downward through the absorber 50 effects an absorption of the C_3 and C_4 hydrocarbons, or any desired portion thereof, from the gases traversing the absorber 50.

The thereby enriched naphtha leaving the absorber 50 and containing C_3 and C_4 hydrocarbons removed by absorption therein, then passes through a line 53, wherein is located a pump 54,

and thence through a heat exchanger 55, a line 56, a heat exchanger 57 and a line 58 into an elongated pipe coil 59 of restricted cross-sectional area located within a heating furnace 60. In passing through the pipe coil 59, the enriched naphtha is subjected to thermal conversion at an elevated temperature and under superatmospheric pressure. Substantial conversion is obtained at various temperatures and pressures ranging from about 950° to 1400° F. and from 100 to 2000 pounds per square inch gauge pressure, but the best results are obtained when the operation is conducted in the manner set forth and claimed in my prior U. S. Patent No. 2,135,014. That is to say, the admixture of naphtha and normally gaseous hydrocarbons is subjected to a high cracking temperature and a high degree of conversion per pass substantially in excess of the maximum temperature and conversion per pass to which the oil alone 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. The actual conversion temperature, for a given oil, will ordinarily range from 25° to 300° F. higher than the aforesaid maximum temperature for the same oil.

During the passage of the naphtha and normally gaseous hydrocarbons through the coil 59, conversion takes place, resulting primarily in the formation of a gasoline product of substantially higher anti-knock value than the original charging stock. The heated products are then discharged through a vapor-transfer line 61, having a pressure-reducing valve 62, into a tar separator 64. Under the influence of this pressure reduction and cooling supplied as will hereinafter be shown, tarry constituents present in the vapors entering the separator 64 are separated in liquid form and as such are withdrawn from the bottom of the separator 64 through a valved line 65 having a cooler 66. The tar-free vapors then pass through a line 67, through the heat exchanger 57 and thence into a fractionating column 68 of more or less conventional design.

As the result of cooling supplied to the fractionating column 68, condensation of constituents heavier than are desired to be retained in the final gasoline condensate is effected. Such cooling is readily supplied by withdrawing a side stream from the tower 68 through a line 69, cooling it in a cooler 70 and returning it by means of a pump 71 and a reflux line 72 to the head of the column 68. It will be obvious, however, that in this and other instances where it is desired to provide cooling in one of the units disclosed herein, such cooling may be effected in any suitable manner, although the apparatus shown in the drawings represents a simple, convenient and advantageous means.

The condensate recovered in the fractionating column 68, which may be referred to as gas-oil, is withdrawn from the bottom of the column 68 through a line 74. All or a portion of this condensate then passes through a valved branch line 75, through heat exchangers 76 and 55 to a pump 77. Part of the thereby cooled gas-oil is returned by means of a line 78 and a valved branch line 79 to the upper part of the tar separator 64 to serve as a refluxing and cooling medium therefor. The remainder of the cooled gas-oil then passes through a line 79 to a pump 80 and thence at least in part through a valved quenching line 82 which communicates with the transfer line 61. The gas-oil thus introduced into transfer line 61 serves as a quenching medium to arrest reactions initiated in the pipe coil 59.

When the stock subjected to thermal cracking consists of naphtha withdrawn from the column 8, comparatively little gas-oil will be formed in the thermal conversion unit. In such instance all of this gas-oil will ordinarily be returned to the separator 64 or the transfer line 61 or both, and it may be supplemented where desired by the use of cool oil from any outside source.

Vapors remaining uncondensed in the column 68 then pass through a line 90, wherein may be located a cooler 91, into a condensing and stabilizing column or rectifier 92, wherein removal of stabilized gasoline condensate is effected. Heat is supplied to the bottom of the column 92 by means of heat exchanger 76, which is in communication with the lower part of the rectifier 92 through a liquid line 93 and a vapor return line 94. Stabilized gasoline leaves the system through a cooler 95 and a valved line 96.

Cooling for the top of the rectifier 92 is provided by removing overhead vapors from the top of the column 92 through a line 97 and passing them to a condenser 98 and a separator 99. A portion or all of the cooled condensate collecting in the separator 99, and comprising mainly condensed C_3 and C_4 hydrocarbons, is returned by means of a pump 101 and a reflux line 102 to the head of the rectifier 92.

In order to provide for the initial recovery of the C_3 and C_4 hydrocarbons, as well as any higher boiling constituents which may be present, from the gases withdrawn from the separators 11 and 41, all or any desired portion of these gases is delivered to a compressor 103 (where the pressure of these gases is raised to a pressure at least equal to that maintained in the rectifier 92) and then passed into the upper section of the rectifier 92 through a line 104.

Uncondensed gases leaving the separator 99 pass through a line 105 to the absorber 50, where C_3 and C_4 hydrocarbons are removed therefrom by absorption in the manner set forth hereinabove. Unabsorbed gases (mainly hydrogen, methane, ethane and ethylene) leave the absorber 50 through a valved gas line 106 and pass out of the system.

In the description set forth hereinabove, I have referred to the cracking or re-forming of straight-run or virgin naphtha recovered in the initial distillation of the crude. I have not referred to any thermal cracking of any other stock. However, the apparatus shown in Fig. 1 also includes means for effecting cracking of such other stocks, for example, a virgin gas-oil fraction recovered in the initial crude distillation, an intermediate gas-oil fraction recovered in the catalytic cracking unit, and also (particularly where the charging stock to the thermal conversion operation comprises oils heavier than naphtha) gas-oil recycle stock produced in the thermal conversion unit itself; all in the presence of recycled normally gaseous hydrocarbons containing 3 to 4 carbon atoms per molecule.

Thus I provide a second pipe coil 110 located within a furnace 111 for cracking either virgin gas oil or intermediate gas oil produced in the catalytic cracking operation, or both. Virgin gas oil is delivered to this coil by means of the line 20, a pump 112 and a line 113 while, either alternatively or simultaneously, all or a portion of the gas oil recovered in the column 36 may be delivered to the coil 110 through a valved branch

line 114 communicating with the line 37 and wherein is provided a pump 115. The gas oil thus introduced into the coil 110 is first admixed with a portion of the C_3 and C_4 hydrocarbons recovered in the separator 99, and which may be delivered for such admixture through a line 120, a pump 121, a line 122 and a valved branch line 123.

The admixture of oil and normally gaseous hydrocarbons is subjected in the coil 110 to thermal conversion under elevated temperature and pressure. The products of conversion then pass through a transfer line 124 having a pressure-reducing valve 125 into the tar separator 64, where they are combined with the hot products of conversion from the naphtha re-forming coil 59. Quenching of the hot products of conversion from the coil 110 is effected by delivering cool oil into the transfer line 124 through a line 126 communicating with the pump 80, and a valved branch line 127 communicating with the transfer line 124.

In view of the relatively high-boiling character of the charging stock delivered to the coil 110, the temperatures and pressures employed therein will, of course, be lower than those employed in the naphtha re-forming coil 59. Typical operating temperatures and pressures will run from 850° to 1000° F. and from 1000 to 2000 pounds per square inch. In any event, however, the best results are secured, as in the coil 59, by operating in the manner disclosed and claimed in my prior Patent No. 2,135,014 and as referred to hereinabove, keeping in mind the character of the individual charging stock.

The entire feed to the coil 110 will in some cases consist of virgin gas oil withdrawn from the column 8. In other cases the feed will consist entirely of gas oil withdrawn from the column 36, and in still other cases a mixture of both of these gas oils may be delivered to the coil 110. The optimum temperatures and pressures in each case may of course vary somewhat, as will be apparent to those skilled in the art, but are within the general ranges set forth hereinabove. Wherever the characteristics of the virgin gas oil and the catalytically produced gas oil are so different that reasonably optimum results could not be secured by subjecting them to conversion in admixture with each other, separate coils may be employed for their conversion. Such separate coils are not illustrated in Fig. 1 but would be generally similar to the coil 110.

In a system of this character, in which the products of conversion entering the vapor separator 64 comprise products of conversion of gas oil as well as products of conversion of naphtha and normally gaseous hydrocarbons, considerable quantities of cracked gas oil may be recovered in the column 68 of the thermal conversion unit. The amount so recovered will usually be in excess of that required for cooling and quenching purposes. Where this is true, the excess gas oil may either be withdrawn from the system or it may be recycled for conversion. It is possible to effect conversion of this stock by recycling it to the coil 110 in admixture with the other oil charged to that coil, but because of the refractory character of the cracked gas oil, it is ordinarily preferable to provide for its conversion in a separate heating coil.

Consequently I have shown in Fig. 1 a heating coil 130 located within a heating furnace 131. That portion of the gas oil removed from the column 68 (over that required as a cooling and quenching medium) is delivered to the coil 130 through a line 132, wherein is located a pump 133. A portion of the normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule recovered in the separator 99 is also delivered to the coil 130 in admixture with the gas-oil charging stock by means of the line 120, the pump 121, the line 122 and a valved branch line 134. The temperatures and pressures employed for conversion in the coil 130 will ordinarily run within the ranges set forth hereinabove with respect to the coil 110, but in each individual case it will usually be found that, because of the refractory character of the recycled cracked gas oil, somewhat different conditions (either time or pressure or temperature or any of these) will give optimum results in the coil 130; for example somewhat higher temperatures may be employed in this coil than in the coil 110. Products of conversion from the coil 130 are quenched by means of cool oil introduced through a branch line 135 which is in communication through the line 126 with the pump 80. The quenched products of conversion then pass through a transfer line 136, having a pressure-reducing valve 137, into the tar separator 64.

Distribution of normally gaseous hydrocarbons (in liquefied form) from the separator 99 for admixture with the various charging stocks entering the coils 110 and 130 is effected in such manner as to provide for a minimum of not less than 15 per cent of normally gaseous hydrocarbons, in terms of the charging stock supplied to each coil on a liquid-liquid volume basis, as set forth in my prior Patent No. 2,135,014. The amount of normally hydrocarbon gases delivered to any of these coils may be increased, but ordinarily it will be desirable to hold these down to the minimum diluent requirements, thereby permitting the larger portion of the C_3 and C_4 hydrocarbons to be recycled to the coil 59. The latter coil ordinarily operates at a higher temperature than any of the other conversion coils, and is therefore effective to secure a higher degree of conversion of gaseous hydrocarbons per pass. The amount of normally gaseous hydrocarbons (over and above any required for refluxing in the column 92) is readily controlled by regulating the temperature and pressure maintained in the condenser 98 and separator 99. Refrigeration may be employed if necessary in the condenser 98 in order to secure a sufficient volume of liquefied condensate in the separator 99 for such refluxing and recycling purposes.

Referring to the system illustrated in Fig. 2, the thermal conversion unit there shown is of the so-called "pressure-coking" type. The products of conversion from the naphtha re-forming coil 59 pass through a transfer line 150, having a valve 151, into an enlarged coking drum or chamber 152. No liquid residue is withdrawn from the drum 152, and where desired, two or more of these drums may be provided, so that one may be kept on stream while one or more additional drums are being freed from coke previously deposited therein. Vapors from the coking drum 152 pass through a vapor line 153, having a valve 154, into the tar separator 64.

In this instance, the large amount of excess heat available in the coking drum 152 is utilized as a means of reducing tars to coke. Thus, tarry residue separated in the tar separator 64 is removed therefrom through a valved line 160 and

is delivered by means of a pump 161 and a line 162 into the transfer line 150. Bottoms withdrawn from the vaporizer 26 of the catalytic cracking unit are removed therefrom through a line 163 and delivered by means of a pump 164 and the line 162 into the transfer line 150, along with tar from the tar separator 64. The tars thus introduced pass (along with the products of conversion from the re-forming coil 59) into the coking drum 152, and are there further cracked and reduced to coke. The latter accumulates in the coking drum 152 and is removed therefrom from time to time.

I have not illustrated in Fig. 2 means for delivering virgin gas oil from the tower 8 to the coil 110, (although this may be effected wherever desired). I have, however, shown means for delivering catalytically produced gas oil recovered in the column 36 to the coil 110.

From the above, it will be apparent that all tars produced in the system are eventually delivered to the coking drum 152 and there reduced to coke. The system as a whole yields only coke, gasoline and dry gas as final products. As in the instance described in connection with Fig. 1, the dry gas is substantially free of C_3 and C_4 hydrocarbons, all the latter (over and above that portion desired to be retained as such in the final gasoline product) being held in the system until converted.

Wherever the heat of the products of conversion from the re-forming coil 59 is insufficient to effect the desired amount or degree of coking in the coking drum 152, the products of conversion from the coil 130 or the coil 110, or both, may also be delivered to the coking drum 152 instead of directly to the tar separator 64. In such instance, no quenching other than that accomplished by means of the tars introduced into the line 162 (or directly into the coking drum 152) need be provided for with respect to the products from the coils feeding the coking drum 152.

By virtue of the retention and conversion of C_3 and C_4 hydrocarbons within the system and by virtue of the increased degree of conversion per pass possible with respect to each stock in the thermal catalytic unit, and also by virtue of the application of catalytic cracking to that type of stock for which it is best suited and the delivery of products (other than gasoline) from the catalytic cracking unit into the thermal conversion unit for further conversion, the systems described hereinabove represent extremely advantageous methods of producing high yields of gasoline of high anti-knock value from petroleum charging stocks. The catalytic and thermal conversion operations are combined in such a manner as to secure the optimum advantages of each and to secure combined effects which could not be secured in either type of operation considered alone.

While I have referred hereinabove, primarily by way of example, to the so-called Houdry process, it will be understood that other types of catalytic cracking processes, and other catalysts, may be employed in those instances where catalytic cracking is indicated. Such catalytic cracking processes are numerous and well known in the art and need not be catalogued here at length. In general, however, they are characterized by the use of low pressures of less than 100 pounds per square inch, temperatures ranging from 700 to 1100° F., and of course the use of a catalyst of one sort or another for promoting thermal decomposition reactions. Among the catalysts which have been proposed for use in processes of this character and which, to the extent that they are individually useful and advantageous in themselves, may be employed in the catalytic cracking zones of the processes described hereinabove, are the following: nickel and compounds thereof, such as nickel oxide; chromium and compounds thereof, such as chromic oxide; compounds of nickel and chromium, such as nickel chromate; phosphorus compounds, especially metaphosphates, including those of chromium and uranium; aluminas; adsorbent clays; floridin; bauxite; molybdenum sulfide; and a wide variety of other compounds, particularly compounds of metals and alkaline earth metals. Many of these catalysts have entirely different specific actions, some favoring hydrogenation, some scission of carbon-carbon linkages, some isomerization, some cyclization reactions, and others alkylation reactions. However, for the purposes of the present invention, all of these may be considered to come under the similar category of catalytic cracking catalysts. And while most of these catalysts are preferably employed at low pressures, with regeneration at periodic intervals, my invention (in so far as it deals with catalytic cracking) is not so limited.

The term "normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule," as used herein, is intended to mean propane, propylene, butane and butylenes, all of which are normally gaseous in a pure state under atmospheric pressure and temperature conditions. It will be understood, however, that these constituents may or may not exist in gaseous form at different points in the system illustrated. Consequently the term referred to is not intended to imply that these constituents are actually present as gases, for at many points they will exist in the liquid form by virtue of the pressures employed, or because of the presence of liquid oils in which they are absorbed, or both.

As used herein, the term "naphtha" is employed to designate low-boiling petroleum fractions which consist largely or predominantly of hydrocarbons boiling within the gasoline boiling-point range.

While I have described and illustrated my invention hereinabove with respect to several operating examples and specific operating details, my invention is not in its broadest aspects limited to such details or exemplifications, and may be variously practiced and embodied within the scope of the claims hereinafter made.

What I claim is:

1. A process of manufacturing gasoline of high anti-knock value from a petroleum crude which comprises; distilling said crude to separate it into a plurality of fractions, including a naphtha fraction and at least one heavy fraction; subjecting said heavy fraction to conversion in a catalytic cracking zone, and fractionating the products of conversion to separate a cycle stock fraction heavier than gasoline, a gasoline fraction and residual gases; contacting said naphtha fraction with gases produced as set forth hereinbelow to recover hydrocarbons having 3 to 4 carbon atoms per molecule by absorption in said naphtha; subjecting the thereby enriched naphtha to conversion in a thermal cracking zone, and fractionating the products of conversion to recover gasoline, a cycle stock fraction heavier than gasoline, and residual gases; cooling combined residual gases produced in said catalytic cracking zone and said thermal cracking zone, under pres-

sure, to recover a liquefied fraction comprising normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule; subjecting gases remaining after separation of said liquefied fraction to contact with said naphtha fraction for absorption as aforesaid; admixing said liquefied fraction with at least one of said recycle stock fractions, produced as aforesaid, subjecting the admixture of oil and gases thereby obtained to conversion in a separate thermal cracking zone, and fractionating the cracked products thereby obtained to recover gasoline constituents therefrom.

2. A process as set forth in claim 1 wherein the cycle stock fraction subjected to conversion in said separate thermal cracking zone is the cycle stock fraction recovered from the products of conversion from said catalytic cracking zone.

3. A process as set forth in claim 1 wherein the products of conversion from both of said thermal cracking zones are combined for fractionation and recovery of gasoline therefrom.

4. The process as set forth in claim 1 wherein hot products of conversion from said first-mentioned thermal cracking zone are delivered, prior to fractionation thereof, into an enlarged coking chamber, and residual products separated from said heavier fraction obtained in the distillation of the petroleum crude prior to the passage of said heavier fraction through said catalytic cracking zone are delivered to said enlarged coking zone and there reduced to coke by the heat of the products of conversion from said thermal cracking zone.

5. A process of manufacturing gasoline of high anti-knock value and coke from a petroleum crude, which comprises: distilling said crude to separate it into a plurality of fractions, including a naphtha fraction and a residual fraction; vaporizing lighter substances of said residual fraction to separate them from heavier constituents of said residual fraction; subjecting the thereby vaporized constituents of said residual fraction to conversion in a catalytic cracking zone, and fractionating the products of conversion to recover a gasoline fraction and residual gases; contacting said residual gases, under pressure, with said naphtha fraction for absorption in said naphtha fraction of normally gaseous constituents having 3 to 4 carbon atoms per molecule; subjecting the thereby enriched naphtha fraction to conversion in a thermal cracking zone; introducing hot products of conversion from said thermal cracking zone and said heavier constituents recovered from said residual fraction into an enlarged coking zone and there reducing said heavier fraction to coke; withdrawing products of conversion from said enlarged coking zone; fractionating them to recover heavier constituents therefrom; and combining residual gases thereby obtained with the residual gases from the catalytic cracking zone, for contact with said naphtha fraction as aforesaid.

6. A process as set forth in claim 5, wherein tarry constituents contained in the vapors withdrawn from the said enlarged coking zone are first separated and returned to said enlarged coking zone while the separated vapors are fractionated, constituents intermediate gasoline and tar, thereby recovered, are subjected to conversion in a separate thermal cracking zone in the presence of normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, and the resultant products of conversion are combined for fractionation with the products of conversion from said first-mentioned thermal cracking zone.

7. A process as set forth in claim 5, wherein a fraction comprising constituents heavier than gasoline is recovered from the products of conversion from the catalytic cracking zone and subjected to conversion in a separate thermal cracking zone in admixture with normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule, and the products of conversion therefrom are combined for fractionation with the products of conversion from the first-mentioned thermal cracking zone.

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