

**H. B. COOKE**  
**CRACKING HYDROCARBON OILS**

4 Sheets-Sheet 1



By G. M. Foughton  
his Attorney

**Sept. 12, 1944.**

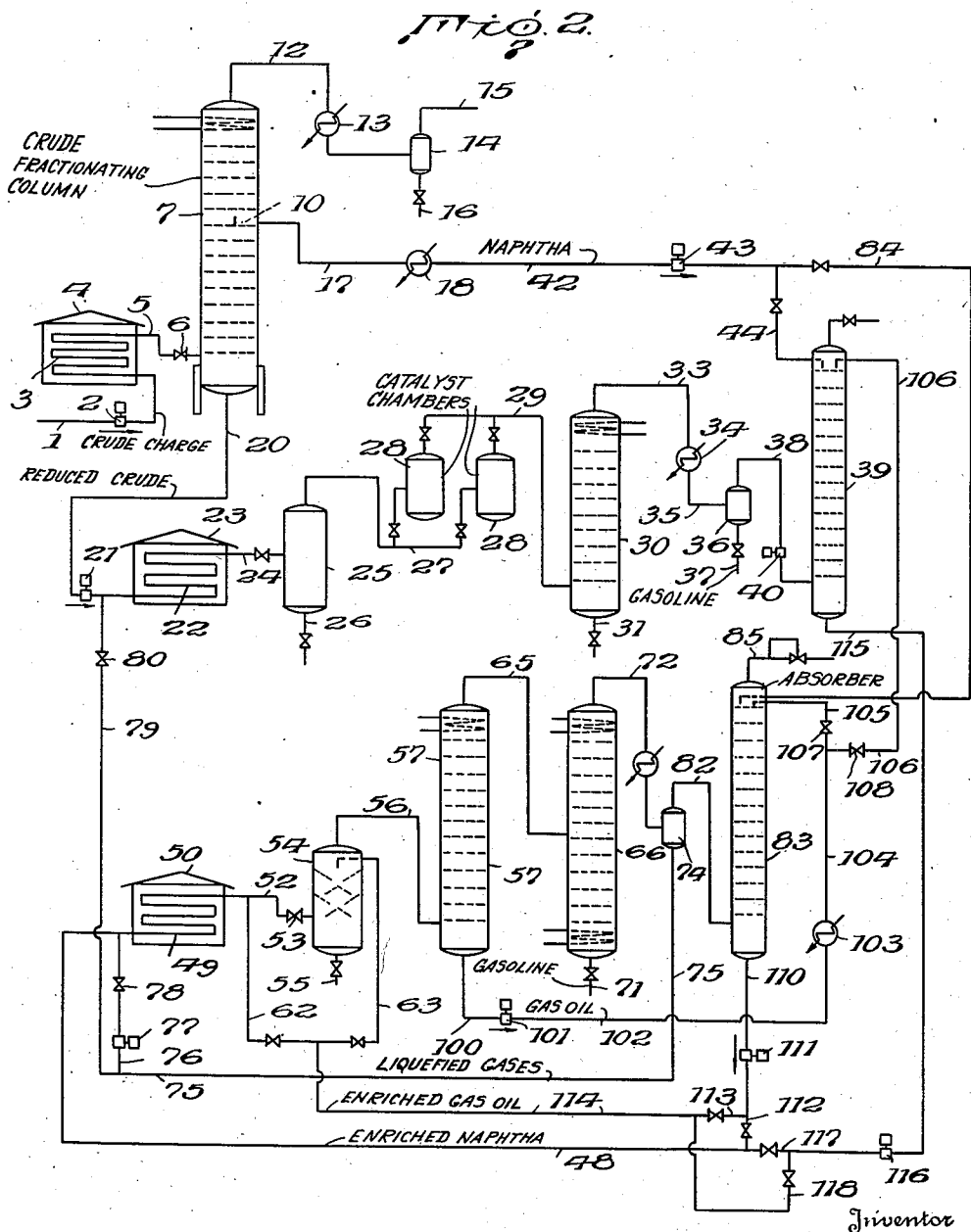
**H. B. COOKE**

**2,358,149**

## CRACKING HYDROCARBON OILS

Filed Dec. 23, 1938

4 Sheets-Sheet 2



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Sept. 12, 1944.

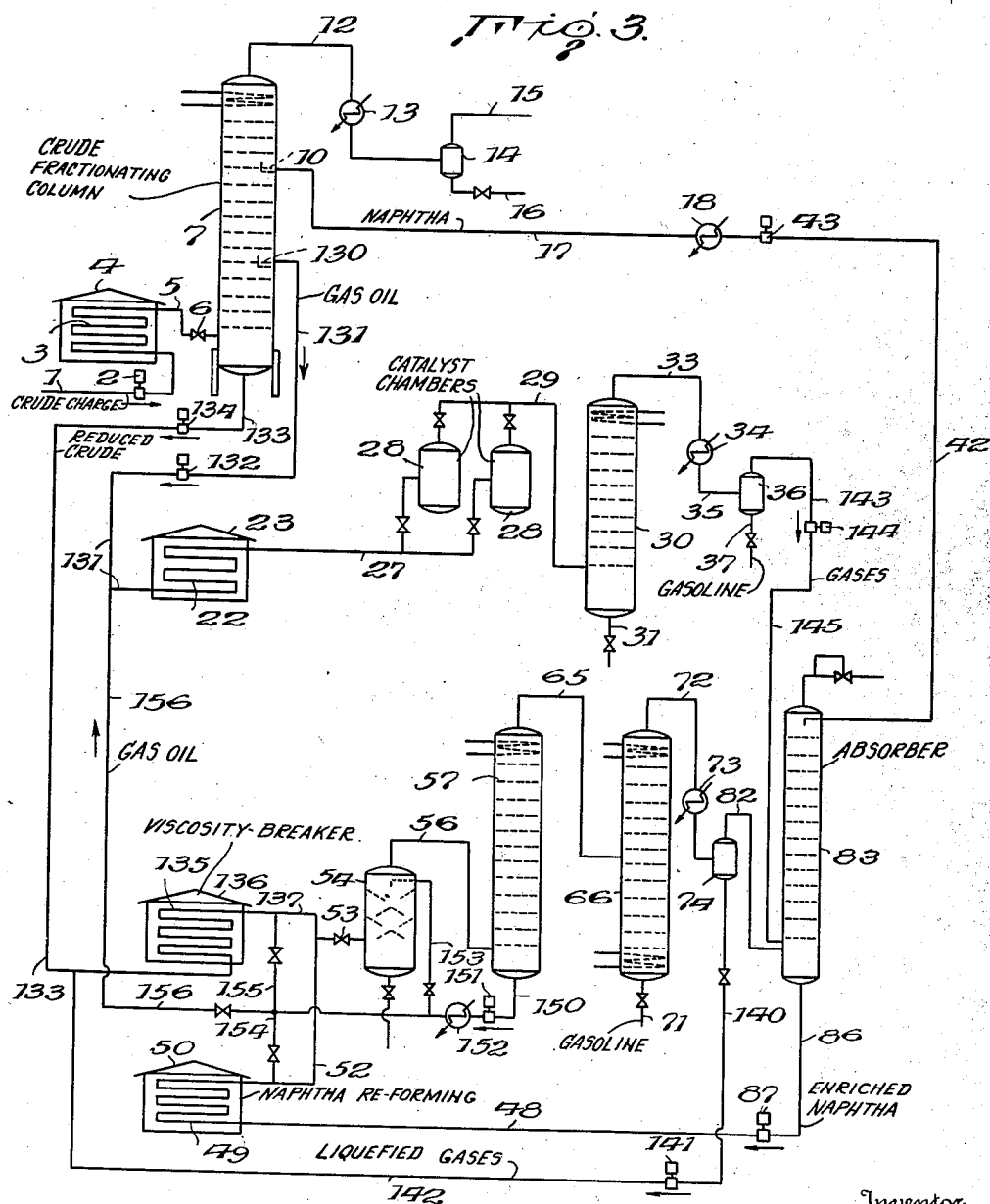
H. B. COOKE

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CRACKING HYDROCARBON OILS

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4 Sheets-Sheet 3



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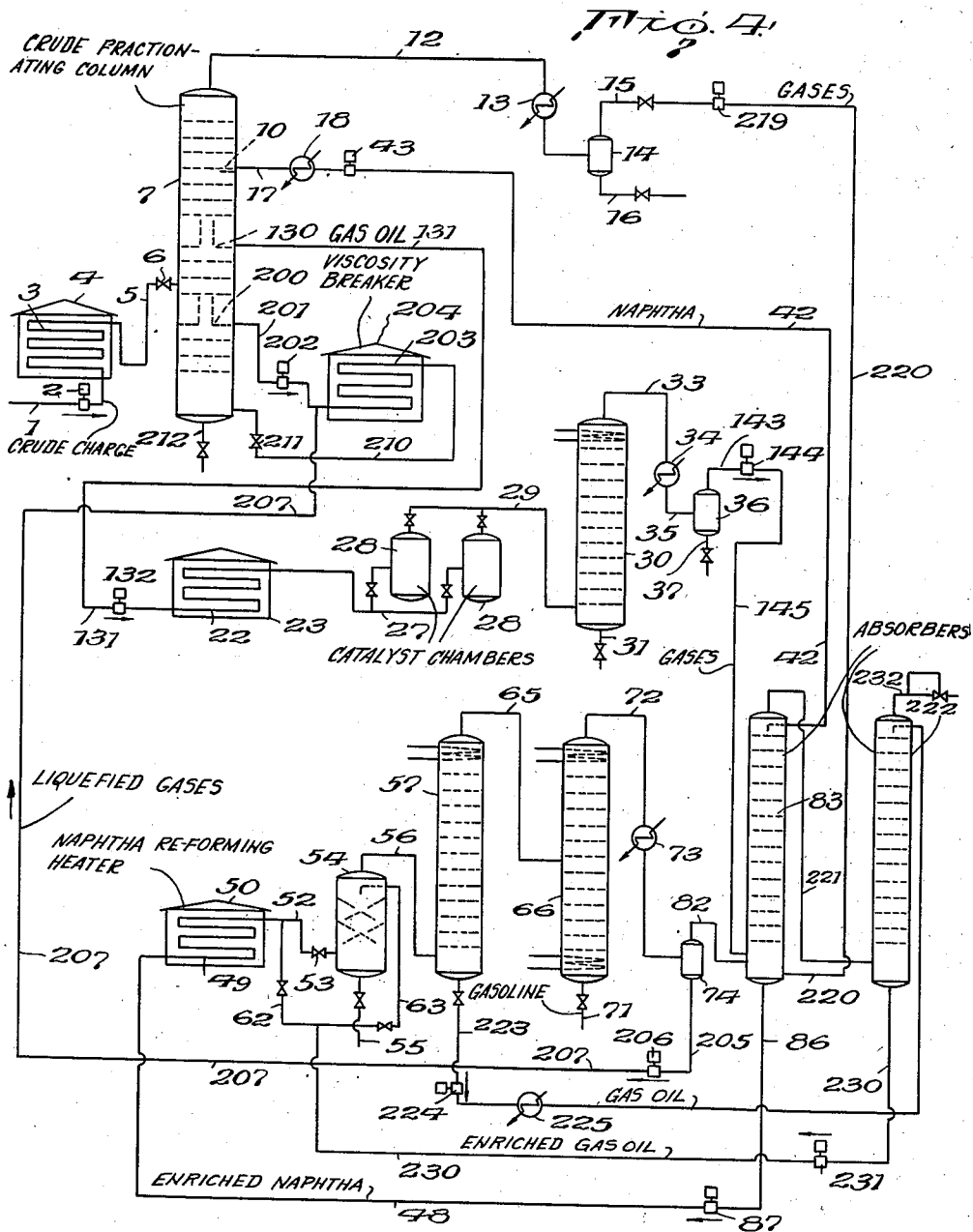
**H. B. COOKE**

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# CRACKING HYDROCARBON OILS

Filed Dec. 23, 1938

4 Sheets-Sheet 4



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## UNITED STATES PATENT OFFICE

2,358,149

## CRACKING HYDROCARBON OILS

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ration of Pennsylvania

Application December 23, 1938, Serial No. 247,504

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, these fractions are segregated and subjected to catalytic cracking and thermal cracking respectively, 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 in further detail.

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 in a unitary conversion operation.

A considerable number of separate 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 relatively small scale manufacture of special fuels, such as iso-octane, 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 process of this character is disclosed in prior U. S. Patents

Nos. 2,135,014, 2,135,108 and 2,135,109 to Povl Ostergaard. Others prior to Ostergaard 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. Ostergaard increased the degree of conversion per pass and the operating temperature in an operation of this kind, above those which would normally obtain and in fact above those which could be maintained under otherwise similar conditions and without carbon deposition, if the same oil were cracked in the same apparatus without recirculation of the reactive normally gaseous hydrocarbons.

The gas-reversion 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 the 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, no doubt partly because of the high temperatures possible when operating on light stocks of this character. On the other hand, this type of process is also especially useful and advantageous in conjunction with the cracking of very heavy or residual stocks, such for example as reduced crudes. The conversion temperatures employed in such operations are, of course, considerably lower than those employed in re-forming or cracking lighter and more refractory stocks, but are nevertheless considerably higher than would be used if the same heavy stock were cracked in the absence of the recirculated normally gaseous hydrocarbons, other conditions remaining the same. For this reason, the gas-reversion process as applied to such heavy stocks is highly advantageous, primarily from the standpoint of the far greater conversion per pass possible with respect to the heavy oil, as distinguished from the conversion per pass of the normally gaseous hydrocarbons. Gas conversion is of course effected, but the conversion per pass of the normally gaseous hydrocarbons is naturally lower when cracking a heavy residual stock than when cracking naphtha or other light stock. This in turn makes it possible to produce a far greater amount of gas-oil charging stock

suitable for subsequent cracking to gasoline. It is not intended to imply that a gas-reversion process is not applicable to the cracking of gas-oil. As a matter of fact the process has been successfully applied to the cracking of gas-oil, and as so applied results in an increase in both the yield and anti-knock quality of the final gasoline produced as compared with thermal cracking processes in which gas recirculation is not employed. However, the advantages of the process are believed to show up more strongly and its economies are believed to be most evident, in connection with the re-forming of naphthas and light stock, on the one hand, and the cracking or so-called "viscosity-breaking" of very heavy stocks, on the other hand.

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 Houdry process, employing as a typical catalyst an activated hydrosilicate of alumina or the like, is a process of this type. 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, there is considerable difficulty in applying a catalytic process of this character to the conversion of heavy residual stocks, which on account of their carbon-forming tendencies tend to interfere with the effectiveness of the catalyst employed.

In accordance with my invention, however, it is possible to secure the maximum advantages and economies of both types of processes described hereinabove, 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 of the Ostergaard type) 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 de-

livered to the naphtha re-forming operation referred to hereinabove.

As will be shown hereinbelow, the heavy fraction thus subjected to catalytic cracking may comprise a reduced or topped crude, or it may comprise a virgin gas-oil fraction. In the latter event, the residual reduced crude is, in accordance with some embodiments of my invention, subjected to cracking in the presence of recirculated  $C_3$  and  $C_4$  hydrocarbons in the manner generally similar to that employed with respect to the naphtha re-forming operation referred to hereinabove. In one embodiment of my invention described hereinbelow, such a reduced crude fraction is subjected to a viscosity-breaking or mild cracking operation conducted in the presence of  $C_3$  and  $C_4$  hydrocarbons and the vaporous products of conversion in this operation are returned to the crude distilling operation in such a manner that the gas-oil produced in this conversion stage is commingled with the gas-oil derived directly from the crude, and subsequently delivered to the catalytic cracking zone.

The segregation of the  $C_3$  and  $C_4$  hydrocarbons produced in the several cracking operations may be variously accomplished but in the main is effected by subjecting the fractionated gasoline-free products of conversion to scrubbing with the naphtha fraction about to be delivered into the thermal conversion zone. In some instances gas-oil condensate may also be withdrawn at one or more points in the system, cooled, and employed as an absorbent for the recovery of  $C_3$  and  $C_4$  hydrocarbons from one or more of the cracking operations. When this is done, it is usually desirable to employ the thereby enriched gas-oil as a quenching and cooling medium in one or more of the thermal conversion units. In order to lighten the load on the final absorber and in order to provide additional flexibility, a pressure condensation step may be provided ahead of the absorber in order to recover a liquefied propane-butane fraction, which is then returned to one or more of the conversion zones in admixture with the oil traversing the same. These and other modifications will be described more fully hereinbelow.

My invention also contemplates such additional 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 a part of this specification, a number of forms and manners in which my invention may be practiced and embodied. In these drawings

Figures 1, 2, 3 and 4 are more or less diagrammatic elevational views of different forms of apparatus for manufacturing gasoline of high anti-knock value from petroleum oil, in accordance with my invention.

These drawings are primarily diagrammatic in character and have been simplified as much as possible in order to show the essential details of operation and without encumbering this disclosure with description and explanation of many more or less obvious minor modifications, such as the use of heat exchangers for exchanging heat between streams of products at different temperatures in various portions of the unit and the like, the application of which will be obvious to those skilled in the art.

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

In the embodiment illustrated in Fig. 1, a crude petroleum charging stock is introduced into the system through pipe 1 by means of a pump 2 and is preheated in a suitable manner, as for example by means of a heated pipe coil 3 located within a furnace 4, to a suitable distilling temperature, usually a temperature at which no substantial cracking is effected. Such preheating temperatures will be of the order of 700° to 750° F. It will be understood that the preheating may be accomplished in various manners, as for example by heat exchange in other portions of the system to be described hereinbelow, and that the same considerations will apply to many instances in which heating and cooling operations are involved.

The preheated crude then passes through a line 5 having a valve 6 into a distilling column or flash tower 7 of more or less conventional design. This column is provided with suitable cooling or refluxing means such as a coil 8, with suitable gas-and-liquid-contact devices such as bell trays 9 and with one or more naphtha trap-out trays 10. By reason of the heat imparted to the crude oil and the low or atmospheric pressure maintained in the column 7, distillation takes place and a considerable portion of the crude oil is distilled. The light products, including any fixed gases which may be present and light virgin gasoline, are withdrawn from the head of the column through a line 12 to a condenser 13 and a separator 14 from which the fixed gases and the light virgin gasoline are removed through lines 15 and 16, respectively. Heavy virgin naphtha suitable for re-forming is withdrawn as a side stream from the trap-out tray 10 and passes through a line 17 to a cooler 18. As will be understood by those skilled in the art, the cooler 18 and all other coolers and condensers subsequently shown are water-cooled devices of more or less conventional type, effective to reduce the temperature of the vapors or oil passing there-through to approximately atmospheric temperature or a little above. However, it will be understood that more drastic cooling may be applied wherever necessary or desirable.

If desired, various cuts may be withdrawn as side streams from the tower 7 in addition to the naphtha cut withdrawn from the trap-out tray 10. Thus kerosene, gasoline and gas-oil cuts may be so withdrawn. In the instance shown, however, all of the crude oil constituents not vaporized and removed through the line 12 or removed as a side stream from the trap-out tray 10 are retained in the reduced or topped crude, which is eventually withdrawn from the bottom of the tower 7 through a line 20.

The reduced crude fraction so withdrawn is then delivered by means of a pump 21 to suitable heating means, such as a still or pipe coil 22 located within a furnace 23, and in passing through the coil 22 is heated to a temperature sufficient to promote conversion in the presence of the catalyst with which the oil or a portion thereof is subsequently to be brought into contact. In the instances shown, in which the cracking of this stock is effected in accordance with the so-called Houdry process, the reduced crude ordinarily emerges from the pipe 22 at a temperature somewhere around 880° F. or at any rate at such temperature as will be sufficient to effect vaporization of all but the very heaviest constituents thereof, and at this temperature passes through a valved line 24 into a vaporizer 25. Tar is withdrawn from the vaporizer 25 through a valved line 26 while the vapors pass through a valved

manifold vapor line 27 into one of a plurality of catalyst cases 28. These catalyst cases are provided with inlet and outlet manifold connections as shown in such a manner that they may be alternated as desired, so that regeneration of the catalyst in one or more of the cases may be effected while the catalyst in another case is on stream.

While I do not wish to limit myself to any particular catalyst or any specific conditions of temperature and pressure, it may be stated that a suitable catalyst used in the Houdry process comprises an activated hydrosilicate of alumina and that typical conditions of temperature and pressure at this point are from 800° to 900° F. and from atmospheric to 20 pounds per square inch gauge pressure. Various modifications of the Houdry process are, however, 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 cracking 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 converted vapors leave the "on-stream" catalyst case 28 through a manifold line 29 and enter a fractionating column 30 which, as shown, may be of more or less conventional design and which is operated to condense and recover constituents having boiling points higher than those desired in the final gasoline fraction. The gas-oil condensate thus obtained is removed from the bottom of the column 30 through a line 31, while the gasoline and lighter vapors pass through a line 33 to a condenser 34, and thence through a line 35 into a separator 36. Condensed gasoline is withdrawn from the separator 36 through a valved line 37, while the gases and vapors remaining uncondensed pass through a line 38 into an absorber 39. A pump or compressor 40 may be provided in the line 38 for the purpose of maintaining elevated pressures, for example pressures of 100 or 200 pounds per square inch gauge, in the absorber 39 wherever this proves desirable for the purpose of promoting efficiency of absorption.

In the instance shown, I provide for the recovery of C<sub>3</sub> and C<sub>4</sub> hydrocarbons from the gases entering the absorber 39 through the introduction to the absorber of a portion of the naphtha recovered in the crude flash tower 7. The naphtha so recovered, after leaving the cooler 18, passes through a line 42 having a pump 43 and communicating with a valved branch line 44 leading into the top of the absorber 39. The gases from the catalytic operation, entering the absorber 39, flow countercurrent to a stream of cool naphtha thus introduced, and the conditions within the absorber are so regulated in accordance with the amount and character of the gases introduced as to effect an absorption of the C<sub>3</sub> and C<sub>4</sub> hydrocarbons, or any desired portion thereof, from the gases. The residual gases, comprising for the most part C<sub>3</sub> and lighter hydrocarbons, leave the top of the absorber through a valved outlet line 45.

The enriched naphtha leaving the absorber 39 and containing C<sub>3</sub> and C<sub>4</sub> hydrocarbons removed by absorption in the absorber 39, then passes through a line 46 to a pump 47 which in turn delivers it through a line 48 into an elongated pipe coil 49 of restricted cross-sectional area

located within a heating furnace 50, and wherein the naphtha is subjected to thermal conversion at an elevated temperature in the presence of the C<sub>3</sub> and C<sub>4</sub> hydrocarbons. Substantial conversion is obtained at various temperatures and pressures, ranging for example from about 950° to 1400° F. and from about 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 U. S. Patent No. 2,135,014 to Povl Ostergaard. That is to say, the admixture of oil and normally gaseous hydrocarbons is subjected to a high cracking temperature substantially in excess of the maximum temperature 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, and ordinarily ranging from about 25° to 300° higher than the aforesaid maximum temperature.

During the passage of the oil and normally gaseous hydrocarbons through the coil 49 conversion takes place and the heated products are then discharged through a vapor-transfer line 52 having a pressure-reducing valve 53 into a tar separator 54. Under the influence of the pressure reduction and cooling, supplied as will hereinafter be shown, vapor separation takes place, tar being withdrawn from the bottom of the separator 54 through a valved line 55. The separated vapors are then passed through a line 56 into a fractionating column 57 which, as shown, may be of more or less conventional design.

In the fractionating column 57, sufficient cooling is effected to cause the condensation of constituents heavier than are desired to be retained in the final gasoline condensate. These condensed constituents, which may be referred to as gas oil, are withdrawn from the bottom of the fractionating column 57 through a line 58. All or a portion of the gas oil thus withdrawn is then delivered by means of a pump 59 to a cooler 60 and thence in part through a valved quenching line 62 to the vapor-transfer line 52, and in part through a valved reflux line 63 into the tar separator 54.

The uncondensed vapors leaving the top of the column 57 pass through a line 65 into a gasoline condenser and rectifier 66. Various types of apparatus may be used at this point for condensing and stabilizing the gasoline produced in the system, such, for example, as that shown and claimed in U. S. Patent No. 2,134,816 to Povl Ostergaard. In the instance shown, however, I have for simplicity's sake shown a conventional rectifying column provided with suitable plates or trays 67, cooling means 68 located in the head of the column and heating means 69 located in the foot of the column. The heat supplied to the heating coil 69 may be obtained from hot oil produced elsewhere in the system, as for example by causing all or a portion of the gas-oil condensate to traverse this coil. In any event, however, rectification takes place in the column 66 with the result that stabilized gasoline condensate is withdrawn from the bottom thereof through a valved line 71 while the remaining gases pass overhead through a line 72 leading to a condenser 73 and a separator or accumulator 74.

By virtue of the pressures maintained in this portion of the system, and which will ordinarily run from 100 to 300 pounds per square inch, a portion of the C<sub>3</sub> and C<sub>4</sub> constituents present in

the gases are caused to be condensed in the condenser 73 and collect in the accumulator 74 in liquefied form. Operation of the cooler 73 at temperatures somewhat below atmospheric may be resorted to in order to condense any desired portion of the C<sub>3</sub> and C<sub>4</sub> hydrocarbons at this point.

The condensate thereby obtained, comprising liquid butane and propane together with their unsaturated analogues, is removed from the accumulator 74 through a line 75. The line 75 is in communication with the inlet to coil 49 through a branch line 76 having a pump 77 and a valve 78, and with the inlet to the pipe coil 22 of the catalytic cracking unit through a branch line 79 having a valve 80. This apparatus makes it possible to deliver any desired portion or all of the liquid condensate from the accumulator 74 either to the coil 49 or to the coil 22, or to distribute the liquid condensate to the two coils mentioned in any desired proportion.

The gas and vapors remaining uncondensed in the condenser 73 leave the accumulator 74 through a line 82 and enter the bottom of an absorber 83. That portion of the virgin naphtha removed in the tower 7 and not used in the absorber 39 is delivered to the upper portion of the absorber 83 through a valved line 84 and in passing downwardly through the absorber 83 effects a removal, by absorption, of C<sub>3</sub> and C<sub>4</sub> hydrocarbons present in the gas traversing the absorber. The gases remaining uncondensed, and comprising for the most part C<sub>3</sub> and lighter hydrocarbons, are removed from the top of the absorber 83 through a valved exit line 85, while the enriched naphtha reaching the bottom of the tower 83 is withdrawn through a line 86 having a pump 87 and communicating with the line 48. This enriched naphtha is delivered to the pipe coil 49 located within the furnace 50 and is there subjected to thermal conversion along with the enriched naphtha from the absorber 39.

The system illustrated in Fig. 2 is generally similar to that illustrated in Fig. 1 and described hereinabove with the exception that provision is made for effecting absorption of C<sub>3</sub> and C<sub>4</sub> hydrocarbons in the absorbers 39 and 83 in a different manner or manners. In some instances, it may be desirable to use all of the virgin naphtha removed from the flash tower 7 as the scrubbing medium in the absorber 83, or in the absorber 39, and in such instance it is, of course, necessary to provide a suitable absorbent for use in whichever one of the two absorbers 39 and 83 is not supplied with this naphtha. As shown in Fig. 2, gas oil condensate removed from the bottom of the fractionating column 57 is delivered after the cooling either to the absorber 39 or to the absorber 83. After absorption, the enriched gas-oil is then returned to the thermal cracking unit at a point subsequent to the conversion zone.

Referring to Fig. 2 in greater detail, gas oil condensed in the fractionating column 57 is withdrawn therefrom through a line 100 and is delivered by means of a pump 101 and a line 102 to a cooler 103 and thence through a line 104 which is in communication with branch lines 105 and 106, having valves 107 and 108 and leading to the tops of the absorbers 83 and 39, respectively. Enriched oil from the bottom of the absorber 83 is removed therefrom by a line 110 having a pump 111 and may be delivered either through a valved branch line 112 into the line 48 and thence into the pipe coil 49, or through a valved branch line 113 and a line 114 into the

valved conduits 62 and 63 and thence into the transfer line 52 and the tar separator 54 in any desired proportions. Similarly, enriched oil withdrawn from the absorber 39 is withdrawn therefrom through a line 115 having a pump 116 and this oil may be delivered either through a valved branch line 117 into the line 48 and the pipe coil 49, or through a valved branch line 118 and the lines 114, 62 and 63 into the transfer line 52 and the tar separator 54.

In the preferred instance, all of the naphtha withdrawn from the trap-out tray 10 of the tower 7 passes through the lines 42 and 84 into the absorber 83 and after passing through the absorber 83 the thereby enriched oil is delivered through the lines 110, 112 and 48 to the pipe coil 49. Gas oil withdrawn from the fractionating column 57, or any desired portion thereof, is delivered through the lines 100, 102, 104 and 106 into the absorber 39 and the enriched oil after absorption of C<sub>3</sub> and C<sub>4</sub> hydrocarbons in the absorber 39 is then returned through lines 115, 118, 114, 62 and 63 into the transfer line 52 of the tar separator 54. The C<sub>3</sub> and C<sub>4</sub> hydrocarbons thus absorbed in the absorber 39 are not in this instance delivered directly to the pipe coil 49, but are eventually picked up in the absorber 83 in the naphtha used therein and then pass to the pipe coil 49. This system has the advantage that it increases the concentration of C<sub>3</sub> and C<sub>4</sub> hydrocarbons in the fractionating system of the thermal cracking unit and hence the efficiency of condensation and absorption of these constituents in that unit.

Alternatively, all of the naphtha removed from the crude flash tower 7 may be passed through the absorber 39, the enriched naphtha then passing through lines 115, 117 and 48 to the pipe coil 49. In this instance, gas-oil withdrawn from the base of the fractionating column 57 is delivered through lines 100, 102, 104 and 105 into the absorber 83 and the enriched gas-oil is then returned through lines 110, 113, 114, 62 and 63 into the transfer line 53 (as a quenching medium) and the tar separator 54 (as a refluxing medium).

In the system illustrated in Fig. 3, provision is made for subjecting a light cut, such as virgin naphtha, and a heavy cut, such as reduced crude, to separate thermal conversion with gas recirculation, and for subjecting an intermediate or gas-oil fraction also recovered in the distillation of the crude to catalytic cracking. The gases in the catalytic cracking unit are combined with the gases from the thermal cracking units for recirculation into the latter. Provision is also made for delivering gas-oil condensate from the thermal cracking unit into the catalytic cracking unit for conversion.

Referring to Fig. 3 in greater detail, one or more trap-out trays 130 are provided in the crude flash tower 7 at a point located below the naphtha trap-out tray 10, and more specifically at such a point as will enable the withdrawal therefrom of a virgin gas-oil fraction. The gas-oil fraction thus withdrawn is delivered through a pipe 131 and a pump 132 to the pipe coil 22 of the catalytic conversion unit, and thence directly through the valved manifold line 27 to one of the catalyst cases 28. A vaporizer, similar to the vaporizer shown in Fig. 2 may be provided, but will ordinarily be unnecessary when cracking such a non-residual stock. Heavy reduced crude unvaporized in the flash tower 7 is withdrawn therethrough through a line 133 having a pump 134 and is delivered to a pipe coil 135 located

within a heating furnace 136. Before being passed through the coil 135, however, this reduced crude is joined by propane-butane condensate recovered in the separator 74, and which in this instance is withdrawn from the separator 74 through a valved line 140 and delivered by means of a pump 141 and a line 142 into the line 133.

The temperatures and pressures employed in the coil 135 will, of course, be lower than those employed in the coil 49, which in this instance receives enriched naphtha from the absorber 83. Typical operating temperatures and pressures will run from 850 to 1000° F. and from 100 to 2000 pounds per square inch. In any event, however, the best results are secured, as in the coil 49, by operating in the manner disclosed and claimed in U. S. Patent No. 2,135,014 to Povl Ostergaard and as referred to hereinabove, keeping in mind the character of each individual charging stock.

The hot products of conversion leaving the coil 135 are discharged through a transfer line 137 into the transfer line 52, where they mingle with the products of conversion of the coil 49 and then pass into the tar separator 54 and subsequent fractionating units. Gases remaining uncondensed in the accumulator 74 are delivered to the absorber 83 where they are scrubbed with virgin naphtha recovered in the crude flash tower 7. The enriched naphtha, containing C<sub>3</sub> and C<sub>4</sub> constituents recovered from the gases in the absorber 83, is then delivered through the line 86, the pump 87 and the line 48 into the pipe coil 49. In the instance shown, the gases remaining uncondensed in the separator 36 of the catalytic cracking unit are passed through a line 143 to a pump or compressor 144 where they are raised to a pressure equal to that obtaining in absorber 83 and then pass through a line 145 into the bottom of the absorber 83. Gas-oil condensate recovered in the fractionating column 57 is withdrawn therefrom through a line 150 and passes through a pump 151 to a cooler 152. One portion of this cooled gas oil may be delivered through a valved line 153 into the tar separator 54, another portion through a valved quenching line 154 into the transfer line 52, and a third portion through a valved quenching line 155 into the transfer line 137, while any remaining gas-oil from this source may be delivered through a valved line 156 into the line 131 where it joins virgin gas-oil withdrawn from the tower 7 and enters the pipe coil 22 of the catalytic conversion unit.

In the apparatus just described in connection with Fig. 3, the fractionated products leaving the heavy oil conversion coil 135 are combined with and fractionated with the products leaving the re-forming coil 49. In the system illustrated in Fig. 4, however, the cracking or viscosity breaking of the heavy oil is accomplished in conjunction with the crude flash tower, and the products from the heavy-oil conversion or viscosity-breaking coil are fractionated in the crude flash tower along with the crude undergoing fractionation.

Referring to Fig. 4 in greater detail, a reduced crude fraction is withdrawn from the tower 7, which in this instance serves as a fractionating tower for the combined products of crude distillation and viscosity-breaking, by means of a trap-out tray 200 located at a point below the point of entry of the preheated crude. This reduced crude fraction is delivered by means of a line 201 and a pump 202 to a pipe coil 203 lo-

cated within a furnace 204. Butane-containing condensate recovered in the accumulator 74 of the thermal re-forming unit is in this instance withdrawn by a line 205 and delivered by means of a pump 206 and a line 207 to the line 201, thereby causing this liquefied gas fraction to be commingled with the reduced crude withdrawn from the trap-out tray 200 before the latter passes to the conversion coil 203. The conversion operation conducted in the coil 203 is essentially similar to that described hereinabove in connection with the operation of the coil 135 of the system shown in Fig. 3. In this instance, however, the products leaving the coil 203 pass through a transfer line 210 having a pressure-reducing valve 211 into the lower part of the flash tower 7. Residue or tar separating in the bottom of the flash tower 7 is withdrawn by a line 212, while the flashed vapors pass upward through the tower 7 and are fractionated therein.

It will be obvious that in this system the fraction withdrawn from the trap-out tray 130 of the tower 7 comprises both virgin gas-oil constituents and gas-oil constituents produced by the mild cracking effect in the coil 203. This fraction passes through the line 131 into the pipe coil 22 of the catalytic conversion unit, as in the system illustrated in Fig. 3.

As in that system, virgin naphtha recovered from the flash tower 7 is delivered by means of the line 17, the pump 43 and the line 42 into the absorber 83 of the thermal cracking unit, and the enriched naphtha leaving the bottom of the absorber 83 is delivered through the lines 86 and 48 into the re-forming coil 49.

In this system, inasmuch as normally gaseous hydrocarbons are delivered to the viscosity-breaking or mild cracking operation conducted in the coil 203, considerable quantities of C<sub>3</sub> and C<sub>4</sub> hydrocarbons are present in the overhead products from the tower 7. I have illustrated in Fig. 4 means whereby these may be recovered. As shown, gases leaving the separator 14 through the line 15 are picked up by a pump or compressor 219, where they are raised to a pressure equal to that obtaining in absorber 83, and the compressed gases are then delivered into the bottom of the absorber 83 through a line 220 provided for that purpose.

I have also illustrated in Fig. 4 a procedure which, while especially suitable for use in conjunction with the rest of the system illustrated in Fig. 4, may also be employed to advantage in conjunction with the other systems described and set forth hereinabove. The gases leaving the absorber 83 sometimes contain substantial quantities of C<sub>3</sub> and higher boiling constituents which it may be desired to recover for use and ultimate conversion in the system. To that end, the gases leaving the top of the absorber 83 are delivered through a line 221 to a second absorber 222. Gas oil recovered in the fractionating column 57, or any desired portion thereof, is withdrawn therefrom through a valved line 223, wherein are located a pump 224 and a cooler 225, and passes to the upper part of the absorber 222. In passing down through the absorber 222, the gas oil thus introduced absorbs C<sub>3</sub> and C<sub>4</sub> hydrocarbons as well as any heavier constituents which may be contained in the gases entering the absorber. The enriched gas oil leaving the bottom of the absorber 222 is delivered through a line 230 having a pump 231 into the lines 62 and 63 leading to the transfer line 52 and the tar separator 54, respectively. In this case, as in all other in-

stances in which oil is delivered to one of the transfer lines leading from one of the conversion zones, the purpose is thus introducing oil is to arrest and control the reactions initiated in the respective conversion zone.

Gases remaining uncondensed in the absorber 222 are removed through a valved exit line 232 and pass out of the system.

With reference to all of the systems shown in Figs. 1 to 4 hereinabove, any gas-oil constituents recovered in the fractionating column 30 of the catalytic conversion unit may be recycled to the catalytic conversion unit or cracked in a separate coil, with or without a catalyst, and the products of cracking may be fractionated along with other products of conversion, in a manner which will be evident to any one skilled in the art from the foregoing. However, for purposes of simplicity, I have omitted the details of such operation from the drawings.

Moreover, the various gasolines recovered in the systems illustrated and described hereinabove, for example at 16, 37 and 71, may be combined and blended in any desired proportions to produce the final motor-fuel product, or they may be used separately. Moreover, these gasolines may be blended with additional agents for use, as for example, with the usual anti-knock agents, such as tetraethyl lead and the like.

In this case it may be noted that in general the lead susceptibility of catalytically cracked gasolines does not usually compare with the lead susceptibility of thermally cracked gasolines such as those produced in the thermal cracking zones of the systems illustrated hereinabove. This fact constitutes one of the reasons why, as I have stated, the re-forming of straight run gasoline is best carried out in a thermal conversion zone of the type indicated hereinabove rather than in a catalytic cracking zone. For this reason, the overall anti-knock value and lead susceptibility of the products obtained in accordance with my invention represent a distinct improvement over prior art processes.

In referring to catalytic cracking processes I have in mind in general those processes, usually carried out at pressures of less than 100 pounds per square inch at elevated temperatures ranging from 700° to 1100° F., wherein a catalyst of some sort or another is employed to promote conversion reactions tending to form gasoline-like hydrocarbons. I have referred principally hereinabove to the Houdry process, but it will be understood that other types of catalytic 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 in full. However, by way of exemplification, it may be stated that 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 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 dehydrogenation, some scission of carbon-carbon linkages, some isomerization, some cyclization reactions, and others alkylation reactions, but for the purposes of the present invention, all of these may be considered to come under the general category of catalytic cracking catalysts. Most of these catalysts are preferably employed at low pressures, with regeneration at periodic intervals, but my invention, in so far as it deals with catalytic cracking, is not so limited.

In referring to "normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule," I mean propane, propylene, butanes 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 systems illustrated, and consequently the expression 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.

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

What I claim is:

1. The process of producing gasoline motor fuel of high anti-knock value from a crude petroleum, which comprises: fractionally distilling a crude petroleum to recover a naphtha fraction and a higher-boiling fraction; subjecting said higher-boiling fraction to conversion at a relatively low pressure in the presence of a catalyst effective to promote pyrolysis reactions, and fractionating the resultant products of conversion to recover gasoline and heavier constituents, including a gas-oil fraction, therefrom; subjecting said naphtha fraction to thermal conversion at a high cracking temperature and under a relatively high super-atmospheric pressure, effective to cause the formation of gasoline-like products having an increased anti-knock value, and separately fractionating the resultant products of conversion to recover gasoline and heavier constituents, including a gas-oil fraction, therefrom; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the thereby fractionated products of conversion of one of the conversion operations referred to above by absorption in said naphtha fraction, prior to conversion thereof as aforesaid; delivering the thereby enriched naphtha fraction containing gaseous hydrocarbons to the thermal conversion operation for conversion as aforesaid; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the products of conversion of the other operation referred to above, by absorption in a gas-oil fraction recovered as aforesaid; and delivering the thereby enriched gas-oil constituents to the hot products of conversion in the thermal conversion operation, as a cooling medium.

2. The process of producing gasoline motor fuel of high anti-knock value from a crude pe-

troleum, which comprises: fractionally distilling a crude petroleum to recover a naphtha fraction and a higher-boiling fraction; subjecting said higher-boiling fraction to conversion at a relatively low pressure in the presence of a catalyst effective to promote pyrolysis reactions, and fractionating the resultant products of conversion to recover gasoline and heavier constituents therefrom; subjecting said naphtha fraction to thermal conversion at a high cracking temperature and under a relatively high superatmospheric pressure, effective to cause the formation of gasoline-like products having an increased anti-knock value, and separately fractionating the resultant products of conversion to recover gasoline and heavier constituents, including a gas-oil fraction, therefrom; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the thereby fractionated products of conversion of the thermal conversion operation referred to above by absorption in said naphtha fraction before conversion thereof as aforesaid; delivering the thereby enriched naphtha containing said normally gaseous hydrocarbons to the thermal conversion operation for conversion as aforesaid; recovering normally gaseous hydrocarbons from the fractionated products of conversion in the catalytic cracking operation by absorption in said gas-oil fraction; and delivering the thereby enriched gas-oil fraction to the hot products of conversion in the thermal cracking operation, as a cooling medium.

3. The process of producing gasoline motor fuel of high anti-knock value from a crude petroleum, which comprises: fractionally distilling a crude petroleum to recover a naphtha fraction and a higher-boiling fraction; subjecting said higher-boiling fraction to conversion at a relatively low pressure in the presence of a catalyst effective to promote pyrolysis reactions, and fractionating the resultant products of conversion to recover gasoline and heavier constituents, including a gas-oil fraction, therefrom; subjecting said naphtha fraction to thermal conversion at a high cracking temperature and under a relatively high super-atmospheric pressure, effective to cause the formation of gasoline-like products having an increased anti-knock value, and separately fractionating the resultant products of conversion to recover gasoline and heavier constituents, including a gas-oil fraction, therefrom; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the thereby fractionated products of conversion of the catalytic conversion operation by absorption in said naphtha fraction prior to conversion thereof; delivering the thereby enriched naphtha fraction containing said normally gaseous hydrocarbons to the thermal conversion operation for conversion as aforesaid; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the fractionated products of conversion in the thermal cracking operation by absorption in a gas-oil fraction produced as aforesaid; and recycling the thereby enriched gas-oil fraction into the thermal conversion operation.

4. The process of producing gasoline motor fuel of high anti-knock value from a crude petroleum which comprises fractionally distilling a crude petroleum to recover a naphtha fraction, a gas-oil fraction and a residual fraction; subjecting said residual fraction to thermal con-

version at a mild cracking temperature and under superatmospheric pressure; separating tarry constituents from the products of conversion thereby obtained and commingling the separated hot products of conversion thereby obtained with the crude petroleum undergoing fractionation; subjecting said gas-oil fraction to conversion at a relatively low pressure in the presence of a catalyst capable of promoting pyrolysis reactions, and separately fractionating the resultant products of conversion to obtain gasoline and heavier constituents therefrom; subjecting said naphtha fraction to thermal conversion at a high cracking temperature and under a relatively high superatmospheric pressure, effective to cause the formation of gasoline-like products having an increased anti-knock value, and fractionating the resultant products of conversion to recover gasoline and heavier constituents therefrom; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the gaseous products leaving the crude fractionating operation, the catalytic conversion operation and the naphtha re-forming operation referred to above; and subjecting said normally gaseous hydrocarbons to conversion in admixture with the residual fraction and the naphtha fraction subjected to conversion as aforesaid, respectively.

5 The process of producing gasoline motor fuel of high anti-knock value from a crude petroleum which comprises fractionally distilling a crude petroleum to recover a naphtha fraction, a gas-oil fraction and a residual fraction; subjecting said residual fraction to thermal conversion at a mild cracking temperature and under superatmospheric pressure; separating tarry constituents from the products of conversion thereby obtained and commingling the separated hot products of conversion thereby obtained with the crude petroleum undergoing fractionation; subjecting said gas-oil fraction to conversion at a relatively low pressure in the presence of a catalyst capable of promoting pyrolysis reactions, and separately fractionating the resultant products of conversion to obtain gasoline and heavier constituents therefrom; subjecting said naphtha fraction to thermal conversion at a high cracking temperature and under a relatively high superatmospheric pressure, effective to cause the formation of gasoline-like products having an increased anti-knock value, and fractionating the resultant products of conversion to recover gasoline and heavier constituents therefrom; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the fractionated gasoline-free products of the naphtha re-forming operation referred to above; subject-

ing said normally gaseous hydrocarbons to conversion in admixture with said residual fraction subjected to conversion as aforesaid; combining the remaining gaseous products from the naphtha re-forming operation with the fractionated gaseous products from the catalytic cracking operation; scrubbing the thus combined products with said naphtha fraction, prior to conversion thereof, to remove normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule by absorption in said naphtha fraction; and delivering the thereby enriched naphtha fraction to the naphtha re-forming operation for conversion as aforesaid.

15 6. A process as set forth in claim 5, wherein gas-oil is recovered by fractionation of the products of conversion of the naphtha re-forming operation, the combined gaseous products after being scrubbed with said naphtha fraction as set forth in claim 18 are scrubbed with said gas-oil fraction, and the thereby enriched gas-oil fraction is introduced into the hot products of conversion leaving the naphtha conversion zone, as a cooling medium.

20 7. The process of producing gasoline motor fuel of high anti-knock value from a crude petroleum which comprises fractionally distilling a crude petroleum to recover a virgin naphtha fraction, virgin gas-oil constituents and a residual fraction; subjecting said residual fraction to thermal conversion at a mild cracking temperature and under superatmospheric pressure; separating tar constituents from the products of conversion thereby obtained and fractionating the products of conversion to recover cracked gas-oil constituents; subjecting virgin and cracked gas-oil constituents recovered as aforesaid to conversion at a relatively low pressure in the presence of a catalyst capable of promoting pyrolysis reactions, and separately fractionating the resultant products of conversion to recover gasoline and heavier constituents therefrom; subjecting said naphtha fraction to thermal conversion at a high cracking temperature and under a relatively high superatmospheric pressure, effective to cause the formation of gasoline-like products having an increased anti-knock value, and fractionating the resultant products of conversion to recover gasoline and heavier constituents therefrom; recovering normally gaseous hydrocarbons having 3 to 4 carbon atoms per molecule from the gaseous products leaving the several cracking operations referred to above; and subjecting portions of said normally gaseous hydrocarbons to conversion in admixture with the residual fraction and the naphtha fraction subjected to conversion as aforesaid, respectively.

HORACE B. COOKE.

CERTIFICATE OF CORRECTION.

Patent No. 2,358,149.

September 12, 1944.

HORACE B. COOKE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 8, second column, line 20, claim 6, for the claim reference numeral "18" read --5--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of November, A. D. 1944.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.