

March 20, 1945.

R. F. RUTHRUFF

2,372,018

CONVERSION OF HYDROCARBONS

Filed June 7, 1939

4 Sheets-Sheet 1

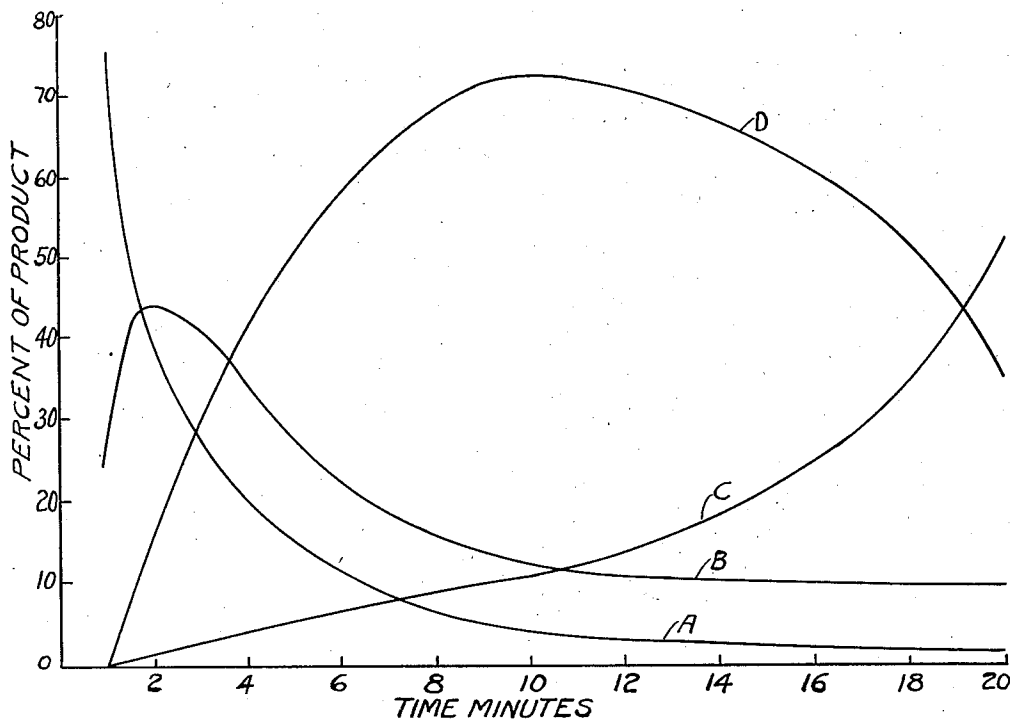


FIGURE 1

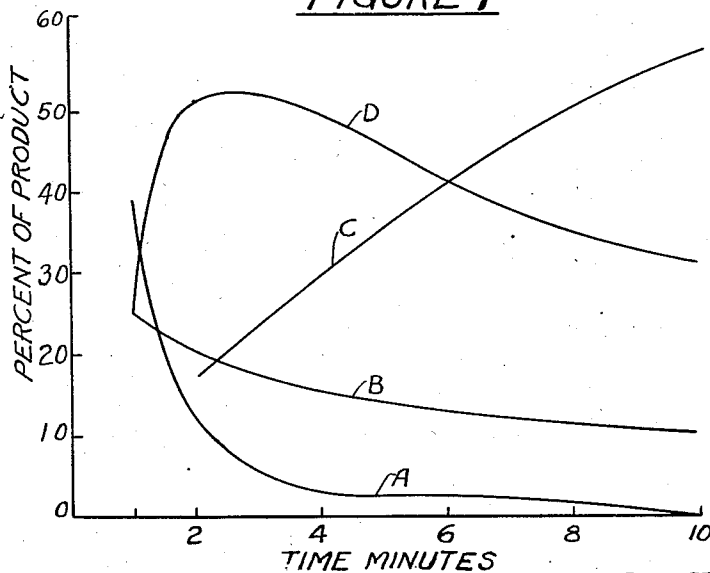


FIGURE 2

ROBERT F. RUTHRUFF

INVENTOR

BY *Walter A. Borchert*

ATTORNEY

March 20, 1945.

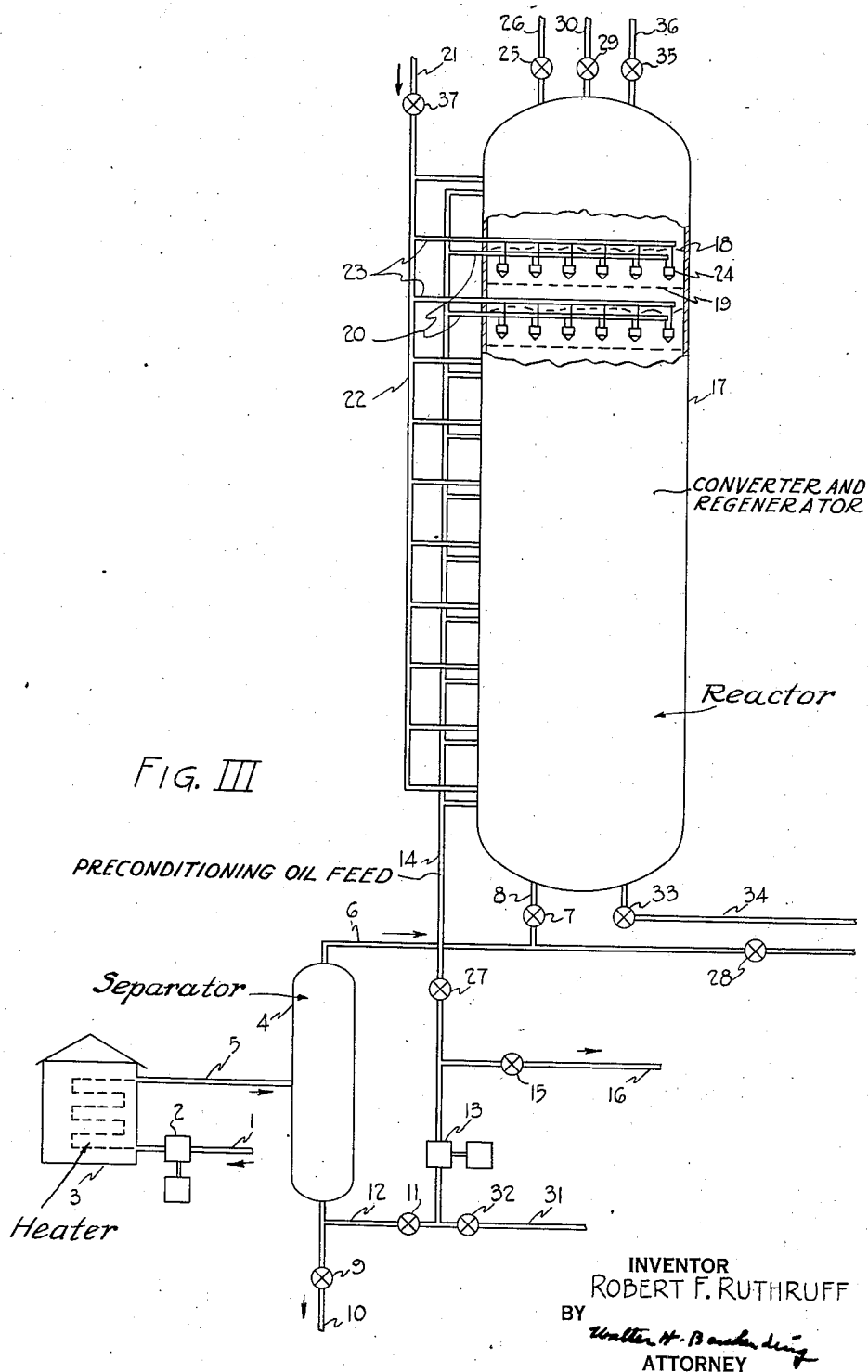
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CONVERSION OF HYDROCARBONS

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4 Sheets-Sheet 2



March 20, 1945.

R. F. RUTHRUFF

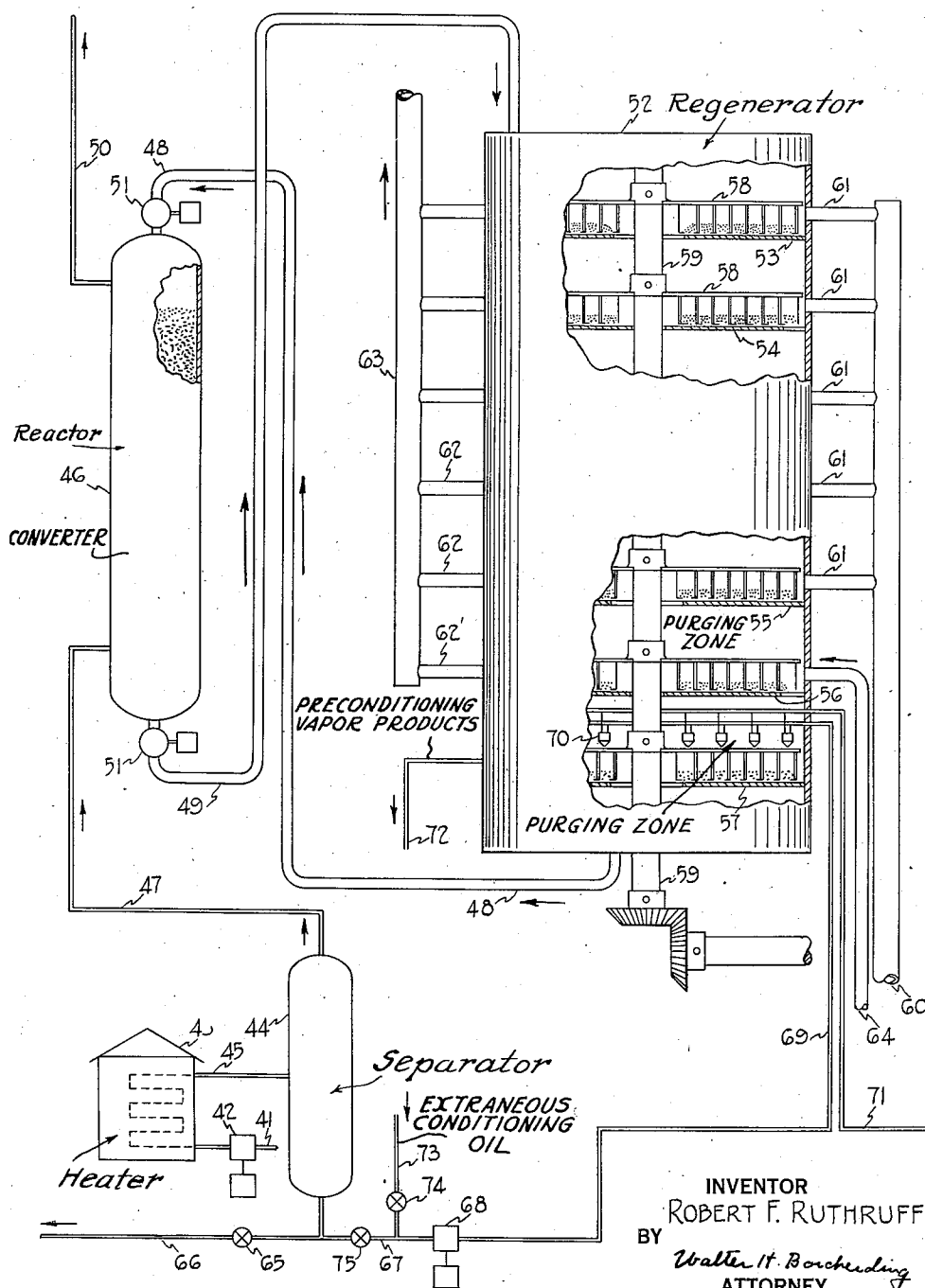
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4 Sheets-Sheet 3

FIG. IV



March 20, 1945.

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CONVERSION OF HYDROCARBONS

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4 Sheets-Sheet 4

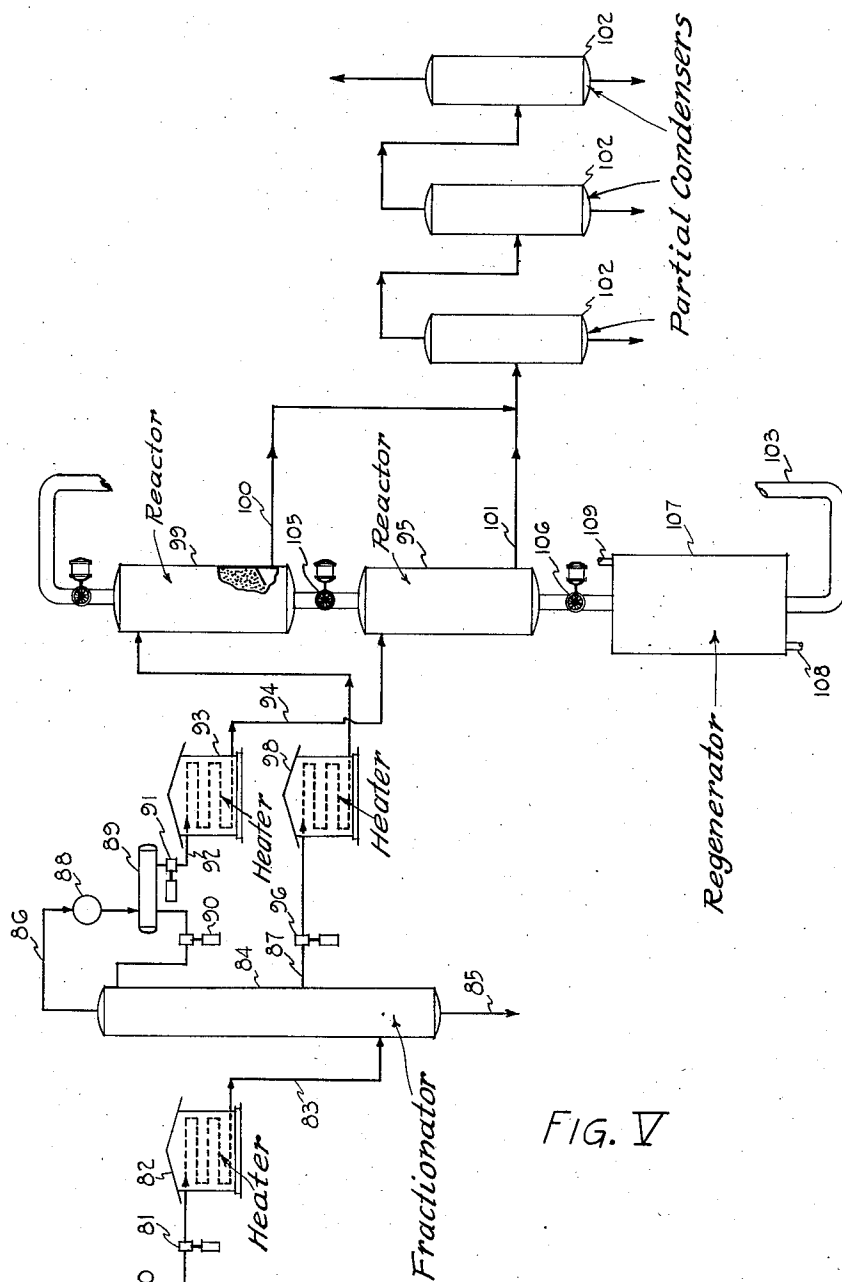


FIG. V

INVENTOR
ROBERT F. RUTHRUFF
BY
Walter H. Borchert
ATTORNEY

UNITED STATES PATENT OFFICE

2,372,018

CONVERSION OF HYDROCARBONS

Robert F. Ruthruff, Nutley, N. J., assignor to The
M. W. Kellogg Company, New York, N. Y., a
corporation of Delaware

Application June 7, 1939, Serial No. 277,885

5 Claims. (Cl. 196—52)

The present invention relates to the conversion of hydrocarbons, particularly the conversion of high-boiling hydrocarbons to low-boiling hydrocarbons. More specifically, my invention relates to the conversion in the presence of a catalyst or contact agent of high-boiling hydrocarbon mixtures such as petroleum crudes or heavy fractions thereof to low-boiling fractions such as gasoline.

It has been common practice to convert high-boiling hydrocarbons to low-boiling hydrocarbons by thermal decomposition or thermal cracking, and this art as applied to hydrocarbons is well known and highly developed.

By subjecting hydrocarbons to elevated temperature, decomposition or cracking sets in with the production of various conversion products. When, for example, a mixture of liquid hydrocarbons boiling in the temperature range 400–750° F., is thermally cracked or decomposed, the following conversion products are obtained: gas, gasoline, cycle stock having approximately the same boiling range as the hydrocarbon charge, tar and coke. By returning the cycle stock to the conversion zone, gas, gasoline, tar and coke are obtained as ultimate conversion products. Usually, gasoline is the desired decomposition product while gas, tar and coke are, under most circumstances, undesirable.

Many advantages follow the use of contact materials or catalysts in the decomposition or cracking of hydrocarbons. For example, the operating temperature required for a given amount of conversion may be considerably lowered in comparison with the temperatures required in operations conducted in the absence of catalysts. Additionally, the quality of the gasoline produced in the presence of catalysts is higher than that of thermally cracked gasoline and also the yield of this superior product is enhanced. In catalytic cracking, gas, gasoline, cycle stock and coke are produced, so the ultimate products are gas, gasoline and coke. It will be observed that in catalytic cracking, no tar is usually produced although it is to be noted that generally the coke production in catalytic cracking is appreciably greater than in thermal cracking and this enhanced coke production may be considered equivalent to part of the tar produced in thermal cracking.

While the catalytic conversion of hydrocarbons is superior to thermal processes, the former operation is not perfect for here too, undesirable products (gas and coke) are formed. By the practice of this invention the production of these undesirable products is decreased, while the production of gasoline is increased.

The coke produced during catalytic conversion progressively increases throughout the conversion, and finally reaches a stage at which it deactivates the catalyst to an extent necessitating its regeneration. Regeneration is usually effected by passing air over the spent catalyst and burning off the deposited coke at a suitable temperature. A great variety of catalytic materials, differing widely in physical structure and chemical composition have been suggested for use as cracking catalysts, and in each instance, these materials have been recognized as requiring periodic regeneration treatments for removal of deposited carbonaceous material in order to enable them to be employed for repeated conversion treatments.

The basis of this invention resides in the observation and discovery that, the alumina-silica type of cracking catalyst exhibits certain distinctive phenomena during the initial portion of the conversion cycle with respect to the products produced, and in the provision of a process arising from this observation whereby a more favorable distribution and enhanced yield of the desired conversion products is obtained.

The catalytic material contemplated for use in the practice of the invention comprises either, naturally occurring or synthetically prepared mixtures or compounds of silica and alumina, suitably prepared so as to exhibit a high degree of catalytic cracking activity. A variety of different methods for the preparation of catalysts of this type have been described heretofore in the art. For example, a suitable type of alumina-silica cracking catalyst for use in accordance with my invention may be artificially prepared by impregnating a hydrogel of silica with a heat-decomposable salt of alumina such as aluminum nitrate, and then heating the impregnated hydrogel to decompose the nitrate, thereby producing a suitable cracking catalyst consisting of a hard porous silica gel impregnated with alumina, this method of preparation being that described in U. S. Patent 1,782,857. Other materials containing alumina and silica such as naturally occurring, or activated adsorbent clay materials such as for example fuller's earth and bentonite, having the effect of catalytically converting the higher-boiling hydrocarbons into lower one, may be employed. An activated bleaching clay sold under the trade name, "Super Filtrol" is particularly suitable for use in accordance with my invention. This product is produced by the conversion of certain types of raw bentonites into highly active adsorbent products by intimately contacting the ground raw clay with mineral acid

under suitable conditions and thereafter removing the products of reaction by successive washings with large volumes of hot water. After dewatering, the pulp is dried under carefully controlled conditions followed by final grinding to desired mesh specification.

The term "alumina-silica cracking catalyst" as employed herein and in the appended claims, designates and is limited to a well recognized class of materials known for their capability of catalyzing the conversion of high boiling hydrocarbons to lower boiling hydrocarbons within the gasoline boiling range characterized by both high yield and quality of the gasoline product. This catalytic conversion is further characterized by the continuous conversion during the catalytic contact of a portion of the charge to produce a carbonaceous deposit on the catalyst. Activated clays such as "Super-Filtrol" and synthetic composites including silica-gel and alumina are well known examples of this class of catalyst material. Other materials such as pumice, although including alumina and silica in some form, are known to lack catalytic activity of the character referred to and are, therefore, expressly excluded from the term "alumina-silica cracking catalyst."

The procedure employed in the practice of my invention, and its various features and advantages will be apparent from the following detailed description thereof, given in connection with the appended drawings, wherein:

Figures 1 and 2 are graphical representations of the per cent production, based on the hydrocarbon charged, of the various products of once-through catalytic cracking over alumina-silica type of cracking catalysts, as a function of the catalyst exposure time; and

Figures 3, 4, and 5, each illustrates diagrammatically a suitable type of apparatus for the practice of specific embodiments of the invention.

Referring to Figures 1 and 2, the curves shown are graphical representations of the instantaneous yields of the per cent production, relative to feed stock, of the conversion products produced by passage of the feed in a once-through operation over alumina-silica type of cracking catalysts as a function of the catalyst exposure or contact time. Referring to the individual curves, curve A, represents coke yield; B, yield of gaseous material; C, yield of cycle stock; and D, yield of gasoline.

It is to be noted that the yields shown are not cumulative, but rather represent the instantaneous yields obtained during any given period of catalyst life. For example, the yield data shown at ten minutes represent the production of conversion products obtaining at the instant when the reactor containing the catalyst has been on-stream ten minutes, and not the cumulative yield over the first ten minutes of the conversion cycle. The specific data shown in Figure 1 were obtained when passing West Texas gas oil over a catalyst consisting of an acid treated clay of the "Super-Filtrol" type. A temperature of 850° F. was employed and the charge was passed at a rate of 0.3 liquid volume per volume of catalyst per hour.

The results in Figure 1 show that when using this catalyst, initially no gasoline or cycle stock is formed, only large amounts of coke and gas. As time on-stream increases, the yields of gas and coke both decrease rapidly, the yield of cycle stock increases slowly while gasoline production rapidly increases to an optimum and then more slowly declines.

The following explanation is suggested to cover the behavior exhibited but it is to be understood that this is theory only, and in no way limits the scope of the invention. It is believed that the contact material charged to the reactor is not of itself the true cracking catalyst but that it is a material capable of producing carbon or carbonaceous residues of peculiar orientation and properties and that it is this carbon or these residues that form the true cracking catalyst. During the first few minutes on-stream the major product formed is this oriented carbon which is of course deposited on the catalyst. As time goes on, production of gasoline increases rapidly, reaching a maximum in the present instance at an on-stream period of approximately ten minutes. At this time, coke production is practically nil while gas production is very low. When the on-stream period is increased beyond ten minutes, the proportion of gasoline in the reaction product decreases with increasing rapidity. It is believed that initially the contact material has little or no ability to make gasoline. As carbon is deposited on the surfaces of this contact material, this carbon, due to its peculiar orientation and properties which are due to the nature of the surface of the contact material upon which it is deposited, has the ability to convert the charge to gasoline. Conversion to gasoline increases rapidly as the contact material becomes covered with carbon; likewise as the contact material becomes covered with carbon, less charge becomes converted to carbon. However, as cracking progresses, it is believed that tar or pitch forms as a byproduct and this material also is deposited on the contact agent, covering the active carbon already thereon. The tar or pitch or carbonaceous material derived therefrom does not, it is believed, possess the required orientation necessary for converting gas oil to gasoline and accordingly gasoline production decreases. As this occurs, the yield of cycle stock increases simultaneously since there is no fresh surface of contact material to convert it to coke and no orientated carbonaceous material to convert it to gasoline. Apparently the contact material during any one cycle acquires a double layer. When fresh, the contact material gives largely coke and gas; when covered with oriented carbon it produces gasoline; and when the carbon is covered with tar or decomposition products thereof, the whole is inactive both as a carbon producer and as a gasoline producer.

Figure 2 is similar to Figure 1 except that Figure 2 represents conditions wherein the gas oil charge was passed over the alumina-silica catalyst at a rate of 1.0 liquid volume per volume of catalyst per hour. The time on-stream yield relationships in the two figures are quite similar, any differences being explainable on the basis of the different charging rates. In Figure 1, maximum gasoline yield was 73%, attained when the catalyst was on-stream 10.5 minutes. In Figure 2, gasoline yield was maximum at 52.5% when the on-stream period was 2.7 minutes, approximately. The lower gasoline yield in this case reflects the shorter contact time. It will be noted that the increase in gasoline yield to the maximum is faster in Figure 2 than in Figure 1, while the decline from the maximum is slower. This last is due to the slower rate at which the oriented carbon surface is blanketed with tar or pitch and reflects in turn the lower extent of cracking at the higher charge rate. It appears, however, that the rate of depositing active, oriented car-

bon on the contact material is not so much a function of contact time as it is of the total amount of charge passed. For example, in Figure 2, maximum activity was reached in 2.7 minutes. This multiplied by the charge rate, gives 2.7 volumes of charge passed to reach maximum activity. In Figure 1, maximum activity was reached in 10.5 minutes and this multiplied by the charge rate 0.3, gives 3.15 volumes of charge passed to reach maximum activity. Within the limit of experimental accuracy, these two values are substantially identical.

It may be observed from Figures 1 and 2 that for any length of cycle X, the gasoline yield could be increased if the initial period could be, in effect, eliminated. In addition, not only is the gasoline yield increased but also the gasoline to gas plus coke ratio is very substantially increased. More specifically, in Figure 1, if the reaction is conducted over the period 6 to 15 minutes shown, the gasoline yield is higher than over the period, 0 to 9 minutes, and the gasoline to gas plus coke ratio is much higher. Likewise, in Figure 2, the yield of gasoline and the product distribution is much more favorable over the period, 2 to 6 minutes than the period, 0 to 4 minutes.

It may be further observed that when conducting a catalytic conversion operation in accordance with the operating conditions obtaining for Figure 1, if the products are sent to waste during the initial period, for example, the first five minutes of the reaction cycle after which the conversion products are collected for use in the production of distillate boiling within the usual gasoline boiling range, the product distribution in the finally collected products is much improved. However, under such conditions no useful result has been attained since the initial product showing poor distribution was sent to waste.

In accordance with my invention the initial period of the cycle characterized by undesirable product distribution and yield is, in effect, eliminated by subjecting the catalyst to a preconditioning treatment prior to the conversion reaction. In accordance with this treatment, a quantity of carbonaceous material is formed or deposited on the particular type of alumina-silica cracking catalyst employed approximating the quantity normally deposited during said initial period above described. The quantity of carbon to be thus formed will, in general, range in quantity from about 0.5% to 2.0%, by weight, of the catalyst, and preferably resides in the somewhat narrower range of about 0.8% to 1.5%. Preconditioning of the catalyst, in accordance with my invention, may be effected by the decomposition of a hydrocarbon mixture which is readily broken down or decomposed to produce a mixture of carbon and other hydrocarbons by a suitable decomposition treatment, and contacting the decomposition products with the fresh or regenerated alumina-silica catalyst in such manner that carbon is deposited thereon to the required extent. Preferably, the conditioning treatment is effected by passing the hydrocarbons selected for the treatment, in contact with the fresh or regenerated catalyst under reacting conditions adapted to decompose it to a mixture of hydrocarbons and carbon, the latter forming the required deposit of activating carbon on the catalyst. The quantity of carbon thus deposited is dependent on the quantity of the selected hydrocarbon passed over the catalyst, and a sufficient quantity is passed to form a deposit of carbon approximating in quantity and distribution, the carbon

deposit normally deposited during said initial period previously described, which is characterized by a gradually increasing yield of gasoline per unit of time up to an optimum value.

The invention may be practiced with a wide variety of types of catalytic reactors and regeneration equipment. One type involves the so-called "static bed" type of operation wherein the catalyst is disposed in the reactor in the form of a stationary or static bed through which the hydrocarbons undergoing treatment are passed. Upon substantial deactivation of the catalyst, the flow of hydrocarbons thereover is discontinued, and a regenerating gas such as air is passed over the spent catalyst to burn off deposited carbon. Usually a plurality of such catalyst reactor chambers are arranged in parallel and suitably manifolded with respect to the incoming stream of treated hydrocarbons and regenerating gas, so that the operation is substantially continuous, one reactor being "on-stream" while another is being regenerated. Accordingly, a complete cycle in a given reactor involves both a conversion period and a regeneration period. In accordance with my invention the complete cycle includes an additional conditioning period. A suitable apparatus for the practice of this embodiment of the invention is shown in Figure 3.

Referring to Figure 3, a single reactor 17 is shown, partly in elevation and partly in section. Charging stock, which may consist of reduced crude or heavy gas oil is passed by line 1 and pump 2 to furnace 3. The preheated charge enters separator 4, through line 5, overhead products passing through line 6 and through opened valve 28 to a reactor or reactors (similar to 17, hence not shown) which are exercising the cracking function, valve 7 in line 8 being closed. Heavy products in the preheated charge accumulate in the bottom of separator 4 from whence they may be eliminated from the system if desired through valve 9 in line 10. Alternatively, these heavy products may be passed through valve 11 in line 12, pump 13 and valve 27 to manifold 14, valve 15 in line 16 being closed. Line 16 leads to manifolds similar to 14 (not shown) serving the other reactor or reactors (not shown) exercising, at this stage, the cracking and/or regeneration operations.

Reactor 17 contains a suitable catalyst 18 disposed on a plurality of perforated trays 19. Manifold 14 is provided with a plurality of branched pipes 20, one or more for each tray. If desired, an atomizing fluid, suitably preheated, such as steam, gas made in the process or from another source, flue gas made in the regeneration process or from an outside source, may be passed through line 21 to manifold 22, said manifold having a plurality of branched pipes 23, each side pipe corresponding to a side pipe 20 from manifold 14.

The heavy charge is distributed to a series of atomizers or sprays 24 by means of the plurality of side pipes 20. Preferably the atomizers or sprays 24 are disposed in the layers of catalyst 18 on the perforated trays 19 although they may also be disposed above the catalyst. Also, it is not necessary to have atomizers or sprays 24 in or near each tray of catalyst. While this arrangement is preferable, satisfactory results can be obtained by atomizing, vaporizing or spraying all of the heavy charge in the bottom of reactor 17. The atomizing, vaporizing or spraying of the heavy charge may be aided by the introduction of fluid through line 21.

In operating the above described apparatus to secure the benefits of this invention, the heavy portion of the charge obtained from the bottom of separator 4 is passed over the freshly regenerated hot catalyst in reactor 17, and is decomposed thereby forming the desired carbon deposit on the catalyst, while the lighter portions of the charge pass through line 6 to another reactor (not shown) which is on the cracking cycle. Passage of the heavy portion of the charge through line 14 and decomposition thereof is continued until the desired amount of carbon is deposited on the catalyst.

Vaporizable products derived by the decomposition of the heavy portion of the charge leave reactor 17 through opened valve 25 in line 26, and may be disposed of as desired. After a short preconditioning treatment, valve 27 in manifold 14, valve 25 in line 26, valve 37 in line 21, and valve 28 in line 6, are closed while valve 7 in line 8 is opened, light product from the top of separator 4 then passing over the preconditioned catalyst in reactor 17, the resulting product then being sent to conventional fractionating or condensing means (not shown) through opened valve 29 in line 30. Also at this stage, valve 15 is opened and the conditioning stock passed through line 16 to a reactor ready for the conditioning treatment, a continuous operation being thus assured.

Because of the heavy nature of the conditioning stock it is readily decomposed into carbon and other hydrocarbons, and the time required for accomplishing the conditioning treatment is very short. For example, when operating under the conditions described in connection with Figure 1, a period of about 2.5 minutes brings the catalyst to a condition similar to that shown by the catalyst after 5 minutes (Figure 1) where a relatively light gas oil was used as charge. In one series of experiments, satisfactory results have been obtained by passing preheated charge to the separator 4 at a rate of 100 volumes in unit time, separating it into 80 volumes of overhead and 20 of bottoms, pumping these bottoms at a rate of 20 volumes in unit time through line 14 for a time of 2.5 minutes which constitutes the conditioning period, and then passing the overhead from separator 4 to the reactor 17 at a rate of 80 volumes per unit of time for a time of 10 minutes which constitutes the conversion or cracking period of the cycle.

If desired, the product withdrawn through line 26 during the conditioning treatment may be recycled in the conditioning operation, for example by introducing this material through line 31 and valve 32. Alternatively, other conditioning materials may be added to the system through line 31 in addition to, or replacing in whole or part material from line 12. Suitable materials for such purposes include non-volatile hydrocarbons such as petroleum pitch, coal tar pitch, wax introduced as such or dissolved in a suitable volatile solvent such as naphtha. These materials may be suitably preheated if desired but it should be borne in mind that these are contacted with the catalyst in reactor 17 immediately after the regeneration step under which conditions the catalyst may be considerably above reaction temperature so that the addition of conditioning feed at relatively low temperatures may be necessary or desirable to aid in bringing the catalyst temperature down to the required operating temperature before the conversion or cracking cycle begins. For this rea-

son, in some cases it is necessary to cool the heavy bottoms from separator 4 before using them as a conditioning means.

It is apparent that when using a light charging stock containing little or no bottoms suitable for conditioning, conditioning materials from outside sources must be used. For convenience, stocks suitable for use in the conditioning of catalysts may be termed carbogens.

At the conclusion of the cracking cycle in which the preconditioned catalyst, prepared as previously described, is employed the regeneration cycle begins. Valve 7 in line 8 is closed as is valve 29 in line 30. Revivification gas enters through valve 33 in line 34 and leaves by valve 35 in line 36. It is apparent that one complete cycle is divided into three portions (a) preconditioning (b) cracking and (c) regeneration.

My invention may be further employed in conjunction with the so-called "moving-bed" type of catalytic cracking operation. In this type of operation, the catalyst is moved through the conversion zone during the conversion period of the cycle, and regenerated in a zone external of the conversion zone. Figure 4 illustrates a suitable apparatus and flow procedure for use in the practice of this embodiment of the invention. Referring to Figure 4, the charge, such as reduced crude or heavy gas oil is introduced by line 41 and pump 42 to furnace 43. The preheated charge enters separator 44 by means of line 45, overhead from said separator 44 passing to reactor 46 through line 47. The contact material or catalyst in reactor 46 is constantly moving downward, contact material being added through conveyor 48 and leaving through conveyor 49. Converted or cracked hydrocarbons leave reactor 46 through line 50, passing to conventional fractionating means or condensing means (not shown) as desired. Suitable feeding means or solids pumps 51 are provided at the top and bottom of reactor 46 for introducing and withdrawing the solid catalyst without substantial escape of vapor therefrom.

Spent catalyst leaving reactor 46 through conveyor 49 is regenerated in any suitable manner, one suitable form of regenerator being illustrated. This regenerator 52 contains a plurality of hearths 53, 54, 55, 56 and 57, each provided with one or more rakes 58 attached to rotatable shaft 59. Spent catalyst falls on the top hearth 53 and is distributed and agitated by means of the rake or rakes 58 which move over the surface of said hearth. The catalyst on hearth 53 is gradually moved down through the regenerator, resting in turn on hearths 54, 55, 56 and 57 and is finally discharged into conveyor 48 and moved to the top of reactor 46 to repeat the cycle.

Means are provided for contacting the catalyst in regenerator 52 with air or dilute air. For example, air or dilute air may pass through duct 60 to ducts 61, over the hearths 53, 54 and 55 and out through ducts 62 and duct 63. The regenerating fluid may be suitably warmed or cooled before entering duct 60 and part or all of the flue gas leaving 63 may be recycled after eliminating a portion which is replaced by make-up air.

A separate duct 64 is shown supplying hearth 56. Inert material such as oxygen-free flue gas is supplied to duct 64 and may suitably be flue gas from duct 63. This inert flue gas is supplied at such a rate that it forms a seal, the inert material forming a partition between hearth 56 and hearth 55. While catalyst can fall from the upper hearth

55 onto hearth 56 and then hearth 57, gaseous products on the hearth 57 and on hearth 58 cannot diffuse into the space occupied by hearth 56. Gaseous material from hearth 56 may suitably leave by duct 62' opening into duct 63.

Heavy products from the bottom of separator 44 may be eliminated in part through valve 65 in line 66 but part or all of said heavy products are passed through valve 75 in line 67, pump 68 and line 69 to sprayers or atomizers 70 in the immediate vicinity of hearth 57. The sprayers or atomizers may suitably form the teeth of the rakes passing over hearth 57. If desired, steam, flue gas, or gaseous hydrocarbons may be employed to aid in the vaporization, spraying or atomization of the heavy material from the bottom of separator 44. This may be added through line 71. The products from hearth 57 may be removed through line 72 and worked up as desired. By this process the catalyst is conditioned in the last hearth.

The conditioning treatment may be effected, wholly or partly, at other points in the cycle if desired. For example, heavy oil may be vaporized, atomized or sprayed into conveyor 48 at one or more points or it may be vaporized, sprayed or atomized into the upper portions of reactor 46.

As in the embodiment previously described, the heavy oil used in conditioning may be supplemented or replaced by material from sources other than the charge and where the charge is comparatively light, such outside sources, preferably, are employed. Conditioning oil from said outside sources may enter the cycle through line 73 and valve 74.

It will be noted that the reactor shown in Figure 4, differs from that shown in Figure 3 in that, with the former, operations are continuous. While the catalyst in reactor 46 differs in activity from top to bottom of said reactor, the integrated activity of all the material in reactor 46 is always constant regardless of the length of time the reactor has been on stream. Accordingly, the processed charge leaving reactor 46 by line 50 has constant characteristics which are highly advantageous.

A further modified embodiment, also, employing a "moving-bed" type of catalytic conversion operation is illustrated in Figure 5. In this embodiment, a suitable feed stock for the process such as a reduced crude oil is picked up from source 80 by pump 81 and passed through heater 82 and line 83 into fractionating column 84 where fractional distillation of the oil is effected. The non-volatile portion, if any, is withdrawn as bottoms through line 85 while the remaining portion is divided into light and heavy fractions which are drawn off through lines 86 and 87 respectively. The light fraction passing overhead through line 86 as a vapor is cooled in exchanger 88; and condensed in condenser 89 and part of the condensate is pumped back from condenser 89 by pump 90 to serve as reflux to column 84. Liquid from condenser 89 is pumped by pump 91 through line 92 through a suitable heater 93 and the resultant vapors passed through line 94 to reactor 95. In reactor 95, conversion to gasoline is effected in the presence of the preconditioned catalyst. If desired, vapors from line 86, may be only partially condensed to supply the required quantity of reflux, and the uncondensed vapors heated to the reaction temperature required in reactor 95. The heavier fraction separated in column 84 is withdrawn by pump 96 and passed through line 87 to heater 98, and thence to heavy

oil reactor 99 where conversion into gasoline is effected in the presence of the catalyst, and the catalyst is conditioned in accordance with my invention, for use in reactor 95.

The conversion products from reactors 99 and 95 are withdrawn through lines 100 and 101 respectively and may be suitably fractionated into tail gas, gasoline, recycle stock and tar, in a conventional system of partial condensers or fractionators 102.

Hot regenerated catalyst is carried by a conveyor system 103 and discharged into reactor 99, travelling therethrough from top to bottom and dropping through a star-feeder or solids pump 105 into reactor 95. The catalyst continues downwardly through reactor 95 and drops through a star-feeder or solids pump 106 into regenerator 107 wherein the accumulated impurities are removed by burning with air or other suitable regenerating gas introduced through 108. The hot regenerated catalyst is returned to reactor 99 through conveyor system 103, and gaseous regeneration products are withdrawn through duct 109.

From the foregoing it will be apparent that the process therein described accomplishes the object of my invention of providing a process for the catalytic conversion of hydrocarbons whereby a more favorable distribution and enhanced yield of the desired conversion products is obtained. It will further be readily apparent to those skilled in the art that while the invention has been illustrated and described with respect to a preferred operation and examples, and with reference to suitable apparatus for its practice, the invention is not limited to such exemplifications but may variously be practiced and embodied within the scope of the claims hereafter made.

What I claim is:

1. In a process for the conversion of high-boiling hydrocarbons into low-boiling hydrocarbons distilling within the gasoline boiling range, wherein said high-boiling hydrocarbons are contacted, in vapor form, with an alumina-silica cracking catalyst under reacting conditions adapted to produce the required extent of conversion into low-boiling hydrocarbons distilling within the gasoline boiling range, and wherein said catalyst in the absence of a conditioning treatment exhibits a catalytic activity characterized by an initial period of gradually increasing yield of gasoline per unit of time up to an optimum value and by the continuous formation of a carbonaceous deposit on the catalyst during said initial period, the steps, including, separating the hydrocarbon charged into a light fraction, and a heavy fraction relatively readily heat-decomposable to produce coke or carbon compared to said light fraction, passing the heavy fraction in contact with said catalyst under carbon-producing reaction conditions until a deposit of carbon is formed thereon approximating that normally deposited during said initial period, and then passing the light fraction, in vapor form, in contact with said catalyst under reacting conditions adapted to produce the required degree of conversion into low-boiling hydrocarbons distilling within the gasoline boiling range.

2. A process of converting high-boiling hydrocarbons to low-boiling hydrocarbons involving contacting said high-boiling hydrocarbons, in the vapor phase, with an alumina-silica cracking catalyst under reacting conditions adapted to continuously produce a carbonaceous deposit on the catalyst with consequent relatively short on-stream periods and a high yield and quality of

hydrocarbons distilling within the gasoline boiling range, which comprises preconditioning said catalyst prior to the conversion treatment by passing a relatively readily heat-decomposable hydrocarbon in contact with said catalyst under reacting conditions adapted to decompose it to a mixture of hydrocarbons and solid carbonaceous material, and in quantity sufficient only to deposit a coating of carbonaceous hydrocarbon material on the catalyst in an amount of about 0.5% to 2.0% by weight of the catalyst, and then passing vaporized high boiling hydrocarbons relatively stable to decomposition by heat in contact with said preconditioned catalyst under reaction conditions adapted to produce a substantial conversion thereof to low boiling hydrocarbons within the gasoline boiling range.

3. A process of catalytically cracking high boiling hydrocarbons to low boiling hydrocarbons within the gasoline boiling range and involving the concurrent production of a carbonaceous deposit on the catalyst with consequent relatively short on-stream periods, which comprises forming a relatively small amount of a carbonaceous hydrocarbon deposit on an alumina-silica cracking catalyst by passing a relatively readily heat decomposable hydrocarbon in contact with the catalyst under reaction conditions adapted to decompose the hydrocarbon to volatile hydrocarbons and carbonaceous material, thereby preconditioning the catalyst and eliminating its tendency to produce excessive coke and fixed gases at the initial portion of the conversion

period, and then passing vaporized high boiling hydrocarbons relatively stable to decomposition by heat in contact with said preconditioned catalyst under reaction conditions adapted to produce a substantial conversion thereof to low boiling hydrocarbons within the gasoline boiling range.

4. A process as defined in claim 3 wherein said readily heat decomposable hydrocarbon comprises a non-volatile fraction of a petroleum crude.

5. In a process of catalytically cracking high boiling hydrocarbons to low boiling hydrocarbons within the gasoline boiling range, the improvement which consists in passing a non-volatile readily heat decomposable fraction of a crude petroleum in contact with an alumina-silica cracking catalyst selected from the group consisting of synthetic composites of silica-gel and alumina, and activated clays, under reaction conditions adapted to decompose the hydrocarbon to volatile hydrocarbons and non-volatile carbonaceous hydrocarbon material with consequent relatively short on-stream periods, thereby preconditioning the catalyst with said non-volatile material and eliminating its tendency to produce excessive coke and fixed gases at the initial portion of a subsequent conversion period wherein hydrocarbons are passed over the catalyst to concurrently produce low boiling hydrocarbons within the gasoline boiling range and a carbonaceous deposit on the catalyst.

ROBERT F. RUTHRUFF.