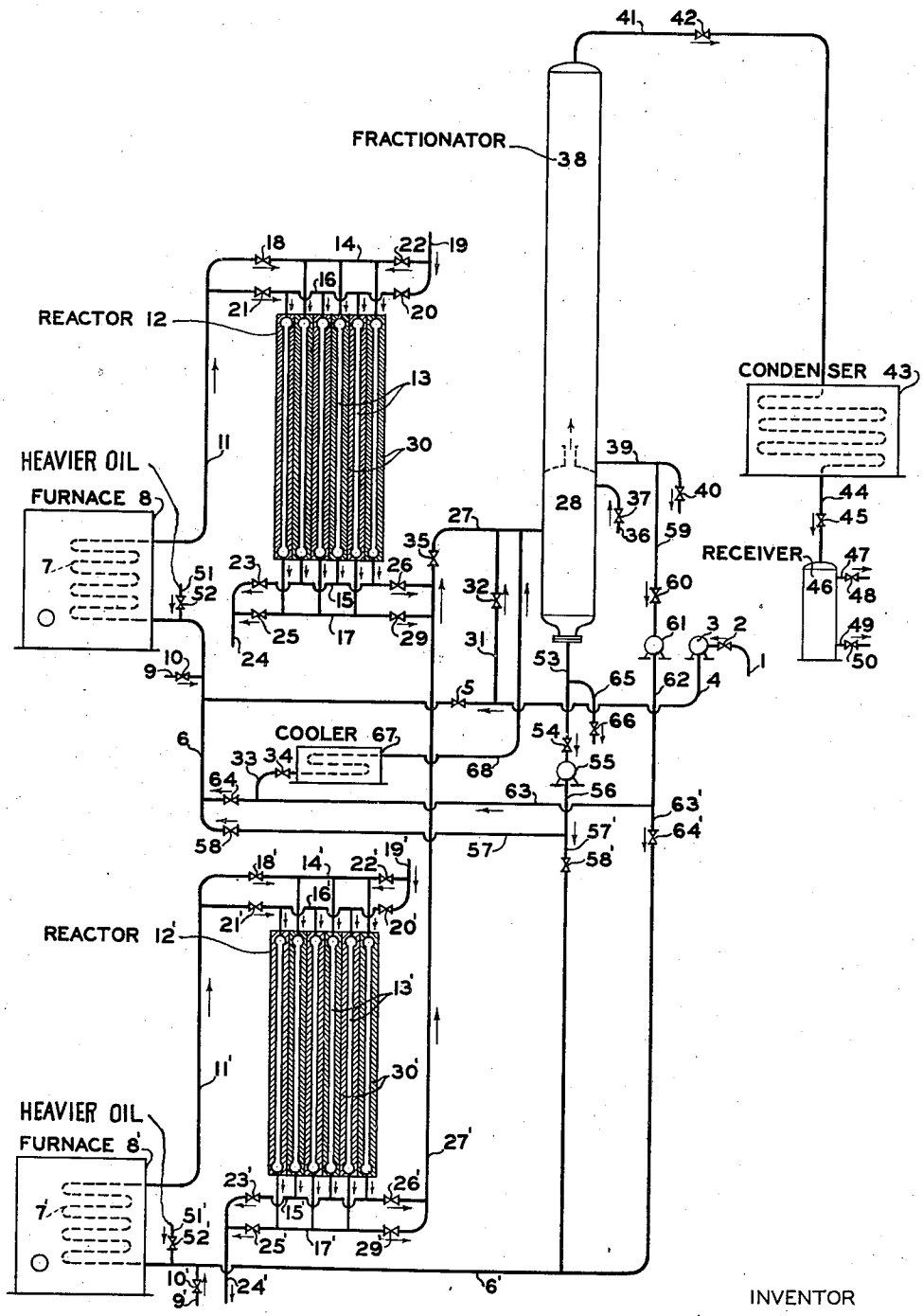
July 28, 1942. L. S. KASSEL 2,291,234

CATALYTIC CONVERSION OF HYDROCARBONS

Filed Feb. 13, 1939



INVENTOR

LOUIS S. KASSEL

BY Lee Gary

ATTORNEY

Patented July 28, 1942

2,291,234

UNITED STATES PATENT OFFICE

2,291,234

CATALYTIC CONVERSION OF HYDROCARBONS

Louis S. Kassel, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application February 13, 1939, Serial No. 256,023

6 Claims. (Cl. 196—52)

The invention relates specifically to an improved method of operation in processes involving simultaneously conducted endothermic and exothermic reactions; the endothermic reaction involving the formation and deposition of heavy carbonaceous material such as coke on a mass of contact material, such as a bed of catalyst, disposed in the zone of endothermic reaction, and the exothermic reaction involving the oxidation of previously deposited carbonaceous material from a bed of catalyst or contact mass in a separate reaction zone, heat being supplied from the exothermic to the endothermic reaction. The purpose of the invention is to regulate the quantity of carbonaceous material deposited in the endothermic reaction zone so as to approximately balance the heat generated by its subsequent oxidation in the exothermic reaction zone with the heat requirements of the endothermic reaction. This is accomplished by controlling the quantity of relatively high coke-forming components in the reactants supplied to the endothermic reaction zone.

The invention is particularly advantageous as applied to processes for the catalytic cracking of hydrocarbon oils and the subsequent more detailed description of the invention, as applied to catalytic cracking, will serve to illustrate its features and advantages. The invention may, however, be employed to advantage in any process of the general type above mentioned, including dehydrogenation, aromatization, isomerization and the like, wherein coke or other carbonaceous material is deposited on a catalyst or contact mass and periodically burned away to renew the contact surface and restore catalytic activity.

Catalytic cracking processes, in common with other processes of the general type above referred to, are of three general classes in so far as the features of the invention are concerned. The first class consists of processes in which the hydrocarbons to be treated are passed only once through the zone of endothermic reaction and the resulting products separated and recovered. The second class consists of processes wherein insufficiently converted intermediate products resulting from initial conversion of the raw charging stock are recycled to the same zone of endothermic reaction whereto the charging stock or a selected portion thereof is supplied. The third class consists of processes in which insufficiently converted intermediate products resulting from initial conversion of the raw charging stock are supplied to and further converted in a separate zone of endothermic reaction. For the sake of simplicity, the first class will be subsequently referred to as a "once through" type of operation, the second class as a "recycle" operation and the third class as a "selective" type of operation, these terms being now rather commonly accepted and understood in the industry.

The invention is applicable to each of the three general classes of processes above outlined. As applied to the once through type of operation, the objects and advantages of the invention are obtained by commingling regulated minor amounts of relatively heavy, high coke-forming hydrocarbons, formed within the system or derived from an external source, with the relatively clean charging stock of lower coke-forming characteristics supplied to the reaction zone when more coke deposition is required in this zone. As applied to a recycle operation, the invention provides for increasing the quantity of coke or carbonaceous material deposited on the contact mass in the reaction zone, when needed, by increasing the quantity of relatively heavy components included in the intermediate conversion products recycled to the reaction zone and decreasing the relative proportion of high coke-forming components in the recycle stock when less coke deposition is desired, this being accomplished by varying the quantity of heavy residual product removed from the system. This variation is reflected in the quality of the residual product with respect to the quantity of relatively light residual fractions included therein and is accomplished by varying the operating conditions employed in that zone of the system wherein the residual product recovered is separated from the lower boiling conversion products. A combination of the two methods above outlined may be employed in the selective type of operation, regulated quantities of relatively heavy, high coke-forming material being commingled with the relatively light, clean charging stock supplied to one reaction zone, when more coke deposition is required therein, and the quantity and quality of the residual product being varied to control the relative proportion of high coke-forming material in the intermediate fractions supplied to the other reaction zone.

The invention also contemplates an alternative but non-equivalent method of operation which may be employed to advantage when it is desirable to recover a residual product of uniform, good quality. In accordance with this alternative method of operation, which is applicable to any of the three classes of systems above men-

tioned, regulated minor amounts of the residual liquid product are blended with the raw charging stock or with the intermediate conversion products or with the mixture of intermediate conversion products and charging stock, as the case may be.

In processes of the general type above referred to, the quantity of heat evolved in the exothermic phase of the system is ordinarily of such magnitude that its efficient recovery is a matter of economic necessity. It is common practice to utilize the same for generating steam in a waste heat boiler but the steam thus generated is usually more than sufficient to satisfy the requirements of the process and, except in special cases where the excess steam can be otherwise usefully employed, a heat recovery system of this type is not feasible. On the other hand, considerable heat is ordinarily required at a relatively high temperature level to carry on the processing step or endothermic phase of the reaction and it is decidedly advantageous, in most instances, to transfer the heat generated in the exothermic phase of the system to the endothermic phase. However, the two phases are ordinarily not in thermal balance and it is still necessary for best economy to recover the excess heat generated in the exothermic phase or, in case there is a deficiency in the heat generated, to supply additional heat to the endothermic phase. In either case, a rather complicated and expensive system is required. When the endothermic and exothermic phases of the system are maintained in substantial thermal balance, as provided by the invention, the initial cost of the installation, as well as the expense of operating the same, is considerably reduced and the reduced cost will, in many instances, constitute the difference between a commercially successful process and an economic failure.

It should be understood that in referring to a substantial thermal balance between the endothermic and exothermic phases of the system, I refer to the reactions simultaneously taking place in the reaction zones containing the contact mass or catalytic material rather than to the overall heat requirements of the process, since the invention contemplates external cooling and heating means in other portions of the system, the object of the invention being to balance the heat evolved in the reaction zone wherein the catalyst or contact mass is being revivified with that required in the reaction zone containing the active catalytic material or contact mass, to which reactants are ordinarily supplied in preheated state and wherefrom the reaction products are ordinarily discharged to separating, condensing and collecting equipment.

Each reaction zone is alternately employed for conducting the endothermic and exothermic reactions, said reactions taking place simultaneously in separate zones. Preferably, heat is transferred from the zone of exothermic reaction to the zone of endothermic reaction through a relatively static heat transfer medium such as a bath of molten metal, molten salt or the like or directly from the metallic walls of one reactor to the other or, when desired, hot combustion gases generated by burning of the carbonaceous material during the exothermic reaction may be passed in contact with a mass of high heat capacity material such as firebrick or the like wherein it is stored and subsequently liberated to the endothermic reaction. Such relatively simple forms of reactors cannot be employed with success in processes of the type described, except when the endothermic and exothermic phases of the process are in substantial thermal balance. Otherwise a more complicated system involving the use of a circulated heating and cooling medium with provision for supplying external heat or extracting excess heat from the same between the exothermic and endothermic reactions is required.

The accompanying drawing diagrammatically illustrates a catalytic cracking apparatus in which the process of the invention may be conducted and, in conjunction with the following description, will serve to more clearly illustrate the features of the invention and various alternative modes of operation which it provides.

Referring to the drawing, hydrocarbon oil charging stock for the process which is preferably a relatively clean distillate such as gas oil, naphtha or the like, susceptible to substantially complete vaporization, is supplied through line 1 and valve 2 to pump 3 wherefrom it is directed through line 4 and may be supplied, all or in part, through valve 5 in this line and line 6 to heating coil 7 wherein it preferably is substantially completely vaporized and heated to a temperature at which the desired cracking reaction will take place upon contact of the heated vapors with the catalyst employed. Heat is supplied to coil 7 from furnace 8 and, preferably, to assist vaporization and repress thermal cracking in coil 7, regulated quantities of relatively low molecular weight material such as steam or normally gaseous hydrocarbons are commingled with the materials supplied to the heating coil, line 9 and valve 10 communicating with line 6 being provided for this purpose.

That hot vaporous hydrocarbons and low molecular weight material commingled therewith are directed from coil 7 through line 11 to reactor 12 which, in the case here illustrated, contains a plurality of elongated fluid passageways 13, each substantially filled with a bed of suitable granular catalytic material capable of promoting the cracking reaction. As indicated in the drawing, the fluid passageways 13 are connected with suitable manifolds 14, 15, 16 and 17 by branch lines in such a manner that fluid passageways 13 form two separate reaction zones, in one of which the endothermic cracking reaction is taking place while the catalyst in the other reaction zone is being revivified by burning therein carbonaceous materials deposited during a previous cracking reaction in this zone. Heated reactants from coil 7 may be supplied from line 11 through valve 18 in manifold 14 to one of the reaction zones, while oxygen-containing gases for revivifying the catalyst are supplied from line 19 through valve 20 in manifold 16 to the other reaction zone. After a predetermined period of operation, during which carbonaceous material is deposited on the catalyst in the reaction zone wherein catalytic cracking is taking place and during which the catalyst in the other reaction zone is restored to a high degree of catalytic activity by burning the carbonaceous material therefrom, the reaction zones are switched with respect to the endothermic and exothermic reactions by closing valve 18 and directing the heated reactants through valve 21 and manifold 16 into the reactor containing the revivified catalyst and by closing valve 20 and directing the revivifying gases through valve 22 and manifold 14 into the reactor containing the catalyst which now requires revivification.

When revivification of the catalyst is taking place in the reaction zone communicating with manifold 15, spent revivifying gases are discharged therefrom through valve 23 and line 24. When revivification is taking place in the reaction zone communicating with manifold 17, spent revivifying gases are discharged therefrom through valve 25 and line 24. When cracking is taking place in the reaction zone communicating with manifold 15, the resulting hot conversion products are directed therefrom through valve 26 and line 27 to separating chamber 28. When catalytic cracking is taking place in the reaction zone communicating with manifold 17, resultant hot conversion products are directed therefrom to valve 29 and line 27 to separating chamber 28.

Reactor 12, in the particular case here illustrated, comprises a nest of metallic sections 30, each containing one or a plurality of the fluid passageways 13 and so arranged that heat is transferred directly through the metallic walls of the several sections from the zone of exothermic reaction to the zone of endothermic reaction, whereby the heat required for conducting the endothermic reaction is supplied by the exothermic reaction. Although not indicated in the drawing, reactor 12 is preferably well insulated to conserve heat. It will be apparent that any other specific form of reactor, wherein efficient heat transfer from the exothermic to the endothermic zone is obtained, may be employed within the scope of the invention and, except for this qualification, the invention is not limited to the type of reactor or reactors employed. However, full advantage of the benefits to be derived from the features of the invention can best be obtained by employing one of the relatively simple and inexpensive forms of reactors which the present invention makes acceptable and satisfactory, but which will not permit efficient operation when the endothermic and exothermic reactions are not in substantial thermal balance. Some of the other forms which may be successfully employed to advantage have been previously mentioned. They include the so-called "regenerative" type and the type employing a bath of molten metal, salt or the like which acts as the heat transfer medium as well as the type illustrated which employs metal-to-metal contact between the walls of the endothermic and exothermic zones.

The stream of hot conversion products passing from the reactor to chamber 28 is preferably cooled to a temperature below that of active thermal cracking and at which the desired separation of their residual liquid and vaporous constituents is assisted in chamber 28. This may be accomplished by commingling a suitable cooling oil with the products passing through line 27. When recycle operation is employed, all or a regulated portion of the charging stock may be employed as cooling oil in line 27 by directing the same thereto from line 4 through line 31 and valve 32. In addition to, or instead of employing charging stock for this purpose, intermediate liquid conversion products formed within the system, as later described, may, when desired, be supplied to line 27 through line 33 and valve 34. Preferably, a superatmospheric pressure is employed in the endothermic reaction zone and by control of valve 35 in line 27, in conjunction with the cooling employed in line 27 and/or chamber 28, the desired separation of vapors and residual liquid is effected in the latter zone and the quantity and characteristics of the residual product thus controlled to suit requirements. Additional cooling may be provided, when required, in chamber 28 by supplying regulated quantities of a suitable cooling oil such as charging stock, intermediate liquid conversion products or the like to the upper portion of the chamber through line 36 and valve 37, suitable fractionating or contacting means of any well known form, not illustrated, being provided in the upper portion of chamber 28, when desired.

In the case here illustrated, the upper portion of the same column, within which separating chamber 28 is disposed, comprises fractionator 38 and the components of the conversion products which are not included in the residual liquid product separated in chamber 28 are supplied in vaporous state from chamber 28 to fractionator 38 wherein their heavy components which boil above the range of the desired final light distillate product, such as gasoline, are condensed to form reflux condensate comprising the intermediate liquid conversion products of the process which are withdrawn from the lower portion of the fractionator through line 39 and may be removed, all or in part, from the system to cooling and storage, or elsewhere, through valve 40 in line 39 or may be returned, as will be later described, via coil 7 to reactor 12 for further cracking treatment in this zone in commingled state with the charging stock, or they may be directed to separate catalytic cracking treatment, as will be later described.

Fractionated vapors of the desired end-boiling point, comprising normally gaseous materials and fractions of the conversion products boiling within the range of the desired gasoline, are directed from the upper portion of fractionator 38 through line 41 and valve 42 to condenser 43 wherefrom the resulting distillate passes together with uncondensed and undissolved gases through line 44 and valve 45 to collection and separation in receiver 46. The uncondensed and undissolved gases are released from the receiver through line 47 and valve 48 and the distillate collected in this zone is removed therefrom to storage or to any desired further treatment through line 49 and valve 50. When desired, regulated quantities of the distillate collected in receiver 46 may be returned by well known means, not illustrated, to the upper portion of fractionator 38 to serve as a cooling and refluxing medium in this zone.

The drawing illustrates an apparatus in which the once-through, recycle or selective cracking type of operation may be accomplished. Any of these three types may be selected to suit requirements and they will be discussed separately in the subsequent description of the drawing.

When once-through operation is employed, the intermediate liquid conversion products condensed from vapors formed in fractionator 38 are removed from the system through line 39 and valve 40. Since a light charging stock is preferably employed in this type of operation, the amount of coke deposited on the catalyst in reactor 12 will ordinarily be insufficient to satisfy the heat requirements of the cracking operation in this zone and to increase the coke deposition to the desired degree, a regulated quantity of relatively high coke-forming oil is supplied through coil 7 to reactor 12 with the light charging stock. Any suitable oil from outside the system may be employed for this purpose and line 51, controlled by valve 52, is provided for supplying the same

through line 6 to coil 7 with the charging stock which, in this type of operation, is supplied directly to coil 7, as previously described.

The invention also contemplates the use of regulated quantities of the residual liquid conversion products separated from the vapors in chamber 28 as the coke-forming material. When this mode of operation is employed, residual liquid withdrawn from the lower portion of chamber 28 through line 53 is directed through valve 54 in this line to pump 55 and supplied therefrom in regulated quantities through line 56, line 57, valve 58 and line 6 to heating coil 7, together with the charging stock which is also supplied to line 6, as previously described, from pump 3. That portion of the residual liquid from chamber 28 not supplied, as described, to coil 7 is removed from the system through line 65 and valve 66 to cooling and storage or elsewhere, as desired.

When recycle operation is employed, all or a regulated portion of the reflux condensate formed in fractionator 38 is directed from line 39 through line 59 and valve 60 to pump 61 wherefrom it is supplied through line 62, line 63, valve 64 and line 6 to coil 7. In this type of operation the charging stock may be either a relatively low-boiling distillate or an oil of relatively wide boiling range and, depending upon its characteristics, may be supplied directly to coil 7 through line 4, valve 5 and line 6 or directed from line 4 through line 31, valve 32 and line 27 into chamber 28. The latter flow is employed in case the charging stock contains a quantity of high-boiling components in excess of that required to give the desired coke deposition in reactor 12. Any such excess of high-boiling components in the charging stock, as well as the excess of high-boiling components in the conversion products discharged from reactor 12, are included with the residual liquid removed from chamber 28 by regulating the temperature and pressure conditions employed therein, the remaining components of the charging stock and of the conversion products which boil above the range of the desired overhead product from fractionator 38 being condensed in this zone as reflux condensate and supplied therefrom, as previously described, to coil 7.

It will be apparent that, when the last described method of operation is employed, the residual liquid removed from chamber 28 may, in some instances, be robbed of desirable low-boiling fractions (which are included as high-boiling components in the reflux condensate formed in fractionator 38) to such an extent that the residual liquid product is of an inferior quality. When this condition would arise, I preferably employ an alternative method of operation in which conditions are so regulated in chamber 28 as to produce a good quality residual liquid product and, to compensate for the deficiency of high coke-forming components in the cracking stock, regulated minor amounts of the whole residual liquid product are returned by a line 53, valve 54, pump 55, line 56, line 57, valve 58 and line 6 to heating coil 7, the remaining quantity of residual liquid being removed from the system to cooling and storage or elsewhere, as desired, through line 65 and valve 66.

When the selective type of cracking operation is utilized, a separate heating coil 7', furnace 8' and reactor 12' are provided, as indicated in the drawing, for separate treatment of the reflux condensate from fractionator 38. This separate cracking equipment may be of the same general form, but not necessarily the same size as the corresponding equipment in which the charging stock is treated. The invention is not limited to the same general type of equipment in the two cracking steps but, to simplify the present description, the same general type of equipment is illustrated for each of the cracking steps in the drawing. The reference numbers designating the different portions of the equipment employed in the charging stock cracking step are duplicated by corresponding prime numbers, indicating corresponding portions, in the reflux cracking step. The functions of the corresponding portions of the equipment are the same and the foregoing description of their functions and operations, as applied to the charging stock cracking step, also apply to the reflux cracking step.

With the selective cracking operation, reflux condensate from fractionator 38 is supplied by means of pump 61 through line 62, line 63', valve 64' and line 6' to coil 7', steam or other light molecular weight material such as hydrocarbon gases being admitted to line 6', when desired, through line 9' and valve 10'. With this type of operation, the charging stock is preferably a light oil which is supplied directly to coil 7 in the manner previously described. When, due to the desirability of producing a good quality liquid residue, the reflux condensate supplied to coil 7' does not contain a sufficient quantity of high coke-forming constituents, regulated minor quantities of the residual liquid product may be supplied from pump 55 through line 56, line 57', valve 58' and line 6' to coil 7' or a suitable relatively heavy high coke-forming oil from an external source may be supplied in regulated quantities to line 6' through line 51' and valve 52'.

The conversion products discharged from reactor 12' are directed through line 27', line 27 and valve 35 to chamber 28 whereby they are separated into the vaporous and residual liquid components in this zone, together with the conversion products from reactor 12.

While the invention is not limited to the use of any specific cracking catalyst, it should be one which will satisfactorily withstand temperatures during revivification within the range or somewhat higher than those suitable for accomplishing the catalytic cracking reaction, in order that heat for the latter may be supplied directly to the reaction zone wherein catalytic cracking is taking place from the reaction zone wherein the catalyst is being revivified, the temperature difference in these two zones being sufficient to effect good heat transfer therebetween. So long as the temperature level at which the catalyst may be successfully revivified is sufficiently high, the temperature level prevailing in the zone wherein catalytic cracking is taking place may be regulated to suit requirements, since the temperature in the revivifying zone may be controlled to suit requirements by regulating the relative proportions of oxygen and inert materials in the revivifying gases and by controlling the rate of flow of the revivifying gases through the catalyst bed being revivified. One specific catalyst which possesses a high degree of activity and meets the requirements of withstanding fairly high revivification temperatures comprises a silica-alumina mixture from which alkali metal ions are substantially eliminiated during its preparation to prevent fusing during revivification. This catalyst may advantageously contain minor amounts of other materials such

as, for example, zirconia which will retard shrinkage of the catalyst particles during revivification at high temperatures.

When employing a catalyst such as above mentioned, and a relatively light charging stock such as gas oil, the catalytic cracking reaction is preferably conducted at a temperature of the order of 900 to 1100° F., preferably with a gauge pressure of the order of 10 to 50 pounds, or more, per square inch with a sufficient quantity of steam or other low molecular weight material present to materially reduce the effective pressure, preferably to approximately atmospheric.

In general, paraffins can be catalytically cracked to produce high yields of gasoline with less coke deposition than oils containing a high proportion of olefins and/or aromatics but conditions within the range above given may be selected for any of the three types of oil mentioned as well as mixtures thereof and for the type of operation employed.

Preferably, the cracking stock is supplied to the catalytic reaction zone at a temperature of the order of 875 to 950° F., or thereabouts, and the heat supplied to this zone from the exothermic phase of the system is sufficient to maintain the desired temperature in the catalytic cracking zone.

The pressure employed in separating chamber 28 may be varied from substantially the same as that employed in the catalytic cracking zone down to substantially atmospheric pressure, depending upon the desired split-up between residual liquid and intermediate liquid conversion products. Controlled cooling of the conversion products prior to their introduction into chamber 28 and within that zone will also assist in controlling the characteristics of the residual liquid product and the intermediate liquid conversion products. Normally, the conversion products are cooled prior to their introduction into chamber 28 to a temperature of the order of 600 to 800° F., or thereabouts, depending upon the pressure employed in chamber 28 and the cooling accomplished within this zone. The temperature of the vapors entering fractionator 38 will range, for example, from 500 to 750° F., or thereabouts, depending upon the pressure employed and the amount of heavy high coke-forming fractions which it is desired to include in the reflux condensate formed in this zone. The quantity of residual liquid recovered from the system may vary from 2 to 20%, or thereabouts, based on the raw oil charging stock, depending upon the operating conditions employed and the desired characteristics of the intermediate liquid products with respect to the quantity of high coke-forming components included therein and upon the quantity of residual liquid returned to the catalytic cracking zone.

As an example of one specific operation of the process, conducted in an apparatus such as illustrated and above described, employing as charging stock a straight run paraffinic gas oil of about 34° A. P. I. gravity, the charging stock is commingled with a small amount of residual liquid, comprising a portion of the residual liquid product removed from chamber 28, and with approximately 100 mol per cent of steam. The mixture is heated in coil 7 to an outlet temperature of approximately 910° F. with a gauge pressure at this point in the system of approximately 75 pounds per square inch and is supplied at approximately this temperature and pressure to reactor 12 wherein it is passed alternately through the two reaction zones in contact with active catalyst, while the catalyst in alternate reaction zones is being revivified. The revivifying gases comprise combustion gases containing approximately 3% of air and are supplied to the reactor at a temperature of approximately 900° F. The catalyst employed comprises catalyst granules or pellets of substantially uniform size and shape containing approximately 89.5% alumina, approximately 3% silica and approximately 7.5% of zirconia. The quantity of catalyst employed amounts to approximately 0.33 cubic foot per cubic foot of hydrocarbon (measured as liquid) contacted with the catalyst per hour and the volume of revivifying gases employed amounts to approximately 2000 cubic feet, per cubic foot of catalyst, per hour. Approximately 60 minute periods of cracking and revivification are employed in each reaction zone. The conversion products leave reactor 12 at a temperature of approximately 950° F. and a superatmospheric pressure of about 18 pounds per square inch. Substantially the same pressure is employed in chamber 28 and conversion products are cooled prior to their introduction into this zone to a temperature of approximately 675° F. by commingling therewith regulated quantities of the reflux condensate formed in fractionator 38 after the latter has been cooled to a temperature of approximately 400° F. Approximately 5% of residual liquid, based on the charging stock, is removed from chamber 28, approximately 3% of this material being recovered and approximately 2% being recycled to heating coil 7. The pressure in fractionator 38 is substantially equalized with that employed in chamber 28. The reflux condensate formed in fractionator 38 has a boiling range of approximately 400 to 700° F. and contains approximately 75% of material boiling from 400 to 600° F. and approximately 10% of material boiling above 650° F. Reflux condensate is supplied, together with approximately 100 mol per cent of steam to heating coil 7' wherein it is heated to an outlet temperature of approximately 930° F. at a gauge pressure of about 75 pounds per square inch. The vapor steam mixture enters reactor 12' at approximately this temperature and pressure and the operation of reactor 12' is similar to that above outlined for reactor 12. The conversion products leave reactor 12' at a temperature of approximately 975° F., are commingled with the conversion products in reactor 12, reduced to a temperature of about 675° F., as above described, and introduced into chamber 28.

The above described operation will yield per barrel of charging stock, approximately 80% of 400° F. end-point gasoline having an octane number of approximately 82 as determined by the motor method and approximately 15% of gases containing a high concentration of readily polymerizable olefins. The residual product comprises a satisfactory fuel oil and, as above indicated, amounts to approximately 3% of the charging stock.

I claim as my invention:

1. In a process wherein endothermic and exothermic reactions are simultaneously conducted, the endothermic reaction involving the formation and deposition of heavy carbonaceous material, such as coke, on a contact mass through which a stream of hydrocarbon reactants is passed and the exothermic reaction involving the oxidation, from a similar mass of contact material, of such carbonaceous material deposited

thereon during a prior endothermic reaction, and heat being transferred from the exothermic to the endothermic reaction, the improvement which comprises increasing the amount of such carbonaceous material deposited on the contact mass in the endothermic phase of the system, so as to maintain the exothermic and endothermic reactions substantially in thermal balance, by adding relatively heavy, high coke-forming constituents to said stream of hydrocarbon reactants.

2. The process defined in claim 1, further characterized in that said stream of hydrocarbon reactants consists essentially of relatively low-boiling hydrocarbons which are supplied to the zone of endothermic reaction in heated substantially vaporous state and to which regulated minor quantities of higher boiling hydrocarbons are added to increase carbon formation and deposition on the contact mass during said endothermic reaction.

3. The process defined in claim 1, further characterized in that said stream of hydrocarbon reactants comprises a mixture of low-boiling hydrocarbons from an external source and intermediate liquid conversion products formed within the system, said mixture being supplied to the zone of endothermic reaction in heated substantially vaporous state and the composition of said intermediate liquid products, with respect to their heavy, high coke-forming constituents, being controlled by varying the quantity of residual liquid fractions separated from the vaporous conversion products prior to their fractionation for the formation of said intermediate liquid fractions.

4. The process defined in claim 1, further characterized in that said stream of hydrocarbon reactants comprises a mixture of low-coke-forming hydrocarbons from an external source and low-coke-forming intermediate liquid conversion products formed within the system, regulated minor quantities of residual liquid conversion products formed within the system being added to asid mixture to increase the amount of carbon formation and deposition in the zone of said endothermic reaction.

5. In the catalytic cracking of hydrocarbon distillates of relatively low coke-forming tendency, wherein carbonaceous matter is deposited on the catalyst during the endothermic cracking reaction, while simultaneously oxidizing from a separate mass of the catalyst carbonaceous matter deposited thereon during a prior cracking reaction, and heat is transferred from the exothermic oxidizing reaction to the endothermic cracking reaction, the improvement which comprises adding to the distillate to be cracked an oil of higher coke-forming tendency than the distillate in an amount such as to maintain the exothermic and endothermic reactions substantially in thermal balance.

6. In the catalytic treatment of hydrocarbons wherein carbonaceous matter is deposited on the catalyst during an endothermic reaction of the hydrocarbons, while simultaneously oxidizing from a separate body of the catalyst carbonaceous matter deposited thereon during a prior endothermic reaction of the hydrocarbons, and heat is transferred from the exothermic oxidizing reaction to the endothermic hydrocarbon reaction, said hydrocarbons being too low in coke-forming tendency to deposit on the catalyst during the endothermic reaction sufficient carbonaceous matter to supply, on oxidation thereof, the heat requirements of the endothermic reaction, the improvement which comprises adding to the hydrocarbons, prior to the catalytic treatment thereof, hydrocarbons of higher coke-forming tendency in an amount such as to maintain the exothermic and endothermic reactions substantially in thermal balance.

LOUIS S. KASSEL.