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HYDROCARBON CONVERSION

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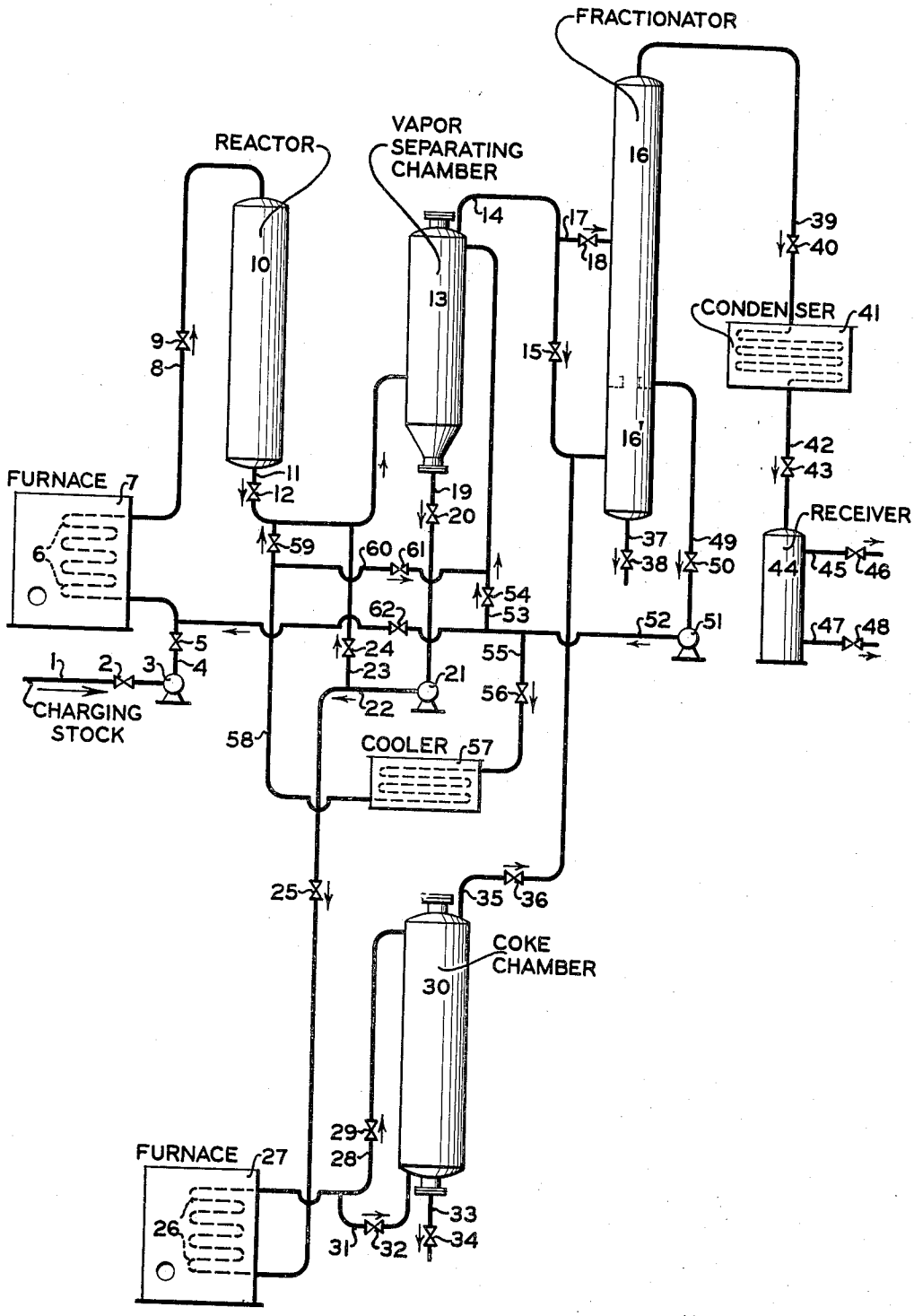

INVENTORS

ROLAND B. DAY

ELMER R. KANHOFER

BY Lee Gary

ATTORNEY

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HYDROCARBON CONVERSION

Roland B. Day and Elmer R. Kanhofer, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates to a process for the production of high octane rating gasoline from hydrocarbon oils heavier than gasoline and more specifically it relates to a process for the catalytic conversion of hydrocarbon oil in which the insufficiently converted hydrocarbons from the catalytic cracking step are subjected to pyrolytic treatment, the heavier ends thereof reduced to a substantially dry coke and the vaporous material separated from the heavier ends returned to the catalytic step for further conversion.

In processes for the catalytic cracking of hydrocarbon oil and especially those in which insufficiently converted hydrocarbons are recycled, it has been shown that a high percentage of aromatic hydrocarbons and particularly polynuclear aromatics such as diphenyl, naphthalene, anthracene, and the like, are formed and that these materials account for a large proportion of the carbonaceous substances deposited upon the catalyst particles resulting in a more rapid lowering of the catalyst activity than is encountered when passing clean unconverted oils in contact with such catalyst. In commercial practice it is not uncommon to subject the charging stock to catalytic conversion in a once-through operation and then thermally crack the insufficiently converted oils in a thermal cracking system. In a once-through operation due to the reduction in the formation of carbonaceous substances upon reactivation of the used catalytic material, lower peak reactivating temperatures are encountered than might be otherwise encountered if recycling were employed, thus minimizing the danger of overheating the catalytic material and permanent loss of catalytic activity

We have found that if the insufficiently converted hydrocarbons in the catalytic conversion step are subjected to thermal treatment under conditions of temperature and pressure optimum for the polymerization of the above mentioned aromatic hydrocarbons, these materials may be removed from the system as a heavy liquid residue or as a substantially dry coke and that the vapors supplied to and evolved in this latter treatment are substantially free of such materials and may be subjected to further catalytic conversion in the absence of any undue formation of carbonaceous substances on the catalytic material.

The principal object of this invention, therefore, is to produce a catalytically cracked gasoline of high octane rating with a minimum deposition or formation of carbonaceous substances on the catalytic material during conversion.

One feature of this invention involves the preparation of catalytic cracking stock from the heavy conversion products formed in the catalytic conversion step by subjecting the insufficiently converted hydrocarbons including those boiling above the gasoline products to a pyrolytic treatment wherein undesirable carbon forming constituents are converted into a heavy liquid residue or reduced to a substantially dry coke.

Another feature of this invention is the method employed in cooling the conversion products from catalytic cracking with the reflux condensate comprising a major proportion of hydrocarbons which have undergone pyrolytic treatment whereby these hydrocarbons may be returned for further pyrolytic treatment to insure substantially complete removal of the undesirabe carbon forming constituents.

In one embodiment the invention comprises heating and vaporizing a charging oil, passing the heated vapors at cracking temperature in contact with a mass of granular cracking catalyst, separating the conversion products into two fractions, a light fraction consisting essentially of gasoline and normally gaseous products and a heavy fraction consisting essentially of insufficiently converted hydrocarbons, supplying said heavy fraction to a coking chamber wherein non-vaporous materials supplied to and formed therein are reduced to a substantially dry coke, commingling the vapors supplied to and generated within said coking chamber with said light fraction, fractionating the mixture to separate fractionated vapors boiling substantially in the range of gasoline from the higher boiling hydrocarbons which are condensed as reflux condensate, supplying said reflux condensate to the catalytic conversion step, and condensing said fractionated vapors.

In a more specific embodiment the invention set forth above is further characterized by the steps which include cooling the conversion products from the catalytic conversion step with a portion of the reflux condensate, said reflux condensate being introduced as quenching oil to the conversion products and as a cooling and refluxing medium to the vapor separating chamber wherein gasoline boiling range materials are separated from the insufficiently converted hydrocarbons, and the insufficiently converted hydrocarbons or heavy fraction are heated to a coking temperature before introduction to the coking chamber.

The accompanying diagrammatic drawing illustrates in conventional side elevation one specific form of the apparatus which may be employed to accomplish the objects of the invention.

Referring to the drawing, charging stock comprising, for example, a hydrocarbon oil amenable to catalytic cracking, such as, for example, naphtha, kerosene, light and heavy gas oils or any mixture thereof is supplied through line 1 containing valve 2 to pump 3. Pump 3 discharges through line 4 containing valve 5 into heating coil 6 which receives heat from furnace 7. Preferably also, reflux condensate separated in the manner to be described is commingled with the charging oil in line 4 and subjected to treatment in commingled state therewith in the manner to be described. The oil in passing through coil 6 is vaporized and heated to a cracking temperature which may range, for example, from 800 to 1200° F., preferably while being maintained at a pressure of the order of substantially atmospheric to 100 pounds or more per square inch. The heated vapors leaving coil 6 are directed through line 8 containing valve 9 into catalytic reactor 10 containing catalytic material capable of effecting the desired conversion reaction.

In the case here illustrated, reactor 10 may comprise, for example, a zone of the heat exchanger type wherein the catalyst is contained in a plurality of elongated tubular elements of relatively small diameter and wherein provisions are made for passing some suitable heat convective medium such as combustion gases in contact with the exterior of said elongated tubular elements whereby to supply heat to the reactants during conversion and to effect cooling of the mass of catalytic material during reactivation. Reactor 10, on the other hand, may comprise a cylindrical vessel which is well insulated to reduce radiation losses and which contains one or a plurality of beds of catalytic material wherein the reaction may be accomplished substantially adiabatically.

In the catalytic cracking of hydrocarbons relatively large amounts of carbonaceous substances are formed which deposit upon the catalytic material thereby reducing its active surface and necessitating reactivation at periodic frequent intervals. The present invention contemplates reactivating the used catalytic material in the usual manner, such as, for example, by passing oxygen-containing reactivating gases in contact with the used catalytic material and removing carbonaceous substances as combustion gases along with the spent reactivating gases. It is desirable, therefore, in order that the operation may be carried out as a continuous process to employ at least two reactors and in some instances more than two reactors so that while the catalytic material in one reactor is being used for effecting conversion of the hydrocarbon reactants the catalytic material in the other or others may be undergoing reactivation.

Catalysts which have been found to be effective in the catalytic cracking of hydrocarbon vapors may comprise pellets or granules of silica or other siliceous and refractory materials composited with compounds selected from the group consisting of alumina, zirconia, and thoria. In addition, the hydrosilicates of alumina, acid treated clays, or the like, have also been found to be effective in the cracking treatment of hydrocarbon vapors. Although the catalysts above recited are generally considered to be the preferred catalysts their use is not to be construed as a limiting feature, for various other catalysts well known to those in the art may be employed within the broad scope of the invention.

The conversion products leaving reactor 10 by way of line 11 containing valve 12 are preferably quenched by commingling therewith any one of several hydrocarbon oil fractions separated in the manner to be described to cool the conversion products to a temperature at which the subsequent separation into light and heavy fractions may be accomplished which may range, for example, from 550 to 750° F. The mixture of cooling oil and conversion product in line 11 is supplied to vapor separating chamber 13 which may be operated at a pressure of substantially the same order as that existing at the outlet of reactor 10. In the accompanying drawing chamber 13 is illustrated as a flash distilling chamber wherein vaporous materials under the operating conditions of temperature and pressure are flash distilled from the heavier liquid hydrocarbons. The invention, however, also contemplates the use of a flash distilling chamber which is provided with one or a plurality of bubble trays, perforated plates or the like which aid in accomplishing the desired separation. When desired, a fractionating device may be employed in the place of a flash distilling chamber, however, the former is generally preferred since only a rough separation is required in chamber 13.

The mixture of cooling oil and conversion products supplied to chamber 13 is substantially separated therein into two fractions, a light fraction consisting essentially of gasoline boiling range hydrocarbons and normally gaseous products and a heavy fraction consisting essentially of the cooling oil and insufficiently converted hydrocarbons. Preferably also, and in accordance with the objects of this invention, cooling oil of the type to be described more fully later is supplied to the upper portion of chamber 13 as a cooling and refluxing medium in controlling the end point of the vapors separated therein.

Vapors separated in chamber 13 may be recovered from this step as a product of the process but, since only a rough separation is accomplished in this chamber the vapors are preferably subjected to fractionation. Fractionation may be accomplished by directing the vapors through line 14 containing valve 15 into vaporizing and separating zone 16' which forms the lower portion of fractionator 16. Preferably, however, since these vapors contain substantially no residual liquid hydrocarbons or only a small proportion thereof they are directed through valve 17 containing valve 18 and introduced to fractionator 16 at some intermediate point where the composition of the vapors present therein is approximately the same as that of the vapors supplied thereto and the fractionation accomplished as subsequently described.

The heavy fraction separated in chamber 13, including both the insufficiently converted hydrocarbons and the cooling oil, is removed from the lower portion thereof by way of line 19 and directed through valve 20 to pump 21. Pump 21 discharges through line 22 and a portion of the heavy fraction in line 22 may be supplied to line 11 as the quenching medium for the conversion products by way of line 23 containing valve 24. If desired, a cooler or heat exchanger may be interposed in line 23 for cooling the heavy fraction to a temperature at which it may be used as the quenching oil. Preferably, however, reflux condensate separated in the man-

ner to be described is employed as a quenching medium in line 11 thus obviating the use of the heavy fraction from line 22, although, in some cases, either or both may be employed, when desired. The residual portion or all of the heavy fraction in line 22 is directed through valve 25 into heating coil 26 which receives heat from furnace 27. The heavy fraction in passing through coil 26 is raised to a temperature at which the desired conversion reaction is accomplished which may range, for example, from 800 to 1000° F., preferably while being maintained under a superatmospheric pressure of the order of 50 to 500 pounds per square inch.

The heated oil leaving coil 26 is directed through line 28 containing valve 29 into coke chamber 30 wherein residual liquid hydrocarbons, including those supplied to and those formed in the pyrolytic treatment, are reduced to substantially dry coke. If desired, the heated heavy fraction in line 28 may be directed through line 31 containing valve 32 into the lower portion of chamber 30, the vapors separated therein passing in contact with the bed of coke or carbonaceous substances formed within this chamber. Intermediate point injection at one or several points in coke chamber 30 may be employed, if desired, to aid in preventing the entrainment of carbonaceous particles or heavy residual liquids with the vapors removed from this chamber, and since means for accomplishing this are well known such means are not illustrated. Chamber 30, on the other hand, may be employed as the vaporizing and separating chamber wherein non-vaporous liquid residue is separated from the vaporous reaction products and in such cases the non-vaporous liquid residue may be removed from chamber 30 by way of line 33 containing valve 34, recovered as a product of the process or subjected to any desired further treatment. When chamber 30 is employed as a coke chamber line 33 and valve 34 may be utilized during the cleaning out period as a cooling line through which steam or water may be introduced. Preferably also, in a coking operation in order that the process may be made continuous two or more coking chambers are employed so that while coke is being formed in one or more chambers the other or others may be cleaned.

Vapors supplied to and those evolved within chamber 30 are directed through line 35 containing valve 36 into line 14 by means of which they are introduced to vaporizing and separating zone 16' in fractionator 16. Non-vaporous liquid residue and in some cases other carbonaceous materials carried from chamber 30 in the vapors are substantially separated from the vaporous reaction products in zone 16' and removed therefrom by way of line 37 containing valve 38, recovered as a product of the process or subjected to any desired further treatment. Vapors separated in zone 16', which in some cases may include the vapors from chamber 13, are subjected to fractionation in the upper portion of fractionator 16 to separate fractionated vapors boiling substantially in the range of gasoline from the higher boiling hydrocarbons and the latter condensed as reflux condensate.

Fractionated vapors from fractionator 16 are conducted through line 39 containing valve 40 to cooling and condensation in condenser 41. Distillate, together with undissolved and uncondensed gases from condenser 41, is directed through line 42 containing valve 43 into receiver 44 wherein the distillate and gases are collected and separated. Undissolved and uncondensed gases collected and separated in receiver 44 are directed through line 45 containing valve 46, recovered as a product of the process or subjected to any desired further treatment. A portion of the distillate collected and separated in receiver 44 may be returned to the upper portion of fractionator 16 by well known means, not illustrated, as a refluxing and cooling medium in controlling the end point of the fractionated vapors, while the residual portion thereof is removed from receiver 44 by way of line 47 containing valve 48, recovered as a product of the process or subjected to any desired further treatment.

Reflux condensate separated in fractionator 16 is directed through line 49 containing valve 50 to pump 51. Pump 51 discharges through line 52 and a portion of the light reflux condensate may be directed through line 53 containing valve 54 into the upper portion of chamber 13 as a refluxing and cooling medium. Preferably, however, since the reflux condensate in line 52 will ordinarily be at a higher temperature than the top temperature of chamber 13, a cooler portion of the reflux condensate supplied to line 53 in the manner to be described is introduced to chamber 13 as the refluxing and cooling medium.

In the preferred embodiment, therefore, a portion of the reflux condensate in line 52 is directed through line 55 containing valve 56 to cooling in cooler 57. Cooled reflux condensate leaves cooler 57 through line 58 and a portion may be directed through valve 59 into line 11 for use in quenching the conversion products as previously described. The residual portion of the cooled reflux condensate in line 58, or all, may be directed through line 60 containing valve 61 into line 53 for use in the manner previously described. The residual portion of the reflux condensate in line 52 is directed through valve 62 into line 4 where it commingles with the charging oil for treatment in the manner previously described.

An example of one specific operation of the process as it may be accomplished in an apparatus such as illustrated and above described is approximately as follows: Charging oil, a 33° A. P. I. gravity Mid-Continent gas oil, is vaporized and heated to a temperature of 950° F. The heated vapors are passed in contact with a mass of synthetically prepared silica-alumina-zirconia catalyst at a superatmospheric pressure of 40 pounds per square inch. The conversion products leaving the catalytic reaction zone are cooled to a temperature of 600° F., by commingling therewith cooled reflux condensate supplied in the manner to be described. The mixture of cooling oil and conversion products are supplied to a vapor separating chamber operated at a superatmospheric pressure of approximately 30 pounds per square inch, cooled reflux condensate being supplied to the upper portion of this chamber as the refluxing and cooling medium to aid in controlling the end point of the vapors separated therein. Vapors of approximately 400° F., end point are separated from the higher boiling products supplied to chamber 13 and the latter, including both insufficiently converted hydrocarbons and cooling oil, are heated to a temperature of approximately 900° F., and supplied to a coking chamber operated under a superatmospheric pressure of 100 pounds per square inch.

Non-vaporous hydrocarbons supplied to the coke chamber and formed in the treatment therein are reduced to a substantially dry coke and the

vapors, including those supplied to the coke chamber and evolved therein, are commingled with the vapors from the vapor separating chamber and the mixture fractionated to separate fractionated vapors of approximately 400° F., end point from the higher boiling hydrocarbons, the former cooled, condensed, and recovered as a product of the process and the latter condensed as reflux condensate in the fractionator. A portion of the reflux condensate is cooled to a temperature of approximately 500° F., and a portion of the cooled reflux condensate commingled with the conversion products as cooling oil while the residual portion thereof is supplied as a cooling and refluxing medium into the upper portion of the vapor separating chamber. The residual portion of the reflux condensate is supplied to the catalytic conversion step for further treatment.

From an operation employing conditions as above described one may obtain approximately 76% of 400° F., end point gasoline of approximately 75 octane number, approximately 30 pounds of coke per barrel of charge, the balance being carbon on the catalyst, gas and loss.

We claim as our invention:

1. A process for the conversion of hydrocarbon oil which comprises passing vapors of said hydrocarbon oil at a cracking temperature in contact with a mass of granular cracking catalyst to effect conversion thereof, cooling the resulting cracked products, separating the cooled products into a light vapor fraction consisting essentially of hydrocarbons in the gasoline boiling range and reflux condensate, supplying said reflux condensate at a coking temperature to a coke chamber and therein reducing non-vaporous materials supplied to and formed therein to substantially dry coke, commingling vapors generated within said coke chamber with said light fraction, fractionating the mixture to separate fractionated vapors boiling substantially in the range of gasoline and reflux condensate, supplying the last mentioned reflux condensate to the catalytic conversion step, and finally condensing the fractionated vapors.

2. A process for the conversion of hydrocarbon oil which comprises heating and vaporizing said hydrocarbon oil, passing the heated vapors at a cracking temperature in contact with a mass of granular cracking catalyst to effect conversion thereof, cooling the resulting cracked products by commingling therewith a cooling oil formed within the system, supplying the mixture of cooling oil and conversion products to a vapor separating zone and therein separating relatively light cracked vapors from heavier hydrocarbons separated as reflux condensate, heating said reflux condensate to a coking temperature and thereafter reducing the non-vaporous liquid portion thereof to substantially dry coke, commingling vapors formed in the coking step with said light cracked vapors, fractionating the mixture to separate fractionated vapors boiling substantially in the range of gasoline and reflux condensate, supplying the last mentioned reflux condensate to the catalytic conversion step, and finally condensing the fractionated vapors.

3. The process defined in claim 2 further characterized in that a portion of the reflux condensate is commingled with the conversion products as the cooling oil to this step.

4. The process defined in claim 2 further characterized in that a portion of the first mentioned reflux condensate is commingled with the conversion products as the cooling oil to this step.

5. A process for the conversion of hydrocarbon oil which comprises heating and vaporizing said hydrocarbon oil, passing the vapors at a cracking temperature through a confined zone containing a cracking catalyst to effect conversion thereof, quenching the resulting cracked products by commingling therewith a cooler hydrocarbon oil, supplying the mixture of conversion products and cooling oil to a vapor separating chamber and therein separating relatively light cracked vapors consisting essentially of hydrocarbons in the gasoline boiling range from heavier hydrocarbons separated as reflux condensate, heating said reflux condensate to a coking temperature, supplying the heated reflux condensate to a coke chamber wherein non-vaporous liquid hydrocarbons introduced and formed within said coke chamber are reduced to substantially dry coke, supplying vapors, formed within said coke chamber to a vaporizing and separating zone and therein separating liquid residue from cracked vapors, fractionating the last mentioned cracked vapors with the first mentioned cracked vapors to form reflux condensate, supplying the last mentioned reflux condensate to the catalytic conversion step, and finally condensing the fractionated vapors.

6. The process defined in claim 5 further characterized in that a portion of the last mentioned reflux condensate is cooled and the cooled reflux condensate supplied to the upper portion of the vapor separating chamber to aid in controlling the end point of the vapors withdrawn therefrom.

7. The process defined in claim 5 further characterized in that a portion of the reflux condensate is cooled and the cooled reflux condensate commingled with the conversion products as the cooling oil.

8. The process defined in claim 5 further characterized in that a portion of the first mentioned reflux condensate is commingled with the conversion products as the cooling oil.

9. A process for the conversion of hydrocarbon oil which comprises subjecting said oil to catalytic cracking, separating from the resultant cracked products a vapor fraction comprising hydrocarbons boiling within the range of gasoline and a heavier fraction including substantially all the hydrocarbons boiling above the range of gasoline, introducing said heavier fraction to a coking zone and therein reducing non-vaporous materials supplied to and formed therein to substantially dry coke, removing vapors introduced to and generated within the coking zone and combining the same with said vapor fraction, fractionating the combined vapors to form reflux condensate, supplying at least a portion of said reflux condensate to the catalytic cracking step and finally condensing the fractionated vapors.

ROLAND B. DAY.
ELMER R. KANHOFER.