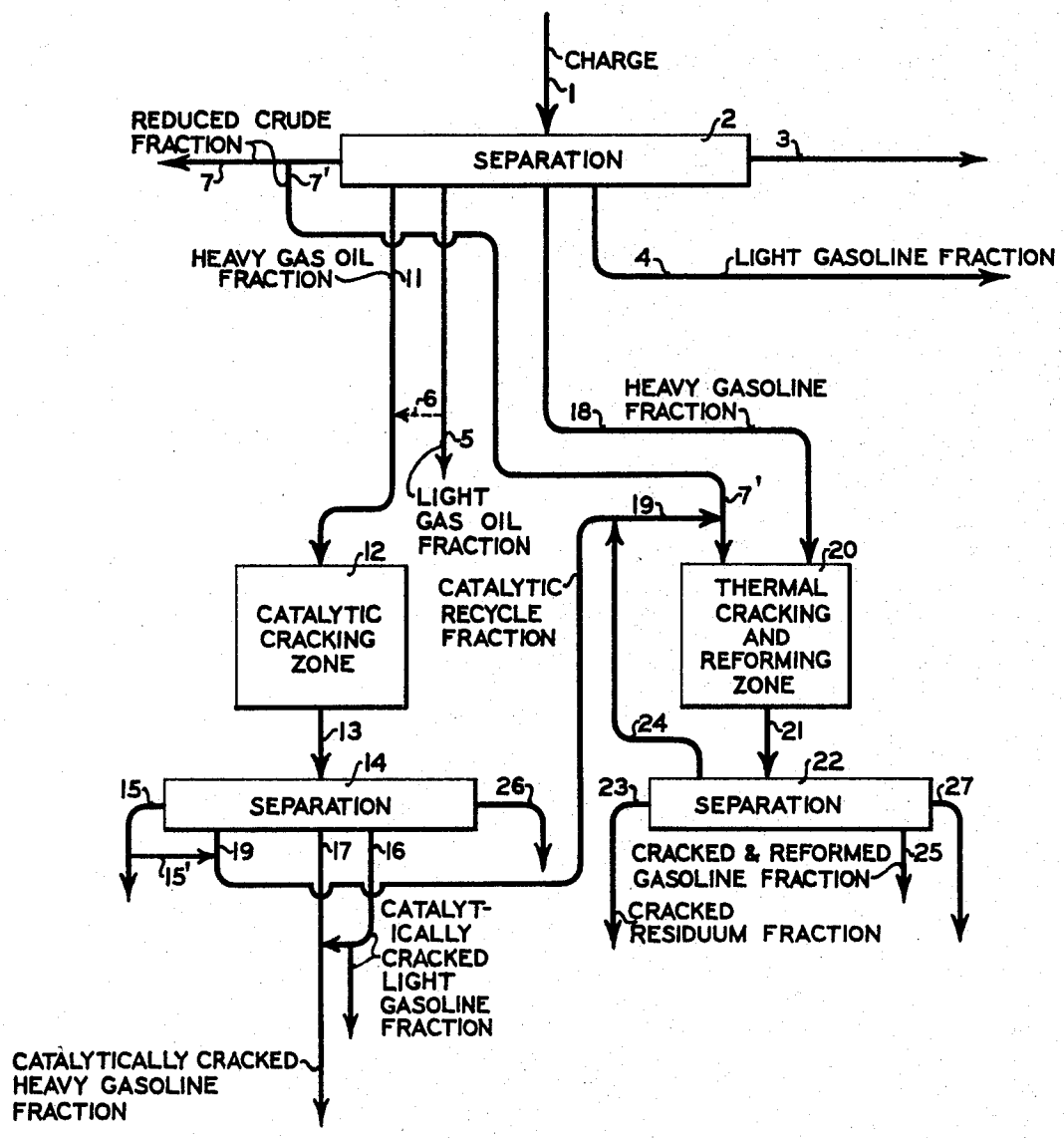
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HYDROCARBON CONVERSION

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HYDROCARBON CONVERSION

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4 Claims. (Cl. 196—52)

This is a continuation-in-part of my co-pending application, Serial No. 280,680.

This invention relates to a process for the selective treatment of hydrocarbon oils and particularly crude mineral oils to produce various gasolines. The invention provides a process for obtaining a range of final products essentially corresponding to the market requirements in respect of nature, quality and proportion and involves a series of individual processing steps which are herein combined in a novel and advantageous manner so that they cooperate to produce the desired result.

The invention involves principally catalytic cracking treatment of a gas-oil fraction of the crude hydrocarbon oil charge, and thermal reforming treatment of the heavy gasoline fraction from the crude oil concurrently with the thermal cracking treatment of the recycle gas-oil from the catalytic cracking treatment.

The term "thermal cracking and reforming treatment" as used throughout the specification and claims refers to the conversion of hydrocarbon oils boiling above the range of gasoline into hydrocarbons boiling within the range of gasoline and to the treatment of gasoline to improve the octane rating of the same without materially altering its boiling range. Catalytic cracking treatment refers to the conversion of hydrocarbons boiling above the range of gasoline and gasoline boiling range hydrocarbons in the presence of catalytic materials.

In a particular embodiment, the present invention comprises fractionally distilling a wide boiling range hydrocarbon oil, such as a crude mineral or synthetic hydrocarbon oil into a relatively light straight-run gasoline fraction, a heavier gasoline or naphtha fraction, one or more gas-oil fractions, and a distillation residue, recovering the relatively light straight-run gasoline fraction, also recovering the distillation residue or subjecting the same in part or all to a cracking treatment for the production of gasoline therefrom, subjecting at least one gas-oil fraction from the fractional distillation to catalytic cracking treatment to convert a substantial portion thereof into gasoline, separating the products from the catalytic cracking treatment into normally gaseous products, catalytically cracked gasoline fractions and recycle gas-oil, subjecting the naphtha fraction from the fractional distillation to pyrolytic reforming treatment and recycle gas-oil from the catalytic cracking treatment to pyrolytic cracking treatment in a combination pyrolytic cracking and reforming system to produce gasoline, separating the conversion products of the pyrolytic cracking and reforming treatment into normally gaseous products, pyrolytically produced gasoline and a cracked residue.

In one manner of operating the process of the invention the fractional distillation of the initial charging stock may be carried out principally in three stages, the straight-run gasoline fraction and lighter products being recovered in the first stage, naphtha and a gas-oil fraction (or several gas-oil fractions) being separated in the second stage and the then remaining higher boiling portion of the charging stock being subjected in a third distilling stage to separation of a gas oil-like distillate, which is supplied to the catalytic cracking treatment, together with one or more gas-oil fractions from the second distilling stage, while the bottoms are recovered as a product of the process. The fractional distillation of the initial charging stock, may, however, be modified without deviating from the spirit of the invention by first recovering a straight-run gasoline fraction and lighter components, if any, in a first distilling stage and separating the remaining charging stock in a second stage of fractional distillation into a naphtha fraction, one or more gas-oil fractions and a distillation residue, one or more of said gas-oil fractions and preferably the whole thereof being supplied to the catalytic cracking treatment and said naphtha fraction and the distillation residue being supplied to the pyrolytic cracking and reforming system to which also recycle gas-oil from the catalytic cracking system is supplied for further conversion.

Since the invention is concerned primarily with the novel and advantageous manner in which the various steps of the process have been combined and not with the apparatus in which the various treatments may be accomplished, the accompanying flow diagram will serve to illustrate the invention in a more comprehensible form than would be possible if the many details of the various steps were inserted. In general, the flow diagram shows the individual steps of the process each bearing their appropriate legends. In the following description, which is to be read in conjunction with the accompanying drawing, the particular steps of the process will be discussed so as to bring out the more essential details.

Referring to the flow diagram, charging stock, preferably comprising a crude oil or a similar wide boiling range hydrocarbon material, is introduced through line 1 to separation zone 2. Separation zone 2 may comprise a fractionating zone wherein the hydrocarbon oil is subjected to fractional distillation to separate a light gasoline fraction containing the normally gaseous hydrocarbons, a heavy gasoline fraction, a light gas-oil fraction, a heavy gas-oil fraction and a reduced crude fraction.

The gas fraction containing normally gaseous hydrocarbons is directed from zone 2, in the case

here illustrated, through line 3 to collection and storage or disposed of in any suitable manner. The light gasoline fraction is directed from zone 2 through line 4 and recovered as a product of the process. The light gas-oil fraction is directed through line 5 and may be recovered in part or all as a product of the process. The reduced crude fraction from separation zone 2 may be directed through line 7. In the treatment of some crude hydrocarbon oil charging stocks, however, it may be preferable for obtaining optimum results to subject the whole of the reduced crude to thermal cracking treatment for the production therefrom of cracked gasoline, cracked residuum and olefin-containing gas and in such embodiment of the invention and the reduced crude directed through lines 7 and 7' to the thermal cracking and reforming system 20, as hereinafter described.

The heavy gas-oil fraction from zone 2 is directed through line 11 to the catalytic cracking system 12, wherein it is subjected to catalytic cracking treatment while in the vapor state. The heavy straight-run gas-oil fraction may also contain, if so desired, the light straight-run gas-oil fraction instead of separately recovering the latter through line 5; or a portion or all of the light straight-run gas-oil fraction may be directed, if so desired, from line 5 through the optional line 6 and commingled in line 11 with the distillate oil fractions supplied to the catalytic cracking system 12.

The production of gasoline and particularly of aviation fuel by catalytic cracking treatment involves the treatment of the catalytic cracking charge in a continuously operated system principally comprising a vaporizing zone in operative communication with two reactors, which contain the cracking catalyst and which are alternately maintained in cracking service and regenerated. The duration of the cycles of cracking service and catalyst regeneration will vary with numerous factors, such as cracking temperature, nature of the catalyst employed, contact time and nature of the cracking charge, and may range, for example, from 10 to 60 minutes. The catalytic cracking system may comprise any desired number of reactors. The conversion of the oil fractions supplied to the system 12 may be effected therein by a single stage treatment or by treatment in several separate stages.

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, vanadia, and thoria. In addition, the hydro-silicates 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. Temperatures during conversion may range, for example, from 800 to 1200° F. while employing a pressure varying from substantially atmospheric to 100 pounds or more superatmospheric.

The conversion products from zone or system 12 are directed through line 13 to separation zone 14. This zone 14 may include a vaporizing and separating zone wherein vaporous conversion products are separated from the heavier liquid residue. In any case, zone 14 will normally include a fractionating zone wherein the vaporous conversion products are subjected to fractionation to separate the components of gasoline and lower boiling range from the components of higher boiling characteristics, the latter being condensed in the fractionating zone as a recycle fraction. The fractionating zone may at the same time serve to separate a heavy gasoline fraction as an intermediate condensate from a fractionated vaporous mixture containing a light gasoline and normally gaseous hydrocarbons. Separation zone 14, in addition to the above mentioned zones, preferably also includes a debutanizing zone to which fractionated vapors are supplied in order to separate the normally gaseous hydrocarbons from the gasoline or light gasoline fraction. The catalytically cracked residuum fraction, in the case here illustrated, is directed from zone 14 through line 15, cooled and recovered as a product of the process. In some cases, however, it may be desirable to direct this residuum fraction from zone 14 through line 15' and 19 to the thermal cracking and reforming system 20, as hereinafter described. The catalytically cracked light gasoline fraction and heavy gasoline fraction are removed from zone 14 by way of lines 16 and and 17, respectively, and recovered as products of the process.

The heavy straight-run gasoline fraction from zone 2 is directed through line 18 and may be commingled with the recycle gas-oil fraction removed from zone 14 by way of line 19, the mixture being subjected to thermal cracking and reforming treatment in the thermal cracking and reforming system 20. The thermal cracking and reforming treatment employed in system 20 preferably provides for converting the heavier hydrocarbon oils to gasoline boiling range hydrocarbons and in addition provides for thermally treating the lower boiling hydrocarbons, such as gasoline and naphtha, to improve their octane rating without excessively altering the boiling range. The pyrolytic cracking and reforming system 20 may be constructed and operated in accordance with the practice well established in the art and, for example, the Dubbs process or any other process wherein relatively heavy oils are cracked thermally for the production of gasoline of high antiknock value, and relatively light oil, such as heavy gasolines or naphthas, are reformed into gasoline of high antiknock value, may be employed within the scope of the present invention. The preferred form of treatment in system 20 consists in thermally cracking the recycle gas-oil fraction in a heating coil and communicating reaction chamber and reforming the heavy gasoline fraction in a separate heating coil. When reduced crude supplied by way of line 7' and or liquid residue supplied from the catalytic cracking system 12 is to be subjected to thermal conversion, these oils are preferably commingled with the fraction of recycle gas-oil undergoing thermal cracking in the heavy oil cracking portion of the combination thermal cracking and reforming system 20 while the heavy straight-run gasoline fraction is reformed in a light oil heating coil of the same system. However, when desired, both the recycle gas-oil fraction and the heavy gasoline fraction may be subjected to treatment in the same heating coil, in which case a reaction chamber may or may not be employed. When separate heating coils are employed, the heating coil to which the re-

cycle gas-oil fraction or this fraction, together with other high boiling oils, is supplied, may employ an outlet temperature ranging for example, from 850 to 1000° F. with a superatmospheric pressure in the range of 200 to 600 pounds or more per square inch, and the heating coil to which the heavy gasoline is supplied may employ an outlet temperature ranging, for example, from 900 to 1000° F. with a superatmospheric pressure in the range of 300 to 1000 pounds per square inch. When both the recycle gas-oil fraction and the heavy gasoline fraction are subjected to treatment in the same heating coil, the outlet temperature on the heating coil may, for example, range from 900 to 1030° F. while employing a superatmospheric pressure ranging, for example, from 400 to 800 pounds or more per square inch.

The conversion products obtained in the thermal cracking and reforming system are directed through one or more lines **21** to separation zone **22**. Separation zone **22** may comprise a vapor separating zone wherein a non-vaporous liquid residue is separated from the vaporous conversion products, and a fractionating zone wherein the vaporous conversion products are subjected to fractionation to separate fractionated vapors boiling in the range of gasoline from the heavier vaporous conversion products, the latter being condensed in the fractionating zone as reflux condensate. In addition, separation zone **22** may include a debutanizing or stabilizing zone wherein the fractionated vapors are substantially freed from the normally gaseous hydrocarbons. The cracked residuum fraction, in the case here illustrated, is removed from separation zone **22** by way of line **23** and recovered as a product of the process. The cracked residuum fraction, however, may, when desired, be subjected to further treatment, such as, for example, to coking treatment or to solvent extraction. The reflux condensate is directed through line **24** and is returned as recycle to the thermal cracking and reforming treatment or, when desired, it may be recovered as a product of the process by well known means, not shown. The cracked and reformed gasoline is directed through line **25** to cooling and storage and recovered as a product of the process.

Normally gaseous hydrocarbons separated in zone **14** are directed through line **26**. Similar fractions separated in zone **22** are removed therefrom by way of line **27**.

An example of one specific operation of the process as accomplished by using the preferred conditions and catalysts is as follows:

The charging stock, comprising a 40.8° A. P. I. gravity crude oil, was heated to a temperature of 700° F. and subjected to fractional distillation at a superatmospheric pressure of 25 pounds per square inch to separate a light gasoline fraction containing normally gaseous hydrocarbons having an end point of approximately 212° F., a heavy gasoline fraction having an end point of approximately 472° F., a gas-oil fraction, and a reduced crude fraction.

The gas-oil fraction from the fractional distillation step is subjected to contact in the vapor phase with a cracking catalyst consisting essentially of silica, alumina, and zirconia at a temperature of 932° F., under a superatmospheric pressure of 60 pounds per square inch, and at a space velocity of 4. The conversion products from the catalytic cracking treatment were supplied to a separating zone maintained at a superatmospheric pressure of 40 pounds per square inch wherein non-vaporous liquid residue was separated from the vaporous conversion products and recovered as a product of the process. The vaporous conversion products were subjected to fractionation at substantially the same pressure as that maintained in the separation zone to separate fractionated vapors having an end point of approximately 300° F. from the heavier vaporous conversion products, the latter being condensed in the fractionating zone as a heavy gasoline fraction and reflux condensate. The fractionated vapors were subjected to cooling and condensation and the resulting distillate and gas collected and separated.

The reflux condensate recycle gas-oil from the catalytic cracking treatment was commingled with the heavy gasoline fraction from the first mentioned fractional distillation and the mixture subjected to thermal cracking and reforming treatment at a temperature of 1000° F. and at a superatmospheric pressure of 600 pounds per square inch. The conversion products from the thermal cracking and reforming treatment were introduced to the fractionating zone maintained at a superatmospheric pressure of 175 pounds per square inch wherein fractionated vapors having an end point of approximately 400° F. were separated from the heavier conversion products, the latter being condensed and recovered from the fractionating zone as a product of the process. Fractionated vapors from the cracking and reforming treatment were introduced to a debutanizing zone maintained at a superatmospheric pressure of 60 pounds per square inch and operated at a top temperature of 130° F. to separate substantially all of the normally gaseous hydrocarbons from the thermally cracked and reformed 400 end point gasoline, the latter having an octane rating of 68 recovered as a product of the process.

I claim as my invention:

1. A conversion process which comprises fractionally distilling hydrocarbon oil of relatively wide boiling range to form a gas-oil fraction and a heavy gasoline fraction, catalytically cracking said gas-oil fraction and fractionating the resultant products to separate gasoline from hydrocarbons heavier than gasoline, combining at least a portion of said heavier hydrocarbons with said heavy gasoline fraction, thermally cracking the resultant mixture, and separating gasoline from the products of the last-mentioned cracking step.

2. A conversion process which comprises fractionally distilling hydrocarbon oil of relatively wide boiling range to separate therefrom a heavy gasoline fraction and a fraction suitable as catalytic cracking stock, catalytically cracking the last named fraction and fractionating the resultant products to separate gasoline from higher boiling hydrocarbons, combining at least a portion of the latter with said heavy gasoline fraction, thermally cracking the resultant mixture, and separating gasoline from the products of the last-mentioned cracking step.

3. The process as defined in claim 1 further characterized in that residual portions of said hydrocarbon oil are supplied to the thermal cracking operation.

4. The process as defined in claim 2 further characterized in that residual portions of said hydrocarbon oil are supplied to the thermal cracking operation.

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