

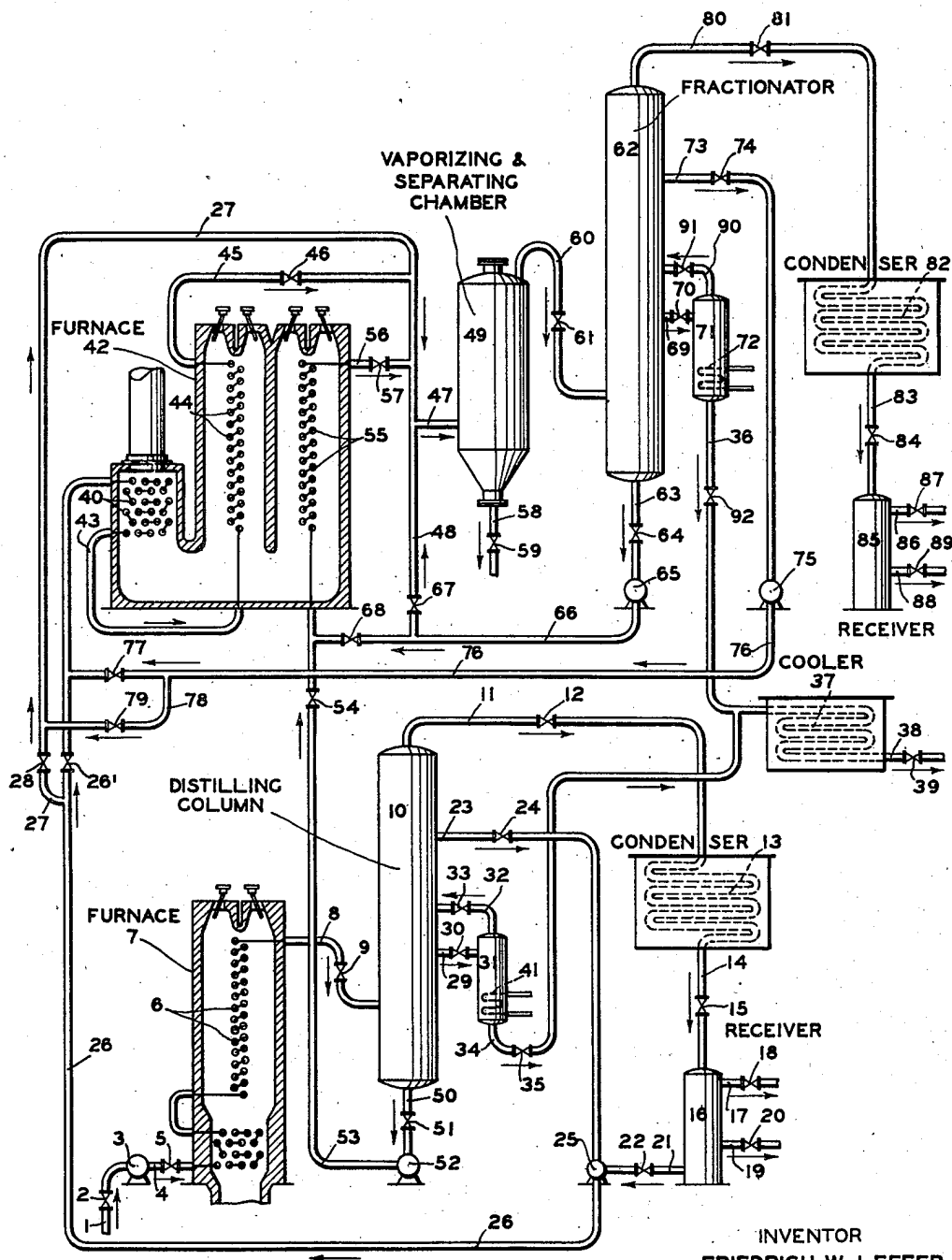
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CONVERSION OF HYDROCARBON OILS

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CONVERSION OF HYDROCARBON OILS

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The invention particularly refers to an improved process for the distillation and pyrolytic conversion of hydrocarbon oils for the production therefrom of high yields of intermediate liquids, such as Diesel fuel and minor yields of lighter and heavier products, such as gasoline and heavy residual liquids.

More specifically, the invention is concerned with a process for the treatment of crude synthetic hydrocarbon liquids produced from the catalytic watergas reaction, such as the product derived from the Fischer-Tropsch synthesis, wherein materials boiling within the range of Diesel fuel may be separately recovered and blended with Diesel fuel produced by cracking to form a final blended product of the desired characteristics without subjecting the straight run product to conversion. The product of the aforesaid Fischer-Tropsch synthesis is known in the art as Kogasin.

The invention is also concerned with a method and means of treating the components of said charging stock which boil intermediate the desired gasoline product and the Diesel fuel product, to produce additional gasoline of good antiknock properties.

Although the process of the invention is more particularly well adaptable to the treatment of crude synthetic hydrocarbon liquids of the class mentioned, it is also adapted to the treatment of other hydrocarbon oils of a predominately aliphatic or paraffinic character and particularly to virgin oils containing materials which boil within the range of Diesel fuel and, in accordance with the provisions of the invention, as stated above, are separately recovered without subjecting them to conversion.

I have found that the Diesel fuel fraction obtained by distillation of the liquid hydrocarbons produced in the catalytic water-gas synthesis has an excessively high cetane number and usually also a high viscosity and is therefore not desirable for direct use as a Diesel fuel. The cracked Diesel fuel, on the other hand, obtained by cracking the bottoms from the distillation of such an oil, has a lower cetane number and lower viscosity, and when blended with the product obtained by distillation, produces a Diesel fuel having the desired properties.

I have found that when cracking relatively high-boiling components of hydrocarbon oils, of either natural or synthetic origin, for maximum yields of Diesel fuel, it is highly advantageous to use relatively mild cracking conditions which, in this particular case, are obtained by employ-

ing relatively high cracking temperature and relatively short time at an active cracking temperature, the short time being obtained by immediate cooling of the conversion products after they are discharged from the heating coil.

In one specific embodiment, the invention comprises subjecting an oil of relatively wide boiling range to fractional distillation, without appreciable cracking, whereby to separate the same into heavy bottoms, including substantially all of its components which boil above the desired Diesel fuel, a distillate Diesel fuel fraction, and lower boiling components such as gasoline and/or naphtha, subjecting the heavy bottoms to relatively mild cracking at superatmospheric pressure for the production of additional Diesel fuel fractions and some lighter and heavier products, subjecting a part or all of said lower boiling components to more severe cracking or reforming treatment to produce therefrom high yields of gasoline of improved antiknock characteristics, cooling and commingling the products of both cracking operations, separating the commingled materials into residual liquid and vaporous products, removing the residual liquid from the system and fractionating the vapors to separate therefrom a heavy reflux condensate, returning the latter to the first mentioned cracking step, further fractionating the remaining vapors to condense therefrom a cracked Diesel fuel, blending the latter with the Diesel fuel recovered in the fractional distilling step, removing fractionated vapors of the desired end-boiling point from the last mentioned fractionating step and condensing the same to form good antiknock gasoline.

The accompanying drawing diagrammatically illustrates one specific form of apparatus embodying the features of the invention and in which the objects of the process may be accomplished.

Referring to the drawing, charging stock for the process, which may comprise any desired type of oil, but is preferably an aliphatic or paraffinic hydrocarbon oil of wide boiling range or a crude synthetic hydrocarbon oil of the type obtained from the catalytic watergas synthesis, may be supplied through line 1 and valve 2 to pump 3 by means of which it is fed through line 4 and valve 5 to heating coil 6. Heat is imparted to the oil in passing through heating coil 6 from a suitable furnace 7 in which the heating coil is disposed. The oil is heated to distillation temperature in coil 6 and the resulting heated materials are discharged therefrom

through line 8 and valve 9 into distilling and fractionating column 10. Non-cracking conditions are preferably employed in coil 6.

The vaporous materials comprising the lower boiling components of the charge are fractionated in column 10 to produce an overhead product comprising either materials boiling within the range of gasoline and gas or all of the components of the charging stock which boil below the desired Diesel fuel fraction. Preferably, however, distilling column 10 is operated with a top temperature controlled to give an overhead gasoline fraction of good antiknock properties. The overhead vaporous stream is directed from the upper portion of distilling column 10 through line 11 and valve 12 to condenser 13. The resulting distillate and uncondensed gases are directed through line 14 and valve 15 to receiver 16. Uncondensed and undissolved gases are separated from the distillate in receiver 16 and are discharged therefrom through line 17 and valve 18 to storage or elsewhere as desired. The distillate, of the desired end-boiling point, is withdrawn from receiver 16 through line 19 and valve 20 to storage or elsewhere as desired.

Any components of the charging stock which boil below the desired Diesel fuel and above the desired overhead distillate product are withdrawn from the upper portion of column 10 through line 23 and are directed through valve 24 to pump 25. When desired, and in the case where liquids recovered in receiver 16 are not suitable as a motor fuel, they may be withdrawn from receiver 16 through line 21 and valve 22 and directed to pump 25 through line 23 commingling therein with heavier fractions separately removed from column 10 through this line.

In either case, oil supplied to pump 25 is discharged therefrom through line 26 and may be directed through valve 26' in the same line to heating coil 40.

When desired, the materials contained in the fraction boiling intermediate to Diesel fuel and the overhead product may be subjected to polymerization and condensation with suitable agents, such as aluminum chloride, in a separate polymerizing system of well known form, not illustrated, for the production of lubricating oils and the remaining non-polymerized constituents returned to the process and introduced to heating coil 40.

The components of the charge supplied to column 10, which boil within the range of the desired Diesel fuel product, are withdrawn from a suitable intermediate point in the column through line 29 and valve 30 to stripping column 31 wherein they are subjected to reboiling to substantially free the same of any desirable lower boiling fractions and dissolved gases. This may be accomplished, for example, by passing a suitable heating medium, such as steam, hot oil, or the like, through coil 41 within the lower portion of column 31. The evolved vapors and gases are returned from column 31 through line 32 and valve 33 to column 10. The reboiled Diesel fuel is withdrawn from the lower portion of column 31 through line 34 and is directed through valve 35 to line 36 and thence to cooler 37. Diesel fuel produced by cracking, as subsequently described, is also supplied to cooler 37, blended and cooled Diesel fuel product being directed from cooler 37 through line 38 and valve 39 to storage or elsewhere as desired.

The oil supplied to heating coil 40, located in the fluid heating zone of furnace 42, receive heat

predominately by convection, are discharged therefrom through line 43 to heating coil 44 which is located in a radiant heating zone of the same furnace. The oil passing through heating coil 44 is heated therein to a high cracking temperature at a substantial superatmospheric pressure and the heated products are discharged from coil 44 through line 45, valve 46, line 27 and line 47 into vaporizing and separating chamber 49.

The heavy components of the charge to column 10, which comprise materials boiling above desired Diesel fuel, are withdrawn from the lower portion thereof and directed through line 50 and valve 51 to pump 52 by means of which they are fed through line 53 and valve 54 to heating coil 55.

The oil in passing through heating coil 55, which is disposed in furnace 42, is subjected therein to relatively mild cracking conditions and the resulting products are discharged therefrom through line 56, valve 57 and line 47 into chamber 49.

In order to definitely control the time during which the oil is maintained at an active cracking temperature and substantially limit such conversion to primary cracking reactions, the heated products which are discharged from heating coil 55 are preferably cooled sufficiently to prevent any substantial continued cracking in chamber 49. Since rapid cooling of the conversion products is desirable, the cooling is preferably accomplished by introducing cooling oil directly into line 47, although substantial pressure reduction and/or indirect heat exchange with any desired cooling material may replace or augment direct commingling of the conversion products with a cooling medium. Any desired oil, which will not cause restriction or plugging of transfer line 47 and will not contaminate the desired final product of the process, may be employed as a direct cooling medium. Regulated quantities of any of the products of the process other than the Diesel fuel may be employed as the cooling oil. An example of the use of such materials and means for supplying the same to line 47 will be later more fully described. Preferably the products discharged from coil 44 are also cooled to below an active temperature before they are introduced into chamber 49 and, preferably, before they are commingled with the products from coil 55. Cooling of this stream from coil 44 may be accomplished in the same manner, above outlined, as the products from coil 55 are cooled and specific means of accomplishing this will be later described.

The conversion products supplied to chamber 49 are separated therein into vapors and residual liquid. The latter is directed from the lower portion of chamber 49 through line 58 and valve 59 to cooling and storage or elsewhere as desired. The vaporous products, comprising gas, gasoline, Diesel fuel and fractions heavier than the desired Diesel fuel which are suitable as stock for further cracking within the system are directed from the upper portion of chamber 49 to fractionator 62 through line 60 and valve 61.

The relatively heavy reflux condensate formed by fractionation of the vaporous conversion products in fractionator 62 comprises substantially all of their components boiling above the desired Diesel fuel, and is removed from the lower portion of the fractionator through line 63 and valve 64 to pump 65 by means of which it is fed through line 66 and may, when desired, be directed all or in part through line 48 and valve 67 into line 47 as a cooling medium for the

hot conversion products with which it is then commingled. Preferably, however, at least a portion of this oil is directed through valve 88 in line 86 and through line 53 to further cracking in coil 55 with the bottoms from column 10.

A selected lighter fraction of the reflux condensate formed in fractionator 62 is removed as the desired cracked Diesel fuel from a suitable intermediate point in fractionator 62 and is directed through line 89 and valve 70 into stripping column 71 wherein it is reboiled to substantially free the same of any undesired low-boiling fractions and dissolved gases. This reboiling is accomplished, in the case here illustrated, by passing a suitable heating medium, such as steam, hot oil or oil vapors or the like, through coiled coil 72, disposed in the lower portion of column 71. The evolved gases and vapors are returned from column 71 through line 90 and valve 91 to fractionator 62. The reboiled Diesel fuel is withdrawn from the lower portion of column 71 through line 36 and valve 92 to cooler 37 to commingle with the Diesel fuel recovered by distillation of the charging oil in column 10 and form the final Diesel fuel product of the process.

It will, of course, be understood that stripping columns 31 and 71, although desirable, are not essential to the operation of the process and that, when desired, reboiling may be accomplished in any other well known manner, not illustrated, or may be dispensed with.

The components of the conversion products supplied to fractionator 62 which boil within the range of the desired gasoline, are withdrawn from the upper portion of fractionator 62 and directed through line 80 and valve 81 to condenser 82. The resulting distillate and uncondensed gases are directed through line 82 and valve 84 to receiver 85. The uncondensed and undissolved gases are removed from the receiver through line 86 and valve 87 to storage or elsewhere as desired. The distillate collected in receiver 85 is directed through line 88 and valve 89 to any desired further treatment or to storage or elsewhere as desired.

Any components of the vapors supplied to column 62 which boil below the desired Diesel fuel and above the desired gasoline are condensed as light reflux condensate in the upper portion of fractionator 62 and directed therefrom through line 73, valve 74 to pump 75 by means of which they are preferably fed, all or in part, through line 76, valve 77 and line 26 to coils 40 and 44 for further cracking. A portion or all of this material may be directed from line 76 through line 78, valve 79 and lines 27 and 47 into chamber 49 to serve as a cooling medium for the conversion products from coils 44 and 55 by directly commingling therewith.

Regulated quantities of the light oil supplied to pump 25 in either or both of the manners previously described may likewise be employed, when desired, as a cooling medium for the conversion products in line 47 in which case they are directed from line 26 through line 27 and valve 28 into line 47.

Although not shown in the drawing, it is within the scope of the invention to employ stripping columns for obtaining more closely cut fractions when removing naphtha and/or heavy gasoline fractions from the distilling and fractionating steps in which case their operation would be similar to that given for columns 31 and 71. Regulated quantities of the distillate collected in receiver 16 and receiver 85 may, when desired,

be returned to the upper portions of the respective columns 10 and 62 to serve as cooling and refluxing liquid therein.

It will, of course, be understood that the various alternative methods of operation illustrated in the drawing are not equivalent but may be selected to suit individual requirements, and that any of the methods illustrated in the drawing may be employed for cooling the conversion products prior to their introduction into the separating chamber, either alone or in conjunction with any other suitable method of cooling, such as, for example, indirect heat exchange between the hot conversion products and charging stock, or other cooling material.

The preferred range of operating conditions which may be employed to accomplish the objects of the invention in an apparatus such as illustrated and above described is approximately as follows:

The temperature at the outlet of the heating coil employed for heating the charge may range, for example, from 600 to 700° F., preferably with a relatively low pressure in the coil and fractionating column ranging, for example, from 50 pounds or thereabouts per square inch, superatmospheric, down to substantially atmospheric pressure. Preferably substantially the same pressure is employed in both coil 6 and column 10 although lower pressure may be utilized in the distilling column, when desired. The temperature employed at the outlet of the heavy oil cracking coil may range, for example, from 850 to 1000° F. or thereabouts, preferably with a relatively low superatmospheric pressure in this zone ranging, for example, from 300 pounds or thereabouts per square inch down to substantially atmospheric pressure and with a reaction time substantially less than 60 seconds and preferably less than 30 seconds based on the cold oil velocity. The heating coil to which the naphtha and/or low antiknock gasoline fractions are supplied may employ an outlet temperature of from 900 to 1050° F., or more, with a superatmospheric pressure ranging, for example, from 300 to 1200 pounds or more per square inch. Vaporizing and separating chamber 49 is preferably operated under temperature and pressure conditions which will not permit any substantial further cracking of the products supplied thereto. The pressure may be substantially reduced in this zone relative to that employed in coil 44 and/or coil 45, said reduced pressure ranging, for example, from substantially atmospheric to 60 pounds or thereabouts per square inch superatmospheric. The temperature employed in chamber 49 may range, for example, from 650 to 790° F. or thereabouts. The pressure employed in chamber 49 may be substantially equalized or reduced in the succeeding fractionating, condensing and collecting portions of the system.

As a specific example of an operation of the process, as it may be conducted in an apparatus, such as illustrated and above described, the charging stock comprising a wide boiling range synthetic hydrocarbon liquid produced in the Fischer-Tropsch synthesis is quickly heated in coil 6 to a temperature of about 650° F. at a superatmospheric pressure of about 30 pounds per square inch and thence introduced into the distilling column wherein it is separated at substantially atmospheric pressure into the desired components. The low-boiling components of the charge having an end-boiling point of about 250° F. are withdrawn from the upper portion of the

distilling column in vaporous state and subjected to condensation and collection for the recovery of a gasoline product of satisfactory antiknock value. Heavier gasoline and naphtha fractions having a boiling range of about 240 to 410° F. are withdrawn as light condensate from the upper portion of the distilling column and subjected to reforming treatment in coil 44, in admixture with recycle stock from fractionator 62. A conversion temperature of approximately 1040° F. and a superatmospheric pressure of about 750 pounds per square inch are employed at the outlet of coil 44. The highly heated reformed products are cooled to a temperature of approximately 750° F. by direct contact with the heavy reflux condensate produced, as hereinafter described, in the fractionator of the cracking system after which they are introduced into a vaporizing and separating chamber. The Diesel fuel fraction recovered from column 10 has a boiling range of about 400 to 650° F. The heavy bottoms from the distilling column, comprising the components of the charge boiling above approximately 650° F. are subjected to conversion in coil 55 at a temperature of approximately 950° F. and a superatmospheric pressure of approximately 60 pounds per square inch, the conversion time in coil 55 being approximately 30 seconds based on the cold oil velocity. The resulting hot conversion products are quickly cooled to a temperature of about 750° F. along with the conversion products obtained from the reforming coil, as hereinbefore described, whereupon they are introduced into the vaporizing and separating chamber which is operated at a pressure of approximately 60 pounds per square inch. The vaporous conversion products are separated from the residual liquid conversion products in chamber 49 and the latter are withdrawn from the chamber, cooled and recovered as a product of the process. The vaporous conversion products are subjected to fractionation for the production of heavy reflux condensate, gasoline, and the desired intermediate products comprising naphtha and cracked Diesel fuel. Vapors boiling up to approximately 380° F. are withdrawn from the upper portion of fractionator 62, subjected to condensation and the resulting good antiknock gasoline recovered. Naphtha fractions boiling within the range of from approximately 380 to 455° F. are withdrawn as a side stream from fractionator 62 and commingled as previously described, with the heavy gasoline and naphtha supplied to coils 40 and 44 from fractionator 10. Cracked Diesel fuel, comprising the components of the vapors supplied to fractionator 62, which boil within the range of about 455° F. to 650° F., is withdrawn from an intermediate point in fractionator 62, commingled with a Diesel fuel obtained from the fractional distilling step and commingled materials are cooled and recovered as the final Diesel fuel product. The heavy reflux condensate, formed in fractionator 62 is recycled, as previously described, to furnish the necessary cooling to the conversion products prior to their introduction into the vaporizing and separating chamber. This operation will produce, per barrel of charging stock, approximately 31% of good quality Diesel fuel, including the cracked and straightrun product, approximately 57% good antiknock gasoline, and about 1% of good quality residual oil, the remainder being chargeable principally to uncondensable gas and loss.

I claim as my invention:

1. The process of treating a synthetic hydro-

carbon oil resulting from the interaction of carbon monoxide and hydrogen, which comprises separating from said oil by fractional distillation thereof, without appreciable cracking, a Diesel fuel of unusually high cetene number, selected lower boiling fractions and fractions boiling above the range of said Diesel fuel, cracking said lower boiling fraction under conditions regulated to produce therefrom high yields of good antiknock gasoline, separately cracking said higher boiling fractions under conditions regulated to produce therefrom high yields of cracked Diesel fuel, commingling the products of both cracking operations and cooling the same to below an active cracking temperature, separating the resulting cooled and commingled products into vapors and non-vaporous residue, fractionating the vapors to form condensate consisting of cracked Diesel fuel having a low cetene number and an overhead vaporous stream comprising materials of good antiknock value boiling within the range of gasoline, condensing said overhead vaporous stream, recovering the resulting distillate, and blending Diesel fuels resulting from said distilling and cracking steps to form a final Diesel fuel product of the desired characteristics.

2. The process defined in claim 1, wherein a condensate heavier than said cracked Diesel fuel is condensed from the vapors in the second mentioned fractionating step, separately removed therefrom and returned to the second mentioned cracking step for further cracking treatment.

3. The process defined in claim 1, wherein a condensate heavier than said cracked Diesel fuel is condensed from the vapors in the second mentioned fractionating step, separately removed therefrom and wherein regulated quantities of said higher boiling condensate are directly commingled with said conversion products to effect at least a portion of said cooling of the latter.

4. The process defined in claim 1, wherein selected fractions of the charging stock, boiling below said high cetene number Diesel fuel, are removed from the distilling step and directly commingled with said conversion products to effect at least a portion of said cooling of the latter.

5. The process defined in claim 1, wherein selected fractions of the vaporous conversion products, boiling intermediate said cracked gasoline and said cracked Diesel fuel, are separately removed as light reflux condensate from the last mentioned fractionating step and directly commingled with said conversion products to effect at least a portion of said cooling of the latter.

6. The process defined in claim 1, wherein selected fractions of the charging stock and selected fractions of the vaporous conversion products, boiling below the Diesel fuels formed in the respective fractionating steps, are removed therefrom and directly commingled with said conversion products to effect at least a portion of said cooling of the latter.

7. The process defined in claim 1, wherein selected fractions of the charging stock and selected fractions of the vaporous conversion products, boiling below the Diesel fuels formed in the respective fractionating steps, are removed therefrom, a regulated portion thereof being commingled with said conversion products to effect at least a portion of said cooling of the latter and another regulated portion thereof being supplied to the first mentioned cracking operation.

8. A process for producing Diesel fuel from Kogasin which comprises fractionally distilling the Kogasin without substantial cracking thereof to separate the fractions thereof boiling in the Diesel fuel range from those heavier than Diesel fuel, the first-mentioned fractions being unsuitable as Diesel fuel because of excessively high cetene number and viscosity, subjecting said heavier fractions to relatively mild cracking

such as to convert the same predominantly into lighter hydrocarbons boiling in the Diesel fuel range, fractionating the resultant conversion products to separate a cracked Diesel fuel therefrom, and blending the latter with said first-mentioned fractions to form a Diesel fuel product of satisfactory cetene number and viscosity.

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