

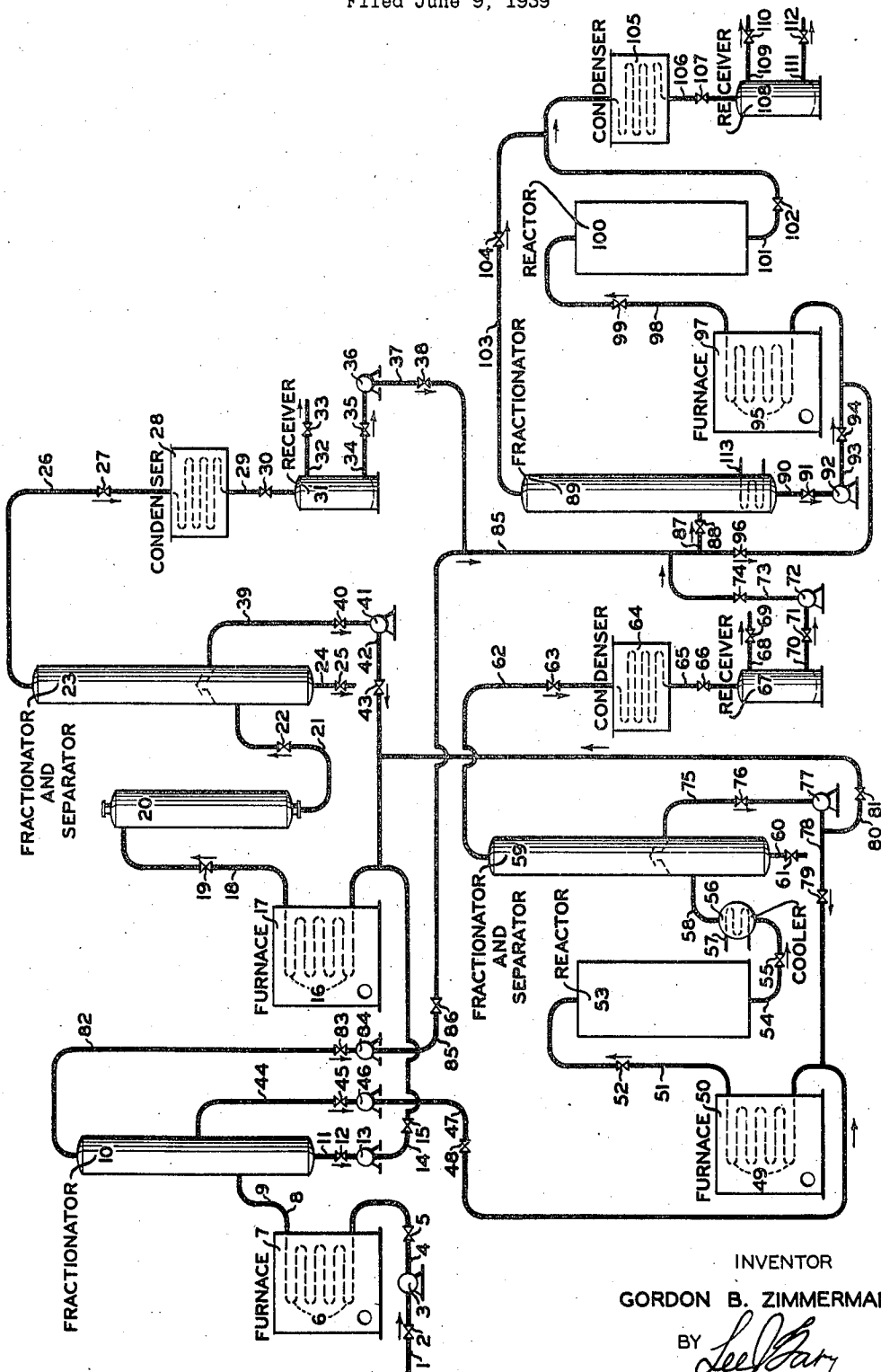
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HYDROCARBON CONVERSION

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## HYDROCARBON CONVERSION

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The invention relates to the conversion of hydrocarbon oil into substantial yields of high octane rating gasoline. More specifically it is concerned with a process for treating a wide boiling range hydrocarbon oil wherein the gasoline mixture, comprising the straight-run product, the gasoline produced in catalytically cracking the gas-oil fraction, and the gasoline from thermally cracking the crude bottoms, is subjected to aromatization treatment to produce a final product with a relatively high concentration of aromatic hydrocarbons of relatively low olefin content and of high octane rating.

The invention particularly involves thermal cracking treatment of the heavy bottoms of the crude oil, catalytic cracking treatment of the straight-run intermediate fraction, separation of the straight run distillate fraction and the distillate fractions from the thermal and the catalytic cracking treatments into a fraction consisting essentially of hydrocarbons containing five carbon atoms and less to the molecule and a fraction containing the higher molecular weight hydrocarbons, catalytic aromatization treatment of the higher molecular weight hydrocarbons and blending of the conversion products from the aromatization treatment with the hydrocarbon fraction containing five carbon atoms and less to the molecule.

In one specific embodiment the invention comprises fractionally distilling a wide boiling range hydrocarbon oil into a light fraction consisting essentially of hydrocarbons boiling in the range of gasoline, an intermediate fraction consisting essentially of hydrocarbons boiling in the range of gas-oil, and a heavy residual fraction containing hydrocarbons boiling above said intermediate fraction, subjecting said heavy residual fraction to thermal cracking treatment to convert a substantial portion to gasoline boiling range hydrocarbons, separating the non-vaporous cracked liquid residue from the thermally cracked vaporous conversion products and recovering the former as a product of the process, subjecting said thermally cracked vaporous conversion products to fractionation to separate fractionated vapors of the desired end boiling point from the heavier vaporous conversion products, condensing the latter as reflux condensate in the fractionating zone and returning the same to further thermal cracking treatment, cooling and condensing said fractionated vapors and collecting the resulting distillate and gas, subjecting said intermediate fraction from the fractional distillation to catalytic cracking treatment to convert a substantial

portion into gasoline boiling range hydrocarbons, separating liquid residue from the catalytically cracked vaporous conversion products and recovering the former as a product of the process, subjecting said catalytically cracked vaporous conversion products to fractionation to separate fractionated vapors of the desired end boiling point from the heavier vaporous conversion products, condensing the latter as reflux condensate in the fractionating zone and subjecting the same to further cracking treatment, cooling and condensing the fractionated vapors and collecting the resulting distillate and gas, commingling the light fraction from the fractional distillation, the distillate fractions from the thermal cracking and catalytic cracking treatments and subjecting the mixture to fractionation to separate hydrocarbons containing 5 carbon atoms and less to the molecule from the heavier components, subjecting said heavier components to aromatization treatment to convert a substantial portion of the aliphatic and naphthenic hydrocarbons to aromatic hydrocarbons, commingling the conversion products from the aromatization treatment with the overhead fractions from the last mentioned fractionation, cooling and condensing the mixture and recovering the resulting distillate and gas as products of the process.

Straight-run gasoline ordinarily is composed of paraffinic and/or naphthenic hydrocarbons and, depending upon the concentration of each, its octane rating may vary over a relatively wide range. For example, the octane rating may be relatively low when it is highly paraffinic, increasing gradually as the concentration of naphthenic hydrocarbons increases. Although the gasolines, having a relatively high concentration of naphthenic hydrocarbons, have a high octane rating as compared with straight-run gasolines with a higher concentration of paraffinic hydrocarbons, the octane ratings of these mixtures is still below those of the gasolines presently employed in the automotive industry. The addition of small amounts of antiknock agents, such as lead tetraethyl, improves the gasoline to some extent, but as yet no material has been found that will improve the antiknock properties of the straight-run gasolines sufficiently for them to become equivalent to or compare favorably with those gasolines produced by catalytic or pyrolytic means.

Thermally cracked gasoline, on the other hand, is highly olefinic, and although the olefins tend to increase the octane rating of the final gasoline, they also increase the potential gum-forming

properties of the gasoline and, in addition, the gasoline has a high acid heat test as compared with that of a paraffinic or aromatic gasoline. Catalytically cracked gasoline, like thermally cracked gasoline, is also rich in olefinic hydrocarbons.

I have found that aromatization treatment of the three types of gasoline, described above, is particularly advantageous because the antiknock rating is increased, the potential gum-forming properties decreased and the acid heat properties improved in some instances, and, in addition, the gasoline makes a suitable base for blending to produce aviation gasoline. In addition, I have found that the aromatization treatment of the three types of gasoline may be conducted simultaneously in the same reaction zone to produce a gasoline containing a relatively high percentage of aromatic hydrocarbons. The invention therefore involves a series of steps combined in a novel and advantageous manner to produce a final product of the desired characteristics.

The term "aromatization" as used through the specification and claims refers to the conversion of aliphatic and/or naphthenic hydrocarbons into aromatic hydrocarbons. The conversion of aliphatic to aromatic hydrocarbons involves dehydrogenation followed by cyclization, whereas the conversion of naphthenic to aromatic hydrocarbons merely involves dehydrogenation. Catalytic cracking refers principally to the splitting of carbon-to-carbon bonds in the presence of catalytic masses, whereas thermal cracking refers principally to the splitting of carbon-to-carbon bonds by heat and pressure.

The accompanying diagrammatic drawing illustrates generally in side elevation the apparatus in which the process of the invention may be accomplished. The fact is recognized, however, that various modifications may be made, such as the addition of stabilizing and condensing equipment where needed or the utilization of other cracking procedures, when desired, but it is the purpose of this invention to cover such modifications within its broad scope.

Referring to the drawing, charging stock for the process, comprising a wide boiling range hydrocarbon oil, such as crude oil, is introduced through line 1 and valve 2 to pump 3, which discharges through line 4 and valve 5 into heating coil 6. The oil in passing through heating coil 6 is raised to a temperature in the range of 400 to 700° F. by means of heat supplied from furnace 7, and is discharged therefrom through line 8 and valve 9 into fractionator 10 maintained at a pressure varying from substantially atmospheric to 100 pounds or more per square inch. The heated oil introduced to fractionator 10 is separated by fractionation into a light fraction consisting essentially of hydrocarbons boiling in the range of gasoline and preferably boiling below 475° F., an intermediate fraction consisting essentially of hydrocarbons boiling above said light fraction and substantially below 750° F., and a heavy residual fraction containing hydrocarbons boiling above said intermediate fraction.

The heavy fraction from fractionator 10 is directed through line 11 and valve 12 to pump 13, which discharges through line 14 and valve 15 into heating coil 16. The oil in passing through heating coil 16 is raised to the desired cracking temperature, which may vary, for example, from 850 to 1000° F. by means of heat supplied from furnace 17, and is discharged therefrom under a superatmospheric pressure ranging, for exam-

ple, from 100 to 500 pounds per square inch, and is directed through line 18 and valve 19 into reaction chamber 20 wherein the oil undergoes substantial further conversion by means of its contained heat. Reaction chamber 20 is preferably maintained at substantially the same or at a slightly reduced pressure relative to that employed on the outlet of the heating coil and is preferably insulated to reduce the radiation losses therefrom, although insulation is not shown in the accompanying drawing.

The resulting conversion products after their prolonged conversion in chamber 20 are discharged from the lower portion thereof through line 21 and valve 22 into the separating zone of fractionator and separator 23. Valve 22 is preferably a pressure control valve by means of which a substantial superatmospheric pressure is maintained in the heating coil and communicating reaction chamber, the pressure on the downstream side of the valve being somewhat lower than that maintained in said heating coil and said reaction chamber. Chamber 23 is preferably maintained at a lower pressure than that maintained in reaction chamber 20 ranging, for example, from 50 to 250 pounds per square inch in order to effect substantial further vaporization of the liquid conversion products introduced thereto. In the separating zone of chamber 23 the vaporous conversion products introduced thereto and evolved therein are separated from the non-vaporous liquid residue, the latter being discharged from the lower portion thereof through line 24 and valve 25 to cooling and storage or to further treatment as desired. The vaporous conversion products introduced to the separating zone, together with the vapors evolved within the same zone, are introduced to the fractionating zone situated in the upper portion of chamber 23. Fractionated vapors of the desired end boiling point are separated from the heavier vaporous conversion products in the fractionating zone, the latter being condensed therein as reflux condensate and the former being withdrawn as an overhead vaporous fraction. The fractionated vapors are directed through line 26 and valve 27 to cooling and condensation in condenser 28. The resulting distillate and gas from condenser 28 is directed through line 29 and valve 30 to collection and separation in receiver 31. The normally gaseous hydrocarbons remaining uncondensed and undissolved in receiver 31 are directed from the upper portion thereof through line 32 and valve 33 to collection and storage or to further treatment. The distillate collected and separated in receiver 31 is directed from the lower portion thereof through line 34 and valve 35 into pump 36, which discharges through line 37 and valve 38 into line 35 for treatment as hereinafter described. The reflux condensate collected in the lower portion of the fractionating zone in chamber 23 is directed therefrom through line 39 and valve 40 into pump 41, which discharges through line 42 and valve 43 into line 14 wherein said reflux condensate commingles with the heavy fraction from fractionator 10 prior to its conversion in heating coil 16 and reaction chamber 20.

The intermediate fraction from fractionator 10 is directed through line 44 and valve 45 to pump 46, which discharges through line 47 and valve 48 into heating coil 49. The oil in passing through heating coil 49 is substantially completely vaporized therein and is raised to a temperature within the range of 800 to 1200° F. without

substantial pyrolytic cracking thereof by means of heat supplied from furnace 50. The heated vapors are discharged from heating coil 49, at a pressure varying from substantially atmospheric to 100 pounds or more per square inch, through line 51 and valve 52 into catalytic reactor 53 wherein the vapors are subjected to contact with a suitable cracking catalyst disposed therein. Reactor 53 may comprise any one of a number of types of reactors now employed in the industry. However, since the invention is concerned primarily with a combination of steps rather than with the design of any particular piece of equipment, no attempt will be made to describe in detail the features of the various reactors that may be employed.

A reactor which may be employed and one which has found wide application in the field of catalysis is that which contains a plurality of relatively small diameter reactor tubes supported within an enclosed zone, preferably equipped for alternate processing and reactivation. It is also of particular importance that provisions be made for introducing heat to the reactor during the processing cycle and for cooling the reactor during the reactivation cycle, catalytic cracking being an endothermic reaction and reactivation an exothermic reaction. During the cracking reaction carbon deposits upon the surface and within the pores of the catalyst lowering its catalytic activity, and in order to restore the catalyst to its active state frequent reactivations are necessary. In order to accomplish continuous operation, a plurality of reactors are preferably employed so that at least one or more may be employed for processing while the other or others is undergoing reactivation.

Catalysts which may be employed in the catalytic cracking treatment may consist of pellets or granules of an inert siliceous and refractory material, such as silica composited with compounds selected from the group consisting of alumina, zirconia, vanadia, and thoria, or the hydrosilicates of alumina, or acid treated clays, or the like. These catalysts are not to be considered exactly equivalent in their catalytic effect, for certain of these catalysts, such as the silica-alumina catalyst, are known to give better results than the others. This fact, however, is not to be considered as a limiting feature to the broad scope of the invention, for it is thoroughly recognized that other catalysts not mentioned may also be employed to obtain favorable results.

The conversion products from reactor 53 are directed through line 54 and valve 55 into and through cooler 56 wherein the conversion products are cooled to the desired temperature by indirect heat exchange with a cooling medium introduced to cooler 56 by way of closed coil 57. Cooled conversion products leaving cooler 56 are directed through line 58 into the separating zone of fractionator and separator 59. The vaporous conversion products are separated from the non-vaporous liquid residue in the separating zone and the latter removed by way of line 60 and valve 61 to cooling and storage or to further treatment as desired. The vaporous conversion products from the separating zone are introduced to the fractionating zone situated in the upper portion of fractionator and separator 59 wherein fractionated vapors of the desired end boiling point are separated from the higher boiling hydrocarbons and the latter condensed as reflux condensate in the fractionating zone. The fractionated vapors separated in chamber 59 are di-

rected from the upper portion thereof through line 62 and valve 63 and subjected to cooling and condensation in condenser 64. The resulting distillate and uncondensed and undissolved gases are directed through line 65 and valve 66 to collection and separation in receiver 67. Normally gaseous hydrocarbons collected and separated in receiver 67 are directed through line 68 and valve 69 to collection and storage or to further treatment as desired. Distillate collected in the lower portion of receiver 67 is directed through line 70 and valve 71 to pump 72, which discharges through line 73 and valve 74 into line 85 for treatment as hereinafter described.

Reflux condensate from the fractionating zone of chamber 59 is directed through line 75 and valve 76 to pump 77, which discharges through line 78 and valve 79 into line 47 for subsequent conversion in commingled state with the intermediate fraction from fractionator 10. When once-through catalytic cracking is desired, or when it is desired to reduce the amount of recycle returned to the catalytic cracking treatment, all or a portion of the reflux condensate in line 78 may be directed through line 80 and valve 81 into line 42, commingling therein with the reflux condensate from the thermal cracking treatment after which the mixture is subjected to further cracking in commingled state with the heavy fraction from fractionator 10.

The light fraction from fractionator 10 is directed through line 82 and valve 83 to pump 84, which discharges through line 85 and valve 86, and said light fraction commingled in line 85 with the distillate fractions from thermal and catalytic cracking treatments introduced as previously described. The mixture in line 85 is then directed through line 87 and valve 88 into fractionator 89 wherein the combined distillates are subjected to fractionation to separate a fraction consisting essentially of hydrocarbons containing 5 atoms of carbon and less to the molecule from the heavier higher boiling components, the former being removed as a vapor and the latter as a liquid. Provision is made for reboiling the distillate collected in the lower portion of fractionator 89 by means of indirect heat exchange with a suitable heating medium introduced by way of closed coil 113. The heavier higher boiling portion of the distillate collected in the lower portion of fractionator 89 is directed through line 90 and valve 91 to pump 92, which discharges through line 93 and valve 94 into heating coil 95. When the distillate in line 85 contains relatively minor amounts of hydrocarbons containing 5 carbon atoms and less to the molecule, fractionator 89 may be by-passed and all of the distillate directed through valve 96 into line 93 by means of which it is introduced to heating coil 95.

The oil in passing through heating coil 95 is substantially completely vaporized therein and is raised to a temperature in the approximate range of 800 to 1200° F. by means of heat supplied from furnace 97. The heated vapors discharged from heating coil 95, under a pressure varying from substantially atmospheric to 100 pounds or more per square inch, are directed through line 98 and valve 99 into reactor 100. Reactor 100 may be of substantially the same design as reactor 53, because although different catalysts are employed in the aromatization reaction the reaction is similar in many respects to the catalytic cracking reaction; that is, relatively short cycles of operation are employed in both reactions and in addition

the aromatization reaction is endothermic while the reactivation of catalysts involves an exothermic reaction.

Catalysts which have been found to be highly efficient for converting aliphatic and/or naphthenic hydrocarbons to aromatic hydrocarbons consist in general of pellets or granules of alumina or inert siliceous and refractory materials composited with compounds of the elements selected from the group consisting of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table. Although these catalysts are the preferred catalysts, various other catalysts not mentioned which are capable of promoting the desired reaction may be employed within the broad scope of the invention.

The conversion products from reactor 100 are directed through line 101 and valve 102, and, when fractionator 89 is employed, commingled with the light hydrocarbons removed therefrom as an overhead fraction through line 103 and valve 104 and the mixture thereafter subjected to cooling and condensation in condenser 105. The resulting distillate, together with uncondensed and undissolved gases, is directed through line 106 and valve 107 to receiver 108. Uncondensed and undissolved gases collected and separated in receiver 108 are directed from the upper portion thereof through line 109 and valve 110 to collection and storage. Distillate collected in the lower portion of receiver 108 is directed through line 111 and valve 112 to storage or to further treatment as desired.

The following is an example of one specific operation of the process as it may be accomplished in an apparatus such as illustrated and above described when using the preferred catalyst and the preferred conditions of temperature and pressure. The example merely illustrates what may be accomplished and is not intended as a limiting feature of the invention, for various other catalysts well known to those versed in the art may be employed within its broad scope and the operating conditions adjusted with each of these catalysts to produce the desired result.

The charging stock, a 36° A. P. I. gravity Mid-Continent crude oil, was subjected to fractional distillation to separate a light fraction equal to approximately 25% by volume of the charge and containing gasoline and naphtha having an end point of approximately 450° F., an intermediate fraction equal to approximately 25% by volume of the charge and consisting essentially of hydrocarbons boiling above said light fraction and below 700° F., and a bottoms fraction comprising the balance of the charging stock containing hydrocarbons boiling above said intermediate fraction.

The bottoms fraction was subjected to thermal cracking treatment in a conventional full flashing coil and chamber unit at a temperature of 935° F. and at a superatmospheric pressure of approximately 150 pounds per square inch on the reaction chamber. The conversion products from the reaction chamber were introduced to a vaporizing and separating zone maintained at a superatmospheric pressure of 75 pounds per square inch wherein the vaporous conversion products were separated from the liquid conversion products and said liquid conversion products subjected to substantial further vaporization to separate a non-vaporous liquid residue which was recovered as a product of the process. The vaporous conversion products, together with the vapors evolved in the separating zone, were subjected

to fractionation to separate fractionated vapors of the desired end boiling point from the higher boiling hydrocarbons, the latter being condensed as reflux condensate in the fractionating zone and returned to the heating coil for further thermal cracking treatment. The fractionated vapors were subjected to cooling and condensation and the resulting distillate and uncondensed and undissolved gases collected and separated into their respective fractions.

The intermediate fraction from the fractional distillation was subjected to catalytic cracking treatment in the presence of a silica-alumina cracking catalyst at a temperature of 932° F. and at a superatmospheric pressure of 60 pounds per square inch. The conversion products from this zone were introduced to a separating zone maintained at a superatmospheric pressure of 40 pounds per square inch wherein the liquid residue was separated from the vaporous conversion products and the former recovered as a product of the process. The vaporous conversion products were subjected to fractionation to separate fractionated vapors of the desired end boiling point from the higher boiling conversion products, the latter condensed as reflux condensate in the fractionating zone and returned for further catalytic cracking treatment. The fractionated vapors were subjected to cooling and condensation and the resulting distillate and uncondensed and undissolved gases collected and separated, said uncondensed and undissolved gases being withdrawn as a product of the process.

The distillate produced in the thermal cracking and the catalytic cracking treatments were commingled with the light fraction from the fractional distillation and subjected to fractionation to separate a light vaporous fraction containing hydrocarbons having 5 carbon atoms and less to the molecule from the higher boiling hydrocarbons containing 6 and more carbon atoms to the molecule. The latter fraction was subjected to aromatization treatment in the presence of an alumina-chromia catalyst at a temperature of 932° F. and at a superatmospheric pressure of 40 pounds per square inch to convert a substantial portion to unsaturated cyclic compounds. The products from the aromatization treatment were commingled with the light vaporous fraction from the last mentioned fractionation, the mixture subjected to cooling and condensation and the resulting distillate and gases collected and separated.

This operation on the basis of 1000 barrels of crude oil charged per 24 hour day resulted in a yield of gasoline equivalent to approximately 67.5% by volume of the charging stock having an octane rating of 75, the remaining 32.5% being liquid residue, gas and loss.

I claim as my invention:

1. A process which comprises fractionating crude petroleum to form a residual fraction, a light fraction containing straight-run gasoline components, and an intermediate fraction heavier than gasoline, thermally cracking said residual fraction, catalytically cracking said intermediate fraction, combining said light fraction with gasoline products of said thermal and catalytic treatments, subjecting the resultant mixture to aromatization, and recovering the aromatized gasoline.

2. A process which comprises fractionating crude petroleum to form a residual fraction, a light fraction containing straight-run gasoline components, and an intermediate fraction heavier

than gasoline, thermally cracking said residual fraction, catalytically cracking said intermediate fraction, combining said light fraction with gasoline products of said thermal and catalytic treatments, aromatizing the resultant mixture in the presence of a dehydrocyclization catalyst, and recovering the aromatized gasoline.

3. A process which comprises fractionating crude petroleum to form a residual fraction, a light fraction containing straight-run gasoline components, and an intermediate fraction heavier than gasoline, thermally cracking said residual fraction, catalytically cracking said intermediate fraction, combining said light fraction with gasoline products of said thermal and catalytic treatments, fractionating the resultant mixture to separate therefrom the hydrocarbons of less than six carbon atoms to the molecule, subjecting the remainder of said mixture to aromatization, and blending the resultant gasoline boiling products with said hydrocarbons of less than six carbon atoms.

4. A process for producing anti-knock motor fuel from crude petroleum which comprises topping the crude to separate straight-run gasoline fractions therefrom, cracking portions of the

crude heavier than gasoline to produce cracked gasoline, combining the latter with said straight-run gasoline fractions, subjecting the resultant mixture to aromatization in the presence of a dehydrocyclization catalyst, and recovering the aromatized gasoline.

5. A process for producing anti-knock motor fuel from crude petroleum which comprises topping the crude to separate straight-run gasoline fractions therefrom, cracking portions of the crude heavier than gasoline to produce cracked gasoline, combining the latter with said straight-run gasoline fractions, fractionating the resultant mixture to separate therefrom the hydrocarbons of less than six carbon atoms to the molecule, subjecting the remainder of said mixture to aromatization in the presence of a dehydrocyclization catalyst, and blending the resultant gasoline boiling products with said hydrocarbons of less than six carbon atoms.

6. The process as defined in claim 3 further characterized in that said remainder of said mixture is subjected to aromatization in the presence of a dehydrocyclization catalyst.

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