

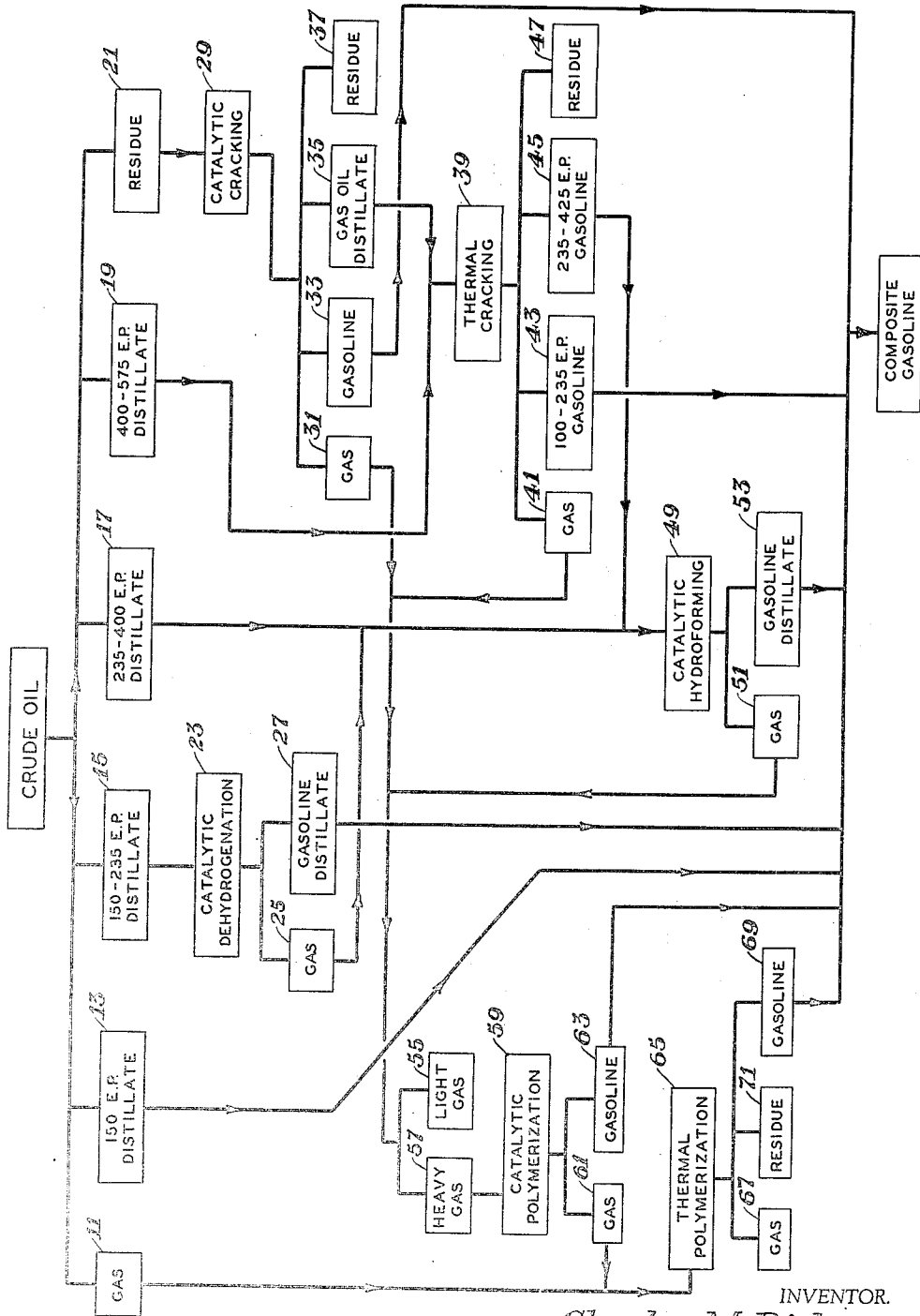
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MOTOR FUEL

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MOTOR FUEL

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This invention relates to the manufacture of high anti-knock gasoline having unusually effective road performance in internal combustion engines at both high and low speeds and more specifically to an integration of steps which involve separately treating by purely thermal and catalytic steps, fractions obtained by fractionation of a relatively wide boiling range charging stock such as crude oil, to produce a high octane gasoline of well-balanced boiling range having a high proportion of unsaturated hydrocarbons in the low boiling portion and a low proportion of unsaturated hydrocarbons in the high boiling portion.

Experience has shown that highly olefinic motor fuels have certain disadvantages with respect to their use in modern automotive engines. Their susceptibility to lead is low as compared with paraffinic hydrocarbons. Furthermore, under high speed operating conditions, olefinic hydrocarbons have a tendency to cause knocking when used in engines having a relatively high compression ratio.

It has been found that these disadvantages may be overcome and unusually effective all-speed performance and high lead susceptibility obtained by controlling the chemical composition-boiling range relationship in motor fuels. The preferred fuels are those fuels which are predominantly olefinic in character in the low boiling portion, that is, that portion of the fuel boiling up to about 140° F. and in which the high boiling portion contains not more than a minor amount of aliphatic unsaturated hydrocarbons. It is particularly advantageous to have the high boiling portion contain substantial amounts, that is, in excess of 30% or 50% by volume of alkylated cyclic, preferably aromatic, hydrocarbons. The high boiling portion is that portion of the fuel boiling between approximately 235° F. and the end point of the fuel. The boiling points are determined using an apparatus having a packed fractionating column and in which a relatively high reflux ratio is employed. At the present time most commercial motor fuels have an end point of about 400° F. The intermediate portion of the fuel may consist of hydrocarbons of any chemical structure so long as the octane number of this fraction is sufficiently high to maintain a relatively high overall octane in the finished fuel. The intermediate portion of the fuel is that portion which distills between approximately 140° F. and 235° F. Fuels which have the aforementioned chemical composition-boiling range relationship produce unusually ef-

fective road performance in modern internal combustion engines. As used throughout this specification and in the claims, the term "unsaturated hydrocarbons" does not include aromatic hydrocarbons.

In a specific embodiment, the present invention comprises separating, preferably by fractionation, hydrocarbon mixtures of wide boiling range such as crude oil to produce gas, light gasoline distillate, intermediate gasoline distillate, heavy gasoline distillate, heavy distillate boiling above the gasoline boiling range and residual cracking stock, subjecting intermediate gasoline distillate to catalytic dehydrogenation to produce unsaturated high octane hydrocarbons of gasoline boiling range, separating gas and gasoline boiling range hydrocarbons from the dehydrogenation reaction products, subjecting the residual cracking stock to catalytic cracking and separating gas, gasoline, gas oil distillate boiling above the gasoline boiling range and residue from the cracked reaction products, combining said gas oil distillate and heavy distillate from the initial crude oil fractionation and subjecting the mixture to thermal (non-catalytic) vapor phase cracking whereby to produce substantial proportions of unsaturated hydrocarbons of gasoline boiling range, separating the thermally cracked reaction products into gas, low boiling gasoline distillate, high boiling gasoline distillate and residue, combining said high boiling gasoline distillate with heavy gasoline distillate obtained from the initial crude oil fractionation step and subjecting the mixture to catalytic hydroforming whereby to produce substantial proportions of high octane alkylated cyclic hydrocarbons of gasoline boiling range, separating the hydroformed reaction products into gas and gasoline, combining gas from the catalytic cracking operation and gas from the thermal vapor phase cracking operation and separating the gaseous mixture into light gas and heavy gas fractions, subjecting the heavy gas fraction to catalytic polymerization, separating gas and gasoline from the catalytically polymerized reaction products, subjecting last-mentioned gas in admixture with gas separated from the initial crude oil fractionation step to thermal (non-catalytic) polymerization, separating thermally polymerized reaction products into gas and gasoline and combining light gasoline distillate from the initial crude oil fractionation operation, gasoline boiling range hydrocarbons from the catalytic dehydrogenation operation, gasoline from the catalytic cracking operation, low boiling gasoline distillate from

the thermal vapor phase cracking operation, gasoline from the catalytic hydroforming operation, gasoline from the catalytic polymerization step and gasoline from the thermal polymerization step to produce a uniform boiling range high anti-knock gasoline having unusual performance characteristics in modern internal combustion engines.

An object of this invention is to provide a unitary process for producing a well-balanced motor fuel capable of producing unusually effective performance in modern internal combustion engines at all engine speeds.

Another object of this invention is to produce motor fuels of high anti-knock rating and smooth curve boiling range having a predominant proportion of unsaturated hydrocarbons in the fraction boiling up to approximately 140° F. and not more than a minor proportion of unsaturated aliphatic hydrocarbons and a major proportion of isoparaffins and/or alkylated cyclic hydrocarbons such as alkylated benzenes in the fraction boiling above approximately 235° F.

A still further object of the invention is to provide a method of treating hydrocarbons of relatively wide boiling range by a combination of purely thermal and catalytic conversion processes wherein each specific process is correlated with other processes to provide maximum thermal and operating efficiency and to efficiently utilize a high proportion of the hydrocarbons in producing a high octane motor fuel having unusually effective performance characteristics.

A still further object of the invention is to provide a method for improving the performance of motor fuels by proper treatment of particular fractions and the blending of the fractions after treatment.

Other objects of the invention will become apparent from the following description when considered in conjunction with the accompanying drawing, the single figure of which is a diagrammatic flow sheet illustrating the process of the invention in such a manner as to eliminate unnecessary complications of processing details of each specific step, since those skilled in the art are now familiar with these details.

Referring to the accompanying drawing, hydrocarbons of relatively wide boiling range such as crude oil are separated, preferably by fractionation, into a gas fraction 11, a light gasoline distillate 13 of high anti-knock value and preferably of about 150° F. end point, an intermediate gasoline distillate 15 preferably boiling in the approximate range of 150 to 235° F., heavy gasoline distillate 17 preferably boiling in the approximate range of 235 to 425° F., heavy distillate 19 boiling above the gasoline boiling range and preferably within the approximate range of 400 to 575° F. and residual cracking stock 21.

The light gasoline distillate 13 is ordinarily relatively small in volume and is cut to a low end point so that it consists largely of high octane hydrocarbons, the particular type of hydrocarbons varying widely depending upon the particular type of crude oil charged to the process. This fraction is employed without further processing in the blending of the desired composite gasoline.

Intermediate gasoline distillate 15 which is ordinarily a predominantly saturated fraction is charged to catalytic dehydrogenation zone 23 and therein dehydrogenated to produce unsaturated high octane hydrocarbons of gasoline boiling range. Such a process may be effectively carried

out at temperatures of about 400 to 700° C. at relatively low superatmospheric pressure and in the presence of catalysts comprising refractory metallic oxides such as aluminum and magnesium oxides supporting compounds of metals such as those in the left-hand columns of groups 4, 5 and 6 of the periodic table. Such a dehydrogenation process is more fully set forth in Grosse Patent No. 2,231,446. The catalytically dehydrogenated reaction products are separated into gas 25 and gasoline 27. The gas 25 which is rich in hydrogen may be withdrawn from the system or may be employed in a catalytic hydroforming operation as will be subsequently described. Gasoline 27 is blended with gasoline fractions obtained from other steps in the process to produce the desired composite gasoline.

Residue 21 which is preferably at elevated temperatures as a result of the initial fractionating step is charged to catalytic cracking zone 29 and therein subjected to suitable conditions of time, temperature and pressure to produce conversion products containing substantial proportions of high octane hydrocarbons of gasoline boiling range. Various catalytic cracking processes are known and that process may be selected which produces a gasoline containing the lowest proportion of unsaturated hydrocarbons in the high boiling fraction and the highest proportion of unsaturated hydrocarbons in the low boiling fraction. Suitable catalytic cracking processes include the so-called "Houdry" process and the "C. R. A." process. The "Houdry" cracking process is described in numerous patents such as, for example, Patent No. 2,161,676. The "C. R. A." cracking process is particularly suitable for producing motor fuel hydrocarbons of the desired chemical composition in accordance with this invention and is adapted particularly well to operate in conjunction with the other operations described herein. In accordance with the operating conditions employed in the "C. R. A." cracking process, the residual cracking stock is subjected to sufficient heat to vaporize a substantial portion of the hydrocarbons, the vaporized hydrocarbons separated from unvaporized residue, admixed with steam and catalyst and brought to a conversion temperature of the order of 950° F. The pressure employed in the reaction zone is of the order of 10 pounds per square inch. A process of this type is covered by the patent to Miller No. 1,799,858. Very finely divided catalyst such as silica, alumina or activated clays is employed and is maintained in suspension in the mixture of vaporized hydrocarbons mixed with a relatively small quantity of steam in a reaction zone and the entire mixture retained in the reaction zone for a sufficient time to produce substantial proportions of high octane conversion products of motor fuel boiling range. The solid catalyst is removed by means of cyclone precipitators or collectors from the effluent from the reaction zone. Irrespective of the particular catalytic cracking process employed, the catalytically cracked reaction products are separated into gas 31, gasoline 33, gas oil distillate 35 consisting of hydrocarbons boiling above gasoline boiling range and residue 37. Gasoline 33 is blended with gasoline fractions obtained from other steps in the process to produce the desired composite gasoline.

Gas oil distillate 35 is combined with heavy distillate 19 obtained from the crude oil separation step and the mixture charged to a high temperature thermal (non-catalytic) cracking zone 39 whereby a substantial portion of the mixture

charged is converted into unsaturated high octane gasoline boiling range hydrocarbons. The cracking operation is preferably conducted at temperatures of the order of 1000 to 1500° F. and at relatively low superatmospheric pressure. No catalyst is employed. Such a thermal vapor phase cracking operation is more fully described in Greenstreet Patent No. 1,886,093. The thermally cracked products are separated into gas 41, low boiling gasoline distillate 43, high boiling gasoline distillate 45 and residue 47. Low boiling gasoline distillate fraction 43 is blended with gasoline fractions obtained from other steps in the process to produce the desired composite gasoline.

High boiling gasoline fraction 45 is combined with heavy gasoline distillate 17 obtained from the initial crude oil separation step and the mixture charged to catalytic hydroforming zone 49. Hydrogen is also supplied to the hydroforming zone preferably in admixture with the oil charging stock. The hydrogen may be obtained from an external source, or gas 25 obtained from the catalytic dehydrogenation zone 23 and which is rich in hydrogen, may be used. The hydrogen-containing mixture in the hydroforming zone is contacted with suitable catalysts such as the oxides of metals of the third, fifth or sixth groups of the periodic table, alone or on a support such as activated alumina, silica or pumice at temperatures of about 950 to 1050° F. and pressures of approximately 300 to 3000 pounds per square inch. Further details of a suitable hydroforming process are set forth in Pier et al. Patent No. 2,045,795. The conversion products of such a process contain a high proportion of alkylated cyclic hydrocarbons, particularly aromatics of the single ring type boiling within the range of the high boiling portion, i. e., 235 to 425° F., of gasoline. Catalytically hydroformed conversion products from hydroforming zone 49 are separated into gas 51 and gasoline distillate 53 which is combined with gasoline fractions produced in other steps of the process to form the desired composite gasoline. Gas 51 may be withdrawn from the system or supplied to a gas separation step to be subsequently described.

Gas 31 from the catalytic cracking zone in combination with gas 41 from the thermal vapor phase cracking zone is separated into a light gas fraction 55 consisting largely of hydrogen, methane and ethane and a heavy gas fraction 57 consisting largely of C₃ and C₄ hydrocarbons. Gas fraction 51 obtained from the catalytic hydroforming zone may also be included in the aforementioned gaseous mixture which is separated into light and heavy gas fractions. The light gas fraction 55 is withdrawn from the system. Heavy gas fraction 57 is charged to catalytic polymerization zone 59 and therein polymerized to produce substantial proportions of high octane gasoline boiling range hydrocarbons. The conditions maintained in the catalytic polymerization zone are temperatures of the order of 50 to 500° F. and pressures of the order of 200 pounds per square inch. The polymerization is effected in the presence of suitable polymerization catalysts such as phosphoric acid catalysts. A more specific description of a suitable catalytic polymerization process is set forth in Holm et al. Patent No. 2,186,021. The catalytically polymerized reaction products are separated into gas 61 and gasoline 63 which is combined with gasoline fractions produced in other steps of the process to form the desired composite gasoline.

Gas fraction 61 in admixture with gas 11 ob-

tained from the initial crude oil separation step is charged to thermal polymerization zone 65 and therein subjected to suitable conditions of elevated temperature and pressure to convert substantial proportions of the hydrocarbons charged to high octane hydrocarbons of gasoline boiling range. Temperatures of the order of 850 to 1100° F. and pressures of 500 to 2000 pounds per square inch are suitable. Such a thermal polymerization process is more fully described in Wagner Patent No. 2,157,225. The thermally polymerized reaction products are separated into gas 67 which is withdrawn from the system, gasoline 69 and residue 71. Gasoline 69 is combined with gasoline fractions produced in other steps of the process to form the desired composite gasoline.

It will be seen from a consideration of the foregoing description that a process has been described wherein a high proportion of the hydrocarbons found in crude oil is efficiently utilized for producing motor fuel containing predominant proportions of unsaturates in the low boiling range and not more than minor proportions of unsaturates together with substantial proportions of alkylated cyclic hydrocarbons in the high boiling range, which motor fuels have been found capable of producing unusually effective road performance in modern internal combustion engines.

The specific operating conditions which may be employed in successfully conducting the various steps of the process will vary considerably depending upon the type of crude oil charging stock employed, the particular composition of the fractions subjected to conversion in each of the individual cooperative steps and the specific type of catalyst employed in the catalytic conversion zones. Since the regulation of the operating conditions in each of the individual steps to accomplish the object herein set forth is within the skill of those working in the art, no attempt has been made to herein define the specific limits of satisfactory operating conditions.

Although reference has been made to specific patents in connection with various steps in the process, it should be understood that the patents have been cited as being merely illustrative of the particular steps. For example, other methods are known for the dehydrogenation of saturated gasoline boiling range hydrocarbons. The same is true of the hydroforming and catalytic cracking steps. The various steps in the process are limited, therefore, only by the following definitions:

Catalytic dehydrogenation.—A process for converting saturated gasoline boiling range hydrocarbons into unsaturated gasoline boiling range hydrocarbons of high anti-knock value, said process being carried out under conditions of elevated temperature and in the presence of a catalyst.

Catalytic cracking.—A process for thermally converting higher boiling hydrocarbons into gasoline boiling range hydrocarbons in the presence of a catalyst.

Thermal vapor phase cracking.—A process for thermally converting, in the vapor phase, higher boiling hydrocarbons into gasoline boiling range hydrocarbons in the absence of a catalyst.

Hydroforming.—A process for catalytically converting non-aromatic hydrocarbons boiling approximately within the gasoline range into alkylated cyclic hydrocarbons boiling approximately within the gasoline boiling range.

Catalytic polymerization.—A process for converting normally gaseous hydrocarbons into high

octane hydrocarbons boiling in the gasoline boiling range in the presence of a catalyst.

Thermal polymerization.—A process for converting normally gaseous hydrocarbons into high octane hydrocarbons boiling in the gasoline boiling range at elevated temperatures and in the absence of a catalyst.

While the invention has been shown and described in connection with a specific form of the invention, it will be understood that the invention is not limited to these conditions and is limited only as defined in the following claims.

I claim:

1. The process for preparing gasoline from crude petroleum oil which comprises separating said oil into light gasoline distillate, heavy gasoline distillate, heavy distillate boiling above gasoline boiling range and residual cracking stock, subjecting the light gasoline distillate before admixture with cracked gasoline to catalytic dehydrogenation suitable for converting said distillate into high octane unsaturated hydrocarbons of gasoline boiling range and separating gasoline boiling range hydrocarbons from the dehydrogenation conversion products, subjecting the residual cracking stock to catalytic cracking, separating gas, gasoline distillate and gas oil distillate boiling above gasoline boiling range from the catalytic cracking conversion products, subjecting said gas oil distillate and said heavy distillate to thermal vapor phase cracking at temperatures of 1000 to 1500° F., recovering gas, low boiling gasoline distillate and high boiling gasoline distillate from the thermal cracking conversion products, subjecting said high boiling gasoline distillate and said heavy gasoline distillate to hydroforming, separating gas and gasoline distillate from the hydroforming conversion products, subjecting higher boiling constituents in the gas from said catalytic cracking and from said thermal vapor phase cracking steps to polymerization, separating gas and gasoline from the polymerization conversion products and combining gasoline boiling range hydrocarbons from the dehydrogenation operation, gasoline distillate from the catalytic cracking operation, low boiling gasoline distillate from the thermal vapor phase cracking operation, gasoline distillate from the hydroforming operation and gasoline from the polymerizing operation to produce a composite uniform boiling range high anti-knock gasoline.

2. Process in accordance with claim 1 in which the polymerization operation includes subjecting said higher boiling constituents to a primary catalytic polymerization step, separating the catalytic polymerization conversion products into gas and gasoline, subjecting said last-mentioned gas to thermal polymerization and separating the thermal polymerization conversion products into gas and gasoline.

3. Process in accordance with claim 1 in which higher boiling constituents in the gas separated from the hydroformed reaction products are charged to the polymerization operation.

4. A process for converting hydrocarbon oil of wide boiling range into gasoline of uniform boiling range and high anti-knock value comprising separating said oil into gas, light gasoline distillate, intermediate gasoline distillate, heavy gasoline distillate, heavy distillate boiling above gasoline boiling range and residue, subjecting intermediate gasoline distillate before admixture with cracked gasoline to dehydrogenation whereby to produce unsaturated hydrocarbons of gasoline

boiling range, separating the dehydrogenation conversion products into gas and gasoline distillate, subjecting said residue to catalytic cracking, separating gas, gasoline, gas oil distillate boiling above gasoline boiling range and residue from the catalytic cracking conversion products, combining said gas oil distillate with said heavy distillate and subjecting the mixture to thermal vapor phase cracking at temperatures of 1000 to 1500° F., recovering gas, low boiling gasoline distillate and high boiling gasoline distillate from the thermal cracking conversion products, combining said high boiling gasoline distillate with said heavy gasoline distillate and subjecting the mixture to hydroforming, separating gas and gasoline distillate from the hydroforming conversion products, combining gas from the catalytic cracking step with gas from the thermal cracking step and separating higher boiling constituents from lower boiling constituents of the gases, subjecting said higher boiling constituents to polymerization, separating gas and gasoline from the polymerization conversion products and combining light gasoline distillate from said initial separation step, gasoline distillate from the dehydrogenation operation, gasoline from the catalytic cracking step, low boiling gasoline distillate from the thermal vapor phase cracking step, gasoline distillate from the hydroforming step and gasoline from the polymerization operation to form the desired composite gasoline.

5. Process in accordance with claim 4 in which gas from the dehydrogenation step is supplied to the hydroforming step.

6. Process in accordance with claim 4 in which gas from the hydroforming step is combined with gas from the catalytic and thermal cracking steps prior to separation of said gases into higher boiling and lower boiling constituents.

7. Process in accordance with claim 4 in which the polymerization operation includes a primary catalytic polymerization step, separating the catalytic polymerization conversion products into gas and gasoline, subjecting said last-mentioned gas to thermal polymerization and separating the thermal polymerization conversion products into gas and gasoline.

8. Process in accordance with claim 4 in which the polymerization operation includes a primary catalytic polymerization step, separating the catalytic polymerization conversion products into gas and gasoline, subjecting said last-mentioned gas in admixture with gas from said initial separation step to thermal polymerization and separating the thermal polymerization conversion products into gas and gasoline.

9. A process for preparing gasoline from crude petroleum oil which comprises separating said oil into gas, light gasoline distillate, intermediate gasoline distillate, heavy gasoline distillate, heavy distillate boiling above gasoline boiling range and residue, subjecting said intermediate gasoline distillate before admixture with cracked gasoline to dehydrogenation whereby to produce unsaturated hydrocarbons of gasoline boiling range, separating the dehydrogenation conversion products into gas and gasoline distillate, subjecting said residue to catalytic cracking, separating gas, gasoline and gas oil distillate boiling above gasoline boiling range from the catalytic cracking conversion products, combining said gas oil distillate with said heavy distillate and subjecting the mixture to thermal vapor phase cracking at temperatures of 1000 to 1500° F., recovering gas, low boiling gasoline distillate and high boiling gasoline dis-

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distillate from the thermal cracking conversion products, combining said high boiling gasoline distillate with said heavy gasoline distillate and gas from said hydrogenation step and subjecting the mixture to hydroforming, separating gas and gasoline distillate from the hydroforming conversion products, combining gas from the catalytic cracking step, gas from the thermal cracking step and gas from the hydroforming step and separating higher boiling constituents from lower boiling constituents of the gases, subjecting said higher boiling constituents to catalytic polymerization, separating gas and gasoline from the catalytic polymerization conversion products, combining said last-mentioned gas with gas separated in the initial separation step and subjecting the mixture to thermal polymerization, separating gas and gasoline from the thermal polymerization conversion products and combining light gasoline distillate from said initial separation step, gasoline distillate from the dehydrogenation step, gasoline from the catalytic cracking step, low boiling gasoline distillate from the thermal vapor phase cracking step, gasoline distillates from the hydroforming step, gasoline from the catalytic polymerization step and gasoline from the thermal polymerization step to form the desired high octane uniform boiling range composite gasoline.

10. The process of converting crude petroleum oil into gasoline of high anti-knock value which comprises fractionating the oil into a light

gasoline fraction, a heavy gasoline fraction, a distillate boiling above the gasoline boiling range and a residue, catalytically dehydrogenating the light gasoline fraction before admixture with cracked gasoline to produce unsaturated gasoline and gas rich in hydrogen, catalytically cracking the residue and separating from the reaction product gasoline and distillate boiling above the gasoline boiling range, combining the last mentioned and first mentioned distillates and subjecting the mixture to thermal cracking at temperatures of 1000 to 1500° F., separating from the thermal cracking reaction products, light and heavy gasoline fractions, combining the last mentioned fraction with the first mentioned heavy gasoline fraction and subjecting the mixture to catalytic hydroforming in conjunction with hydrogen rich gas from the dehydrogenation step, recovering gasoline boiling hydrocarbons from the reaction mixture and combining them with the gasoline from the dehydrogenating and catalytic cracking steps and the light gasoline fraction from the thermal cracking step to form the desired high anti-knock gasoline.

11. Method in accordance with claim 10 in which the light gasoline fraction subjected to catalytic dehydrogenation boils within the approximate range of 150-235° F. and the fractions subjected to catalytic hydroforming boil within the approximate range of 235-425° F.

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