

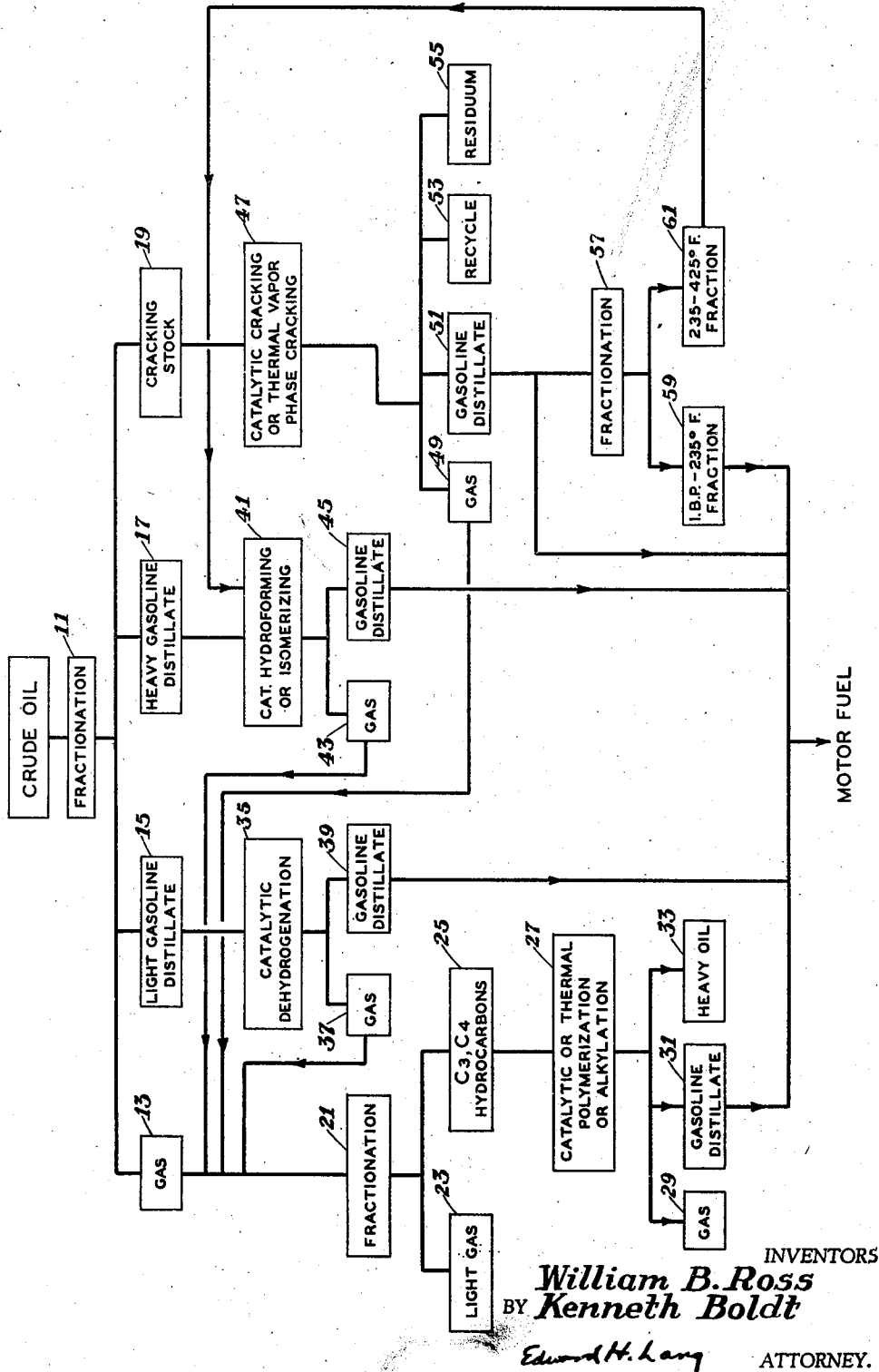
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MOTOR FUELS

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MOTOR FUEL

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This invention relates to the manufacture of high anti-knock gasoline having a well-balanced distillation range and unusually effective road performance in modern internal combustion engines, and more particularly to an integration of steps which involve separately treating by thermal and catalytic steps fractions obtained by fractionation of relatively wide boiling range hydrocarbon mixtures such as crude oil, particularly crude oil in which the gasoline boiling constituents are of the saturated type, whereby to obtain a well-balanced boiling range gasoline of high anti-knock properties having a high proportion of unsaturated hydrocarbons in the low boiling fraction and not more than a minor amount of unsaturated hydrocarbons in the high boiling portion.

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

It has been found that these disadvantages may be overcome and particularly effective all-speed performance and high lead susceptibility may be obtained by controlling the chemical composition-boiling range relationship in the gasoline. The preferred gasolines are those in which the low boiling portion of the gasoline—that is, the portion boiling from approximately 100° to 140° F.—is predominantly unsaturated in character and in which the high boiling portion—that is, the portion boiling from approximately 235° to 400° F.—contains not more than a minor amount of aliphatic unsaturated hydrocarbons. The intermediate portion of the fuel—that is, the portion boiling from approximately 140° to 235° F.—may consist of any type of hydrocarbons so long as the octane number of this fraction is sufficiently high to maintain a high overall octane number in the finished motor fuel. The boiling points of the aforementioned fractions are determined using an apparatus having a packed fractionating column and in which a relatively high reflux ratio is employed. Fuels which have the aforementioned chemical composition-boiling range relationship produce unusually effective 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 fractionating a mixture of hydrocarbons of widely divergent boiling range such as, for example, crude oil, particularly highly paraffinic crude oil of the type obtained from Michigan and Pennsylvania producing areas, to produce gas, light gasoline distillate, heavy gasoline distillate and residual cracking stock; supplying said gas in admixture with gases from other steps of the process to be subsequently described, to a fractionation zone and therein separating non-condensable gases consisting largely of hydrogen, methane and ethane from normally gaseous hydrocarbons of higher molecular weight such as C₃ and C₄ hydrocarbons; supplying said last-mentioned hydrocarbons to a catalytic or thermal polymerization or alkylation zone to convert a substantial portion of the hydrocarbons charged into high octane hydrocarbons of motor fuel boiling range; separating the conversion products of the polymerization or alkylation zone into gas, gasoline distillate and heavy oil boiling above the gasoline boiling range and blending the gasoline distillate with other gasoline fractions to produce a composite motor fuel; charging light gasoline distillate separated in the initial fractionation step to a catalytic dehydrogenation zone whereby to produce substantial proportions of high octane unsaturated hydrocarbons of gasoline boiling range and a gas fraction; supplying the gas fraction to the first-mentioned gas fractionating step and blending the gasoline fraction with other gasoline fractions to produce a composite motor fuel; charging the heavy gasoline distillate separated in the initial fractionation step to a catalytic hydroforming or isomerizing zone to convert a substantial proportion of the hydrocarbons charged into high octane hydrocarbons boiling in the upper portion of the gasoline boiling range and containing only a relatively small amount of unsaturated hydrocarbons; separating the conversion products from said hydroforming or isomerizing zone into gas and gasoline; supplying the gas to the first-mentioned gas fractionating step and blending the gasoline with other gasoline fractions to produce a composite motor fuel; charging the residual cracking stock separated in the initial fractionation step to a catalytic cracking or thermal vapor phase cracking step whereby to produce substantial proportions of gasoline boiling range hydrocarbons of high octane value; separating the conversion products from the aforementioned cracking zone into gas, gasoline distillate, recycle stock and

residuum; supplying the gas to the first-mentioned gas fractionating step and blending the gasoline distillate with other gasoline fractions to produce a composite motor fuel. The resultant composite gasoline blend is of high octane number, contains a predominant amount of unsaturated hydrocarbons in the low boiling fraction and only a minor amount of unsaturated hydrocarbons in the high boiling fraction.

An object of this invention is to provide a method for producing a balanced motor fuel capable of producing unusually effective all-speed performance in internal combustion engines.

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 benzenes in the fraction boiling above approximately 235° F.

A further object of this invention is to provide a method for efficiently converting high proportions of wide boiling range hydrocarbon mixtures by thermal and catalytic steps wherein each specific step is correlated with other steps to provide maximum thermal and operating efficiency to produce motor fuel possessing unusually high road performance characteristics.

A further object of the invention is to produce motor fuel of high anti-knock rating having a predominant proportion of unsaturated hydrocarbons in the low boiling range and not more than a minor proportion of unsaturated aliphatic hydrocarbons in the high boiling range.

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

Other objects of the invention will become apparent from the following description considered in conjunction with the accompanying drawing, the single figure of which is a diagrammatic flow sheet illustrating a specific form of the invention. A flow sheet has been used in order to illustrate the invention without complicating the drawing with unnecessary processing details of each specific step, since those skilled in the art are familiar with the details of these steps.

Referring to the accompanying drawing, hydrocarbon oil of wide boiling range, particularly Michigan or Pennsylvania type crude oil, is supplied to a fractionation zone 11 and therein separated into gas 13, light gasoline distillate 15, heavy gasoline distillate 17 and residual cracking stock 19. The gas fraction 13 in admixture with gases obtained from other steps of the process as will be subsequently described, is supplied to a gas fractionation zone 21 and therein fractionated into light gases 23 consisting largely of hydrogen, methane and ethane and heavy gases 25 such as C₃ and C₄ hydrocarbons. The heavy gases are supplied to a catalytic or thermal polymerization or alkylation zone 27 in order to convert a substantial proportion of the hydrocarbons charged to this zone into high octane hydrocarbons of motor fuel boiling range. It is preferred to employ catalytic or thermal polymerization. In subjecting the heavier gaseous hydrocarbons 25 to catalytic polymerization, the gases may be

contacted with phosphoric acid catalyst at temperatures of about 50-400° F. for a sufficient time to produce substantial amounts of gasoline boiling range hydrocarbons, all as is more particularly described in Holm et al. Patent No. 2,186,021. When a thermal, or non-catalytic, polymerization step is employed, the gases are subjected to temperatures of the order of 850-1100° F. at pressures of about 400 to 2000 pounds per square inch for a sufficient time to produce substantial quantities of gasoline boiling range hydrocarbons. Further specific details of conditions suitable for thermal polymerization are set forth in Wagner Patent No. 2,157,225. In the event that it is desired to subject the heavy gases 25 to an alkylation step, the gases are contacted with a sulfuric acid catalyst at low super-atmospheric pressures and temperatures of about 15-150° F., as is more particularly described in the patent to Holm et al. No. 2,244,556.

Irrespective of the particular process to which the heavy hydrocarbon gases are subjected, the conversion products from the catalytic or thermal polymerization or alkylation zone 27 are separated into gas 29, gasoline distillate 31 and heavy oil 33. The gasoline distillate thus obtained is blended with other gasoline fractions obtained in the process to produce a composite motor fuel.

The light gasoline distillate obtained from the initial crude oil fractionation step usually has a boiling range of about 100° to 235° F., and when Michigan or Pennsylvania type crude oils are employed, is highly paraffinic in character and of relatively low octane number. This distillate is supplied to catalytic dehydrogenation zone 35 and therein subjected to temperatures of the order of 752° to 1292° F. in contact with suitable catalysts such as aluminum or magnesium oxides supporting oxides of elements in the left-hand columns of the fourth, fifth and sixth groups of the periodic table to produce unsaturated high octane hydrocarbons of substantially the same boiling range as the fraction charged. Suitable dehydrogenating conditions are more particularly described in Grosse Patent No. 2,231,446. Conversion products from the catalytic dehydrogenation step 35 are separated into gas 37 and gasoline distillate 39. Gas 37 is admixed with gas obtained from the initial crude oil fractionation step and supplied to gas fractionation zone 21. Gasoline distillate 39 which is of high octane number and of relatively high unsaturate content is blended with other gasoline fractions produced in the process to form the composite gasoline.

Heavy gasoline distillate 17 obtained from the initial crude oil fractionation step preferably has a boiling range of approximately 235° to 425° F. This distillate when employing crude oils of the aforementioned type is also highly paraffinic in character and of very low octane number. The distillate is supplied to a catalytic hydroforming or isomerizing step 41 wherein the hydrocarbons charged are converted into substantial proportions of high octane hydrocarbons boiling in the upper portion of gasoline boiling range and containing not more than minor amounts, usually very small amounts, of unsaturated hydrocarbons. When employing a catalytic hydroforming step the heavy gasoline distillate is subjected to temperatures of about 950° to 1050° F. and pressure of about 300 to 3000 pounds per square inch in contact 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. Further specific details of suitable operating conditions are more fully 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 of the single ring type boiling within the range of the high boiling portion of gasoline. In the event that the heavy gasoline distillate is subjected to isomerization, the distillate is contacted with suitable catalysts such as sulfuric acid or chlor-sulfonic acid at temperatures between about -25° and $+70^{\circ}$ F., whereby to produce high yields of substantially saturated gasoline boiling range high octane hydrocarbons. Further specific details of such a process are found in Lynch et al. Patent No. 2,223,180. Conversion products from the catalytic hydroforming or isomerizing step 41 are separated into gas 43 and gasoline 45. The gas is admixed with gas obtained from the initial crude oil fractionation step and supplied to gas fractionation zone 21. Gasoline 45 is blended with other gasoline distillates produced in the process to form the composite gasoline.

Residual cracking stock 19, preferably at elevated temperature as a result of the initial fractionating step, is supplied to cracking zone 47 and therein subjected to catalytic cracking or thermal vapor phase cracking in order to produce high yields of high octane number gasoline boiling range hydrocarbons. When catalytic cracking of the cracking stock 19 is employed, any one of several processes may be used, the preferable ones being those that produce the highest proportions of unsaturated hydrocarbons in the low boiling portion and minimum amounts of unsaturated hydrocarbons in the high boiling portion. Suitable cracking processes include the "Houdry" and "C. R. A." processes. The Houdry process is described in numerous patents as, for example, Patent No. 2,161,676. The C. R. A. process is particularly suitable for producing gasoline hydrocarbons in accordance with this invention and is very suitable for operation in conjunction with the other processes described herein. In this process the cracking stock is subjected to temperatures of the order of 830° F. in order to vaporize a substantial portion of the hydrocarbons, the vaporized hydrocarbons separated from unvaporized liquid, admixed with steam and catalyst and maintained in a reaction zone under conditions of temperature of the order of 950° F. and low superatmospheric pressures of about 10 pounds per square inch for a time suitable to effect the desired conversion into high octane hydrocarbons. Very finely divided catalyst such as silica, alumina or activated clays is employed and is maintained in suspension in the mixture of vaporized hydrocarbons and steam. The solid catalyst is removed by means of cyclone precipitators or collectors from the effluent from the reaction zone. A process of this type is described in Miller Patent No. 1,799,858. Suitable catalysts include silica, alumina and various clays, particularly activated clays. The hydrocarbon reaction products pass through a fractionation step and are separated into the desired fractions. When thermal vapor phase cracking of the cracking stock 19 is employed, the cracking stock is subjected to elevated temperatures to vaporize a substantial portion of the hydrocarbons and the vaporized hydrocarbons maintained in a conversion zone at temperatures of about 1100° to 1500° F. under low

superatmospheric pressure for a sufficient time to produce substantial proportions of high octane gasoline boiling range hydrocarbons. Suitable conversion conditions are more fully set forth in Greenstreet Patent No. 1,886,093.

Irrespective of the particular cracking process employed, the conversion products are separated into gas 49, gasoline distillate 51, recycle stock 53 and residuum 55. The gas fraction 49 is admixed with gases separated from the initial crude oil fractionating step and supplied to gas fractionation zone 21. Gasoline distillate 51 is blended with other gasoline distillates produced in the process to form the composite gasoline.

In the event that gasoline distillate 51 contains high proportions of unsaturated hydrocarbons boiling in the upper portion of the gasoline range, it is desirable to convert a substantial proportion of these compounds into saturated compounds of high octane number and of gasoline boiling range. In this case gasoline distillate 51 is subjected to fractionation in fractionating zone 57 and therein separated into a low boiling gasoline fraction 59 having an end point of approximately 235° F. and a high boiling gasoline fraction 61 having a boiling range of approximately 235 to 425° F. The low boiling gasoline fraction 59, being of a highly unsaturated character, is blended direct with other gasoline fractions to form the composite gasoline. The high boiling unsaturated gasoline fraction 61 is subjected to catalytic hydroforming or isomerizing in conversion zone 41. The hydroforming or isomerizing step may be carried out separately from or preferably in admixture with heavy gasoline distillate 17 obtained from the initial crude oil fractionating step.

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 gasoline containing predominant proportions of unsaturates in the low boiling range and not more than minor proportions of unsaturates in the high boiling range, which gasolines 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 step 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 isomerization of paraffins to iso-paraffin hydrocarbons. The same is true of the hydro-forming 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 in the presence 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.

Isomerization.—A process of catalytically converting straight chain hydrocarbons boiling approximately within the gasoline boiling range into branched chain hydrocarbons of approximately the same boiling range.

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

Thermal vapor phase cracking.—A process for converting higher boiling hydrocarbons in the vapor state into gasoline boiling hydrocarbons by purely thermal means, i. e., without the use of a catalyst.

Catalytic polymerization.—A process for converting normally gaseous hydrocarbons into gasoline boiling range hydrocarbons in the presence of a catalyst.

Thermal polymerization.—A process for converting normally gaseous hydrocarbons into hydrocarbons of gasoline boiling range by purely thermal means, i. e., without the use of a catalyst.

Alkylation.—A process for catalytically converting mixtures of normally gaseous saturated and unsaturated hydrocarbons into substantially saturated high octane gasoline boiling range hydrocarbons.

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.

What is claimed is:

1. A process for preparing gasoline from crude oil which comprises fractionating said oil into gas, light gasoline distillate, heavy gasoline distillate and residual cracking stock, subjecting said light gasoline distillate to dehydrogenation in the presence of a dehydrogenating catalyst at temperatures of approximately 752 to 1292° F. to produce unsaturated hydrocarbons of gasoline boiling range, separating gas and gasoline distillate from the dehydrogenation conversion products, subjecting said heavy gasoline distillate to hydroforming in the presence of a hydroforming catalyst and hydrogen at elevated pressures and at temperatures of approximately 950 to 1050° F., separating gas and gasoline distillate from the hydroforming conversion products, subjecting said residual cracking stock to thermal vapor phase cracking, separating gas, low boiling gasoline distillate and high boiling gasoline distillate from the cracking conversion products, supplying said high boiling gasoline distillate to said hydroforming step, subjecting heavy constituents of the gas from the initial crude oil fractionating step, gas from the dehydrogenation step, gas from the hydroforming step and gas from the cracking step to polymerization to produce substantial amounts of high octane gasoline boiling range hydrocarbons, separating gas and gasoline from the polymerization conversion products, and combining gasoline distillate from the dehydrogenation step, gasoline distillate from the hydroforming step, low boiling gasoline

distillate from the cracking step and gasoline from the polymerization step to produce the desired high octane composite gasoline.

2. In a process for converting crude oil into gasoline, the steps of separating from the crude oil a light gasoline and a heavy gasoline fraction subjecting the light fraction to dehydrogenation in the presence of a dehydrogenating catalyst at temperatures of approximately 752 to 1292° F. in order to convert the paraffinic hydrocarbons to unsaturated hydrocarbons, subjecting the heavy gasoline fraction to hydroforming in the presence of a hydroforming catalyst and hydrogen at elevated pressures and at temperatures of approximately 950 to 1050° F. whereby paraffinic hydrocarbons are converted into high octane number alkylated ring hydrocarbons, and blending the gasoline fractions recovered from the two steps to make a high anti-knock quality gasoline.

3. In a process for converting crude oil into gasoline, the steps of separating from the crude oil a light gasoline fraction boiling within the range of about 100° to 235° F. and a heavy fraction boiling within the range of approximately 235° to 425° F., dehydrogenating the light fraction in the presence of a dehydrogenating catalyst at temperatures of approximately 752 to 1292° F. to convert paraffinic hydrocarbons into olefinic hydrocarbons, hydroforming the heavy fraction in the presence of a hydroforming catalyst and hydrogen at elevated pressures and at temperatures of approximately 950 to 1050° F. into aromatic hydrocarbons of high anti-knock and blending the fractions after conversion to produce a gasoline of high anti-knock quality.

4. In a process in accordance with claim 2, the steps of subjecting crude oil fractions boiling above the gasoline range to high temperature cracking, separating a light and a heavy gasoline fraction from the reaction products, converting the heavy fraction together with the heavy gasoline fraction separated from the crude oil and blending the resulting converted gasoline from the hydroforming operation with the light straight run and cracked gasoline fractions to make the finished gasoline.

5. In a process for converting crude oil into anti-knock gasoline, the steps of separating from the crude oil a light gasoline fraction boiling in the range of about 100° to 235° F., a heavy gasoline fraction boiling within the range of approximately 235 to 425° F. and a fraction heavier than gasoline, subjecting the latter fraction to high temperature cracking in order to produce a fraction boiling up to about 235° F. of highly unsaturated character and a fraction within the approximate boiling range of 235 to 425° F., combining the two fractions boiling within the range of 235 to 425° F. and subjecting them to hydroforming in the presence of a hydroforming catalyst and hydrogen at elevated pressures and at temperatures of approximately 950 to 1050° F., subjecting the initial light fraction to dehydrogenation in the presence of a dehydrogenating catalyst at temperatures of approximately 752 to 1292° F. and combining the converted hydrocarbons from the foregoing steps to produce the desired anti-knock gasoline.

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