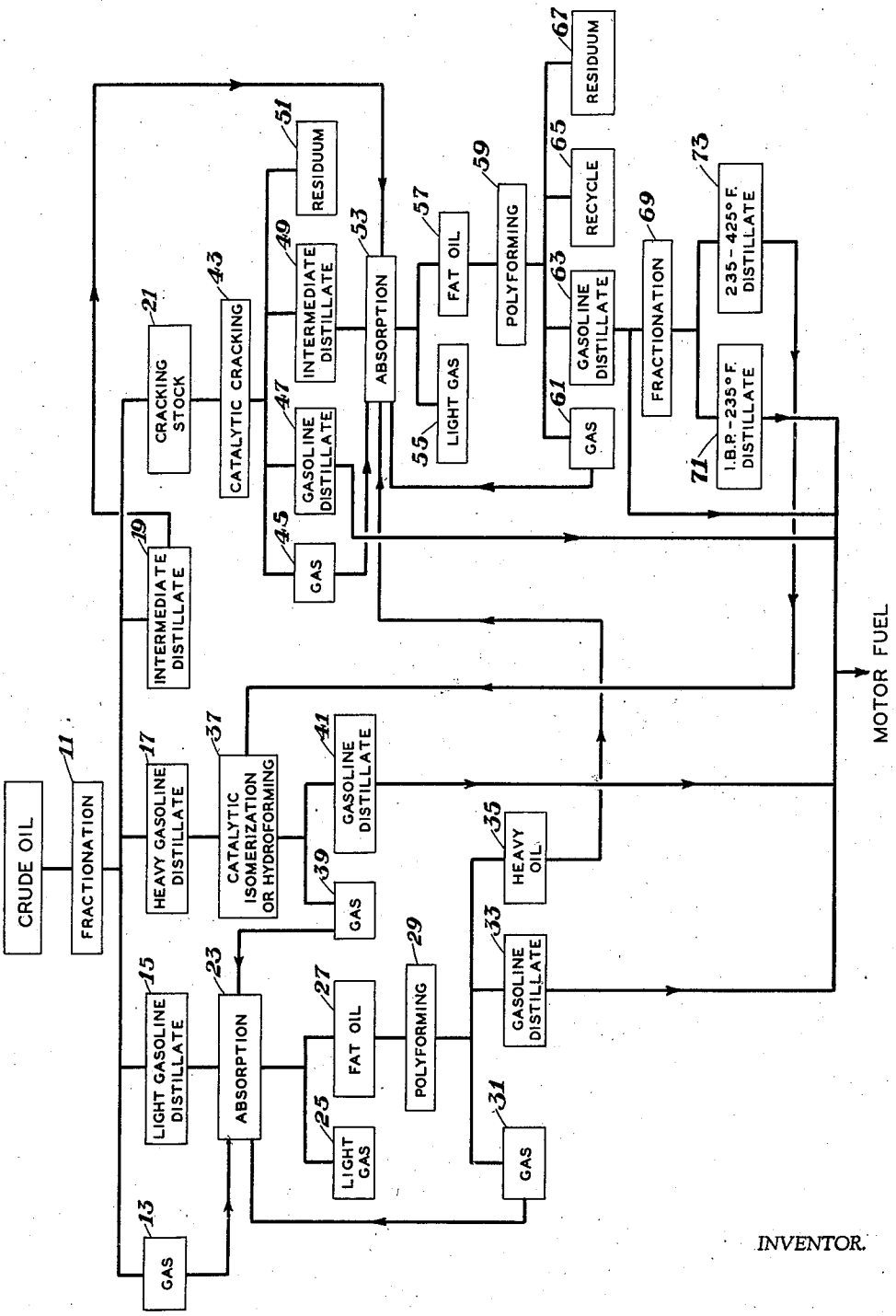
Aug. 1, 1944. E. H. LANG 2,354,866

PROCESS FOR THE MANUFACTURE OF IMPROVED MOTOR FUELS

Filed Nov. 1, 1941



INVENTOR.

Edward H. Lang

Patented Aug. 1, 1944

2,354,866

UNITED STATES PATENT OFFICE

2,354,866

PROCESS FOR THE MANUFACTURE OF IMPROVED MOTOR FUELS

Edward H. Lang, Chicago, Ill., assignor to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

Application November 1, 1941, Serial No. 417,442

11 Claims. (Cl. 196—9)

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 conversion, fractions obtained by fractionation of a relatively wide boiling range charging stock such as crude oil, particularly one in which the gasoline boiling constituents are of the straight chain paraffin type, 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. 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 over-all 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 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 crude oil to produce gas, light gasoline distillate, heavy gasoline distillate, intermediate distillate and residual cracking stock, commingling light gasoline distillate and gas in admixture with gas obtained from other steps of the process as will be subsequently described, in an absorption zone and therein absorbing a substantial portion of the gases in the light gasoline distillate, removing unabsorbed light gases consisting chiefly of hydrogen, methane and ethane from the system, withdrawing enriched light gasoline distillate as a fat oil from the absorption zone and charging it to a polyforming zone, separating the polyformed products into gas, gasoline distillate and heavy oil, charging the last-mentioned gas to the absorption zone, withdrawing the gasoline for blending with other gasoline fractions to produce motor fuel and supplying the heavy oil to a second absorption zone to be subsequently described, charging heavy gasoline distillate obtained from the initial crude oil fractionation to a catalytic isomerizing or hydroforming zone, separating the conversion products from the isomerizing or hydroforming zone into gas and gasoline distillate, charging the gas to the aforementioned absorption zone and blending the gasoline distillate with other gasoline fractions to produce motor fuel, supplying said residual cracking stock to a catalytic cracking zone, separating catalytic cracked products into gas, gasoline distillate, intermediate distillate and residuum, blending the last-mentioned gasoline fraction with other gasoline fractions to produce a finished motor fuel, contacting the gas and intermediate distillate fractions obtained from the catalytic cracking zone in admixture with said first-mentioned intermediate distillate and heavy oil obtained from the polyforming zone in a second absorption zone and therein absorbing a substantial portion of the normally gaseous hydrocarbons, separating the unabsorbed light gases consisting chiefly of hydrogen, methane and ethane from the system, withdrawing fat oil from the absorption zone and supplying it to a polyforming zone, separating the polyformed products into gas, gasoline distillate, recycle stock and residuum, returning the gas fraction to said second absorption zone and blending the gasoline with other gasoline fractions produced in the process to obtain a finished motor fuel.

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 iso-paraffins and/or 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 charged to a fractionation zone **11** and separated by fractionation into a gas fraction **13**, a light gasoline distillate fraction **15**, a heavy gasoline distillate fraction **17**, intermediate distillate **19** and residual cracking stock **21**.

The light gasoline fraction is ordinarily of about 100 to 235° F. boiling range and usually consists predominantly of paraffinic hydrocarbons and is of relatively low octane number, although these characteristics may vary widely depending upon the particular crude oil employed. This fraction is charged to absorption zone **23** and therein contacted with gas fraction **13** under suitable conditions of temperature and pressure to absorb the heavier portions of the gas fraction, principally, hydrocarbons of 3 and 4 carbon atoms. Gas fractions obtained from other steps in the process are also charged to absorption zone **23**, as will be subsequently described. The mixture of gases and light gasoline fraction in the absorption zone are separated into light gas **25** and fat oil **27**. The light gas consisting chiefly of hydrogen, methane and ethane is withdrawn from the system. The fat oil is charged to a polyforming zone **29** and therein subjected to suitable conditions of time, temperature and pressure to produce a substantial proportion of unsaturated hydrocarbons of motor fuel boiling range. The polyforming zone is preferably maintained at pressures of about 500 to 3000 lbs. per sq. in. and at temperatures of about 900 to 1450° F., but preferably 1000° to 1100° F. Further details of such a process are set forth in Ostergaard Patent No. 2,134,926. By such a process the straight run light gasoline distillate can be cracked to a very high degree with a relatively low gas loss, the conversion products containing a high proportion of high octane unsaturated hydrocarbons of motor fuel boiling range. Conversion products from the polyforming zone are separated into gas **31**, gasoline distillate **33** and heavy oil **35** of higher boiling range than that useful in motor fuel. Gas fraction **31** is returned to absorption zone **23** and therein contacted with light gasoline distillate as previously described and gasoline distillate **33** is blended with gasoline fractions obtained from other steps in the process to produce a finished motor fuel. Heavy oil fraction **35** is supplied to an absorption zone as will be subsequently described.

Heavy straight run gasoline distillate **17** preferably having a boiling range of about 235 to 425° F. is supplied to a catalytic isomerization or hydroforming zone **37** and therein converted into hydrocarbons of higher anti-knock value, the conversion products containing a relatively small amount of unsaturated hydrocarbons. When an isomerization step is carried out, the heavy gasoline distillate is contacted with a suitable catalyst such as sulfuric acid or chlorsulfonic acid at temperatures of about −25 to +70° F., and at relatively low superatmospheric pressure. The details of such a process are more completely set forth in Lynch Patent No. 2,223,180. The conversion products of such an isomerizing operation contain a high proportion of saturated high octane hydrocarbons boiling in the high boiling portion of the motor fuel boiling range. In the event a hydroforming step is employed instead of the isomerizing step just described, the heavy gasoline distillate in admixture with hydrogen 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 lbs. per sq. in. Further details of such a 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 aromatics of the single ring type boiling within the range of the high boiling portion, i. e., 235–425° F., of gasoline. Conversion products from the isomerizing or hydroforming step **37** are separated into gas **39** and gasoline distillate **41**. The gas is supplied to absorption zone **23** and therein contacted with light gasoline distillate as previously described. Gasoline distillate **41** is blended with other fractions of motor fuel boiling range obtained from other steps of the process to produce a finished motor fuel.

Residual cracking stock **21**, which is at elevated temperatures as a result of the initial fractionating step, is supplied to a catalytic cracking zone **43** 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 major portion of the hydrocarbons, the vaporized hydrocarbons separated from unvaporized residue are 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 lbs. per sq. in. 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, the steam condensed and the hydrocarbon vapors fractionated into gas **45**, gasoline distillate **47**, intermediate distillate **49** and residuum **51**. The gasoline fraction **47** is blended with other gasoline fractions obtained from other steps in the process to produce a finished motor fuel. Intermediate distillate **49** is charged to an absorption zone **53** in admixture with intermediate distillate **19** from the initial crude oil fractionating step and heavy oil **35** obtained from polyforming operation **29** and therein contacted with gas **45** obtained from the catalytic cracking zone as well as gases obtained from a later step in the process, as will be subsequently described. Heavy oil **35** may also be charged to absorption zone **53**. Products issuing from the absorption zone **53** are separated into light gas **55**, consisting largely of hydrogen, methane and ethane, which is withdrawn from the system and fat oil **57** which is supplied to a second polyforming zone **59** and therein subjected to temperatures of the order of 950 to 1250° F., preferably 950 to 1050° F., and pressures of 100 to 2000 lbs. per sq. in. for a sufficient time to convert a substantial portion of the hydrocarbons charged into high octane hydrocarbons of motor fuel boiling range. The details of such a process are more specifically described in Ostergaard Patent No. 2,135,108. Conversion products from the polyforming zone **59** are separated into gas **61**, gasoline distillate **63**, recycle stock **65** and residuum **67**. The gas fraction **61** is returned to absorption zone **53** in order to effect a separation between non-condensable gases consisting principally of hydrogen, methane and ethane and normally gaseous hydrocarbons of higher molecular weight, principally C_3 and C_4 hydrocarbons. Gasoline distillate **63** will ordinarily contain high proportions of unsaturated hydrocarbons, a large proportion of which are in the low boiling portion of the gasoline. This gasoline fraction, therefore, may be suitable for direct blending with other gasoline fractions to produce the desired finished motor fuel. However, in the event that the gasoline contains more unsaturated hydrocarbons boiling in the high boiling portion of the gasoline range than it is desired to add to the finished motor fuel, the gasoline is subjected to fractionation in fractionating zone **69** and therein separated into a low boiling portion, boiling from about the initial boiling point of fraction **63** to approximately 235° F., and a high boiling gasoline fraction **73** boiling from approximately 235° F. to 425° F. The low boiling gasoline fraction **71** containing a high proportion of unsaturated hydrocarbons is suitable for blending with other gasoline fractions to produce the finished motor fuel while the relatively highly unsaturated high boiling gasoline fraction **73** is supplied to the catalytic hydroforming zone **37** and therein hydroformed in admixture with the straight run heavy gasoline distillate to produce high proportions of alkylated benzene hydrocarbons boiling in the upper portion of the gasoline boiling range as previously described. When distillate **73** is charged to step **37**, the latter is operated as a hydroforming step in order to convert the olefins to aromatic hydrocarbons.

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 a motor fuel containing predominant proportions of unsaturates in the low boiling range and not more than minor proportions of unsaturates 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 step. For example, other methods are known for the isomerization of paraffin to isoparaffin 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:

Polyforming.—A process for converting a mixture of normally liquid and normally gaseous hydrocarbons into gasoline boiling hydrocarbons having good anti-knock qualities, under relatively high superatmospheric pressure and temperature without catalyst.

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.

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 cracking.—A process for thermally

converting higher boiling hydrocarbons into gasoline boiling hydrocarbons in the presence of a catalyst.

Although the invention as described and shown indicates the return of gas from particular steps of the process to one of two absorption steps, it will be understood that the gas from any particular step may be charged to either absorption step or divided between the two absorption steps. It will be understood also that gas from any step may in whole or part be discharged from the system without being returned to an absorption operation.

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. The process for preparing gasoline from crude petroleum oil which comprises separating said oil into low boiling gasoline distillate, high boiling gasoline distillate, distillate heavier than gasoline and heavy cracking stock, subjecting the high boiling gasoline distillate to a catalytic conversion operation suitable for converting said distillate into hydrocarbons which are predominantly non-olefinic but which boil within the gasoline boiling range and have materially higher octane numbers than the charging stock, separating gasoline boiling hydrocarbons from the conversion products of said conversion step, subjecting said low boiling gasoline distillate to purely thermal conversion to increase the octane value thereof, separating gas and gasoline boiling hydrocarbons from the reaction products of said thermal conversion step, subjecting said heavy cracking stock to catalytic cracking, separating gas, gasoline boiling distillate and hydrocarbons boiling above the gasoline boiling range from the conversion products of said catalytic cracking step, subjecting said hydrocarbons boiling above the gasoline boiling range together with said distillate heavier than gasoline to a separate purely thermal cracking operation, recovering gas and gasoline distillate from said last-mentioned operation, subjecting higher boiling constituents in the gas from said thermal operations and from said catalytic cracking operation to conversion in the aforesaid purely thermal conversion steps in admixture with distillate separated from the crude oil and combining the predominantly non-olefinic gasoline boiling range hydrocarbons from the first-mentioned conversion operation, gasoline boiling range hydrocarbons from the purely thermal conversion steps and gasoline boiling range distillate from the catalytic cracking operation to make a composite gasoline.

2. Process in accordance with claim 1 in which the first-mentioned catalytic conversion operation is a hydroforming step.

3. Process in accordance with claim 1 in which the first-mentioned catalytic conversion operation is a hydroforming step, the gasoline distillate from the separate purely thermal conversion operation is separated into a low boiling and a high boiling fraction, the low boiling fraction is blended with the composite gasoline and the high boiling fraction is subjected to hydroforming prior to being blended with the composite gasoline.

4. Process in accordance with claim 1 in which higher boiling constituents of the gas separated in the first-mentioned purely thermal operation are recycled to the first-mentioned purely thermal operation and the higher boiling constituents of the gas separated from the second-mentioned purely thermal operation are recycled to the second-mentioned purely thermal operation.

5. A process for converting hydrocarbons of wide boiling range into gasoline of high antiknock value comprising separating the hydrocarbons of wide boiling range into gas, light gasoline distillate, heavy gasoline distillate, intermediate distillate and cracking stock, contacting light gasoline distillate with said gas in an absorption zone whereby to absorb a substantial portion of the gas, separating fat oil from unabsorbed gases, subjecting said fat oil to a polyforming operation, separating polyformed conversion products into gas, gasoline fraction and hydrocarbons heavier than gasoline, subjecting said heavy gasoline distillate to a hydroforming operation, separating the hydroformed conversion products into gas and gasoline fraction, supplying said last-mentioned gas to said absorption zone whereby to absorb a substantial portion thereof in said light distillate, catalytically cracking said cracking stock, separating the reaction products from the catalytic cracking step into gas, gasoline fraction, intermediate condensate and residuum, absorbing the heavier constituents of said last-mentioned gas in a mixture of intermediate distillate and intermediate condensate in a second absorption zone and subjecting the thus enriched oil to a separate polyforming operation, separating conversion products from the last-mentioned step into gas, gasoline fraction and higher boiling hydrocarbons and blending the gasoline fractions to produce a uniform boiling range high antiknock gasoline.

6. Process in accordance with claim 5 in which gas from the first-mentioned polyforming operation is supplied to said first-mentioned absorption zone and gas from said second-mentioned polyforming operation is supplied to said second-mentioned absorption zone.

7. Process in accordance with claim 5 in which the gasoline fraction obtained from the second-mentioned polyforming operation is fractionated before blending into lower and higher boiling fractions and a high boiling fraction separated and supplied to said hydroforming operation.

8. A process for converting hydrocarbon oil of wide boiling range into gasoline of high antiknock value comprising separating said oil into gas, light gasoline distillate, heavy gasoline distillate, intermediate distillate and cracking stock, absorbing higher boiling hydrocarbons in said gas in said light gasoline distillate and subjecting the thus enriched oil to a polyforming operation, separating the polyformed conversion products into gas, gasoline fraction and hydrocarbons heavier than gasoline, subjecting said heavy gasoline distillate to a catalytic isomerization operation, separating isomerized conversion products into gas and gasoline fraction, supplying said last-mentioned gas to said absorption zone whereby to absorb the higher boiling constituents of the gas in said light gasoline distillate, subjecting said cracking stock to a catalytic cracking, separating cracked conversion products into gas, gasoline fraction, intermediate condensate and residuum, absorbing higher boiling constituents of said last-mentioned gas in a mixture of intermediate condensate and intermediate distillate in a second absorption zone and subjecting the thus enriched oil to a separate polyforming operation, separating the polyformed conversion products from the last-mentioned polyforming operation into gas, gasoline fraction

and hydrocarbons heavier than gasoline and blending the gasoline fractions to produce a uniform boiling range high antiknock gasoline.

9. Process in accordance with claim 8 in which unabsorbed gases are removed from the system.

10. A process for converting hydrocarbon oil of wide boiling range into high yields of gasoline of high antiknock value comprising separating said oil in a fractionating zone into gas, light gasoline distillate, heavy gasoline distillate, intermediate distillate and cracking stock, absorbing higher boiling constituents of said gas in said light gasoline distillate and subjecting the thus enriched oil to a polyforming operation, separating the polyformed conversion products into gas, gasoline fraction and hydrocarbons heavier than gasoline, subjecting said heavy gasoline distillate to a hydroforming operation, separating hydroformed conversion products into gas and gasoline fraction, absorbing higher boiling constituents of said last-mentioned gas in said light gasoline distillate, subjecting said cracking stock to a catalytic cracking, separating cracked conversion products into gas, gasoline fraction, intermediate condensate and residuum, absorbing higher boiling constituents of said last-mentioned gas in a mixture of intermediate condensate and intermediate distillate and subjecting the thus enriched oil to a separate polyforming operation, separating the conversion products from the last-mentioned polyforming operation into gas, gasoline distillate and hydrocarbons heavier than gasoline, separating said last-mentioned gasoline distillate into a low boiling gasoline fraction and a portion boiling in the upper part of the gasoline boiling range, supplying said last-mentioned gasoline portion to said hydroforming operation and blending the gasoline fractions to produce a uniform boiling range high antiknock gasoline.

11. Process in accordance with claim 10 in which gases from the first and second-mentioned polyforming operations are supplied to the first and second-mentioned absorption steps respectively, and the unabsorbed gases are removed from the system.

EDWARD H. LANG.