

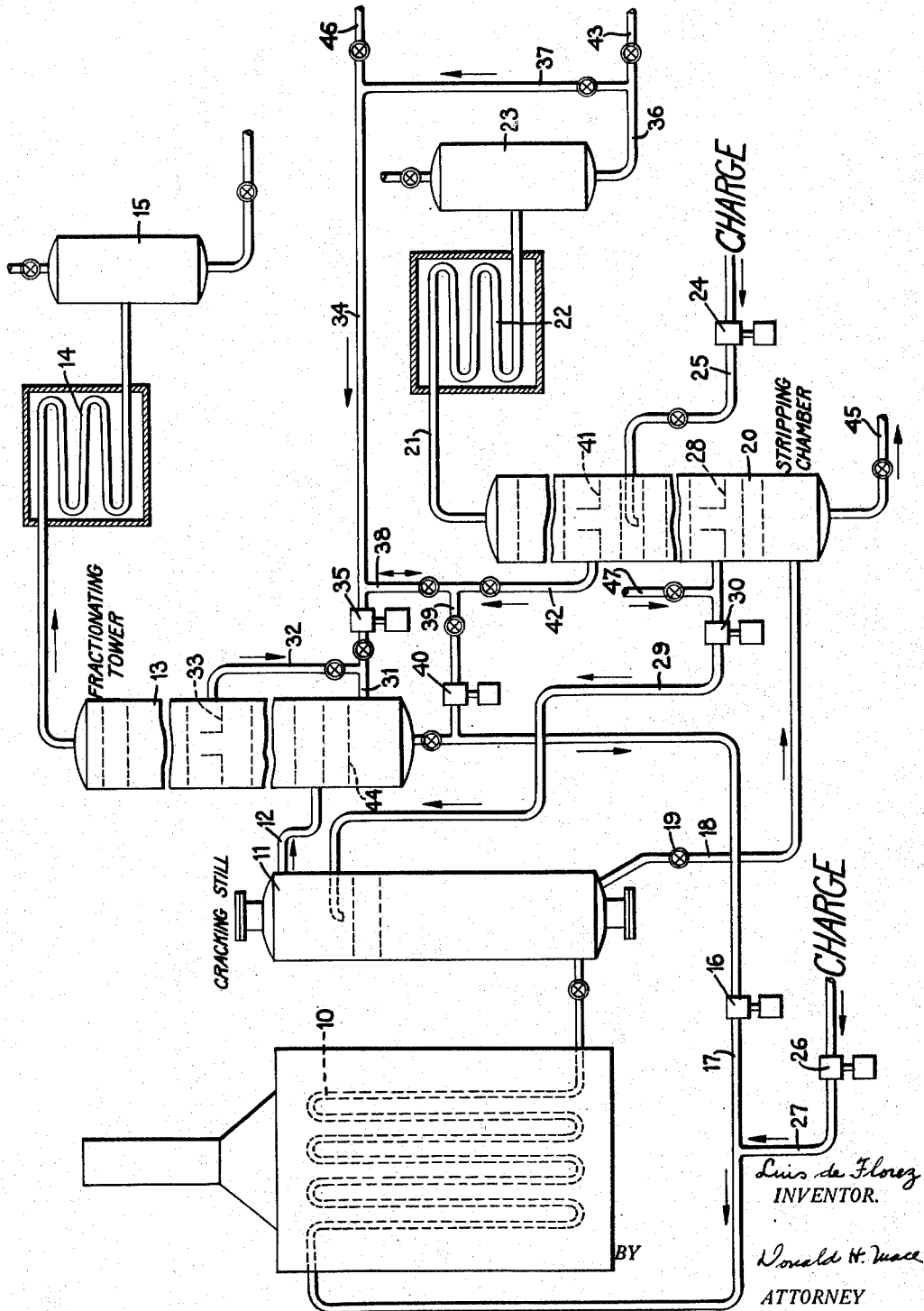
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L. DE FLOREZ

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MANUFACTURE OF ANTIKNOCK GASOLINE

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MANUFACTURE OF ANTIKNOCK GASOLINE

Luis de Florez, Pomfret, Conn., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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This invention relates to the manufacture of gasoline of superior anti-knock value.

The invention contemplates the reforming of gasoline having no appreciable anti-knock value, or having a low anti-knock value, into gasoline of superior anti-knock value and may be practiced in conjunction with a cracking process in which higher boiling hydrocarbon oils are converted into lower boiling ones or, it may be practiced on gasoline material alone.

In practicing the invention in connection with the cracking of a higher boiling stock into a lower boiling product such as gasoline, gasoline or naphtha having a relatively low anti-knock value, such as straight-run gasoline which may be present in charging stock for the process and/or tar stripper distillate resulting from stripping the residual products from the cracking zone may be added to the higher boiling charging stock, such as gas oil, for introduction into a cracking and reforming zone so that the gasoline constituents may be transformed into products of increased anti-knock value while at the same time the gas oil or higher boiling constituents may be converted into lower boiling products of the gasoline boiling range.

In one of its more specific aspects, the invention contemplates a process in which gasoline constituents are added to a cycle stock being cycled to the cracking zone or in which the fractionation resulting in the production of such cycle stock is modified or controlled in such a way as to insure that the cycle stock will contain material quantities of gasoline constituents.

In another aspect of the invention a gasoline charging stock may be charged to a heating zone wherein it is subjected to a sufficient temperature to effect a transformation into products of increased anti-detonating qualities and products of the reaction subjected to distillation and fractionation to form a cycle condensate adapted for returning to the reforming zone, the fractionation being carried on in such a way that the cycle condensate may contain material quantities of gasoline constituents.

In another phase of the invention, off-grade naphtha or gasoline produced from the process which normally possesses undesired motor knocking properties, with or without being first stripped of lighter ends, is cycled to the cracking zone and subjected to treatment resulting in material improvement in anti-knock properties thereof.

As an additional feature the invention contemplates a process in which the fresh charging

oil containing gasoline constituents such as crude or reduced crude or gas oil containing gasoline constituents is introduced into the fractionating zone of a stripping chamber employed for stripping the residual products from the cracking zone so that the gasoline constituents of the fresh charge are vaporized and are condensed with the gasoline constituents stripped from the residual products and in which the gasoline distillate so formed, which normally possesses low anti-knock characteristics, is cycled to the cracking zone for transformation into gasoline products possessing materially improved anti-knock properties.

Another feature of the invention consists in introducing the vapors to be fractionated to an intermediate point of the fractionating tower employed in producing the cycle condensate and carrying on the operation in the tower in such a manner that the bottom of the tower, wherein the final pool of reflux condensate accumulates, may be at a temperature below the maximum temperature obtaining in the tower to thereby increase the solubility factor of the higher boiling hydrocarbons for the hydrocarbons of the gasoline boiling range so that the cycle condensate withdrawn from the tower will contain material quantities of gasoline constituents.

The invention will be understood from the following detailed description thereof, reference being had to the accompanying drawing which is a diagrammatic view in elevation of a particular embodiment of the invention.

In the drawing 10 is a heating or cracking coil discharging into a cracking still 11. A vapor line 12 extends from the cracking still to a fractionating tower 13 which may be a bubble tower. A condenser 14 is provided for condensing the overhead vapor fraction from the tower 13, which condensate is collected in a receiving drum 15. A pump 16 serves to remove cycle condensate from the tower 13 and pass it through line 17 to the heating coil 10.

Unvaporized residual products are withdrawn from cracking still 11 through line 18 provided with a pressure reducing valve 19 and introduced into the stripping chamber 20 wherein further vaporization of the residual products is effected, preferably by contained heat of the products under a pressure materially below that maintained in the still chamber 11. The upper portion of the chamber 20 is provided with suitable fractionating elements such as baffle plates or bubble trays so that the vapors released from the residual products are subjected to dephlegma-

tion or fractionation to condense heavier constituents thereof.

The uncondensed vapors containing gasoline components are withdrawn from chamber 20 through line 21 leading to a condenser box 22 wherein the gasoline constituents are condensed. After passing through the condenser box the products are discharged into a receiver 23 wherein liquid and gaseous products separate.

Two different methods of introducing the raw charging stock to the system are indicated in the drawing. In one method the fresh charging stock is introduced into an intermediate section of the fractionating zone in the upper portion of stripping chamber 20 by means of pump 24 and charging line 25. In the other method the fresh charge may be introduced by means of pump 26 and charging line 27 directly into the line 17 leading from the tower 13 to the heating coil 10. The two methods of charging may be used as alternatives or both may be used concurrently as desired.

The charging oil introduced into the stripping chamber 20 may be a crude, reduced crude or gas oil and may, and preferably does, contain gasoline components. The charging stock introduced into line 17 through charging line 27 should be a clean condensate stock relatively free of dirty, coke-forming, residual products normally present in crude oil and may or may not contain hydrocarbons within the gasoline range.

The fresh charging stock introduced into the stripping chamber 20 is heated to a distilling temperature by the hot vapors released from the residual products withdrawn from the cracking still 11 so that lighter constituents of the fresh charge including gasoline components are vaporized.

The undistilled constituents of the fresh charge introduced into chamber 20 and the condensed heavier constituents of the vaporized residual products and fresh charge are collected on trap-out tray 28 located in chamber 20 below the point of entry of the fresh charging stock and are withdrawn from the chamber 20 through line 29 provided with a pump 30 which forces these products into a primary dephlegmating zone in the upper part of the cracking chamber 11 in which they serve to reflux the vapors evolved in the cracking still before the vapors pass to the fractionating tower 13. The fresh charging stock so introduced into still 11 in flowing downwardly therethrough is subjected to distillation and/or cracking by the heat imparted to it from the highly heated cracked products from coil 10.

A line 31 is indicated for introducing gasoline or naphtha stock into the lower part of the fractionating tower 13. The line 31 is branched, one branch 32 extending to a trap-out tray 33 located at an intermediate point in the tower 13, and another branch 34 provided with a pump 35 which serves to introduce additional gasoline or naphtha stock.

As shown, this additional gasoline or naphtha stock may consist in whole of distillate recovered from the stripping operation or may also include straight run gasoline from the fresh stock distilled in the upper portion of tower 20 and/or additional gasoline stock from an extraneous source. According to one mode of operation the total gasoline distillate from the stripping operation is collected in the receiver 23 and a part or all of this gasoline or naphtha fraction is then passed through line 36 and branch line 37 to line 34. In accordance with this mode of operation

I prefer to pass the gasoline or naphtha from the stripping operation through line 34, pump 35 and line 31 to the fractionating tower 13 wherein the lighter ends may be vaporized. However, if desired, for example when the gasoline or naphtha distillate from the stripping operation contains a relatively large proportion of heavy ends, a portion or all of this distillate may be transferred from line 34 through lines 38, 39, pump 40, and line 17, directly to the heating coil 10.

According to another mode of operation the temperature in the upper part of the stripping chamber 20 is controlled to condense the heavier ends of the gasoline or naphtha fraction and a trap-out tray 41 is provided in the upper end of the chamber for collecting this heavy naphtha fraction. The fraction thus collected may be withdrawn from the trapout tray through line 42 and passed through lines 39 and 17 directly to the heating coil 10 or through lines 38, 34 and 31 to the tower 13. In carrying out this mode of operation uncondensed vapors from the stripping chamber 20 containing the lighter ends of the gasoline are passed through line 21 and condenser 22 to the receiver 23 and may be cycled to the fractionating tower 13 in the manner hereinbefore described or may be withdrawn from the system through line 43.

In a preferred manner of practicing the invention, a suitable charging stock of the character hereinbefore specified, is introduced to the system by either or both of the pumps 24 and 26 and the oil is subjected to cracking in the coil 10 and in the cracking still 11. The still 11 may be held under approximately the same pressure as that of the coil 10 or the pressure may be reduced in the still 11. The evolved vapors pass from the still 11 to the fractionating tower 13 wherein they are fractionated to separate out the cycle stock, which is passed to the heating coil, and a vapor fraction which is condensed in the condenser 14 and collected as a light distillate in the receiver 16. Cooling is preferably supplied to the upper part of the tower 13, such as by pumping back a portion of the distillate collected in the receiver 16 or 23 so as to regulate the end point of the product desired to be collected in the receiver. This end point may for example be 400° F. or any other suitable temperature for the particular gasoline or naphtha product desired.

The gasoline material introduced into the lower portion of the tower 13 preferably consists predominantly of components boiling within the higher boiling range of gasoline. Thus for example the fraction directed through line 31 to the final pool of condensate in the tower 13 may consist mainly of constituents boiling within a range of 300° F. to 400-450° F. By thus positively admitting into this final pool of condensate constituents of the gasoline range, and more particularly components within the higher boiling range of gasoline, an equilibrium condition may be established tending to the retention in the pool of gasoline constituents and particularly the heavier fractions of gasoline.

In order to obtain the maximum solution effect it is desirable that agitation of the pool of condensate be avoided and that the pool be blanketed as far as possible against evaporation. The provision of one or more trays, as at 44, intermediate the pool of condensate and the point of entry of the vapors into the tower promotes this effect. The use of superatmospheric pressure in the tower increases the solution effect and the tower

may be held under several hundred pounds pressure.

The fractionating operation carried on in the tower 13 may be so conducted that the temperature in the bottom of the tower beneath the trays 44 is lower than the maximum temperature obtaining in the tower. Thus the point of maximum temperature in the tower may be at the point of entrance of the vapors from the vapor line 12 with a progressive decrease in temperature upwardly through the tower, while the bottom pool of condensate in the tower is maintained at a lower temperature than that of the intermediate point where the vapors enter the tower, by reason of the relatively cool gasoline constituents introduced through line 31 from an intermediate point in the tower and/or from the other sources as has been explained. The temperature in the bottom of the tower may, for example, be about 550° F. to 650° F. by cooling the bottom of the tower in this way, the solution effect of the higher boiling constituents for the gasoline constituents and particularly for the heavier fractions of gasoline is increased. It may be observed that even though the temperatures employed may be above the boiling range of the gasoline constituents, nevertheless by positively directing gasoline constituents to this relatively cool pool of condensate, the solution factor will insure that considerable quantities of the gasoline, and especially the heavier fractions of gasoline, will be withdrawn in the cycle condensate.

The temperature conditions maintained in the dephlegmating section of the stripping chamber 20 will depend upon the type of operation desired to be carried out as before explained. When operating according to the first method described, wherein the total gasoline distillate from the stripping operation is collected in receiver 23, the temperature at the top of the chamber or tower 20 may be controlled to produce a gasoline having an end point ranging from 400° to 500° F. or thereabouts, and when operating in accordance with the second method, wherein the heavy ends of gasoline are separately collected in trap-out tray 41, the temperature may be controlled to produce a final gasoline distillate having an end point ranging from 300 to 400° F. or thereabouts and the fraction collected in trap-out tray 41 may have a boiling point range of from 300 to 500° F. or thereabouts. As before mentioned the pressure within the stripping chamber 20 is preferably maintained materially lower than the pressure within cracking still 11 and may range from atmospheric to fifty or seventy-five pounds per square inch. The residual products of the cracking operation will be withdrawn from the system through line 45 leading from the stripping chamber 20.

The cycle stock withdrawn from the tower 13 thus enriched with gasoline constituents, particularly the higher boiling components of gasoline, is passed to the cracking coil 10 and still 11 to be therein subjected to the cracking temperature so as to not only convert the higher boiling or gas oil constituents into lower boiling products but also to reform the gasoline constituents into hydrocarbons of greatly increased anti-knock quality. It is preferable to withdraw an extremely clean cycle stock from the tower 13, the cleanliness of which may be judged by a color test or a carbon residue test so that high cracking temperatures, such as those of the order of 900° F. to 1000° F. or even higher may be employed to thus insure a high rate of cracking per pass and

to further insure that the gasoline constituents in the charge will be transformed or reformed into products of increased anti-knock value.

In a modification of the invention, instead of charging a high boiling oil into the system to be converted into lower boiling products, a gasoline or naphtha fraction may constitute the main charge for the purpose of reforming gasoline constituents into products of increased anti-detonating properties. Thus, for example, a straight run gasoline or other gasoline of inferior anti-knock quality (including cracked gasoline), or a heavy fraction of such gasoline, may be charged to the system through line 46 forming an extension of line 34. When conducting such a reforming operation I prefer to omit the use of pumps 24 and 26 and to introduce the gasoline or naphtha charge by pump 35 to the bottom of the tower 13, although in some cases it may be desirable to introduce some reflux, which may be gasoline or a higher boiling stock, into the chamber 11, which is preferably operated as a primary dephlegmating zone, by means of line 47, pump 30 and line 29. The gasoline constituents may be subjected to temperatures, as of the order of 900° F. or higher, to effect the transformation and reformation of the hydrocarbon compounds into products of increased anti-knock value.

In addition to the gasoline constituents being introduced to the bottom of the tower 13 by the pump 35, an intermediate cut consisting of gasoline or the heavier fractions thereof may be withdrawn from the tower through line 32 and passed into the bottom of the tower. Fractionation is carried on in the tower 13 to separate out a final gasoline distillate of desired boiling range, and this product of superior anti-knock value may be collected in the receiver 15.

In an example of the invention in carrying on the modification in which the gasoline material constitutes the main charging stock for the purpose of reforming the gasoline constituents into products of increased anti-knock quality, there may be a considerable reduction in pressure between the coil 10 and chamber 11, in which case this chamber serves primarily as a separating and primary dephlegmating chamber. Thus, for example, the outlet of the coil 10 may be held at temperatures of the order of 1050° F. under several hundred pounds pressure and the pressure may be reduced in the separator to about 100 pounds, which pressure may likewise be maintained on the tower 13. The temperature in the upper region of the separating chamber 11 may be about 600° F., the temperature in the vapor line 12 about 550° F., and the temperature in the intermediate point in the tower 13 adjacent the point of entry of vapors from the line 12 may be about 500° F. When introducing the gasoline charging stock through the line 46, with or without the addition of the intermediate cut withdrawn through line 32, the temperature in the bottom of the tower 13 may be about 340° F. The temperature of the top of the tower 13 may be about 380° F. while taking off an overhead vapor fraction which is condensed in the condenser 14 which has an end point of about 400° F. It may be observed that when treating a gasoline or naphtha charging stock there will ordinarily be present a relatively large proportion of gas, the presence of which very materially affects the partial pressure in the fractionating tower. The figures stated are given by way of example as to conditions of temperature and pressure obtaining in various parts of the apparatus which are be-

lieved to be satisfactory in operation but it is understood that the invention may be practiced without using the specific temperatures and pressures stated.

When operating the equipment solely for reforming of gasoline, the stripping chamber 20 and the appurtenant equipment connected thereto may be dispensed with if desired.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

1. In a process for producing gasoline having a high anti-knock value wherein hydrocarbon oil is subjected to conversion in a conversion zone maintained at a temperature adequate to convert higher boiling hydrocarbons into lower boiling hydrocarbons and to improve the anti-knock properties of gasoline constituents and wherein the converted products are separated into vapors and unvaporized residuum; the improvement which comprises, subjecting the separated vapors to fractionation in a fractionating tower to form an overhead gasoline distillate of high anti-knock value and a pool of reflux condensate at the bottom of the tower, subjecting unvaporized residuum to further vaporization in a separate zone, fractionating the vapors resulting from said last-named vaporization in direct contact with fresh charging oil containing gasoline constituents whereby said fresh charging oil is heated by said vapors to distilling temperature adequate to vaporize higher boiling gasoline constituents therefrom, separately collecting an overhead distillate fraction containing gasoline constituents from said residuum and fresh charging oil, introducing said last-named distillate into said pool of reflux condensate, the level of said pool being below and spaced from the point of entry of the vapors and separated from direct physical contact with the vapors entering the fractionating tower so as to prevent these vapors from transmitting heat directly to said pool, withdrawing the mixture of reflux condensate and distillate from said pool and cyclically passing said withdrawn mixture to the conversion zone.

2. In a process for producing gasoline having a high anti-knock value wherein hydrocarbon oil is subjected to conversion in a conversion zone maintained at a temperature adequate to convert higher boiling hydrocarbons into lower boiling hydrocarbons and to improve the anti-knock properties of gasoline constituents and wherein the converted products are separated into vapors and unvaporized residuum; the improvement which comprises, subjecting the separated vapors to fractionation in a fractionating tower to form an overhead gasoline distillate of high anti-knock value and a pool of reflux condensate at the bottom of the tower, subjecting unvaporized residuum to further vaporization in a separate zone, fractionating the vapors resulting from said last-named vaporization in direct contact with fresh charging oil containing gasoline constituents whereby said fresh charging oil is heated by said vapors to distilling temperature adequate to vaporize higher boiling gasoline constituents therefrom, further fractionating the vapors from said residuum and fresh oil to condense heavy components thereof including higher boiling gasoline constituents, separately collecting said higher boiling gasoline constituents, introducing said last-named higher boiling gasoline con-

stituents into said pool of reflux condensate, the level of said pool being below and spaced from the point of entry of the vapors and separated from direct physical contact with the vapors entering the fractionating tower so as to prevent these vapors from transmitting heat directly to said pool, withdrawing a mixture of higher boiling gasoline constituents and reflux condensate from said pool and passing the same to the conversion zone.

3. A process for producing gasoline having a high anti-knock value which comprises heating a confined stream of hydrocarbon oil to cracking temperature adequate to improve the anti-knock value of gasoline constituents therein while under relatively high superatmospheric pressure, passing the heated products to an enlarged zone maintained under superatmospheric pressure wherein the products separate into vapors and unvaporized residuum, subjecting the separated vapors to fractionation in a fractionating zone to form an overhead gasoline distillate of high antiknock value and a pool of reflux condensate at the bottom of the zone, passing said unvaporized residuum to a zone of lower pressure wherein further vaporization of the residuum is effected, separately fractionating the vapors from said residuum in direct contact with fresh charging oil containing gasoline constituents to heat said charging oil to a temperature adequate to vaporize higher boiling gasoline constituents therefrom, separately collecting an overhead gasoline distillate from said fresh oil and residuum, introducing said last-named distillate into said pool of reflux condensate, the level of said pool being below and spaced from the point of entry of the vapors and separated from direct physical contact with the vapors entering the fractionating tower so as to prevent these vapors from transmitting heat directly to said pool, withdrawing a mixture of said reflux condensate and distillate and subjecting said withdrawn mixture to said first-mentioned heating operation.

4. In a process for producing gasoline having a high anti-knock value, the process that comprises passing higher boiling hydrocarbon oil through a heating coil wherein the oil is subjected to a cracking temperature to effect conversion into lower boiling hydrocarbons comprising gasoline constituents, maintaining the temperature in said heating coil adequate to effect transformation of gasoline constituents into gasoline constituents of increased anti-knock quality, passing the heated products from said heating coil into an enlarged chamber wherein separation of vapors from unvaporized residue takes place, maintaining a cracking temperature under superatmospheric pressure in said enlarged chamber, subjecting the separated vapors to fractionation to separate out a gasoline distillate of high anti-knock quality as a final product, withdrawing unvaporized residue from said enlarged chamber and subjecting it to vaporization in a flashing zone, subjecting the resultant vapors to fractionation in a fractionating zone, introducing fresh charging stock containing gasoline constituents into said fractionating zone to dephlegmate the vapors therein and effect vaporization of the gasoline constituents contained in said charging stock, withdrawing a fraction from said fractionating zone comprising combined reflux condensate and unvaporized constituents of said charging stock and directing said fraction to said enlarged chamber, subjecting the vapors dephlegmated in said fractionating zone to further frac-

tionation to separate out a gasoline distillate and directing said gasoline distillate to aforesaid cracking zone in admixture with said higher boiling oil being converted to subject the gasoline to reforming therein.

5 5. In a process for producing gasoline having a high anti-knock value, the process that comprises passing higher boiling hydrocarbon oil through a heating coil wherein the oil is sub-
10 jected to a cracking temperature to effect conversion into lower boiling hydrocarbons comprising gasoline constituents, maintaining the temperature in said heating coil adequate to effect transformation of gasoline constituents into gaso-
15 line constituents of increased anti-knock quality, passing the heated products from said heating coil into an enlarged chamber wherein separation of vapors from unvaporized residue takes place, maintaining a cracking temperature under super-
20 atmospheric pressure in said enlarged chamber, subjecting the separated vapors to fractionation to separate out a gasoline distillate of high anti-knock quality as a final product and a heavier
25 reflux condensate, directing said heavier reflux condensate to said heating coil, withdrawing unvaporized residue from said enlarged chamber and subjecting it to vaporization in a flashing zone, subjecting the resultant vapors to frac-
30 tionation in a fractionating zone, introducing fresh charging stock containing gasoline constituents into said fractionating zone to dephlegmate the vapors therein and effect vaporization of the gasoline constituents contained in said
35 charging stock, withdrawing a fraction from said fractionating zone comprising combined reflux condensate and unvaporized constituents of said charging stock and directing said fraction to said enlarged chamber, subjecting the vapors dephlegmated in said fractionating zone to further frac-
40 tionation to separate out a gasoline distillate and directing said gasoline distillate to aforesaid cracking zone in admixture with said higher boiling oil being converted to subject the gasoline to reforming therein.

45 6. In a process for producing gasoline having a high anti-knock value, the process that comprises passing higher boiling hydrocarbon oil through a heating coil wherein the oil is subjected to a cracking temperature to effect conversion
50 into lower boiling hydrocarbons comprising gasoline constituents, maintaining the temperature in said heating coil adequate to effect transformation of gasoline constituents into gasoline constituents of increased anti-knock quality, passing
55 the heated products from said heating coil into an enlarged chamber wherein separation of vapors from unvaporized residue takes place, maintaining a cracking temperature under super-atmospheric pressure in said enlarged chamber, subjecting the separated vapors to fractionation
60 in a fractionating tower maintained under super-atmospheric pressure to separate out a gasoline distillate of high anti-knock quality as a final product and form a pool of heavier reflux con-

densate, withdrawing unvaporized residue from said enlarged chamber and subjecting it to vaporization in a flashing zone, subjecting the resultant vapors to fractionation in a fractionating zone, introducing fresh charging stock containing gaso-
5 line constituents into said fractionating zone to dephlegmate the vapors therein and effect vaporization of the gasoline constituents contained in said charging stock, withdrawing a fraction from
10 said fractionating zone comprising combined reflux condensate and unvaporized constituents of said charging stock and directing said fraction to said enlarged chamber, subjecting the vapors dephlegmated in said fractionating zone to fur-
15 ther fractionation to separate out a gasoline distillate and introducing said gasoline distillate into said pool of heavier reflux condensate, the level of said pool being below and spaced from the point of entry of the vapors and separated
20 from direct physical contact with the vapors to maintain said pool at such temperature under the pressure in the fractionating tower to maintain conditions tending to the retention of gaso-
25 line constituents therein, withdrawing said heavier reflux condensate from said pool containing retained gasoline constituents and directing it to aforesaid cracking zone.

7. In a process for producing gasoline having a high anti-knock value, the process that
30 comprises subjecting higher boiling hydrocarbon oil to cracking temperature under superatmospheric pressure in a cracking zone to effect conversion into lower boiling hydrocarbons, maintaining the temperature in said cacking zone
35 adequate to effect transformation of gasoline constituents into gasoline constituents of increased anti-knock quality, separating the products of the cracking into vapors and unvaporized residue in a separating zone, maintaining a cracking temperature under superatmospheric pressure in said
40 separating zone, subjecting the separated vapors to fractionation in a first fractionating zone to form a reflux condensate and a gasoline distillate of high anti-knock quality as a final product, directing said reflux condensate to said cracking
45 zone, subjecting said unvaporized residue to vaporization under lower pressure in a flashing zone, passing resultant vapors from the flashing zone to a second fractionating zone, introducing fresh charging stock containing gasoline con-
50 stituents into said second fractionating zone for partial vaporization by contact with the hot vapors therein and fractionating resultant vapors with vapors from the flashed residue therein, withdrawing a fraction from the second frac-
55 tionating zone comprising resultant reflux condensate and unvaporized constituents of the charging stock and directing said fractionation into aforesaid separating zone, withdrawing another fraction from the second fractionating
60 zone comprising gasoline constituents and directing it to said cracking zone to effect reforming thereof.

LUIS DE FLOREZ.