

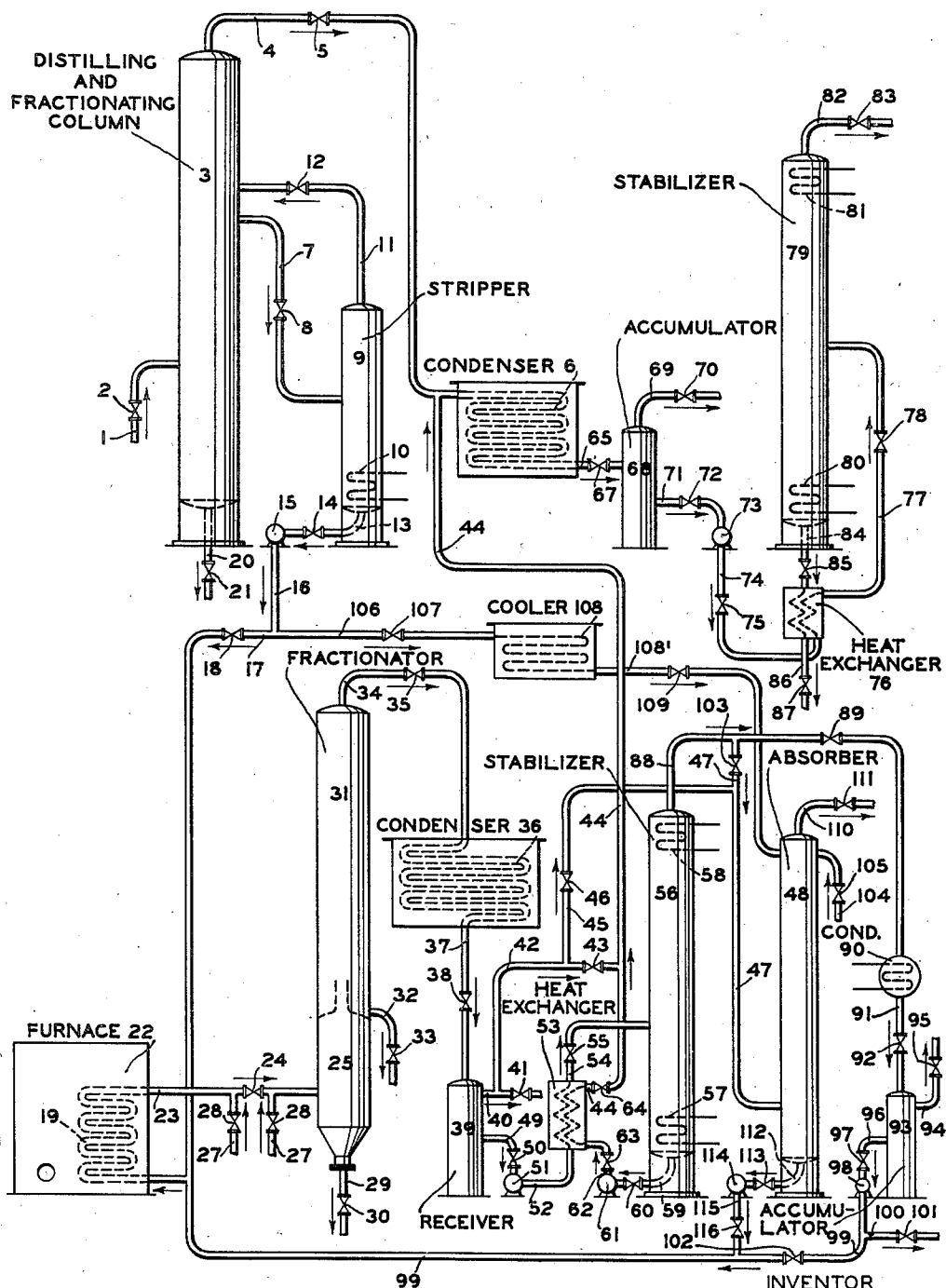
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TREATMENT OF HYDROCARBON OILS

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TREATMENT OF HYDROCARBON OILS

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This is, in part, a continuation of my co-pending applications Serial No. 661,242, filed March 17, 1933, and Serial No. 171,871, filed October 30, 1937.

5 The invention embodies a novel and advantageous combination of distilling, cracking, stabilization and absorption steps which are interdependent and cooperate to produce high yields of good antiknock gasoline of the desired vapor pressure. Readily polymerizable normally gaseous olefins produced in the cracking operation and which are ordinarily left dissolved in the gasoline to give it the desired vapor pressure are replaced by essentially paraffinic gases contained in the charging stock and recovered from the distilling step. The liberated gases or selected high-boiling fractions thereof may be recovered as a separate product of the process which is suitable for catalytic polymerization, to produce additional yields of high antiknock gasoline, or they may be absorbed in the distillate from the distilling operation which is subsequently supplied to the cracking or reforming step of the system, wherein they undergo conversion in commingled state with said distillate under conditions which result in the production of higher yields of gasoline and/or gasoline of higher antiknock value.

While the invention is particularly advantageous as applied to the treatment of crude petroleum, any type of charging stock which contains gasoline or gasoline fractions of unsatisfactory antiknock value and substantial quantities of essentially paraffinic gases may be utilized. Such charging stocks often contain some low-boiling gasoline fractions of sufficiently good antiknock value that they may be advantageously included with gasoline produced within the system by pyrolytic conversion or reforming to form the final gasoline product of the process. Such light gasoline fractions and normally gaseous components of the charging stock are separated in the distillation step from its higher boiling components and commingled under suitable conditions with the gasoline resulting from said conversion, after the latter has been stabilized to a low vapor pressure by liberating therefrom substantial quantities of dissolved gases which contain a high percentage of readily polymerizable olefins, such as propene and butenes. Substantial quantities of high-boiling paraffinic gases are thus dissolved or absorbed in the gasoline resulting from commingling the light products of the distillation step and the low vapor pressure cracked gasoline to replace the olefin-containing gases previously liberated therefrom by said stabilization and this

commingled gasoline product is preferably stabilized in a zone separate from the first mentioned stabilization step to produce a final gasoline product of the desired vapor pressure.

When it is desired to subject the total gasoline components of the charging stock to reforming treatment for the purpose of improving their antiknock value, only normally gaseous components of the charging stock are commingled with the low vapor pressure distillate resulting from the first mentioned stabilization step.

The olefinic-containing gases liberated in the first mentioned stabilization step may be recovered or directly supplied, all or in part, to a well known catalytic polymerization process or they may be subjected to condensation and the resulting condensate supplied, all or in part, to catalytic polymerization or to the pyrolytic conversion step of the system for treatment in commingled state with the low-boiling fractions of the charging stock supplied to this zone. Preferably, however, when it is desired to supply olefin-containing gases to the conversion step, gases liberated from the first mentioned stabilization step are intimately contacted with absorber oil, which comprises regulated quantities of said low-boiling fractions of the charging stock which are to be converted, and the resulting enriched absorber oil is supplied to the conversion step.

As previously indicated, the selected low-boiling fractions of the charging stock to be subjected to cracking or reforming treatment may include or substantially exclude low-boiling gasoline fractions and, in either case, this cracking stock may include, when desired, somewhat higher boiling materials such as, for example, heavy naphtha fractions, kerosene or kerosene distillate and the like which can be advantageously treated, under reforming conditions of high cracking temperature and superatmospheric pressure, to produce substantial yields of good antiknock gasoline.

One specific embodiment of the invention comprises heating a charging stock comprising gasoline and essentially paraffinic gases to distillation temperature and separating therefrom, by fractional distillation, a light vaporous stream consisting essentially of paraffinic gases and selected light gasoline fractions and a condensate comprising heavier gasoline fractions of unsatisfactory antiknock value, reforming said heavier gasoline fractions under controlled time, temperature and pressure conditions regulated to produce therefrom high yields of good antiknock gasoline and substantial quantities of olefinic

gases, recovering from the reforming step, by fractionation of the vaporous products thereof and condensation of the fractionated vapors, a distillate comprising said good antiknock gasoline and containing, as dissolved gases, at least a major portion of the desired readily polymerizable olefins produced in the reforming step, stabilizing said distillate to a lower vapor pressure than that of the desired final gasoline product by liberating therefrom regulated quantities of said dissolved gases, intimately contacting gases thus liberated from the distillate with regulated quantities of said higher boiling gasoline fractions from the distilling step, whereby to absorb in the latter substantial quantities of said readily polymerizable olefinic gases, supplying the resulting enriched absorber oil to the reforming step, cooling and commingling the low vapor pressure distillate resulting from said stabilization and said light vaporous stream from the distilling step to condense the light gasoline fractions of the vaporous stream and absorb therein and in said stabilized distillate substantial quantities of said paraffinic gases and liberating from the gas-containing distillate resulting from said cooling and commingling regulated quantities of the absorbed gases to produce said final gasoline product of the desired vapor pressure.

Numerous modifications of the specific embodiment of the invention above described, and several alternative modes of operation, which have been previously mentioned and are not to be considered equivalent, are within the broad scope of the invention. Its primary object is to provide a cooperative combination of distilling and cracking steps which will result in the production of high yields of good antiknock gasoline of the desired vapor pressure, said vapor pressure resulting to a large extent from inclusion in the final gasoline product of paraffinic gases resulting from the topping operation, and the operation further resulting in recovery, from the cracked products, of substantial quantities of readily polymerizable normally gaseous olefins suitable for polymerization treatment within or external to the system, to produce additional quantities of high antiknock gasoline.

The accompanying drawing diagrammatically illustrates one specific form of apparatus in which various embodiments of the process of the invention may be successfully conducted.

Referring to the drawing, the charging stock, which in this particular case is a crude oil of relatively wide boiling range, is supplied in heated state through line 1 and valve 2 to distilling and fractionating column 3. Heating of the charging stock to distillation temperature may be accomplished in any well known manner, not illustrated, and, when desired, heat for this purpose may be recovered from within the system.

In the case here illustrated, the crude is separated in column 3 into three selected fractions, one of which is an overhead vaporous stream consisting primarily of light gasoline fractions of satisfactory antiknock value and gaseous components of the charging stock. This overhead stream is directed from column 3 through line 4 and valve 5 to condenser 6, the function of which will be later described.

An intermediate fraction comprising gasoline of unsatisfactory antiknock value and which may, when desired, include somewhat higher boiling materials such as heavy naphtha fractions, kerosene, kerosene distillate and the like is removed

as a side stream from column 3 and directed through line 7 and valve 8 to stripper 9, wherein it is substantially freed of dissolved gases and desirable low-boiling fractions by reboiling in this zone. Reboiling is accomplished, in the case here illustrated, by passing a suitable heating medium through closed coil 10 in the lower portion of stripper 9. The evolved vapors and gases may be returned, as shown, from stripper 9 through line 11 and valve 12 to fractionator 3, or they may, when desired, be supplied from stripper 9 to condenser 6, by well known means not illustrated. The reboiled condensate is directed from the lower portion of stripper 9 through line 13 and valve 14 to pump 15 by means of which it is fed through line 16, and, when desired, may be directed therefrom, all or in part, through line 17 and valve 18 to heating coil 19, the function of which will be later described, or the reboiled distillate may, when desired, be cooled and utilized in regulated quantities, as will be later described, for absorbing gaseous products of the conversion step of the system and thence supplied, in the manner later described, to heating coil 19.

The remaining higher boiling components of the crude are removed as bottoms from the lower portion of column 3 through line 20 and valve 21 wherefrom they may be directed, by well known means not illustrated, to storage, cracking treatment or elsewhere, as desired. It will, of course, be understood that the particular separation of the charging stock effected in the distilling step may be varied, depending upon the specific charging stock employed and the desired products, and that any desired separation may be accomplished within the scope of the invention so long as a relatively light distillate, suitable for conversion to produce high yields of good antiknock gasoline, and predominantly paraffinic gases are separately recovered from the charging stock.

Heating coil 19 is disposed within a furnace 22 whereby the materials supplied to this zone are heated preferably to a relatively high cracking temperature at substantial superatmospheric pressure. The conditions of temperature, pressure and time employed in this step of the system are regulated to materially improve the antiknock value of the gasoline fractions supplied thereto without excessively altering their boiling range and to produce substantial yields of good antiknock gasoline from any higher boiling distillate fractions supplied thereto. When olefinic gases are supplied to coil 19, in the manner later described, substantial quantities thereof are also converted, under the conditions maintained in this zone, into appreciable additional yields of good antiknock gasoline. This conversion of the olefinic gases is probably due to some extent to their polymerization under the temperature and pressure conditions employed in coil 19, but other reactions, such as alkylation, for example, are probably also involved. It is also considered quite probable that there are secondary reactions between the various primary conversion products formed in coil 19, although the exact nature of this reaction and the reactants involved cannot be definitely stated at the present time.

The highly heated products formed in coil 19 are discharged therefrom through line 23 and these materials are discharged into separating chamber 25, preferably after they have been cooled sufficiently to prevent excessive continued cracking and undesirable secondary reactions.

This cooling is preferably accomplished, in part, by materially reducing the pressure imposed upon the stream of heated products as they pass through valve 24 in line 23 and additional cooling, when required, may be accomplished in any well known manner such as, for example, by indirect heat exchange between the conversion products and a suitable cooling medium or by directly commingling regulated quantities of a suitable cooling oil with the stream of conversion products. When desired, heat for the distilling operation may be recovered at this point in the system by passing all or regulated quantities of the charging stock in indirect heat exchange with the stream of relatively hot conversion products discharged from coil 19. However, the well known provisions whereby cooling of the products discharged from coil 19 by indirect heat exchange are, for the sake of simplicity, omitted from the drawing. Provision is made, in the case here illustrated, for supplying any suitable cooling oil to line 23 by means of lines 27 controlled by valve 28, the cooling oil being introduced on either or both sides of pressure reducing valve 24.

Heavy liquid conversion products are separated from vaporous conversion products in chamber 25 and the residual liquid is removed from the lower portion of this zone to cooling and storage or elsewhere, as desired, through line 29 and valve 30.

The vaporous conversion products from chamber 25 enter fractionator 31 wherein their components boiling above the range of the desired gasoline product are condensed as reflux condensate. The reflux condensate is removed from the lower portion of the fractionator through line 32 and valve 33 and may be directed to cooling and storage, to further conversion in heating coil 19 or in a separate cracking coil or supplied elsewhere, as desired.

Fractionated vapors of the desired end-boiling point, comprising gasoline of the desired end-boiling point produced by conversion in coil 19 and normally gaseous products of the conversion step, are directed from the upper portion of fractionator 31 through line 34 and valve 35 to condenser 36 wherein they are cooled sufficiently to condense substantially all of their normally liquid fractions and to retain substantial quantities of dissolved gases in the resulting distillate. This distillate is pressed together with uncondensed and undissolved gases from condenser 36 through line 37 and valve 38 to receiver 39, wherein the uncondensed and undissolved gases are separated from the gas-containing distillate.

The temperature and pressure conditions employed in condenser 36 and receiver 39 are preferably such that at least a major portion of the desired readily polymerizable olefinic gases (such as propene and/or butenes) contained in the overhead vaporous stream from fractionator 31 are retained in the distillate collected in receiver 39. The uncondensed and undissolved gases removed from receiver 39 preferably comprise a major portion of the gases produced by conversion which have two and less carbon atoms to the molecule but will ordinarily also contain a minor portion of the heavier gases. This material is directed through line 40 and may be discharged through valve 41 in this line to storage or elsewhere, as desired, or it may be directed, all or in part, from line 40 through line 42, valve 43 and line 44 to condenser 6 or, from line 42, through line 45, valve 46 and line 47 to absorber 48.

The distillate collected in receiver 39 is sta-

bilized to reduce its vapor pressure to a value substantially below that of the final gasoline product by liberating therefrom regulated quantities of the dissolved gases. To accomplish this, in the particular case here illustrated, distillate is directed from receiver 39 through line 49 and valve 50 to pump 51 wherefrom it is fed through line 52, heat exchanger 53, line 54 and valve 55 to stabilizer 56. Sufficient heat is imparted to the distillate in heat exchanger 53 to effect appreciable vaporization thereof and, in accordance with conventional practice, reboiling may be accomplished in stabilizer 56 or in a reboiler external to the stabilizing column. In the case here illustrated, closed coil 57, through which any suitable heating medium may be passed for reboiling the unvaporized distillate in stabilizer 56, is provided in the lower portion of this zone. Reboiling may, of course, be accomplished in any other well known manner, not illustrated. Provision is also made for controlling stabilization by cooling in the upper portion of column 56, this being accomplished, in the case here illustrated, by passing any suitable cooling medium through closed coil 58, provided therein. Any other conventional method of cooling may, of course, be substituted.

The low vapor pressure stabilized distillate resulting from the liberation of gases in stabilizer 56 is directed from the lower portion of this zone through line 59 and valve 60 to pump 61 and is supplied therefrom to condenser 6. In the case here illustrated, it first passes through heat exchanger 53 in indirect heat exchange with the distillate from receiver 39, whereby the stabilized distillate is partially cooled and the unstabilized distillate is heated, the flow from pump 61 being through line 62, valve 63, heat exchanger 53, line 44 and valve 64 to condenser 6. It is not essential to cool the stabilized distillate prior to its introduction into condenser 6, since all of the required cooling may be accomplished in the latter zone. The specific manner of cooling the stabilized distillate in heat exchanger 53 conforms with conventional practice.

The mixture of vapors, gases and stabilized distillate supplied to condenser 6, in the manner previously described, is cooled sufficiently in this zone to effect condensation of substantially all of the normally liquid gasoline fractions of the mixture and to effect the absorption of substantial quantities of the gases supplied to this zone from column 3 in the distillate condensed in and supplied to condenser 6. At least a portion of the heat of absorption is also extracted in condenser 6, so that the distillate supplied therefrom through line 65 and valve 67 to accumulator 68 will retain a relatively large quantity of dissolved gases and particularly high-boiling normally gaseous fractions of the overhead stream from column 3. The uncondensed and unabsorbed gases, which consist predominantly of relatively light fractions, are discharged from accumulator 68 through line 69 and valve 70 to storage or elsewhere, as desired.

The quantity of gases dissolved in the distillate collected in accumulator 68 will normally be in excess of that required to produce the desired vapor pressure in the final gasoline product and this distillate is, therefore, preferably stabilized to the desired vapor pressure in a stabilizing zone separate from stabilizer 56. To accomplish this, in the case here illustrated, distillate is directed from accumulator 68 through line 71 and valve 72 to pump 73 wherefrom it is fed through line 74, valve 75, heat exchanger 76, line 77 and valve 78

into stabilizer 79. The function of heat exchanger 76 is to reheat and partially vaporize the distillate supplied to stabilizer 79 and cool the stabilized gasoline removed from this zone. Other well known means of accomplishing either or both of these steps may, of course, be employed within the scope of the invention.

Stabilizer 76 is a conventional stabilizing column employing suitable means, such as closed coil 80 in the lower portion thereof, for reboiling and suitable means, such as, for example, closed coil 81 in the upper portion of this zone, for cooling, a suitable heating medium being passed through coil 80 and a suitable cooling medium through coil 81. The gases liberated from the distillate in stabilizer 79 are released from the upper portion of this zone through line 82 and valve 83 to storage or elsewhere as desired. The distillate which has been stabilized in column 79 to the desired vapor pressure is removed as the final gasoline product from the lower portion of this zone and, in the particular case here illustrated, is directed through line 84 and valve 85 to and through heat exchanger 76, wherein it passes in indirect heat exchange with the distillate from accumulator 68 and wherefrom it is discharged through line 86 and valve 87 to further cooling and storage or to any desired further treatment. This stabilized product is of higher vapor pressure than the distillate resulting from separate stabilization in stabilizer 56.

The gases liberated in stabilizer 56 from the distillate supplied to this zone may comprise either an intermediate or a final product of the process and, depending upon the specific mode of operation desired, may be handled in several different manners. In accordance with one embodiment of the invention, the gases released from the upper portion of stabilizer 56 are directed through line 88 and valve 89 to condenser 90 wherein they are cooled sufficiently to effect substantial condensation thereof and wherefrom the resulting condensate and uncondensed gases are directed through line 91 and valve 92 to accumulator 93. Uncondensed gases may be removed from accumulator 93 through line 94 and valve 95 to storage or elsewhere, as desired, or they may be supplied by well known means, not illustrated, to condenser 6. The condensate collected in accumulator 93 will contain a high proportion of readily polymerizable normally gaseous olefins such as propene and/or butenes and is highly suitable as polymerization stock for a well known catalytic polymerization process operated to produce high antiknock gasoline from the heavy olefins. It is also suitable stock for treatment in coil 19, to produce appreciable quantities of high antiknock gasoline in the manner previously described. It is directed, in the case here illustrated, from accumulator 93 through line 96 and valve 97 to pump 98 wherefrom it is fed through line 99 and may be discharged from the system to storage or to polymerization in a separate system through line 100 and valve 101 or it may be supplied, all or in part, through valve 102 in line 99 to heating coil 19.

Another manner of handling the gases from stabilizer 56 and/or the gases previously separated from the distillate in receiver 39 involves the absorption therefrom of high-boiling components, comprising substantial quantities of readily polymerizable olefins such as propene and/or butenes, in absorber 48. Provision is made for supplying gases from stabilizer 56 to absorber 48 through line 47 and valve 103, while gases from

receiver 39 may be supplied to this zone, when desired, either alone or together with gases from stabilizer 56, in the manner previously described.

Any desired relatively light distillate capable of absorbing the desired high-boiling components of the gases supplied to absorber 48 and suitable for cracking treatment in heating coil 19 may be employed within the scope of the invention. When absorber oil from an external source is utilized in absorber 48, it may be supplied to the upper portion of this zone through line 104 and valve 105. The stripped distillate from column 9 is particularly suitable as absorber oil in absorber 48 and the use of regulated quantities of this distillate as absorber oil is specifically contemplated in the present invention. The use of this material as absorber oil is particularly advantageous due to its relatively low vapor pressure and its consequent good absorbing efficiency and due to the fact that its use in this manner provides a simple and efficient method of supplying polymerizable gases to coil 19.

Provision is made, in the case here illustrated, for directing regulated quantities of the light distillate supplied from column 9 to pump 15 and line 16 through line 106 and valve 107 to cooler 108 wherein its temperature is reduced to the desired degree and thence through line 108' and valve 109 to the upper portion of absorber 48, wherein it comes in intimate countercurrent contact with the gases supplied to this zone as previously described, and absorbs desirable high-boiling components thereof. The gases remaining unabsorbed in absorber 48 will consist predominantly of relatively light gases and are released from the upper portion of this zone through line 110 and valve 111 to storage or elsewhere, as desired. The enriched absorber oil which will contain a substantial quantity of dissolved heavy gases rich in readily polymerizable olefins such as propene and butenes, is directed from the lower portion of absorber 48 through line 112 and valve 113 to pump 114 wherefrom it is supplied through line 115, valve 116 and line 99 to conversion coil 19, in the manner previously described, in heating coil 19.

It will, of course, be understood that the invention is not limited to the use of the specific form of apparatus illustrated in the drawing, but that the latter simply represents one specific means of successfully accomplishing the desired process steps. As an example of one alternative, not illustrated, an absorber similar to absorber 48, for example, may be substituted for condenser 6, the low vapor pressure stabilized distillate from stabilizer 56 being cooled and supplied as absorber oil to the upper portion of this zone, while the overhead vaporous stream from column 3 is supplied, with or without prior cooling, to the lower portion of the absorber or, when desired, distillate may be first condensed and separated from this overhead vaporous stream and the uncondensed gases supplied to an absorber in which stabilized distillate from stabilizer 56 is utilized as absorber oil. However, the use of condenser 6 in the manner illustrated, provides a simple and efficient means of accomplishing the desired results and this is the preferred mode of operation.

In an apparatus, such as illustrated and above described, the preferred range of operating conditions which may be employed to produce the desired results, may be exemplified as follows: Any desired pressure ranging from substantially atmospheric to a superatmospheric pressure of

several hundred pounds per square inch may be employed in the distilling and fractionating column. The temperature utilized in this zone will depend upon the characteristics of the charging stock employed and, with a wide boiling range crude, for example, may range from 400 to 700° F., or thereabouts. Higher temperatures are, of course, necessary in column 3 when this zone is operated at substantial superatmospheric pressure, as compared with those required to give similar results at lower pressure. With a substantially atmospheric or low superatmospheric pressure up to 35 pounds, or thereabouts, per square inch in column 3, condenser 6 and accumulator 68, the condenser is preferably operated to give an outlet temperature from this zone in the neighborhood of 100° F., or thereabouts. The temperature employed in stripper 9 is preferably sufficient to remove substantially all gases and good antiknock light gasoline fractions from the material supplied thereto and, when desired, stripping may be assisted in column 9 by utilizing a lower pressure in this zone than that employed in column 3, when the latter is operated at superatmospheric pressure. The temperature employed in stripper 9 may range, for example, from 150 to 350° F., or thereabouts, depending upon the end boiling point of the good antiknock light gasoline components of the charging stock. The temperature employed at the outlet of coil 19 is preferably of the order of 925 to 1100° F. with a superatmospheric pressure at this point in the system of from 200 to 1000 pounds, or thereabouts, per square inch. The heated products discharged from this zone are preferably cooled to a temperature of the order of 600 to 750° F. prior to their introduction into chamber 25 and/or within the latter zone. A superatmospheric pressure substantially lower than that employed at the outlet of coil 19 is preferably utilized in chamber 25 and fractionator 31 and may range, for example, from 100 to 200 pounds, or thereabouts, per square inch. Preferably, condenser 36 is operated to cool the products discharged therefrom to a temperature of the order of 90 to 110° F., or thereabouts, and receiver 39 is preferably operated at substantially the same pressure as that employed in fractionator 31. Stabilizer 56 is preferably operated at a substantial superatmospheric pressure of the order of 200 to 300 pounds, or thereabouts, per square inch with a bottom temperature of the order of 400° F., for example, when the superatmospheric pressure employed in this zone is in the neighborhood of 250 pounds per square inch and with a top temperature, under these conditions, of approximately 130-145° F. Condenser 90 and accumulator 93 are preferably operated at a superatmospheric pressure substantially the same as that employed in stabilizer 56 and at a temperature of the order of 70 to 90° F. or less. When absorber 48 is employed, it is preferably operated at a superatmospheric pressure of the order of 70 to 150 pounds or more. Stabilizer 79 is preferably operated at a superatmospheric pressure of from 100 to 150 pounds per square inch, or more, with a bottom temperature in this zone of the order of 300 to 325° F. and a top temperature of approximately 120° F., or less. In each of the various steps, the temperatures employed are, of course, closely allied with the pressure employed and either may be varied to give substantially the same or similar results when the other is correspondingly varied.

As an example of one specific operation of the process, as conducted in an apparatus such as illustrated and above described, the charging stock is a light mixed base crude containing approximately 15% of satisfactory antiknock gasoline fractions boiling up to approximately 250° F. and containing more than 40% of materials boiling up to 437° F. This charging stock is heated to a temperature of approximately 650° F. and fractionated at substantially atmospheric pressure. Gases and light vapors having an end-boiling point of approximately 250° F. are removed as the overhead vaporous product from the fractional distilling step, cooled in commingled state with the low vapor pressure reformed gasoline from the stabilizer of the reforming system to a temperature of about 100° F., the resulting distillate separated from the uncondensed and undissolved gases and supplied to a separate stabilizer wherein its vapor pressure is reduced to approximately 10 pounds per square inch as determined by the Reid method. This stabilizer is operated with a bottom temperature of approximately 315° F. and a top temperature of approximately 120° F.

A light side stream having an end-boiling point of approximately 540° F. is removed from the distilling and fractionating column to a stripping column wherein it is reboiled at a temperature of approximately 275° F., the evolved vapors and gases being returned to the distilling column and the reboiled distillate supplied to the reforming coil of the system wherein it is heated to an outlet cracking temperature of approximately 980° F. A superatmospheric pressure of about 800 pounds per square inch is employed at the outlet of the reforming coil and the products discharged therefrom are cooled to a temperature of about 670° F. and introduced into a separate chamber operated at a superatmospheric pressure of about 125 pounds per square inch, wherein their vaporous components are separated from residual liquid. The vapors are fractionated at a superatmospheric pressure of about 125 pounds per square inch to condense their components boiling above the range of approximately 400° F. The fractionated vapors and gases are subjected to condensation at a temperature of about 100° F. The resulting distillate, containing dissolved gases, is separated from the uncondensed and undissolved gases and supplied to the first mentioned stabilizer which is operated at a superatmospheric pressure of about 250 pounds per square inch. A bottom temperature of approximately 400° F. and a top temperature of approximately 135° F. is employed in this zone. The resulting stabilized, reformed gasoline, which has a vapor pressure of approximately 4 pounds per square inch, is supplied to the aforementioned condenser to which overhead vaporous products and gases from the distilling step are supplied. Gases liberated in the stabilization step to which the reformed gasoline is supplied are substantially condensed to recover, as condensate, a normally gaseous product containing a high proportion of propene and butenes and desirable as charging stock for a catalytic polymerization process.

Neglecting approximately 15%, based on the crude charging stock of light, straight-run gasoline fractions included in the final blended gasoline product, the above described operation will yield, per barrel of distillate supplied to the reforming coil, approximately 76% of 400° F. end-point gasoline. The final blended gasoline product has an octane number of approximately 68

and a Reid vapor pressure of approximately 10 pounds per square inch. In addition, approximately 7.6 gallons of liquified gases, highly suitable as polymerization stock, are produced per barrel of distillate supplied to the reforming coil.

As an example of another specific operation of the process, the charging stock and operating conditions are substantially the same as those above described, except that the gaseous products from the stabilizer to which the reformed distillate is supplied are directed to an absorber to which regulated quantities of the reboiled sidestream from the stripping column of the distilling step are supplied, after cooling, as absorber oil and the resulting enriched absorber oil supplied to the reforming coil.

On the same basis as given in the first example, the last described operation will produce approximately 78% of 400° F. end-point gasoline having an octane number of approximately 72 when substantially all of the gases from the stabilizer of the reforming system are supplied to the absorber and no catalytic polymerization stock is recovered.

I claim as my invention:

1. A process of converting hydrocarbons which comprises, distilling an oil containing poor antiknock gasoline and essentially paraffinic gases to recover therefrom as separate fractions a distillate, comprising said poor antiknock gasoline, and lighter fractions comprising at least a major portion of said paraffinic gases, subjecting said distillate to conversion conditions regulated to effect the production therefrom of high yields of good antiknock gasoline and substantial quantities of readily polymerizable normally gaseous olefins, recovering said good antiknock gasoline from the resulting conversion products in the form of a distillate substantially free of dissolved normally gaseous olefins, adding to the last named distillate substantial quantities of the heavy paraffinic gases resulting from the distillation step to form a gasoline product of materially increased vapor pressure, and separately recovering from said conversion products a mixture of normally gaseous hydrocarbons containing a high concentration of readily polymerizable olefins.

2. A process such as defined in claim 1, wherein at least a portion of the readily polymerizable olefinic components of said conversion products is returned to said conversion step and therein further converted in commingled state with the first named distillate to produce additional yields of good antiknock gasoline.

3. A process of converting hydrocarbons which comprises, distilling an oil containing poor antiknock gasoline and essentially paraffinic gases to recover therefrom as separate fractions a distillate, comprising said poor antiknock gasoline, and lighter fractions comprising at least a major portion of said paraffinic gases, subjecting said distillate to conversion conditions regulated to effect the production therefrom of high yields of good antiknock gasoline and substantial quantities of readily polymerizable normally gaseous olefins, recovering said good antiknock gasoline from the resulting conversion products in the form of a distillate substantially free of dissolved normally gaseous olefins, adding to the last named distillate substantial quantities of the heavy paraffinic gases resulting from the distillation step to form a gasoline product of materially increased vapor pressure, contacting normally gaseous components of said conversion

products with regulated quantities of the first named distillate to absorb in the latter substantial quantities of readily polymerizable olefinic gases, and supplying the resulting gas-containing distillate to said conversion step.

4. A process of converting hydrocarbons which comprises, distilling an oil containing poor antiknock gasoline and essentially paraffinic gases to recover therefrom as separate fractions a distillate comprising said poor antiknock gasoline, and lighter fractions comprising at least a major portion of said paraffinic gases, subjecting said distillate to conversion conditions regulated to effect the production therefrom of high yields of good antiknock gasoline and substantial quantities of readily polymerizable normally gaseous olefins, recovering said good antiknock gasoline from the resulting conversion products in the form of a distillate substantially free of dissolved normally gaseous olefins, contacting the last named distillate with said lighter fractions resulting from the distillation step at a sufficiently low temperature to absorb therein substantial quantities of said paraffinic gases, stabilizing the resulting gas-containing distillate to a vapor pressure materially in excess of that of the second named distillate, recovering the stabilized distillate, and separately recovering from said conversion products a mixture of normally gaseous hydrocarbons containing a high concentration of readily polymerizable olefins.

5. A process such as defined in claim 4, wherein at least a portion of the readily polymerizable olefinic components of said conversion products is returned to said conversion step and therein further converted in commingled state with the first named distillate to produce additional yields of good antiknock gasoline.

6. A process of converting hydrocarbons which comprises, distilling an oil containing poor antiknock gasoline and essentially paraffinic gases to recover therefrom as separate fractions a distillate, comprising said poor antiknock gasoline, and lighter fractions comprising at least a major portion of said paraffinic gases, subjecting said distillate to conversion conditions regulated to effect the production therefrom of high yields of good antiknock gasoline and substantial quantities of readily polymerizable normally gaseous olefins, recovering said good antiknock gasoline from the resulting conversion products in the form of a distillate substantially free of dissolved normally gaseous olefins, contacting the last named distillate with said lighter fractions resulting from the distillation step at a sufficiently low temperature to absorb therein substantial quantities of said paraffinic gases, stabilizing the resulting gas-containing distillate to a vapor pressure materially in excess of that of the second named distillate, recovering the stabilized distillate, contacting normally gaseous components of said conversion products with regulated quantities of the first named distillate to absorb in the latter substantial quantities of readily polymerizable olefinic gases, and supplying the resulting gas-containing distillate to said conversion step.

7. A process of converting hydrocarbons which comprises, distilling an oil containing straight-run gasoline and essentially paraffinic gases to separately recover therefrom a distillate, comprising substantially all of its poor antiknock, straight-run gasoline fractions, and a lighter product containing good antiknock, straight-run gasoline fractions and at least a substantial

quantity of said paraffinic gases, subjecting said distillate to conversion conditions regulated to effect the production therefrom of high yields of good antiknock gasoline and substantial quantities of readily polymerizable olefinic gases, recovering the last named good antiknock gasoline from the resulting conversion products in the form of a distillate devoid of at least a major portion of said normally gaseous olefins, commingling the last named distillate with said lighter product of the distillation step to include therein, with said last named distillate, as the gasoline product, said good antiknock straight-run gasoline and a substantial quantity of said paraffinic gases, and separately recovering from said conversion products a mixture of normally gaseous hydrocarbons containing a high concentration of readily polymerizable olefins.

8. A process such as defined in claim 7, wherein at least a portion of the readily polymerizable olefinic components of the conversion products is returned to said conversion step and therein further converted in commingled state with the first named distillate to produce additional yields of good antiknock gasoline.

9. A process of converting hydrocarbons which comprises, distilling an oil containing straight-run gasoline and essentially paraffinic gases to separately recover therefrom a distillate, comprising substantially all of its poor antiknock straight-run gasoline fractions and a lighter product containing good antiknock straight-run gasoline and at least a substantial quantity of said paraffinic gases, subjecting said distillate to conversion conditions regulated to effect the production therefrom of high yields of good antiknock gasoline and substantial quantities of readily polymerizable olefinic gases, recovering the last named good antiknock gasoline from the resulting conversion products in the form of a distillate devoid of at least a major portion of said normally gaseous olefins, commingling the last named distillate with said lighter product of the distillation step to include with said last named distillate, as the gasoline product, said good antiknock, straight-run gasoline and a substantial quantity of said paraffinic gases, contacting normally gaseous components of said conversion products with regulated quantities of the first named distillate to absorb in the latter substantial quantities of readily polymerizable olefinic gases, and supplying the resulting gas-containing distillate to said conversion step.

10. A process of distilling and converting hydrocarbon oils which comprises, heating charging oil containing poor antiknock gasoline fractions and essentially paraffinic gases to distillation temperature and separating therefrom by fractionation a substantially gas-free condensate comprising said poor antiknock gasoline fractions, converting said condensate under conditions of high cracking temperature and substantial superatmospheric pressure to produce therefrom substantial yields of gasoline of improved antiknock value and olefinic gases, separating said good antiknock gasoline and gaseous products of the conversion step from higher boiling products thereof, recovering said good antiknock gasoline in the form of a distillate containing substantial quantities of dissolved relatively heavy gases including readily polymerizable olefins, stabilizing said distillate to a low vapor pressure by liberating therefrom at least a major portion of the dissolved gases, removing as liberated gases from the stabilizing step a mixture

of normally gaseous materials containing a high proportion of readily polymerizable olefins, separately removing from the charging stock in the distillation step a low-boiling vaporous stream comprising substantially all of the gaseous components of the charging stock, commingling said vaporous stream with the stabilized distillate, cooling the mixture sufficiently to retain said stabilized distillate in liquid state and absorbing therein substantial quantities of the heavy gaseous components of the charging stock, and stabilizing the resulting gas-containing distillate to form a final gasoline product of the desired vapor pressure.

11. A process such as defined in claim 10, wherein gases liberated in the first mentioned stabilization step are condensed to form a normally gaseous condensate containing a high concentration of readily polymerizable olefins.

12. A process such as defined in claim 10, wherein gases liberated in the first mentioned stabilization step are condensed to form a normally gaseous condensate containing a high concentration of readily polymerizable olefins and wherein regulated quantities of said condensate are returned to said conversion step for further treatment in commingled state with the first mentioned condensate.

13. A process such as defined in claim 10 wherein gases liberated in the first mentioned stabilization step are intimately contacted with regulated quantities of the first mentioned condensate to absorb in the latter substantial quantities of readily polymerizable normally gaseous olefins and the resulting gas-containing condensate supplied to said conversion step.

14. A process such as defined in claim 10, wherein said vaporous stream recovered from the distillation step includes good antiknock gasoline components of the charging stock which are condensed in said cooling step and included, with said heavy paraffinic gases and the good anti-knock gasoline resulting from said conversion, in the gasoline product resulting from the final stabilization step.

15. A process of distilling and converting hydrocarbon oils which comprises, heating crude petroleum containing gasoline and paraffinic gases to distillation temperature and separating the same by fractionation into a condensate, comprising poor antiknock gasoline fractions, and lower boiling and higher boiling fractions, substantially stripping the condensate of desirable light components including dissolved gases and thereafter converting the same by heat and pressure treatment into high yields of good antiknock gasoline and substantial quantities of olefinic gases, cooling the heated products of the conversion step sufficiently to prevent excessive further conversion thereof and separating the same into vapors and non-vaporous residue, fractionating the vapors to condense therefrom components boiling above the range of the desired gasoline, subjecting the fractionated vapors to condensation, separating the resulting distillate and uncondensed gases under conditions regulated to include in the distillate at least a major portion of the heavy, readily polymerizable, normally gaseous olefins produced by said conversion, stabilizing the distillate to a vapor pressure substantially lower than that of the desired final gasoline product by liberating therefrom regulated quantities of its gaseous components, removing as thus liberated gases from the stabilization step a mixture of nor-

- mally gaseous materials containing a high proportion of readily polymerizable olefins, removing said lower boiling fractions of the crude as a vaporous stream from the first mentioned fractionating step, subjecting the same to condensation in commingled state with distillate resulting from said stabilization, separating resultant distillate from uncondensed and undissolved gases under conditions regulated to retain in the distillate a substantial quantity of the heavy paraffinic gaseous components of the charging stock, and separately stabilizing the last named distillate to form said final gasoline product of the desired vapor pressure.
- 15 16. A process such as defined in claim 15, wherein gases liberated in the first mentioned stabilization step are contacted with an absorber oil comprising regulated quantities of the stripped condensate recovered from the crude oil distilling step and the resulting enriched absorber oil supplied to said conversion step.
- 20 17. A process such as defined in claim 15, wherein gases liberated from the distillate in the first mentioned stabilization step and gases previously separated therefrom are contacted with an absorber oil comprising regulated quantities of the stripped condensate recovered from the crude oil distilling step and the resulting enriched absorber oil supplied to said conversion
- 25 30 step.

18. A process such as defined in claim 15, wherein gases separated from the first named distillate prior to its stabilization are supplied to the same condensation step to which the first named stabilized distillate and said lower boiling fractions of the charging stock are supplied.

19. A process for treating hydrocarbon oil containing low anti-knock gasoline and paraffinic gases which comprises fractionally distilling said oil and separating the paraffinic gases from the low anti-knock gasoline fractions, subjecting the latter to reforming conditions of temperature and pressure and separating from the resultant products a gasoline distillate containing a substantial amount of dissolved olefinic gases, stabilizing said distillate to a lower vapor pressure than commercial gasoline, thereby separating from the distillate normally gaseous olefins suitable for polymerization, and combining with the stabilized distillate a sufficient amount of said paraffinic gases to raise its vapor pressure to that of commercial motor fuel.

20. The process as defined in claim 19, further characterized in that at least a portion of said normally gaseous olefins is subjected to the reforming conditions together with said low anti-knock gasoline fractions whereby substantial polymerization thereof is effected.

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