

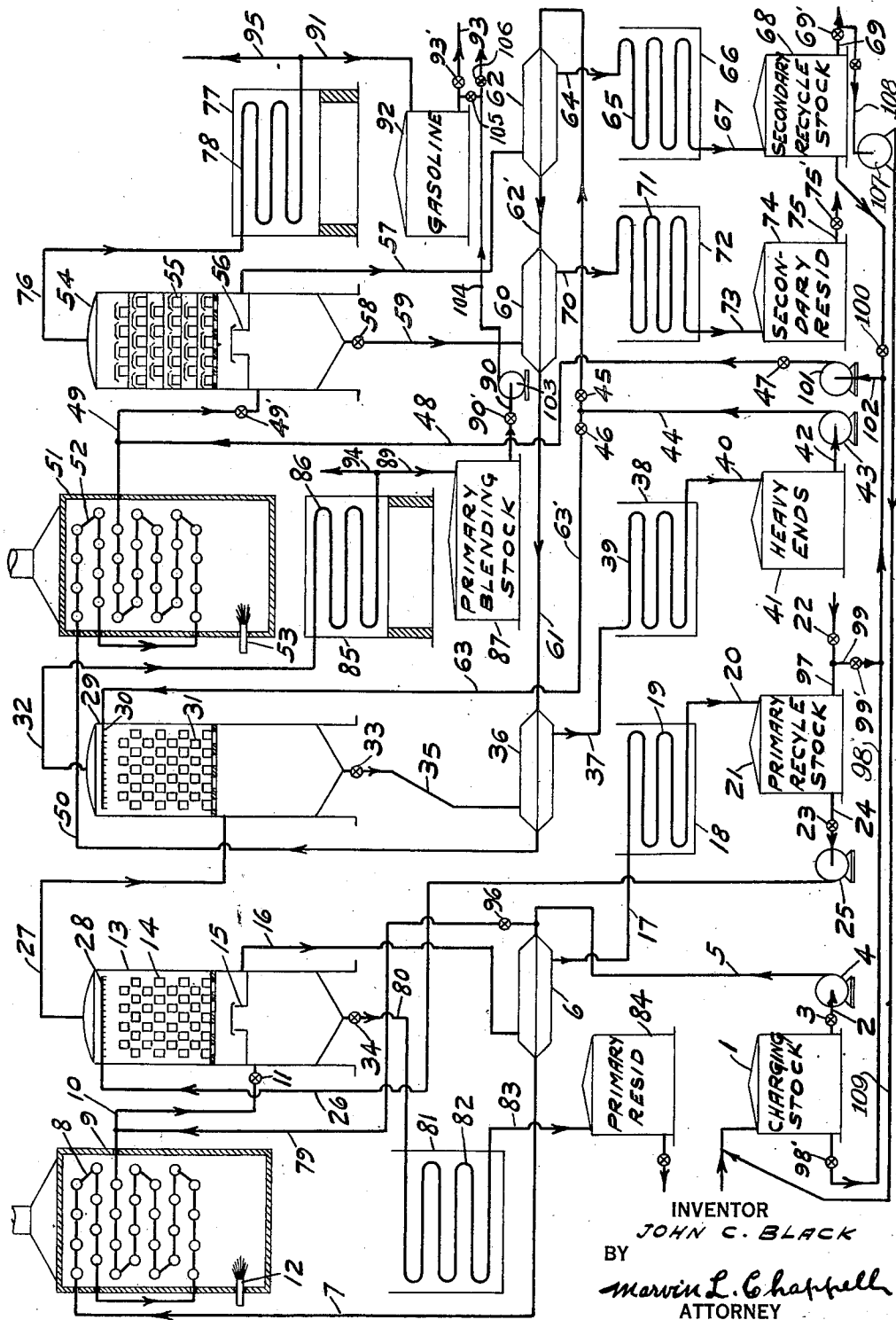
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PROCESS OF PRODUCING AN IMPROVED MOTOR FUEL AND SOLVENT OIL

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PROCESS OF PRODUCING AN IMPROVED
MOTOR FUEL AND SOLVENT OILJohn C. Black, Beverly Hills, Calif., assignor
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This invention relates to a method of processing mineral oil products, such as petroleum oils, shale oils, or distillates of the same, to produce an improved motor fuel or gasoline stock suitable as a fuel for internal combustion engines with a high compression ratio, or as a solvent for the extraction of oils from vegetable products and the like; this product being lower in sulphur content and containing a higher percentage of carbocyclic hydrocarbons than is usually obtained by any of the well-known thermo cracking processes using super-atmospheric pressure.

Briefly stated, my invention comprises separating by fractionation and condensation, a higher boiling fraction and a lower boiling fraction from a vaporized naphtha stock derived by cracking a higher boiling petroleum oil by any of the processes known in the art, or derived by the distillation of a crude-petroleum oil, then subjecting the said separated higher boiling naphtha fraction to a temperature sufficiently high to dehydrogenate and convert a substantial portion of the same into carbocyclic hydrocarbons, then separating by fractionation that portion of the said dehydrogenated hydrocarbons which have boiling points up to approximately 450 degrees F. or any other end point desired, and then commingling the same with the lower boiling fraction separated from the said first naphtha stock, with or without the addition of casinghead gasoline stock, in quantities sufficient to produce gasoline stocks having any desired range of boiling points within the limits of the stocks blended. In case a solvent for the extraction of oil from vegetable products, or a cleaners' solvent is desired, the dehydrogenated hydrocarbons having boiling points up to approximately 450 degrees F. may be employed after a purification and fractionation operation.

As an illustration of the process I will take a naphtha vapor from a pressure cracking process, this vapor having passed through fractionating equipment to produce if it were condensed, a gasoline or naphtha stock having an end boiling point of 425 to as high as 500 degrees F., depending upon the degree of cracking or the quantity of carbocyclic hydrocarbons required in the finished blend. This vaporized naphtha stock is now further fractionated by any of the well-known fractionating processes but the one shown in the accompanying drawing is a wash tower equipment in which a portion of the separated or condensed oil after cooling, is used as the condensing medium. The wash oil in this case is of the same character as the oil I wish

to separate from the naphtha vapors and was previously a part of them. The separated or condensed portion consists of the higher boiling fractions of the vapor, say from 250 degrees F. up to the end boiling point of the naphtha stock entering the fractionating equipment. The lower boiling fractions, or the uncondensed portion of the naphtha vapors pass out of the tower and are separately condensed to form the primary blending constituent of the final product. This primary portion of the naphtha vapors may have, as an illustration, boiling points of from 90 degrees F. to 250 degrees F. or even higher, say to 284 degrees F. which is the boiling point of the 50 per cent fraction of the U. S. motor gasoline. This primary fraction is already rich in hydrocarbons having non-detonating qualities and I have found it is not necessary to further process this fraction to get a satisfactory motor fuel when blended with the secondary blending stock. The high boiling fractions separated by the wash oil are further treated and changed in the process into a range of boiling points starting as low as that of the original naphtha stock and as high or higher than in the original stock. These processed or re-treated hydrocarbons are fractionated and the proper boiling point hydrocarbons are separated to form the secondary blending stock which may range in boiling points from 100 degrees F. or lower to as high as 400 degrees F. or higher. The two stocks, the primary and the secondary blending stocks, when blended will form a gasoline or motor fuel entirely different from the original stock from which they were derived, as for instance, the original stock may have boiling points having an initial of 95 degrees F. or less, 18 to 20 per cent boiling at 212 degrees F., the 50 per cent fraction boiling at approximately 284 degrees F. and a final boiling point of 437 degrees F., whereas the blended stock may have an initial of 95 degrees F., 30 to 35 per cent boiling at 212 degrees F. and 65 or 70 per cent boiling at 284 degrees F., and the final boiling point may be 437 degrees F. or lower, this latter depending upon the desired characteristics of the finished product, or for other consideration such as market requirements or the use for which the fuel is intended.

The best non-detonating fuels as a rule (except where tetra ethyl lead is used) are those having a large percentage of their fractions boiling under 300 degrees F. and 30 per cent or more boiling at 212 degrees F., so it is evident that the boiling points of this improved blended mo-

tor fuel fulfill this requirement. This end is attained by the conversion of a portion of the higher boiling fractions into lower boiling fractions of the benzol series, or hydrocarbons of similar characteristics, it being well-known that benzol gasoline mixtures make a most satisfactory non-detonating motor fuel.

The gasoline made by this process may be chemically treated and purified by any of the well-known vapor phase processes, or the blended stock may be treated and purified by any of the well-known treating and sweetening processes.

An object of the invention is to produce gasoline boiling point stock or motor fuel for use in internal combustion engines with a high compression ratio.

Another object of the invention is to produce a motor fuel suitable for use in internal combustion engines with a high compression ratio without requiring the use of anti-knock compounds.

Another object of the invention is to produce a solvent which may be employed to extract oils from vegetable products or may be used as a cleaning fluid.

Another object of the invention is to provide a continuous process for converting by a dehydrogenation operation a higher boiling fraction of a gasoline or naphtha stock into a non-detonating motor fuel containing a high percentage of carbocyclic hydrocarbons such as benzol, toluol, xylol, etc.

Another object of the invention is to increase the non-detonating properties of cracked gasoline stocks by a continuous process, while the same is in the process of manufacture.

Various other objects and advantages of the present invention will be apparent from the description of the preferred form or example of the process embodying the invention. For this purpose, reference is made to the accompanying drawing, in which there is illustrated a form of apparatus in which the invention may be performed.

The drawing represents a diagrammatic view of the apparatus in which the parts are in vertical section.

In the drawing, 1 represents generally a tank for holding the hydrocarbon oil to be processed, which is termed "charging stock", and may be any petroleum oil distillate such as a gas oil stock. Pipe 2, controlled by valve 3, connects charging stock tank 1 near the bottom to the inlet side of pump 4. Pipe 5 connects the discharge side of pump 4 to heat exchanger 6. Pipe 7 connects heat exchanger 6 to heater coil 8 which is stationed in the furnace 9. The furnace 9 is provided with a burner 12 which leads to a source of fuel supply not shown. Pipe 10 controlled by pressure relief valve 11 connects heater coil 8 to fractionating tower 13. Fractionating tower 13 is provided with a separator plate 15, contact material 14, such as tile, and a spray pipe 28. Pipe 16 connects fractionating tower 13 just above the separator plate, to heat exchanger 6. Pipe 17 connects heat exchanger 6 to cooling coil 19, which is stationed in the condenser box 18. Pipe 20 connects cooling coil 19 to re-cycle stock tank 21. Pipe 23, controlled by valve 22 connects re-cycle stock tank 21 to a storage not shown. Pipe 24, controlled by the valve 23, connects re-cycle stock tank 21 near the bottom to the inlet side of pump 25. Pipe 26 connects the discharge side of pump 25 to spray pipe 28. Pipe 30, controlled by the valve 34, connects fraction-

ating tower 13 at the bottom to cooling coil 22 which is stationed in the condenser box 21. Pipe 33 connects cooling coil 22 to primary residuum tank 34. Pipe 39, controlled by valve 36, connects pipe 5 to pipe 10. Pipe 27 connects fractionating tower 13 at the top to fractionating tower 29. Fractionating tower 29 is provided with contact material such as tile 31 and a spray pipe 30. Pipe 35, controlled by the valve 33, connects fractionating tower 29 at the bottom to exchanger 36. Pipe 37 connects exchanger 36 to cooling coil 39, which is stationed in the condenser box 38. Pipe 40 connects cooling coil 39 to "heavy ends" tank 41. Pipe 42 connects "heavy ends" tank 41 near the bottom to the inlet side of pump 43. Pipe 44 connects the discharge side of pump 43 to pipe 63'. Pipe 63', controlled by valves 45 and 46, connects the pipe 63 to exchanger 62. Pipe 63 connects the pipe 63' to spray pipe 30 in the fractionating tower 29. Pipe 62' connects exchanger 62 to exchanger 60. Pipe 61 connects exchanger 60 to exchanger 36. Pipe 50 connects exchanger 36 to heater coil 52. The heater coil 52 is stationed in the furnace 51 which is provided with a burner 53. Burner 53 leads to a source of fuel not shown. Pipe 32 connects fractionating tower 29 at the top to condenser coil 86 which is stationed in the condenser box 85. Pipe 89 connects cooling coil 86 to "primary blending stock" tank 87. Pipe 94 connects pipe 89 to an absorber not shown. Pipe 90, controlled by valve 90', connects "primary blending stock" tank 87 near the bottom to pump 103. Pipe 104, controlled by valve 106 connects pump 103 to a storage not shown. A branch pipe controlled by valve 105 connects pipe 104 to pipe 93. Pipe 49, controlled by valve 49', connects heater coil 52 to fractionating tower 54. Fractionating tower 54 is provided with a separator plate 56 and bubble trays 55. Pipe 76 connects fractionating tower 54 at the top to condenser coil 78, which is stationed in the condenser box 77. Pipe 91 connects condenser coil 78 to gasoline tank 92. Pipe 93, controlled by the valve 93', connects gasoline tank 92, near the bottom, to a storage not shown. Pipe 57 connects fractionating tower 54 just above the separator plate 56 to exchanger 62. Pipe 64 connects exchanger 62 to cooling coil 65 which is stationed in the condenser box 66. Pipe 67 connects cooling coil 65 to re-cycle stock tank 68. Pipe 69, controlled by the valve 69', connects re-cycle stock tank 68 near the bottom to a storage not shown. Pipe 59, controlled by the valve 58, connects fractionating tower 54 at the bottom to exchanger 60. Pipe 70 connects the exchanger 60 to cooling coil 71 which is stationed in the condenser box 72. Pipe 73 connects cooling coil 71 to secondary residuum tank 74. Pipe 75, controlled by the valve 75', connects secondary residuum tank 74 near the bottom, to a storage not shown. Pipe 48, controlled by the valve 47, connects the discharge side of pump 101 to pipe 49. Pipe 102 connects the inlet side of pump 101 to pipe 98. Pipe 98, controlled by valves 98' and 100, connects charging stock tank 1 to re-cycle stock tank 68. Pipe 99, controlled by valve 99', connects pipe 98 to re-cycle stock tank 21 through the pipe 97. Pipe 95 connects pipe 91 to an absorber not shown by means of which the gasoline stock retained by the hydrocarbon gases may be separated and returned to the gasoline tank 92.

The preferred process as carried out in the apparatus just described is as follows:

Tank 1 is filled with the petroleum oil to be

processed, such as gas oil stock, from a source not shown. The gas oil stock, termed "charging stock" contained in tank 1, is caused to pass in a regulated stream flow through pipe 2 into the inlet side of pump 4, by operation of valve 3. Pump 4 continuously discharges the gas oil stock through pipe 5, heat exchanger 6, pipe 7 and heater coil 8, under a pressure sufficient to prevent any substantial vaporization during the passage through heater coil 8, preferably using a terminal pressure of approximately 1000 pounds, although higher or lower pressure may be used, depending upon the stock to be cracked and the temperature employed. This oil passing through heater coil 8 is heated to a temperature of approximately 800 to 900 degrees F. to efficiently crack the oil to the required degree. From heater coil 8 the oil cracked to the desired degree passes into pipe 10 and is therein cooled below an active cracking temperature by the continuous introduction of a bypassed portion of the charging stock coming through pipe 79, which connects pipe 5 to pipe 10, the flow being regulated by operation of valve 96. This introduced oil not only cools the cracked oil stream to a temperature below an active cracking temperature of approximately 800 to 875 degrees F., depending upon the oil to be cracked, but is itself partially cracked with the formation of gasoline stock. From pipe 10 the cracked oil stream passes through pressure relief valve 11 and into fractionating tower 13 wherein the naphtha having boiling points up to approximately 450 degrees F., produced by the primary cracking operation, is separated from a primary higher boiling distillate termed "recycle stock". This primary "recycle stock" passes from fractionating tower 13 through pipe 16, exchanger 6, pipe 17, cooling coil 19, which is stationed in the condenser box 18, then through pipe 20 and into "recycle stock" tank 21.

The "primary residuum" which separates in the fractionating tower 13, below the separator plate 15, passes out of the said tower 13 at the bottom through pipe 80, cooling coil 81, pipe 83 and into "primary residuum" tank 84, the flow being controlled by operation of valve 34. The "primary residuum" on passing through cooling coil 82, is cooled to approximately 80 to 150 degrees F. by the introduction of a cooling fluid such as water, into cooler box 81. This "primary residuum" which collects in tank 84 may be conducted to a storage not shown and may be used for fuel purposes or other purposes known in the art.

The "recycle stock" collecting in the tank 21 is employed as a wash oil to assist in the fractional separation of the naphtha vapors from the higher boiling oils, in which a regulated quantity of this stock continuously passes from tank 21 in a regulated stream flow, controlled by valve 23, through pipe 24 and into the suction side of pump 25. Pump 25 continuously discharges this "recycle stock" through pipe 26, which ends in a spray pipe 28 stationed in the top of fractionating tower 13. This spray oil or "recycle stock" after passing through contact material 14, collects on the separator plate 15 and is returned to tank 21, as heretofore described. The excess "recycle stock" which collects in tank 21 may be employed alone or mixed with charging stock as an injection oil, to lower the temperature of the cracked oil vapors leaving cracking coil 52, in which case the required amount is permitted to flow continuously through pipe 99 and into pipe 98 by operation of valve 99'. Pipe 98 conducts this recycle stock into branch pipe 102, which is con-

nected to the inlet side of pump 101. Pump 101 discharges this recycle or injection oil through pipe 48 and into pipe 49, the flow being controlled by operation of valve 47. By operation of valve 100 the secondary recycle stock in tank 68 may be used as an injection oil. By a regulated opening of valve 98' any desired percentage of charging stock in tank 1 may be mixed with the recycle stock coming from tank 21 and/or tank 68 and employed as an injection oil into the pipe 49, to cool the cracked vaporized oil leaving the heater coil 52, as heretofore described. Pipe 69, controlled by valve 69', conducts the excess recycle stock to a storage not shown, from whence this stock may be returned to the system along with other petroleum oil stock to be again processed. As illustrated, recycle stock may be drawn from the tank 68 by a pump 107 through lines 69 and 108 and conducted through line 109 to the charging tank 1.

The naphtha vapors separated in fractionating tower 13 pass through pipe 27 and into fractionating tower 29 wherein further fractionation is effected in which a higher boiling fraction termed "heavy ends" is separated from the lower boiling naphtha vapors. The "heavy ends" separated in fractionating tower 29, pass out of tower 29 at the bottom through pipe 35, the rate of flow being controlled by operation of valve 33, and then pass through exchanger 36, pipe 37 and into cooling coil 39, which is stationed in the condenser box 38. From cooling coil 39 the cooled "heavy ends" pass through pipe 40 and are collected in "heavy ends" tank 41. In order to facilitate the fractionation operation in tower 29 a portion of the "heavy ends" collecting in tank 41 are used as a wash oil. The heavy ends continuously collecting in tank 41 are continuously permitted to flow through pipe 42 and into the inlet side of pump 43—which discharges the same through pipe 44 into pipe 63'. By means of regulated openings of valves 45 and 46, the flow of "heavy ends" passing into pipe 63' is divided into two parts, one part passing into and through the pipe 63 which terminates in spray pipe 30 in the top of fractionating tower 29; and the other portion passing from pipe 63' through exchanger 62, pipe 62', exchanger 60, pipe 61, exchanger 36, pipe 50 and into cracking coil 52, which is stationed in the furnace 51. That portion of the "heavy ends" which passes out through spray pipe 30 into fractionating tower 29, assists in the fractional separation and condensation of the "heavy ends" contained by the naphtha vapors entering tower 29. The wash oil, together with the heavy ends separated from the naphtha vapors, pass out of tower 29 and into heavy ends tank 41, as heretofore described.

The "heavy ends" produced by the aforesaid fractionation operation pass through heater coil 52 under a pressure sufficient to obtain the desired rate of flow and to control the volume of vapors passing therethrough, which may range from approximately atmospheric up to 100 pounds terminal pressure. The "heavy ends" passing through this coil 52 are vaporized and heated in a vapor state to a temperature of approximately 900 to 1200 degrees F. and maintained at this temperature for a period of time sufficient to crack the same with the production of carbocyclic hydrocarbons similar to benzol, toluol, xylol, etc. The products of the cracking reaction pass from coil 52 into pipe 49 wherein they are commingled with a cool oil coming from "recycle" stock tank 21 and/or tank 68, or

"charging stock" tank 1, as heretofore described. The regulated amount of cool oil introduced into the cracked oil vapors leaving heating coil 52 is sufficient to cool the products of the cracking reaction below an active cracking temperature and at the same time partially crack the introduced oil. The products of the secondary cracking operation pass through pipe 49, pressure reducing valve 49' and into fractionating tower 54 wherein the gasoline boiling point stock produced is separated from the higher boiling oil and passes in a vapor state out of fractionating tower 54 through pipe 76, and into condenser coil 78 wherein the gasoline boiling point stock is condensed to a liquid and collected in tank 92, passing from the said condenser coil 78 through pipe 91 which is connected to tank 92. The gasoline stock collected in tank 92 may be conducted to a storage not shown, through the pipe 93, controlled by the valve 93' and may be thereafter commingled with the primary blending stock and purified by methods known in the art to produce a motor fuel having a desired range of boiling points and containing a high percentage of carbocyclic hydrocarbons in quantities sufficient to render the blended gasoline stock suitable for use in motors with a high compression ratio.

Pipe 59, controlled by the valve 58, conducts the residual oil separated by the fractionation operation in tower 54, through exchanger 60, pipe 70, cooling coil 71, pipe 73 and into tank 74 termed "secondary residuum". This secondary residuum which collects in the tank 74 may be conducted to a storage not shown by opening valve 75' in the pipe 75, and may thereafter be utilized as a fuel oil, or for other purposes known in the art. The higher boiling distillate resulting from the fractionation operation in tower 54 which collects above the separator plate 56, passes out through pipe 57, heat exchanger 62, pipe 64, cooling coil 65 and into re-cycle stock tank 68. The recycle stock tank 68 contains the higher boiling distillate from the secondary cracking operations and as heretofore stated, this stock may be used as an injection oil to cool down the products of reaction leaving the cracking coil 52, either alone or in conjunction with the charging stock from tank 1; or the recycle stock may be conducted to a storage not shown by opening valve 69' in the pipe 69, and may thereafter be utilized as a cracking stock or for other purposes known in the art.

In my copending application Serial No. 371,859, I describe a method of producing a motor fuel wherein the total original naphtha vapors are processed to produce a new product rich in carbocyclic hydrocarbons, but by the above described process the original vapors are divided into two fractions, one a low boiling fraction which may amount to as much as 50 per cent of the total naphtha cut and a second fraction consisting of the balance of the naphtha cut. This latter fraction is subjected to a cracking treatment at high temperature and the resultant gasoline fractions are blended with the first mentioned low boiling fractions which are not treated with the higher heat as are the high boiling fractions; in this way a great economy is effected as practically one half of the hydrocarbons are eliminated from the high heat treatment and yet the final product in both processes will result in a motor fuel of high non-detonating qualities which is the object of the two inventions.

Furthermore, I have discovered that by the elimination of the low boiling fractions that the

higher boiling fractions are more readily cracked at the elevated temperature employed and a greater yield of carbocyclic hydrocarbons are produced than if the low boiling fractions were present during the cracking operation.

The primary blending stock collected in tank 87 may be mixed with the secondary blending stock in tank 92, or tanks 87 and 92 may be the same tank and the blending of the stocks could be made as the stocks are produced, but for simplicity and clearness of the operation, I have shown the two tanks separately; also if the primary and secondary blending stocks should require separate chemical treatments, the two stocks may be kept separate. Furthermore, it may be desired to use the secondary blending stocks as a motor fuel by itself without being blended with the primary blending stock, or if mixed with the primary blending stock it may be done in various proportions.

While the process herein described is well adapted for carrying out the objects of the present invention, it is to be understood that various changes and modifications may be made without departing from the invention, such for example, as the use of various heat exchangers or fractionating devices known in the art, and the invention includes all such modifications and changes as appear within the scope of the appended claims.

What I claim is:

1. In the conversion of higher boiling hydrocarbon oils into lower boiling ones, the process that comprises subjecting higher boiling oil in a primary reaction zone to cracking temperature to effect cracking, primarily separating the resultant naphtha stock from higher boiling materials, secondarily separating by fractionation the higher boiling portions of said naphtha stock consisting mainly of hydrocarbons in the gasoline boiling range from the lower boiling portion thereof, passing the said separated gasoline hydrocarbons through a heating coil wherein the gasoline constituents are subjected to a temperature sufficient to effect conversion into products of increased anti-knock value, passing the resultant products from said heating coil to a fractionating zone wherein said products are fractionated to separate out a gasoline stock and a higher boiling oil and introducing said higher boiling oil into contact with the products passing to said fractionating zone to subject the higher boiling oil thus introduced to cracking.

2. In the conversion of higher boiling hydrocarbon oils into lower boiling ones, the process that comprises subjecting higher boiling oil in a primary reaction zone to cracking temperature to effect cracking, subjecting the resultant cracked products to fractionation to separate out a gasoline fraction, a higher boiling condensate and a residual stock, passing said gasoline fraction through a heating coil wherein the gasoline constituents are subjected to a temperature sufficient to effect conversion into products of increased anti-knock value, passing the resultant products from said heating coil to a fractionating zone wherein said products are fractionated to separate out a gasoline stock and introducing at least a portion of aforesaid higher boiling condensate into contact with the products passing to said fractionating zone to lower the temperature of the stream of products entering therein.

3. In the conversion of higher boiling hydrocarbon oils into lower boiling ones, the process

that comprises subjecting higher boiling oil in a primary reaction zone to cracking temperature to effect cracking, subjecting the resultant cracked products to fractionation to separate out a gasoline fraction, a higher boiling condensate and a residual stock, passing said gasoline fraction through a heating coil wherein the gasoline constituents are subjected to a temperature sufficient to effect conversion into products of increased anti-knock value, passing the resultant products from said heating coil to a fractionating zone wherein said products are fractionated to separate out a gasoline stock and a higher boiling oil and introducing at least portions of aforesaid higher boiling condensate and of said higher boiling oil into contact with the products passing to said fractionating zone to lower the temperature of the stream of products entering therein.

4. In a process for the conversion of hydrocarbon oil wherein a hydrocarbon mixture containing gasoline components and higher-boiling components is fractionated to separate therefrom a light fraction containing gasoline components and a higher-boiling fraction, said light fraction is passed through a heating zone and therein heated to a temperature adequate to increase the anti-knock value of its gasoline components, the products are separated into vapors and residue, the vapors are subjected to fractionation in a second fractionating zone for the removal of their insufficiently converted high-boiling fractions which are condensed as reflux condensate, fractionated vapors of the desired end boiling point are subjected to condensation and the resulting distillate and gas are collected, the improvement which comprises commingling at least a portion of said higher-boiling fraction

and said reflux condensate and introducing the thereby commingled oils into the stream of heated oil from the heating zone prior to the separation of vaporous and residual conversion products and effecting cracking of the commingled oils thus introduced by the heat of the heated oil from the heating zone, whereby the commingled oils are subjected to somewhat milder conversion conditions than those employed in said heating zone.

5. In a process for the conversion of hydrocarbon oil wherein a hydrocarbon mixture containing gasoline components and higher-boiling components is fractionated to separate therefrom a light fraction containing gasoline components and a higher boiling fraction, said light fraction is passed through a heating zone and therein heated to a temperature adequate to increase the anti-knock value of its gasoline components, the products are separated into vapors and residue, the vapors are subjected to fractionation in a second fractionating zone for the removal of their insufficiently converted high-boiling fractions which are condensed as reflux condensate, fractionated vapors of the desired end boiling point are subjected to condensation and the resulting distillate and gas are collected, the improvement which comprises introducing at least a portion of said higher-boiling fraction into the heated oil from said heating zone prior to the separation of vaporous and residual conversion products and effecting cracking of the oil thus introduced by the heat of the heated oil from said heating zone, whereby the oil thus introduced is subjected to somewhat milder conversion conditions than those employed in said heating zone.

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