

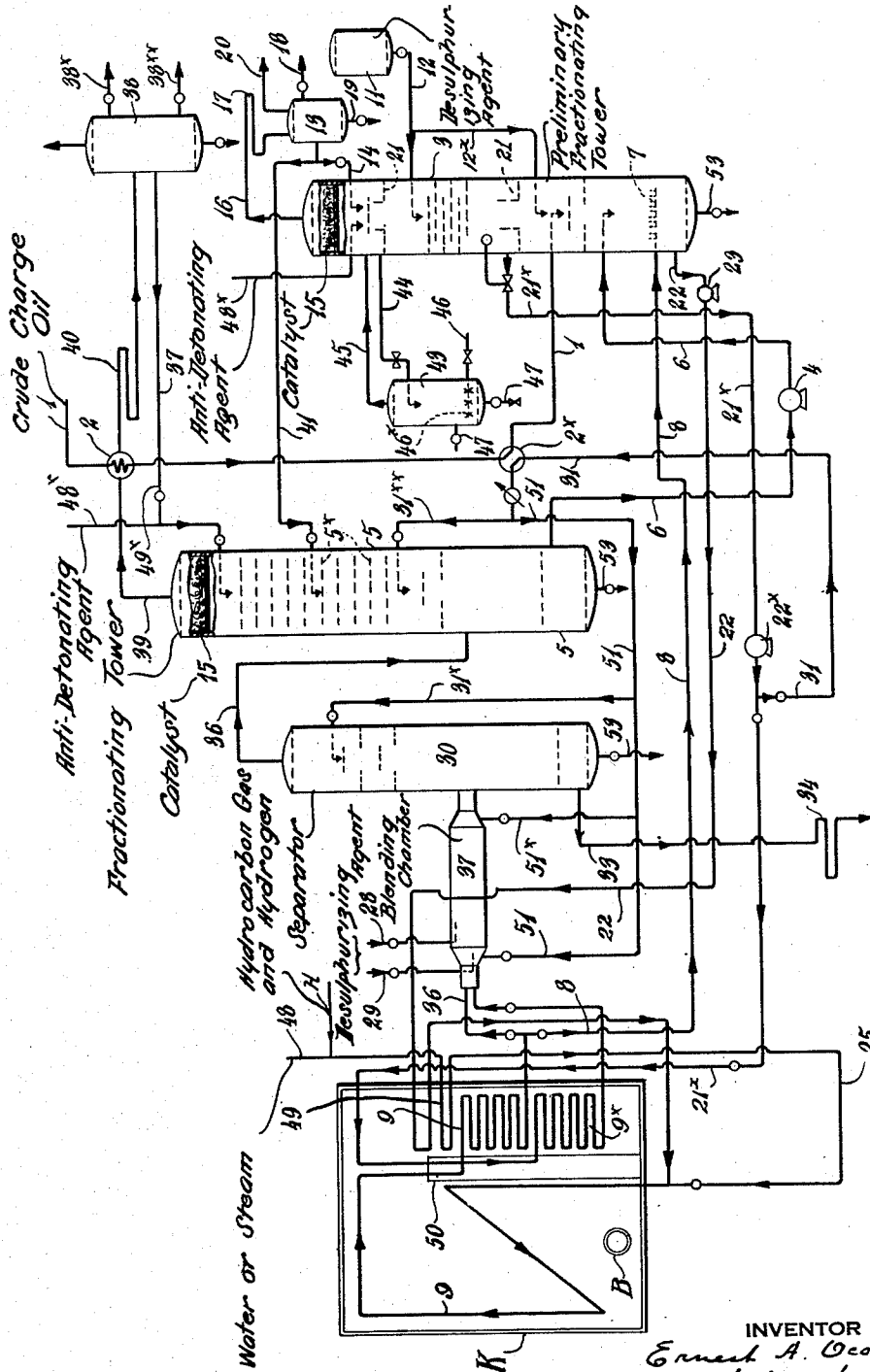
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E. A. OCON
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METHOD FOR TREATING A PLURALITY OF HEAVY HYDROCARBON
OILS FOR SUBSEQUENT CRACKING
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INVENTOR

Ernest A. O'Connor

BY

W Lee Helms.

ATTORNEY

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METHOD FOR TREATING A PLURALITY OF
HEAVY HYDROCARBON OILS FOR SUBSE-
QUENT CRACKING

Ernest A. Ocon, New York, N. Y.

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The object of this invention is to provide a novel method for treating hydrocarbon materials preliminary to cracking, characterized by the preliminary common vaporization treatment by the aid of highly heated gas or vapors or both, in a preliminary blending, vaporizing and fractionating tower, of a plurality of charging stocks of different characteristics, such as (a) uncracked hydrocarbon stock, which may be crude oil, topped oil, liquefied coal, shale oil and the like, (b) insufficiently converted or intermediate condensed fractions free of heavy tarry material, of a previously cracked and fractionated hydrocarbon stock, for example, gas oil, heavy naphtha, kerosene and the like; and (c) insufficiently cracked or intermediate cracked liquid products such as fuel oil, tower bottoms and the like, free of coke and tar, to form with the vaporized and unvaporized fractions two purified clean streams of different characteristics and boiling range, each stream being adapted as a separate charging stock body for subsequent conversion or cracking. Thus the two bodies may be led to different cracking zones and subjected, preferably to different thermal treatment under conditions of cracking temperature and pressure most efficient, to each body, for maximum conversion into low boiling point products with the minimum formation of gas and almost complete absence of formation of coke.

For example, in the preliminary tower for the formation of said two purified charging stock bodies, there are passed two streams, to wit: a regulated stream of preheated crude oil, and a regulated stream of hot heavy fractions from previously cracked hydrocarbon, such as gas oil, fuel oil, and the like. The two streams are blended and subjected to a higher thermal action by means of a blast of highly heated hydrocarbon vapors, but preferably subjected to a blast of highly heated hydrocarbon products that have been cracked admixed with water vapors, and having a temperature of not less than 800° F., which serve a three-fold purpose; first, the reduction of viscosity of the blended uncracked and previously cracked stocks; secondly, increase in the degree of vaporization of the uncracked stock so as to release therefrom the lower boiling point fractions without cracking; thirdly, stripping light fractions from the condensate of the previously cracked stock led into the treating zone, as aforesaid.

The preliminary zone may contain catalysts of the desulfurizing type through which the vaporized fractions may pass, or the vaporized fractions in some cases may be subjected to the successive action of the purification agent and catalytic agent in the said preliminary tower. The catalysts may advantageously be mixed or bound with materials such as Floridin clay,

Attapulugus clay, fuller's earth, bentonite, bauxite and the like.

The pressure employed within the said preliminary blending and fractionating tower will be atmospheric or substantially atmospheric, and preferably from 1 to 10 atmospheres, and in some cases higher pressure may be utilized, if desired.

Part of the purified, blended, uncracked and cracked light fractions of gasoline boiling range drawn off from the preliminary blending, vaporizing and fractionating tower may be subjected to further fractionation, or may all, or part, be refluxed back into said preliminary tower, and into the final fractionating tower for the cracked products, to act as a cooling medium for separation of the desirable light fractions of gasoline range of the blended vapors in said towers.

The process will be described in conjunction with the accompanying drawing in which the figure is a diagrammatic view of an apparatus adapted for operating the method.

Referring to the drawing, the charging stock, for example, crude oil, flows through pipe 1 to heat exchanger 2, thence to heat exchanger 2x, and is thereby heated to a temperature, for example, from 400 to 700° F., more or less. The charged stock thus substantially vaporized passes into the preliminary blending, vaporizing and fractionating tower 3. Simultaneously, there is passed into the said preliminary tower 3 by means of pump 4, through pipe 6, hot purified clean heavy condensate fractions from fractionating tower 5, having a temperature, say from 400 to 700° F., more or less, and consisting of insufficiently converted or intermediate products below naphtha range and above tarry residue. The unvaporized portion of the crude oil and the clean heavy condensate fractions pass into the preliminary fractionating tower 3 in a direction counter-current to a blast of highly heated cracked hydrocarbon products and steam having a temperature preferably between 1000 and 1300° F., discharged through jets 7 connected with a pipe 8 connected with a cracking coil 9 at the convection section of a furnace K. By this means, the hot heavy condensate cracked fractions and substantially vaporized crude oil within the fractionating tower 3 are in turn blended with the highly heated cracked products, the degree of vaporization in the tower being increased and the viscosity of the bodies being reduced. If desired, the vapors meet a purification agent, such as a sulfur precipitation and/or sulfur absorption agent from tank 11 through pipes 12 and 12x, and also meet reflux condensate from tank 13 via pipe 14 and from any other suitable source, the reflux serving as a cooling medium to separate the light fractions of substantially gasoline boiling range of the uncracked and cracked materials and to condense the relatively heavier fractions

of the blend. The gasoline fractions pass upward, preferably through a catalyst 15, and are led off through pipe 16 to a condenser 17, thence into the reflux tank 13. Part of the condensed fractions may pass from tank 13 through pipe 18 to storage. The water is drawn off through pipe 19 and uncondensed gas through pipe 20.

The condensed fractions of relatively higher molecular weight that form one of the continuous charging stock bodies, are drawn off from lower draw-off pan 21, disposed within the primary blending, vaporizing and fractionating tower 3, and are passed through pipe 21x, by means of pump 22x into the cracking furnace coil 9x receiving the lower heat and heated preferably under super-atmospheric pressure range from 5 to 50 atmospheres to a temperature from 850 to 950° F.

The blended, unvaporized fractions in the said tower 3 are withdrawn from the lower part of said tower forming the other continuous separately controlled charging stock body which is passed through pipe 22 by means of pump 23 into a second cracking coil 9 and heated under pressure at a temperature of from 950 to 1300° F., and generally between 1000 and 1100° F. and preferably in the presence of steam. The water or steam from any suitable source is passed through pipe 48 into superheating steam coil 49 and then jointly with the said unvaporized fractions, into the higher heated coil 9 through pipe 25. The steam may be superheated admixed with gases such as gas produced by cracking hydrocarbon material, natural gas or a mixture of said gases or fractions of such gases and if desired, the steam-gas mixture may be superheated under superatmospheric pressure, in the presence of reactive catalysts and passed into the superheating coil 49 to accelerate the decomposition or conversion of said mixture.

The coils 9, 9x and 49 are disposed in a furnace K, having a burner B. The furnace is divided into two chambers by bridge wall 50 open at the top to permit the passage of the hot gases from the combustion chamber to the convection chamber. It will be noted that the preliminary leads for the higher heating coil 9 start in the upper part of the convection chamber of the furnace, then passed near the walls and top of the combustion chamber and thence return to the convection chamber, between the steam coil 49 and coil 9x, and that the preliminary leads of the coil 9x start at the top of the furnace convection chamber and thence pass to a point below the outlet of coil 9 in the convection chamber and lead out at the base of said chamber. These arrangements are preferable, but not essential in the apparatus.

Leaving coil 9 the cracked products are divided into two controlled streams under regulated pressure and one of the streams passes through pipe 36 into a purifying and blending chamber 37, which may be disposed vertically if desired, where it is blended, under expansion, with the products from the lower heated furnace coil 9x. The other stream passes through pipe 8 and discharges under expansion into the lower part of preliminary blending, vaporizing and fractionating tower 3, through spray 7. Provision is made in chamber 37 for the introduction of sulphur reagent and sulphur absorbent material through pipes 28 and 29 for further purification of the products if desired. The sulphur reagent that may be used in the process is preferably selected from a group comprising lead acetate,

sodium plumbite, ethylenediamine $C_2H_4(NH_2)_2$, ammonia sulphide, calcium hydroxide, sodium hydroxide, potassium hydroxide and the like, singly or in compound, and preferably in solution, as with alcohol, gasoline, water, etc. Similar purification materials may be passed into the preliminary vaporizing and fractionating tower 3, through pipes 12 and 12x and tank 11. The pressure employed in said tower 3 will be atmospheric or may be from 1 to 10 atmospheres and in towers 30 and 5 will preferably be from 2 to 20 atmospheres.

Chamber 37 discharges into the vapor separating tower 30 into which a reflux of purified clean blended stock is passed through pipes 31, 51, and by-pass 31x by means of pump 22x to control the temperatures of the vapors. Clean reflux may also be passed to chamber 37 through pipe 51x. The fuel oil product from the separating tower 30 may be withdrawn to storage through pipe 33 and cooler 34x, which may be a heat exchanger to heat water for the steam or may be passed free of coke and tar, into the preliminary purification and fractionating tower 3 for further treatment jointly with the heavy condensate fractions passed from the fractionating tower 5 and the crude oil charging stock.

The cracked vapors in tower 30 pass overhead through pipe 36 and enter, free of tar and any chemical sludge, into the lower part of the fractionating tower 5 wherein the vapors pass through bubble decks 5x in contact with liquid reflux, supplied through pipes 41 and 37, and consisting of purified condensed fractions of substantially gasoline boiling range from tanks 13 and 38. The vapors also may meet purified blended condensate supplied through pipe 21x, pump 22x and pipes 31 and 31xx from lower pan 21 of the tower 3. The light fractions of gasoline boiling range finally pass overhead, free of intermediate fractions below the gasoline boiling range, preferably through catalytic material 15, such as may be employed in the tower 5 and through pipe 39 and heat exchanger 2 and condenser equipment 40 into tank 38, in which the gasoline is subsequently separated from the fixed gases, leaving through pipe 38x and run to storage. The condensing water is withdrawn through pipe 38xx. The gasoline is partly refluxed back through pipe 37 into the upper part of the fractionating tower 5.

Hydrogen from any suitable source may be passed with the hydrocarbon gas and steam into the superheating steam coil 49 through pipe H when a higher saturation of hydrogen of the treated charging bodies is desired.

Suitable catalysts to employ in the process, are those immune to sulphur poisoning. As an example of the said catalysts are the oxides of tungsten and molybdenum, preferably admixed with heavy metal sulphides of the iron group. Other catalysts that can be used advantageously are the oxides or sulphides of nickel, chromium, aluminum, vanadium, uranium, titanium, magnesium, tantalum, calcium, tin, cobalt, zinc and the like, one or a compound of two or more of such metals or derivatives.

The selected catalyst when used in the towers 3 and 5 may be a fixed catalyst, and/or may be used also in finely divided form, or colloidal condition with the steam and hydrocarbon gas as a carrier. The catalysts in towers 3 and 5 may be in the form of beads, rings, wire gauge, lumps, briquettes, baffles or any suitable form to present the greatest contact surface, and if desired, may

be mixed or bound with material such as Floridin clay, Attapulugus clay, cement, fuller's earth, active charcoal, bauxite, bentonite and like materials.

5 The preliminary blending, vaporizing and fractionating tower 3 was conceived with the idea of forming from a plurality of hydrocarbon materials of different characteristics such as uncracked hydrocarbon stock and heavy condensate fractions, from previously cracked oil, two streams of blended purified clean fractions for subsequent cracking.

10 Any solid material, organic sulfur compounds or tar sediment that may drop at the base of the towers are drained through valve controlled pipes 53 as is well known in the art. The exact size of furnace, length and diameter of cracking coils, size of vessels and pipes, height of towers, temperature and time of heating, etc., depend upon the capacity of the unit plant to be operated and final products desired.

15 When kerosene is desired, it may be drawn off from the kerosene condensate structure 43 receiving kerosene condensate from the upper draw-off pan 21 disposed in the preliminary blending, vaporizing and fractionating tower 3 via pipe 44, any naphtha light ends being returned through pipe 45 into the tower 3. The kerosene may be brought up to specifications by means of superheated steam injected through jets 46x of pipe 46. The kerosene is drawn off through line 47 to storage.

20 An anti-detonating agent may be added to the vapors of the gasoline boiling range for common condensation, such as nitrous ether, diphenyl ditelluride, isopropylbenzene, nitrobenzol, lead tetraethyl, ethyl benzene, ethylenediamine monohydrate, ethyl benzol, iron penta carbonyl, butyl nitrite, nickel carbonyl and the like, if desired, mixed with anti-oxidants such as alphanaphthylamine, alphanaphthol, to which dyes may be added, for example, fluorescein, rosaniline, fuchsin hydrochlorate, magenta rosein and the like. The anti-detonating agent may be one or a compound of two or more and if desired, admixed or in solution with a suitable solvent, for example, ethyl alcohol, methyl alcohol, methyl butanol, acetone and the like materials, and may be injected into the fractionating towers at the top thereof, through pipe 48x alone or mixed with the reflux from tank 38 if desired. The anti-detonating agent or compounds thereof, may be from 0.02 to 10.0% of the gasoline by weight and generally in the range of 0.05 to 5.0%. The quantity of anti-detonating material added to the vapors will depend on the nature of said vapors, which may be of cracked gasoline, naphtha, straight run gasoline, or a blend of such vapors and naturally on the anti-knock value of the final product desired.

25 It is to be understood that additional heat may be applied to the preliminary tower 3, if desired, by any suitable means such as electric heaters, flue gases from furnace duct, and the like. Also it is to be understood that pumps, temperature controls, heat exchangers, etc., may be used in the apparatus where desirable, as it is well known in the art.

30 Although the heretofore described method is preferred, the system of operation may vary considerably as there are characteristics in structure and apparatus which make my invention one of broad application; and I do not desire to limit the apparatus to use in connection with the process, nor to the details of construction. For ex-

ample, various other means for cooling the vapors in towers 3, 5 and 30 may be employed, such as; by direct or indirect contact with cooling material such as crude oil, hydrocarbon products of semi-refined nature, water and the like. Also the crude oil charging stock and the heavy condensed fractions may be preheated by other suitable means as is well known in the art.

35 In some cases it will be advantageous to pass the vapors of gasoline mixed with the volatile anti-detonating agent through a hot catalytic zone by heating the catalysts with suitable means, such as an electric heater and the like.

What I claim is as follows:

1. A process for converting hydrocarbon oils into relatively lower boiling hydrocarbon oil suitable for use as motor fuel, which comprises distilling petroleum oils including a virgin crude petroleum oil in a preliminary fractionating zone to produce a residual oil and a fractional condensate higher boiling than naphtha, separating some sludge from the residual oil, heating said residual oil free from thus separated sludge in the presence of steam under cracking conditions of temperature and pressure, heating said fractional condensate under cracking conditions selectively different from those imposed on the residual oil and effective for converting a substantial part of the fractional condensate constituents into gasoline hydrocarbons, fractionating vapor products of the thus treated fractional condensate in a secondary fractionating zone to separate and condense a substantially tar free heavy oil fraction higher boiling than naphtha, passing hot products from the heat treatment of the residual oil and said substantially tar free heavy oil fractional condensate from the secondary fractionating zone into the preliminary fractionating zone to form part of the petroleum oils subjected to distillation therein.

2. A process for converting hydrocarbon oils into relatively low boiling hydrocarbon oil suitable for use as motor fuel, which comprises distilling petroleum oils including a virgin crude petroleum oil in a preliminary fractionating zone to produce a residual oil and a fractional condensate higher boiling than naphtha, separating some sludge from the residual oil, subjecting said residual oil free from thus separated sludge to cracking conditions, commingling a portion of the hot products from the thus treated residual oil with the oils undergoing distillation in the preliminary fractionating zone, subjecting said fractional condensate to cracking conditions different from those imposed on said residual oil, commingling another portion of the hot products from the residual oil subjected to cracking conditions with hot products of the thus treated fractional condensate, separating vapors from the commingled products of the two cracking treatments, fractionating said separated vapors in a secondary fractionating zone to condense out a heavy oil substantially tar free condensate higher boiling than naphtha, and using such tar free heavy oil condensate as a part of the petroleum oils subjected to distillation in the preliminary fractionating zone by passing said condensate into the preliminary fractionating zones.

3. A process for converting hydrocarbon oils into relatively low boiling hydrocarbon oil suitable for use as motor fuel, which comprises distilling an initial crude mineral oil and a substantially tar free heavy oil distillate higher boiling than gasoline containing partially converted products of cracking in a preliminary fraction-

ation zone with the aid of highly heated products from a heat treatment passed into contact with said crude oil and said substantially tar free distillate undergoing distillation, separating a residual oil produced in said distillation from some tar and coke, heating said residual oil composed mainly of reduced unvaporized crude and heavy oil fraction distillates containing partially converted products of cracking under conditions of temperature and pressure adequate for cracking to produce said highly heated products used to aid the distillation in the preliminary fractionation zone, separating and condensing intermediate condensate of higher boiling range than naphtha from the mixed vapors produced by the distillation and released in the preliminary fractionation zone, heating said intermediate condensate in a separate zone under conditions of temperature and pressure effective for producing motor fuel separately from said residual oil, fractionating vapor products from the thus heated intermediate condensate in a secondary fractionation zone to separate said heavy oil distillate containing partially converted products, and sending such tar and coke free distillate separated in the secondary fractionation zone directly and without further heating to the preliminary fractionation zone as said substantially tar free heavy oil distillate.

4. A process for converting purified hydrocarbon oil into relatively low boiling hydrocarbon oil suitable for use as motor fuel, which comprises cracking a hydrocarbon oil, passing hot products from said cracking together with a virgin crude petroleum oil to a preliminary fractionating zone, separating vapors therefrom in said zone, subjecting the mixture of vapors from the virgin crude petroleum oil and vapors from the cracked hydrocarbon oil to desulfurization in said preliminary fractionation zone, separating a tar free intermediate condensate of higher boiling range than naphtha from said desulfurized mixed vapors, heating said intermediate sulphur treated condensate in a stream of restricted cross sectional area under cracking conditions adequate to convert a substantial portion of its constituents into gasoline, fractionating vapor products of said cracking in a secondary fractionation zone to condense out a heavy tar and coke free oil condensate higher boiling than naphtha, and subjecting said tar and coke free heavy oil condensate to vaporization in said preliminary fractionation zone to form part of the vapors included in said mixture of vapors subjected to desulfurization.

5. A process for converting a purified hydrocarbon oil into relatively low boiling hydrocarbon oil suitable for use as a motor fuel, which comprises cracking a hydrocarbon oil, passing hot products from said cracking together with a virgin crude petroleum oil to a preliminary fractionating zone, separating vapors therefrom in said zone, subjecting the mixture of vapors from the virgin crude petroleum oil and vapors from the cracked hydrocarbon oil to desulfurization in said preliminary fractionating zone, separating a tar free condensate from said desulfurized mixture, heating such condensate in a stream of restricted cross sectional area under cracking conditions adequate to convert a substantial portion of the condensate into gasoline, fractionating vapor products of said cracking to condense out a tar

and coke free heavy oil condensate higher boiling than naphtha, and subjecting said tar and coke free heavy oil condensate to vaporization in said preliminary fractionation zone to form part of the vapors included in said mixture of vapors subjected to desulfurization.

6. A process for converting clean and purified hydrocarbon oils into relatively lower boiling hydrocarbon oil suitable for use as motor fuel, which comprises distilling petroleum oils including a virgin crude petroleum oil in a preliminary fractionating zone to produce residual oil and vapors, subjecting the vapors to desulfurization, condensing out a thus purified intermediate condensate of higher boiling range than naphtha from the desulfurized vapors, separating some sludge from the residual oil, heating said residual oil free from thus separated sludge under cracking conditions of temperature and pressure, heating said purified intermediate condensate free of sludge under cracking conditions different from those imposed on the residual oil and effective for converting a substantial part thereof into gasoline hydrocarbons, commingling hot products from the heat treatments of the sulphur purified residual oil and the intermediate condensate subjecting the commingled products to further desulphurization, separating vapors from the commingled hot products, fractionating in a secondary fractionating zone said vapors separated from the commingled hot products to condense out a purified, tar and coke free heavy oil condensate higher boiling than naphtha, and discharging said purified, tar and coke free heavy oil condensate into the preliminary fractionating zone to form part of the petroleum oils subjected to distillation therein.

7. A process of producing from relatively high boiling point hydrocarbons, lower boiling point hydrocarbons of the motor fuel type, which comprises cracking heavy oil under mild conversion conditions distilling in a preliminary fractionating zone a plurality of petroleum oils, including a substantially tar free fractional condensate of higher boiling point than gasoline, and hot products from said cracking step, and thereby producing an unvaporized residual fraction, and a fractional condensate mixture higher boiling than naphtha separating some sludge from said residual fraction, heating the unvaporized residual fraction free from thus separated sludge under said mild conversion conditions of temperature and pressure, heating said fractional condensate mixture under rigorous cracking conditions different from those imposed on the unvaporized residual fractions, and effective for converting a substantial part of the fractional condensate mixture into gasoline hydrocarbons, fractionating vapor products of the thus treated fractional condensate mixture in a secondary fractionating zone to separate and condense out a heavy oil fraction higher boiling than naphtha and overhead lighter products, passing at least a portion of the condensate as said substantially tar free fractional condensate first mentioned from the secondary fractionating zone into the preliminary fractionating zone for distillation therein.

8. A process in accordance with claim 7 in which the unvaporized residual fraction is heated under conversion conditions in the presence of gaseous compounds containing hydrogen.

ERNEST A. OCON.