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PROCESS FOR REFINING AND CRACKING OIL

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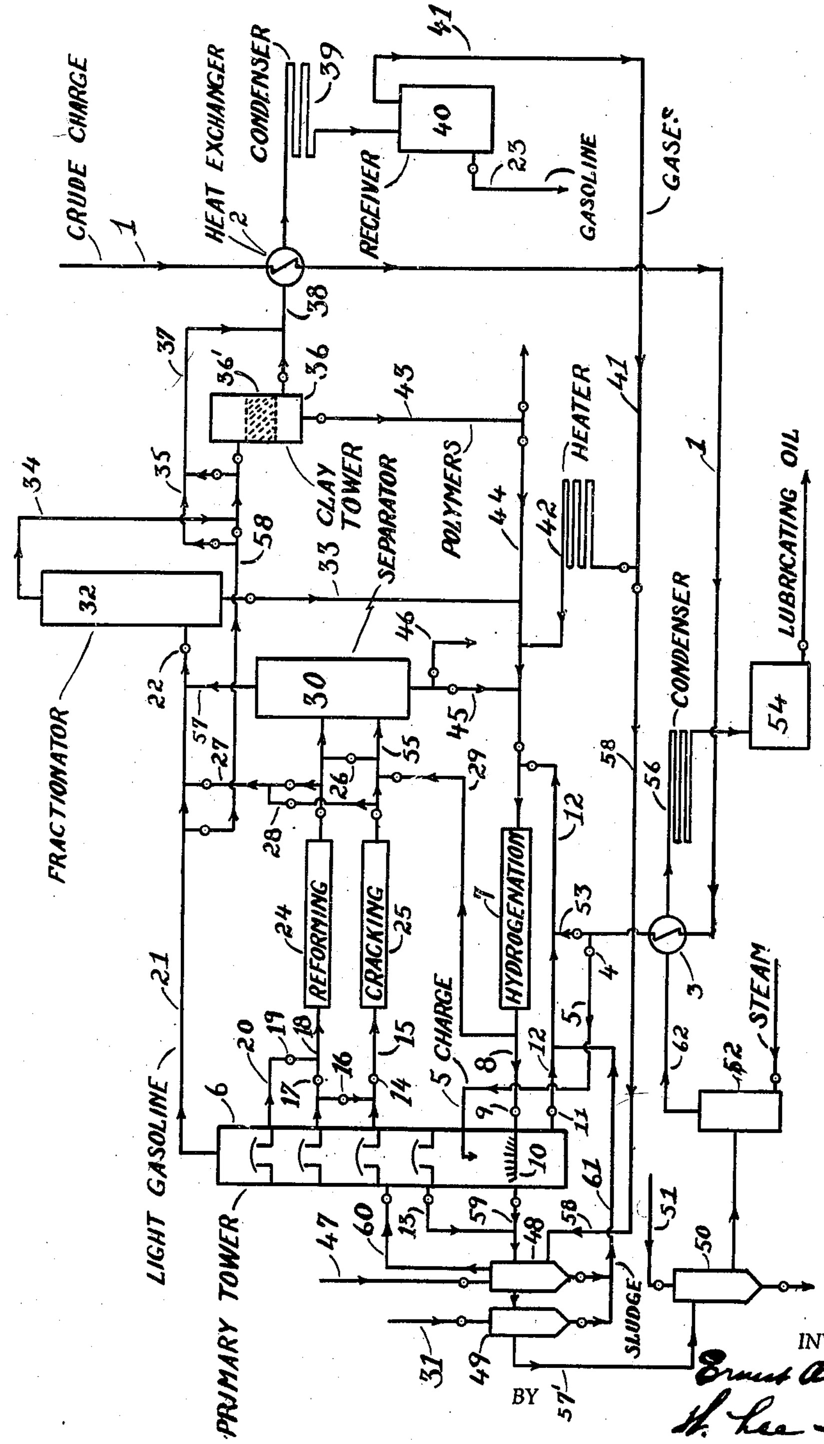

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PROCESS FOR REFINING AND CRACKING OIL

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13 Claims. (Cl. 196—53)

This invention relates to treatments of bituminous materials, such as crude oils, topped crude mineral oils, materials from extraction, and liquefaction of coal, to form therefrom commercial products such as anti-knock gasoline, fuel oils and lubricants, by the use of a simple and flexible arrangement of apparatus in which operations are carried out to permit ready utilization of ordinary waste products, such as residues, polymer-liquids and gases.

According to this invention, an economy in apparatus, space and handling of materials is obtained with the conservation of energy and materials, while at the same time, the apparatus can be adapted to treat various types of initial materials to obtain products which the initial material is most suited to produce or which the market demand makes more desirable. This economy and flexibility is especially valuable in small refineries, and it is obtained through the use of the cooperating operations performed on the materials. A conservation of heat is principally obtained by the use of heat evolved and put into one reaction for aiding in carrying out another operation which is generally necessary in refineries, namely; distillation of initial charging stocks, with an enhancing of the efficiency and yield of the distillation, and elimination of or simplification of apparatus. At the same time, the resulting distillation products are especially suitable for further treatments or use and can be changed by merely making changes in operating conditions. A conservation in material is also obtained in that the heat evolving reaction is a hydrogenating reaction and can be used to transform by-products of the further treatments into oils which can be mixed with fractions of the charging stock with an improvement rather than an impairment of their qualities for further use or treatments.

More particularly, the invention relates to improvements in process and apparatus in which bituminous liquids relatively free from compounds present in cracked materials in much larger quantities than in straight run petroleum products, which compounds insofar as the complexity of the material permits analysis, appear to be cyclic and unsaturated hydrocarbons, are subjected to distillation to produce distillates and residual oils without substantial cracking and with the aid of heat and products from a hydrogenation treatment. Since the products from the hydrogenation are relatively saturated, this distillation is comparable to a straight distillation, especially with the aid of the gaseous products of the hydrogenation, in lowering the partial pressure of the distillates. This results in the formation of a gas oil substantially unmixed with cracked materials, which kind of oil is easy to crack with low coke formation, in distillates lighter than gas oil which are easy to reform or dehydrogenate, and in heavier distillates and residuals which are of such purity as to make them good lubricating oils or Diesel fuel stocks depending upon conditions and the nature of the charging stock. The materials which may be used for the hydrogenation are the ready available by-products of the cracking, reforming, and purification treatments, to which the products of the distillation may be subjected.

The term "bituminous" is to be understood as meaning the materials are relatively highly saturated as in paraffinic hydrocarbons and naphthenic hydrocarbons. If extraction products, such as, raffinates from extractions by solvents of the nature of sulphur dioxide, are used, they can be directly distilled, but when the more unsaturated extracted oil in such extractions are used, which oil may be aromatic or unsaturated, such oil would first be subjected to hydrogenation. Similarly, saturated liquid products of the liquefaction of coal, from shale oils, from heavy synthetic hydrocarbon products produced by reaction of hydrogen with carbon monoxide, and products produced by saturating, partly or wholly, products from the polymerization of unsaturated hydrocarbons can be considered as coming under the term of bituminous materials. Also natural asphalts, paraffins, naphthenes, waxes, etc., in contradistinction to cracked hydrocarbon, aromatics, unsaturated hydrocarbons, and pyrogenous (cracked) asphaltic residues, such as are obtained from cracking stills.

One object of the present invention is to provide a novel and efficient process and apparatus to subject any residual product from cracking and refining treatments imposed on hydrocarbon liquids and vapors to a hydrogenation treatment in order to substantially saturate such residual product so that more valuable materials for use as lubricating oil, fuel oil, and cracking stocks are obtained, in a manner in which they can be readily separated by fractionation, while they at the same time can be admixed with fresh charging oil which they may aid in distilling by virtue of their heat content together with the vaporizing effect of the gaseous products of the hydrogenation.

A further object of this invention is to provide a novel method and apparatus for making a more efficient use of homogeneous catalysts or polymerizing agents through the use of a hydrogenation treatment on the residuals containing the used polymerizing agent or catalyst, in which hydrogenation, the used polymerizing agent or catalyst is of further use or at least is not objectionable.

A further object of this invention is to provide a novel and efficient process and apparatus to utilize the ordinary waste by-products of residues, polymer-liquids and gases in a novel method of distilling a fresh charging stock to produce a high octane gasoline substantially free of sulphur and gum forming substances.

A further object of the invention is to provide a novel and efficient process and apparatus for the utilization of residual distillates such as Diesel fuel stocks or cracking stocks, especially when the initial charge is more suitable for making fuel oils than lubricating oils, and especially with the distillation involving some viscosity breaking, and with the recovery of more desirable products from the heavy unvaporized residue by hydrogenation if its components are deficient in hydrogen.

A further object of this invention is to provide a novel and efficient process and apparatus for the utilization of residual oils and heavy residual distillates, obtained especially when the distillation is performed on suitable charging stocks, such as, paraffin or mixed base crudes without appreciable cracking as lubricating oil stocks which can be readily refined by ordinary chemical treatments, such as aluminum chloride, zinc chloride, boron fluoride or solvent extraction, making possible a good recovery of the otherwise wasted gummy oils.

A further object of this invention is to provide a novel and efficient process and apparatus for the utilization of the lighter distillates, such as, the gas oil, kerosene and naphtha for cracking and reforming and to separate out the products from these operations unsuitable for motor fuels but may be hydrogenated to make possible the recovery of more suitable products.

A further object of this invention is to provide a novel and efficient process and apparatus for advantageously utilizing the heat energy of residues and waste products more efficiently than they have hitherto been used to distill a fresh charging stock and provide an especially suitable treatment of ordinarily wasted by-products which can be used in conjunction with the distillation to aid in the removal of sulphurous and other injurious compounds from the cracked vapor products.

The process will be described with reference to the accompanying drawing, in which:—

The figure diagrammatically illustrates the conventional apparatus involved.

The charging stock from any suitable source is passed by line **1** by means of a pump (not shown), through a heat exchanger **2** and **3** to either of the valve joined lines **5** or **53**, preferably to **5**, which leads into the flash distillation tower **6**. In the lower part of said tower **6** the charging stock, preheated by heat exchange, is discharged into a blast of products from a hydrogenation zone **7**, which products include large volumes of hydrogenous gas, such as excess hydrogen, and are at a temperature in the range of approximately 500 to 850° F., upon entering through a spray inlet **10**. In the upper part of said tower **6** are the conventional dephlegmation means for fractionating out in ascending order a residual distillate, a gas oil fraction, a kerosene fraction or heavy naphtha, and a lighter naphtha fraction, with regulation permitting light ends of gasoline and normally gaseous materials to pass overhead. The residual oil distillate will have a suitable boiling range of 650 to 850° F.; the gas oil fraction will have suitably a boiling range of about 500 to 650° F.; the kerosene fraction will have suitably a boiling range of 350 to 500° F.; and the naptha cut a range of about 200 to 350° F.

The gas oil is led by valved line **15** to a heating and cracking unit **25**, conventionally shown, and which is preferably a system of heated tubes for raising the temperature of the gas oil to about 750 to 900° F., the oil being maintained in a vapor or partly vapor and liquid state at these temperatures for a period of 10 to 2 minutes, with less time as the temperature is increased, and a pressure of about 30 to 350 lbs., per square inch. The thus treated gas oil products are sent by a valved line **55** to an enlarged zone **30**, where vapors are separated from liquids and time for further reaction may be given. Methanol synthesis products can be used for quenching the cracking products passing from the cracking unit **25** to the separator **30**.

The fraction of the nature of kerosene mixed with heavy naptha is led by valved line **18** to a reforming unit, conventionally shown, and designated by **24**, which may be a system of heated tubes, or heated tubes connected with an enlarged zone for containing catalysts. The lighter naphtha cut may also be passed together with the kerosene cut by valved line **29** and valved line **18** to the reforming unit. When no catalysts are employed the oils are subjected to heating to a temperature of about 1000° F., at a pressure of about 400 pounds per square inch for a sufficient period to form anti-knock constituents without too much gas, say a period of less than two minutes. When a catalyst is used, such as activated alumina, activated magnesia, chromium oxide, potassium oxide, limestone, halogen compounds, difficultly reducible oxides, such as oxidizable metals with halogens or other oxidants, halogens with metal oxides, or other difficultly reducible oxides alone or promoted by other oxides such as alkaline oxides which increase porosity and prevent sintering, lower temperature and pressures and shorter periods may be used. In particular, with sensitive catalysts, such as copper-nickel, cobalt, iron-copper, and similar metals or their mixtures which cause mainly a dehydrogenation reaction, the temperatures may be as low as about 850° F., and the periods less than one minute; that is, with space velocities of one volume of vapors per minute, per volume of catalyst space, approximately. It may be preferable to subject only the lighter naphtha cut to the dehydrogenation with the use of sensitive catalysts, especially when the cut is free from poisons which may be removed by the hydrogenation and other chemical treatment imposed upon the oil, and in this event, the heavier naphtha and kerosene oil can be separately reformed to obtain splitting; for example they may be passed through valved line **16** to join the gas oil passing to **25**, which is operated in this event at high vapor phase cracking temperatures. The products of reforming may also be sent to enlarged zone **30** or be by-passed by line **27** to a fractionator **32**. Vapors from zone **30** pass by line **57** and through valve **22** to the fractionating tower **32**, in which constituents higher boiling than gasoline constituents are refluxed out. A kerosene reflux may be collected in an intermediate section of the fractionator to be recycled to the reforming unit to increase the anti-knock and gasoline by-product by a line (not shown) leading from the fractionator 32 to the reforming unit 24.

Overhead vapors and gases from tower 6 may be passed by line 21 to join either the reforming or cracked products passed to separator 30, by valved line 28 or valved line 27, or the vapors entering the fractionator 32, or be made to by-pass the fractionator and a clay treating zone 36, by valved lines 58 and 35. The by-passing of the fractionator and treating zone is preferable when the light gasoline vapors contain too much gas and particularly sulphur compounds.

The overhead gasoline vapors from fractionator 32 may be led by line 34 to a treating tower 36 which may have an inlet (not shown) and an acid treated clay 36′ or metal salt such as zinc chloride or tin chloride, or other adsorbents and chemicals to remove gum forming constituents and other undesirable substances, and from 36, the purified gasoline vapors are led by line 38 through heat exchanger 2 to a condenser 39, to condense out a gasoline product. The condensate and uncondensed material is passed from the condenser to a receiver 40 for separation of the liquids from uncondensible vapors and gases. The gasoline is withdrawn from the system through valved line 23.

Liquid polymers formed in the treating tower 36, reflux condensate formed in the fractionator 32, and residual liquids separated in 30 may be passed by lines 43, 33 and 45, respectively, to a hydrogenation unit 7, conventionally shown, to be subjected to hydrogenation individually, intermixed one with the other or others, or with other residual oils of the operation. Line 44 is a means for conveying the above mentioned liquids to the hydrogenation unit 7, and a pump (not shown) may be provided for increasing the pressure on the liquids. The hydrogenation unit 7 may be constructed of heated tubes, or heated tubes leading to an enlarged zone, with catalysts in the tubes, the enlarged zone, or both. Hydrogen, hydrogen-containing gases, or hydrogenous gas or vapor is supplied to the hydrogenation unit. Recycled uncondensed gas such as removed from receiver 40, may be led by line 41 to a heating or gas decomposing coil 42, thence to the hydrogenation zone, or steam, or steam jointly with reducing gases may be used, especially with agents capable of decomposing the steam. About 600 cu. ft. of hydrogen or more may be used per gallon of liquids treated. Temperatures of 500 to 900° F. may be used; pressures may range from about 5 to 20 atmospheres and higher. Catalysts to be employed in the hydrogenation are metal halides or metal oxides, such as iron oxide, magnesia or nickel oxide; metal sulphides such as cadmium sulphide, molybdenum sulphide, or tinned iron, etc. The catalysts may be fixed in the reaction zone, as on carriers of charcoal, activated carbon, or clay, or be suspended in the oil treated in amounts of 1 to 10% of the oil. The hydrogenation reaction is controlled so that small amounts of gasoline are formed, especially when a saturated product is desired. The time of reaction is about 1 to 5 minutes, or more.

Products from the hydrogenation may be sent by valved line 29 to the separator 30, or a portion may be so sent, but preferably they are led by line 8, through valve 9 into the lower part of tower 6, being discharged through spray 10, from which vapor and gas products ascend to aid in the distillation of liquids discharged into tower 6. Unvaporized residuals collect at the bottom of tower 6, and may be withdrawn through valved line 12 to be resubjected to hydrogenation or to be used as fuel oil or, when of high quality, to be used for obtaining lubricants. Especially, when the initial charge oil is of high quality, such as, a paraffin base or mixed base crude products, and other oils entering tower 6 as from the hydrogenation zone are highly saturated, residual oils may be led by valved line 59 to chemical treatment units. The residual oil may first be subjected to a dewaxing, if necessary, and then treated in vessel 48 with a refining agent, such as aluminum chloride, zinc chloride, boron fluoride, at temperatures of 200 to 450° F., the aluminum chloride being led into 48 admixed with oil through line 47 and stirred with the oil to be treated for about 4 hours or over. The aluminum chloride should be used in amounts of about 2 to 10% of the oil treated, depending upon the amount needed. Vapors generated may be returned to the tower 6 by line 60. Following the treatment in 48, the refined oil is decanted into vessel 49, and separated thus from sludge, which may be sent by lines 61 and 12 to the hydrogenation zone 7. In 49 the aluminum chloride treated oil is washed with about 9% of concentrated sulphuric acid, or about that amount of a 98% sulphuric acid which may be led through valved line 31. It is then passed through line 57′ into vessel 50 to be further washed with water and caustic soda led through valve line 51 to neutralization, and then blown bright or reduced in 52, with steam at above 500° F. to obtain the desired viscosity. The oil is then passed through line 62, heat exchanger 3 and condenser 56 into the receiver 54 from which it is withdrawn from the system. Clay may also be used in the distillation. Any wax separated in dewaxing may be used as charging stock for the cracking unit, since it is of highly saturated nature. To aid in removing volatiles from the treating vessel 48 and in forming some desirable polymers in the lubricating oil, normally gaseous hydrocarbons from the cracking operation may be led into vessel 48 through valved line 58. The sludge, containing partially spent aluminum chloride, can be readily subjected to hydrogenation in 7 through valve line 61, for the aluminum chloride itself will still have catalytic activity, and even with water present which hydrolyzes it to aluminum hydroxide, it aids rather than detracts from the hydrogenation. The lower viscosity residual oil distillate may also be passed through valved line 59 from the tower 6 to vessel 48 for treatment. Other halides such as zinc or stannous chloride may be used, and in some cases other treatments such as with solvents which extract asphaltic constituents may be used, and in the solvent treatments solvent tars are recoverable which may be sent to the hydrogenation unit.

When the initial stock is of lower quality, it may first be partly directed, as by line 12 to the hydrogenation zone, and partly by line 5 to discharge into tower 6. In this instance, the hydrogenation zone may be operated under little more rigorous conditions and the tower 6 may have what approaches to a viscosity breaking at its base. More naphthenic, mixed base, or somewhat asphaltic base crude oils would be considered as having lower quality. The operations with regard to the distillates formed in tower 6, other than the heaviest, may remain the same as described, but the heaviest, called distilled residuals, may be of such quality as to be useful as Diesel fuels, or otherwise as cracking stock which may be treated in the cracking unit 25.

Charging stocks which come into contemplation for use besides crude and topped crude mineral oils are bituminous materials from extractions, liquefaction of coal, shale oils, products of water gas synthesis, polymerized products, etc.

Besides the hydrogenous gases mentioned for use in the hydrogenation, it is contemplated that other reducing gases or vapors, such as water gas, methanol, and natural gas, etc., can be used. When steam is used, it is preferably superheated, mixed with a reducing agent such as carbon monoxide, hydrocarbon vapors, or the like, and in the presence of decomposing contact materials, such as hydrides of calcium, spongy iron, alloys of chromium, etc. Methanol and other low alcohols have been found very suitable because they decompose at low temperatures to liberate hydrogen and carbon monoxide, especially in the presence of catalytic agents such as zinc oxide, vanadium oxide, copper, iron oxide, nickel-alumina, zinc oxide-chromium oxide, etc., which while present in the hydrogenation zone also may accelerate the hydrogenation of the oils, and at the same time alcohols appear to have alkylating effects desirable in the final products.

In the gasoline treatment may also be used metal halides, such as aluminum chloride, zinc chloride, etc., especially, since by providing of the hydrogenation, use can be made of the particular spent catalyst.

The exact sizes of apparatus and conditions depend upon the capacity of the plant, the character of the charging stock, and types of products desired. Instruments, valves, pumps and other of such engineering equipment are not all mentioned, but it is understood that they will be used as required and as understood in the art.

The polymerization in tower 36 is mainly one carried out to free the gasoline vapors from gum forming constituents such as diolefins. The chemical polymerizing agent such as clay, metal halides, or whatever is used, causes the highly unsaturated hydrocarbons such as the diolefins to polymerize into tarry oils, which may be led to the hydrogenation zone 7, where they can be treated to form more saturated oils. These more saturated oils are valuable in that a portion can be used to form lubricating oil, fuel oil or Diesel fuel, that is, the portion remaining as residual oil or heavy reflux in tower 6, while the lighter saturated parts are susceptible to more ready cracking and reforming without excessive coke formation. This treatment therefore makes possible a good recovery of the otherwise wasted gummy oils from the polymerization treatment in 36.

It will be understood that the above examples and illustrations are not to be considered limitations on the principles of the invention set forth.

This application is a continuation in part of my copending application, Serial No. 26,835, applied for June 15th, 1935 now Patent No. 2,088,756.

Having described my invention, what I claim and desire to secure by Letters Patent, is as follows:—

1. A process for treating bituminous materials such as mineral oils of wide boiling range substantially free from cracked materials to produce cracking stocks and valuable residual oils, which comprises vaporizing the initial bituminous charging stock with the aid of hot products from a saturating hydrogenation of hydrocarbon oils deficient in hydrogen by directly contacting said products while hot with the bituminous oil undergoing vaporization to form vapors and residual products, and fractionating the vapors to form non-refractory cracking stock distillates and valuable residual stocks substantially free from cracked materials.

2. A process for treating bituminous materials to produce high quality lubricating oils, comprising subjecting initial bituminous oils containing lubricating oil constituents to vaporization with the aid of hot products of hydrogenation by directly contacting said hot products with the bituminous oil undergoing vaporization to produce vapors and residual oils, subjecting residual oils of the vaporization to refining to produce refined lubricating oils and undesirable tars, subjecting tars separated in the refining to hydrogenation to produce more valuable saturated products, and using products of the hydrogenation for aiding the vaporization of the initial oils as hereinbefore stated.

3. A process in accordance with claim 1, in which non-refractory distillates higher boiling than gasoline are formed in the fractionation and are subjected to cracking conditions to produce gasoline, passing products of the cracking to a separation zone to separate vapors from liquids, subjecting vapors separated in the separation zone to fractionation to condense out liquids higher boiling than gasoline and to obtain overhead gases and vapors of the gasoline range, subjecting liquids condensed out in the fractionation to hydrogenation without substantial cracking, and using products of the hydrogenation in aiding the vaporization of the initial oils in the vaporization zone by directly contacting said hydrogenated products while hot with the initial bituminous oil undergoing vaporization.

4. A process for treating bituminous materials, such as mineral oils of wide boiling range, which comprises subjecting the initial oils to vaporization with the aid of the products of hydrogenation, fractionating the vapors formed in the vaporization to produce a condensate intermediate gas oil and light gasoline, subjecting the intermediate condensate to reforming to produce anti-knock gasoline constituents, separating out liquid products of the reforming boiling above the desired motor fuel end point, hydrogenating liquid products thus separated without substantial cracking, and using products from the hydrogenation while hot to aid in vaporization of the initial oils by directly contacting said hot products with the initial oils undergoing vaporization.

5. A process in accordance with claim 4, in which residuals formed in the vaporization are subjected to refining to produce refined oils and tars, separating the tars from the refined oils, subjecting tars thus separated to hydrogenation without substantial cracking with liquid products of the reforming boiling above the end point of the desired motor fuel, and using said hydrogenated products while hot to aid in the vaporization of the initial oils by direct contact therewith.

6. A process for treating bituminous materials, such as mineral oils of wide boiling range, which comprises subjecting the initial material to vaporization with the aid of products of hydrogenation, separating vapors from liquids produced in the vaporization, fractionating the vapors to produce cracking stock condensates containing

constituents higher boiling than gasoline constituents, subjecting the thus separated condensates to cracking, separating liquid products of cracking of higher boiling point than gasoline constituents, subjecting vapors from this separation to chemical treatment to polymerize out gum forming constituents as liquid polymers, subjecting liquid polymers from the chemical treatment to hydrogenation without substantial cracking, and using products of the hydrogenation to aid in the vaporization of the initial material by directly contacting said hydrogenated products while hot with the initial material undergoing vaporization.

7. A process in accordance with claim 6, in which hydrogenation products are mixed with the cracked products of cracking prior to separation of liquid products.

8. A process for treating bituminous materials, such as mineral oils of wide boiling range including gasoline constituents, comprising subjecting such initial material to vaporization with the aid of hot products from a non-destructive hydrogenation by directly contacting said hot products with the initial bituminous material undergoing vaporization, separating the vapors from liquids unvaporized, fractionating the vapors to procure cracking stock condensates and overhead light gasoline ends and normally uncondensed vaporous and gaseous materials, subjecting cracking stock condensates thus produced to cracking without destructive hydrogenation, separating vapor from liquid products of higher boiling range point than gasoline of the cracking, treating separated vapor products of cracking with a polymerizing agent to remove polymerizable constituents, then blending the refined vapor products of cracking with the light gasoline of the overhead products.

9. A process for treating bituminous materials, which comprises subjecting the initial bituminous materials containing gas oil constituents to vaporization with the aid of hot products of a saturating hydrogenation, fractionating vapors formed in the vaporization to form a distillate for cracking, subjecting the distillate to a heat treatment under cracking conditions to form gasoline constituents, separating out vapor products of the cracking from the liquid products of the cracking in a zone distinct from the zone in which the initial materials are vaporized, subjecting liquid products of the cracking of higher boiling range than gasoline to a saturating hydrogenation, and using products of the hydrogenation while hot to aid in the vaporization of the initial materials by direct contact therewith.

10. A process for treating bituminous materials, such as mineral oils of wide boiling range including cracking stock fractions, comprising subjecting such initial materials in a preliminary zone to distillation by direct contact with hot uncracked hydrogenated products to produce a distillate cracking stock and a residual oil, subjecting a portion of the distillate to cracking under cracking conditions to form a motor fuel product, subjecting a portion of the residual oil to a saturating hydrogenation without cracking, and passing hot products from the cracking and hydrogenation to a separation zone to separate mixed vapor products of motor fuel boiling range from liquid products.

11. A process as in claim 10, in which liquid products from the separation zone are subjected to a saturating hydrogenation jointly with a portion of the residual oil and a portion of the hot products from the hydrogenation are used to aid in the vaporization of the initial material.

12. A process for treating bituminous materials, such as mineral oils of wide boiling range including cracking stock fractions, comprising subjecting such material in a preliminary zone to distillation to produce a cracking stock distillate and a residual oil, subjecting such residual oil to a saturating hydrogenation without cracking to add hydrogen to constituents deficient in hydrogen, and passing the resulting products while hot into direct contact with the initial materials to aid in the vaporization of said initial materials and fractionating the vapors formed in said vaporization to produce said cracking stock distillate.

13. A process for treating bituminous materials which comprises subjecting a bituminous material of a type suitable for cracking or catalytic reforming to heat under conversion conditions to produce anti-knock gasoline, subjecting vapor products of the conversion to a chemical treatment with a metal halide type catalyst to remove polymerizable constituents as liquid polymers, subjecting such liquid polymers to a saturating hydrogenation without substantial cracking to produce saturated hydrocarbons of higher boiling range than gasoline, and using a portion of said saturated hydrocarbons as at least part of said bituminous materials subjected to conversion.

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