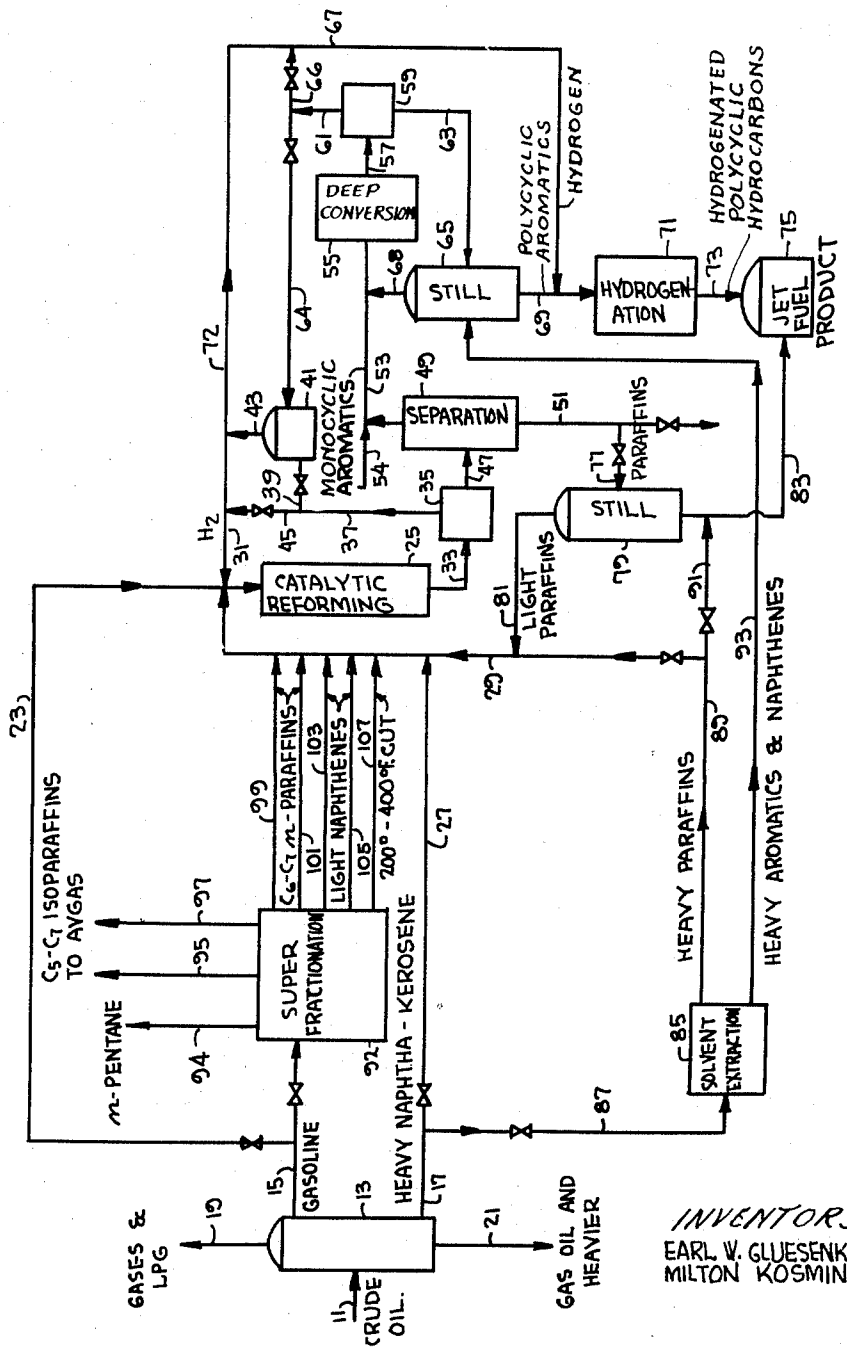
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PROCESS FOR PRODUCING HIGH ENERGY FUELS

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# PROCESS FOR PRODUCING HIGH ENERGY FUELS

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This invention relates to a process for producing improved high energy fuels and in particular to fuels suitable for use in turbo jet and turbo prop engines.

One object of this invention is to provide a process for producing a hydrocarbon fuel having substantially increased energy content per unit volume over hydrocarbon fuels of the prior art.

Another object of this invention is to provide a process for producing a hydrocarbon fuel for jet engines having a heat of combustion of from 125,000 to 160,000 B.t.u.'s per gallon and more specifically from 136,000 to 150,000 B.t.u.'s per gallon. Another object of this invention is to provide a process for producing a hydrocarbon fuel having a pour point (ASTM D 97–34 M) below —40° C.

An additional object of this invention is to provide a process for producing a hydrocarbon fuel for jet engines having a specific gravity from 0.85 at 30° C. to 1.5 at 30° C., and preferably from 0.90 at 30° C. to 1.00 at 30° C.

A still further object is to provide a process for producing a hydrocarbon fuel having a heat of combustion of from 125,000 B.t.u.'s to 160,000 B.t.u.'s per gallon and a pour point below —40° C. from naphthenic and paraffinic hydrocarbons boiling in the gasoline and/or kerosene boiling range.

As pointed out in our copending application, Serial No. 316,312, filed October 22, 1952, now U. S. Patent 2,765,617, issued October 9, 1956, of which the present application is a continuation-in-part, present jet fuels have a heat of combustion of about 112,000 B.t.u.'s per gallon and a relatively high pour or crystallization point. They are prepared from petroleum hydrocarbons in the naphtha and kerosene boiling range and accordingly consist largely of paraffinic and naphthenic hydrocarbons.

We have now found that high energy fuel having an extremely low pour point can be prepared from naphthenic hydrocarbons or from mixtures of naphthenic and paaffinic hydrocarbons by subjecting such mixtures to a catalytic reforming process, preferably in the presence of a noble metal catalyst of the platinum group, separating monocyclic aromatic hydrocarbons from the resulting mixture, and then subjecting the resulting aromatic hydrocarbon mixture to deep thermal conversion at a temperature of at least 1100° F., whereby polycyclic hydrocarbons are formed, then hydrogenating said polycyclic hydrocarbons to a substantially complete saturation.

The naphthenic hydrocarbons or mixtures of naphthenic and paraffinic hydrocarbons employed are essentially cyclic hydrocarbons including methyl cyclopentane, cyclohexane and methyl cyclohexane in admixture with straight or slightly branched open chain compounds. Aromatic compounds such as benzene, toluene and the xylenes may be present in the starting material.

The starting materials for the present process comprises petroleum distillates, such as naphthas or gasoline fractions having an initial boiling point ranging from about 70° F. to 150° F. and an end boiling point ranging from 250° F. to about 425° F. Such fractions generally



comprise mixtures of naphthenic and paraffinic hydrocarbons.

In the reforming step the naphthenic hydrocarbons are dehydrogenated forming aromatic hydrocarbons and hydrogen, while the straight chain paraffins are hydrocracked and cyclicized and dehydrogenated likewise to aromatic hydrocarbons. The reforming step may be carried out with catalysts of known compositions. Generally suitable catalysts comprise alumina or silica or mixtures thereof formed by heat-treating suitable hydrous oxide gels, containing a minor percentage of platinum or palladium. Suitable catalysts contain from 0.01% to 1.5% platinum and are usually employed in the range of from 650° F. to 900° F. at pressures ranging from 150 to 800 pounds per square inch.

The hydrocracking reactions are those in which paraffin chains are severed, the reaction occurring in the presence of hydrogen. Cyclization occurs to some extent during this reaction. Generally, the catalyst is sufficiently selective so as to accomplish the desired cracking without the formation of excessive quantities of normally gaseous hydrocarbons such as methane, ethane and propane. It is necessary in order to obtain maximum selectivity to correlate the type of gasoline or naphtha fraction with the space velocity, temperature and pressure of the reaction. When this is done, it is possible to obtain good conversions of the essentially paraffinic hydrocarbons to cyclic compounds and eventually to aromatic hydrocarbons.

With certain catalysts and charge stocks it is possible to carry out the reforming operation simultaneously with the hydrocracking step. Generally, however, in order to obtain greater selectivity in these operations, it is desirable to carry out these processes separately, i.e., in separate reactors, whereby the precise conditions for maximum conversion can be maintained.

The drawing is a schematic flow diagram showing apparatus elements and flow of materials therethrough, suitable for the practice of some preferred embodiments of this invention.

In the drawing a crude petroleum oil is passed via line 11 into a fractionation system represented diagrammatically by the element 13. From such system, which will ordinarily be made up of a plurality of fractional distillation columns and associated equipment as is well-understood in the art, a gasoline fraction is obtained via line 15 and a fraction higher boiling than gasoline composed of heavy naphtha and/or kerosene is obtained via line 17. Light gases and liquefied petroleum gas can be removed as indicated by line 19, and the topped crude containing gas oil and heavier components is removed through line 21.

In one embodiment of our invention a full boiling range gasoline or a single selected cut thereof is introduced as by line 23 into a catalytic reforming operation of the nature described herein, represented by unit 25. A single cut rich in naphthenes can be subjected in unit 25 to simple naphthene dehydrogenation to form aromatic hydrocarbons. Part or all of the material characterized as heavy naphtha and/or kerosene can also be introduced to the catalytic reformer as by lines 27 and 29. Catalytic reforming unit 25 comprises one or more catalyst cases, into which there is also introduced a hydrogen-rich gas from line 31. Hydrocarbon charging stock and hydrogen are preheated by means not shown, to the desired reaction temperature.

A catalyst case (or cases) in reforming unit 25 contains a stationary bed of reforming catalyst, preferably one containing a small quantity of platinum or palladium supported on a synthetic silica-alumina gel having a comparatively low surface area, for example, 10 to 65 square meters per gram. This catalyst is mentioned here as an example of a suitable reforming catalyst, but

it will be understood from the discussion herein that a variety of reforming catalysts can be employed provided they at least effect dehydrogenation of naphthenes to aromatics, and preferably also effect dehydrocyclization of paraffins containing at least 6 carbon atoms per molecule to aromatics, dehydroisomerization of alkyl cyclopentanes to form aromatics and/or hydrocracking of heavy paraffins in the charge stock to lower molecular weight normally liquid paraffins, some of which in turn may undergo dehydrocyclization. It will be understood that one catalyst will not be the full equivalent of another, and that the extent of conversion of charging stock to aromatic hydrocarbons will be dependent not only on the catalyst chosen but also on the characteristics of the feed stock and the conversion conditions employed. While a stationary bed of catalyst is the simplest embodiment, other methods of contacting reactants with solid catalysts, e.g., in a "fluidized bed" or with a moving catalyst bed, can be used if desired.

Total effluent from reforming unit **25** passes through line **33** into separator **35**, first being cooled by means not shown. In separator **35** hydrogen-rich gas is separated as a gas phase and passed via lines **37** and **39** into a gas holder **41**. Hydrogen-rich gas from gas holder **41** is passed via lines **43** and **31** back to the reforming reaction being effected in unit **25**. Alternatively, part or all of the hydrogen for the reforming can be recycled directly from line **37** via lines **45** and **31**. Liquid is removed from separator or accumulator **35** through line **47** and passed to unit **49** wherein a separation is effected between aromatic hydrocarbons on the one hand and paraffinic hydrocarbons on the other hand. Usually essentially complete conversion of naphthenes to aromatics is effected in the catalytic reforming, but when substantial amounts of naphthenes are present in the liquid feed to separation uit **49**, that unit is preferably operated so that residual naphthenes are recovered in admixture with the paraffins.

In unit **49** can be employed any procedure known to the art for effecting aromatic-paraffin separation. For example, the liquid hydrocarbons recovered from the catalytic reforming operation can be contacted in liquid phase with a liquid solvent selective for aromatics. Alternatively, the liquid hydrocarbons can be subjected to extractive distillation whereby a paraffin-rich distillate is recovered and a liquid bottoms comprising aromatics dissolved in solvent is recovered, from which the aromatic hydrocarbons are then separated in known manner. Another alternative is to subject the liquid product of the catalytic reforming operation to contact with silica gel or other suitable adsorbent whereby aromatic hydrocarbons are adsorbed while paraffins pass through unadsorbed; the aromatic adsorbate is then desorbed by suitable means from the gel.

Numerous examples of each of these methods for separating aromatic hydrocarbons from paraffinic hydrocarbons are well-known in the art and hence need not be discussed in great detail here. Thus, for example, brief discussions of a silica gel adsorption process, and extractive distillation process, and a liquid-liquid solvent extraction process, are found in the Petroleum Refiner, vol. 30, No. 9, September 1951, at pages 227, 233, and 237, respectively.

In any event, a paraffin hydrocarbon product as free from aromatic hydrocarbons as economically feasible is recovered from separation unit **49** through line **51**, and a highly aromatic hydrocarbon product is recovered through line **53**. In the practice of our invention, it is not necessary that individual aromatic hydrocarbons produced in the catalytic reforming be separated one from the other as all can be recovered as a single stream of mixed aromatic hydrocarbons in line **53**. However, in some instances it will be preferred to separate benzene, toluene, xylene, etc., from each other and subject each to optimum conditions in the deep pyrolysis step now to be discussed.

Aromatic hydrocarbons from line **53**, mixed if desired with aromatic hydrocarbons from line **54** obtained by thermal or catalytic cracking of petroleum hydrocarbons including deep cracking of naphthas or of light hydrocarbon gases are obtained from coal tar, are heated by means not shown and subjected in unit **55** to a pyrolysis which is a non-catalytic deep thermal conversion at conditions including a temperature of at least 1100° F. and preferably at least 1400° F., resulting in the formation of polynuclear aromatic hydrocarbons, e.g., biphenyl, terphenyl and complex mixtures of polycyclic hydrocarbons, some of which may contain several benzene nuclei attached to and/or fused with each other and/or joined with each other by one or more methylene groups.

The conditions for obtaining good yields of polynuclear hydrocarbons will depend somewhat upon the particular stock which is subjected to said deep thermal conversion. The temperatures will range upwardly from 1100° F. to say 1550° F., the higher temperatures within this range being employed when the stock is predominantly benzene, while the lower temperatures within the range are employed when substituted benzenes such as toluene, the xylenes or the ethylbenzenes are present in appreciable amounts in the charging stock. The time of sojourn of the hydrocarbon vapor within the pyrolysis tube is maintained within the range from about 4 seconds to about 30 seconds, the operating sojourn being related to the temperatures of the vapor undergoing conversion in such a manner that the shorter times of sojourn are employed with the higher temperatures and vice versa.

While the chemical reactions occurring during the deep thermal conversion step are not completely understood, it is thought that the aromatic hydrocarbons undergo dehydrogenation followed by fusion of the aromatic residues.

The gaseous product of the deep thermal conversion operation consists largely of hydrogen together with minor amounts of hydrocarbons such as methane, ethane, ethylene, etc. It is desired, however, to keep the formation of such normally gaseous hydrocarbon products at a minimum by suitable control of temperature and sojourn time in the deep thermal conversion tube. By so doing, the loss of valuable hydrocarbons is prevented and formation of carbon held to a minimum. It should be recognized that some charging stocks are more susceptible to the deposition of carbon or coke deposition in the pyrolysis tube than are others. In the event that coke-like deposits are formed within the pyrolysis tube, they can usually be removed simply by interrupting the stream of hydrocarbon vapors and passing an oxidizing gas such as air through the tubes until the carbon deposits have been burned off.

Apparatus suitable for the deep thermal conversion operation herein described is generally known to those skilled in the art. It comprises a preheater section in which the hydrocarbon vapors are brought up to the conversion temperature, and then introduced into the pyrolysis tubes. The preheater and pyrolysis tubes are heated by gas or oil burners, provision being made to maintain the latter tubes at a substantially uniform temperature throughout their length. The preheater serves to heat the hydrocarbon vapor to the pyrolysis temperature without permitting any substantial amount of pyrolysis to occur therein. Indeed all of the heat necessary to convert the hydrocarbons may be added in the preheating section and only so much heat supplied to the pyrolysis section as to prevent normal heat losses. When the vapors have reached the desired conversion temperature in the preheater, they enter the pyrolysis section and are then maintained at this temperature for a required time in order to permit the desired amount of deep thermal conversion to take place. The vapors leaving the pyrolysis tube are

quickly cooled in order to stop any further reaction. Further cooling resulting in the production of a liquid condensate is then applied.

Total effluent from deep thermal conversion unit **55** is passed via line **57** and cooling means not shown into a separator **59** from which hydrogen is recovered overhead in line **61** and pyrolyzed liquid product is recovered in line **63**. Hydrogen in line **61** is preferably passed via line **64** into gas holder **41** for admixture with hydrogen recovered from the reforming step and for use in the reforming step and in the dehydrogenation step to be described hereinbelow. If desired, part or all of the hydrogen in line **61** can be passed via lines **66** and **67** to the hydrogenation step.

Liquid is passed from line **63** into still **65** in which a separation is made between lower boiling unconverted aromatic hydrocarbons which are passed via lines **68** and **53** back to deep thermal conversion unit **55**, and the polycyclic hydrocarbon mixture which is the product of the deep thermal conversion.

Polycyclic hydrocarbon mixture is recovered as bottoms through line **69** and passed to hydrogenation zone **71**. Also into hydrogenation zone **71** is passed hydrogen from gas holder **41** via lines **72** and **67**. This hydrogen can be derived in whole or in part from the hydrogen obtained by deep thermal conversion in unit **55** and hydrogen obtained by the dehydrogenation effected in reformer **25**. Such hydrogen is passed into hydrogenation unit **71** through line **67** having been compressed by known means not shown to an effective hydrogenation pressure, e.g., 250 to 1000 pounds per square inch. In unit **71** the polycyclic hydrocarbon mixture is catalytically hydrogenated using any known hydrogenation catalyst, for example, metallic nickel obtained by decomposition of nickel formate, nickel-copper oxide-alumina, copper chromate. Hydrogenation is effected at such temperature, time and hydrogen pressure as to effect preferably substantially complete hydrogenation of the polycyclic hydrocarbons. Less preferably the hydrogenation can be carried only part way to form a partially hydrogenated polycyclic hydrocarbon mixture. This is a nondestructive hydrogenation and essentially theoretical yields of hydrogenated liquid polycyclic hydrocarbons are obtained.

The partially, or preferably completely, hydrogenated polycyclic hydrocarbon mixture thus formed is separated from catalyst and hydrogen by known methods not shown and passed by line **73** into storage **75**. This product from line **73** constitutes a high energy content jet fuel product of the present invention. It can be used per se as jet fuel, or blended with other fuel components, preferably hydrocarbons, to form a blended jet fuel.

By way of example, a few combinations of petroleum hydrocarbon charging stocks and reforming conditions will be discussed. It will be appreciated that numerous variations can be used in the catalytic reforming within the broad scope of the invention. For example, a Mid-Continent light naphtha cut having an initial boiling point of 130° F., 30 percent over boiling temperature of 240° F. and end point of 350° F., and containing about 50 percent paraffins, 35 percent naphthenes and 15 percent aromatics, can be contacted at 850 to 950° F., 500 p.s.i.g., a weight space velocity (weight of charge per weight of catalyst per hour) of 2 to 4, and a hydrogen:naphtha mol ratio of 10:1, with a reforming catalyst composed of a steam treated synthetic silica-alumina having a surface area of 40 square meters per gram to which has been added about 0.5 weight percent platinum by impregnation of the steam-treated silica-alumina base with a solution of chloroplatinic acid followed by drying and reduction with hydrogen gas at an elevated temperature. The resulting reformate product is recovered almost without loss of volume and contains 50 weight percent aromatic hydrocarbons. As another example, a Mid-Continent straight run naphtha having a boiling range of 180° to 400° F. is reformed at 850° F., 500 p.s.i., a weight space velocity of 2, and a hydrogen:hydrocarbon mol ratio of 3:1, over a catalyst prepared by treating hydrous alumina with aqueous hydrogen fluoride, drying, pelleting, and then treating with chloroplatinic acid and ammonium hydroxide, followed by drying and calcining in air; the weight percent aromatic hydrocarbons in the product is 45 to 50 percent.

A less preferred but operable reforming catalyst is a synthetic chromia-alumina gel, preferably in bead form. For example, such catalysts can be used to reform a wide variety of straight run naphthas, at a pressure of 200 pounds per square inch gauge, a temperature of 950–1000° F., and a 3:1 to 5:1 mole ratio of recycled hydrogen rich gas to naphtha feed stock, to produce a reformed gasoline containing from 35 to 50 volume percent aromatic hydrocarbons. Maximum percentage aromatics in the product is obtained with naphthas boiling within the range of 200° F. to 300° F.

Another very effective type of reforming catalyst includes those whose principal active constituent is molybdena, the commonest form being molybdena-alumina. Temperatures of 850° F. to 1050° F. are suitable, and ordinarily hydrogen-rich gas is recycled.

The foregoing description of flow of materials relates to the treatment of a full range gasoline by catalytic reforming or single cut thereof by catalytic reforming or simple naphthene dehydrogenation. The remaining portion of the drawing now to be described illustrates additional and preferred embodiments of the invention.

While the paraffins separated from the catalytic reforming effluent by separating means **49** can be employed in any desired manner, it is preferred that this material be passed via line **51** and line **77** to distillation unit **79** wherein a separation is effected between the lighter paraffins recovered in line **81** and heavier paraffins recovered in line **83**. A cut-point between two fractions is chosen to give in the light fraction only those paraffins most susceptible to dehydroaromatization, which occurs on passing the light cut from line **81** via line **29** back to reforming unit **25**. The heavier paraffins can if desired also be returned by means not shown to reforming unit **25** for hydrocracking, but it is preferred that they be passed from line **83** into product storage tank **75** and blended therein with the hydrogenated polycyclic hydrocarbons to produce a blended jet fuel. In this manner that portion of the paraffins recovered from the catalytic reforming operation by means of separation unit **49**, lines **51** and **77**, still **79**, and line **83**, and which boil above, say, 250° F., are utilized as components of a final jet fuel blend.

A further feature of the invention involves passage of the heavy naphtha and/or kerosene recovered from still **13** via line **17**, to a solvent extraction unit **85** via line **87**. By well-known solvent extraction procedures a separation is effected between the paraffinic components on the one hand and the aromatic and naphthenic components on the other hand; this often may require a multi-stage separation treatment. The heavy paraffins are recovered via line **89** and if desired can be passed via lines **91** and **83** into storage unit **75**, becoming part of a final blended jet fuel product. Alternatively, part or all of the heavy paraffins can be passed from line **89** via line **29** to the catalytic reforming unit **25** for hydrocracking either in a single reforming operation or as a catalytic operation separate from naphthene dehydrogenation. Heavy aromatic and naphthenic hydrocarbons recovered by solvent extraction in unit **85** are passed via line **93** to still **65**, wheel in admixture with the liquid effluent of the deep thermal conversion step, monocyclic hydrocarbons are recovered as a lighter fraction and passed via line **68** to deep thermal cracking unit **55** while polycyclic hydrocarbons are recovered by line **69** and passed to hydrogenation unit **71**. By the described procedure of solvent extracting (in unit **85**) the material in the crude oil boiling above the gasoline boiling range, and then separating

the resulting aromatic-naphthenic extract by distillation (in unit 65), the polycyclic hydrocarbon content of this heavier fraction of the crude oil is recovered and directly utilized without the disadvantage of its being passed through catalytic reforming and/or hydrocracking procedures. Any heavy naphthene content of the extract passes unchanged through the hydrogenation reaction effected in unit 71.

More selective reactions can be obtained in the catalytic reforming step of our process by first subjecting the gasoline from line 15 to a treatment termed "super-fractionation" represented diagrammatically by element 92 which can be fractional distillation procedures aided if desired by azeotropic distillation, extractive distillation, and/or solvent extraction procedures of known character. Normal pentane is removed by line 94 as it does not undergo useful reactions in catalytic reforming. Branched chain paraffins containing 5, 6 and 7 carbon atoms per molecule are recovered in a plurality of fractions indicated diagrammatically by lines 95 and 97 and employed as aviation gasoline blending stocks. Normal hexane and heptane are recovered as by lines 99 and 101 and these stocks can be subjected to dehydroaromatization. This reaction can be effected in a general catalytic reforming or such conditions and catalysts optimum for dehydroaromatization can be applied to n-hexane and n-heptane, apart from the presence of other hydrocarbons. One or more fractions of low molecular weight naphthenic hydrocarbons containing at least 6 carbon atoms per molecule are obtained as via lines 103 and 105, and passed to a general catalytic reforming reaction or subjected to catalytic reforming conditions particularly adapted for and optimum for formation of aromatic hydrocarbons from these naphthenic hydrocarbons by dehydrogenation of cyclohexane rings and combined isomerization and dehydrogenation of alkyl cyclopentanes to form aromatic hydrocarbons. It is not feasible to attempt detailed segregation of components boiling above, say, 200° F. to 250° F., and therefore the heavier portion of the gasoline, boiling from temperatures in the neighborhood of 200° F. to 250° F. up to about 400° F., is recovered via line 107 and subjected to catalytic reforming in unit 25. It is thus apparent that one or more fractions of desired chemical and physical characteristics can be separated out from the gasoline material in order to obtain the most beneficial effects from the catalytic reforming, which reforming can be of the type wherein several different reactions occur concomitantly, or can be restricted to a straight-forward single reaction for the purpose of forming aromatic hydrocarbons and/or hydrocracking as the case may be a plurality of such single reactions often being effected simultaneously but in separate reactors.

While the invention has been described herein with particular reference to various preferred embodiments thereof, it will be appreciated that variations from the details given herein can be effected without departing from the invention in its broadest aspects.

We claim:

1. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a hydrocarbon stock of relatively high naphthene content to catalytic reforming, whereby contained naphthenes are substantially dehydrogenated and isomerized to aromatics, separating monocyclic aromatic hydrocarbons from the resulting product, subjecting said monocyclic aromatic hydrocarbons to non-catalytic deep thermal conversion at conditions including a temperature of at least 1100° F. resulting in the formation of higher boiling polycyclic aromatic hydrocarbons, and hydrogenating said polycyclic aromatic hydrocarbons to substantially complete saturation thereby forming a high energy fuel product higher boiling than the initial feed to the process.

2. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a hydrocarbon stock of relatively high naphthene content to catalytic dehydrogenation, whereby contained naphthenes are substantially dehydrogenated to aromatics, separating monocyclic aromatic hydrocarbons from resulting product, subjecting said monocyclic aromatic hydrocarbons to non-catalytic deep thermal conversion at conditions including a temperature of at least 1100° F. resulting in the formation of higher boiling polycyclic aromatic hydrocarbons, and hydrogenating said polycyclic aromatic hydrocarbons to from partial to substantially complete saturation thereby forming a high energy fuel product higher boiling than the initial feed to the process.

3. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a petroleum naphtha of relatively high naphthene content to catalytic reforming in the presence of hydrogen and in the presence of a platinum-containing catalyst whereby contained naphthenes are substantially dehydrogenated and isomerized to aromatics and contained paraffins are dehydroaromatized, under conditions effecting a net production of hydrogen, separating monocyclic aromatic hydrocarbons from the resulting product, subjecting said monocyclic aromatic hydrocarbons to non-catalytic deep thermal conversion at conditions including a temperature of at least 1100° F. resulting in the formation of higher boiling polycyclic aromatic hydrocarbons, and hydrogenating said polycyclic aromatic hydrocarbons to substantially complete saturation with hydrogen derived from said deep thermal conversion and from said catalytic reforming thereby forming a high energy fuel product higher boiling than the initial feed to the process.

4. The process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a petroleum naphtha containing naphthene hydrocarbons and paraffin hydrocarbons to catalytic reforming under conditions effecting dehydrogenation of cyclohexane naphthenes to aromatics, dehydroisomerization of alkyl cyclopentane naphthenes to aromatics, hydrocracking of high-boiling paraffins to lower-boiling normally liquid paraffins, and dehydroaromatizing paraffins to aromatics, separating monocyclic aromatic hydrocarbons from the resulting product, subjecting said monocyclic aromatic hydrocarbons to non-catalytic deep thermal conversion at conditions resulting in the formation of higher boiling polycyclic aromatic hydrocarbons therefrom, and catalytically hydrogenating said polycyclic aromatic hydrocarbons to produce a high energy fuel having a heat of combustion of from 125,000 to 160,000 B.t.u.'s per gallon and higher boiling than the initial feed to the process.

5. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a hydrocarbon stock of relatively high naphthene content to catalytic reforming in the presence of hydrogen, whereby contained naphthenes are substantially dehydrogenated and isomerized to aromatics and a net production of hydrogen is effected, separating monocyclic aromatic hydrocarbons from the resulting product, subjecting said monocyclic aromatic hydrocarbons to non-catalytic deep thermal conversion at conditions resulting in the formation of higher boiling polycyclic aromatic hydrocarbons and hydrogen, said hydrogen for catalytic reforming being obtained from both said net production of hydrogen therein and said deep thermal conversion, and hydrogenating said polycyclic aromatic hydrocarbons to from partial to complete saturation to form said high energy fuel product higher boiling than the initial feed to the process.

6. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a hydrocarbon stock of relatively high naphthene content to catalytic reforming in the presence of hydrogen, whereby contained naphthenes are substantially

dehydrogenated and isomerized to aromatics and a net production of hydrogen is effected, separating monocyclic aromatic hydrocarbons from the resulting product, subjecting said monocyclic aromatic hydrocarbons to non-catalytic deep thermal conversion at conditions resulting in the formation of higher boiling polycyclic aromatic hydrocarbons and hydrogen, said hydrogen for catalytic reforming being obtained both from said net production of hydrogen therein and said deep thermal conversion, and hydrogenating said polycyclic aromatic hydrocarbons with hydrogen derived from said net hydrogen production in said catalytic reforming and from said deep thermal conversion to from partial to complete saturation to form said high energy fuel product higher boiling than the initial feed to the process.

7. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a hydrocarbon stock of relatively high naphthene content to catalytic reforming whereby contained naphthenes are substantially dehydrogenated and isomerized to aromatics, separating resulting product into a monocyclic aromatic hydrocarbon rich portion and a paraffinic hydrocarbon rich portion, subjecting the former to non-catalytic deep thermal conversion at conditions including a temperature of at least 1100° F. resulting in the formation of higher boiling polycyclic aromatic hydrocarbons, hydrogenating said polycyclic aromatic hydrocarbons to from partial to substantially complete saturation thereby forming a high energy fuel product higher boiling than the initial feed to the process, and blending same with at least part of said paraffinic hydrocarbon rich portion to produce a blended high energy jet fuel.

8. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a hydrocarbon stock of relatively high naphthene content to catalytic reforming whereby contained naphthenes are substantially dehydrogenated and isomerized to aromatics, separating resulting product into a monocyclic aromatic hydrocarbon rich portion and a paraffinic hydrocarbon rich portion, subjecting the former to non-catalytic deep thermal conversion at conditions including a temperature of at least 1100° F. resulting in the formation of higher boiling polycyclic aromatic hydrocarbons, hydrogenating said polycyclic aromatic hydrocarbons to from partial to substantially complete saturation thereby forming a high energy fuel product higher boiling than the initial feed to the process, separating said paraffinic hydrocarbon rich portion into a lower boiling cut and a higher boiling cut, returning said lower boiling cut to said catalytic reforming, and blending said higher boiling cut with said high energy fuel product resulting from said hydrogenation to form a blended high energy jet fuel.

9. A process for producing a high boiling hydrogenated polycyclic hydrocarbon high energy fuel which comprises subjecting a gasoline boiling range hydrocarbon stock of relatively high naphthene content to catalytic reforming whereby contained naphthenes are substantially dehydrogenated and isomerized to aromatics, separating monocyclic aromatic hydrocarbons from the resulting product, subjecting said monocyclic aromatic hydrocarbons to non-catalytic deep thermal conversion at conditions including a temperature of at least 1100° F. resulting in the formation of higher boiling polycyclic aromatic hydrocarbons, subjecting effluent from said deep thermal conversion to distillation to separate monocyclic hydrocarbons from polycyclic hydrocarbons, subjecting a hydrocarbon stock higher boiling than said gasoline range stock and derived from the same source material to solvent extraction and thereby obtaining an extract comprising heavy aromatic and naphthenic hydrocarbons, introducing said extract into said distillation, passing monocyclic hydrocarbons obtained from said distillation to said deep thermal conversion step, and subjecting polycyclic hydrocarbons obtained from said distillation to hydrogenation to form a high energy fuel product higher boiling than the initial feed to the process.

10. A process according to claim 9, wherein a raffinate comprising heavy paraffinic hydrocarbons obtained by said solvent extraction is passed to said catalytic reforming.

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