

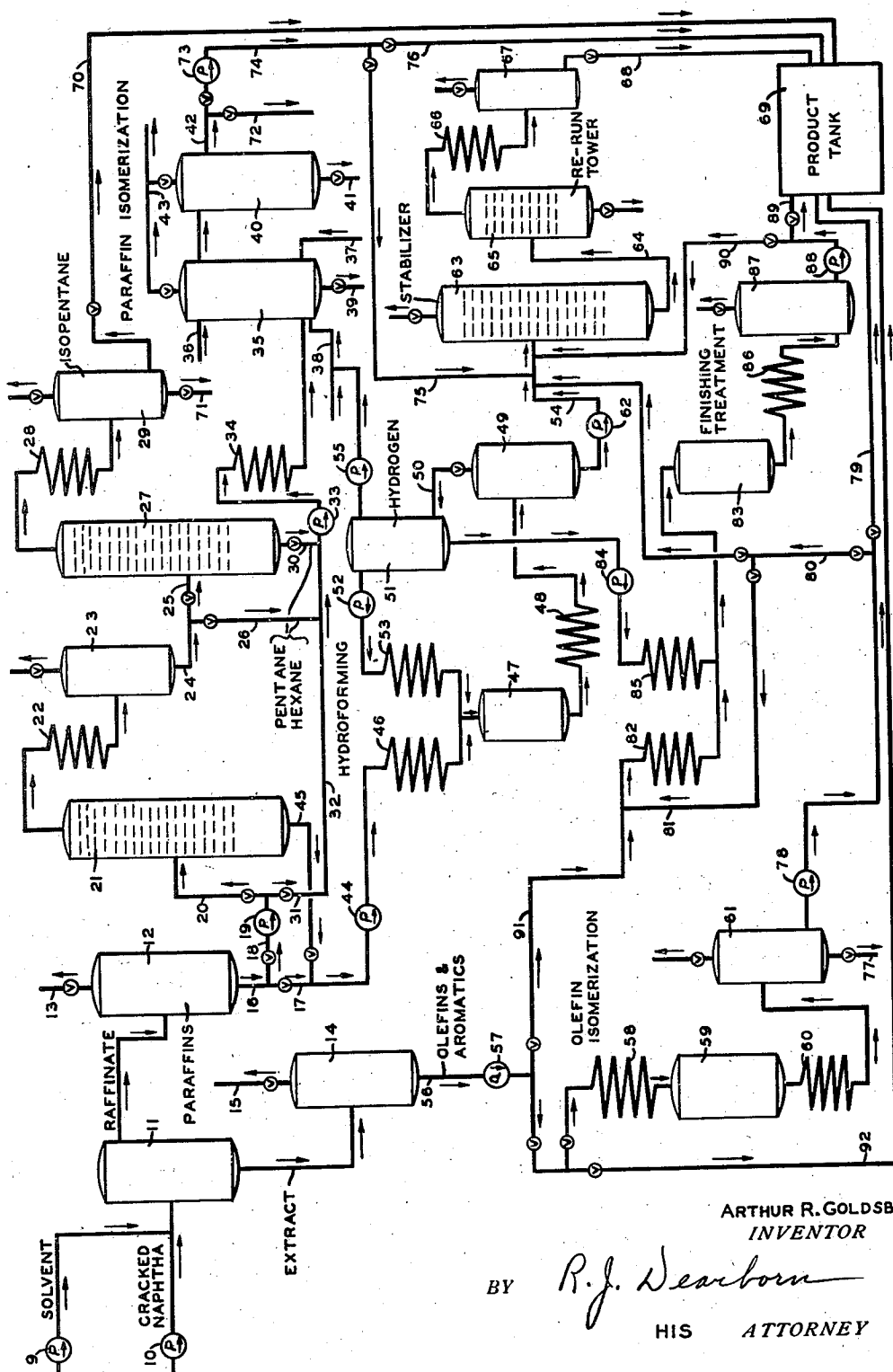
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MANUFACTURE OF MOTOR FUELS

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MANUFACTURE OF MOTOR FUELS

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This invention relates to the treatment of cracked naphtha for the production of high grade motor fuel of high antiknock quality.

The gasoline product produced in commercial thermal cracking processes does not ordinarily have an octane value in excess of about 70-72 A. S. T. M. and considerable quantities of cracked gasoline produced in the thermal cracking processes, particularly the cracked gasolines produced in viscosity breaking and coking operations, have antiknock values below 70 octane. My invention contemplates the treatment of such cracked naphthas to produce high yields of products having octane values of the order of 80-90 and to produce motor fuel products adapted for aviation motor fuel.

In accordance with the invention the cracked gasoline is treated with a selective solvent to separate paraffins from olefins, the paraffinic fraction is subjected to thermal or catalytic reforming or to hydroforming or paraffin isomerization and the olefinic fraction is subjected to olefin isomerization or isoforming.

In a preferred embodiment of the invention the paraffinic fraction, obtained in the solvent treatment of the cracked naphtha, is subjected to fractionation to separate lower boiling or intermediate fractions rich in normal hydrocarbons, such as pentane and hexane, from higher boiling hydrocarbons. The lower boiling or intermediate paraffinic fractions are subjected to catalytic isomerization while the higher boiling paraffinic fractions are subjected to thermal or catalytic reforming or hydroforming, and the olefinic fractions, obtained in the solvent treatment, are subjected to catalytic isomerization.

In aviation motor fuel it is desirable that the fuel contain relatively minor proportions of olefin hydrocarbons and the invention contemplates a special method of treating the olefinic fractions to reduce the olefin content thereof and increase susceptibility to tetraethyl lead. In accordance with the invention the cracked naphtha is treated with a selective solvent to obtain a raffinate fraction comprising paraffin hydrocarbons and an extract fraction comprising olefin and aromatic hydrocarbons. The entire paraffinic fraction is subjected to a conversion or reforming treatment to raise the antiknock quality thereof, or is subjected to fractionation to obtain a lower boiling or intermediate fraction and a higher boiling fraction, and the lower boiling or intermediate fraction is subjected to a treatment to effect isomerization of normal paraffin hydrocarbons, while the higher boiling fraction is subjected to reform-

ing or hydroforming to raise the antiknock quality thereof. The olefin-aromatic fraction, obtained in the solvent treatment, may be subjected to a two-stage treatment, in the first of which the fraction is subjected to treatment to effect isomerization of olefins and in the second of which the products from the first stage are subjected to a finishing treatment to effect conversion of olefins to isoparaffins and to increase the lead susceptibility, or the olefin-aromatic fraction may be subjected to a single-stage treatment in which it is subjected to treatment to effect both an isomerization of olefins and a conversion of olefins to isoparaffins and to effect reactions causing an increase in lead susceptibility.

The invention will be understood from the following description thereof, reference being had to the accompanying drawing which is a flow diagram illustrating a particular embodiment of the invention.

Referring to the drawing, cracked naphtha is directed by a pump 10 to a treating vessel 11 into which is introduced a selective solvent by a pump 9. Such solvents as sulfur dioxide, mixtures of sulfur dioxide and methyl alcohol, benzyl alcohol, or diacetone alcohol or phenol and mixtures of phenol and cresol are recommended as solvents to be used. The solvent treatment is ordinarily carried on in the liquid phase with sulfur dioxide at temperatures of 10° F. to -60° F. The solvent treatment produces a raffinate fraction comprising paraffins and an extract fraction comprising olefins and aromatics. The raffinate fraction is collected in a vessel 12 from which the solvent may be distilled off through a line 13 and the extract fraction is collected in a vessel 14 from which the solvent may be distilled off through a line 15. In using the phenol-cresol solvent the naphtha is introduced as a vapor into the liquid solvent and an extractive distillation is carried on, the paraffins being removed as a vapor and the olefins and aromatics remaining in the liquid.

The raffinate or paraffinic fraction is withdrawn from the vessel 12 through a line 16 having branch lines 17 and 18. Describing the operation when passing the paraffinic fraction through the line 18, this fraction is directed by a pump 19 through a line 20 to a fractionating tower 21 wherein fractionation takes place to separate from higher boiling constituents, a lower boiling paraffinic fraction containing the paraffin hydrocarbons which are especially susceptible to treatment for catalytic isomerization. This low boiling fraction will ordinarily have an

end point of 160-170° F. so as to include the pentanes and hexanes which are well adapted for the isomerization treatment. The low boiling fraction taken off as a vapor from the tower 21 is condensed in the condenser 22 and collected as a distillate in the receiver 23. The pentane-hexane fraction is withdrawn through a line 24 and directed through either of branch lines 25 and 26. When the cracked gasoline contains a material quantity of isopentane it is desirable to remove the isopentane from the stock which is to be subjected to isomerization and for this purpose the pentane-hexane fraction is directed through the line 25 to a fractionator 27 from which the isopentane, together with any lighter fractions, is taken overhead to a condenser 28, thence to a receiving drum 29. The pentane-hexane fraction is withdrawn from tower 27 through a line 30. When it is not desired to fractionate the paraffinic fraction, obtained in the solvent treatment of the cracked naphtha, this fraction withdrawn through lines 18, 19 and 20 is directed through a branch line 31 for the isomerization treatment. The lines 31, 26 and 30 communicate with a manifold line 32 so that either the entire paraffinic fraction obtained in the solvent treatment of the cracked naphtha or the entire light fraction obtained in fractionating the solvent treated paraffinic product or the pentane-hexane fraction from which the isopentane has been removed may be utilized as the charge to the isomerization operation.

A pump 33 withdraws the paraffinic fractions through line 32, from either of the lines 31, 26 and 30, and directs the hydrocarbons through a heating coil 34 thence to a contact or treating vessel 35. The catalyst employed therein comprises anhydrous metallic halides, particularly the chlorides and bromides of aluminum, usually with small amounts of hydrogen halides such as hydrogen chloride as a promoter. Aluminum chloride is the catalyst recommended. This catalyst is preferably used in the form of an aluminum chloride hydrocarbon complex and may be directed to the treating vessel 35 through a line 36 while the hydrocarbons are introduced to the lower portion of the vessel and are caused to bubble up through the liquid complex. The operation is improved by the addition of hydrogen chloride, introduced through line 37, as well as hydrogen, introduced through line 38, under superatmospheric pressures such as about 150-1000 lbs. The reaction is carried on at temperatures of about 150° F.-300° F. Complex may be withdrawn from time to time from the chamber through a line 39 and fresh aluminum chloride may be added to maintain catalyst activity. The treated hydrocarbons overflow to a settling vessel 40 from which any catalyst present may be withdrawn through a line 41 while the isomerizate is withdrawn through a line 42. Gases may be withdrawn through a gas release line 43.

In lieu of subjecting the paraffinic fraction or pentane-hexane fractions thereof to catalytic isomerization the entire paraffinic fraction obtained in the solvent treatment or the higher boiling constituents of such fraction may be subjected to thermal or catalytic reforming or hydroforming. For this purpose the line 17 extends to a pump 44 and a line 45 conducts higher boiling constituents of the paraffinic fraction from the fractionating tower 21 to the line 17. Thus either the entire paraffinic fraction from vessel 12 or higher boiling constituents thereof from fractionator 21 may be directed by the pump 44

through a heating coil 46 thence to a reaction chamber 47 wherein the hydrocarbons are subjected to either thermal or catalytic reforming or to hydroforming. In the thermal reforming operation the gasoline fractions are subjected to temperatures upwards of 850° F., preferably temperatures of the order of 900° F. or 1000° F., under pressures usually within a range of about 200 lbs. to 800 lbs. In the catalytic reforming operation the paraffinic constituents are subjected to temperatures of about 850-1000° F. under pressures of about 50-300 lbs. in the presence of catalysts such as bauxite or clays. In the hydroforming operation the paraffinic hydrocarbons are subjected to reaction temperatures in the presence of hydrogen and a suitable catalyst to effect reactions involving conversion of paraffinic hydrocarbons to aromatic hydrocarbons. The catalysts which are particularly recommended for hydroforming are molybdena-alumina catalysts and chrome-alumina catalysts. Temperatures of the order of 900° F. or 1000° F. under pressures of the order of 200-300 lbs. are quite satisfactory for effecting the desired conversion into higher antiknock hydrocarbons. The products of reaction pass from the reaction chamber 47 through a cooler 48 thence to an accumulating drum 49 from which the lighter gases, more particularly, the hydrogen and methane, may be withdrawn through a line 50 to a hydrogen accumulator 51. A pump 52 directs the hydrogen-containing gases to a heating coil 53 wherein the hydrogen-containing gases are preheated to approximately reaction temperatures before being combined with the heated paraffinic hydrocarbons passing from the heating coil 43 and the combined products are subjected to reaction temperatures in the presence of the molybdena-alumina or chrome-alumina catalyst in the reaction chamber 47. The reformate or hydroformate is withdrawn from the accumulator 49 through a line 54.

In the hydroforming operation an excess of hydrogen is produced over that required for recycling to the hydroforming zone and in accordance with the invention hydrogen containing gases may be withdrawn from the accumulator 51 and directed by a pump 55 to the hydrogen line 38 for introduction to the paraffin isomerization zone. Normally, sufficient hydrogen is produced in the hydroforming operation to provide the hydrogen necessary for the paraffin isomerization operation, as well as for the finishing treatment which is described hereinafter.

Referring now to the treatment of the extract fraction, obtained in the solvent treating of the cracked naphtha, this fraction, which comprises predominantly olefinic and aromatic hydrocarbons, is withdrawn from the chamber 14 through a line 56 and is directed by a pump 57 through a heating coil 58 thence to a reaction chamber 59 wherein the olefinic hydrocarbons are subjected to isomerization or isoforming to effect a conversion of olefin hydrocarbons into isomers thereof. The catalyst adapted for this isomerization operation consists advantageously of a synthetic silica-alumina type of catalyst, clay catalysts and the like. The catalyst may either be disposed as a stationary bed or fixed mass through which the hydrocarbon vapors pass or it may be used as a powder in which case the hydrocarbon vapors are contacted with a stream of the powdered catalyst. Temperatures of the order of 800° F. or 900° F. to 1000° F. with high space velocity and under

moderate superatmospheric pressures preferably under 100 p. s. i. are employed. The lower temperatures have the advantage of effecting the isomerization of the olefins with a minimum of cracking and polymer formation. The products of reaction pass from the catalyst chamber 59 through a cooler 60 thence to an accumulator or gas separator 61. The liquid product collected in the accumulator 61 consists largely of isomerized olefins together with the aromatics contained in the charge to the isomerization unit.

The reformate or hydroformate produced in the thermal or catalytic reforming or hydroforming operation will ordinarily require some fractionation to remove polymer products of higher boiling point than desired for the gasoline or motor fuel product and also to remove normally gaseous hydrocarbons. For this purpose the reformate or hydroformate withdrawn from the accumulator 49 through line 54 is directed by a pump 62 to a rectifying tower 63 wherein the hydrocarbons are subjected to rectification to produce a liquid product of desired vapor pressure. This liquid product may then be directed through a line 64 to a re-run still 65 for the removal of any constituents of higher boiling point than desired for the gasoline product. The liquid product is redistilled in the tower 65, the desired gasoline constituents being taken off as a vapor, condensed in a condenser coil 66 and collected in a distillate accumulator 67. The distillate is passed from the accumulator through a line 68 to a product tank 69.

The isopentane fraction collected in accumulator 29 will ordinarily have an A. S. T. M. octane number approximating 90 and this fraction may be passed directly through a line 70 to the product tank to be blended with the products therein, or withdrawn through a branch line 71 for other blending purposes.

The isomerizate produced in the isomerization of the paraffinic hydrocarbons, flowing through line 42, may be withdrawn through a branch line 72 or directed by pump 73 through a line 74 thence either through branch line 75 to the stabilizer 63 or through branch line 76 directly to the product tank.

The isomerizate collected in the accumulator 61 may be withdrawn through a line 77 or directed by a pump 78 through a line 79 to the product tank 69. In case it is desired to fractionate or stabilize the isomerizate it may be directed through the branch line 80 to the stabilizer 63.

When the isomerizate product collected in the tank 61 is to be used for aviation gasoline it sometimes is desirable to treat this product for the purpose of reducing the olefin content and increasing susceptibility to tetraethyl lead. In a preferred embodiment of the invention the isomerizate is subjected to a finishing treatment capable of effecting a conversion of olefins into isoparaffins and of effecting an increase in lead susceptibility. By subjecting the isomerizate at elevated temperatures to contact with a solid adsorbent cracking or hydroforming catalyst, such as the synthetic silica-alumina catalysts, adsorbent clays and the like, in the presence of hydrogen-containing gases, olefin hydrocarbons are converted into isoparaffins and the reduction in olefin content of the product increases the lead susceptibility thereof. For the purpose of giving the isomerizate this finishing treatment the product collected in tank 61 may be directed by the pump 78 and line 80 through a branch line 81 thence through a

heating coil 82 to a reaction chamber 83 containing the catalytic material. The hydrocarbons are subjected to temperatures within a range of about 600° F.-950° F. under pressures of the order of 100-300 pounds in the presence of the catalyst. Hydrogen containing gas is drawn from the tank 51 and is directed by a pump 84 through a heating coil 85 wherein the gas is heated to approximately the temperature of reaction and is delivered thence into the reaction chamber 83. The reaction products pass through a cooler 86 to an accumulator or gas separator 87 from which the hydrogen containing gases may be recycled to the heating coil 85, while any excess of such gases may be returned to the hydrogen tank 51. The liquid product is directed by a pump 88 either through branch line 89 to the product tank 69 or through branch line 90 to the stabilizer 63.

In a modification of the invention the extract fraction withdrawn from tank 14, instead of being passed to the olefin isomerization step (coil 58 and reaction chamber 59), is directed through a line 91 to the heating coil 82 and reaction chamber 83 for the finishing treatment which has just been described, the extract fraction being subjected to the conditions of temperature and treatment in the presence of the catalyst and in the presence of hydrogen in the manner described in the preceding paragraph to accomplish conversion of olefins into isoparaffins and to effect an increase in lead susceptibility. In this modification it is advantageous to use cracking catalysts, such as the silica-alumina catalysts, so as to effect in a common reaction zone both an isomerization of olefins and a conversion of olefins to isoparaffins to obtain a product of high octane number and of increased lead susceptibility. In another modification of the invention the olefin-aromatic fraction withdrawn from tank 14 through line 56 is passed through a branch line 92 directly to the product tank 69 to be used in blending with the products obtained in the paraffin isomerization and hydroforming operations. In another modification of the invention the olefin aromatic fraction is treated with a selective solvent for aromatics such as water so as to separate this fraction into an olefin fraction and an aromatic fraction and in this case the olefin fraction is passed to either the olefin isomerization operation or to the finishing treatment or to the olefin isomerization operation and finishing treatment in succession, while the aromatic fraction is blended with the final product in the product tank.

In a specific example of the invention a cracked gasoline stock of 400° F. end point obtained from the thermal cracking of gas oil and having an A. S. T. M. octane number of 70 is treated with sulfur dioxide to produce a raffinate fraction constituting 60% of the gasoline stock and having an octane number of 58 and an extract fraction constituting 40% of the gasoline stock and having an octane number of 85. The raffinate or paraffinic fraction is fractionated to produce the following fractions:

	Per cent
Isopentane cut—90 octane number.....	2.5
Pentane-hexane cut—68 octane number.....	17.5
Higher boiling fraction.....	80.0

The normal pentane-hexane cut is subjected to catalytic isomerization in contact with aluminum chloride hydrocarbon complex together with added free aluminum chloride to produce a product yield, based on the charge to the isomerization

unit, of 98% of 80 octane number, or a yield of 10.3% based on the original cracked gasoline charge. The high boiling fraction is subjected to hydroforming in the presence of a molybdena-alumina catalyst with recycling of hydrogen to produce a product yield, based on the charge to the hydroforming unit, of 80% of 80 octane number, or a yield of 38.4% based on the cracked gasoline charge. The extract fraction obtained in the solvent treatment containing olefin and aromatic hydrocarbons is subjected to olefin isomerization in contact with a synthetic silica-alumina catalyst to produce a product yield, based on the charge to the olefin isomerization unit, of 97% having an octane number of 88, or a yield of 38.8% based on the cracked gasoline charge. In blending the isopentane cut (constituting 1.5% of the cracked gasoline charge) with the hydroformate and the isomerizates from the olefin and paraffin isomerizing operations, a yield of gasoline amounting to 89% of the original cracked gasoline charging stock is produced having an octane number of 84. The yield in the complete process, based on the cracked naphtha charge, may be tabulated as follows:

	Per cent
Isopentane	1.5
Paraffinic isomerizate.....	10.3
Hydroformate	38.4
Olefinic isomerizate	38.8
Total product.....	89.0

In a second example of the invention, the process is conducted in accordance with the example just described, except that instead of subjecting the extract fraction, collected in tank 14, to isomerizing or isomerization this fraction is subjected directly to a finishing treatment at a temperature of 600° F. under 300 lbs. pressure in contact with a molybdena-alumina catalyst in the presence of hydrogen, or at temperatures of 800° F.-950° F. under about 100 lbs. pressure in contact with a synthetic silica-alumina cracking catalyst in the presence of hydrogen. In either of these operations a gasoline product of 84 octane number is produced in a quantity amounting to 95% of the charge to the finishing operation or 38% based on the original cracked gasoline charge, with the result that in the complete process the gasoline yields are as follows:

	Per cent
Isopentane	1.5
Paraffinic isomerizate.....	10.3
Hydroformate	38.4
Gasoline from finishing operation.....	38.0
Total.....	88.2

The total gasoline product constituting 88.2% of the cracked gasoline charge has an octane number of 82. This product is better suited for aviation gasoline stock than that of the first example due to the lower olefin content. It may be led to values closely approaching 100 octane and by blending with small proportions of straight run gasoline or with alkylate from a sulfuric acid alkylation process may readily be led to values even above 100 octane. The technical advantage of the process may be seen by comparing it with ordinary reforming. In thermal reforming an octane number of about 75-76 is about the limit obtainable in a commercial operation and to produce a product of that octane value a yield loss of about 15% and even higher is necessary and, moreover, the product is not adapted for aviation

stock on account of the relatively high olefin content.

In a third example of the invention the process is conducted in the same manner as in the first example, except that the extract fraction instead of being given a catalytic treatment is blended directly with the final product and the high boiling fraction of the paraffinic raffinate instead of being subjected to hydroforming is subjected to thermal reforming at temperatures of 950° F.-1000° F. under 200 lbs. pressure to produce a gasoline product of 72 octane number amounting in quantity to 85% of the charge to the thermal reforming operation or 40.8% based on the original cracked gasoline charging stock, the yields of the complete process being as follows:

	Percent
Isopentane	1.5
Paraffinic isomerizate.....	10.3
Olefinic aromatic extract.....	40.0
Thermally reformed gasoline.....	40.8
Total.....	92.6

The composite gasoline product has an octane number of 79.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, but only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of treating cracked naphtha stocks consisting essentially of olefin and aromatic hydrocarbons to produce an improved blending stock adapted as a component of aviation gasoline that comprises contacting the olefin-aromatic naphtha with a solid catalytic material, selected from the group consisting of silica-alumina and adsorptive clays, at a temperature within a range of about 800° F.-1000° F. and under a relatively low pressure of under 100 pounds to effect isomerization of olefin hydrocarbons and contacting resultant products of reaction with a solid catalytic material, selected from the group consisting of silica-alumina and adsorptive clays, in the presence of hydrogen while at a temperature within a range of about 600° F.-950° F. and under a pressure of the order of 100-300 pounds to effect conversion of olefins to isoparaffins and produce a naphtha product rich in aromatic hydrocarbons and of high lead susceptibility.

2. The method of treating cracked naphtha stocks consisting essentially of olefin and aromatic hydrocarbons to produce an improved blending stock adapted as a component of aviation gasoline that comprises contacting the olefin-aromatic naphtha with a silica-alumina catalyst at a temperature within a range of about 800° F.-1000° F. and under a relatively low pressure of under 100 pounds to effect isomerization of olefin hydrocarbons and contacting resultant products of reaction with a catalyst composed of silica-alumina in the presence of hydrogen while at a temperature within a range of about 600° F.-950° F. and under a pressure of the order of 100-300 pounds to effect conversion of olefins to isoparaffins and produce a naphtha product rich in aromatic hydrocarbons and of high lead susceptibility.

3. The method of treating cracked naphtha stocks to produce an improved blending stock adapted as a component of aviation gasoline that

comprises treating the cracked naphtha with a selective solvent for olefins and aromatics to separate paraffin hydrocarbons from an extract fraction rich in olefin and aromatic hydrocarbons, treating said extract fraction with a solid catalytic material, selected from the group consisting of silica-alumina and adsorptive clays, at a temperature within a range of about 800° F.-1000° F. and under a relatively low pressure of under 100 pounds to effect isomerization of olefin hydrocarbons and contacting resultant prod-

ucts of reaction with a solid catalytic material, selected from the group consisting of silica-alumina and adsorptive clays, in the presence of hydrogen while at a temperature within a range of about 600° F.-950° F. and under a pressure of the order of 100-300 pounds to effect conversion of olefins to isoparaffins and produce a naphtha product rich in aromatic hydrocarbons and of high lead susceptibility.

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