

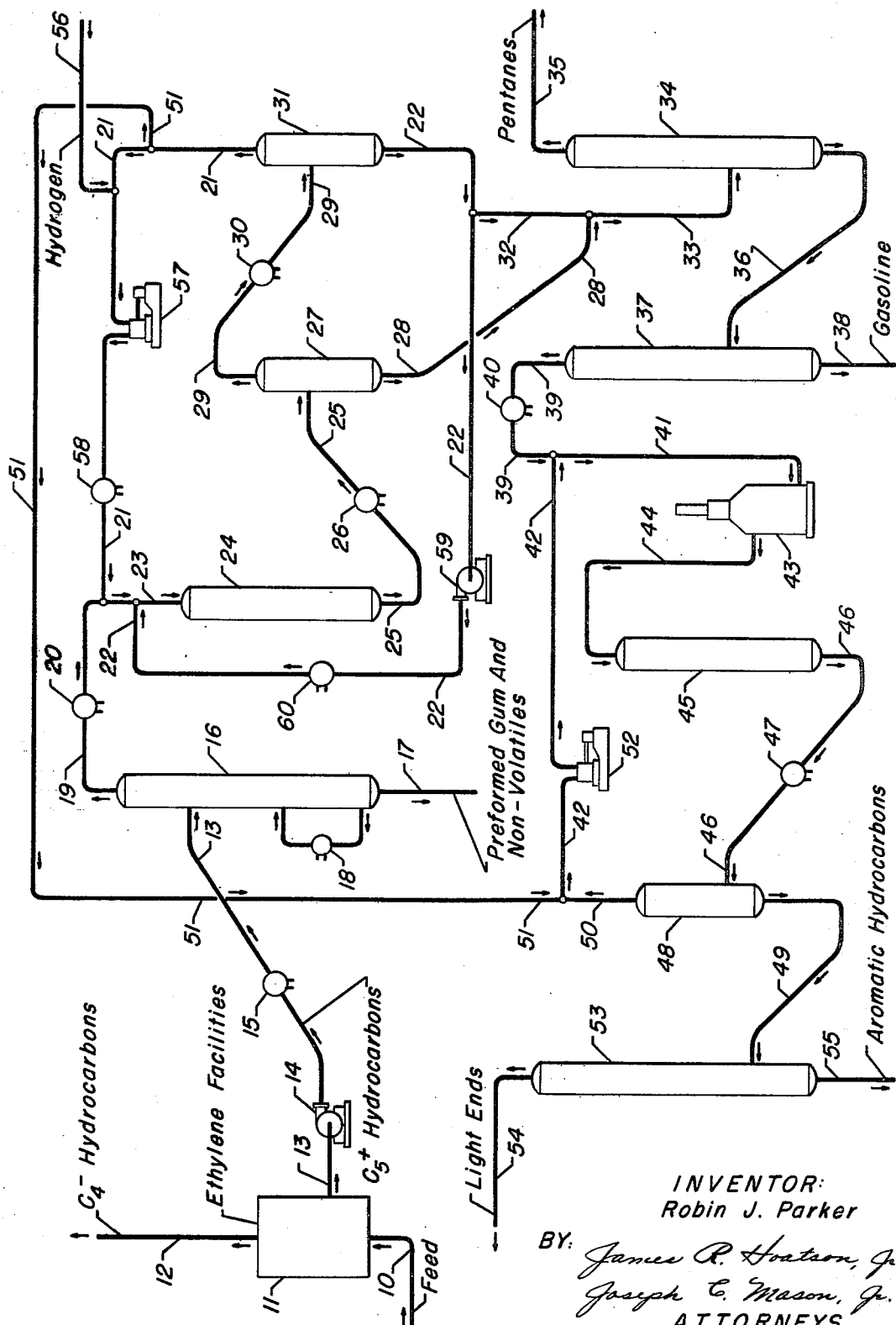
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TWO-STAGE HYDROGENATION OF AN AROMATIC HYDROCARBON FEEDSTOCK
CONTAINING DIOLEFINS, MONOOLEFINS AND SULFUR COMPOUNDS

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TWO-STAGE HYDROGENATION OF AN AROMATIC HYDROCARBON FEEDSTOCK CONTAINING DIOLEFINS, MONOOLEFINS AND SULFUR COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

An aromatic hydrocarbon feedstock containing diolefins, monoolefins and sulfur contaminants is hydro-generated at a relatively low temperature of 200–500° F. with a composite catalyst of lithium in palladium-alumina to convert the diolefins to monoolefins. The effluent is separated and an aromatic hydrocarbon is then hydrogenated at a relatively high temperature of 550–750° F. with a conventional desulfurization catalyst to saturate olefins and convert sulfur compounds to hydrogen sulfide. Hydrocarbons suitable for gasoline blending and aromatic hydrocarbons suitable for, say, solvent extraction are recovered as separate product streams. The method finds particular utility in stabilizing pyrolysis gasoline.

BACKGROUND OF THE INVENTION

This invention relates to the hydrogenation of hydrocarbons. It particularly relates to the stabilization of pyrolysis gasoline. If specifically relates to a method for selectively removing diolefins and olefins from the product gasoline obtained in light olefin manufacture.

It is known in the art that one of the commercially attractive routes to the production of valuable normally gaseous olefinic hydrocarbons such as ethylene, propylene, etc. is the thermal cracking or pyrolysis of hydrocarbons such as the light paraffin hydrocarbons and/or naphtha fractions obtained from petroleum. Usually, the pyrolysis reaction is effected in the substantial absence of a catalyst at high temperatures often in the presence of a diluent such as superheated steam utilizing a tubular reactor or a plurality of cracking furnace coils. Depending upon the charge stock and specific pyrolysis operating conditions employed, the effluent from the cracking zone may comprise light olefinic hydrocarbons such as ethylene, propylene, butylene, etc. or mixtures thereof, all of which may constitute the principal product or products. In addition to these light olefinic gases there is also produced a significant quantity of pyrolysis gasoline which contains undesirable quantities of diolefin hydrocarbons and/or sulfur compounds. The pyrolysis gasoline frequently is rich in aromatic hydrocarbons, but it has been found that usually the aromatic portion of the pyrolysis gasoline is also heavily contaminated with olefin hydrocarbons which renders recovery of the aromatics in high purity extremely difficult.

Conventional prior art schemes for producing light olefin gases, such as ethylene, may charge ethane, propane, or a straight-run naphtha fraction containing about 5% aromatic hydrocarbons, to a pyrolysis unit. The pyrolysis effluent is separated into desired fractions, one fraction of which usually comprises a C₅–400° F. pyrolysis gasoline which represents, for example, approximately 1% to 40% by weight of the original naphtha feed depending upon the charge stock and severity of cracking. Since the pyrolysis gasoline is heavily contaminated, as previously mentioned, it is hydrotreated for saturation of olefin and/or diolefin compounds and for re-

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moval of sulfur compounds. Not infrequently the prior art schemes also charge the hydrotreated pyrolysis gasoline fraction to an aromatic extraction unit for recovery of the aromatic hydrocarbons such as benzene, toluene, and xylene therefrom. Typical extraction procedures utilizing a solvent such as sulfolane or the glycols are well known to those skilled in the art for aromatic extraction purposes.

However, as is known by those skilled in the art, the diene content of such pyrolysis gasoline, as measured by its well known diene value, is usually within the range from 20 to 70 for C₅–400° F. gasolines. The diolefin compounds pose particular difficulty in the operation of the hydrotreating facilities since these compounds cause extensive equipment fouling and catalyst bed fouling. So far as is known, the prior art hydrotreating process will experience this fouling from polymer formation to some extent. Usually, the prior art will attempt to improve the on-stream efficiency of the hydrotreating unit by either promoting the polymerization reaction prior to the hydrotreating step thereby preventing the polymer from reaching downstream equipment and/or utilizing operating techniques and schemes which tend to minimize polymer formation. None of the prior art approaches are completely successful in overcoming the fouling difficulty resulting from the diolefin compounds present in the pyrolysis gasoline.

More important, however, the prior art schemes do not provide selectivity in the hydrotreating unit. For example, the hydrogenation reaction may not stop with the conversion of diolefins to olefins but will frequently saturate the amount of olefins completely and even hydrogenate substantial portions of aromatic hydrocarbons. Such non-selectivity, of course, results in a decreased yield of desirable products in the pyrolysis gasoline. Even though aromatic hydrocarbons may not be hydrogenated, more frequently, olefin hydrocarbons are completely saturated, thereby significantly decreasing the octane blending value of that portion of the pyrolysis gasoline which is normally utilized in motor fuel.

Therefore, it would be desirable to provide a process for selectively hydrogenating pyrolysis gasoline which minimizes polymer formation, minimizes product degradation, and operates in a facile and economical manner.

Summary of the invention

Accordingly, it is an object of this invention to provide a method for hydrogenating hydrocarbons.

It is another object of this invention to provide a method for stabilizing pyrolysis gasoline.

It is a specific object of this invention to provide a method for removing diolefins from pyrolysis gasoline without destroying the olefins while simultaneously removing diolefins, olefins, and sulfur compounds from the aromatic portion of the pyrolysis gasoline in a facile and economical manner.

Therefore, the practice of the present invention provides a method for hydrogenating hydrocarbons which comprises admixing an aromatic hydrocarbon feedstock containing diolefin and olefin compounds, boiling within the range from C₅ to 400° F., with hydrogen and a hereinafter specified recycle stream; passing said admixture into a first reaction zone maintained under hydrogenating conditions including relatively low temperature and the presence of a palladium-containing catalyst sufficient to convert diolefin compounds to olefin compounds without substantial saturation of olefin compounds; separating the total effluent from said first reaction zone into a first gaseous fraction comprising hydrogen and a liquid fraction; returning a portion of said liquid fraction to the first reaction zone as the specified recycle stream; passing the remainder of said liquid fraction into a separation zone

maintained under conditions sufficient to produce an aromatic hydrocarbon concentrate stream and hydrocarbons suitable for gasoline blending; admixing said concentrate stream with at least a portion of said first gaseous fraction; passing the gaseous fraction-concentrate stream into a second reaction zone maintained under hydrogenation conditions including a relatively high temperature and the presence of a desulfurization catalyst sufficient to substantially saturate olefin compounds and convert sulfur compounds to hydrogen sulfide; and, recovering a product stream comprising aromatic hydrocarbons from the effluent of said second reaction zone.

Another broad embodiment of the invention includes the method hereinabove wherein said liquid fraction is separated into a relatively light liquid fraction and a relatively heavy liquid fraction and wherein said relatively light liquid fraction is recycled to said first reaction zone as specified in an amount such that the combined hydrocarbon charge to the first reaction zone has a diene value substantially less than that of said aromatic hydrocarbon feedstock.

The selectivity of the present invention is based on the discovery that the unique two-stage system for hydrogenation accomplishes the desired results of removing diolefins, selectively removing olefins, and removing sulfur compounds simultaneously from various fractions of pyrolysis gasoline so that maximum recovery of desired products may be obtained from the pyrolysis of ethane, propane and/or naphthas to produce, for example, ethylene. This invention achieves these results in an economical and facile manner. For example, the use of the palladium catalyst and a relatively low temperature in the first reaction zone achieves selectively the conversion of diolefins to olefins without either substantial desulfurization or substantial saturation of the olefins. The relatively low temperature is that which is below desulfurization temperatures for the same system.

Therefore, satisfactory operating conditions for the first reaction zone include a temperature from 200° F. to 500° F., a pressure from 100 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity from 1 to 10, based on combined charge, and a molar excess of hydrogen typically within the range from 500 to 2,000 standard cubic feet of hydrogen per barrel of combined charge.

The operation performed in the second reaction zone of the present invention is primarily one of desulfurization and saturation of olefins boiling within the C₆ to C₈ boiling range, utilizing any of the well known desulfurization catalysts. It was found that the conventional nickel-containing desulfurization catalyst was particularly satisfactory in removing sulfur from the C₆ to C₈ aromatic concentrate fraction while simultaneously saturating any olefin compounds therein. By proper selection of operating conditions it was found that no substantial saturation of the aromatic hydrocarbons was achieved. Particularly satisfactory operating conditions for the second reaction zone of the present invention include a relatively high temperature in the range from 550° F. to 750° F., a pressure from 400 p.s.i.g. to 800 p.s.i.g., a liquid hourly space velocity from 1 to 10, and a molar excess of hydrogen such as from 500 to 2,000 scf hydrogen/barrel of charge. A particularly useful catalyst for desulfurization and olefin saturation in the second reaction zone is, for example, nickel-molybdate supported on alumina.

It is noted from the description of the embodiments to the invention presented hereinabove that a portion of the liquid effluent from the first reaction zone is recycled in admixture with the feed to the first reaction zone to produce a combined charge to the reactor. The purpose of this admixing is to reduce the diene value of the total feed to the reaction zone to a relatively low figure. Preferably, the diene value of the combined charge to the first reaction zone is less than 30 and, typically, will be less than 20, e.g. from 10 to 15. It has been found that the pyrolysis gasoline contains, for example, 5% to 35% by weight conjugated diolefin hydrocarbons, generally con-

centrated in the C₅ fraction. These diolefins would contribute significantly to polymer formation in the reactor; however, utilizing the operating conditions previously mentioned and the satisfactory palladium catalyst, the diolefins are selectively converted to olefins at a temperature from 200° F. to 500° F., preferably from about 360° F. to 500° F.

It is also to be noted from the recited embodiments that the entire fresh hydrogen is added to the system only through the first reaction zone. Thus, the sole source of hydrogen for the second reaction zone is obtained from the first zone. That is not to say, however, that there is not a recycle stream set-up around the second reactor. However, the amount of hydrogen necessary to make-up for the hydrogen consumed in the second reactor comes only from the first reaction zone by way of cascade. By operating in this manner an important benefit is obtained. The hydrogen to the first reaction zone is substantially free of hydrogen sulfide; therefore, there is virtually no chance of forming mercaptans from hydrogen sulfide passing over the palladium catalyst of the first reaction zone. Similarly, the desulfurization catalyst in the second reaction zone is notably sulfur resistant. Therefore, the recycle hydrogen stream to the second reactor contains hydrogen sulfide with substantially no adverse effects being noticed on the desired reactions.

By way of emphasis it is to be further noted that the present invention is based on the discovery that the palladium-containing catalyst is particularly useful in effectuating the desired reactions in the first reaction zone. Contrary to teachings found in the prior art, a platinum-containing catalyst was not satisfactory in the practice of the present invention. It was also distinctly discovered that palladium deposited on lithiated alumina support produced excellent results. The amount of lithium on the support achieved remarkable results in reducing gum formation caused by polymerization of the dienes on the acid sites of the catalyst.

The preferred palladium-containing catalyst employed in the present invention is prepared utilizing spherical alumina particles formed in accordance with the well known oil drop method as described in U.S. Patent No. 2,620,314, issued to James Hoekstra. These preferred catalysts contain either 0.75% or 0.375% by weight of palladium incorporated by way of an impregnation technique using the proper quantities of dinitro-dianisole palladium. Following evaporation to visual dryness and drying in air for about an hour at 100° F. the palladium impregnated alumina is calcined at about 1100° F. for about two hours. The lithium component is then incorporated using the necessary quantities of lithium nitrate to produce catalysts of 0.33% and 0.5% lithium in an impregnation procedure and the composite again is dried and calcined. A distinctly preferred diene catalyst includes 0.4% by weight palladium, 0.5% by weight lithium on a 1/16 inch spherical base. Broadly, then, the particularly preferred catalyst for the first reaction zone of the present invention comprises lithiated alumina containing from about 0.05% to about 5.0% by weight of palladium.

The practice of the present invention, as previously noted, is particularly applicable to an aromatic hydrocarbon feedstock obtained from the pyrolysis of hydrocarbons such as naphthas for the production of light olefinic gases such as ethylene. As used herein, the term "aromatic hydrocarbon feedstock" is intended to include those feedstocks containing sufficient quantities of aromatic hydrocarbons to warrant the desirability of recovering these aromatic hydrocarbons as a separate product stream substantially free of olefin hydrocarbons and sulfur compounds.

The pyrolysis reaction for the conversion of hydrocarbons into normally gaseous olefinic hydrocarbons is generally obtained at operating conditions including a temperature from 1000° F. to 1700° F., preferably, 1350° F. to 1550° F.; a pressure from 0 to 20 p.s.i.g., preferably 5

to 10 p.s.i.g.; and a residence time in the pyrolysis reaction zone of from 0.5 to 25 seconds, preferably from 3 to 10 seconds. In order for the pyrolysis reaction to proceed subsequently without undue plugging of the reaction, an inert diluent such as steam, light gases, and the like, is used. The prior art distinctly prefers to use superheated steam as the diluent which is added to the pyrolysis reaction zone in an amount from 0.2 to 1.0 pounds of steam per pound of hydrocarbon, preferably from 0.3 to 0.7 pound per pound, and typically, about 0.5 pound per pound.

The invention may be more fully understood with reference to the appended drawing which is a schematic representation of apparatus which may be utilized in practicing one embodiment of the invention.

Description of the drawing

Referring now to the drawing, a typical naphtha stream is introduced into the system via line 10 and pyrolyzed to desirable light olefinic gases in ethylene production facilities 11. The desirable C_4 minus hydrocarbons including the particularly desired ethylene stream is separated from the system via line 12. A typical pyrolysis gasoline comprising C_5+ material separated from the effluent of the steam pyrolysis reaction zone is passed via line 13, pump 14, heater 15, into prefractionation or separation facilities 16. Typically, the separation zone 16 comprises a distillation column maintained under conditions to separate gum materials and relatively non-volatile materials (such as those boiling above about 400° F.) may be removed via line 17. The desirable feedstock fraction comprising, say, C_5 to 400° F. hydrocarbons is withdrawn from separation zone 16 via line 19.

The feedstock is heated to substantially reaction temperature in heater 20, admixed with hydrogen from line 21, and further admixed with a hereinafter specified recycle stream from line 22. This admixture comprising hydrogen and a combined hydrocarbon charge is passed via line 23 into reactor 24.

It has been found that optimum reaction conditions may be obtained by minimizing the degree to which the feedstock is heated and maximizing the heat input through the recycle liquid stream and hydrogen stream; these conditions being consistent with effective vaporization and preferable limiting of temperature of any single stream to 550° F. and further limiting preferably the temperature of the fresh feed in line 19 to a temperature of no higher than about 420° F. It should be further noted that although the invention has been described as admixing the materials in lines 19, 21, and 22 prior to introduction into the reactor, the term "admixing said feedstock" is intended to embody first admixing the feedstock and hydrogen, or first admixing the hydrogen and recycle liquid which is then admixed with the feedstock or any other combination of introducing these three streams into the first reaction zone.

The combined charge material plus a molar excess of hydrogen is passed through reactor 24 over the preferred palladium catalyst under conditions sufficient to substantially convert diolefin compounds to olefin compounds without substantial saturation of olefin compounds. The total effluent from reactor 24 is cooled in exchanger 26 in an amount sufficient to produce in separator vessel 27 a significantly quantity of relatively heavy liquid. Preferably, the amount of relatively heavy liquid, more fully discussed hereinafter, which is separated in separator 27 comprises from 30% to 70% by weight, typically about 50% by weight of the hydrocarbons in the effluent stream.

Operating conditions suitable for the achievement of the proper liquid phase in separator 27 include a temperature from 250° F. to 450° F., typically, about 330° F.

Operating under these conditions a relatively light fraction is withdrawn from separator 27 via line 29, passed through condenser 30 into secondary separator 31. The

relatively light liquid which is condensed is withdrawn from separator 31 via line 22 and passed in part to first reactor 24, as previously mentioned, utilizing pump 59 and heater 60. The separated gaseous phase or first gaseous fraction is withdrawn from separator 31 via line 21 and recycled to reactor 24, as previously mentioned, utilizing compressor 57 and heater 58. The material in line 21 comprises hydrogen, and sufficient make-up hydrogen is added to the system via line 56.

The relatively heavy liquid portion produced in separator 27 is withdrawn via line 28, admixed with the remainder of the relatively light liquid in line 22 from line 32, and the admixture passed via line 33 into fractionating column 34. These streams, of course, can be introduced separately into column 34 at different column locations, if desired.

Fractionating column 34 is maintained under suitable conditions to separate, as an overhead product, the C_5 portion of the effluent which is subsequently passed via line 35 to, for example, stabilization and further handling in accordance with well known practices in the art. The bottoms from fractionating column 34 comprises the C_6+ material and is withdrawn via line 36 and passed into second fractionating column 37. Suitable distillation conditions are maintained in column 37 to separate as a bottoms product a relatively heavy gasoline fraction which is suitable for blending into motor fuel. It should also be noted that the material in line 38 comprises generally C_9+ hydrocarbons and the material in line 35 generally comprises C_5 olefin-containing hydrocarbons. Both of these streams comprise hydrocarbons suitable for gasoline blending stock. The overhead from distillation column 39 comprises an aromatic hydrocarbon concentrate and is withdrawn via line 39 through exchanger 40 into heater 43 via line 41 after admixture with hydrogen from line 42. The heated aromatic concentrate-hydrogen mixture is passed via line 44 into second reactor 45 containing the preferred nickel-molybdate desulfurization catalyst. Proper operating conditions are maintained in reactor 45, as previously mentioned, to effectuate saturation of the olefins contained in the aromatic concentrate stream as well as the substantial conversion of any sulfur compounds present therein to hydrogen sulfide.

The total effluent from reactor 45 is withdrawn via line 46, passed through cooler 47 into separator 48, wherein a hydrogen fraction containing hydrogen sulfide gas is withdrawn via line 50 and recycled to reactor 45 utilizing compressor 52 in line 42. It should also be noted at this point that sufficient make-up hydrogen is cascaded from the first reaction zone system via lines 21 and 51. Thus, no fresh make-up hydrogen need be added to the reactor 45 system thereby enabling the confinement of the H_2S gases to the second reaction zone which contains a traditionally sulfur resistant catalyst. Otherwise, should hydrogen sulfide be passed through reactor 24, there would be a strong tendency for the palladium catalyst to convert or effectuate reaction between the hydrocarbons and hydrogen sulfide to produce undesirable mercaptans.

Referring again to separator 48, the condensed aromatic product stream is withdrawn from separator 48 via line 49 and passed into fractionating column 53. Suitable operating conditions are maintained in fractionating column 53 to produce a light ends fraction containing hydrogen and H_2S which is removed via line 54 and an aromatic hydrocarbon products stream which is removed via line 55 and which may be sent, for example, to solvent extraction for recovery of benzene, toluene, and/or xylene therefrom utilizing techniques well known to those skilled in the art.

As a matter of preference, the amount of relatively light liquid material in line 22 which is recycled to reactor 24 via line 23 is sufficient to produce a combined charge to reactor 24 which has a diene value less than

30 and particularly has a diene value less than 20 and which typically is about 15. Those skilled in the art, of course, from the teachings presented herein and general knowledge may adjust the amounts and operating conditions for the practice of this invention to accomplish the desired results described herein.

Preferred embodiment

Thus, a preferred embodiment of the present invention provides a method for stabilizing sulfur-containing pyrolysis gasoline which comprises the steps of: (a) separating said gasoline into a feedstock fraction comprising C_5 to 400° F. hydrocarbons; (b) admixing said feedstock with hydrogen and a hereinafter specified recycle stream and introducing the admixture into a first reaction zone containing hydrogenating catalyst comprising palladium on lithiated alumina under conditions including a temperature from 200° F. to 500° F., a pressure from 100 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity from 1 to 10 based on combined charge, and a molar excess of hydrogen, sufficient to convert dienes to olefins without substantial conversion of sulfur compounds to hydrogen sulfide; (c) separating the total effluent from the first reaction zone into a first gaseous fraction comprising hydrogen, a relatively light liquid fraction, and a relatively heavy liquid fraction under conditions whereby said relatively heavy liquid fraction comprises from 30% to 70% by weight of the hydrocarbons in said effluent; (d) introducing said relatively heavy liquid fraction and a portion of said relatively light liquid fraction into a separation zone maintained under conditions sufficient to produce an aromatic hydrocarbon concentrate stream and hydrocarbons suitable for gasoline-blending stock; (e) returning the remainder of said relatively light liquid fraction to the first reaction zone as the specified recycle stream in an amount sufficient to produce a combined hydrocarbon charge to the reactor having a diene value of less than 30; (f) passing said aromatic concentrate stream into a second reaction zone containing desulfurization catalyst under hydrogenating conditions including the presence of a molar excess of hydrogen, a temperature from 550° F. to 750° F., a pressure from 400 p.s.i.g. to 800 p.s.i.g., and a liquid hourly space velocity from 1 to 10, sufficient to substantially convert olefins to saturates and sulfur compounds to hydrogen sulfide; and, (g) recovering a product stream comprising aromatic hydrocarbons substantially free of olefin hydrocarbons.

Another preferred embodiment of the invention includes the preferred embodiment hereinabove wherein the hydrogen introduced into said first reaction zone is substantially free of hydrogen sulfide and wherein the hydrogen present in said second reaction zone contains hydrogen sulfide.

The invention claimed is:

1. Method for hydrogenating and desulfurizing hydrocarbons which comprises:

- (a) admixing an aromatic hydrocarbon feedstock, containing diolefin, monoolefin, and sulfur compounds, boiling within the range from C_5 to 400° F. with hydrogen and a sufficient amount of a hereinafter specified recycle stream to reduce the diene value of the resulting feed mixture to less than 30;
- (b) passing said mixture into a first reaction zone maintained under hydrogenating conditions sufficient to convert diolefin compounds to olefin compounds without substantial saturation of olefin compounds, said conditions at a relatively low temperature in the range of from about 200° F. to about 500° F., and in contact with a catalyst composite comprising lithium in a palladium alumina;
- (c) separating the total effluent from said first reaction zone into a first gaseous fraction comprising hydrogen and a liquid fraction;
- (d) returning a portion of said liquid fraction to the first reaction zone as the specified recycle stream;

- (e) passing the remainder of said liquid fraction into a separation zone to separate an aromatic hydrocarbon stream from a hydrocarbon stream comprising monoolefins suitable for gasoline blending;
 - (f) admixing said aromatic stream with at least a portion of said first gaseous fraction;
 - (g) passing said admixture of gaseous fraction and aromatic stream in the liquid phase into a second reaction zone maintained under hydrogenating conditions at a relatively high temperature in the range of from about 550° F. to about 750° F. and in contact with a desulfurization catalyst sufficient to substantially saturate olefin compounds and convert sulfur compounds to hydrogen sulfide, substantially all of the hydrogen requirements of said second reaction zone being met by hydrogen present in said first gaseous fraction; and
 - (h) recovering a product stream comprising aromatic hydrocarbons from the liquid effluent of said second reaction zone.
2. Method according to claim 1 wherein said desulfurization catalyst comprises nickel on an alumina support.
3. Method according to claim 1 wherein the sole source of hydrogen to said second reaction zone is said first gaseous fraction.
4. Method according to claim 1 wherein said hydrogenating catalyst in the first reaction zone comprises from 0.05 to about 5.0% by weight palladium on lithiated alumina.
5. Method according to claim 1 wherein said liquid fraction is separated into a relatively light liquid fraction and a relatively heavy liquid fraction, and wherein said relatively light liquid fraction is recycled to said first reaction zone in an amount such that the combined hydrocarbon charge to the first reaction zone has a diene value substantially less than that of said aromatic hydrocarbon feedstock.
6. Method according to claim 5 wherein the diene value of said combined charge is less than 20.
7. Method for stabilizing sulfur-containing pyrolysis gasoline which comprises the steps of:
- (a) separating said gasoline into a feedstock fraction comprising C_5 to 400° F. hydrocarbons;
 - (b) admixing said feedstock with hydrogen and a hereinafter specified recycle stream and introducing the admixture into a first reaction zone containing hydrogenating catalyst comprising lithium in a palladium alumina at a temperature from 200° F. to 500° F., a pressure from 100 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity from 1 to 10 based on combined charge, and a molar excess of hydrogen, sufficient to convert dienes to olefins without substantial saturation of olefin compounds and without substantial conversion of sulfur compounds to hydrogen sulfide;
 - (c) separating the total effluent from the first reaction zone into a first gaseous fraction comprising hydrogen, a relatively light liquid fraction, and a relatively heavy liquid fraction under conditions whereby said relatively heavy liquid fraction comprises from 30% to 70% by weight of the hydrocarbons in said effluent;
 - (d) introducing said relatively heavy liquid fraction and a portion of said relatively light liquid fraction into a separation zone to separate an aromatic hydrocarbon stream from a hydrocarbon stream comprising monoolefins suitable for gasoline-blending stock;
 - (e) returning the remainder of said relatively light liquid fraction to the first reaction zone as the specified recycle stream in an amount sufficient to produce a combined hydrocarbon charge to the reactor having a diene value of less than 30;
 - (f) passing said aromatic stream in liquid phase into a second reaction zone containing desulfurization catalyst under hydrogenating conditions including the

presence of a molar excess of hydrogen, at a temperature from 550° F. to 750° F., pressure from 400 p.s.i.g. to 800 p.s.i.g., and a liquid hourly space velocity from 1 to 10, sufficient to substantially convert olefins to saturates and sulfur compounds to hydrogen sulfide; and,

(g) recovering a liquid product stream comprising aromatic hydrocarbons substantially free of olefin hydrocarbons.

8. Method according to claim 7 wherein said desulfurization catalyst comprises nickel.

9. Method according to claim 7 wherein the hydrogen introduced into said first reaction zone is substantially free of hydrogen sulfide and wherein the hydrogen present in said second reaction zone contains hydrogen sulfide.

10. Method according to claim 9 wherein said hydrocarbons suitable for gasoline blending include a C₅ ole-

fin-containing fraction and a fraction comprising C₉+ hydrocarbons.

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