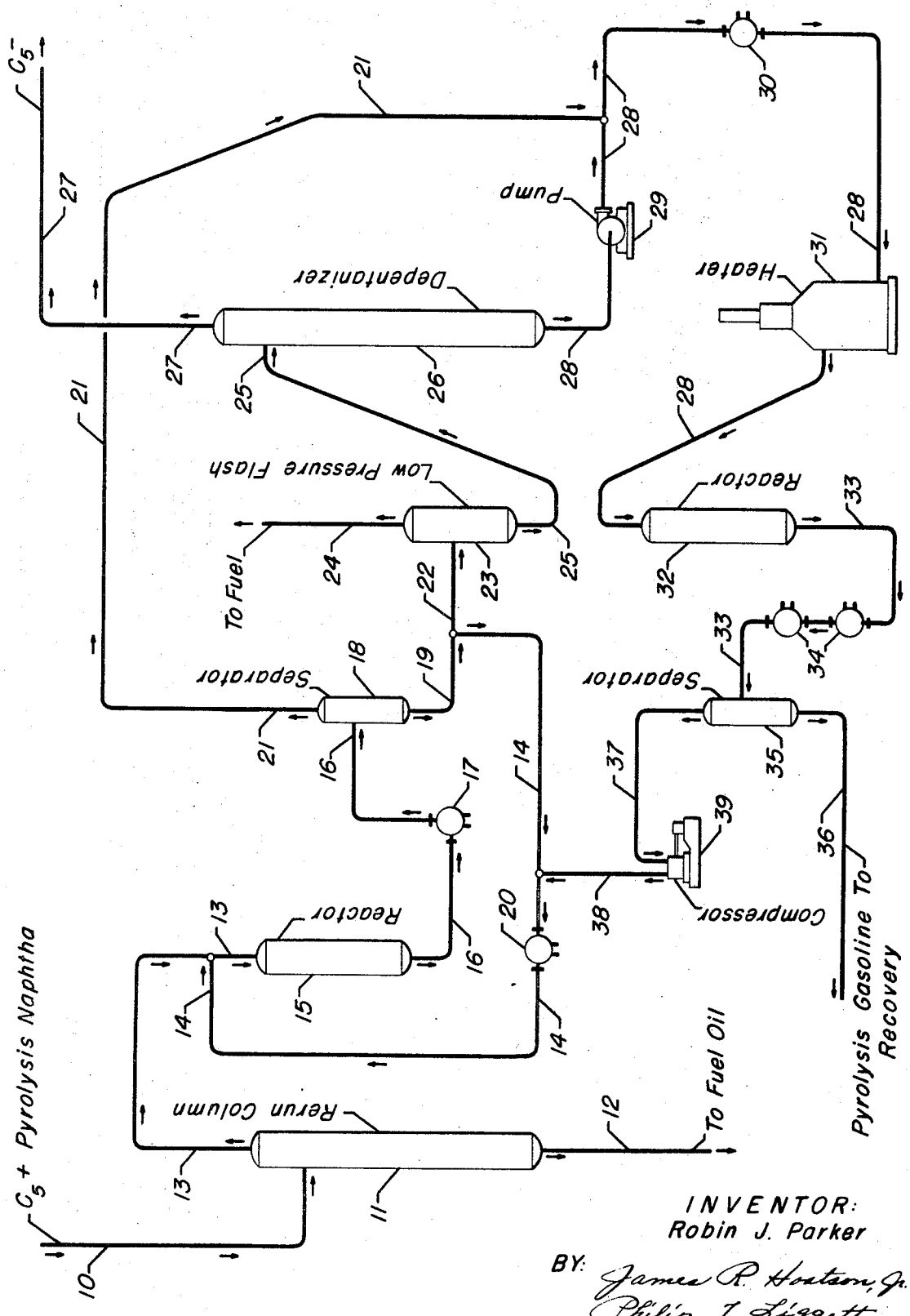
Nov. 3, 1970 R. J. PARKER 3,537,981

METHOD FOR STABILIZING PYROLYSIS GASOLINE

Filed May 7, 1969



INVENTOR:
Robin J. Parker

BY: James R. Hoatson, Jr.
Philip T. Liggett
ATTORNEYS

United States Patent Office 3,537,981 Patented Nov. 3, 1970

3,537,981

METHOD FOR STABILIZING PYROLYSIS GASOLINE

Robin J. Parker, Western Springs, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

Continuation-in-part of application Ser. No. 684,173, Nov. 20, 1967. This application May 7, 1969, Ser. No. 822,537

The portion of the term of the patent subsequent to Sept. 30, 1986, has been disclaimed

Int. Cl. C10g 35/18, 35/08; C07g 5/06

U.S. Cl. 208—143 7 Claims

ABSTRACT OF THE DISCLOSURE

Method for stabilizing pyrolysis gasoline via a two-stage selective hydrogenation technique. The first stage utilizes a palladium catalyst and the second stage utilizes a nickel catalyst for desulfurization. The invention is uniquely applicable to feedstocks having a Diene Value in excess of 30, typically, in the 50 to 60 range. Olefinic hydrocarbons, hydrocarbons suitable for gasoline blending, and aromatic hydrocarbons may, if desired, be recovered as separate product streams.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my copending application Ser. No. 684,173, filed Nov. 20, 1967, now U.S. Pat. No. 3,470,085.

BACKGROUND OF THE INVENTION

This invention relates to the hydrogenation of hydrocarbons. It particularly relates to the stabilization of pyrolysis gasoline.

It is known in the art that one of the commercially advantageous 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, often at high temperatures and usually in the presence of a diluent such as super-heated steam utilizing a tubular reactor or a plurality of cracking furnace coils. Depending upon the characteristics of 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 normally produced a significant quantity of pyrolysis gasoline which contains undesirable quantities of conjugated diolefins, styrenes 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 olefinic hydrocarbons which renders recovery of aromatics in high purity extremely difficult.

Conventional prior art schemes for producing light olefinic gases, such as ethylene, may charge ethane, propane, or straight-run naphtha fractions containing about 5% by weight aromatic hydrocarbons to a pyrolysis unit. The pyrolysis effluent is separated into desired fractions, one fraction of which usually comprises a debutanized C_5–400° F. gasoline fraction which represents for example, aproximately 1% to 40% by weight of the original naphtha feed depending, of course, upon the charge stock

characteristics and severity of cracking. Since the pyrolysis gasoline fraction is heavily contaminated, as previously mentioned, it is usually hydrotreated for saturation of the olefins and/or diolefins and/or removal of sulfur compounds. Not infrequently, the prior art schemes also charge the hydrotreated pyrolysis gasoline fraction to an aromatic extraction unit for recovery of aromatic hydrocarbons, such as benzene, toluene, and xylene therefrom. Typical extraction procedures utilizing a selective solvent, such as sulfolane or the glycols are well known to those skilled in the art for aromatic extraction purposes.

However, as is well 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 of from 20 to 70 for C_5–400° F. gasolines. The conjugated diolefins and styrenes 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 considerable extent. Usually, the prior art will attempt to improve the on-stream efficiency of the hydrotreating unit by either promoting the polymerization prior to the hydrotreating step thereby preventing the polymer from reaching downstream equipment and/or by utilizing operating techniques and schemes which tend to minimize polymer formation. None of the prior art approaches, however, are completely successful in overcoming the fouling difficulties resulting from the conjugated diolefins and styrenes in pyrolysis gasoline.

More important, perhaps, the prior art schemes do not provide selectivity in the hydrotreating unit. Such non-selectivity, of course, results in a decrease of desirable products in the pyrolysis gasoline. 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 conjugated diolefins and styrenes from pyrolysis gasoline without destroying the mono-olefins while simultaneously removing conjugated diolefins, mono-olefins, styrenes 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 stabilizing sulfur-containing pyrolysis gasoline with comprises: (a) introducing an unstable pyrolysis gasoline feedstock comprising mone-olefinic hydrocarbons, conjugated diolefins, styrenes, sulfur compounds, and pre-formed gum-like compounds into a first separation zone maintained under distillation conditions; (b) withdrawing from said first zone a distillate fraction having a Diene Value in excess of 30 and comprising C_5 to 400° F. hydrocarbons, mono-olefinic hydrocarbons, conjugated diolefins, styrenes and sulfur compounds, and a residual fraction containing gum-like compounds; (c) admixing said distillate fraction with a hereinafter specified liquid recycle stream and introducing the admixture into a first reaction zone containing a palladium catalyst under hydrogenating conditions including a temperature in the range of from 250° F. to 500° F., a pressure in the range of from 100 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity from 1 to 10 based on total hydrocarbon charge, and a molar excess of hydrogen, said

conditions being sufficient to convert said conjugated diolefins to saturated hydrocarbons and to convert said styrenes to alkylaromatic hydrocarbons without substantial conversion of sulfur compounds to hydrogen sulfide and without substantial conversion of said mono-olefinic hydrocarbons to saturated hydrocarbons so that the hereinafter specified liquid stream of step (d) has a Diene Value of less than 1.0 and a styrene content of less than 1.0 percent by weight; (d) introducing the total effluent from said first reaction zone into a second separation zone maintained under conditions sufficient to produce a vaporous stream comprising hydrogen and a liquid stream comprising C_5+ hydrocarbons containing mono-olefinic hydrocarbons and sulfur compounds; (e) recycling a portion of said liquid stream of step (d) to step (c) as said specified recycle liquid; (f) passing another portion of said liquid stream of step (d) into a second reaction zone maintained under desulfurization conditions including the presence of said vaporous stream of step (d) sufficient to convert sulfur compounds to hydrogen sulfide, said mono-olefinic hydrocarbons to saturated hydrocarbons; and (g) subsequently recovering stabilized pyrolysis gasoline.

Another embodiment of this invention includes the method hereinabove wherein said palladium catalyst comprises palladium or compounds disposed on lithiated alumina base.

The selectivity of the present invention is based on the discovery that the unique two-stage system utilizing a palladium catalyst in one stage and a desulfurization catalyst in another stage for hydrogenation accomplishes the desired results of selectively removing conjugated diolefins and styrenes, selectively removing mono-olefins, and removing sulfur compounds simultaneously from various fractions of pyrolysis gasoline including the aromatic portion of such gasoline such that the maximum recovery of the products may be obtained. With respect to the hydrogenation reactions in the first stage utilizing a palladium catalyst and relatively low temperature, these conditions selectively convert conjugated diolefins to saturated hydrocarbons and styrenes to alkylaromatic hydrocarbons without substantial desulfurization and without substantial saturation of the mono-olefinic hydrocarbon. This relatively low temperature is that temperature which is below desulfurization temperature for the same system. It was surprising to discover that the palladium catalyst and relatively mild operating conditions could achieve these results to an extent such that the liquid recycle stream obtained from the effluent of the first reaction stage has a Diene Value of less than 1.0, e.g., about 0.2, and a styrene content of less than 1.0 percent by weight, typically about 0.2 weight percent, and, therefore, can be recycled directly to the reaction zone for diluent purposes. Also, by the use of this recycle stream it was found advantageous to supply maximum heat to the recycle stream and minimum heat to the unstabilized charge stock in order to achieve sufficient temperature for reaction purposes. Operating in this manner, of course, minimizes the formation of gum in the charge stock prior to introduction into the palladium catalyst reaction zone.

Therefore, satisfactory operating conditions for the first reaction zone include a temperature in the range of from 250° F. to 500° F., preferably, 270° F. to 470° F., a pressure in the range of from 100 p.s.i.g. to 1200 p.s.i.g., preferably, 350 p.s.i.g. to 850 p.s.i.g., a liquid hourly space velocity in the range of from 1 to 10 based on combined charge, and a molar excess of hydrogen typically within the range of 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 diesulfurization and saturation of the mono-olefinic hydrocarbons boiling within the C_6 to C_8 boiling range utilizing any of the well known desulfurization catalysts. It was found that the conventional nickel-containing desulfurization

catalyst (hereinafter referred to as "nickel catalyst") was particularly satisfactory in removing sulfur from the C_6 to C_8 aromatic concentrate fractions while simultaneously saturating any mono-olefinic hydrocarbons 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 500° F. to 700° 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 s.c.f. hydrogen/barrel of charge. A particularly useful catalyst for desulfurization and mono-olefin saturation in the second reaction zone is, for example, nickel-molybdate supported on alumina.

It was noted from the description of the embodiments of the invention presented hereinabove that a portion of the C_5+ hydrocarbons obtained from the effluent of the first reaction zone is recycled directly to the reaction zone in a manner which minimizes the formation of gum-like compounds. Since the preformed gum in the feedstock has been removed in the first separation zone, the entire system is now maintained substantially gum or polymer-free. This gum-like compound formation is not exactly understood by those skilled in the art. However, it is known that the dimer or polymer material of which these compounds generally resemble lead to undesirable product quality or to coking or fouling of the second reactor system in the present invention. These difficulties are particularly acute if the second reactor system in operating at an appreciably higher temperature. Those skilled in the art also are aware that it is frequently desirable to admix a diluent with the feed material to the first reactor system in order 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 25 and, typically, will be about 20. It has been found that the pyrolysis gasoline contains, for example, 5% to 35% by weight conjugated diolefin hydrocarbons generally concentrated in the C_5 fraction. These conjugated diolefins, as previously mentioned, will contribute significantly to polymer formation in the reactor; however, utilizing the operating conditions previously mentioned, and the satisfactory palladium catalyst including the two-stage separation feature of the present invention these conjugated diolefins are selectively converted to saturated hydrocarbons and the styrenes are converted to alkylaromatic hydrocarbons at a temperature from 250° F. to 500° F., preferably, from 270° F. to 470° F. and therefore problems resulting from polymer formation are minimized.

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 particularly when the system is operated in accordance with the practices of the present invention. 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. Pat. No. 2,620,314 issued to James Hoekstra. These preferred catalyst contain either 0.75% or 0.375% by weight of palladium incorporated by way of an impregnation technique using the proper quantities of dinitrodianisole palladium. Following evaporation to visual dryness and dry-

ing in air from 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 2.0% lithium in an impregnation procedure and the composite is again dried and calcined. A distinctly preferred catalyst contains 0.4% by weight palladium, 0.5% by weight lithium on a 1/16 spherical alumina base. Broadly, then, the prefered catalyst for the first reaction zone of the present invention comprises lithiated alumina containing from 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. In other words, the term "stabilized pyrolysis gasoline" is intended to include aromatic hydrocarbons substantially free of olefins as well as fractions obtained from a suitable feedstock which may be subsequently used in gasoline blending.

The pyrolysis reaction for the conversion of hydrocarbons into normally gaseous olefinic hydrocarbons is generally obtained at operating conditions including a temperature in the range of from 1000° F. to 1700° F., preferably 1350° F. to 1550° F.; a pressure in the range of from 0 to 20 p.s.i.g., preferably from 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 zone an inert diluent such as steam, light gases, and the like, is used. The prior art distinctly prefers to use super-heated steam as the diluent which is added to the pyrolysis reaction zone in an amount from 0.2 to 1.0 pound 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 one embodiment of my invention.

DESCRIPTION OF THE DRAWING

Referring now to the drawing, a typical C_5+ pyrolysis naphtha stream obtained from a conventional ethylene facility is introduced into the system via line **10** and passed into distillation colum **11** which is maintained under distillation conditions. Preferably, the residual fraction containing pre-formed gum-like compounds are removed from column **11** via line **12** and conventionally passed into a fuel oil system. A distillate fraction comprising C_5 to 400° F. hydrocarbons, mono-olefinic hydrocarbons, conjugated diolefins, styrenes and sulfur compounds is withdrawn from distillation column **11** via line **13**.

This distillate fraction is heated to substantially reaction temperature by means of heaters not shown, admixed with a hereinafter specified liquid recycle stream from line **14** which also contains hydrogen gas and the mixture passed into reactor system **15** containing a palladium catalyst. The amount of liquid material being admixed via line **14** is generally that amount sufficient to reduce the Diene Value of the material in line **13** to a suitably low level, for example, about 20 Diene Value.

As previously mentioned, it was found that optimum reaction conditions may be obtained by minimizing the degree to which the feedstock is heated, e.g., the material in line **13**, and maximizing the heat input through the recycled liquid and hydrogen stream; these conditions being consistent with effective vaporization and preferably limiting of temperature of any single stream to 550° F. and further limiting, preferably, the temperature of fresh feed in line **20** to a temperature of no higher than about 420° F. By utilizing these procedures it was found that formation of gum in the system was minimized.

The charge material, including recycle liquid and hydrogen, is passed through reactor **15** over a bed of the preferred palladium catalyst under conditions sufficient to substantially convert conjugated diolefins to saturated hydrocarbons and without substantial staturation of mono-olefinic hydrocarbons and without substantial conversion of sulfur compounds present therein to hydrogen sulfide. The total effluent from reactor **15** is passed via line **16** into cooler-condenser **17** for removing heat and the cooled effluent is passed into separator **18** under conditions to produce a vaporous stream in line **21** comprising hydrogen gas and a liquid stream in line **19** having now a Diene Value of about 0.2.

Operating conditions suitable for the achievement of the proper liquid phase in separtor **18** include a temperature from 250° F. to 450° F., typically about 330° F.

Operating under these conditions, a stablized liquid stream is passed from the material in line **19** via line **14** into admixture with hydrogen gas from line **38**, more fully discussed hereinbelow, and the mixture of recycle liquid and hydrogen passed into heater **20** which supplies sufficient heat for reaction purposes to the recycle liquid and hydrogen. The heated mixture of hydrogen and recycle liquid is passed via line **14** into admixture with the incoming feed material in line **13**, as previously mentioned.

The remaining material in line **19** is passed via line **22** into a relatively low pressure flash chamber **23**, according to a preferred embodiment of this invention. The conditions maintained in separator **23** are sufficient to produce a gas fraction in line **24** which comprises residual dissolved hydrogen gas and light hydrocarbon, such as methane and ethane. These are removed from the system via line **24** and sent, for example, to a fuel system. The remaining liquid stream comprising sulfur-containing hydrocarbons including C_5 minus material is withdrawn from vessel **23** and passed via line **25** into distillation column **26**. Distillation column **26** is maintained under suitable conditions to separate as an overhead product the C_5 minus material which is withdrawn via line **27** and sent to recovery facilities. A bottoms material comprising C_6+ material having included therein aromatic hydrocarbons and sulfur compounds are passed through pump means **29** into admixture with the hydrogen-containing vapor stream in line **21** which is being passed from first separator **18**. The admixture of hydrogen gas and C_6+ material is passed through exchanger **30** and heater **31** into second reaction zone **32**. Second reactor **32** contains the preferred nickel-molybdate desulfurization catalyst. Proper operating conditions are maintained in reactor **32**, as previously mentioned, to effectuate saturation of the mono-olefins contained in the aromatic portion of the liquid charge to the reactor as well as to effectuate substantial conversion of any sulfur compounds present therein to hydrogen sulfide.

The total effluent from reactor **32** is withdrawn via line **33**, condensed and cooled in exchangers **34** and passed into separation zone **35**. Sufficient conditions are maintained in separation zone **35** to produce a gaseous fraction in line **37** which contains hydrogen gas and hydrogen sulfide gas which is withdrawn from the separator via line **37**. The pyrolysis gasoline fraction is withdrawn from separator **35** via line **36** and sent to, for example, stripping or recovery facilities, such as, for example, a sulfolane solvent extraction system, for the recovery therefrom of high purity aromatic hydrocarbons, such as benzene, toluene and xylene. These recovery facilities are well known to those skilled in the art and have not been shown for convenience.

If desired, the gaseous material in line **37** comprising

useful hydrogen gas can be passed through compressor means **39** and the compressed hydrogen-containing gas can be passed therefrom via line **38** into admixture with the liquid recycle stream in line **14**, as previously mentioned, for passage into the first reaction zone **15**. Also, if desired, by means not shown, the hydrogen sulfide gas may be removed from the hydrogen gas by conventional treating facilities, such as an amine treating unit. In such case, the hydrogen-containing gas in line **38** may be of significantly higher purity than would perhaps otherwise be the case.

PREFERRED EMBODIMENT

A preferred embodiment of the present invention includes broadly the process or method referred to hereinabove with reference to the attached drawing. For example, it is distinctly preferred to practice this invention utilizing the two-reactor system wherein the first reactor contains palladium catalyst and operates at relatively low temperature with the second reactor containing a nickel catalyst with operations being performed at relatively high temperature. It is also distinctly preferred that the gasoline portion of the pyrolysis gasoline which is passed through the first reaction zone be separated prior to the second reaction zone so that the desirable high octane blending value olefin hydrocarbons may be retained and recovered for use in gasoline blending.

Specifically, then a preferred embodiment of the present invention provides a method for stabilizing a sulfur-containing pyrolysis gasoline feedstock comprising mono-olefinic hydrocarbons, conjugated diolefins, styrenes, sulfur compounds and pre-formed gum-like compounds and having a Diene Value in excess of 30 which comprises the steps of: (a) admixing said feed sotck with hereinafter specified liquid recycle stream in an amount sufficient to produce an admixture having a Diene Value of less than 25; (b) passing said admixture into a first reaction zone containing a hyrogenating catalyst comprising from 0.05% to 5.0% by weight palladium on an alumina base containing from 0.3% to 2.0% by weight lithium maintained under hydrogenating conditions including a temperature in the range of from 250° F. to 500° F., a pressure in the range of from 100 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity in the range of from 1 to 10 based on said admixture, and a molar excess of hydrogen, said conditions being sufficient to convert said conjugated diolefins to saturated hydrocarbons and to convert said styrenes to alkylaromatic hydrocarbons without substantial conversion of sulfur compounds to hydrogen sulfide and without substantial conversion of said mono-olefinic hydrocarbons to saturated hydrocarbons and sufficient to produce a hereinafter specified liquid stream having a Diene Value of less than 1.0; (c) introducing the total effluent from said first reaction zone into a first separation zone maintained under conditons sufficient to produce a vaporous fraction containing hydrogen and a first liquid stream having a Diene Value of less than 1.0 as said specified liquid stream; (d) recycling a portion of said liquid to step (a) as said specified recycle stream; (e) passing the remaining portion of said liquid stream into a second separation zone maintained under conditions sufficient to produce a light product stream comprising C_5 hydrocarbons and a second liquid stream comprising sulfur compounds and C_6+ components; (f) introducing said second liquid stream into a second reaction zone containing desulfurization catalyst under conditions including the presence of said vaporous fraction of step (d) to provide a molar excess of hydrogen, a temperature in the range of from 500° F. to 700° F., a pressure in the range of from 400 p.s.i.g. to 800 p.s.i.g., and a liquid hourly space velocity in the range of from 1 to 10, said conditions being sufficient to substantially convert sulfur compounds to hydrogen sulfide and said mono-olefinic hydrocarbons to saturated hydrocarbons; and, (g) subsequently recovering stabilized pyrolysis gasoline.

I claim as my invention:

1. Method for stabilizing sulfur-containing pyrolysis gasoline which comprises:

(a) introducing an unstable pyrolysis gasoline feedstock comprising mono-olefinic hydrocarbons, conjugated diolefins, styrenes, sulfur compounds and pre-formed gum-like compounds into a first separation zone maintained under distillation conditions;

(b) withdrawing from said first zone a distillate fraction having a Diene Value in excess of 30 and comprising C_5 to 400° F. hydrocarbons, mono-olefinic hydrocarbons, conjugated diolefins, styrenes and sulfur compounds, and a residual fraction containing gum-like compounds;

(c) admixing said distillate fraction with a hereinafter specified liquid recycle stream and introducing the admixture into a first reaction zone containing a palladium catalyst under hydrogenating conditions including a temperature in the range of from 250° F. to 500° F., a pressure in the range of from 100 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity in the range of from 1 to 10 based on total hydrocarbon charge, and a molar excess of hydrogen, said conditions being sufficient to convert said conjugated diolefins to saturated hydrocarbons and to convert said stryrenes to alkylaromatic hydrocarbons without substantial conversion of sulfur compounds to hydrogen sulfide and without substantial conversion of said mono-olefinic hydrocarbons to saturated hydrocarbons so that the hereinafter specified liquid stream of step (d) has a Diene Value of less than 1.0 and a styrene content of less than 1.0 weight percent;

(d) introducing the total effluent from said first reaction zone into a second separation zone maintained under conditions sufficient to produce a vaporous stream comprising hydrogen and a liquid stream comprising C_5+ hydrocarbons containing mono-olefinic hydrocarbons and sulfur compounds;

(e) recycling a portion of said liquid stream of step (d) to step (c) as said specified recycle liquid;

(f) passing another portion of said liquid stream of step (d) into a second reaction zone maintained under desulfurization conditions including the presence of said vaporous stream of step (d) sufficient to convert sulfur compounds to hydrogen sulfide and said mono-olefinic hydrocarbons to saturated hydrocarbons; and,

(g) subsequently recovering stabilized pyrolysis gasoline.

2. Method according to claim **1** wherein said palladium catalyst comprises palladium or palladium compound deposited on a lithiated alumina base.

3. Method according to claim **1** wherein said distillate fraction of step (b) has a Diene Value in excess of 50.

4. Method according to claim **2** wherein said stabilized pyrolysis gasoline includes aromatic hydrocarbons substantially free of olefins.

5. Method for stabilizing a sulfur-containing pyrolysis gasoline feedstock comprising mono-olefinic hydrocarbons, conjugated diolefins, styrenes, sulfur compounds and pre-formed gum-like compounds and having a Diene Value in excess of 30 which comprises the steps of:

(a) admixing said feedstock with hereinafter specified liquid recycle stream in an amount sufficient to produce an admixture having a Diene Value of less than 25;

(b) passing said admixture into a first reaction zone containing a hydrogenating catalyst comprising from 0.05% to 5.0% by weight palladium on an alumina base containing from 0.3% to 2.0% by weight lithium maintained under hydrogenating conditions including a temperature in the range of from 250° F. to

500° F., a pressure in the range of from 100 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity in the range of from 1 to 10 based on said admixture, and a molar excess of hydrogen, said conditions being sufficient to convert said conjugated diolefins to saturated hydrocarbons and to convert said styrene to alkylaromatic hydrocarbons without substantial conversion of said mono-olefinic hydrocarbons to saturated hydrocarbons and sufficient to produce a hereinafter specified liquid stream having a Diene Value of less than 1.0;

(c) introducing the total effluent from said first reaction zone into a first separation zone maintained under conditions sufficient to produce a vaporous fraction containing hydrogen and a first liquid stream having a Diene Value of less than 1.0 as said specified liquid stream;

(d) recycling a portion of said liquid to step (a) as said specified recycle stream;

(e) passing the remaining portion of said liquid stream into a second separation zone maintained under conditions sufficient to produce a light product stream comprising C_5 hydrocarbons and lighter components and a second liquid stream comprising sulfur compounds and C_6+ components;

(f) introducing said second liquid stream into a second reaction zone containing desulfurization catalyst under conditions including the presence of said vaporous fraction of step (d) to provide a molar excess of hydrogen, a temperature in the range of from 500° F. to 700° F., a pressure in the range of from 400 p.s.i.g. to 800 p.s.i.g., and a liquid hourly space velocity in the range of from 1 to 10, said conditions being sufficient to substantially convert sulfur compounds to hydrogen sulfide and said mono-olefinic hydrocarbons to saturated hydrocarbons; and,

(g) subsequently recovering stabilized pyrolysis gasoline.

6. Method according to claim 5 wherein said desulfurization catalyst comprises a nickel-containing catalyst.

7. Method according to claim 6 wherein a hydrogen-containing gas stream is separated from the effluent of said second reaction zone and returned to the first reaction zone of step (b) as at least part of said molar excess of hydrogen.

References Cited

UNITED STATES PATENTS

3,004,914	10/1961	White	260—677
3,470,085	9/1969	Parker	260—677

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—57; 260—677