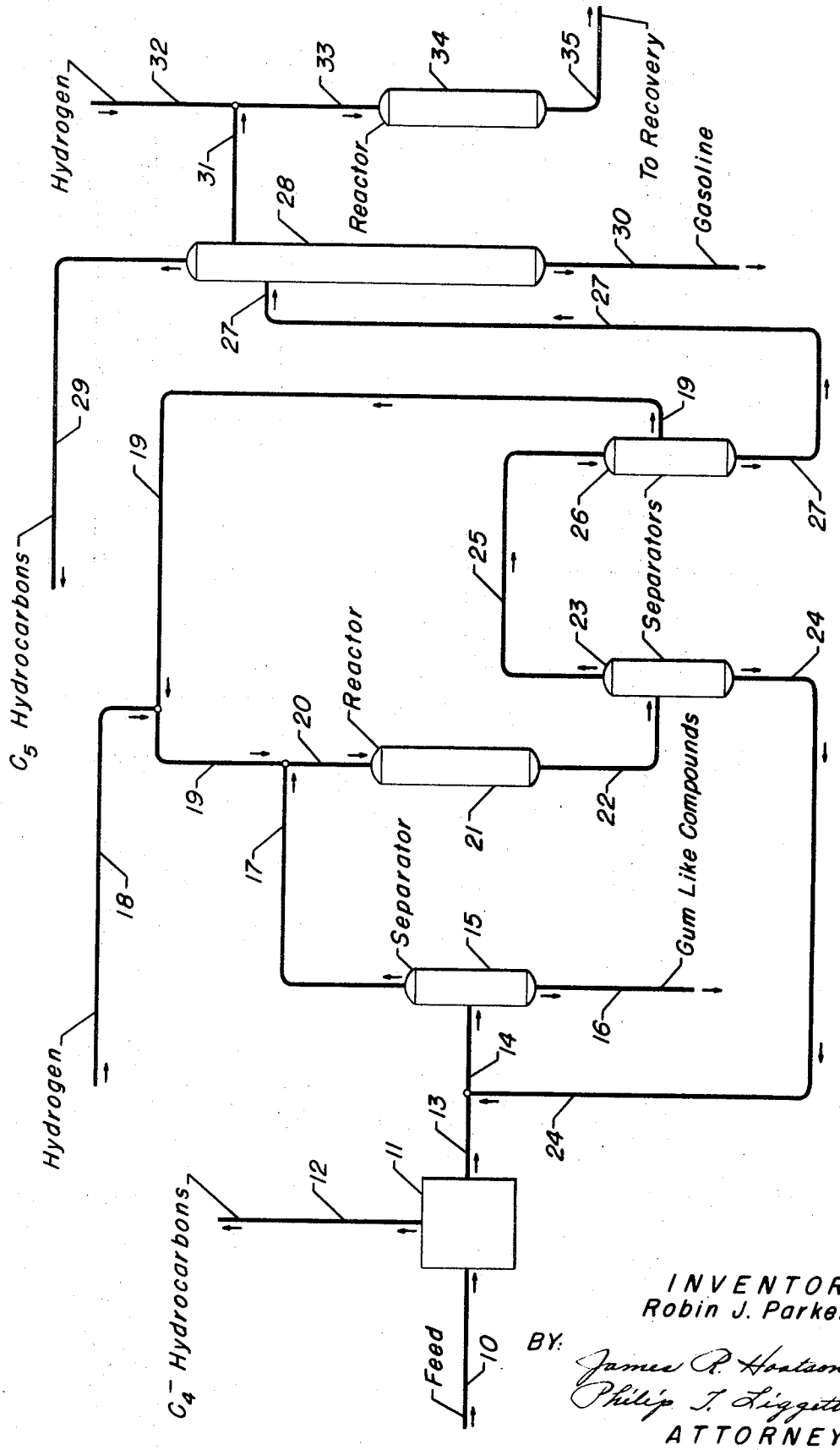
Nov. 3, 1970 R. J. PARKER 3,537,982

METHOD FOR HYDROGENATION

Filed April 28, 1969



INVENTOR:
Robin J. Parker

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

United States Patent Office 3,537,982 Patented Nov. 3, 1970

3,537,982

METHOD FOR HYDROGENATION

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. 646,707, June 6, 1967, now Patent No. 3,457,163, dated July 22, 1969. This application Apr. 28, 1969, Ser. No. 819,675

The portion of the term of the patent subsequent to July 22, 1986, has been disclaimed

Int. Cl. C07c 5/02; C10g 23/04

U.S. Cl. 208—255 9 Claims

ABSTRACT OF THE DISCLOSURE

Method for stabilizing pyrolysis gasoline via selective hydrogenation. Gum-like compounds, both pre-formed and subsequent-formed, are removed by distillation. The method separates pre-formed gum-like compounds prior to the first reaction zone and by judicious separation recycles a portion of the reactor effluent containing gum-like compounds formed in the reaction zone to a first separation zone for combining with the pre-formed gum-like compounds and the removal thereof from the system.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my co-pending application Ser. No. 646,707, filed June 6, 1967, now U.S. Pat. No. 3,457,163, issued July 22, 1969.

BACKGROUND OF THE INVENTION

This invention relates to the hydrogenation of hydrocarbons. It particularly relates to the stabilization of pyrolysis gasoline. It specifically relates to a method for selectively removing conjugated diolefins and mono-olefinic hydrocarbons from the product gasoline obtained in light olefin hydrocarbon 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 optained from petroleum. Usually, the pyrolysis reaction is effected in the substantial absence of a catalyst at high temperature 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 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 also produced a significant quantity of pyrolysis gasoline which contains undesirable quantities of conjugated diolefinic hydrocarbons, 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 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 straight-run naphtha fractions containing about 5% aromatic hydrocarbons to a pyrolysis unit. The pyrolysis effluent is separated into desired fractions, one fraction of which usually comprises a C_5-400° F. pyrolysis gasoline which represents, for example, approximately 1% to 40%

by weight of the original naphtha feed, depending upon the charge stock characteristics and severity of cracking. Since the pyrolysis gasoline 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 the aromatic hydrocarbons such as benzene, toluene, and xylene therefrom. Typical extarction 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 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 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 difficulties resulting from the conjugated diolefins and styrenes present in the 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 decreased yield of desirable products in the pyrolysis gasoline. Therefore, it would be desirable to provide a process for selectivity 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 gasolines.

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 hydrogenating hydrocarbons which comprises the steps of: (a) introducing an unstable hydrocarbon feedstock comprising mono-olefinic hydrocarbons, conjugated diolefins, styrenes, and preformed gum-like compounds and a hereinafter specified stabilized liquid stream into a first separation zone maintained under separation conditions; (b) withdrawing from said first zone a first fraction containing hydrocarbons contaminated with mono-olefinic hydrocarbons, conjugated diolefins, styrenes, and a residual fraction comprising hydrocarbons contaminated with gum-like compounds; (c) passing said first fraction into a hydrogenation reaction zone maintained under conditions sufficient to hydrogenate said conjugated diolefins to saturated hydrocarbons and to hydrogenate said styrenes to alkyl aromatic hydrocarbons; (d) introducing the total effluent from said reaction zone in substantially vaporous form into a second separation zone maintained under conditions sufficient to produce from 1% to 25% by volume of stabilized liquid

based on the C_5 plus hydrocarbons in said effluent, said liquid containing gum-like compounds; (e) returning said stabilized liquid stream formed in the second separation zone to said first separation zone as feed thereto; and (f) recovering hydrogenated hydrocarbons from the remaining vapor stream from the second separation zone.

Thus, it is noted that the present invention provides a facile and economical manner for removing gum-like compounds in a manner which separates pre-formed gum-like compounds prior to the first reaction zone and by judicious separation, recycles a portion of the reactor effluent containing gum-like compounds formed in the reaction zone to the first separation zone for combining with the pre-formed gum-like compounds and removal thereof from the system.

In addition, the present invention provides a two-stage method for stabilizing sulfur-containing prolysis gasoline which comprises the steps of: (a) introducing an unstable pyrolysis gasoline feedstock comprising mono-olefinic hydrocarbons, conjugated diolefins, styrenes, sulfur compounds, and pre-formed gum-like compounds, and a hereinafter specified liquid recycle stream into a first separation zone maintained under distillation conditions; (b) withdrawing from said first zone a distillate fraction comprising C_5-400° F. hydrocarbons, mono-olefinic hydrocarbons, conjugated diolefins, styrenes, sulfur compounds, and a residual fraction containing gum-like compounds; (c) admixing said distillate fraction with hydrogen and introducing the admixture into a first reaction zone containing a palladium catalyst under 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 said styrenes to alkyl aromatic hydrocarbons without substantial conversion of sulfur compounds to hydrogen sulfide and without substantial conversion of said mono-olefinic hydrocarbons to saturated hydrocarbons; (d) introducing the total effluent from said first reaction zone in substantially vaporous form into a second separation zone maintained under conditions sufficient to produce a liquid stream comprising from 1% to 25% by volume based on the C_5+ hydrocarbons in said effluent, said liquid stream containing gum-like compounds; (e) recycling entirely said liquid stream from step (d) to step (a) as said specified recycle stream; (f) passing remaining hydrocarbons containing sulfur compounds from said second separation zone into a second reaction zone containing desulfurization catalyst under hydrogenating conditions including the presence of a molar excess of hydrogen, a temperature in the range of from 500° F. to 750° 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) recovering stabilized pyrolysis gasoline in high concentration.

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 conjugated diolefins, selectively removing mono-olefins, and removing sulfur compounds simultaneously from various fractions of pyrolysis gasoline including the aromatic portion of such 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 while operating to remove the deleterious gum-like compounds from the system in a manner not heretofore contemplated. With respect to the hydrogenation reactions the use of the palladium catalyst and relatively low temperature in the first

reaction zone achieves selectively the conversion of the conjugated diolefins to saturated hydrocarbons and the styrenes to alkyl aromatic hydrocarbons without substantial desulfurization or substantial saturation of the mono-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 in the range of from 250° F. to 500° F., and preferably in the range of from 270° F. to 470° F., a pressure in the range of from 100 p.s.i.g. to 1200 p.s.i.g., and preferably in the range of from 350 p.s.i.g. to 800 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 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 mono-olefins 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-olefin hydrocarbon 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 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., a liquid hourly space velocity in the range of 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 olefin saturation in the second reaction is, for example, nickel-molybdate supported on alumina.

It is noted from the description of the embodiments of the invention presented hereinabove that a portion of the C_5+ hydrocarbons contained in the effluent from the first reaction zone is recycled to the pre-separation zone in a manner such that gum-like compounds are effectively removed from the effluent of the first reaction zone. The gum-like compounds are similar in nature to those which have been pre-formed in the feedstock following the pyrolysis reaction, for example, to produce ethylene. 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 is 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 30 and, typically about 20 Diene Value. 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 and styrenes, 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 at a temperature from 250° F. to 500° F., preferably, from 270° F. to 470° F. and the styrenes are also selectively converted to alkyl aromatic hydrocarbons, 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 catalysts 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 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 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 preferred 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 fedestocks containing sufficient quantities of aromatic hydrocarbons to warrant the desirability of recovering these aromatic hydrocarbons as a separate product stream substantially fee 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 superheated 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 apparatus which may be used 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 system **11** via line **12**. A typical pyrolysis gasoline comprising C_5+ material, separated from the effluent of the steam pyrolysis reaction zone, is passed through line **14**, admixed with a hereinafter specified stabilized liquid stream from line **24**, and the admixture passed via line **14** into first separation zone **15**. Typically, the separation zone **15** comprises a distillation column maintained under distillation conditions to separate gum-like compounds and relatively non-volatile materials (such as those boiling above about 400° F.) may be removed via line **16**. As more fully explained hereinafter, the material in line **16** contains both the pre-formed gum-like compounds and the subsequent-formed gum-like compounds from the reaction zone. The desirable feedstock fraction comprising, say, C_5 to 400° F. hydrocarbons is withdrawn from separation zone **15** via line **17**.

The feedstock is heated to substantially reaction temperature by means of heaters (not shown), admixed with hydrogen from line **19** with make-up hydrogen being added as needed from line **18**, and the mixture passed via line **20** into reactor system **21** containing a palladium catalyst. As previously mentioned, those skilled in the art may find it desirable to utilize a liquid diluent stream in admixture with the feed to reactor **21** in order to reduce the diene value of the feed to a value of about 20. The means for providing the liquid diluent to the first reaction zone **21** has not been shown.

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 usually desired recycle liquid stream and the recycled 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 the fresh feed in line **20** to a temperature of no higher than about 420° F. By utilizing these procedures it has been found that formation of gum in the transfer system between separator **15** and reactor **21** may be minimized.

The charge material plus a molar excess of hydrogen is passed through reactor **21** over the preferred palladium catalyst under conditions sufficient to substantially convert the conjugated diolefins to saturated hydrocarbons and the styrenes to alkyl aromatic hydrocarbons without substantial saturation of mono-olefinic hydrocarbons and without substantial conversion of any sulfur compounds present to hydrogen sulfide. The total effluent from reactor **21** is passed via line **22** in substantially vaporous form into second separator **23** which is maintained under conditions such that from 1% to 25% by volume of the C_5+ hydrocarbons contained in the effluent of line **22** may be reduced to liquid phase.

Operating conditions suitable for the achievement of the proper liquid phase in separator **23** include a temperature from 250° F. to 450° F., typically, about 330° F.

Operating under these conditions a stabilized liquid stream is withdrawn from separator **23** via line **24** and returned in admixture with the incoming feed in line **13** as previously mentioned. Any gum-like compounds formed inthe system between separator **15** and separator **23** are removed by this technique of returing this relatively small portion of liquid stream to separator **15** from whence the undesirable gum-like compounds are removed via line **16** as previously mentioned.

The remaining material from separator **23** is passed via line **25**, cooled to a suitably low temperature, and introduced into a third separator **26** which is operated under conditions sufficient to separate a hydrogen-containing gas from the hydrocarbon phase. The hydrogen-containing gas is withdrawn from separator **26** via line **19** and returned to reactor **21** as recycle, as previously mentioned.

The relatively heavy liquid portion produced in separator **26** is passed via line **27** into separation zone **28**, which is operating under distillation conditions.

Fractionating column **28** is maintained under suitable conditions to separate as an overhead product the C_5 portion of the reactor **21** effluent. This material is removed via line **29** and passed, for example, into stabilization facilities, not shown, in accordance with well known practices in the art. A bottoms material comprising C_9+ gasoline is withdrawn from fractionating column **28** via line **30** also for handling in accordance with methods well known to those skilled in the art.

It should be noted at this point that the gasoline portion of the pyrolysis gasoline which has now been stabilized and represented by the material in line **29** and in line **30** still contains high octane blending value mono-olefinic compounds.

The aromatic concentrate portion of the pyrolysis gasoline is wtihdrawn from fractioning column **28** via line **31** wherein it is admixed with additional hydrogen from line **22** and the hydrogen-hydrocarbon mixture is passed via line **33** into second reaction zone **34**. Second reactor **34** contains the preferred nickel-molybdate desulfurization catalyst. Proper operating conditions are maintained in reactor **34**, as previously mentioned, to effectuate saturation of the mono-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 **34** is withdrawn via line **35** and passed into recovery facilities which would include a separation zone wherein a hydrogen fraction containing hydrogen sulfide gas may be recovered, the hydrogen sulfide gas separated, and the hydrogen-containing fraction preferably recycled to reactor **34**. These recovery facilities are well known to those skilled in the art and have not been shown for convenience.

PREFERRED EMBODIMENT

A preferred embodiment of the present invention includes broadly the process or method referred to hereinabove with reference to the drawing. However, in actual practice, it is distinctly preferred to maintain conditions in separator **23** such that the stabilized liquid stream formed therein comprises from 3% to 10% by volume of the C_5+ hydrocarbons in the total effluent from reactor **21**. Also it is distinctly preferred to practice this invention utilizing the two reactor systems 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 a relatively high temperautre. It is also distinctly preferred that the gasoline portion of the pyrolysis gasoline which is to be used in gasoline blending be separated prior to the second reaction zone so that the desirable high octane blending value olefin hydrocarbons may be retained and recovered and utilized in gasoline blending.

With reference to the appended claims, it is to be noted that the portion of the effluent passing from the second separator to the second reactor may go to the second separator directly following the separation of hydrogen or may be distilled to separate out the gasoline fraction, as previously mentioned. In some cases, those skilled in the art may find it desirable to send the C_5 and C_9+ olefin materials through the second reaction zone. In addition, when recovery of stabilized pyrolysis gasoline is referred to, it is intended to include in such phraseology the recovery of an aromatic concentrate stream which is substantially free of olefins and sulfur compounds and the separation of a gasoline blending stock such as previously mentioned, including the C_5 olefin constituents therein.

I claim as my invention:

1. Method for hydrogenating hydrocarbons which comprises the steps of:

(a) introducing an unstable hydrocarbon feedstock comprising mono-olefinic hydrocarbons, conjugated diolefins, styrenes and pre-formed gum-like compounds and a hereinafter specified stabilized liquid stream into a first separation zone maintained under separation conditions;

(b) withdrawing from said first zone a first fraction containing hydrocarbons contaminated with mono-olefinic hydrocarbons, conjugated diolefins, styrenes and a residual fraction comprising hydrocarbons contaminated with gum-like compounds;

(c) passing said first fraction into a hydrogenation reaction zone maintained under conditions sufficient to hydrogenate said conjugated diolefins to saturated hydrocarbons and to hydrogenate said styrenes to alkyl aromatic hydrocarbons;

(d) introducing the total effluent from said reaction zone in substantially vaporous form into a second separation zone maintained under conditions sufficient to produce from 1% to 25% by volume of stabilized liquid based on the C_5+ hydrocarbons in said effluent, said liquid containing gum-like compounds;

(e) returning said stabilized liquid stream formed in the second separation zone to said first separation zone as feed thereto; and

(f) recovering hydrogenated hydrocarbons from the remaining vapor stream from the second separation zone.

2. Method according to claim **1** wherein said unstable feedstock comprises pyrolysis gasoline boiling from C_5 to 400° F.

3. Method according to claim **2** wherein said conditions in said second separation zone include a temperature from 250° F. to 450° F.

4. Method according to claim **3** wherein said conditions in said second separation zone are sufficient to produce said liquid stream comprising from 3% to 10% by volume of the C_5+ hydrocarbons in the total effluent from the reaction zone.

5. Method for stabilizing sulfur-containing pyrolysis gasoline which comprises the steps of:

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

(b) Withdrawing from said first zone a distillate fraction comprising C_5 to 400° F. hydrocarbons, mono-olefinic hydrocarbons, conjugated diolefins, styrenes, sulfur compounds, and a residual fraction containing gum-like compounds;

(c) admixing said distillate fraction with hydrogen and introducing the admixture into a first reaction zone containing a palladium catalyst under 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. ot 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 said styrenes to alkyl aromatic hydrocarbons without substantial conversion of said sulfur compounds to hydrogen sulfide and without substantial conversion of said mono-olefinic hydrocarbons to saturated hydrocarbons;

(d) introducing the total effluent from said first reaction zone in substantially vaporous form into a second separation zone maintained under conditions sufficient to produce a liquid stream comprising from 1% to 25% by volume based on the C_5+ hydrocarbons in said effluent, said liquid stream containing gum-like compounds;

(e) recycling entirely said liquid stream from step (d) to step (a) as said specified recycle stream;

(f) passing remaining hydrocarbons containing sulfur compounds from said second separation zone into a second reaction zone containing desulfurization catalyst under hydrogenating conditions including the presence of a molar excess of hydrogen, a temperature in the range of from about 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 said sulfur compounds to hydrogen sulfide and said mono-olefinic hydrocarbons to saturated hydrocarbons; and

(g) recovering stabilized pyrolysis gasoline in high concentration.

6. Method according to claim 5 wherein said stabilized pyrolysis gasoline includes aromatic hydrocarbons substantially free of olefins.

7. Method according to claim 5 wherein said desulfurization catalyst comprises nickel.

8. Method for stabilizing sulfur-containing pyrolysis gasoline which comprises the steps of:

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

(b) withdrawing from said first separation zone a distillate fraction comprising C_5 to 400° F. hydrocarbons, aromatic hydrocarbons, mono-olefinic hydrocarbons, conjugated diolefins, styrenes and sulfur compounds and a residual fraction containing gum-like compounds;

(c) admixing said distillate fraction with hydrogen and introducing the admixture into a first reaction zone containing a palladium catalyst under 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 said styrenes to alkyl aromatic hydrocarbons without substantial conversion of said sulfur compounds to hydrogen sulfide and without substantial conversion of said mono-olefinic hydrocarbons to saturated hydrocarbons;

(d) introducing the total effluent from said first reaction zone in substantially vaporous form into a second separation zone maintained under conditions sufficient to produce a liquid stream comprising from 1% to 25% by volume based on the C_5+ hydrocarbons in said effluent, said liquid stream containing gum-like compounds;

(e) recycling entirely said liquid stream from step (d) to step (a) as said specified recycle stream;

(f) passing remaining hydrocarbons into a third separation zone maintained under conditions sufficient to produce a fraction comprising C_5 compounds including mono-olefinic hydrocarbons, a bottoms material comprising C_9+ gasoline, and an aromatic hydrocarbon concentrate fraction containing sulfur compounds;

(g) introducing said aromatic hydrocarbon concentrate fraction into a second reaction zone containing desulfurization catalyst under hydrogenation conditions including the presence of 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

(h) recovering aromatic hydrocarbons substantially free of olefins and sulfur compounds from the effluent of said second reaction zone.

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

References Cited

UNITED STATES PATENTS

3,457,163	7/1969	Parker	208—255
3,429,804	2/1969	Sze et al.	208—144
3,448,039	6/1969	Tarhan	208—255
3,239,453	3/1966	Halik et al.	208—210
3,179,586	4/1965	Honerkamp	208—216

DELBERT E. GANTZ, Primary Examiner

J. M. NELSON, Assistant Examiner

U.S. Cl. X.R.

208—143, 211