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METHOD FOR HYDROGENATION

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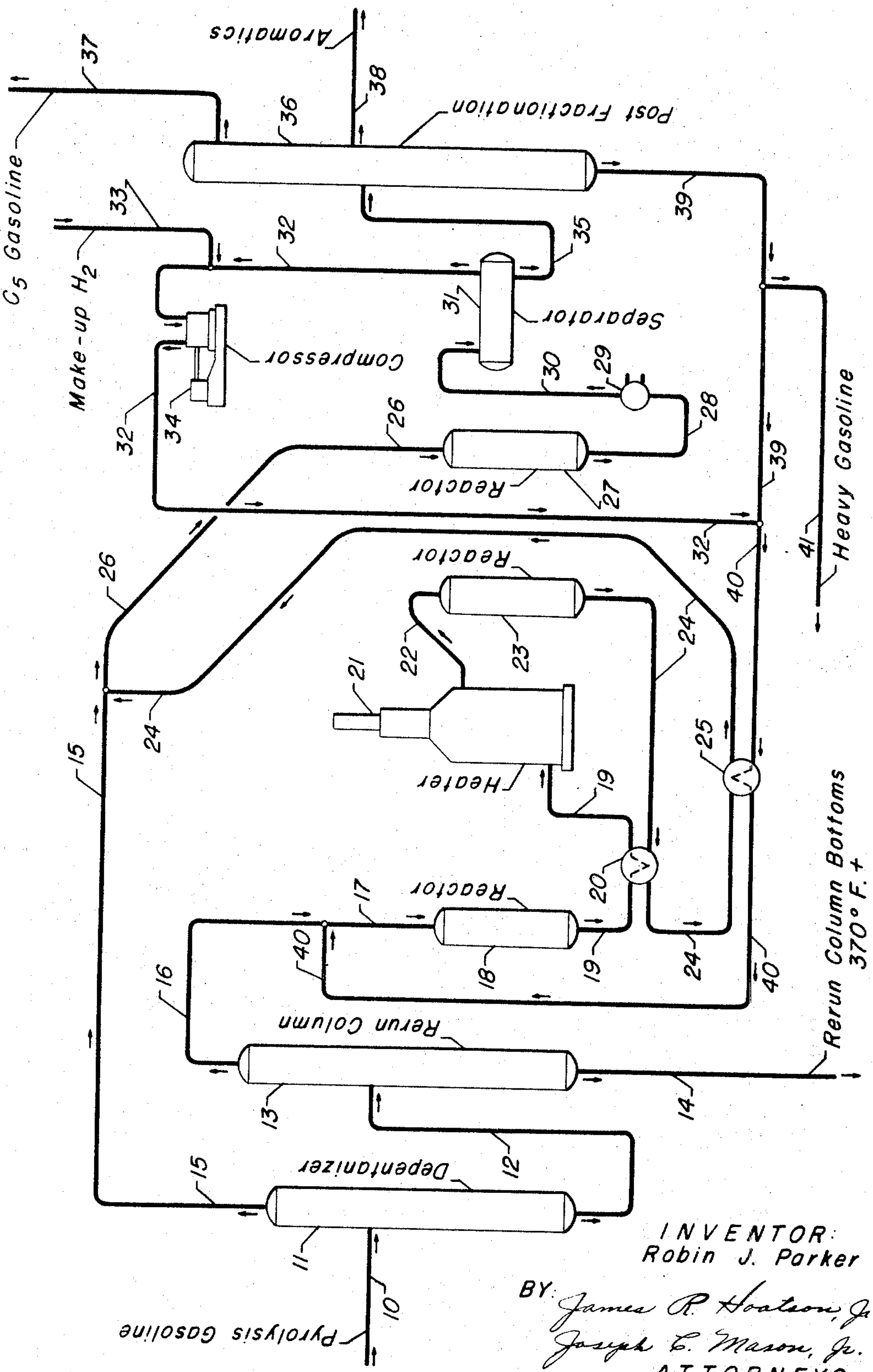

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METHOD FOR HYDROGENATION

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ABSTRACT OF THE DISCLOSURE

Method for stabilizing pyrolysis gasoline via hydrogenation. The C_5 and C_6–370° F. fractions of the gasoline are separately treated with hydrogen as follows: the heavier fraction is first hydrogenated over palladium catalyst and then desulfurized over nickel catalyst; this hydrogenated heavy fraction is mixed with the light fraction and the mixture subjected to hydrogenation over palladium catalyst.

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 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 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 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 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 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 C_5–400° F. gasolines. The diolefin compounds pose particular difficulty in the operation of the hydro-treating 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 povide 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 nonselectivity, 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 introducing a relatively heavy hydrocarbon feedstock containing diolefin and olefin compounds into a first reaction zone maintained under hydrogenation conditions including a relatively low temperature and the presence of a palladium-containing catalyst sufficient to convert diolefin compounds to olefin compounds; passing the total effluent from the first reaction zone 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; admixing the total effluent from the second reaction zone with a relatively light hydrocarbon feedstock containing diolefin and olefin compounds; passing said admixture into a third reaction zone maintained under hydrogenation conditions including a relatively low temperature and the presence of a palladium-containing catalyst sufficient to convert diolefin compounds; to olefin compounds; and recovering hydrogenated hydrocarbons in high concentration from the effluent of the third reaction zone.

Another embodiment of the invention includes the method hereinabove wherein said relatively heavy hydrocarbon feedstock comprises the C_5–400° F. fraction of pyrolysis gasoline and said relatively light hydrocarbon feedstock comprises the C_5 fraction of said pyrolysis gasoline.

A particular embodiment of this invention includes the methods hereinabove wherein said desulfurization catalyst comprises a nickel-containing catalyst.

The selectivity of the present invention is based on the discovery that the unique three-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 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 in the first reaction zone achieves selectively the conversion of diolefins to olefins without substantial desulfurization. This is accomplished by maintaining the temperature in the first stage below desulfurization temperatures. Satisfactory operation may be achieved in the first reaction zone at a temperature from 200° F. to 400° F., a pressure from 200 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity from 1 to 10 based on combined feed, and a molar excess of hydrogen. Usually, hydrogen in an amount from 500 to 5,000 standard cubic feet per barrel (s.c.f./b.) based on combined or total feed to the reactor will be satisfactory.

The operation performed in the second reaction zone of the present invention is primarily one of desulfurization 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 relatively heavy fraction of pyrolysis gasoline while simultaneously saturating the olefin compounds. By proper selection of operating conditions it was found that no substantial aromatic saturation was achieved. Particularly satisfactory operating conditions for the second reaction zone include a temperature from 600° F. to 800° F., a pressure substantially the same as the pressure in the first reaction zone and a catalyst particularly useful for desulfurization such as, for example, nickel-molybdate supported on alumina.

The operating conditions for the third reaction zone are particularly important. It is noted that in the practice of the invention the entire hydrocarbon effluent from the second reaction stage is admixed with the relatively light fraction obtained from the pyrolysis gasoline. The purpose of this admixing is to reduce the Diene Value of the total feed to the third reaction zone to a relatively low figure. It has been found that the C_5 fraction of pyrolysis gasoline contains, for example, from 50% to 80% by weight conjugated diolefin hydrocarbons. These diolefins would contribute significantly to polymer formation in the third reaction zone. Accordingly, it was found that the use of the substantially saturated hydrocarbon effluent from the second reaction zone as diluent was particularly advantageous. Again, the third reaction zone utilizes the particularly satisfactory palladium catalyst. The diolefins are selectively converted to olefins at a temperature from 290° F. to 550° F., preferably, 360° F. to 500° F. It was found that operating outside of these temperature limits did not produce a particularly desirable result. Therefore, it is important that the temperature of the third reaction zone be maintained within these temperature limits for otherwise the olefin hydrocarbons would be unduly saturated and/or the dienes would be converted to undesirable dicyclopentadiene which is extremely difficult to remove from the gasoline fraction. Frequently increased liquid hourly space velocity (LHSV) over those of the first reaction zone may be utilized herein. An LHSV of from 5 to 20 based on combined feed is satisfactory. Again, the pressure on the third reaction zone is substantially the same as that on the other two reaction zones allowing for normal pressure drop through the system.

Normally, the entire fresh hydrogen is added to the system only through the first reaction zone; although, the addition of fresh hydrogen to the other two reaction zones may be desirable from time to time.

By way of emphasis, it is to be noted that the present invention is based on the discovery that the palladium-containing catalyst is particularly useful in selectively converting dienes to olefins. 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 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 hydrogenation catalyst includes 0.4 weight percent palladium, 0.5 weight percent lithium on a $\frac{1}{16}$ inch spherical base. Broadly, then, the particularly preferred catalyst for the first and third reaction zones 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 a feedstock obtained from the pyrolysis of naphthas for the production of light olefinic gases such as ethylene. The pyrolysis reaction for the conversion of hydrocarbons into normally gaseous olefinic hydrocarbons is 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 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 tube, an inlet 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 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 utilized in practicing one embodiment of the invention.

DESCRIPTION OF THE DRAWING

Referring now to the drawing, a typical pyrolysis gasoline comprising C_5+ material separated from the effluent of a steam pyrolysis reaction zone is passed via line **10** into depentanizer tower **11**. Suitable conditions are maintained in depentanizer tower **11** to separate the feed to a C_5 fraction and a C_6+ fraction. The C_5 fraction contains primarily hydrocarbons comprising C_5 paraffins and naphthenes, C_5 olefins and C_5 diolefin hydrocarbons. There may in some cases be small amounts of light hydrocarbons such as the C_4 present, but usually this light hydrocarbon contaminant is not significant. The C_5 fraction is removed from depentanizer tower **11** for further use in the third reaction zone more fully discussed hereinbelow. The heavy portion of the feed is removed via line **12** and, preferably, is introduced into rerun column **13**. The purpose of column **13** is to produce a distinctly desired fraction, namely, a C_6–370° F. fraction of the pyrolysis gasoline which contains the greatest concentration of desirable aromatic hydrocarbons such as benzene, toluene, and xylene. In some instances columns **11** and **13** may be merged into a single column, but generally, it is preferable to maintain them as separate columns. The undesirable 370° F.+ material is removed from rerun column **13** via line **14** and disposed of by means known to those skilled in the art.

The desired C_6–370° F. fraction is passed via line **16** into admixture with a hereinafter described diluent stream from line **40** through line **17** into reactor **18** containing the preferred palladium catalyst. The total effluent from reactor **18** is withdrawn via line **19**, heated in exchanger **20**, raised considerably in temperature by heater **21**, and the heated effluent passed via line **22** into reactor **23**. It is to be noted that the entire effluent including hydrogen is passed directly from reactor **18** to reactor **23** without any intervening separation thereof. Normally, sufficient hydrogen has been added to the system, as hereinbelow discussed, so that additional quantities of hydrogen are not needed for the desulfurization reaction in reactor **23**.

The effluent from reactor **23** is passed through heat exchanger **20** wherein it gives up heat to the effluent from reactor **18** in line **19**, passes through heat exchanger **25** where it gives up additional heat to the hereinafter described diluent stream and into admixture with the previously mentioned C_5 fraction in line **15**. Generally, the entire effluent from reactor **23** is passed directly into reactor **27**; however, in some cases, it may be advisable to remove, by means not shown, hydrogen sulfide gas prior to introduction to reactor **27** since an excessive amount of hydrogen sulfide may cause mercaptan formation in the third reaction zone. Normally, however, as long as the feed in line **16** contains below 1,000 parts per million by weight (p.p.m.) of hydrogen sulfide, and typically, less than about 500 p.p.m., no separation of H_2S between reactor **23** and reactor **27** is necessary.

The combined mixture of C_5 hydrocarbons from line **15** and C_6+ saturated hydrocarbons in line **24** is passed via line **26** into reactor **27** wherein conditions are maintained to selectively convert the C_5 diolefins and C_5 olefin hydrocarbons. The presence of the saturated effluent in line **24** effectively reduces the Diene Value of the combined feed to reactor **27** so that polymer and gum formation in the third reaction zone are minimized. The effluent from reactor **27** is removed via line **28**, cooled in cooler **29**, and passed via line **30** into separation zone **31**.

Conditions are maintained in separation zone **31** whereby a gaseous fraction comprising hydrogen is removed

via line **32** and a normally liquid hydrocarbon fraction containing the desired hydrogenated products is removed via line **35**. The hydrogenated product containing stream in line **35** is then passed into post-fractionation facilities **36** for separation into desired fractions. A C_5 gasoline fraction is removed via line **37** and is suitable for gasoline blending since it still contains a substantial quantity of olefin hydrocarbons. An aromatics fraction rich in benzene, xylene, and toluene (BTX) is withdrawn via line **38** and is suitable for feed to a, for example, sulfolane solvent extraction unit since the material in line **38** is substantially olefin-free.

The remaining portion of the hydrogenated hydrocarbons represents recovered C_9+ material and is withdrawn via line **39**. If desired, a portion of this material is removed via line **41** and since it is substantially sulfur-free and diolefin-free, it may be mixed with the C_5 gasoline fraction from line **37** and passed into gasoline motor fuel blending facilities, not shown. Preferably, however, the material in line **39** is admixed with hydrogen from separator **31** which has been compressed in compressor **34** and being recycled via line **32**. The combined hydrogen and C_9+ material is passed via line **40** through heat exchanger **25** wherein it is heated significantly to reaction temperature and passed into admixture with the C_6–370° F. material from line **16** as discussed hereinabove. The amount of material returned via line **39** into reactor **18** is chosen so that the Diene Value of the combined feed to reactor **18** is less than 15, preferably, less than 12, and typically, from 5 to 10. It was found that by operating in this manner that polymer and gum formation in reactor **18** did not occur to any significant extent.

Thus, it is seen that in substance the present invention provides a method for stabilizing pyrolysis gasoline wherein diolefins are removed from the gasoline fraction without destroying the olefins while simultaneously removing diolefins, olefins, and sulfur compounds from the BTX aromatic fraction.

The following example is furnished to demonstrate the operation of the present invention. These typical operating conditions were chosen:

	Reactor #18	Reactor #23	Reactor #27
Temperature, ° F.	300	650	360
Pressure, p.s.i.g.	800	800	800
LHSV	3	3	6
Catalyst	Pd	Ni-moly	Pd

The feed to reactor **18** was a C_6–370° F. fraction separated from pyrolysis gasoline and the fresh feed to reactor **27** was a C_5 fraction separated from the same pyrolysis gasoline. The following material balances were obtained while operating under the conditions above and with the distinctly preferred catalyst previously mentioned:

TABLE I

	Raw Charge, Wt. Percent	Reactor #18 Fresh Charge, Wt. Percent	Reactor #18 Fresh Charge Product, Wt. Percent	Reactor #23 Fresh Charge Product, Wt. Percent	Reactor #27	
					C₅ Charge, Wt. Percent	Tot. Product (F.C.) Wt. Percent
Chemical Hydrogen Consumption		0.09		0.38	0.18	
C_5 P plus N	0.30				0.30	0.30
C_5 O	2.10				2.10	7.08
C_5 DiO	4.80				4.80	
C_6 P plus N	1.80	1.80	1.80	8.62		8.62
C_6 O	4.70	4.70	6.33			
C_6 DiO	1.60	1.60				
Benzene	26.40	26.40	26.40	26.14		26.14
C_7 P plus N	1.20	1.20	1.20	4.36		4.36
C_7 O	1.10	1.10	2.33			
C_7 DiO	1.20	1.20				
Toluene	25.40	25.40	25.40	24.65		24.65
C_8 P plus N	0.70	0.70	0.70	2.61		2.61
C_8 O	0.60	0.60	1.22			
C_8 DiO	0.60	0.60				
Xylenes	13.70	13.70	13.70	13.05		13.05
C_9–370° F. P plus N	0.40	0.40	0.40	2.04		2.04
C_9–370° F. O	0.40	0.40	0.81			
C_9–370° F. DiO	0.40	0.40				
C_9–370° F. Arom	8.50	8.50	8.50	7.70		7.70
370° F. Plus	4.10					
	100.00	88.70	88.79	89.17	7.20	96.55

Rerun Col. Bottoms 4.10.

It was noted from the above example that BTX available was not reduced, the olefin content of the gasoline portion of the C_5's was not significantly lessened, and the olefin content for the aromatic portion was effectively removed.

PREFERRED EMBODIMENT

Thus, a preferred embodiment of the present invention provides a method for stabilizing pyrolysis gasoline which comprises the steps of: (a) separating pyrolysis gasoline into a relatively light fraction and a relatively heavy fraction; (b) introducing said heavy fraction into a first hydrogenation reaction zone under conditions including the presence of a palladium-containing catalyst sufficient to convert diolefins to olefins; (c) passing the total effluent from the first reaction zone into a second hydrogenation reaction zone under conditions including the presence of a desulfurization catalyst sufficient to substantially saturate olefins and convert sulfur compounds to hydrogen sulfide; (d) admixing the total effluent from said second zone with said relatively light fraction; (e) passing said admixture into a third hydrogenation reaction zone under conditions including the presence of a palladium-containing catalyst sufficient to convert diolefins to olefins; and, (f) recovering stabilized pyrolysis gasoline from the effluent of the third reaction zone.

Another preferred embodiment of the invention includes the preferred embodiment hereinabove wherein a portion of said stabilized gasoline from Step (f) is returned to Step (b) as diluent in said heavy fraction in an amount sufficient to maintain the combined feed to said first reaction zone at a Diene Value of less than 12.

A distinctly preferred embodiment of this invention provides a method for hydrogenating a sulfur-containing pyrolysis gasoline which comprises the steps of: (a) separating said gasoline into a relatively light fraction comprising C_5 hydrocarbons and a relatively heavy fraction comprising C_6 to 400° F. hydrocarbons; (b) admixing said heavy fraction with hydrogen and a hereinafter specified recycle stream and introducing said admixture into a first reaction zone containing hydrogenation catalyst comprising palladium on lithiated alumina under conditions including a temperature from 300° F. to 400° F., a pressure from 200 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity from 1 to 10 based on combined feed and a molar excess of hydrogen sufficient to convert dienes to olefins without substantial conversion of sulfur compounds to hydrogen sulfide; (c) introducing the total effluent from the first reaction zone into a second reaction zone containing desulfurization catalyst comprising nickel-molybdate on alumina under conditions including a temperature from 600° F. to 800° F. sufficient to substantially convert olefins to saturates and sulfur compounds to hydrogen sulfide; (d) passing the total effluent from the second reaction zone together with said relatively light fraction into a third reaction zone containing hydrogenation catalyst comprising palladium on lithiated alumina under conditions including the presence of hydrogen at a temperature from 290° F. to 550° F. and a liquid hourly space velocity from 5 to 20 based on combined feed sufficient to convert dienes to olefins; (e) separating the total effluent from the third reaction zone into a gaseous fraction comprising hydrogen, a C_5 olefin containing hydrocarbon fraction suitable for gasoline blending, an olefin free aromatic hydrocarbon rich fraction suitable for aromatics extraction, and a gasoline fraction comprising C_9+ hydrocarbons; (f) returning at least a portion of said gasoline fraction to the first reaction zone as said specified recycle stream; and, (g) recycling gaseous fraction of Step (e) to the first reaction zone of Step (b).

The invention claimed:

1. Method for hydrogenating sulfur-containing pyrolysis gasoline which comprises the steps of:
   (a) separating said gasoline into a relatively light fraction comprising C_5 hydrocarbons and a relatively heavy fraction comprising C_6 to 400° F. hydrocarbons;
   (b) admixing said heavy fraction with hydrogen and a hereinafter specified recycle stream and introducing said admixture into a first reaction zone in the presence of a palladium-containing catalyst under conditions including a temperature from 200° F. to 400° F., a pressure from 200 p.s.i.g. to 1200 p.s.i.g., a liquid hourly space velocity from 1 to 10 based on combined feed, and a molar excess of hydrogen, sufficient to convert dienes to olefins without substantial conversion of sulfur compounds to hydrogen sulfide;
   (c) introducing the total effluent from the first reaction zone into a second reaction zone containing desulfurization catalyst comprising nickel-molybdate on alumina under conditions including a temperature from 600° F. to 800° F. sufficient to substantially convert olefins to saturates and sulfur compounds to hydrogen sulfide;
   (d) passing the effluent from the second reaction zone together with said relatively light fraction into a third reaction zone under conditions including the presence of a palladium-containing catalyst, a molar excess of hydrogen, a temperature from 290° F. to 550° F., and a liquid hourly space velocity from 5 to 20 based on combined feed, sufficient to convert dienes to olefins;
   (e) separating the total effluent from the third reaction zone into a gaseous fraction comprising hydrogen, a C_5 olefin-containing hydrogen fraction suitable for gasoline blending, an olefin-free aromatic hydrocarbon-rich fraction suitable for aromatics extraction, and a gasoline fraction comprising C_9+ hydrocarbons;
   (f) returning at least a portion of said gasoline fraction to the first reaction zone as said specified recycle stream; and,
   (g) recycling gaseous fraction of Step (e) to the first reaction zone of Step (b).

2. Method according to claim 1 wherein the hydrogen admixed with the heavy fraction in Step (b) is in an amount from 500 to 5,000 s.c.f./b. based on combined feed.

3. Method according to claim 1 wherein said palladium-containing catalyst comprises palladium on lithiated alumina.

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HERBERT LEVINE, *Primary Examiner.*

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