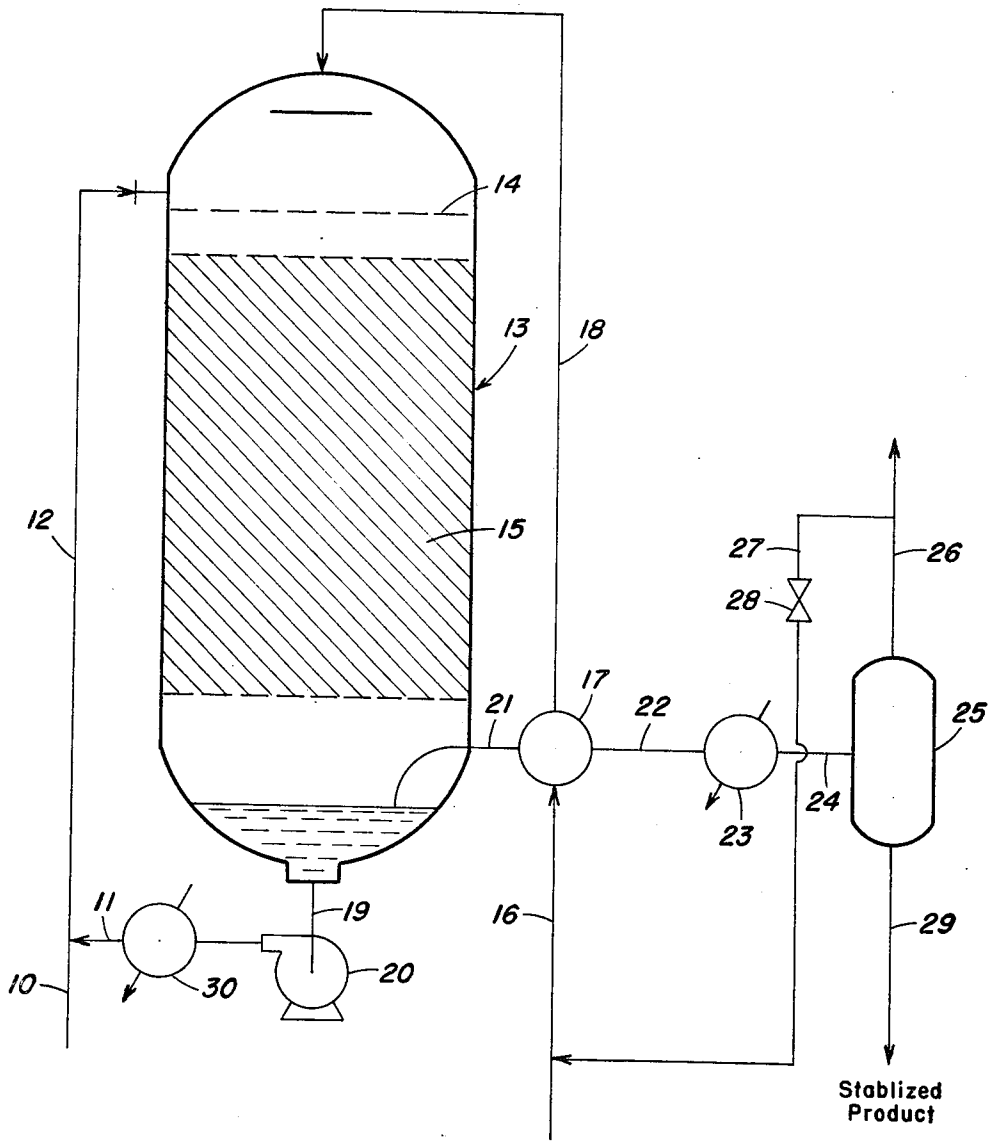
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HYDROTREATING OF PYROLYSIS GASOLINE (DRIPOLENE)

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HYDROTREATING OF PYROLYSIS GASOLINE (DRIPOLENE)

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Continuation-in-part of application Ser. No. 585,990, Oct. 11, 1966, which is a continuation-in-part of application Ser. No. 376,358, June 19, 1964. This application Aug. 20, 1968, Ser. No. 754,065

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ABSTRACT OF THE DISCLOSURE

A process for hydrotreating a pyrolysis gasoline fraction, containing diolefins, mono-olefins, styrenes and other aromatic hydrocarbons, to selectively hydrogenate the diolefins and styrenes wherein the pyrolysis gasoline fraction is hydrogenated in the liquid phase in the presence of a noble metal catalyst, in a reactor having an inlet temperature between 120° F. and 400° F., and a portion of the hydrotreated product is recycled to the feed to both preheat the feed to the hydrogenation temperature and limit the temperature rise within the reactor to 100° F. or less. A hydrogen containing gas stream is introduced into the reactor to provide a logarithmic mean partial pressure of hydrogen of 80–500 p.s.i.g.

This application is a continuation-in-part of application Ser. No. 585,990, filed Oct. 11, 1966, which in turn is a continuation-in-part-of application Ser. No. 376,358, filed June 19, 1964 both applications now abandoned.

This invention relates to the hydrotreating of pyrolysis gasoline, commonly referred to in the art as dripolene, and more particularly, to the selective hydrogenation of diolefins and styrenes contained in the by-product pyrolysis gasolines obtained from the production of olefins, particularly ethylene, by the pyrolysis of a hydrocarbon.

During the production of olefins, particularly ethylene by the pyrolysis of hydrocarbons, there is produced in addition to the desired olefins, a considerable quantity of a by-product boiling in the gasoline range (herein sometimes referred to as "pyrolysis gasoline" or "dripolene"). Pyrolysis gasoline contains considerable amounts of diolefins, such as butadiene, isoprene, cyclopentadiene, etc., as well as residual amounts of olefins, such as pentenes, hexenes, heptenes, styrenes, etc. The pyrolysis gasoline also contains large quantities of aromatic compounds, such as benzene, toluene, ethylbenzene and xylenes. Such aromatic compounds are of value if recovered in high purity.

The presence of considerable amounts of diolefins and styrenes in the pyrolysis gasoline is undesirable, since such diolefins and styrenes are unstable and tend to polymerize to higher molecular weight compounds. The tendency of the diolefins to polymerize is particularly influenced by air and light. Gummy materials, which are formed, tend to deposit on feed lines, carburetors, valves and the like, when a pyrolysis gasoline, containing diolefins and styrenes, is blended with other gasolines and subsequently utilized as fuel in internal combustion engines.

In order to use pyrolysis gasolines in gasoline blending, it is necessary to eliminate substantially all of the diolefins and styrenes, and this can be accomplished by hydrogenating the styrenes to the corresponding aromatics, and the conjugated diolefins to the corresponding mono-olefins. In fact, for gasoline blending purposes, it is not desirable to hydrogenate the diolefins completely to form saturated hydorcarbons, since saturated hydrocarbons of the paraffin type usually have lower octane ratings than the corresponding mono-olefins.

As hereinbefore mentioned, a pyrolysis gasoline also contains valuable aromatic compounds if the same can be recovered in high purity. The presence of minor quantities of olefins in the pyrolysis gasoline hinders the effective separation of such aromatic compounds from the pyrolysis gasoline by known recovery processes. Consequently, in this instance, it is desirable to hydrogenate the olefins completely to form saturated hydrocarbons thereby permitting the recovery of aromatics in high purity from the pyrolysis gasoline by known recovery processes.

At present, the processes available for hydrotreating of pyrolysis gasolines to selectively hydrogenate the diolefins may be classified into two groups. The first group of processes uses a nickel sulfide type catalyst, and operates at temperatures in the range of 300° F. to more than 600° F. The reactor used contains a number of catalyst beds in series and the exothermic heat of reaction is controlled by injecting cold recycled hydrogen gas in between the various beds. As a result of the higher operating temperatures in the reactor design, the feed, prior to hydrotreating, must be preheated to 300° F. or higher, and thus there is a great tendency for the formation of gummy materials in the reactor preheater exchangers. Additionally, the life of nickel sulfide type catalyst is relatively short and decreases steadily during operation requiring gradually increasing operating temperature as a result of deposits on the catalyst. These deposits can be removed by controlled oxidation, but the oxidized catalyst cannot be regenerated to its full initial activity. Temperature control of reactors in plants of this type is not satisfactory and on-stream efficiency is poor.

The second group of processes utilizes a noble metal catalyst and generally operates at temperatures below about 125° F. At such temperatures, the feed is in the liquid phase and need not be preheated to any high temperature, and the tendency for the diolefins to polymerize is greatly minimized. As a result of such low temperatures, however, the catalyst cannot tolerate a feed stock with any significant sulfur content, say two hundred to three hundred p.p.m., or more. Additionally, in order to maintain such low temperatures, the reactor is designed similar to a tubular heat exchanger with catalyst inside the tubes and a circulating coolant outside the tubes. This is satisfactory for relatively small sized plants, but becomes extremely costly for large sized plants. Also, because of this particular reactor system, regeneration of catalyst by controlled burning off of the carbonaceous deposits presents a difficult mechanical design since regeneration must be conducted at temperatures of from 850° F. to 1050° F.

It is an object of my invention to provide an improved process and reactor system for hydrogenating diolefins and styrenes contained in a pyrolysis gasoline (dripolene).

A still further object of my invention is to selectively hydrogenate the diolefins and styrenes present in a pyrolysis gasoline.

A still further object of my invention is to provide a hydrogenation reactor system such that the reaction temperature can be controlled within narrow limits at the optimum range for selective hydrogenation of the diolefins and stryrenes contained in pyrolysis gasoline.

Another object of my invention is to selectively hydrogenate the diolefins and styrenes present in a pyrolysis gasoline in a manner that essentially eliminates coke and gum formation.

Further objects and advantages of my invention will become apparent from the following description taken in conjunction with the accompanying drawing which is a schematic flow diagram of my invention.

In accordance with my invention, a pyrolysis gasoline, is hydrotreated in the liquid phase with a noble metal catalyst to selectively hydrogenate the diolefins and styrenes contained in the pyrolysis gasoline. The reactor is operated at an inlet temperature of from about 120° F. to about 400° F., and a pressure of from 200 to 1000 p.s.i.g., depending upon the feed stock, its sulfur content and the hydrogen gas purity (i.e., contents of inerts, such as methane or nitrogen). The preferred reaction inlet temperature range is between about 180 F. and about 400° F. It is to be understood that the reaction inlet temperature will generally be increased as the catalyst on-stream time increases to compensate for loss of catalyst activity. Fresh feed to the reactor is mixed with recycled hot hydrotreated gasoline from the bottom of the reactor to heat the feed to the hydrotreating reaction conditions and the mixture is introduced into the top of the reactor and passed co-currently with hydrogen in the presence of the noble metal catalyst. In this manner, the fresh feed is brought to reaction temperature without indirect preheat above 175° F. preferably not above 125° F., at which temperatures the tendency to polymerize is essentially nil. In many cases, the pyrolysis gasoline to be hydrotreated is at a temperature of around 125° F. as a result of previous processing steps and therefore by proceeding in accordance with the process of the invention, no indirect preheating of the feed is required. The net reactor effluent is cooled and the treated product separated from the uncondensed gases. The noble metal catalyst, is generally platinum or palladium on a suitable support.

The hydrogenation of diolefins contained in a pyrolysis gasoline is highly exothermic, and depending on the quantity of diolefins and styrenes contained in the pyrolysis gasoline, such hydrogenation may result in severe temperature increases within the reactor. In accordance with the process of the invention, such temperature increases are minimized by the recycle of a portion of hydrotreated product, as hereinabove described, resulting in a minimization of catalyst deposits. By maintaining a recycle ratio of from 1:1 to 10:1, reactor effluent to reactor fresh feed, it is possible to reduce the temperature rise within the reactor to 100° F. or less, preferably 50° F. or less. With lower diolefins content and gasolines requiring less hydrogen absorption, the heat liberated is less, and lower recycle ratios may be used to give the desired temperature control. With higher hydrogen absorption, a higher recycle ratio is needed. Thus, the pyrolysis gasoline may be easily hydrotreated in the liquid phase with high selectivity at the preferred temperature range and with the elimination of a need for a tubular reactor. Additionally, the reactor system is readily adaptable to periodic regeneration of the catalyst in situ since there is no requirement of a tubular reactor. Also, because of the excellent temperature control, it has been found that small increments in temperature rise can be easily effected to compensate for the increased sulfur content of the feed stock. For example, when the reactor is shifted from a feed containing 40 p.p.m. sulfur to one containing 300 p.p.m. an increase in operating temperature of about 10° F. compensates for the deactivating effect of sulfur on the catalyst. In fact, hydrogenation of the diolefins and styrenes appear to be more selective. It is actually advantageous at times to add some sulfur purposely to a low sulfur feed and operate at a higher temperature in order to obtain better selectivity.

The hydrogen containing gas generally comprises between about 40% and about 100% hydrogen, with the remainder of the gas being an inert, such as methane, and the gas is introduced into the reactor in a quantity which is at least sufficient to produce a hydrotreated product having the desired diolefine and styrene content; i.e., a diene number of less than 3.0, as hereinafter described. As a distinct feature of the invention, the hydrogen-containing gas is introduced in an amount to provide a hydrogen excess, with hydrogen excess being defined as the amount of hydrogen introduced into the reactor over the amount of hydrogen consumed in the reactor in producing an effluent having the desired diene number. The hydrogen excess employed is sufficient to achieve a logarithmic mean partial pressure of hydrogen within the reactor of between about 80 and about 500 p.s.i.g. which corresponds to an excess of hydrogen of between about 1% and about 200%, preferably between about 4% and about 60%. It has been found that for most pyrolysis gasoline feeds the actual hydrogen consumption is between about 200 and about 600 s.c.f. per barrel of feed stock.

As another distinct feature of the invention at least 75% of the pyrolysis gasoline and recycle is maintained in the liquid phase in the hydrotreating reactor. The degree of vaporization of total liquid feed to the reactor; i.e., pyrolysis gasoline plus recycle, is a function of the temperature, pressure, composition of the total liquid feed and ratio of light gas (e.g., hydrogen plus methane) flow to the total liquid feed. The ratio of hydrogen rich gas to pyrolysis gasoline feed determines the logarithmic mean partial pressure and therefore, must be sufficient to provide a logarithmic mean partial pressure within the hereinabove described range. This ratio, however, also affects the degree of vaporization of the total liquid feed and consequently the ratio actually employed is chosen between a lower limit imposed by the logarithmic mean hydrogen pressure requirements, and an upper limit imposed by the necessity to limit vaporization of total liquid feed so as not to exceed 25%.

The pyrolysis gasoline (dripolene) employed in the invention, obtained as a by-product in the pyrolysis of a hydrocarbon, is a normally liquid product which boils between 75° F.–500° F., generally between 120° F.–400° F. and is characterized by a large proportion of aromatic hydrocarbons, styrenes, diolefins and mono-olefins. The pyrolysis gasoline generally has a bromine number of at least 30, generally within the range of 40 to about 80, and a diene number of at least 10, generally within the range of 20 to about 50. After hydrotreating the pyrolysis gasoline, the hydrotreated product has a diene number of less than 3, generally less than 2, indicating that the product is essentially free of diolefins, and a bromine number of between 20 and about 70, indicating that the product still contains mono-olefinic components of the pyrolysis gasoline. The term "pyrolysis gasoline" or "dripolene" as used herein refers to the hereinabove described fraction or a portion thereof.

Referring to the drawing, a pyrolysis gasoline or dripolene in line **10** at a temperature below about 175° F., preferably below 125° F., is mixed with hot recycle reactor effluent in line **11** to heat the feed to the hydrotreating reactor inlet temperature as more fully hereinafter described, and the mixture is introduced through line **12** into a reactor, generally indicated as **13**.

The reactor **13** includes a vapor-liquid distributor plate **14** and catalyst bed, generally indicated as **15**. The catalyst bed is filled with a noble metal catalyst, such as platinum or palladium on a suitable support. Hydrogen, or a mixture of hydrogen and an inert, such as methane in line **16** is heated during passage through heat exchanger **17** and introduced through line **18** into reactor **13** and passes co-currently through reactor **13** with the feed from line **12**. The reactor is operated at an inlet temperature of between about 120° F. and about 400° F., preferably between about 180° F. to about 400° F., and the reactor is operated at a pressure of from 200 to 1000 p.s.i.g., preferably 400 to 900 p.s.i.g.

As hereinbefore described, the preferred reactor inlet temperature depends upon the feed stock and its sulfur content; a higher sulfur content requiring a higher operating temperature. The reactor pressure depends upon hydrogen purity and reactor temperature. Lower hydrogen purity requires higher total pressure to provide the same

hydogen partial pressure. In order to keep at least 75% of the feed in the liquid phase, higher pressure is needed with higher temperature.

A portion of the liquid effluent, essentially free of diolefins and styrenes and containing aromatic and monoolefinic components of the pyrolysis gasoline, is withdrawn from reactor **13** through line **19** by pump **20** and constitutes the liquid recycle injected into line **11** to heat the feed in line **10** to the desired reaction inlet temperature. The ratio of recycled reactor effluent to fresh feed is generally adjusted to between about 1:1 to 10:1 preferably 2:1 to 5:1 in order to limit the temperature rise within the reactor **13** to 100° F. or less, preferably 50° F. or less. Net reactor effluent consisting of vapor and liquid is withdrawn from reactor **13** through line **21** and cooled in heat exchanger **17** by passing in indirect heat exchange with the gaseous feed in line **16**. The net reactor effluent is withdrawn from heat exchanger **17** through line **22** and passed through heat exchanger **23** wherein the effluent is cooled to near ambient temperatures of from 85° F. to 100° F. so as to condense substantially all of the hydrocarbons boiling above methane.

The now cooled effluent is withdrawn from heat exchanger **23** through line **24** and passed to separator **25**. An overhead gaseous stream including methane and unreacted hydrogen is withdrawn through line **26** and may be returned through line **27** under the control of valve **28** to line **16** should a low partial pressure of hydrogen be desired. A stabilized product is withdrawn from separator **25** through line **29** and may be used to blend with other gasoline fractions, or passed to subsequent processing units (not shown) in order to later recover the aromatic hydrocarbons contained in the stabilized product.

The recycle line **11** is provided with a cooler **30** to provide temperature control of the recycle. Thus, the exothermic heat of reaction in the reactor **13**, in most cases exceeds that required to maintain the reactor inlet temperature at the desired level. In such cases, the recycle is cooled in cooler **30** so as to provide the desired inlet temperature in line **12**. It is to be understood, however, that the recycle is never cooled to a temperature below the desired reactor inlet temperature.

As hereinbefore mentioned, should the quantity of aromatic compounds contained in the pyrolysis gasoline be sufficient to justify recovery thereof, the stabilized product in line **29** or a subsequently fractionated portion thereof, is passed to a subsequent unit wherein all the olefins contained in the product are selectively hydrogenerated to saturated hydrocarbons without affecting the aromatics. Thus, the aromatic hydrocarbons can be conveniently separated from the other saturated hydrocarbons contained in the stabilized product by conventional techniques, such as, liquid-liquid extraction, azeotropic distillation, and adsorption. Hydrogenation of the olefins may be effected at known operating conditions using commercially available catalyst compositions.

The following examples are illustrative of the invention but the scope of the invention is not to be limited thereby.

EXAMPLE I

To further illustrate my invention, 308 pounds per hour of a pyrolysis gasoline at a temperature of 85° F. and having characteristics and composition set forth in Table A is mixed with 1080 pounds per hour of recycle reactor effluent at a temperature of 320° F. and introduced into reactor **13** at 270° F.

Table A

Feed stock:	
Sp. gr.	0.882
Avg. mol. wt.	84
Diene value [1]	37
Existent gum, mg./100 cc.	29.8
Octane No. (research method, clear)	100

Composition:	Wt. percent
Butadine	1.7
C_4 olefins	0.3
Butanes	0.1
Cyclopentadiene	3.3
Isoprene	2.3
C_5 olefins	2.3
Pentanes	0.2
Benzene	52.0
C_6 diolefins	0.9
C_6 olefins	0.4
Toluene	10.7
C_7 diolefins	0.7
C_7 olefins	0.2
Styrene	5.7
C_2 benzenes	1.3
Vinylcyclo-Hexene	0.3
C_8 olefins	0.3
Octanes	0.4
Indene	1.6
Indane	1.1
C_3 benzenes	0.2
Naphthalenes	1.4
Dicyclopentadiene	8.3
Substituted dicyclopentadienes	2.5
Substituted naphthalenes	1.2
Other	0.6
Total	100.0

[1] Calculated from component analysis.

2.065 pound mols per hour of a gaseous stream in line **18** at a temperature of 150° F. and comprising 65.7 mol percent hydrogen and 34.3 mol percent methane is introduced into the reactor **13**. The reactor is maintained at an inlet temperature of 270° F. and an outlet temperature of 320° F. and at a pressure of 880 p.s.i.g. 310.5 pounds per hour of net reactor effluent consisting of hydrotreated feed along with unreacted hydrogen and methane is withdrawn through line 21 and subsequently cooled to a temperature of 315° F. and 100° F. during passage through heat exchangers **17** and **23**, respectively. Approximately 474 s.c.f. of hydrogen is found to have combined with the feed stock. The thus cooled reactor effluent is introduced into separator **25** from which an overhead gaseous stream containing hydrogen and methane is withdrawn. A stabilized product having the properties set forth in Table B is withdrawn from separator **25** and passed to subsequent processing units.

Table B

Product:	
Sp. gr.	0.881
Diene value	0.48
Existent gum, mg./100 cc.	1.6
Octane No. (research method clear)	100

EXAMPLE II

To further illustrate my invention, 1700 cc. per hour of a liquid dripolene stream at a temperature of 85° F. obtained from the pyrolysis of propane and having the characteristics set forth in Table C was mixed with 5950 cc. per hour of recycle reactor effluent at a temperature of 320° F. and introduced into reactor 13 at a resulting temperature of 270° F. The catalyst bed of the reactor contained 283 cc. of 3/16" x 1/8" catalyst pellets of palladium supported on alumina.

Table C

Boiling range, °F.	124–377
Octane No. (research method, clear)	100+
Bromine No.	65
Diene Value [1]	46
Sulfur, p.p.m.	80
Existent gum, mg./100 cc.	47
Induction period, min.	120

[1] Calculated from component analysis.

A gaseous stream in line **18**, at a temperature of 150° F. and comprising 11.12 s.c.f. per hour of 65 mol. percent hydrogen and 35 mol. percent methane, was introduced into the reactor **13**. The outlet temperature of the reactor was 320° F. and the outlet pressure was 880 p.s.g. The net reactor effluent consisting of hydrotreated feed plus unreacted hydrogen was withdrawn through line **21** and subsequently cooled to a final temperature of 100° F. during passage through heat exchanger **23**. Approximately 70 percent of the hydrogen was found to have combined with the feed stock.

The thus cooled reactor effluent was introduced into separator **25** from which an overhead gaseous stream containing hydrogen and methane was withdrawn. A stabilized product having the properties set forth in Table D was withdrawn from separator **25**.

Table D

Boiling range, °F.	124–377
Octane No. (research method, clear)	100
Bromine No.	26
Diene value	0.7
Sulfur, p.p.m.	N.A.
Existent gum, mg./100 cc.	1.6
Induction period, min.	1400+

EXAMPLE III

A pyrolysis gasoline at a temperature of 85° F. and a feed rate of 600 cc./hr. is combined with 2100 cc./hr. of recycled reactor effluent at a temperature of 320° F. and introduced into hydrotreating reactor **13**, operated at a pressure of 880 p.s.i.g., at a temperature of 270° F. The pyrolysis gasoline has a diene number of 46 and a bromine number of 65. A hydrogen containing gas stream, containing 65 percent hydrogen, is introduced into reactor **13** at the rate of 3.94 s.c.f. per hour.

The outlet temperature of reactor **13** is 320° F. and the hydrotreated product has a diene number of 0.7 and bromine number of 26.

The process of the invention is extremely effective for the selective hydrogenation of diolefins and styrenes in a pyrolysis gasoline fraction (dripolene). The use of a portion of the hydrotreated effluent to heat the hydrotreating feed to hydrotreating reaction conditions, in combination with the other processing conditions of the invention, essentially eliminates coke and gum formation and in addition prevents severe temperature increases within the hydrotreating reaction; i.e., generally a temperature increase of no greater than 100° F., preferably no greater than about 50° F.

While I have shown and described a preferred embodiment of m invyention, I am aware that variations may be made thereto and, therefore, desire a broad interpretation of my invention within the scope of the disclosure herein and the following claims.

What is claimed is:

1. A process for hydrotreating pyrolysis gasoline, containing mono-olefins, diolefins, styrene and other aromatic compounds, to hydrogenate the diolefins and styrenes contained therein with the essential elimination of coke and gum formation which comprises:

(a) mixing heated hydrotreated product with a pyrolysis gasoline to directly heat said pyrolysis gasoline to a hydrotreating inlet temperature of between about 120° F. and about 400° F.;

(b) introducing said mixture from step (a) and a gaseous fraction containing hydrogen into a hydrotreating reaction zone containing a noble metal catalyst, said reaction zone being maintained at an inlet temperature between about 120° F. and about 400° F.;

(c) withdrawing a hot hydrotreated product, essentially free of the diolefins and styrenes of the pyrolysis gasoline and containing the other aromatic hydrocarbons and the mono-olefins of the pyrolysis gasoline from said zone, said hydrotreated product being at a temperature greater than the temperature of the pyrolysis gasoline mixed in step (a);

(d) passing a portion of said hot hydrotreated product from step (c) to step (a) without separation of any component and without cooling thereof to a temperature below the temperature of the pyrolysis gasoline in step (a) as the heated hydrotreated product to heat said pyrolysis gasoline;

(e) recovering the remaining portion of said hydrotreated product.

2. The process of claim **1** wherein the ratio of said portion of hydrotreated product combined with said pyrolysis gasoline is from about 1:1 to about 10:1.

3. The process of claim **2** wherein the pyrolysis gasoline is at a temperature below about 175° F. prior to being mixed with the hydrotreated portion.

4. The process of claim **3** wherein the pressure in the reaction zone is maintained at between about 200 to about 1000 p.s.i.g.

5. The process of claim **4** wherein the gaseous fraction introduced into the reaction zone is in an amount sufficient to provide a logarithmic mean hydrogen partial pressure of 80 to 500 p.s.i.g., the logarithmic mean pressure employed being an amount whereby at least 75% of the pyrolysis gasoline and recycle is in the liquid phase.

6. The process of claim **5** wherein the amount of hydrotreated product portion passed to step (a) is sufficient to maintain the temperature rise within the reactor at no greater than about 50° F.

7. The process as defined in claim **5** wherein the gaseous fraction contains between about 40% and about 100% hydrogen.

8. The process as defined in claim **5** wherein the reactor inlet temperature is between about 180° F. and about 400° F.

9. The process as defined in claim **5** wherein the hydrotreated product has a diene number of less than about 3.0 and a bromine number of between about 20 and about 70.

10. The process as defined in claim **3** wherein at least 75% of the pyrolysis gasoline is maintained in the liquid phase in the reaction zone.

11. The process as defined in claim **10** wherein the catalyst is a supported palladium catalyst.

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