METHOD FOR HYDROGENATION

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

Filed Apr. 28, 1967, Ser. No. 634,554

Int. Cl. C10G 23/04, 23/02, 31/14

U.S. Cl. 286—57

3 Claims

ABSTRACT OF THE DISCLOSURE

Method for stabilizing pyrolysis gasoline via hydrogenation. The C₄ and C₅-370° 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 diolefins and olefins 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 C₄-400° 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 C₅-400° F. gasoline. 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 provide selectivity in the hydrotreating unit. For example, the hydrotreatment reaction may not match with the conversion of diolefins to olefins but will frequently saturate the amount of olefins completely and even hydrotreat 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 hydrotreated, 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.

Therefor, 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 C₅-400° F. fraction of pyrolysis gasoline and said relatively light hydrocarbon...
feedstock comprises the C₅ fraction of said pyrolysis gasoline.

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

The selectivity of the present invention is based on the discovering any of the well-known 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 naphtha 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 maximum excess of hydrogen. Usually, hydrogen in an amount from 500 to 5000 standard cubic feet per barrel (s.e.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 that 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 olefinic 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 zone is admixed with the relatively light fraction obtained from the pyrolysis gasoline. The purpose of this admixing is to reduce the Dienes Value of the total feed to the third reaction zone to a relatively low figure. It has been found that the C₅ fraction of pyrolysis gasoline contains, for example, from 5% to 80% by weight of conjugated diolefins. The 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, 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 heavy olefin fraction of gasoline 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 catalysts are 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 3.75% by weight of palladium incorporated by way of an impregnation technique using the proper quantities of diintri-dianiisole 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. Distinctly preferred catalyst for the first and third reaction zones of the present invention comprises lithiated alumina containing from about 0.05% to about 5% by weight of palladium.

The practice of the present invention as previously noted is particularly applicable to a feedstock obtained from the pyrolysis of naphtha 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 3 to 10 seconds. Preferably, 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 C₅+ material separated from the effluent of a steam pyrolysis reaction zone is passed via line 10 into dephenanizer tower 11. Suitable conditions are maintained in dephenanizer tower 11 to separate the feed to C₅ fraction and a C₅+ fraction. The C₅ fraction contains primarily hydrocarbons comprising C₅ paraffins and naphthenes, C₅ olefins and C₅ diolefins hydrocarbons. There may in some cases be small amounts of light hydrocarbons such as the C₅ present, but usually this light hydrocarbon contaminant is not significant. The C₅ fraction is removed from dephenanizer 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 col-
The purpose of column 13 is to produce a distinctly desired fraction, namely, a C$_{370}$° 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 reaction column 13 via line 14 and disposed of by means known to those skilled in the art.

The desired C$_{370}$° 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 hereinafter 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 whereby 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$_{6}$ 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 except in 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$_{2}$S between reactor 23 and reactor 27 is necessary.

The combined mixture of C$_{6}$+ saturated 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$_{6}$ diolefins and C$_{6}$ 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 via line 35 is then passed into post-fractionation facilities for separation into desired fractions. A C$_{6}$ 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, sulfonate solvent extraction unit since the material in line 38 is substantially olefin-free.

The remaining portion of the hydrogenated hydrocarbons represents recovered C$_{6}$+ 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$_{6}$ 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$_{6}$+ 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$_{370}$° F. material from line 16 as discussed hereinafore. 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 sulfate compounds from the BTEX aromatic fraction.

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

<table>
<thead>
<tr>
<th>Reactor #18</th>
<th>Reactor #23</th>
<th>Reactor #27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F.</td>
<td>900</td>
<td>650</td>
</tr>
<tr>
<td>Pressure, p.s.i.</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>LHSV</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pd</td>
<td>Ni-moly</td>
</tr>
</tbody>
</table>

The feed to reactor 18 was a C$_{370}$° F. fraction separated from pyrolysis gasoline and the fresh feed to reactor 27 was a C$_{6}$ 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>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{6}$ P plus N.</td>
<td>0.09</td>
<td>0.38</td>
<td>0.18</td>
<td>0.20</td>
<td>0.70</td>
</tr>
<tr>
<td>C$_{6}$ O</td>
<td>2.10</td>
<td>2.10</td>
<td>2.10</td>
<td>2.10</td>
<td>2.10</td>
</tr>
<tr>
<td>C$_{6}$</td>
<td>4.90</td>
<td>4.90</td>
<td>4.90</td>
<td>4.90</td>
<td>4.90</td>
</tr>
<tr>
<td>C$_{6}$ P plus N.</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>C$_{6}$ DIO</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>C$_{6}$ P plus N.</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>C$_{6}$ O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>C$_{6}$ P plus N.</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>C$_{6}$ DIO</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>C$_{6}$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C$_{6}$ P plus N.</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C$_{6}$ DIO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C$_{6}$ P plus N.</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Rerun Col. Bottoms 6.16.
It was noted from the above example that BTX available was not reduced, the olefin content of the gasoline portion of the C₅'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 C₅ hydrocarbons and a relatively heavy fraction comprising C₆ to 300° 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 containing hydrogenation catalyst comprising nickel-molybdate on alumina under conditions including a temperature from 600° F. to 800° F. sufficient to substantially convert olefins 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 350° F., 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 C₅ olefin-containing hydrogen fraction suitable for gasolene blending, an olefin-free aromatic hydrocarbon-rich fraction suitable for aromatics extraction, and a gasoline fraction comprising C₆+ 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 C₅ hydrocarbons and a relatively heavy fraction comprising C₆ 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 substantially 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 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 C₅ olefin-containing hydrogen fraction suitable for gasolene blending, an olefin-free aromatic hydrocarbon-rich fraction suitable for aromatics extraction, and a gasoline fraction comprising C₆+ 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.

References Cited

UNITED STATES PATENTS

3,133,013 5/1964 Watkins 208—143
3,161,586 12/1964 Watkins 208—143
3,221,078 11/1965 Keith et al. 208—143
3,239,454 3/1966 Streed et al. 208—143
3,388,055 6/1968 Craig et al. 208—143

HERBERT LEVINE, Primary Examiner.

U.S. Cl. X.R.

208—80, 93, 143, 677