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SELECTIVE HYDROGENATION OF HYDROCARBONS

Howard S. Bryant, Jr., Beaumont, Tex., assignor to Mobil Oil Corporation, a corporation of New York

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The present invention relates to the selective, non-destructive hydrogenation of mixtures containing highly unsaturated hydrocarbons and olefins in which the highly unsaturated substances are preferentially hydrogenated. Thermally cracked petroleum hydrocarbons are a preferred feedstock for said selective hydrogenation. In a particular embodiment, it is concerned with subjecting a pyrolysis gasoline to a mild hydrogenation treatment of improved selectivity to form a stabilized liquid product suitable for use either as a motor fuel blending stock or as an intermediate from which aromatic hydrocarbons may be recovered after further processing.

In the production of olefins, especially ethylene and propylene, by subjecting petroleum fractions, such as naphthas, to severe thermal cracking, usually in the presence of steam, a considerable quantity of pyrolysis gasoline is produced which is unsuitable for use in motor fuels due to its tendency to form excessive quantities of gum during storage. This thermally cracked gasoline contains substantial proportions of both diolefins and mono-olefins as well as some aromatic compounds (typically about 6 to 50% by volume or more) and perhaps some acetylenic materials. The more reactive diolefins among the diolefins therein are particularly undesirable by reason of their known tendency to polymerize and form gums upon prolonged standing. Mono-olefins in general are desirable constituents of motor fuels as they have relatively high octane ratings, and aromatic hydrocarbons are superior in this regard.

Conventional hydrogen treatments for stabilizing such hydrocarbon mixtures are not entirely satisfactory because of their lack of adequate selectivity and also the usual relatively high operating temperatures. For example, the hydrogenation may not end with simply partial saturation of the diolefins to olefins but also frequently saturates the mono-olefins completely and even hydrogenates substantial proportions of the aromatic hydrocarbons to less valuable naphthenes. Polymerization of diolefins with consequent contamination and deactivation of the catalyst with gummy deposits or coke often occurs. Such polymerization may be of the thermal type induced by high temperatures, or it may be of a catalytic type inaugurated by the hydrogenation catalyst, as good hydrogenation catalysts frequently possess substantial polymerization activity also. The polymeric deposits are highly undesirable as they not only reduce the hydrogenation activity of the catalyst, thereby requiring frequent regeneration but also tend to plug up piping and other equipment.

Selective hydrogenation is also employed in multi-stage hydrogenation reactions as for instance in the preparation of pyrolysis gasoline for the extraction of its aromatic hydrocarbon content by well-known solvent extraction techniques as exemplified by extraction with diethylene glycol. To prepare a suitable feed for the solvent extraction, it is necessary to convert the organic sulfur compounds to a readily separable material, such as hydrogen sulfide gas, to saturate the unstable gum forming diolefins and also to saturate the mono-olefins without at the same time converting aromatic hydrocarbons into naphthenes by excessive hydrogenation.

It is not feasible to completely saturate and desulfurize such feedstocks in a single operation because the relatively high temperatures suitable for hydrodesulfurization (typically at least about 450° F.) also promote the formation of coke and polymers or gums, and such temperatures may hydrogenate aromatics to naphthenes under certain conditions. Even conducting the hydrogenation reactions in several stages to avoid or minimize the aforesaid difficulties has not been entirely satisfactory by reason of the accumulation of polymeric deposits that reduce the activity of hydrogenation catalysts, thereby requiring frequent regeneration. In addition, such deposits also plug up piping and other equipment. Not only thermal polymerization but also catalytic polymerization must be minimized as many good hydrogenation and desulfurization catalysts also catalyze the polymerization of diolefins. While various techniques are known for at least partially reducing the polymer formation of hydrocarbons at elevated temperatures, nevertheless polymer formation remains a critical problem in commercial plants for the selective hydrogenation of charging stocks of the type described.

The present invention involves the selective non-destructive hydrogenation (that is, without substantial cracking or hydrocracking) under mild conditions of hydrocarbons which comprises treating an essentially hydrocarbon mixture containing a conjugated diolefin and an olefin with hydrogen at hydrogenation temperatures below desulfurization temperatures in the presence both of a catalyst containing palladium and also of a sulfide of the group consisting of carbon disulfide and hydrogen sulfide wherein said sulfide substantially increases the selectivity of said catalyst for hydrogenating said highly unsaturated hydrocarbons.

Narrower aspects of the invention relate to the presence of carbon disulfide as the preferred agent for improving catalyst selectivity, desirable concentrations of the selected sulfide, the composition of the preferred palladium composite catalyst, maintaining a substantial liquid phase in the reaction and supplying the selected sulfide either by conversion in the pyrolysis reaction or by at least intermittent addition to the hydrogenation reaction or both. Other aspects of the invention will be apparent to those skilled in the art upon consideration of the detailed disclosure which follows.

Unless otherwise indicated herein, all proportions are expressed in terms of weight, all temperatures in degrees Fahrenheit (° F.), all boiling points and ranges are determined according to the ASTM procedure at normal atmospheric pressure and the term "olefins" refers to mono-olefins. The expression "highly unsaturated hydrocarbons" may be defined for the instant purposes as highly reactive hydrocarbons containing aliphatic unsaturation and having a strong tendency toward polymerization at moderately elevated temperatures such as conjugated diolefins, acetylene and substituted acetylenes. Unconjugated diolefins are less reactive and generally treated as mono-olefins.

In performing the instant process a hydrogenation feedstock with a pronounced tendency toward undesired polymerization is subjected to a selective hydrogenation process in which it is hydrogenated mildly in what may be described as essentially the liquid phase although the reactor contains a minor proportion of vaporized gasoline along with large amounts of hydrogen and usually lower hydrocarbon gases. The reaction is conducted at a temperature sufficiently low to avoid or minimize both thermal and catalytic polymerization while hydrogenating a substantial proportion (usually all or a predominant proportion) of the conjugated diolefins, including all of the more reactive ones, to form either olefins or paraffins. In addition, the degree of saturation of mono-olefins in the process is desirably kept as low as may be feasible.

Typically the liquid feed has substantial contents of

diolefins and olefins as evidenced by diene numbers of about 10 to 22, which measure the proportion of conjugated diolefins as determined by the maleic anhydride condensation method, and bromine numbers of about 15 to 30, which represent the total content of unsaturated aliphatic hydrocarbons. Feeds with diene and bromine numbers as high as about 40 and about 75, respectively, may also be processed according to the present invention. A feed containing 6 to 20% of aromatic hydrocarbons is often employed but higher proportions of these compounds are even more desirable for use in motor fuel components and especially for feedstocks for the production of aromatic hydrocarbons.

Feedstocks of the nature described are unstable as they tend to form polymeric gums readily. It has been found desirable to keep the period of storing them as brief as possible in order to minimize the introduction of gum in liquids involved in the present process and into the equipment. In addition, it is recommended that the liquid charge stock be free of dissolved oxygen and be stored in the substantial absence of oxygen or air, for example, under a blanket of an inert gas such as nitrogen, methane, etc. These precautions prolong the activity of the catalyst.

The pyrolysis reaction employed in one embodiment of the instant invention is carried out in conventional equipment under noncatalytic and relatively severe thermal cracking conditions for petroleum stocks, as exemplified by temperatures in the range of about 1250 to 1600° F., pressures of 0 to 40 pounds per square inch gage (p.s.i.g.) and reaction times of about 0.2 to 4.0 seconds. A wide variety of pyrolysis feeds may be utilized including gas oils, naphthas, middle distillates, pentanes and light, normally gaseous hydrocarbons such as ethane, propane and butanes. Thsee may be of varying degrees of purity. A substantial proportion of the organic sulfur compounds therein are converted by pyrolysis into carbon disulfide which may be recovered by condensation of the normally liquid fraction of the pyrolysis product or by fractional distillation thereof to produce a cut with an initial boiling point below 115° F. Excessive concentrations of carbon disulfide in the pyrolysis product may be reduced to the desired extent by scrubbing with aqueous caustic soda with the rate of introducing caustic soda solution adjusted to produce the desired reduction of organic sulfur, including carbon disulfide. Accordingly, it is possible to obtain a pyrolysis product containing a substantial portion or all of the sulfide agent required in the hydrogenation step by selection of pyrolysis feedstocks or by blending high and low sulfur content stocks to make up the pyrolysis feed. It is generally not as convenient to attempt to retain any hydrogen sulfide formed in the pyrolysis reaction in the liquid charge to the hydrogenation reaction, so this gas is usually withdrawn along with other gaseous products of the pyrolysis reaction.

While pyrolysis gasoline is the prefrered charge to the hydrogenation reaction and the material to be hydrogenated is preferably maintained chiefly in the liquid phase during hydrogenation, other materials may also be selectively hydrogenated. For example, propylene streams containing small percentages of methy acetylene and propadiene may be subjected to similar selective hydrogenation in the vapor phase to convert those two contaminants without saturating the propylene to an unacceptable level. Also undesired acetylene in an ethylene stream may be converted by selective hydrogenation.

When charging a pyrolysis gasoline as the hydrogenation feed, a gasoline boiling somewhere within the range between about 60 and 400° F. is usually desirable, and preferably one boiling between about 90 and 240° F. In general, the initial boiling point should desirably not exceed 115° F. And the maximum gum content of the hydrogenation charge stock is preferably less than 15 milligrams per 100 milliliters in order to minimize deactivation of the hydrogenation catalyst. It is usually desirable to retain the carbon disulfide formed in the pyrolysis reaction in the liquid to be hydrogenated. Carbon disulfide is not a typical constituent or contaminant of petroleum crudes for it is seldom present therein in quantities greater than a few parts per million.

The liquid feed typically contains about 20 to 90% of aromatic hydrocarbons, mainly as benzene and toluene, when the product is desired as an intermediate suitable for further processing in the production of aromatic hydrocarbons. Relatively mild hydrogenation conditions are used in this process because of the high hydrogenation activity of pallidium catalysts in general as well as the fact that the presence of the sulfide agent enhances the activity of palladium for hydrogenating highly unsaturated hydrocarbons.

In all cases, the maximum temperature in the hydrogenation zone should be kept below the point at which hydrodesulfurization, that is the conversion of organic sulfur compounds to hydrogen sulfide, takes perhaps which is usually at temperatures of 450° F. and higher. It is generally preferable to maintain the average hydrogenation temperature (the mean of the inlet and outlet temperatures of the hydrogenation zone) below about 250° F. The average temperature of the exothermic hydrogenation reactions may be readily controlled by regulating the temperature of the materials charged and by adjusting the space velocity in the reactor. Although ambient temperatures are usually preferred for the charge, this material may be gently heated to temperatures not exceeding about 200° F. under certain substances such as cold weather operations or when the activity of the catalyst is declining significantly.

The liquid hourly space velocity is desirably maintained within the range of about 0.2 to 15.0, and preferably between about 0.5 and 8.0. In the case of a gaseous charge, the space velocity may be between about 0.3 and 25.0 volume of vapor charge per hour per volume of catalyst (VHSV).

The selectivity of a palladium catalyst for catalyzing hydrogen addition to highly unsaturated hydrocarbons, especially conjugated diolefins, in preference to saturating olefins is substantially enhanced by the presence of certain sulfides, namely carbon disulfide and hydrogen sulfide. Carbon disulfide is greatly preferred as it appears to have a considerably greater effect than hydrogen sulfide and moreover is capable of actually decreasing the undesired saturation of mono-olefins while simultaneously increasing the desired hydrogenation of conjugated diolefins. The reason for this strange increase in selectivity is not known, and it seems to be specific in nature as hydrogenation reactions over platinum are not similarly affected and organic sulfur compounds in general do not improve the selectivity of a palladium catalyst.

A large excess of hydrogen is charged to reactions of the type described herein, usually in the form of a hydrogen-rich gas containing C_{1-3} hydrocarbons. When treating a liquid feed, such as pyrolysis gasoline, the hydrogen charge may be within the range of about 500 to 5000 standard cubic feet per barrel (s.c.f./b.) of the gasoline and the range of about 1200 to 3000 s.c.f./b. is preferred. For hydrogenating gaseous hydrocarbon mixtures, the hydrogen may be charged at an equivalent rate of about 0.5 to 4.8 s.c.f. per s.c.f. of the gaseous hydrocarbon feed.

The total consumption of hydrogen in this process varies of course with the particular feedstock employed; but in general, it is in the range of about 150–800 s.c.f./b. of liquid feedstock. A typical value is 300 s.c.f./b. with a charging stock of diene and bromine numbers of 15 and 24, respectively; and the consumption is usually found to be less than 500 s.c.f./b. Substantial excesses of hydrogen have been specified hereinbefore to avoid a drop in the hydrogenation rates as a result

of an inadequate supply of hydrogen. Although pure hydrogen may be used, it is customarily supplied as a mixture of hydrogen and gaseous hydrocarbons in the off gases of units for reforming naphthas of hydrodesulfurizing gas oils, etc. The gas charge preferably has a hydrogen content of at least 60% by volume but gaseous mixtures with as little as 40% hydrogen may be used. In describing the charging and the consumption of hydrogen in s.c.f. or other units, reference is made only to the hydrogen content in the case of gaseous mixtures and not to the total quantity of a mixed gas which includes a component other than hydrogen.

The total pressure in the reactor is not critical but the partial pressure of hydrogen at the inlet of the reactor is important in avoiding undesired side reactions, such as the formation of gum or coke on the catalysts. The hydrogen partial pressure is desirably maintained within the range of about 200 to 1000 p.s.i. and about 400 to 700 p.s.i. is generally preferred. A major proportion of the product gases with much unconsumed hydrogen is preferably recycled to the process, and this usually constitutes a major proportion of the total quantity of gases charged to the reactor. Another part of the product may be bled off for use as a fuel gas, etc., to avoid accumulating excessive amounts of contaminants or insert substances in the system.

A palladium catalyst possesses the high hydrogenation activity required in order to hydrogenate at relatively low temperatures the more reactive conjugated diolefins; and this quality is substantially improved by the presence of carbon disulfide or hydrogen sulfide according to the present invention. Its polymerization activity is relatively low so that the formation of gums on the catalyst is minimized or eliminated. Furthermore, this catalyst is substantially devoid of alkylation activity and thus does not promote the undesired alkylation of aromatics with olefins.

The improvement in a selectivity is obtainable with palladium catalysts in general. However, the catalytic metal is desirably dispersed upon the surface of various inert, porous carrier materials in particle form such as tablets or pellets, extruded cylinders or crushed and screened material of random shape in concentrations of about 0.05 to 10% palladium based on the total weight, and the range of about 0.2 to 2.0% is preferred. Various aluminas are preferred for the purpose, especially gamma or chi alumina, and a particle size of about 1/16 to 3/8 inch is generally recommended for fixed bed operations. Catalysts of substantial acid activity are not desirable for this process since they produce unwanted cracking reactions, hence silica-alumina catalyst supports are usually avoided. While it is preferable that the catalyst support be substantially free of halogens, a relatively low halogen content up to about 0.5% may be tolerated. Optionally, but desirably, the palladium catalyst composite may include a promoter such as chromium oxides deposited thereon in an amount, for example, such that the chromium content of the catalyst is about equal to the palladium content. The manufacture of such catalyst composites is well known in the art and accordingly need not be further described here.

Regeneration of the catalyst is required when the diene number reduction gradually falls off to an unacceptable level. The inlet temperature may be increased somewhat to delay the need for regeneration but not to the extent of raising the temperature anywhere in the reactor up to the range where substantial hydrodesulfurization occurs.

Although palladium-on-alumina catalysts retain their activity for extremely long periods, as for instance, a year or more, regeneration is eventually necessary; and this may be readily accomplished by heating the reactor to a temperature of about 700 to 900° while passing a gas containing 1 or 2% oxygen through the catalyst bed. A diluent is usually introduced with the air to avoid excessive regeneration temperatures which can reduce catalyst activity considerably. Nitrogen, flue gas or the generally more convenient medium of steam may be utilized as the diluent.

Purging the catalyst with hydrogen at a partial pressure 200 to 500 p.s.i. and 750 to 850° F. for between 4 and 16 hours sometimes serves to regenerate it almost as effectively as the aforesaid combustion. Accordingly, it is contemplated that, in the absence of severe deactivation, this catalyst may be regenerated several times by such treatment with a hydrogen-rich gas before it is necessary to regenerate the contact agent by the combustion technique.

When treating a pyrolysis gasoline, the relatively mild hydrogenating conditions described hereinbefore, and especially the use of relatively low temperatures no higher than necessary to obtain the desired hydrogenation of highly unsaturated hydrocarbons, are also supplemented by maintaining a substantial portion of the charge liquid in the liquid phase throughout the hydrogenation reaction. With such liquid feeds, it is preferable to maintain at least 15% and preferably at least 30% by volume of the normally liquid constituents of the reaction mixture in the liquid phase. In many operations only a small percent of the liquid charge is in vapor form during this hydrogen treatment.

Consequently, despite the unstable nature of the hydrocarbon feedstock, very little if any gum is formed in the reactor. The relatively low reaction temperatures are not conducive to thermal polymerization, and the catalyst has little or no polymerization activity. Maintaining a substantial proportion of the reaction mixture in the liquid phase avoids approaching the point of dryness in the reactor, and thereby further lessens the tendency toward polymerization. In addition, the usually substantial aromatic content of this liquid makes it a good solvent for polymeric gums, so the liquid phase flowing downwardly through this mixed phase reactor dissolves and carries along in solution most of any polymer formed therein.

The reaction conditions may be regulated and balanced against one another to provide the degree of selective hydrogenation needed to yield a product of the desired qualities. When the diene number reduction tends to become too small to provide the desired stability in the product, a more severe or greater degree of hydrogenation of the pyrolysis liquid is required. This may be obtained by decreasing the feed rate in order to correspondingly reduce the space velocity thereby lengthening the time of contact between charge and catalyst. However, in order to maintain the maximum productive capacity in a commercial plant, instead of reducing the charging rate, it will usually be found more desirable to gently preheat the charge to a temperature not exceeding about 150° F. This practice is likely to be particularly beneficial while operating under severe winter weather conditions.

If it is desired to diminish the degree of hydrogenation, this is desirably accomplished by increasing the feed rate. This adjustment, of course, increases the space velocity (i.e., lowers the residence time) and consequently lowers the reaction temperature somewhat since the exothermic hydrogenation reactions do not proceed as far as before. Also diene number reduction may be increased by increasing the concentration of sulfide agent within the ranges indicated elsewhere. Both the lower temperature and the higher production rate are beneficial. While the severity of hydrogenation can also be decreased by decreasing the partial pressure of hydrogen at the reactor inlet, for instance, by reducing the total pressure, this is a less practical manner of adjusting the reaction conditions in commercial practice.

The diene number of the normally liquid fraction of the reaction products is generally far less than that of the feedstock, and such reduction is maintained high enough to inhibit any substantial tendency for reactive diolefins

to form gums even during prolonged storage. This stabilizing of the originally unstable hydrocarbon feed against significant polymerization is better illustrated in terms of a substantial reduction in diene number (e.g. at least 80% reduction for certain purposes) which accurately denotes a proportionate decrease in the content of the most readily polymerizable monomers, rather than in asserting a relatively low diene number as the maximum permissible since the latter could include undesirable charges to the reactor in which a small but significant content of dienes is composed almost entirely of the most easily polymerizable diolefins. In the hydrogenation of mixtures containing both conjugated and unconjugated diolefins, the latter have reactivities and qualities similar to mono-olefins and thus may be present in the product in substantial amount.

As indicated earlier, the sulfide agent for enhancing the selectivity of the palladium catalyst may be either added at least intermittently to the charge to the hydrogenation reaction or, in the case of carbon disulfide, it may be formed in the pyrolysis reaction and retained in the fraction of cracked products, which is selected for the hydrogen treatment. Both of these techniques may be employed in combination in order to maintain the desired concentration of sulfide agent in the hydrogenation charge. Also, carbon disulfide and hydrogen sulfide may be used together or alternately in the process of this invention, in general, while, any addition of the sulfide agent is preferably carried out continuously to maintain a steady concentration thereof, intermittent addition at frequent intervals may also be employed, inasmuch as the effect of the agent seems to last for an appreciable period. Accordingly, during the continuous hydrogen treatment, the concentration of such agent may be expressed as the average concentration over a substantial period of such agent in the material undergoing hydrogenation. The concentration of the sulfide agent should be sufficient to substantially increase the selectivity of the palladium catalyst for hydrogenating highly unsaturated hydrocarbons in preference to saturating olefins, and suitable amounts may be expressed as those providing at least 100 parts per million (p.p.m.) of sulfur in the form of either carbon disulfide or hydrogen sulfide based on the weight of the hydrocarbon charge; the range of about 200 to 500 p.p.m. being usually preferred. While said average concentration may range up to 1000 p.p.m. or more in some cases, it is seldom if ever desirable to allow such concentration to reach a level at which the activity of the catalyst for hydrogenating conjugated diolefins, etc. is substantially decreased even if the catalyst selectivity remains the same or is increased. Usually little or nothing is to to be gained by using said agents in amounts corresponding to more than about 500 p.p.m. of sulfur.

In the case of hydrogen sulfide, this agent is often available in refineries, in admixture with hydrogen which is also utilized in the process, for example, the unscrubbed off-gas of a catalytic hydrodesulfurization unit.

The improvement in selectivity obtained with the instant hydrogenation process is realized not only with fresh palladium catalysts but also with those which have been partially deactivated in long service. Since not only the selectivity but also the activity of a palladium catalyst in hydrogenating highly unsaturated hydrocarbons, such as the conjugated diolefins, is increased at the same average reaction temperature, the space velocity of the hydrogenation reaction may be increased in maintaining any previously acceptable level of selective hydrogenation thereby increasing production. Also the catalyst may be kept on stream longer in maintaining such a level of hydrogenation before it is necessary to lower the space velocity to the rate used in the absence of the sulfide agent.

After hydrogenating pyrolysis gasoline, the reaction effluent, a gaseous-liquid mixture, is cooled and separated in conventional apparatus and the normally liquid fraction is withdrawn as the stabilized product of the process. This material may be blended in varying proportions depending on the ultimate use with other blending stocks suitable for that use. For example, the hydrogenated pyrolysis gasoline may be thoroughly mixed with one or more gasolines of the alkylate type or those derived from catalytic cracking, reforming or coker operations.

In general, it is not necessary to subject the hydrogenated liquid fraction to distillation prior to blending it into other motor fuel components. However, if the gum content is above a desirable level, the product liquid may be distilled in order to eliminate the gum in the bottoms while the overhead fraction is utilized in gasoline. If such a distillation is found necessary, it is usually preferable to distill the entire blended gasoline rather than the hydrogenated component thereof because of the relatively small amount of nonvolatile matter in the latter fraction.

For a better understanding of the nature and objects of this invention, reference should be had to the following detailed example.

Example

A chromia-promoted palladium catalyst on a gamma-alumina support in the form of 3/16 inch diameter cylindrical particles 3/16 inch long is employed as the fixed or stationary bed in a closed reaction vessel for the hydrogenation of pyrolysis gasoline with relatively pure commercial grade hydrogen (90 p.p.m. carbon monoxide on a molar basis). Based on the total weight of the contact mass, there are surface deposits on the alumina of 0.51% of chromium present in oxidized form and 0.50% by weight of palladium metal.

After operating for 11 weeks with pyrolysis gasolines of the same or similar characteristics, a 57° API thermally cracked gasoline with a boiling range of 95 to 230° F., a diene number of 21 and a bromine number of 48 is charged to the reactor. This gasoline is derived from thermal cracking a mixture of light straight run gasolines and light reformed naphtha originating from a variety of crude oils. The sulfur content of this mixture is reduced to a total of about 200 p.p.m. by scrubbing with aqueous caustic soda solution subsequent to the pyrolysis step. The hydrogenation feedstock contains only about 25 to 35 p.p.m. of carbon disulfide and no significant amount of hydrogen sulfide, for most of the sulfur is present as thiophene. In a single pass continuous operation, this pyrolysis liquid is charged to the reactor at a liquid hourly space velocity of 2.0 while the commercial hydrogen is introduced at a rate of 1500 s.c.f./b. of liquid feed. The average reaction temperature is 221° F. and the hydrogen partial pressure amounts to about 450 p.s.i.g. in a total reaction pressure of 500 p.s.i.g. Under these conditions, about 40% of the reaction mixture, based on the volume of pyrolysis liquid charged, is retained in the liqud phase as it flows downward through the catalyst bed. The reaction products are drawn off at the bottom of the reactor and cooled to about 100° F. before the gaseous and liquid phases are separated in a conventional separator. Although suitable for the purpose, the hydrogen-rich product gas is not returned to the reactor in the instant series of runs. The liquid product is found to have a diene number of 5.5 and a bromine number of 26.5 which amount to reductions of 74% in the diene number and 45% in the bromine number, respectively.

A second pyrolysis gasoline of generally similar nature and origin is then substituted for the original feedstock. This particular charge has a boiling range of 95 to 195° F. and a considerably higher sulfur content of 380 p.p.m. resulting from less scrubbing of the pyrolysis material, it also contains approximately 65% by volume of aromatic hydrocarbons, chiefly toluene and benzene. More than three-fourths of this sulfur is in the form of carbon disulfide, that is about 350 to 400 p.p.m. of carbon disulfide, with the balance composed essentially of thiophene plus small amounts of other organic sulfur compounds. Again, no significant amount of hydrogen sulfide is pres-

ent as this substance is separated beforehand along with the gaseous products of the pyrolysis reaction. When steady state conditions are reached after a substantial period in which the average reaction temperature drops to 215°, it is found that the diene number of the normally liquid fraction of the hydrogenation product is 0.5 to 1.0 and its bromine number is 38.5. Thus, the diene number reduction is over 95% and the bromine number reduction is only 20% in this hydrogen treatment, and this represents a saturation of only about 32% of the olefins formed by hydrogenation of the diolefins. Also no appreciable hydrogenation of aromatic hydrocarbons takes place. The aforesaid liquid hydrogenation product is an excellent motor fuel blending stock—clean, noncorrosive and having a high antiknock rating.

It is evident that the presence of carbon disulfide substantially increases both the activity and selectivity of the palladium catalyst for hydrogenating conjugated diolefins and also decreases the activity of the catalyst in saturating monoolefins even though the palladium catalyst is already considered relatively highly selective in this regard.

Another portion of the second pyrolysis gasoline is charged to a reactor containing a platinum catalyst consisting of 0.8% platinum supported on gamma alumina particles for comparison under generally similar conditions except for employing a higher average reaction temperature of 235° F. to at least partially compensate for the lower hydrogenation activity of platinum. However, it is readily apparent that enhanced selectivity is not realized in hydrogenating unsaturated hydrocarbons over platinum while carbon disulfide is present. Instead the platinum catalyst is deactivated greatly, for after carrying out this treatment for only 24 hours, the bromine number of the liquid product is the same as that of the charge and the diene number is reduced only 12%.

While the instant method has been described in detail hereinabove, it will be appreciated by those skilled in the art that the invention is capable of broad utilization with a great variety of unsaturated hydrocarbon charging stocks and that the present process is not restricted to any particular details disclosed other than those specifically recited in the appended claims.

I claim:

1. A process for the selective nondestructive hydrogenation of hydrocarbons which comprises treating an essentially hydrocarbon mixture containing a conjugated diolefin and an olefin with hydrogen at hydrogenation temperatures below desulfurization temperatures in the presence both of a catalyst containing palladium and of a sulfide of the group consisting of carbon disulfide and hydrogen sulfide wherein said sulfide substantially increases the selectivity of said catalyst for hydrogenating said diolefin.

2. A process according to claim 1 in which said sulfide is carbon disulfide.

3. A process according to claim 1 in which a substantial proportion of said mixture is maintained in liquid phase.

4. A process according to claim 1 in which the average concentration of said sulfide corresponds to at least 100 parts of sulfur per million parts by weight of said mixture.

5. A process according to claim 1 in which the average hydrogenation temperature is below about 250° F.

6. A process according to claim 1 in which said catalyst comprises between about 0.05 and 10% by weight of palladium on a porous carrier.

7. A process according to claim 1 in which said catalyst comprises an oxide of chromium and between about 0.2 and 2.0% by weight of palladium on a particle form porous carrier.

8. A continuous process according to claim 1 in which said sulfide is added at least intermittently to said mixture in sufficient quantity to maintain an average concentration of at least 100 parts of sulfur in the form of said sulfide per million parts by weight of said mixture.

9. A continuous process according to claim 1 in which carbon disulfide is added at least intermittently to said hydrocarbon mixture in sufficient quantity to maintain an average concentration of at least about 200 parts of sulfur in the form of carbon disulfide per million parts by weight of said hydrocarbon mixture.

10. A process according to claim 1 in which said sulfide is carbon disulfide and a substantial proportion of said mixture is maintained in the liquid phase.

11. A process according to claim 1 in which thermally cracked petroleum hydrocarbons are employed as said hydrocarbon mixture.

12. A process for the selective nondestructive hydrogenation of hydrocarbons which comprises treating an essentially hydrocarbon mixture containing a conjugated diolefin and an olefin with hydrogen at hydrogenation temperatures below desulfurization temperatures while retaining a substantial liquid phase in the presence both of a catalyst containing between about 0.05 and 10% palladium on a porous carrier and of carbon disulfide in an average concentration corresponding to at least 100 parts of sulfur per million parts by weight of said mixture wherein said carbon disulfide substantially increases the selectivity of said catalyst for hydrogenating said diolefin.

13. A process according to claim 12 in which said mixture contains an average concentration of carbon disulfide corresponding to between about 200 and 500 parts of sulfur, the average hydrogenation temperature is below about 250° F. and at least about 15 percent by volume of said mixture is retained in the liquid phase during said treatment.

14. A process according to claim 12 in which said hydrocarbon mixture is a pyrolysis gasoline.

15. A process for the selective nondestructive hydrogenation of hydrocarbons which comprises treating a gasoline boiling below about 240° F. and containing conjugated diolefins and olefins with hydrogen at an average reaction temperature below about 250° F. in the presence of a catalyst comprising an oxide of chromium and between about 0.2 and 2.0% by weight of palladium on a particle form alumina carrier while maintaining at least about 30 volume percent of said gasoline in the liquid phase and introducing carbon disulfide at least intermittently in sufficient quantity to maintain an average concentration of between about 200 and 500 parts of sulfur in the form of carbon disulfide per million parts by weight of said gasoline to substantially increase the selectivity and activity of said catalyst for hydrogenating said diolefins and to decrease the activity of said catalyst for saturating olefins.

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DELBERT E. GANTZ, *Primary Examiner.*

S. P. JONES, *Assistant Examiner.*